Final report on CarboEurope 'Cucumber' intercomparison programme

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16 February 2009

Executive Summary

The World Meteorological Organisation has specified an "inter-laboratory comparability" of 0.1 ppm for background atmospheric CO_2 measurements. This means that any two given laboratories (or field stations) measuring the same air sample should obtain values within 0.1 ppm of each other. Several intercomparison programmes have existed for many years quantifying (and improving) such comparability between the major CO_2 analysis laboratories around the world. No programme existed, however, for assessing comparability between field stations (with the exception of some field stations run by a common laboratory, where that laboratory may have made internal intercomparisons). The "Cucumber" intercomparison programme was established to address this deficiency, via circulating high pressure cylinders ("Cucumbers") of air of known concentrations to field stations and laboratories. As shown in this report, we have now quantified the CO_2 comparability from 21 European field stations and 9 laboratories, including 4 non-European laboratories. As a "bonus", in addition to CO_2, we report comparability from up to 8 additional species, depending on the analytical capabilities at each field station or laboratory. By highlighting concentration offsets, the programme has also assisted in improving the analytical procedures and thus the precision and accuracy at some stations. Finally, comparability between any two given stations or laboratories is not constant over time. For this reason, the programme consists of several "loops" of Cucumbers, with each loop consisting of a small number of stations, enabling relatively fast circulation and thus for each station to build up a time-history of comparability. For the same reason, we are continuing the Cucumber intercomparison programme into the foreseeable future.

Aims and description of the programme

The Cucumber intercomparison programme is one of several which were run in the CarboEurope project. The other programmes, while extremely insightful and fruitful, were somewhat limited in that they intercompared only central laboratories, with no comparisons made of the many atmospheric CO_2 monitoring field stations within Europe. It was this limitation that the Cucumber programme aimed to address, by including 22 field stations as well as 10 laboratories.

The aim of all such intercomparison programmes is to assess and quantify possible offsets in calibration scales. Two overarching goals are: 1) to use the results to improve laboratory and field analytical procedures and reduce calibration scale offsets over time; and 2) to use the established offsets to facilitate merging of datasets from different laboratories, for example in atmospheric inversion modelling studies.

A "Cucumber" is a 20 L Luxfer aluminium cylinder filled with natural air to high pressure (200 bar)*. The programme consists of 7 fast-circulating loops, each loop consisting of 3 Cucumbers spanning a range of CO_2 concentrations from about 360 to 400 ppm. The 7 loops are shown in Figure 1, with station codes defined in Appendix 1. Each of the 5 "Euro" loops consists of one central laboratory and several CO_2 field stations. The two "Inter" loops consist of central laboratories, where Inter-1 is a fast loop of only the European laboratories, and Inter-2 is a slower loop which includes partners from USA, Canada, Australia, and Japan.

* In the special case of the Inter-2 loop, Cucumbers are 29.5 L Luxfer aluminium cylinders, initially filled to about 130 bar. These are US-manufactured cylinders, whereas all 20 L cylinders used in the other loops were manufactured in the UK.

Within each loop the Cucumbers cycle perpetually between several field stations or laboratories, and are analysed at each, according to common procedures as detailed in Appendix 2. As soon as data are received, they are incorporated into graphs shown on a dedicated website at: http://cucumbers.webapp2.uea.ac.uk. This rapid dissemination of results allows field stations to quickly identify possible problems. The primary limitation is delays from participants in submitting their data.

Whereas the programme was specifically established for the purpose of CO_2 intercomparison it has been expanded to include 8 other atmospheric species: CH_4, CO, N_2O, SF_6, H_2, O_2/N_2, $\delta^{13}C$-CO_2, $\delta^{18}O$-CO_2, with stations and laboratories analysing these additional species as their analytical capabilities and time allow. Results from all species are shown on the website. Euro-3 has been particularly setup to include all field stations which make O_2/N_2 measurements. One other O_2/N_2 field station, WAO, was unable to fit into Euro-3 without make the loop too large, thus it was included in the Inter-1 loop which also reports O_2/N_2 results.

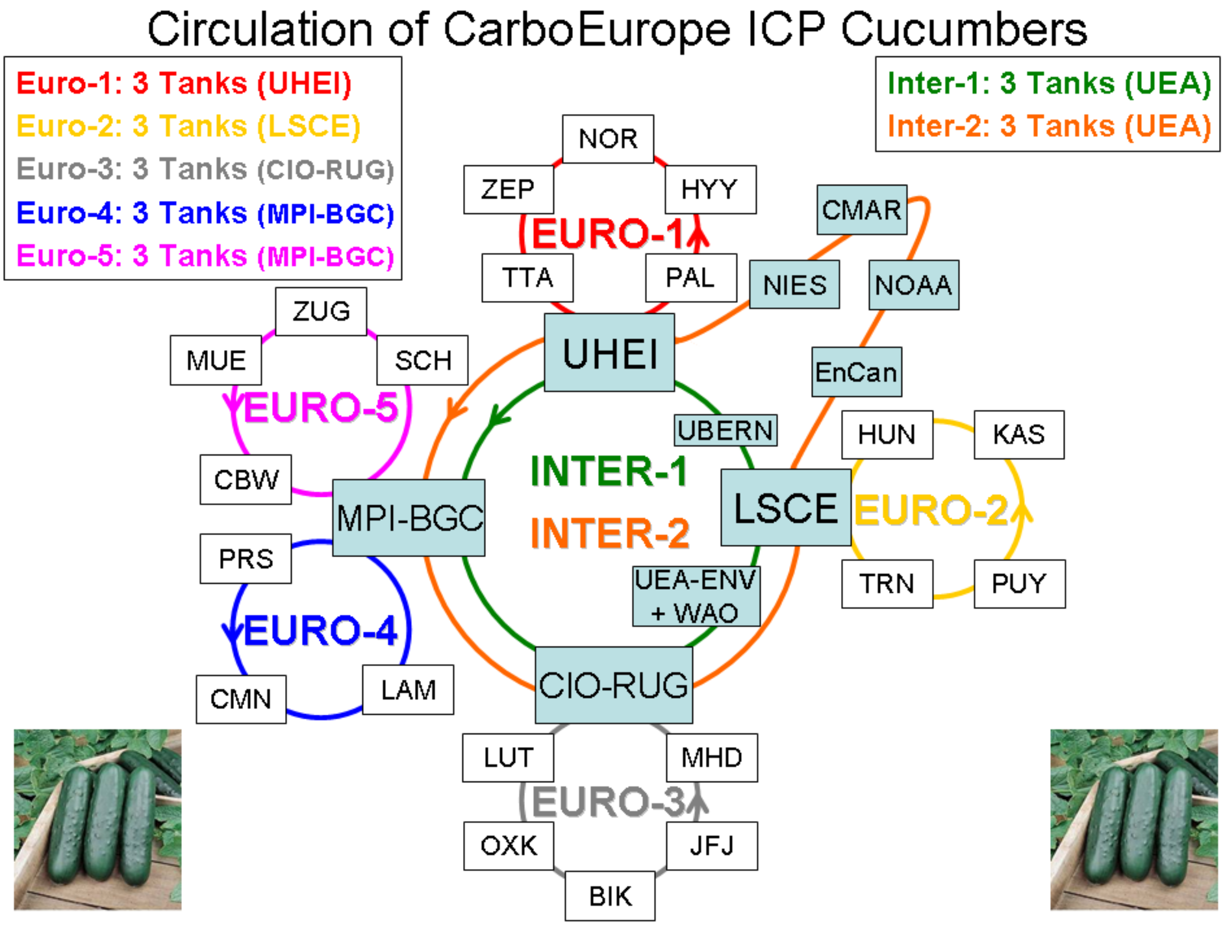

Figure 1: Schematic of the 7 Cucumber loops. Station codes are defined in Appendix 1. Note that there is a small inconsistency with Euro-3 in this schematic: CIO-RUG are indeed responsible for this loop, however, MPI-BGC have been added to the loop, and data from this loop are shown as offsets to MPI, not CIO. This was done because the CIO laboratory does not have capability to measure all of the species reported from some of the field stations (e.g. N_2O).

Progress

Circulation of all Cucumbers initially started in October 2005, with strict deadlines being enforced: 4 weeks to analyse the Cucumbers then ship them to the next participant, and an additional 4 weeks to report data. Shipping times are not included in the deadline. Analysis deadlines were reasonably well adhered to, but unfortunately reporting deadlines were widely ignored. This situation appears to be slowly improving since the launching of the website in early 2008.

There were several very unfortunate logistical problems in the programme in 2005 and 2006, such as repeated damage to the expensive regulators, cylinder damage in one case which required a new cylinder being prepared, new international shipping laws regarding our custom-made wooden shipping boxes, and finally, concerns over laws regarding the use of US-manufactured high pressure cylinders in Europe. Because of this last issue, the programme was suspended in August 2006. New European cylinders were purchased, filled, and initial concentrations established. The programme finally got underway again in January 2008 (following further delays caused by difficult problems with regulator-cylinder seals). The international loop, Inter-2, was not suspended, and consists of a continuous dataset spanning now over 3 years.

Since the resumption of the programme in 2008, it has run much more smoothly, to the extent that the programme is able to continue to this day, despite the fact that CarboEurope IP has concluded. The "Cucumber Responsibles" (see Appendix 2) ensure that the Cucumbers continue to circulate around the loops, and that the data are submitted to the website.

Results

The main results from the field stations since the programme restarted in 2008 are shown in Figures 2 to 8 below. For each of these figures, "zero" is defined as the initial analyses (of all 3 Cucumbers) made at the central laboratory. In this manner, subsequent analyses at the central laboratory are also shown. Each data point represents the average difference (of all 3 Cucumbers) of the field station analyses from the initial central laboratory analyses. Error bars show the minimum and maximum differences. Lines are drawn connecting data points from a single station (or laboratory), showing subsequent analyses by that station in the same loop. Red lines and symbols show central laboratory data for all loops. Dashed horizontal lines show the World Meteorological Organisation (WMO) inter-laboratory comparability goals.

Thus, for example, PUY (Puy de Dome; blue asterisk) shown on the left hand side of Figure 2, in the Euro-2 loop, from analyses made in Aug2007, shows an average offset from LSCE of about -0.35 ppm. Of the 3 Cucumbers analysed, the biggest offset was about -0.45 ppm and the smallest offset was about -0.15 ppm. It is important to note that, as displayed in these Figures, it is not possible to directly compare all field stations with each other. For example, the PUY data show an average offset of about -0.35 ppm, whereas BIK (Bialystok; cyan square; also on left hand side of Figure) data show an average offset of about -0.20. But PUY data are relative to LSCE, whereas BIK data are relative to MPI-BGC. Only from a consideration of LSCE to MPI-BGC offsets can PUY and BIK stations be compared. Indirectly, such comparisons are possible, owing to the existence of the Inter-1 and Inter-2 loops, where we establish offsets between the various central laboratories.

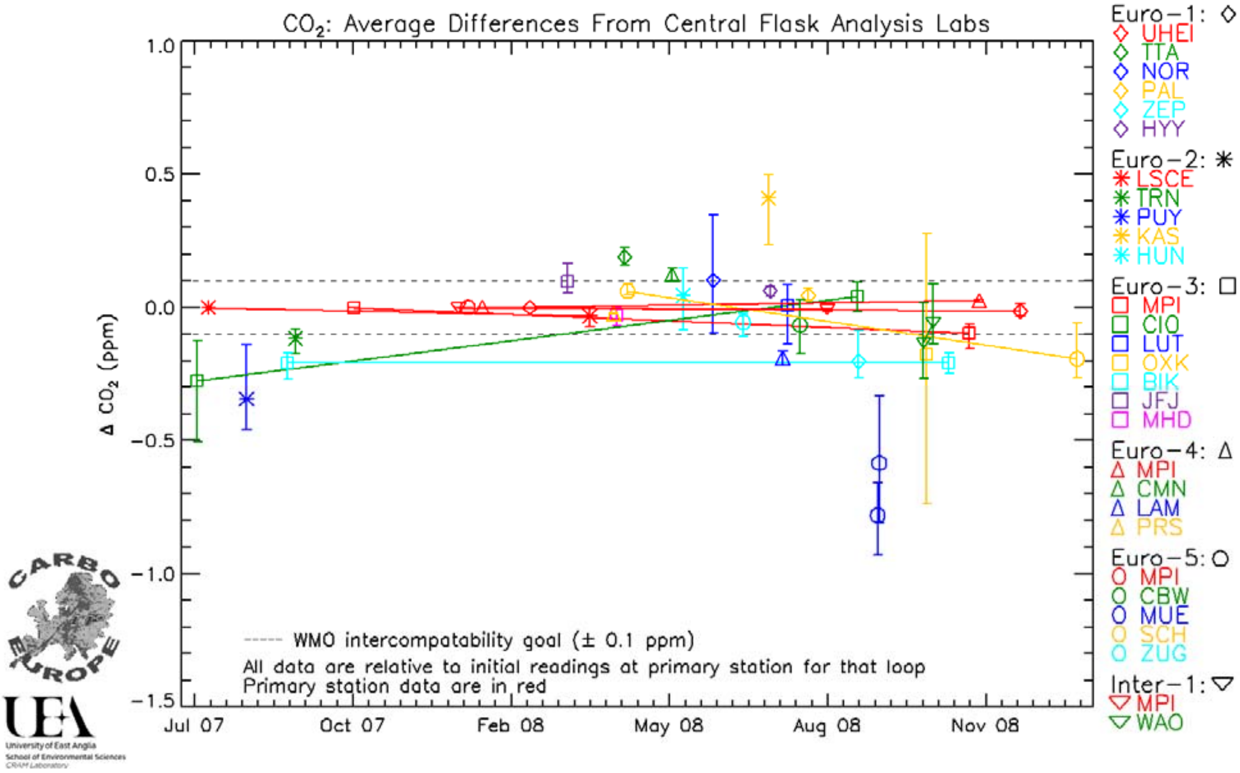

Figure 2: CO₂ field station differences from central laboratories. In Euro-4, one cylinder proved to be unstable, thus results shown are averages from two cylinders only. MUE are presently investigating their calibration scale and analysis protocols in an effort to improve results. Data shown as JFJ and ZEP were in fact from analyses made in University of Bern and Stockholm Univeristy laboratories respectively.

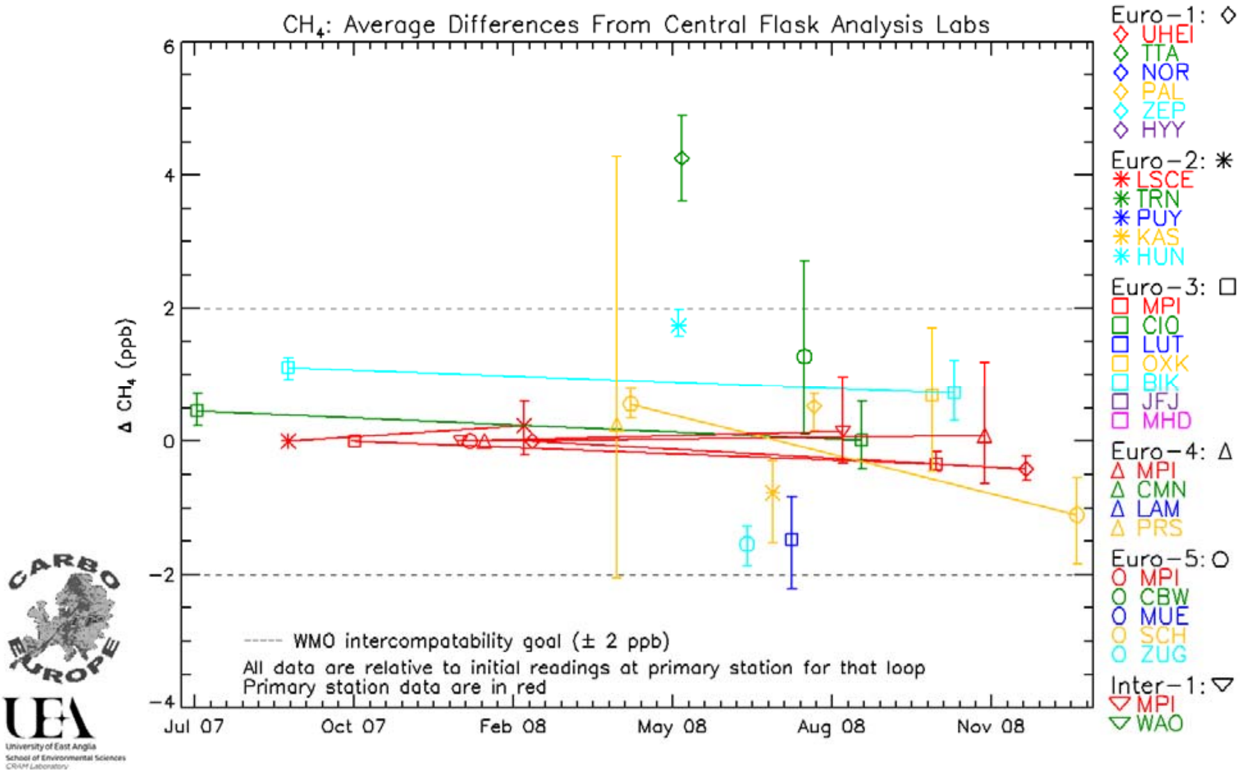

Figure 3: CH_4 field station differences from central laboratories. TRN data are off scale and not shown. TTA had known instrumental problems during their analysis.

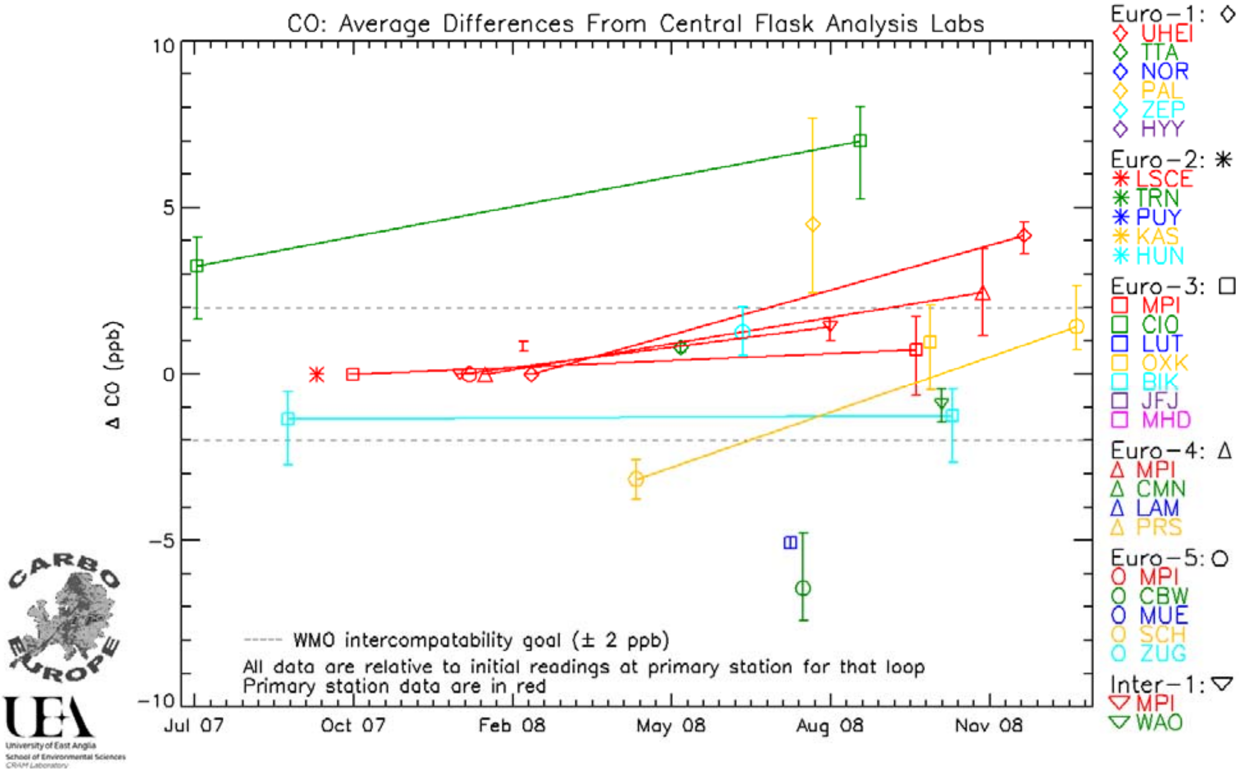

Figure 4: CO field stations differences from central laboratories. There are possible problems with central laboratory scales and/or cylinder stability for CO, most notably from the Euro-1 cylinders analysed at UHEI. PAL results are negatively influenced because one cylinder (350 ppb) is outside of the calibrated range.

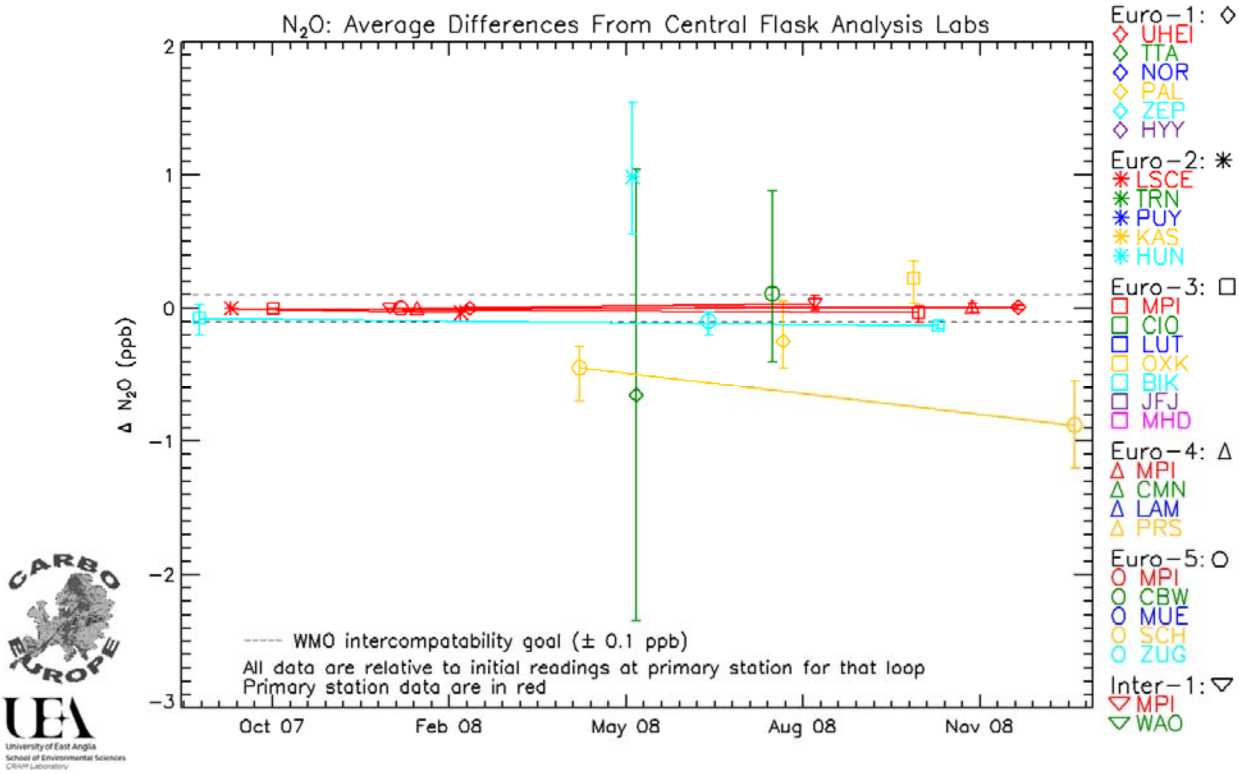

Figure 5: N_2O field stations differences from central laboratories. LUT data are off scale and not shown; TTA had known instrumental problems during their analysis.

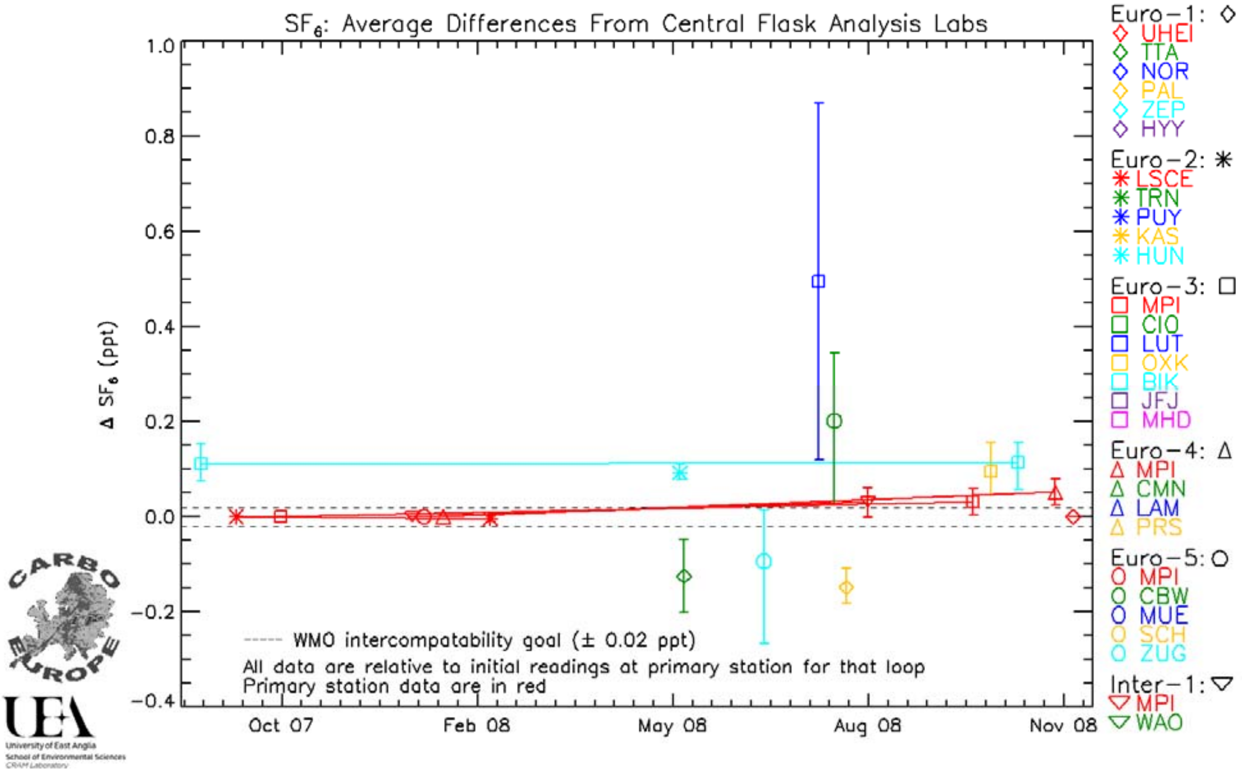

Figure 6: SF_6 field stations differences from central laboratories. SCH data are off scale and not shown.

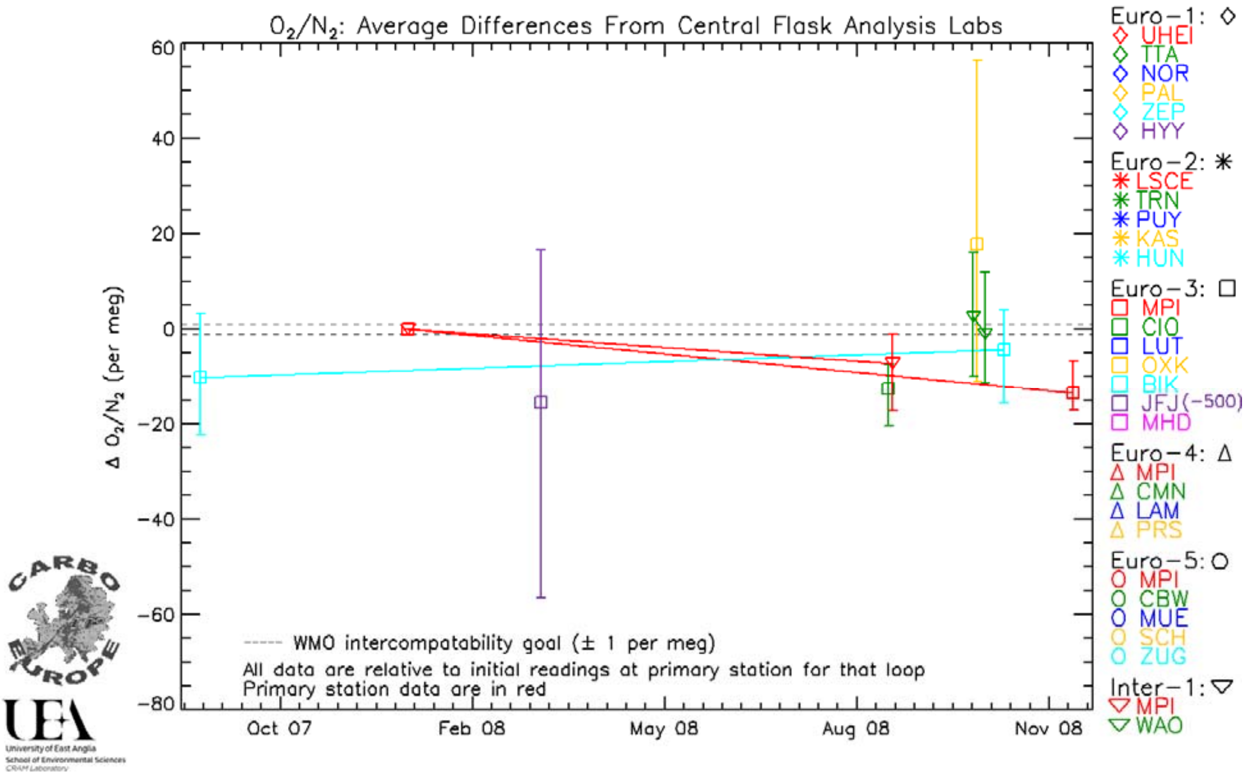

Figure 7: O_2/N_2 field stations differences from central laboratories. As for CO, there is some evidence for possible problems with central laboratory scales and/or cylinder stability for O_2/N_2. The data point shown as JFJ was in fact from analyses made in the University of Bern laboratory.

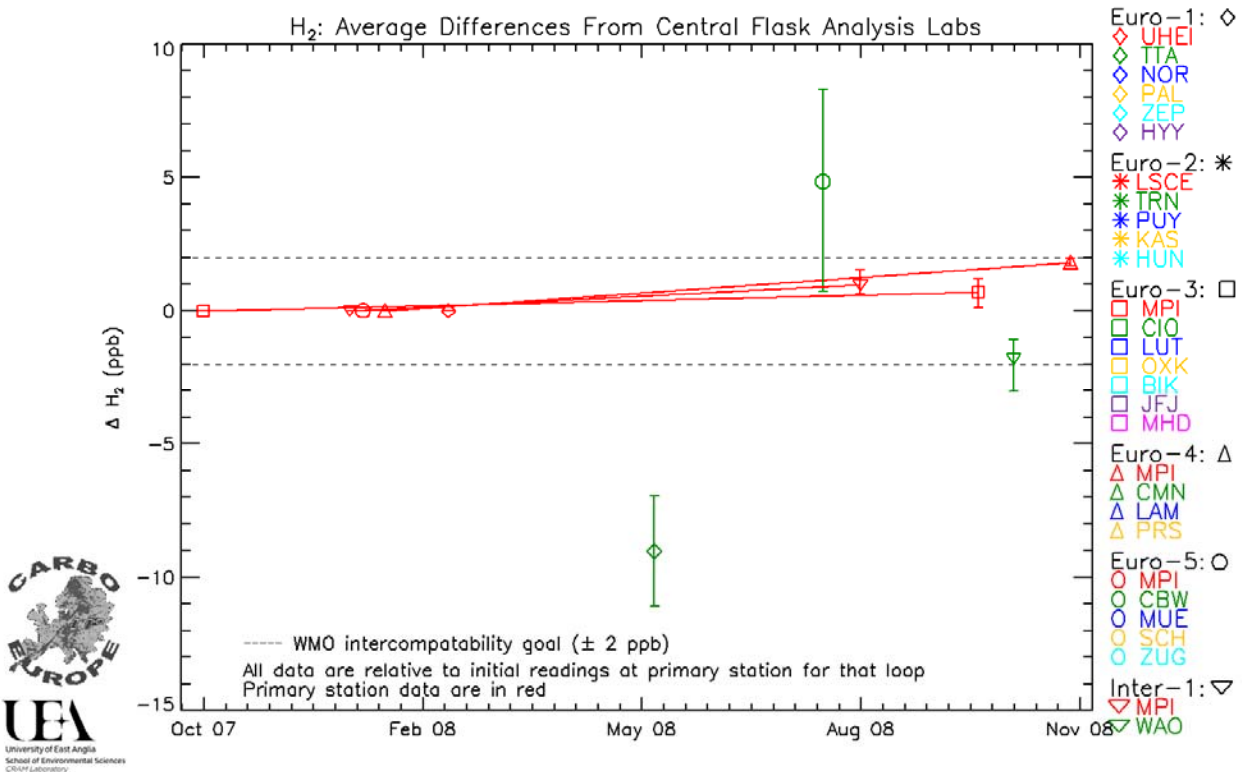

Figure 8: H_2 field stations differences from central laboratories. TTA had known instrumental problems during their Cucumber analysis.

The 3 Cucumbers of each loop span a range in CO_2 concentration, thus one can also observe possible concentration-dependent offsets from a field station. These can not be seen in the summary Figures 2-8, but additional figures on the website allow such studies. One example is shown in Figure 9, showing individual CO_2 analyses made at Environment Canada (EnCan) in the Inter-2 loop. From the first set of analyses in January 2007, there is slight evidence of a very small concentration-dependent offset of EnCan data relative to MPI-BGC. This is only visible owing to the very high precision obtained from the measurements. From the subsequent analyses in September 2008, however, there is no longer evidence of a concentration dependency. The conclusion in this example is that these very small offsets are due to laboratory imprecisions (at both laboratories). Nevertheless, this example illustrates the additional information that can possibly be gleaned from the analyses. Finally, we point out that in this particular example, EnCan and MPI-BGC are well within the WMO CO_2 intercomparability goal. For the other non-CO_2 species, when preparing the Cucumber cylinders it was not always possible to obtain a range in concentration for all cylinders in all loops. Nevertheless, for some species in some loops, such information does also exist.

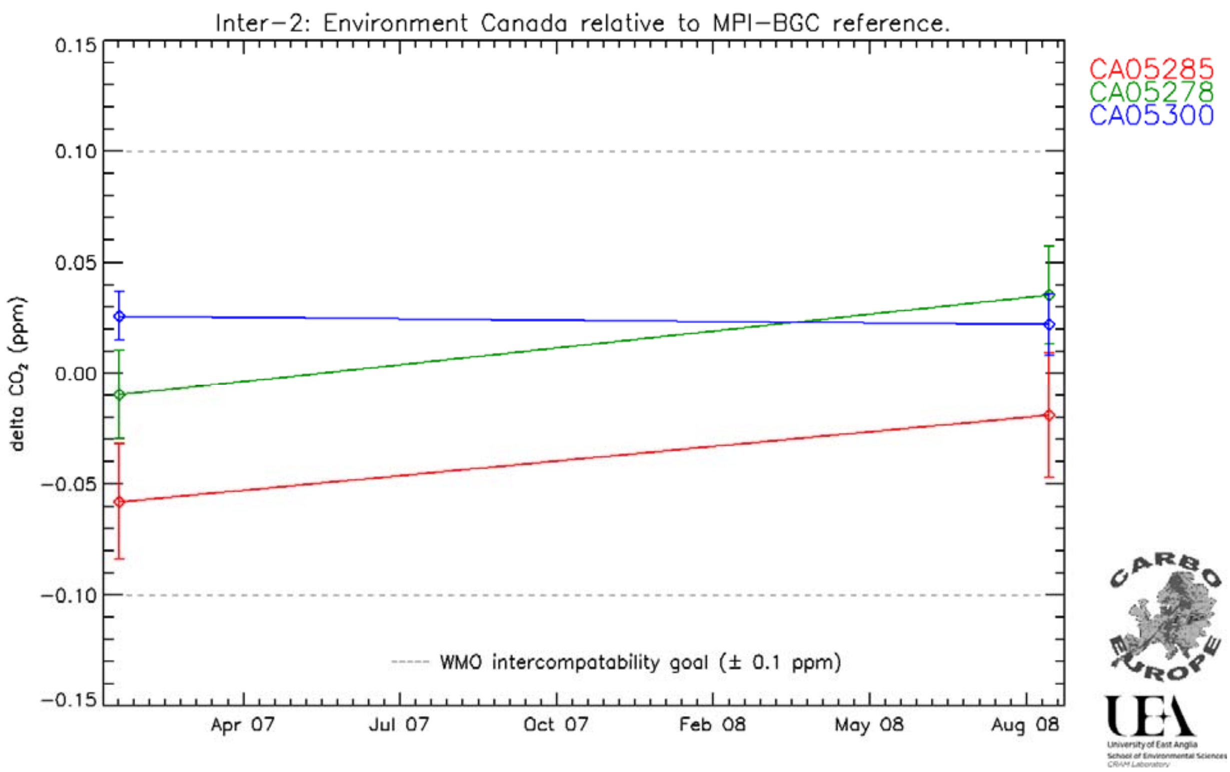

Figure 9: Individual cylinder analyses for CO_2 from Environment Canada (Inter-2 loop). Nominal concentrations are: CA05285 ~400 ppm; CA05278 ~380 ppm; CA05300 ~360 ppm.

We also have results from the initial circulations in 2005-2006. For CO_2, a summary from all field stations is shown in Figure 10. As a generalisation, offsets in 2008-09 have improved since these earlier results.

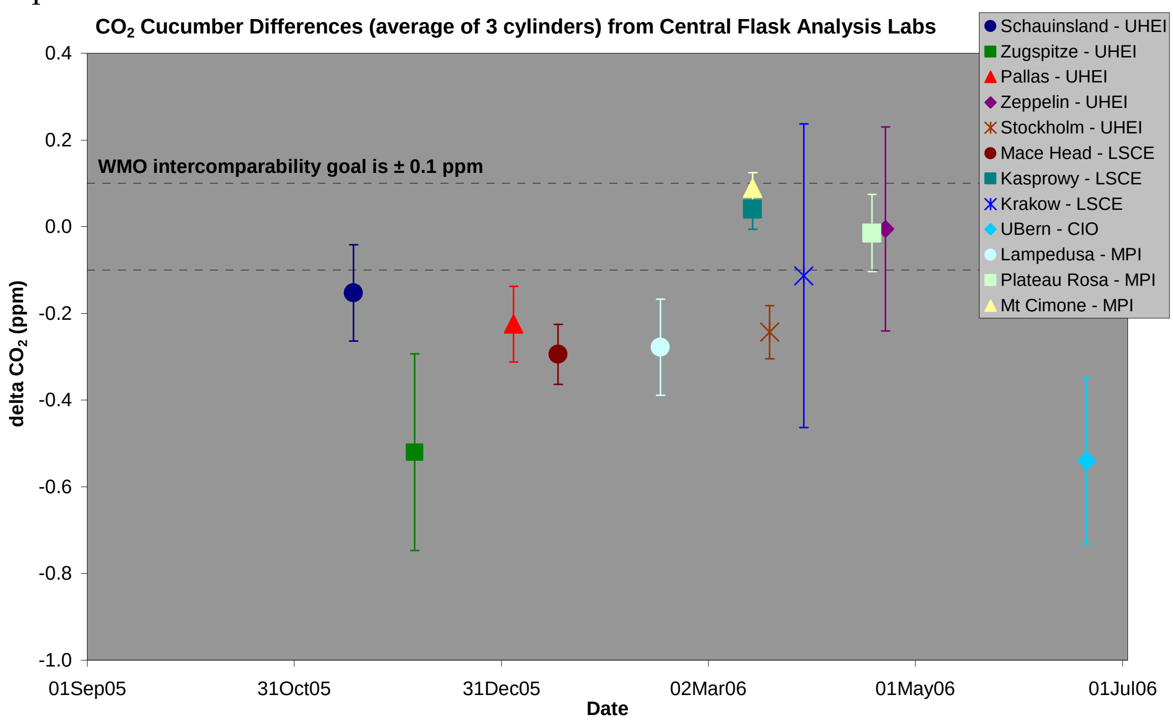

Figure 10: CO_2 field stations differences from central laboratories in 2005 and 2006.

Note: some caution must be taken in comparing these 2005-06 results with later results, since some stations were moved to different loops with different central laboratories. The legend in this figure states the central laboratory for each station.

Figures 2 to 8 and 10 above present the offsets found at the European field stations. Figures 11 to 16 below present the inter-laboratory offsets, including from the 4 non-European partners, over more than 3 years from the Inter-2 loop. CO and H_2 data are not shown, owing to one cylinder having very high values (~900 ppb CO and ~1200 ppb H_2) which were outside of all calibration ranges, and thus intercomparison results had the impression of being very poor.

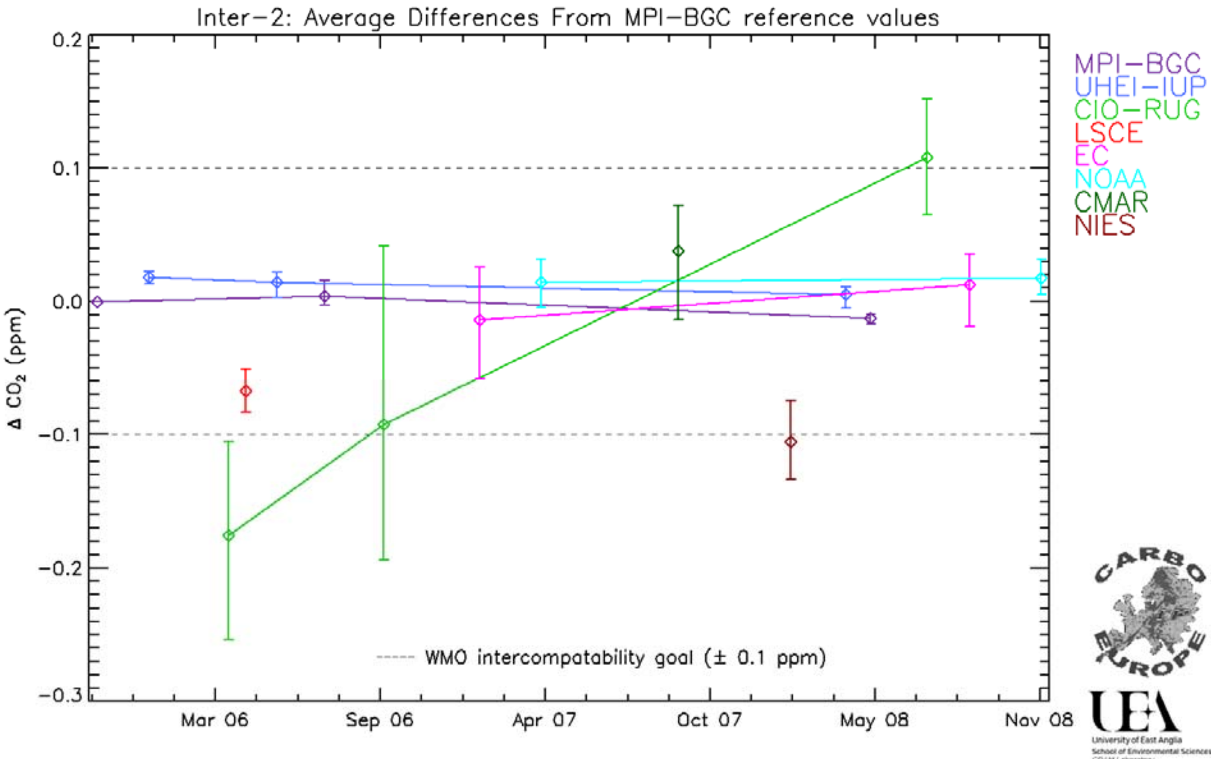

Figure 11: Central laboratory CO_2 differences from MPI-BGC in the Inter-2 loop. All data are on the NOAA X2007 scale, with the exception of NIES who are on their own gravimetric scale.

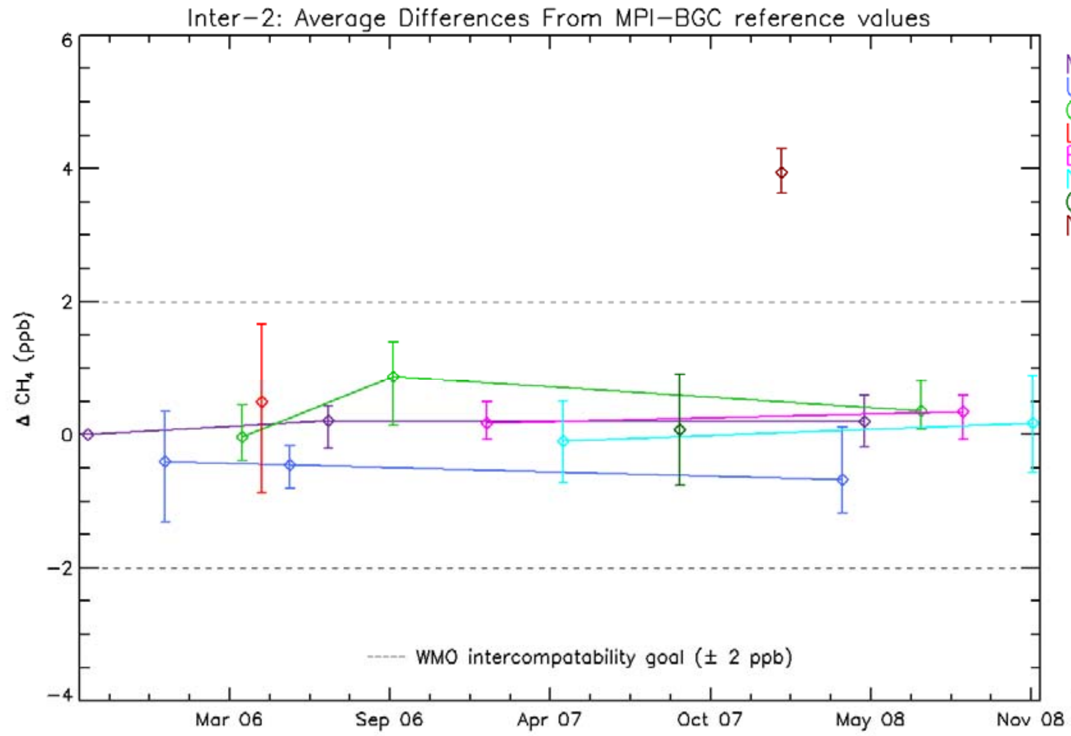

Figure 12: Central laboratory CH_4 differences from MPI-BGC in the Inter-2 loop. As for CO_2, NIES are on an independent Japanese gravimetric scale. Although having a large offset from the NOAA04 scale (which all the other laboratories are using), the offset has proven to be very stable over time, as demonstrated in the "Sausages" intercomparison programme.

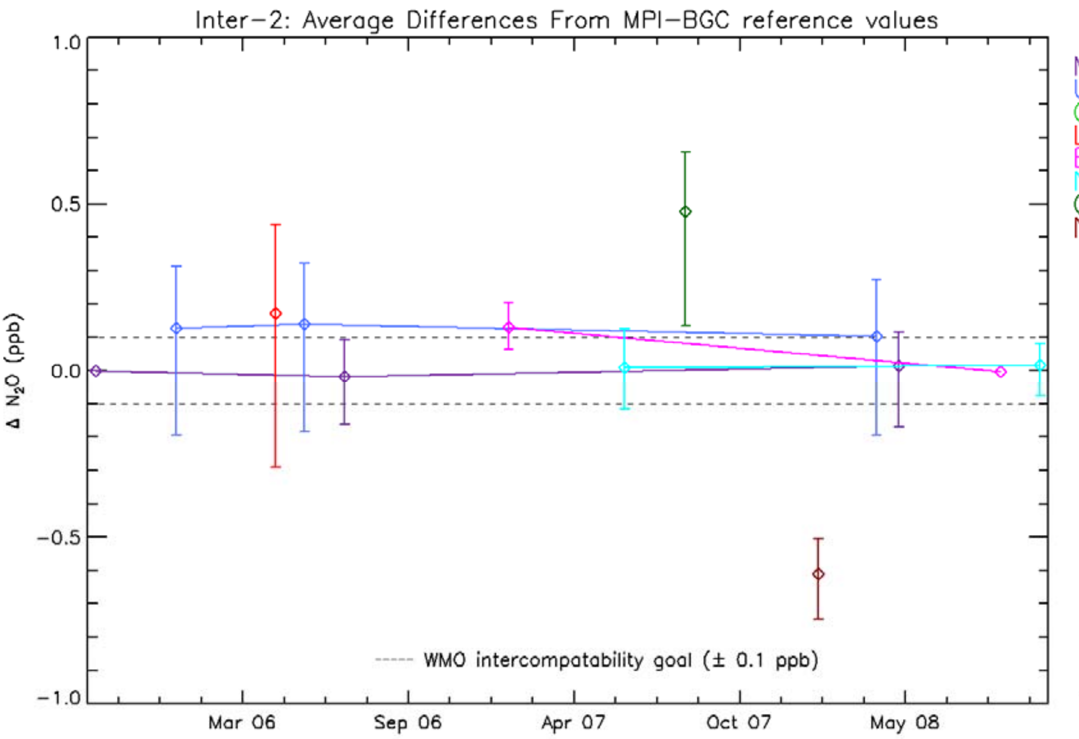

Figure 13: Central laboratory N_2O differences from MPI-BGC in the Inter-2 loop. As for CO_2 and CH_4, NIES are on an independent gravimetric scale.

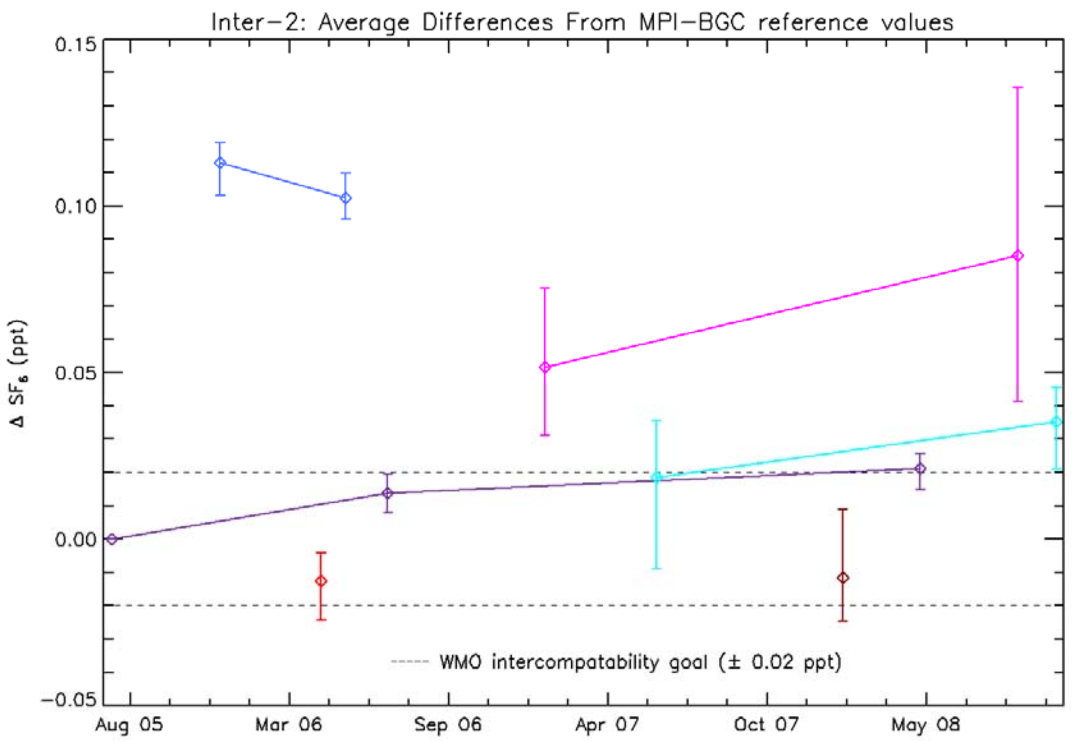

Figure 14: Central laboratory SF_6 differences from MPI-BGC in the Inter-2 loop.

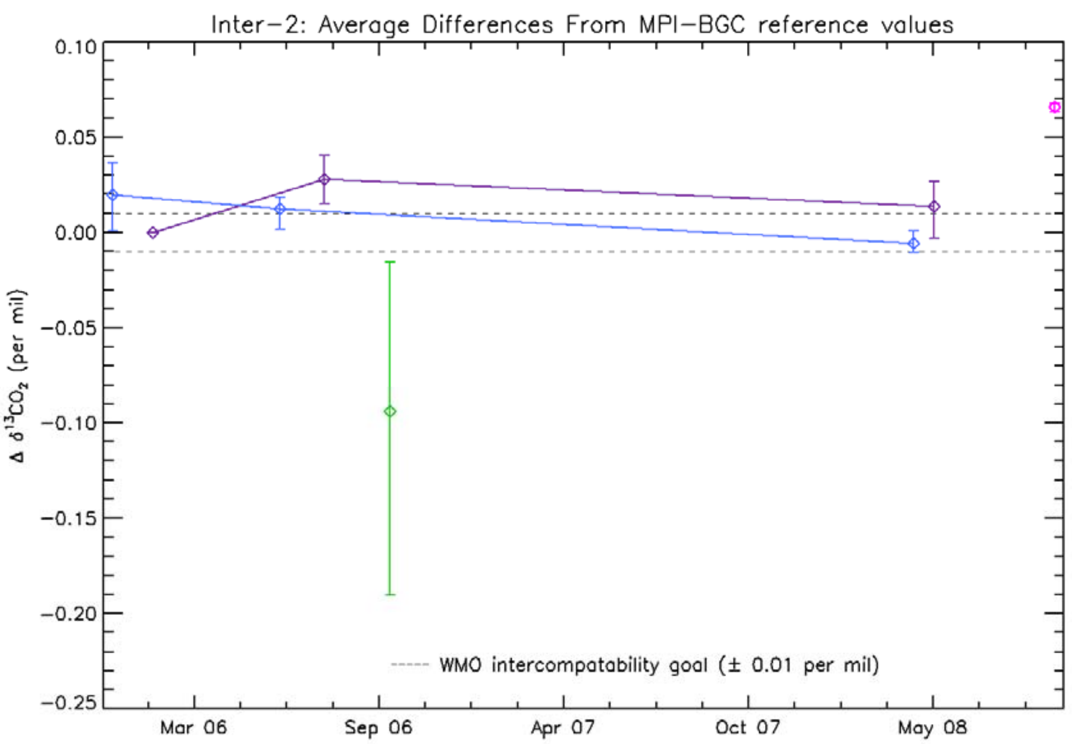

Figure 15: Central laboratory $\delta^{13}C$-CO_2 differences from MPI-BGC in the Inter-2 loop.

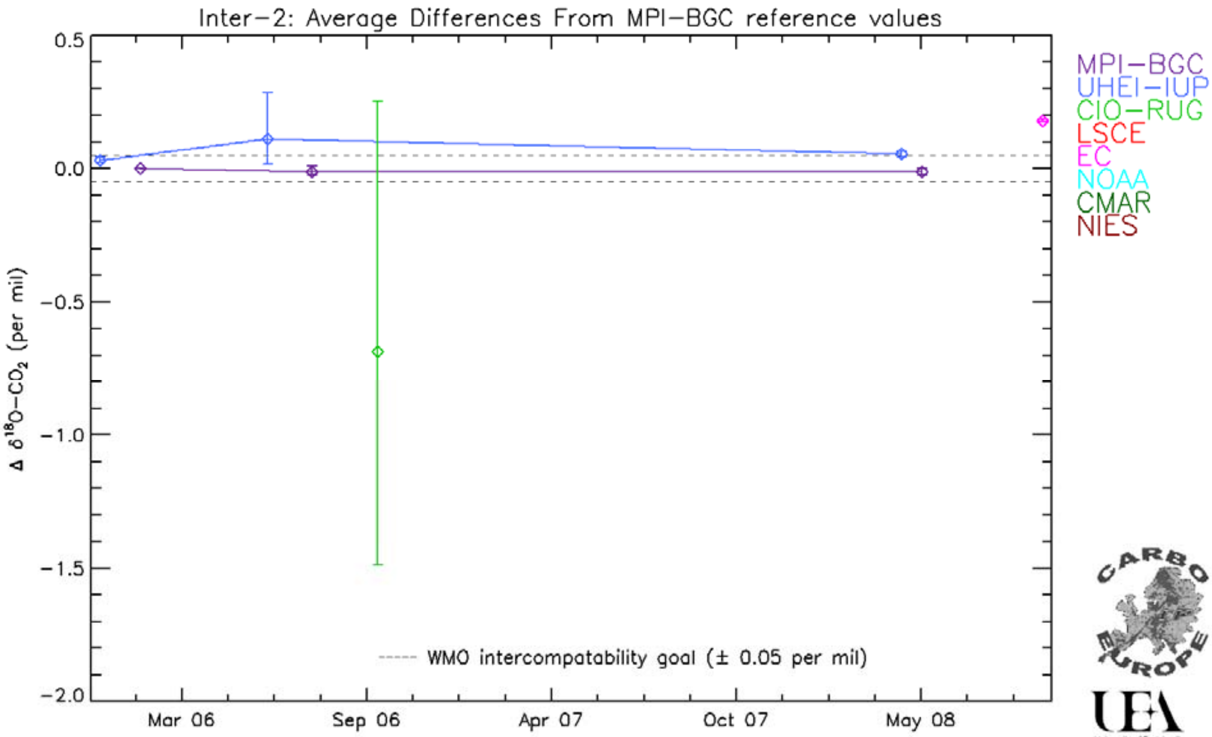

Figure 16: Central laboratory $\delta^{18}O$-CO_2 differences from MPI-BGC in the Inter-2 loop.

<u>**Conclusions and overall assessment:**</u>

The most important conclusion is that, for the first time ever, we have quantified CO_2 concentration comparability offsets between almost all high precision atmospheric CO_2 monitoring stations in Europe. These offsets for all field stations and all species are summarised in Table 1 below. It is important to be aware that this table presents only average offsets from each station, and that offsets are reported against different central laboratories depending on the loop which the station belongs to. Table 2 below presents average offsets between the central laboratories, including our non-European partners. Information from this table can assist in making comparisons between field stations in different loops, but again, one must be aware that Table 2 also only presents average offsets. A more thorough comparison would take into consideration the time-history of relative offsets.

A second important conclusion is that it is vital to continue this programme into the future, both to observe how offsets may change over time, and to assist efforts to improve analytical procedures at those stations with larger offsets. The programme has also collected a wealth of information on species other than CO_2, and has provided data comparing the central European laboratories with 4 non-European laboratories, complementing similar intercomparisons between these laboratories made from low pressure flask samples.

After a long and arduous setup, the programme has been running smoothly since early 2008, and continues to this day. The primary problem still remaining is that some participants are too slow in submitting their data. With CarboEurope IP having terminated, the programme now receives support from the EU IMECC programme, and with the expectation that it will be supported by the EU ICOS project in the longer-term future.

Concerning species other than CO_2 (which had not been the primary focus of this programme) there are a few small issues which need to be improved, for example, the very high CO cylinder in Inter-2. Inter-1 and Euro-3 each have one cylinder with very low O_2/N_2 values, significantly outside of all calibration scales. As yet, however, it has not been resolved if this presents problems for the O_2/N_2 intercomparisons (O_2/N_2 measurements generally have a very high linearity). The validity of SF_6 intercomparisons is limited by anomalously high values exceeding usual calibration ranges in many cylinders. This may contribute to larger offsets in this species. This is not the case for Inter-2 cylinders, however, so can not explain the offsets found in Figure 14 above.

In addition to monitoring, quantifying and attempting to improve offsets between stations, these Cucumber data can also be used in modelling sensitivity studies. One such study has already been carried out in Peters *et al.* [2009], a study of European terrestrial biosphere carbon fluxes constrained by atmospheric observations. Table 3 below shows the CO_2 data that were used in the Peters *et al.* [2009] "O4" sensitivity simulation. In this table, all station offsets are shown relative to MPI-BGC. For stations which do not have MPI-BGC as their central laboratory, these offsets were calculated by incorporating average inter-laboratory offsets from the Inter-1 and Inter-2 loops. As shown in Table 2, in the particular case of CO_2, these offsets are very small. It is important to note that, as for Tables 1 and 2, this table presents only averaged "snapshots" of the offsets between stations and the central laboratories.

Table 1: Summary of all field station offsets from central laboratories.

	Station:	TTA	NOR	PAL	ZEP	HYY	TRN	PUY	KAS	HUN	LUT	OXK	BIK	MHD	PRS	CMN	LAM	SCH	ZUG	MUE	CBW	WAO
CO_2	avg offset	0.19	0.10	0.05	-0.20	0.06	-0.12	-0.34	0.41	0.04	0.01	-0.17	-0.21	-0.03	-0.02	0.12	-0.19	-0.07	-0.06	-0.68	-0.07	-0.09
	std dev	0.05	0.22	0.02	0.10	0.02	0.05	0.18	0.15	0.12	0.12	0.51	0.05	0.04	0.00	0.03	0.04	0.18	0.05	0.19	0.10	0.13
	number	1	1	1	1	1	1	1	1	1	1	1	2	1	1	1	1	2	1	2	1	2
CH_4	avg offset	2.84		0.53			3.58		-0.77	1.74	-1.48	0.69	0.92		0.26			-0.27	-1.54		1.28	
	std dev	0.90		0.33			11.46		0.66	0.21	0.70	1.08	0.31		3.49			1.18	0.30		1.33	
	number	1		1			1		1	1	1	1	2		1			2	1		1	
CO	avg offset	0.81		4.50							-5.08	0.95	-1.30					-0.86	1.26		-6.43	-0.92
	std dev	0.19		2.80							0.16	1.29	1.22					3.25	0.72		1.44	0.51
	number	1		1							1	1	2					2	1		1	1
N_2O	avg offset	-0.65		-0.25						0.99	-3.12	0.23	-0.10					-0.66	-0.10		0.11	
	std dev	2.40		0.26						0.50	1.37	0.17	0.07					0.31	0.09		0.68	
	number	1		1						1	1	1	2					2	1		1	
SF_6	avg offset	-0.13		-0.15						0.09	0.49	0.09	0.11					0.94	-0.09		0.20	
	std dev	0.11		0.04						0.02	0.37	0.06	0.05					1.13	0.15		0.16	
	number	1		1						1	1	1	2					2	1		1	
O_2/N_2	avg offset											17.82	-7.19									0.78
	std dev											34.65	11.47									12.40
	number											1	2									2
H_2	avg offset	-9.03																			4.85	-1.81
	std dev	2.92																			3.83	1.07
	number	1																			1	1
Central lab:		UHEI	UHEI	UHEI	UHEI	UHEI	LSCE	LSCE	LSCE	LSCE	MPI	MPI	MPI	MPI	MPI	MPI	MPI	MPI	MPI	MPI	MPI	MPI

Units are: CO_2 in ppm; CH_4, CO, N_2O, H_2 in ppb; SF_6 in ppt; O_2/N_2 in per meg; TTA analysers had known problems, now resolved. ZEP analyses were in fact made at the Stockholm University laboratory. "Number" refers to how many analyses have been made at the given station from which the average offset and standard deviation were derived.

The WMO intercomparability goals are:

CO_2	± 0.10 ppm	SF_6	± 0.02 ppt
CH_4	± 2 ppb	O_2/N_2	± 1 per meg
CO	± 2 ppb	H_2	± 2 ppb
N_2O	± 0.1 ppb		

Table 2: Summary of all central laboratory offsets from MPI-BGC.

	Laboratory:	UHEI	LSCE	CIO	UBERN	EnCan	NOAA	CMAR	NIES	MPI
CO_2	avg offset	-0.01	-0.06	-0.08	-0.21	0.00	0.02	0.04	-0.11	-0.01
	std dev	0.04	0.02	0.13	0.43	0.04	0.02	0.05	0.03	0.01
	number	4	2	7	2	2	2	1	1	3
CH_4	avg offset	-0.42	0.31	0.39		0.26	0.04	0.08	3.94	0.18
	std dev	0.57	0.75	0.45		0.32	0.67	0.83	0.33	0.49
	number	4	2	7		2	2	1	1	3
CO	avg offset	-4.59	-7.48	5.18		-0.59	-1.63	-7.66	6.65	0.00
	std dev	3.82	0.71	1.58		2.85	1.70	3.60	2.43	1.41
	number	4	1	7		2	2	1	1	3
N_2O	avg offset	0.14	-0.11			0.06	0.01	0.48	-0.61	0.01
	std dev	0.23	0.68			0.09	0.10	0.30	0.12	0.11
	number	4	2			2	2	1	1	3
SF_6	avg offset	0.15	-0.16			0.07	0.03		-0.01	0.02
	std dev	0.07	0.21			0.03	0.02		0.02	0.01
	number	3	2			2	2		1	3
O_2/N_2	avg offset			-8.64	-17.68					-10.29
	std dev			6.65	40.38					7.32
	number			2	2					2
H_2	avg offset	1.46					-6.90	1.58	16.10	0.44
	std dev	3.51					14.12	0.69	3.29	1.74
	number	4					2	1	1	3
$\delta^{13}C$	avg offset	0.00		-0.16		0.07				0.00
	std dev	0.03		0.13		0.00				0.04
	number	4		3		1				3
$\delta^{18}O$	avg offset	0.02		-0.89		0.18				-0.06
	std dev	0.11		0.60		0.01				0.09
	number	4		2		1				3

- Units are: CO_2 in ppm; CH_4, CO, N_2O, H_2 in ppb; SF_6 in ppt; O_2/N_2 in per meg; $\delta^{13}C$-CO_2 and $\delta^{18}O$-CO_2 in per mil.
- "Number" refers to how many analyses have been made at the given laboratory from which the average offset and standard deviation were derived.
- NIES data are on independent gravimetric scales for CO_2, CH_4, CO, and N_2O.
- EnCan, NOAA, CMAR, and NIES data are from the Inter-2 loop only.
- UHEI and LSCE data are averaged results from the Inter-1 and Inter-2 loops.
- UBERN data are averaged results from the Inter-1 and Euro-3 loops.
- CIO data are averaged results from Inter-1, Inter-2 and in some cases also Euro-3.
- The MPI column gives offsets of reanalyses at MPI-BGC from the initial "declared" values (also determined at MPI-BGC).
- For Inter-2 CO and H_2 results, one high (~900 ppb CO; ~1100 ppb H_2) cylinder has been removed from the calculations. We also note that some concern has been raised regarding the stability of H_2 in US Luxfer cylinders from Scott Marrin Inc., which is where the Inter-2 cylinders were purchased.
- WMO intercomparability goals are as given above, with these additions:
  $\delta^{13}C$-CO_2 ± 0.01 ‰ $\delta^{18}O$-CO_2 ± 0.05 ‰

Table 3: Average field station CO_2 offsets from MPI-BGC, used in model sensitivity study. These are the data that were available in late 2008, when the modelling study was undertaken.

Station	orig. offset lab	Offset/ppm	stddev/ppm
PAL	UHEI	0.03	0.04
HYY	UHEI	0.05	0.03
TRN	LSCE	-0.18	0.05
PUY	LSCE	-0.40	0.18
KAS	LSCE	0.35	0.15
HUN	LSCE	-0.02	0.12
BIK	CIO-RUG	-0.03	0.17
MHD	CIO-RUG	0.15	0.19
PRS*	MPI-BGC	-0.21	0.32
CMN*	MPI-BGC	-0.04	0.28
LAM*	MPI-BGC	-0.22	0.06
SCH	MPI-BGC	0.06	0.02
ZUG	MPI-BGC	-0.06	0.05
CBW	MPI-BGC	-0.13	0.15
WAO	MPI-BGC	-0.09	0.13
UHEI	MPI-BGC	-0.02	0.03

* Unfortunately the misbehaving cylinder in the Euro-4 loop was not identified until after these data were supplied for the modelling study. Ignoring this cylinder would give offsets of -0.02, +0.12, and -0.19 ppm for PRS, CMN, and LAM respectively, as given in Table 1.

Acknowledgements:

The following colleagues have contributed to the analyses of the Cucumbers at the field stations and central laboratories. Their affiliations are given by numbered superscripts which correspond to the affiliations given on the title page, with one further addition listed below: A. Bath[14], Z. Barcza[10], P. van den Bulk[20], A. Chivulescu[11], L. Chmura[19], M. Ernst[11], L. Fialdini[7], G. Forster[1], S. Hammer[3], J. Hatakka[6], D. Heltai[7], M. Hielscher[2], R. Howard[17], F. Haensel[2], K. Katsumata[15], B. Kers[5], A. Lanza[7], A. Macdonald[1], F. De Nile[21], B. Noone[22], S. Piacentino[8], J. M. Richter[2], M. Rothe[2], M. Sabasch[3], U. Schultz[2], D. Sferlazzo[8], G. Spain[23], I. Szilagyi[10], U. Treffert[16], and P. Vestin[14].

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Appendix 1: List of participants

Euro-1

UHEI	University of Heidelberg, GERMANY, Ingeborg Levin
TTA	Tall Tower, Angus, UNITED KINGDOM, John Moncrieff
NOR	Norunda, SWEDEN, Anders Lindroth
HYY	Hyytiälä, FINLAND, Tuula Aalto
PAL	Pallas, FINLAND, Tuula Aalto
ZEP	Zeppelin, NORWAY, Johan Strom

Euro-2

LSCE	Lab. des Sciences du Climat et de l'Environ., FRANCE, Martina Schmidt
TRN	Trainou Tower, FRANCE, Martina Schmidt
PUY	Puy de Dome, FRANCE, Martina Schmidt
KAS	Kasprowy Wierch, POLAND, Kazimierz Rozanski
HUN	Hegyhatsal, HUNGARY, Laszlo Haszpra

Euro-3

CIO-RUG	University of Groningen, THE NETHERLANDS, Rolf Neubert
LUT	Lutjewad, THE NETHERLANDS, Rolf Neubert
OXK	Ochsenkopf, GERMANY, Uwe Schultz
BIK	Bialystok, POLAND, Falk Haensel
JFJ	Jungfraujoch, SWITZERLAND, Markus Leuenberger
MHD	Mace Head, IRELAND, Martina Schmidt

Euro-4

MPI-BGC	Max Planck Institute for Biogeochemistry, GERMANY, Armin Jordan
PRS	Plateau Rosa, ITALY, Francesco Apadula
CMN	Monte Cimone, ITALY, Riccardo Santaguida
LAM	Lampedusa, ITALY, Alcide Giorgio di Sarra

Euro-5

MPI-BGC	Max Planck Institute for Biogeochemistry, GERMANY, Armin Jordan
SCH	Schauinsland, GERMANY, Frank Meinhardt
ZUG	Zugspitze, GERMANY, Ludwig Ries
MUE	La Muela, SPAIN, Josep Anton Morguí
CBW	Cabauw, THE NETHERLANDS, Alex Vermeulen

Inter-1

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UEA-ENV	University of East Anglia, UNITED KINGDOM, Andrew Manning

WAO	Weybourne, UNITED KINGDOM, Michael Patecki
LSCE	Lab. des Sciences du Climat et de l'Environ., FRANCE, Martina Schmidt
UBERN	University of Bern, SWITZERLAND, Markus Leuenberger

Inter-2

UHEI	University of Heidelberg, GERMANY, Ingeborg Levin
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CIO-RUG	University of Groningen, THE NETHERLANDS, Rolf Neubert
LSCE	Lab. des Sciences du Climat et de l'Environ., FRANCE, Martina Schmidt
EnCan	Environment Canada, CANADA, Doug Worthy
NOAA	National Oceanic and Atmospheric Admin., USA, Duane Kitzis
CMAR	CSIRO Marine Atmospheric Research, AUSTRALIA, Paul Steele
NIES	National Institute for Environ. Studies, JAPAN, Toshinobu Machida

Appendix 2: Protocols

A) Cucumber cylinder analysis protocols

1. Immediately email your "Responsible Scientist" to notify receipt of shipment (Responsible Scientists are listed at the end of this document). You now have **4 weeks** to complete all analyses and to ship the cylinders to the next participant.
2. Position the cylinders in your laboratory, ensuring that there are no significant heat sources near the cylinders (for example, cryo-chillers, air conditioners, heaters).
3. Remove cap nuts from the cylinders (with 27 mm wrench). Note: these caps have been installed both to prevent and test for leaks. A leak could be present if you have severe difficulty removing the cap. In such a case, please inform your Responsible Scientist immediately.
4. Check the white plastic gasket (PCTFE) on the regulator DIN14 connectors for scratches or damage. If it is necessary, replace the gasket using a new gasket which you can find underneath the foam cube (below the regulator) in the high concentration Cucumber box. Please also inform your Responsible Scientist, if you replace any of the gaskets. If there are no gaskets left, contact Armin Jordan.
5. Install the 3 regulators supplied, and open the cylinders to the high pressure side of the regulators.
6. Record the pressure in each cylinder, noting it in the Cucumber Logsheet Excel file.
7. Make a leak check of the DIN14 regulator connections to the cylinders. This should be done with the regulators at high pressure, with the main cylinder valves closed, and the regulator outlets closed (turn black knobs fully anti-clockwise, with nothing connected to the female Quick Connect on the outlets). Leave this for **at least half a day**, then check for any pressure drop on the high pressure side of the regulators. If the pressure has dropped, then all pressure should be released from the regulator (use the male Quick Connect which was supplied to your lab), and the connection carefully re-tightened (overwinding of the connection will destroy the PCTFE gasket). Then repeat the at-least-half-a-day leak check.
8. If you continue to have difficulty making a leak-tight seal, please do not over tighten. The PCTFE gasket should be examined, and replaced if necessary, for example, if it has become too "flat" (see 4. above). If problems continue, please contact your Responsible Scientist.
9. Now do a pressure flush of the regulators 4 times. This means filling the regulators to the cylinder pressure, closing the cylinders, emptying all air from the regulators (use the male Quick Connect which was supplied to your lab), and then repeating, for a total of 4 times for each cylinder.
10. After installing regulators, leak checking, and pressure flushing, **wait a minimum of 2 days with the cylinders in the same lab where the analyses will take place, and with the high pressure side of the regulator at cylinder pressure, but with the main cylinder valve closed**, before the first analysis from the cylinders. After 2 days, check again for leaks by looking for any pressure drop on the high pressure side of

the regulators. (If your measurements are at a remote field site and do not allow a 2-day wait, please discuss with your Responsible Scientist).

11. Each laboratory should then follow their normal procedures for analysis from unknown high pressure cylinders. Our recommendations are:
    a) Flush between 5 and 10 Litres of air out of each cylinder and regulator (at low flow rate, that is, less than 500 mL/min) before you start your proper analyses.
    b) Perform as high level on-site calibration as possible immediately before or after you analyse the Cucumbers.
12. Each laboratory may conduct more than one analysis from the cylinders, but we ask that no laboratory remove more than a total of 40 Litres of air from each cylinder.
13. If a laboratory conducts more than one analysis, we encourage, if possible, to do them on different days, but ensuring to keep the 4 week deadline.
14. After final analysis, remove the regulators, first noting again the cylinder pressures and writing them on the Logsheet, reinstall the cylinder DIN14 cap nuts, and place cylinders back in their boxes.
15. Ship the cylinders to the next participant in the round robin (if you are not sure who this is, ask your Responsible Scientist – usually it will be as indicated in the schematic below).
16. Email your Responsible Scientist when the cylinders are shipped out to the next participant.

** Please note, for O_2/N_2 analysis, there are a few additional requirements. Contact Andrew Manning if you are not sure about these.

** Inter-2 loop is still with the old CGA-type cylinders, and so protocols should be slightly different where DIN14 specifications are given above.

B) Cucumber cylinder data reporting protocols

1. After analysing a set of Cucumber cylinders, you should report your results to both your Responsible Scientist and to Andrew Manning. There is a **4 week reporting deadline** for these results. We understand that some labs require 6 months or more before they can report final concentration numbers, however, at least provisional numbers are required 4 weeks after analysis.
2. Please use the Excel template provided for reporting your results.
3. Any change or update in concentration data for these analyses should be reported in a new copy of the same Excel template, and sent to your Responsible Scientist and Andrew Manning.
4. CO_2 results are required to be reported in the programme. Reporting (and analysis) of other species is optional.
5. Your analysis results, combined with results from other participants, may be presented at international meetings and workshops. If you have any concerns about this, you should contact Andrew Manning and Philippe Ciais (Philippe.Ciais@cea.fr)

directly.

C) Responsible scientists

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