INFRASTRUCTURE FOR MEASUREMENTS OF THE EUROPEAN CARBON CYCLE

Project no. 026188

IMECC

Infrastructure for Measurement of the European Carbon Cycle

Instrument: Integrated Infrastructure Initiative (I3)

Thematic Priority: Research infrastructures

Deliverable D_NA3_2
Establishment of experimental protocols for each task

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Organisation name of lead contractor for this deliverable:
MPG-Jena, Armin Jordan

NA 3: Experimental Protocols for Intercomparison Activities

NA3.T1 Sausage Flask Intercomparison

Sample Preparation

Every two months 18 flasks (as at September 2007) are connected in series ("Sausage") with two flasks from each participating lab of their regular flask type, and four flasks from the filling lab (MPI-BGC) in a mixed order according to the scheme shown in Figure 1. They are flushed and finally filled with dried ambient air which was compressed into a 50-litre high pressure tank and analysed for trace gas mixing ratios before being used for Sausage filling. Mixing ratios in the tank air used for Sausage flask filling are adjusted to cover a CO_2 range of 360-410 ppm to span a range for three individual Sausages of 20-40 ppm. A drying trap ($Mg(ClO_4)_2$) is mounted before the first flask of a Sausage to remove possible remaining traces of water in the tank air (the dew point of the tank air is normally below -60°C). Each of the three Sausages is flushed once for at least two hours at a flow rate of about 2 litres per minute. Because different laboratories are using different sampling pressures for their routine atmospheric flask samples the Sausage flasks are then pressurised to different pressures. A first set of flasks is filled to 2 bar, a second set to 1.5 bars absolute pressure, whereas the flasks for one group is left at ambient pressure (Figure 1). After this first filling the Sausage flasks are stored for 16 hours (overnight). On the second day the Sausage is flushed again from the same tank for 2 hours and flasks are then finally filled to their respective pressures. They are shipped to the different laboratories with a sheet specifying the Sausage No. and the filling date.

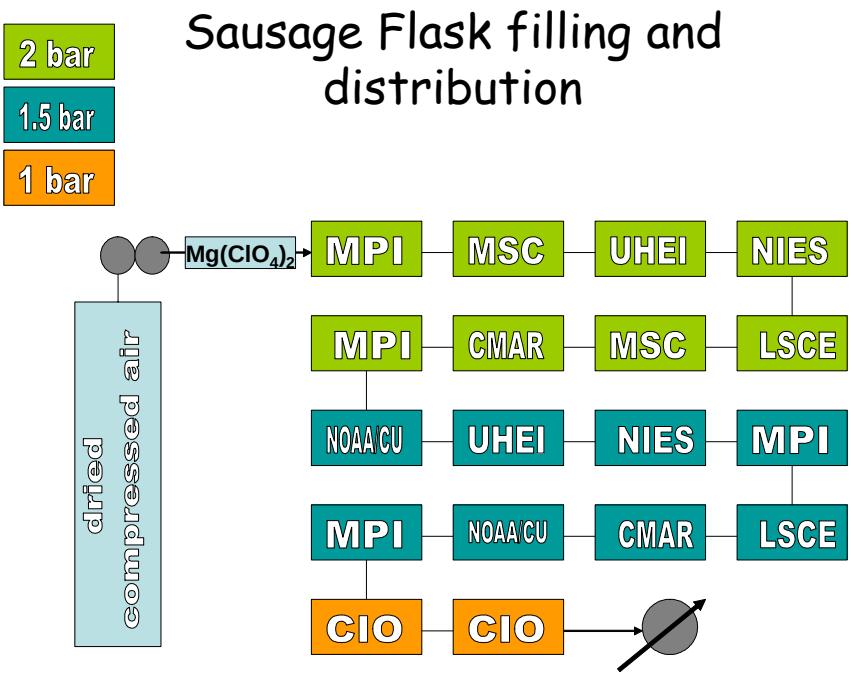


Figure 1: Sausage flask filling scheme at MPI-BGC

Analysis
Soon after receipt of the flasks each laboratory analyses the Sausage samples in the identical way they use to analyse atmospheric field samples for CO_2, CH_4, CO, H_2, N_2O, SF_6, $^{13}CO_2$ and $C^{18}O_2$.

Data Reporting
The analysis results for the Sausage samples are to be reported within about two months. Due date is the end of the following month after the arrival of the sausage set. The report file has to be submitted as a space separated text-file to martina.schmidt@ispl.lsce.fr in the format specified below.

```
Site Year MO D h mm Flask id F CO2(ppm) Flag In Year Mo D h mm pres Range
ICP 2002 02 22 12 00 0E326-27 D  387.416 ... GC 2002 04 30 11 13    6 H ICP   1
ICP 2002 02 22 12 00 0E326-27 D  387.429 ... GC 2002 04 30 11 18 -999 H ICP   1
ICP 2002 02 22 12 00 0E188-27 D  387.379 ... GC 2002 04 30 11 22 -999 H ICP   1
ICP 2002 02 22 12 00 0E188-27 D  387.383 ... GC 2002 04 30 11 27 -999 H ICP   1
ICP 2002 02 22 12 00 00E45-27 D  371.503 ... GC 2002 04 30 12 10 -999 M ICP   1
ICP 2002 02 22 12 00 00E45-27 D  371.507 ... GC 2002 04 30 12 15 -999 M ICP   1
ICP 2002 02 22 12 00 0E492-27 D  366.607 ... GC 2002 04 30 13 08 -999 L ICP   1
ICP 2002 02 22 12 00 0E492-27 D  366.573 ... GC 2002 04 30 13 13 -999 L ICP   1
ICP 2002 02 22 12 00 0E297-27 D  371.530 ... GC 2002 04 30 13 18 -999 M ICP   1
ICP 2002 02 22 12 00 0E297-27 D  371.595 ... GC 2002 04 30 13 22 -999 M ICP   1
ICP 2002 02 22 12 00 0E479-27 D  366.530 ... GC 2002 04 30 14 06 -999 L ICP   1
ICP 2002 02 22 12 00 0E479-27 D  366.494 ... GC 2002 04 30 14 10 -999 L ICP   1
ICP 2002 04 25 12 00 0E534-27 D  370.496 ... GC 2002 06 12 18 15 -999 M ICP   2
ICP 2002 04 25 12 00 0E534-27 D  370.531 ... GC 2002 06 12 18 20 -999 M ICP   2
ICP 2002 04 25 12 00 0E118-27 D  370.639 ... GC 2002 06 12 18 25 -999 M ICP   2
ICP 2002 04 25 12 00 0E118-27 D  370.600 ... GC 2002 06 12 18 29 -999 M ICP   2
ICP 2002 06 27 12 00 0E326-27 D  401.820 ... GC 2002 09 05 14 31 -999 H ICP   3
ICP 2002 06 27 12 00 0E326-27 D  401.874 ... GC 2002 09 05 14 35 -999 H ICP   3
ICP 2002 06 27 12 00 0E188-27 D  401.730 ... GC 2002 09 05 15 19 -999 H ICP   3
ICP 2002 06 27 12 00 0E188-27 D  401.788 ... GC 2002 09 05 15 23 -999 H ICP   3
ICP 2002 08 21 12 00 0E118-27 D  378.133 ... GC 2002 09 11 11 42 -999 L ICP   4
ICP 2002 08 21 12 00 0E118-27 D  378.125 ... GC 2002 09 11 11 46 -999 L ICP   4
```

The contents each column is as follows:
Column 1 has to be "ICP".
The entries in columns 2-6 are filling year, month, day, hour, minute. These entries have to be exactly as written on the sheet enclosed as the software for automatic data comparison matches the sample results using the filling date.
Column 7 reports the flask name.
Column 8 is fixed for Sausage data files as "D" (=decanting).
Column 9 gives the analysis result specified with 3 digits.
Column 10 contains flag information that consists of three characters. The code follows the flagging scheme set by NOAA-GMD: good data points are represented by "...". Any character other than a period "." as first character indicates a problem with the analysis. This data point is then excluded from the comparison.
Column 11 is a two character description of the instrument.
Column 12-16 specify the analysis year, month, day, hour, minute.
Column 17 gives the sample pressure before analysis (mbar).
Column 18 indicates the CO_2 level of the respective Sausage flask. Samples that have the highest CO_2 mixing ratio should be marked "H" with the medium level "M" and the low level of CO_2 "L".
The last column specifies the Sausage number.

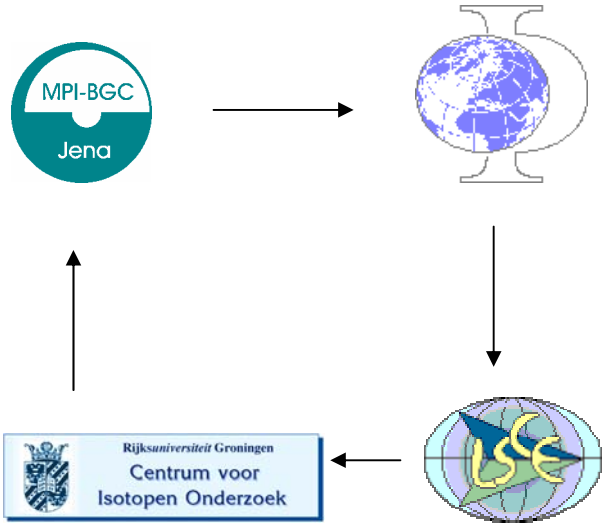
NA3.T2 Grapefruit Flask Intercomparison

Sample preparation

Sets of two different intercomparison samples are prepared in 5 L Duran glas flasks equipped with a single valve sealed with a PCTFE sealing (="Grapefruit flask"). The samples are made with dried, natural air that has been compressed into a 50 L high pressure tank containing CO_2 mixing ratios in the range of its atmospheric abundance (350-410 ppm). A drying trap ($Mg(ClO_4)_2$) is mounted between the source gas tank and the Grapefruit flask to remove possible remaining traces of water in the tank air (the dew point of the tank air is normally below -60°C). The Grapefruit flasks are either completely evacuated prior filling or residual sample from a previous Grapefruit sample is mixed with the new standard gas to obtain different air mixtures. The two Grapefruit samples ("high" and "low") span a CO_2 concentration range of 15-40 ppm. A variation of the CO_2 mixing ratio level is being made by filling the source gas cylinder under different weather conditions. To prepare air samples with subambient concentrations of CO_2 some air is admixed that has been depleted in CO_2. This is achieved by passing the air through big cartridges (1000ccm³) filled with molecular sieve 13X while compressing the air in high pressure.

Circulation

In the beginning of each month the sets of grapefruit flasks are circulated in the constant order MPI-BGC, UHEI, LSCE, CIO.



Each laboratory has 3 weeks for performing the analysis of the intercomparison set before having to forward the set to the next partner. The dates of arrival, analysis and shipment are to be reported on a logsheet that is shipped together with the Grapefruit flasks. At the end a final analysis is made by MPI-BGC. The flask necks have to be sealed with rubber caps after analysis and shipped in dedicated aluminium boxes with special foam inserts to assure the sound condition of the equipment. Both the next participant and the Grapefruit providing lab should be notified on the shipment.

Analysis
The grapefruit flasks shall be analysed in an identical way to any atmospheric air sample. Each group should measure and report the pressure of the incoming flask on the logsheet. The maximum amount of sample volume each laboratory may consume is 800 ml.

Data Reporting
The analysis results for the Grapefruit samples are to be reported within one month after the sending deadline that is two months after receipt of the Grapefruits samples. The report file has to be submitted as a space separated text-file to martina.schmidt@ispl.lsce.fr in the format specified below:

```
Site Year MO D  h  mm Flaskid F CO2 (ppm) Flag In Year Mo D  h mm pres Range GRF#
GPF 2005 02 18 12 00 45-J3079 D  354.721 ..1 G1 2005 03 10 00 32   1620 l Grapefruit 01
GPF 2005 02 19 12 00 45-J3070 D  398.102 ..1 G1 2005 03 10 00 46   1610 h Grapefruit 01
GPF 2005 02 18 12 00 45-J3086 D  354.673 ..1 G1 2005 04 22 13 04   1530 l Grapefruit 02
GPF 2005 05 10 12 00 45-J3085 D  397.892 ..1 G1 2005 05 10 15 59   1900 h Grapefruit 02
GPF 2005 02 19 12 00 45-J3040 D  354.702 ..1 G1 2005 05 06 12 44   1400 l Grapefruit 03
GPF 2005 02 18 12 00 45-J3063 D  398.368 ..1 G1 2005 05 06 12 30   1390 h Grapefruit 03
GPF 2005 02 19 12 00 45-J3084 D  397.291 ..1 G1 2005 08 30 01 49   1100 h Grapefruit 04
GPF 2005 11 08 12 00 45-J3088 D  382.793 ..2 G1 2006 05 24 01 50   1650 l Grapefruit 05
GPF 2005 11 08 12 00 45-J3088 D  382.740 ..1 G1 2005 11 08 19 35   1910 l Grapefruit 05
GPF 2005 11 08 12 00 45-J3090 D  389.571 ..1 G1 2005 11 08 23 56   1910 h Grapefruit 05
GPF 2005 11 08 12 00 45-J3090 D  389.513 ..2 G1 2006 05 24 01 23   -999 h Grapefruit 05
GPF 2005 11 08 12 00 45-J3089 D  382.711 ..2 G1 2006 06 01 22 02   1660 l Grapefruit 06
GPF 2005 11 08 12 00 45-J3091 D  389.644 ..1 G1 2006 06 01 22 16   1900 h Grapefruit 06
GPF 2005 11 08 12 00 45-J3089 D  382.751 ..1 G1 2005 11 09 00 09   1900 l Grapefruit 06
GPF 2006 01 10 12 00 45-J3087 D  387.017 ..1 G1 2006 01 11 16 24   1740 h Grapefruit 07
GPF 2006 01 10 12 00 45-J3087 D  386.987 ..2 G1 2006 06 15 15 46   1400 h Grapefruit 07
GPF 2006 01 09 12 00 45-J3086 D  345.964 ..2 G1 2006 06 15 15 59   1280 l Grapefruit 07
```

The contents each column is as follows:
Column 1 has to be "GPF".
The entries in columns 2-6 are filling year, month, day, hour, minute. These entries have to be exactly as written on the sheet enclosed as the automatic data comparison by the software matches the sample results that have to be compared using the filling date.
Column 7 reports the flask name.
Column 8 specified the filling strategy and is fixed for Grapefruits as "D" (=decanting).
Column 9 gives the analysis result specified with 3 digits.
Column 10 contains flag information that consists of three characters. The code follows the flagging scheme set by NOAA-GMD: good data points are represented by "...". Any character other than a period (".") as first character indicates a problem with the analysis. This data point is then excluded from the comparison.
Column 11 is a two character description of the instrument.
Column 12-16 specify the analysis year, month, day, hour, minute.
Column 17 gives the sample pressure before analysis (mbar).
Column 18 indicates whether the flask contains the grapefruit sample with the higher level of CO_2 ("h") or with the lower level of CO_2 ("l").
Column 19 specifies the Grapefruit number.

NA3.T3 Cucumber cylinder High pressure inter-comparison

Sample Preparation
Dried, natural air is filled into a 20 L high pressure cylinder ("Cucumber cylinders") using a Rix compressor. Each cucumber set consists of three cylinders that contain CO_2 levels of 360, 380, and 400 ± 5 ppm, respectively. These CO_2 mixing ratio levels are obtained primarily by filling under different weather conditions and are then adjusted by dilution or spiking. Dilution is being made with air that has been depleted in CO_2 by passing the air through big cartridges (1000ccm³) filled with molecular sieve 13X while compressing the air.
Spiking of the air with additional CO_2 or other compounds is made using the spiking system built at the MPI-BGC (see Figure 2). The procedure is as follows:
After filling the cylinder with outside air a first analysis is made. The remaining amount of CO_2 that is needed to meet the target concentration is calculated. To add this amount of gas a precisely calibrated volume is filled with CO_2 to the pressure. This CO_2 is then transferred with a small amount of compressed air. After allowance is made for good mixing within the cylinder, it is then re-analyzed.

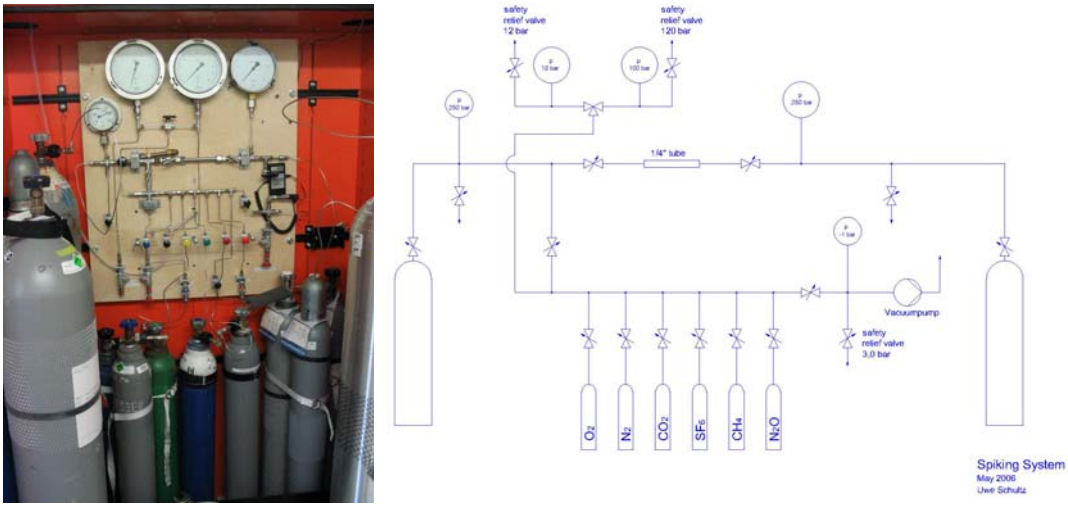


Figure 2: Spiking system for adjustment of mixing ratios in natural air samples

Circulation
There are seven sets of each three cucumbers. Each set is linking a group of laboratories and stations (Euro-1 to Euro-5 loop, Inter-1 and Inter-2 loop). Each of the Euro-loops has a central laboratory that is part of the Inter-loops and the NA3.T1 and NA3.T2 exercises to ensure the comparability of intercomparison data from the different Euro loops. The grouping of these "loops" and the order of rotation is depicted in Figure 3.

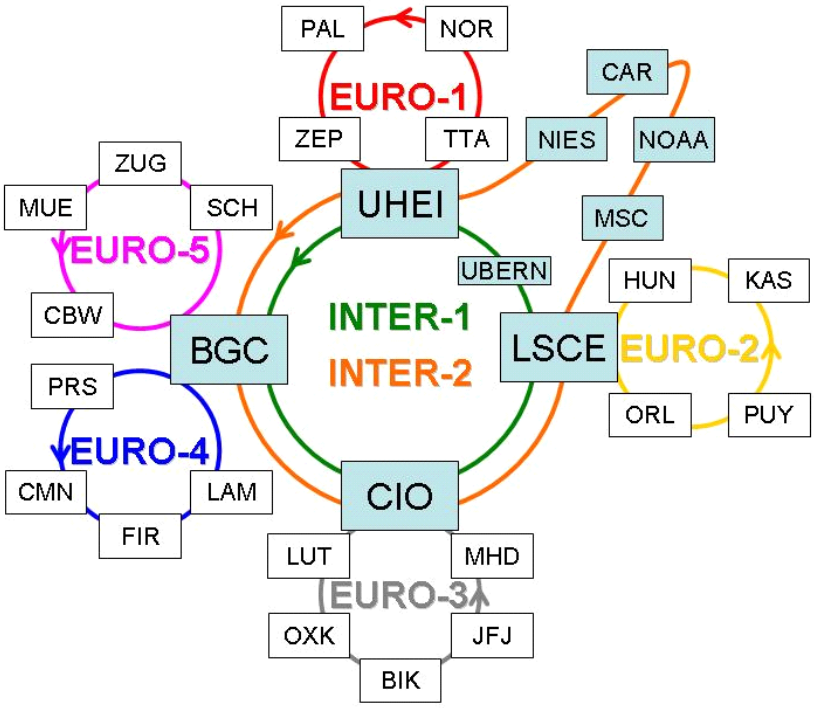


Figure 3: Circulation scheme for Cucumber samples in different loops. The stations and laboratories included are (station name, institution responsible, country of the staion site): UHEI = University of Heidelberg, TTA = Tall Tower Angus, University of Edinburgh (UK); NOR = Norunda tower, University of Stockholm (Sweden); PAL = Pallas, Finnish Meteorological Institute; ZEP = Zeppelin station, Spitsbergen (Norway), University of Stockholm; SCH = Schauinsland, Umweltbundesamt (Germany); ZUG = Zugspitze, Umweltbundesamt (Germany); MUE = La Muela, University of Barcelona (Spain); CBW = Cabauw, ECN (Netherlands); PRS = Plateau Rosa, CESI (Italy); CMN = Monte Cimone, IMS (Italy); LAM = Lampedusa, ENEA (Italy); FIR = Firenze, UNITUS (Italy); CIO= Centre for Isotope Research University Groningen (Netherlands); LUT = Lutjewad, CIO (Netherlands); OXK = Ochsenkopf, MPI-BGC (Germany); BIK = Bialystok , MPI-BGC (Poland); JFJ = Jungfraujoch, University of Bern (Switzerland); MHD = Mace Head, LSCE (Ireland); ORL = Trainou tower, LSCE (France); PUY = Puy de Dome, LSCE (France); KAS = Kasprowy Wierch, University of Krakow (Poland); HUN = Hegyhatsal, Hungarian Meteorological Service (Hungary); MSC = Meteorological Service of Canada/Environment Canada; NOAA = Global Monitoring Devision, National Atmospheric and Oceanic Administration (USA); CAR = CSIRO Marine and Atmospheric Research (Australia); NIES = National Institute for Environmental Studies (Japan)

Each cucumber is shipped in a dedicated aluminium box equipped with a special foam insert to assure the sound condition of the equipment.
Upon receipt of a set of cylinders each participant has to immediately email the central laboratory of the respective loop to notify receipt of the shipment. Within 4 weeks all analyses should be completed and after final analysis the cylinder pressures should be noted again. The pressure regulators should be removed and capped at both ends before

being placed in the cylinder boxes. After reinstalling the cylinder plugs the cylinders should be put back in their boxes.
The cylinders then have to be shipped to the next participant in the round robin according to the rotation plan. For shipment addresses the central laboratory of the loop should be contacted. The subsequent laboratory should be enquired whether it is prepared to receive the cucumbers and notified when the cylinders are shipped out to the next participant. In case the next participant is unavailable the further proceeding should be discussed with the central laboratory.

Analysis

The cylinders should be positioned in the laboratory ensuring that there are no significant heat sources near the cylinders (for example, cryo-chillers, air conditioners, heaters). The supplied regulators should be mounted on the 3 cylinders, and the main valves opened to check the pressure in each cylinder. This should be noted in the Cucumber Logsheet Excel file. The pressure regulators should be stored under high pressure with the main cylinders valve shut and closed regulator outlet for at least half a day and checked for a pressure drop. If the pressure has dropped the pressure should be released and the connection carefully tightened (overwinding of the connection will destroy the PCTFE gasket). The leak test should be repeated. If the problem persists the PCTFE seal should be examined. In case it needs to be replaced the contact person of the respective loop should be informed immediately. A replacement gasket can be requested from MPI-BGC (ajordan@bgc-jena.mpg.de). If the connections are leak tight the regulators should be "pressure flushed" four times. This means filling the regulators to the cylinder pressure, closing the cylinders and emptying all air from the regulators. This should then be repeated for a total of four times for each cylinder. After installing the regulators, leak checking, and pressure flushing, the cylinders should be kept for a minimum of two additional 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, before the first analysis from the cylinders is made. (If your measurements are at a remote field site and do not allow a 2-day wait, this should be discussed with the contact person of the loop).

Each laboratory should then follow their normal procedures for analysis from unknown high pressure cylinders. The recommended procedure is:

- Flushing of 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 the start of the proper analyses.
- Performing of a high level on-site calibration immediately before or after analyses of the Cucumbers.
- Repetition of the analysis from the cylinders on different days, if this remains in compliance with the shipment deadlines and a maximum consumption of a total of 40 litres of air from each cylinder.

Data Reporting

The analysis of CO_2 results (and optionally other species data) for the Cucumber samples are to be reported within one month after the sending deadline that is two months after official receipt of the cucumbers. The data should be sent both to the central laboratory of the respective loop and to Andrew Manning. The expectation of calibration updates should not delay the data reporting but provisional numbers are required 4 weeks after analysis that may be updated later.

The reporting has to be done using an Excel template that is provided on the intercomparison webpage that can be accessed from http://www.imecc.org.

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 the central lab of the respective loop and Andrew Manning.

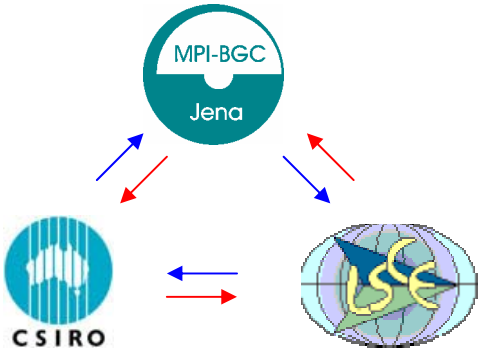
NA3.T4 Loflo high precision CO_2 intercomparison

Sample preparation

Sets of each three intercomparison samples are being prepared at MPI-BGC. 20 bar (300 psi) of dried, natural air containing CO_2 at different mixing ratio levels are filled in Essex Cryogenics 4.5 L internally electropolished stainless steel containers from 50 L cylinders filled at 200 bar. A variation of the CO_2 mixing ratios covering the range of its natural atmospheric abundance is achieved mixing ambient air with air that has been depleted in CO_2. This latter is prepared passing the air through big cartridges (1000ccm³) filled with molecular sieve 13X while compressing the air in high pressure cylinders.

Circulation

Two sets of are circulated in opposite direction between MPI-BGC, LSCE, CSIRO-DMAR:



The dates of arrival, analysis and shipment have to be reported on a logsheet that is shipped together with the canisters. Each laboratory has 6 weeks for making the Loflo analysis of the intercomparison set before having to forward the set to the next partner. This will allow a double full circle of each set of samples per year.

The canisters have to be shipped in dedicated aluminium boxes that are equipped with special foam inserts with plugged valves to assure the integrity of the equipment.

Cylinder handling

The cylinder valves are equipped with stainless steel ¼" Swagelok elbow connectors that are attached to stainless steel ¼" Swagelok pipe connections which are sealed with brass plugs. The ¼" Swagelok connectors that link the cylinders with the tubing to the pressure regulators have to be tightened with extreme care to avoid degradation of the seals. In case of a leak at the pipe connection this should be replaced. For other material failure the samples have to be returned to MPI-Jena.

Analysis

Prior to analysis the cylinders are to be connected to the pressure regulators (Tescom two stage 64 series regulator). The regulators have to be flushed three times before being finally pressurized. A leak test has to be performed assuring that the connections are tight. The regulator then is kept under pressure for at least two days prior to analysis. Each group may analyse the sample until a stable signal is reached (accounting for initial

pressure regulator effects) provided a total volume of 10 L per occasion is not exceeded (corresponding to 2 bar / 30 psi pressure decrease).

Data Reporting
The analysis results for the are to be reported within one month after the sending deadline that is three months after the official receipt of the . The report file has to be submitted to martina.schmidt@ispl.lsce.fr in the format that can be downloaded from the IMECC webpage.