

InGOS: Questionnaire for evaluation of "historic" and recent Non-CO₂ Greenhouse Gases measurements in Europe

In preparation of the first workshop on evaluation of historic non-CO₂ data, which will take place in Heidelberg in March 2012, we promised to compile a questionnaire preparing the information needed for each individual station to re-evaluate its time-series and estimate their uncertainty. It was requested at the Haarlem meeting to distribute, together with the empty template, a filled-in template of the questionnaire which you find below for the Heidelberg measurement site. The questionnaire aims to be usable for different calibration strategies but some aspects of your individual calibration approach might be missing. Please include any information you think might be useful for the purpose of correcting the historic data.

1. System overview

Table 1 contains basic information on the periods where data are available, on the used instrumentation as well as rough estimates of the measurement reproducibility for each species. The calibration strategy used for GC measurements has direct implications on data evaluation and correction. Most evaluation strategies of GC measurements have to address three main issues: a) slightly varying sample amounts caused by changing environmental parameters like e.g. atmospheric pressure and laboratory temperature, b) the instrument response functions, which might be nonlinear and could change in time and c) the accurate assignment of peak area or peak height to the corresponding mole fraction. Widely used calibration strategies in our community are:

i. Instrument response function (IRF):

The instrument response functions are determined frequently (e.g. daily) via a set of calibrated tanks, hereafter referred to as "response function standards" (RFS). The response function links peak area/height to the corresponding calibrated mole fraction, considering the nonlinearities of the instrument. Potential temporal changes of the nonlinearities are accounted for by the high frequency of the IRF determinations. To account for short-term environment changes in the laboratory a hereafter called "working -tank¹" (WT) is measured alternating to the samples. This working tank is afterwards used to normalize the sample signals.

ii. Single working standard (WS):

A calibrated working standard is measured alternating to the samples to track changes in the laboratory environment. All sample measurements are normalised with respect to WS. This corresponds to a single point calibration neglecting any nonlinearities or cross-

¹ In contrast to a working-STD the concentration of a working tank is not used for data evaluation. In some laboratories this working tank is referred to as target tank. We promote the usage of the term "working tank" since in the WMO terminology a target tank is a quality assurance tank which is treated as an unknown sample.

sensitivities of the system. The instrument response function has to be determined in dedicated nonlinearity/cross-sensitivity experiments using a suitable range of calibrated tanks. The temporal stability of the nonlinearities/cross-sensitivities has to be checked frequently.

iii. Multiple working standards (MWS)

Similar to the single working standard approach, several calibrated working standards are measured alternating with the sample. These measurements are used to track the environmental changes in the laboratory. In contrary to the single WS approach a multi-point calibration can be performed which thus includes a certain share of the instrument response function. Depending on the number of the WS used and the actual shape of the instrument response function further nonlinearity corrections may or may not be required.

iv. ...

If your laboratory uses a different calibration strategy, we will add it to the list above. A detailed description of your calibration strategy shall be given in section 4. In addition to this, the calibration scales, the covered ranges, as well as the number of primary laboratory standards have to be specified in Table 1. If additional nonlinearity corrections are applied, please list them as well.

Information concerning data quality assurance is summarized in the third block. Please state your target gas measurement frequency and procedure. List any other quality assurance measures available at your site like e.g. secondary targets or co-located flask measurements.

Please indicate in the last block in which inter-comparison activities your station regularly participates.

Table1: Overview of the GC system, the available data periods, calibration and QC strategies.

| | | | | |
|---|--|---|--|--|
| Station Name: | Heidelberg | | | |
| Responsible Scientist: | Samuel Hammer | | | |
| Organisation: | UHEI-IUP | | | |
| Email: | shammer@iup.uni-heidelberg.de | | | |
| | Methane: | Nitrous Oxide: | Sulfur Hexafluoride: | Hydrogen: |
| Start of measurements: | 1996, ongoing | 1996, ongoing | 1998, ongoing | 2005, ongoing |
| Instrument type: | HP5890II_FID | HP5890II_ECD | HP5890II_ECD | RGA-3 |
| Drying system: | Cryocooler -40°C | Cryocooler -40°C | Cryocooler -40°C | Cryocooler -40°C |
| 1σ reproducibility first year: | 4 | 0.5 | 0.15 | 5 |
| 1σ reproducibility today: | 3 | 0.1 | 0.15 | 3 |
| Calibration | | | | |
| Calibration scheme: | single working STD | single working STD | single working STD | single working STD |
| Calibration scale: | WMO 2004-CH4 | WMO 2006 | Heidelberg | MPI 2009 |
| Calibrated range: | 1764 to 1935 ppb | 307 to 327 ppb | 2.2 to 15.8 ppt | 220 to 822 ppb |
| No. of primary lab. standards 1st year: | 1 | 1 | 1 | 6 |
| No. of primary lab. standards today: | 6 | 5 | 4 | 6 |
| Frequency of working STD/tank measurements: | 15min | 15min | 15min | 15min |
| Measurement pattern: A=ambient, WS(n)=working STD, WT=working tank | WS-A-A-WS-A-A-... | WS-A-A-WS-A-A-... | WS-A-A-WS-A-A-... | WS-A-A-WS-A-A-... |
| Frequency of response func. measurements: | two-monthly | two-monthly | monthly | monthly |
| No. of calibrated mole-fractions for resp. func. det. | 6 | 5 | 10 | 10 |
| Shape of the nonlinearity correction: | none | linear in this range | none | exponential-linear |
| Quality assurance checks: | | | | |
| Target gas: | Target gas since 1996 at least 6 inj.per day | Target gas since 1996 at least 6 inj. per day | Target gas since 2004 at least 6 inj.per day | Target gas since 2005 at least 6 inj.per day |
| Additional target gases: | mid 2002 at least 6 inj. every 2nd week | mid 2002 at least 6 inj. every 2nd week | mid 2002 at least 6 inj. every 2nd week | mid 2005 at least 6 inj. every 2nd week |
| co-located flask measurements: | no | no | no | no |
| ... | | | | |
| Intercomp. activities at the | | | | |
| Cucumbers | Yes | Yes | Yes | Yes |
| WMO Round Robin | Yes | Yes | Yes | Yes |
| IHALICE | Yes | Yes | Yes | No |
| Sausages | Yes | Yes | Yes | Yes |

3. Nonlinearities and cross-sensitivities.

The extent of the nonlinearity corrections (NLC) depends on each individual GC system as well as on the chosen calibration strategy. Depending on the shape of the instrument response function a different number of calibration points is needed to describe the NLC adequately. Basic information on the determination and handling of the NL correction functions is listed in Table 3.1.

Table 3.1: NL corrections

| <i>Nonlinearity in the ambient range</i> | | | | |
|--|------------|-------------------|-----------------------|--------------------------------|
| | CH4 | N2O | SF6 | H2 |
| shape of the NL | no NL | linear function | currently not applied | exponential-linear combination |
| method used to derive correction function | n/a | tank measurements | n/a | dynamic dilution |
| No. of tanks or dilution steps | n/a | 6 | n/a | 10 |
| Is the NL constant in time? | n/a | yes | n/a | no |
| Frequency of NL measurements or checks | n/a | two-monthly | n/a | monthly |

To which extent, if at all, your GC system is subject to cross-sensitivities depends on the chromatographic separation of the investigated species. Especially for N₂O, cross-sensitivities to CO₂ and/or SF₆ can be significant. Testing and quantifying the CO₂-cross-sensitivity can be done by scrubbing CO₂ from a tank using Ascarite. Quantifying the SF₆ cross-sensitivity is more complicated and requires for example a set of tanks with different SF₆ concentrations but similar N₂O concentrations. This latter approach is currently tested by LSCE. To estimate the potential influence of the SF₆ cross-sensitivity to N₂O it is helpful to check the chromatograms, e.g. if similar baseline levels are reached for a range of SF₆ concentrations. An example with very high SF₆ mole fractions is shown in Figure 3.1.

If applicable, please provide a similar example for your system as well.

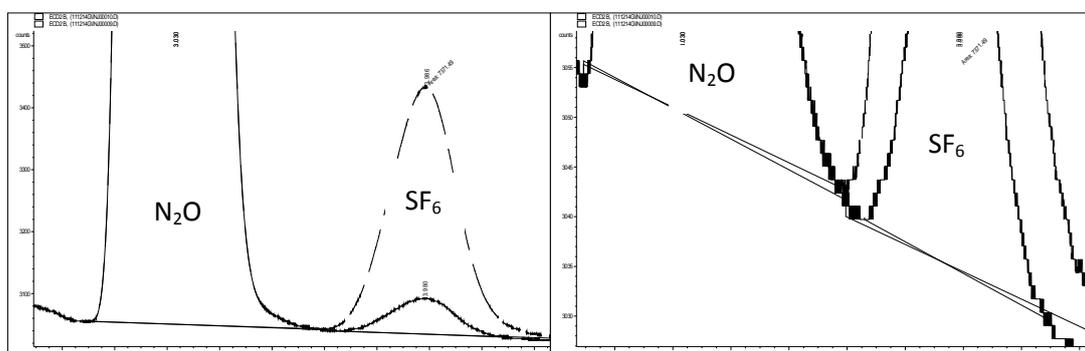


Figure 3.1: Comparison of two ECD chromatograms with different SF₆ concentrations. The solid line corresponds to a sample with 7ppt whereas the dashed line represents ~50ppt. The right picture shows a zoomed version. No interference from SF₆ to N₂O was found.

In Table 3.2 general information on the cross-sensitivities of your GC system are summarised.

Table 3.2: Cross-sensitivities

| <i>Cross-sensitivities</i> | | | | |
|---|------------|------------------------------------|------------|-----------|
| | CH4 | N2O | SF6 | H2 |
| Are cross-sensitivity known? | no | yes | no | no |
| Are cross-sensitivity corrections applied? | no | yes | no | no |
| If yes, which are the interfering substances? | n/a | CO2 | n/a | n/a |
| Were dedicated experiments performed in order to determine the x-sens? How often? For which substance? | n/a | Once (1998) for CO2 using Ascarite | no | no |
| Are new x-sens experiments planned? For which interfering substance? | n/a | yes (CO2) using Ascarite | n/a | no |
| | | | | |

4. Calibration strategy

Please describe your calibration procedure to derive the mole fractions for an unknown sample. This section will depend very much on your chosen calibration strategy:

Heidelberg: Single working standard

For **CH₄** and **SF₆**, where no nonlinearity or cross-sensitivity corrections are applied, the calibrated mole-fractions are derived according to Eq. 1 only:

$$C_{sample} = C_{WS} \cdot \frac{A_{sample}}{A_{WS(interpolate)}} \quad \text{Eq. 1}$$

here $A_{WS(interpolate)}$ is the linearly interpolated area of the two bracketing WS measurements which are 15min apart.

For **H₂** in addition to Eq. 1 the nonlinearity correction is accounted for by using the following equation with parameters p1 to p4 being determined in dedicated NL determinations (Table3.1).

$$\Delta H_2 = p1 * \exp\left(-\frac{H_2 \text{ meas}}{p2}\right) + p3 + p4 * H_2 \text{ meas}$$

For **N₂O** in addition to Eq. 1 the CO₂-cross-sensitivity and the nonlinearity of the detector are taken in to account. Thus first correction due to the CO₂-cross-sensitivity is estimated by using the difference in CO₂ between sample and WS:

$$\Delta N_2O_{CO2corr} = a \cdot (CO_{2(WS)} - CO_{2(sample)}) + b$$

Thereafter the ECD nonlinearity correction is accounted for by using again a linear function:

$$\Delta N_2O_{NL} = \alpha \cdot N_2O_{CO2corr} + \beta$$

Temporally changing primary scales raise the necessity to perform additional scale corrections especially for historic data. These scale corrections are calculated for each WS based on the measurements of the primary laboratory standards.

5. Internal Quality Assurance

This is the most important part of this questionnaire; please compile your data in a similar way.

For each species the target measurements and, if available, the sub-target measurement, should be compiled in a uniform manner. Since the mole fractions of the individual target cylinders might differ from each other, plotting the deviation from the mean mole fraction of each cylinder is advised. The graph should contain ambient air measurements as well (upper panel of the Figures), in order to link potential drifts or jumps in the ambient air record to concurrent target measurements.

In addition to this, the graph should highlight changes of working standards and targets and should provide a rough indication of the target gas concentrations.

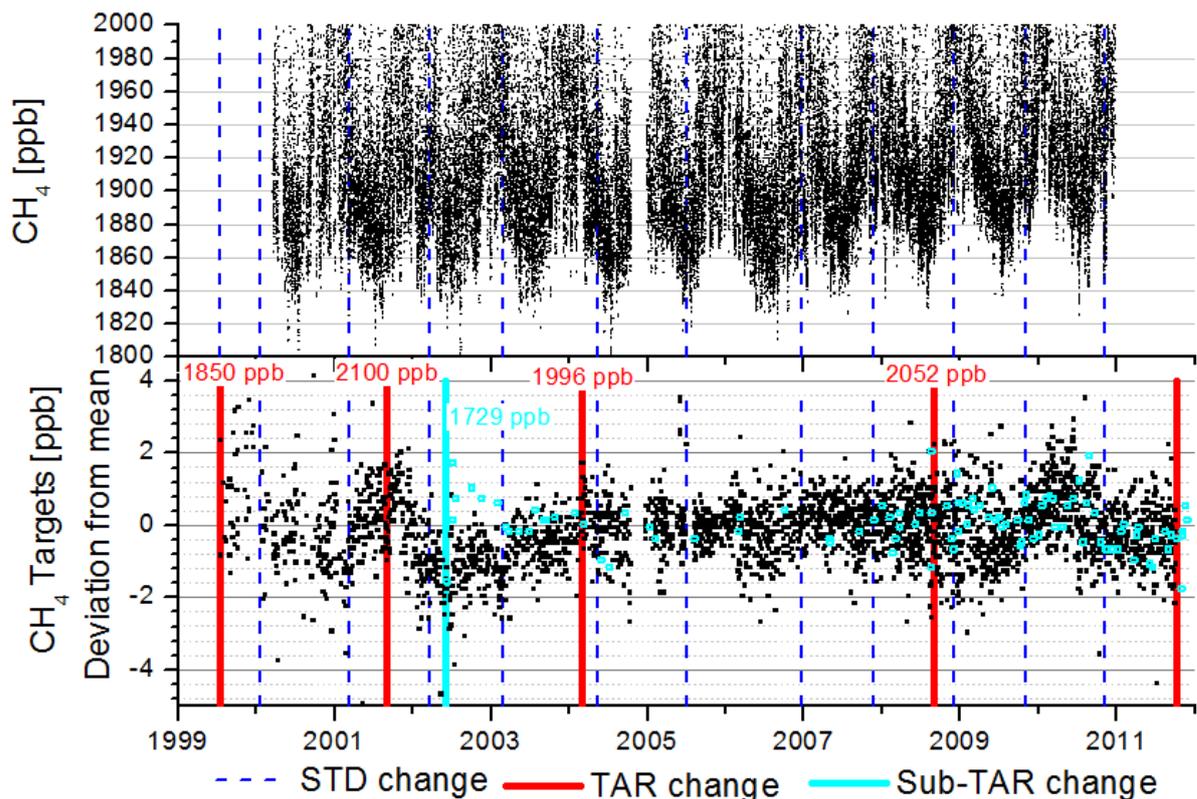


Figure 4.1: Methane ambient air measurements and target gas deviations from the mean value. Dashed lines represent WS changes.

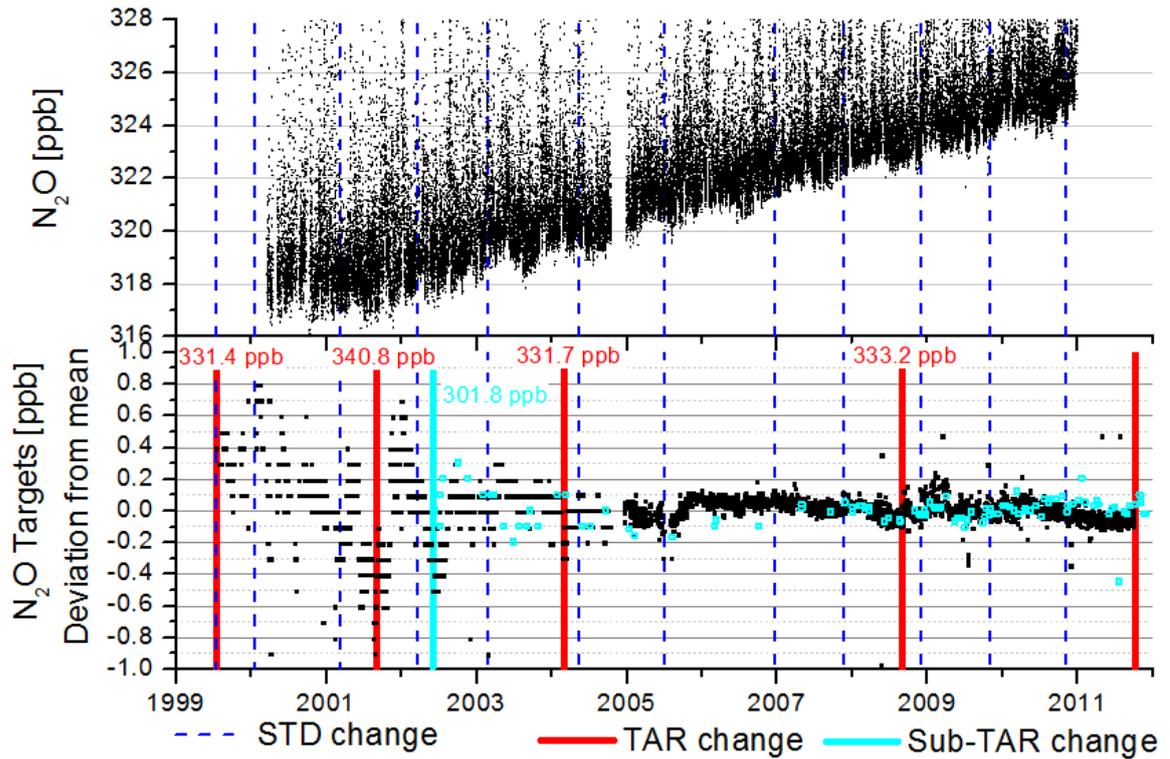


Figure 4.2: Nitrous Oxide ambient air measurements and target gas deviations from the mean value. Dashed lines represent WS changes.

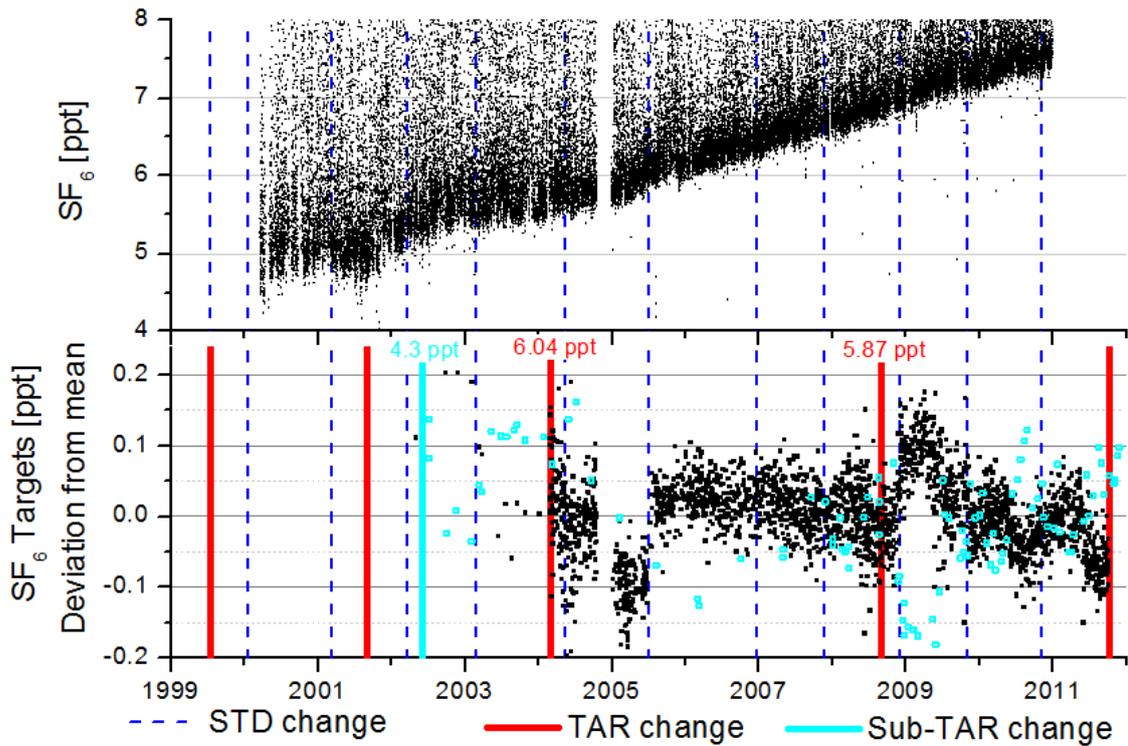


Figure 4.3: Sulfur Hexafluoride ambient air measurements and target gas deviations from the mean value. Dashed lines represent WS changes.

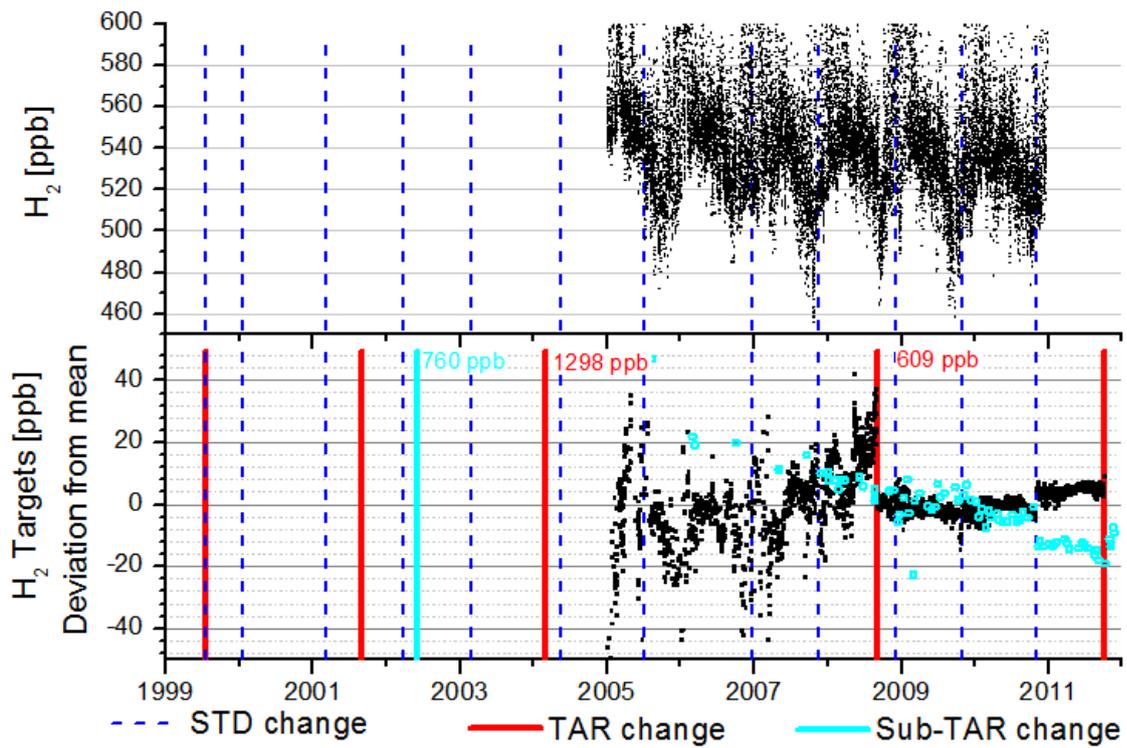
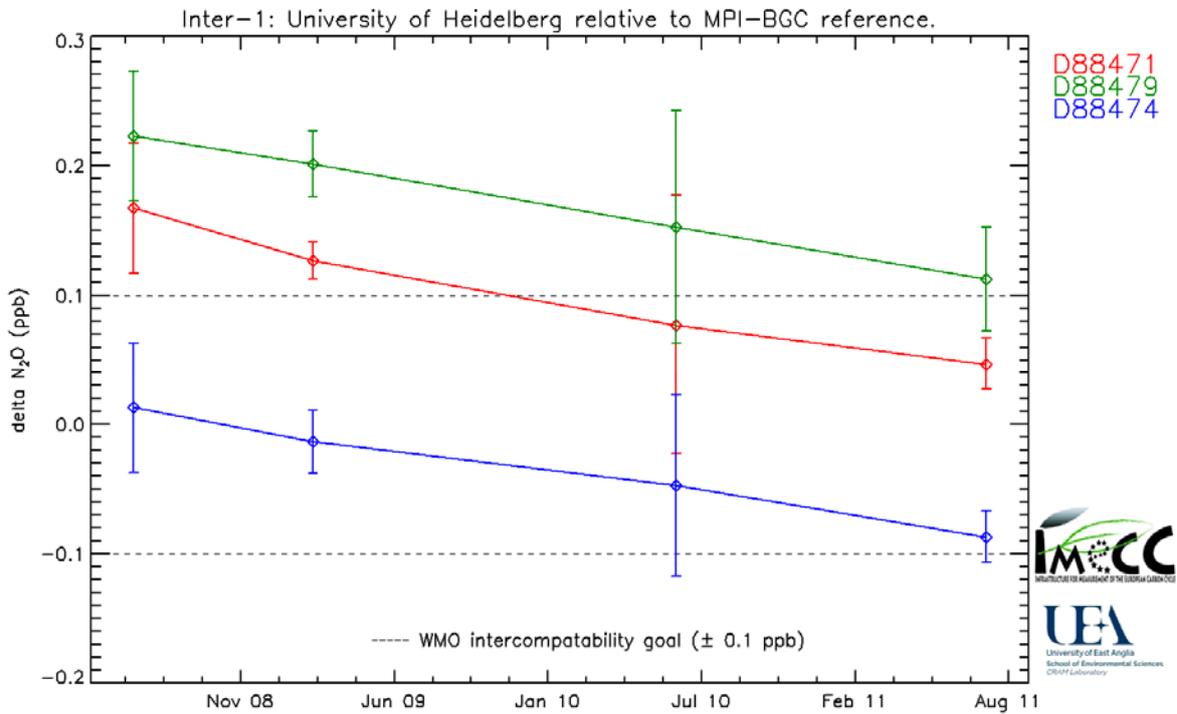


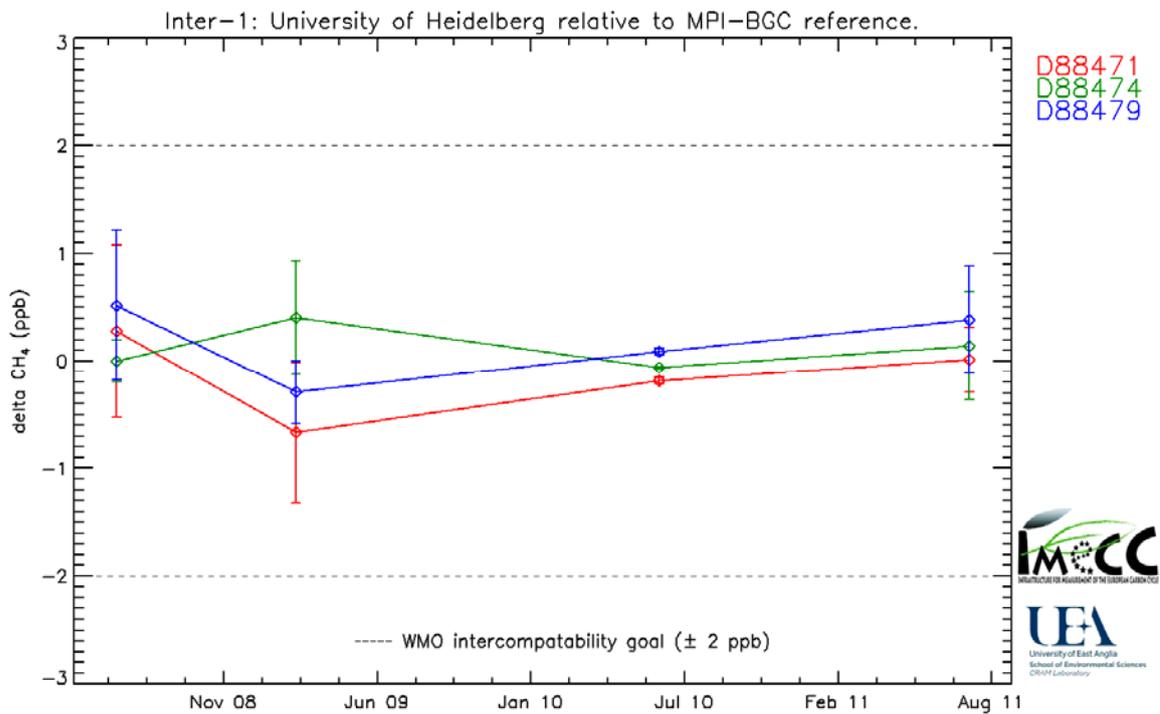
Figure 4.4: Hydrogen ambient air measurements and target gas deviations from the mean value. Dashed lines represent WS changes.

6. Intercomparison activities

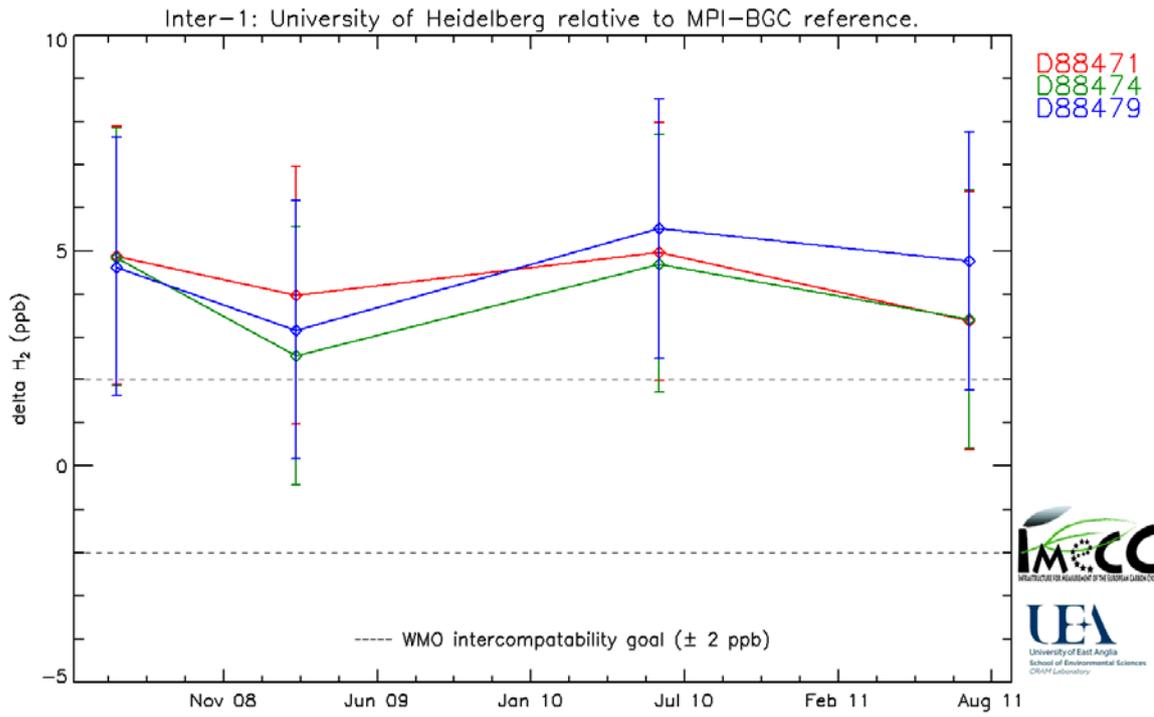
If your station participates in intercomparison activities please paste the results here.
As an example the cucumber results of the Heidelberg station relative to MPI-BGC are shown.



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