**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 is available 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:

* + 1. 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 -tank[[1]](#footnote-1)” (WT) is measured alternating to the samples. This working tank is afterwards used to normalize the sample signals.

* + 1. 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-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.

* + 1. 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.

* + 1. …

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.*

1. Working standards/Response function standards

Each changeover as well as the assigned mole fractions of the used working standards or response function standards have to be listed in Table 2. If the instrument response function (IRF) calibration strategy is used, please list the changes and, where possible, the mole fractions of the working tanks as well.

Please indicate the composition of the gas mixture in the tanks: ambient air, spiked ambient air or artificial mixture as well as the tank material: aluminium (alu), stainless steel (ss) or any other.

“No. of cals” states how often a cylinder has been measured against the set of primary laboratory standards within its lifetime. If independent measurements of these cylinders have been made by external laboratories please name them.

**Please describe your strategy to propagate the official scales to the used working- or response function standards:**

Station: ......

*Table 2: Changes and parameters of either the used working standards or the response function standards. If applicable please list working-tanks changes as well.*

1. 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*



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.

**If applicable, please provide an example chromatogram of your system.**

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

*Table 3.2: Cross-sensitivities*



1. 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:**

1. 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, 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.

1. Intercomparison activities

If your station participates in intercomparison activities please paste the results here.

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.

 [↑](#footnote-ref-1)