# InGOS – Integrated non-CO2GHG Observing System

Detailed workplan, appendix to the online application. Request for access to an infrastructure (TNA1-TNA2-TNA3). The plan must not exceed 6 pages in 12 pt single line spacing, applications exceeding this limit will not be evaluated. The following information should be included in order to be evaluated:

1. **Project name (acronym), name and contact information of the researcher(s), duration of the project (dates, number of working days), type and name of the infrastructure requested**

**Project:** H2 isotope measurements at Kasprowy Wierch

**Researcher:** Elena Popa, IMAU, Utrecht University, Utrecht, The Netherlands

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**Infrastructure:** station, Kasprowy Wierch, Poland

**Station access:** 16 days, May-2014 – July- 2015

1. **Background**
   1. Significance of the research

Atmospheric molecular hydrogen (H2) is an important component of the atmosphere and a participant to atmospheric chemistry. H2 is emitted to the atmosphere from natural processes, but it has also important anthropogenic sources, mainly from burning processes. The main sinks for the atmospheric H2 are uptake by soil and reaction with OH radicals. Through its reaction with OH, which affects the lifetimes of methane and tropospheric ozone, H2 is an indirect greenhouse gas; its GWP has been estimated at 5.8 (Derwent et al., 2006).

The isotopic composition of atmospheric H2 is a powerful tool to identify sources, sinks and processes, because most of these are associated with large isotopic signatures (due to the large relative mass differences between molecules, e.g. mass(HH) = 2 and mass(HD) = 3).

Among the sinks, the oxidation by OH is associated with very large fractionation, the HH molecules reacting almost twice faster than the HD molecules, while the uptake by soil occurs with almost equal speeds for HH and HD. In the absence of large local sources, measurements of the isotopic composition of H2 can thus help partitioning the contribution of the two main sinks of H2, namely soil uptake and oxidation by OH.

* 1. Previous research relevant to the topic and how the proposed project links to this

Measurements of atmospheric H2 mole fractions have been performed at Kasprowy Wierch since 2009, when a PP1 instrument was installed (Necki et al., 2012). Local and regional H2 flux components have been studied extensively at AGH Krakow (e.g. Bartyzel et al., 2013). Work is currently being done at AGH Krakow for a thorough assessment of the H2 budget on regional scale.

Measurements of H2 isotopic composition are routinely performed at IMAU and have been used extensively for a variety of studies (e.g. Batenburg et al., 2011, 2012, Röckmann et al., 2010, Vollmer et al., 2012, Walter et al., 2012). Although very useful for understanding the H2 cycle, isotopic measurements are difficult to perform and thus only few laboratories have this capability worldwide. Thus not many H2 isotope data are available, compared to other atmospheric tracers.

The global H2 loss by reaction with OH has been estimated based on average H2 and OH abundances and their reaction rate. The local contribution of this loss process is more difficult to estimate, which translates in difficulties in interpreting measurements and estimating local to regional budgets. The only measurement-based studies dealing with this subject are the ones of Rhee et al., 2006 and Batenburg et al., 2011. They computed the relative contributions of soil uptake and oxidation by OH to the total H2 sink, based on the apparent fractionation factor resulted from measurements. They showed that the OH oxidation dominates the total sink at low latitudes, while at high NH latitudes the soil uptake is responsible for up to 90% of H2 destruction. The results of Rhee et al., 2006 are based on a small number of upper troposphere samples. Batenburg et al., 2011 used six EuroHydros stations, of which four in NH: Alert, Cape Verde, Mace Head and Schauinsland.

* 1. Links with current research of the applicant

Elena Popa is currently responsible for the H2 isotope measurements at IMAU, and involved in research on various aspects of the H2 cycle, e.g. emission rates and isotopic composition of H2 from vehicles, isotopic signatures associated with uptake and emissions by soil, and regional modeling of H2 with Lotos-Euros. The research group of Thomas Röckmann is currently one of the strongest in the global research on H2, and one of the very few that can perform isotope measurements in atmospheric H2. The results of the current study will complement the previous estimation of H2 oxidation by OH of Batenburg et al., 2011, and will help to constrain the regional H2 budget.

1. **Objectives**
   1. Hypothesis and research objectives

The two main sinks affect the isotopic composition of the remaining H2 in very different ways: the oxidation by OH leads to the remaining H2 being strongly enriched in deuterium, while the soil uptake leaves the composition of the remaining H2 almost unchanged. The apparent (net) fractionation during H2 destruction can be computed using a so-called “Rayleigh fractionation plot”. If the dataset is longer than one year, the influence of concurrent sources on the fractionation result is relatively small. By comparing our resulted fractionation line with the known values for fractionation during soil uptake (0.94) and during Oh oxidation (0.58), we will be able to estimate the relative contribution of the two sinks.

* 1. Connection with the InGOS objectives and the ‘fitness’ of the use of the requested infrastructure to the objectives

This work will help quantify the contribution of oxidation by OH to the total H2 sink, and thus the regional H2 budget. A better understanding of its contribution would also help to constrain the possible effects of H2 variations on the lifetime of methane, tropospheric ozone and carbon monoxide, and thus the possible effects on climate.

Kasprowy Wierch is a mountain top station, with relatively clean air, and carefully selecting the sampling times can help us obtain air with little or no contamination from local sources. The behavior of atmospheric H2 at this location is quite well known, asH2 measurements are already performed here since many years.

Trained personnel from AGH Krakow make regular visits to the station. The necessary inlets already exist, and the sampling equipment can be installed relatively easy.

1. **Methods and materials (legal and ethical issues)**
   1. Research method, explaining how to reach the objective

**Sampling**

Atmospheric samples will be taken about twice per month, and shipped to IMAU for H2 isotope measurements. The sampling will be done in clean air conditions; meteorological information and in-situ measurements of H2 and other trace gases will be used to decide the sampling times. The samples will be taken in pairs, in standard 1-L glass flasks. The planned sampling extent is May-2014 to July-2015.

**Measurements**

The measurements of H2 isotopes will be done at IMAU following the standard procedure (Batenbug et al., 2011). Depending on the quantity of gas available in flasks, and on the availability of other instruments, CO and/or CH4 mole fractions and isotopes will be analyzed in selected samples.

**Data interpretation**

Data interpretation will be done by IMAU and AGH in collaboration. The contribution of OH oxidation to the H2 budget will be estimated following the approach of Batenburg et al., 2011.

* 1. Research materials, instrumentation

A flask sampler will be prepared and tested in collaboration with AGH, and will be connected to the existing inlet lines. Power, tools and basic consumables are available at the station. Online measurements of other gas species (CO2, CH4, N2O, SF6, CO) are needed for assessing the cleanness of the air masses, and will be made available by AGH. Meteo data are as well available at the station. Flask samples will be partially provided by IMAU. Transport to and from the station, and flask shipment to IMAU, will be organized by AGH.

* 1. Governance procedures, safety precautions, permit requirements and procedures

None

1. **Implementation: timetable, budget, distribution of work**
   1. Timetable for the research including personnel efforts, favorably table wise

|  |  |  |
| --- | --- | --- |
| Date | Action | Effective work (days) |
| Apr – May-2014 | Prepare sampler, power, sampler tests, sampling protocol | 1 (AGH) |
| May-2014 – Jul-2015 | - Flask sampling at Kasprowy Wierch, 2 /month,  total 30 samplings  - shipment flasks to IMAU (4 samples / month = one box every 4 months) | 15 (AGH)  (0.5 days / sampling) |
| Jun – 2014 – Sep -2015 | - H2 isotope measurements at IMAU – 60 samples  - additional species measurements as possible | 9 – 14 (IMAU)  not estimated |
| Jul – Sep-2015 | Data analysis | (IMAU / AGH) |

* 1. Total budget for travel and logistical support as requested

|  |  |
| --- | --- |
| Subject | Maximum expected cost |
| 1. Flask samples transport Utrecht – Krakow – Utrecht,  4 boxes, 300 €/box | 1200€ |
| 2. Travel for data analysis / discussion /publication  (E. Popa to Krakow, or J. Necki to Utrecht)  - transport  - accommodation + food (5 days) | 400  50 x 5 = 250 |
| **Total** | **1850€** |

* 1. Plan for specific logistic needs like visa, import/export licenses etc.

Not needed

1. **Expected results and possible risks**
   1. Expected scientific impact of the research

Using the samples from Kasprowy Wierch, we expect to be able to quantify the contribution of the oxidation by OH to the total sink of H2 and its seasonality. This result, combined with the on-going research of the AGH group, will lead to a better estimation of the regional H2 budget. Comparing our results on the OH sink with average global estimates, and with results from other stations from Batenburg et al., 2011, will provide information on the spatial variability of the H2 sink. We will also look into a possible application of our results for constraining the contribution if OH oxidation to the budget of other species, e.g. CO and CH4.

* 1. Applicability and feasibility of the research results

Due to the large difference in fractionation between the two major sinks of H2, it is in principle possible to distinguish their contribution based on the isotopic composition of the remaining H2. Several condition must be fulfilled, for this approach to be successful: (1) a dataset of at least one year is needed, to cover the full seasonal variation; (2) the contribution of local sources during sampling must be minimal; (3) the loss of H2 by reaction with OH or soil uptake must be large enough to produce clear signals in H2 mole fractions and isotopic signatures.

* 1. Publication plan

A publication on the H2 regional budget is planned, which will include the results of this project.

* 1. Data access plan

The data will become public immediately after publication.

1. **Key literature**
   1. List of references used in the working plan

Bartyzel, J., J. Necki, D. Zieba, K. Rozanski & M. Gasiorek 2013, European Journal of Soil Science, 64, 597.

Batenburg, A., T. Schuck, A. Baker, A. Zahn, C. Brenninkmeijer & T. Röckmann 2012, Atmospheric Chemistry and Physics, 12, 4633.

Batenburg, A., et al. 2011, Atmospheric Chemistry and Physics, 11, 6985.

Derwent, R., P. Simmonds, S. O'Doherty, A. Manning, W. Collins & D. Stevenson 2006, International Journal of Nuclear Hydrogen Production and Applications, 1, 57.

Necki, J. & L. Chmura Year, in, EGU General Assembly Conference Abstracts

Rhee, T. S., C. A. M. Brenninkmeijer & T. Roeckmann 2006, Atmos Chem Phys, 6, 1611.

Röckmann, T., et al. 2010, Atmospheric Chemistry and Physics, 10, 5343.

Vollmer, M. K., S. Walter, J. Mohn, M. Steinbacher, S. W. Bond, T. Röckmann & S. Reimann 2012, Atmospheric Chemistry and Physics, 12, 6275.

Walter, S., S. Laukenmann, A. Stams, M. Vollmer, G. Gleixner & T. Röckmann 2012, Biogeosciences, 9, 4115.