**InGOS TNA 5 Activity Report**

**Determine isotopic signatures (13C and 2H) of CH4 at a representative urban site**

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**Application number: 745**

Please limit the report to max 3-5 pages, including tables and figures.

The report should be sent as a pdf document and include the following subheadings:

* Introduction, motivation and scientific objectives

Methane (CH4) is the most important anthropogenically emitted non-carbon dioxide (CO2) greenhouse gas. Its mixing ratio has increased since pre-industrial time from around 722 to 1824 ppb (parts-per-billion, 10-9 moles of trace gas per mole of dry air) in 2013 and the anthropogenic fraction is estimated to be 60 % of the total emissions. While the trend of the tropospheric methane mixing ratio and the most important source and sink processes, wetlands, ruminants, rice agriculture, fossil fuel exploitation, landfills and biomass burning, are relatively well known, much uncertainty remains on the strength and spatio-temporal variability of individual sources.

CH4 source processes can be distinguished measuring the most abundant methane isotopologues: 12CH4, 13CH4 and CH3D. Analysis of CH4 mixing ratios and isotopic composition with inverse modelling techniques and chemical transport models has been applied to validate emission scenarios. Current modelling approaches, however, are restricted by the limited continuity of 13C-CH4 measurements and the limited availability of D-CH4 data. Isotope ratio mass spectrometry (IRMS) is the standard technique to analyze 13C- and D-CH4 in ambient air. However, IRMS is a laboratory based technique and therefore relies on flask sampling which severely limits its temporal and spatial resolution capability.

At Empa a completely new measurement technique for real-time high precision isotopic measurements of methane isotopic composition (13C-CH4, D-CH4) in ambient air was developed funded within InGOS JRA4 (WP16). It consists of an innovative preconcentration device, named trace gas extractor (TREX) and a state-of-the-art quantum cascade laser absorption spectrometer (QCLAS). The TREX unit can increase CH4 mole fractions by a factor of 500 from ambient levels to 1000 ppm (parts-per-million, 10-6 moles of trace gas per mole of dry air) [1]. Preconcentration of CH4 was shown to be quantitative without significant fractionation effects. Additionally spectral interfering trace gases (N2O and CO2) are eliminated by temperature-controlled stepwise desorption. The developed preconcentration device (TREX) can also be applied for N2O, VOCs and other trace gases. Preconcentrated CH4 is analyzed by state-of-the-art QCLAS consisting of two thermo-electrically cooled (TE) continuous wave (cw) DFB QCL sources, an astigmatic multipass-cell and a TE-MCT detector. The QCLAS demonstrates an Allan precision of 0.1 ‰ for 13C-CH4 and <0.5 ‰ for D-CH4 with 600 s spectral averaging. For repeated measurements of preconcentrated pressurized air a reproducibility of 0.19 ‰ and 1.7 ‰ for 13C and D-CH4 was achieved.

In June 2014 a field campaign was organized by Empa to assess the compatibility of real-time measurements for 13C-CH4, D-CH4 and CH4 mixing ratio by different laser spectrometers and validate the measurements by off-line IRMS on air samples collected during the campaign. Additionally, the precision and stability of field instruments and the added value of high-frequency measurements compared to traditional flask measurements was evaluated.

The TNA 5 activities funded within application 745 include IRMS analysis of 48 bag samples for 13C-CH4 and CH4 mixing ratios at RHUL of 50 bags filled at Empa.

* Method and experimental set-up

The field campaign was conducted from June 6th to June 22nd 2014 in the densely populated area of Dübendorf, Switzerland (47°24′11″ N / 8°36′48″ E, elevation 432 m above sea level). A main road passes 100 m south and a highway around 750 m north of the sampling site. Air was continuously sampled from the rooftop of a five-story building at a flow rate of about 25 standard liters per minute (slpm) through a 25 m long unheated polyethylene-coated aluminum tubing (ID 9 mm) using a piston pump (Gardner Denver Thomas GmbH). Upstream of the sampling pump the measuring gas was split for the different analyzers (see Figure 1).



Figure 1: Experimental setup during the field campaign in June 2014 in Dübendorf.

The following laser spectroscopic techniques were deployed: combined preconcentration (TREX) [1] + QCLAS (13C-CH4, D-CH4 and CH4 mixing ratio, Empa), off-axis integrated cavity output spectroscopy (OA-ICOS, 13C-CH4 and CH4 mixing ratio, Model MCIA-24e-EP, Los Gatos Research, Utrecht University) and cavity ring-down spectroscopy (CRDS, 13C-CH4, 13C-CO2, CH4 and CO2 mixing ratio, Model G2201-I, Picarro Inc., Eawag; CH4, CO2, H2O mixing ratio, Model G1301, Picarro Inc., Empa). The OA-ICOS and the two CRDS instruments were calibrated twice per day with two working standards, named CG1 and CG2, 30 minutes each (Table 1). The reproducibility was assessed based on repeated analysis of pressurized air (target gas) every six hours for 30 minutes.

Glass flasks were purged for 10 minutes with sample gas at 2 slpm using a membrane pump. Afterwards the down-stream valve was closed and the flasks were filled to 2 bar overpressure. These air samples were analyzed by IRMS at Utrecht University and MPI. Parallel to the glass flask sampling, 3 liters Tedlar bags (SKL) were also filled after purging the glass flasks at the outflow of the flasks. These bags were analyzed by IRMS at RHUL.

Table 1: CH4 mixing ratios and isotopic composition of the working standards (CG1 and CG2) and the pressurized air deployed as target gas as analyzed by IRMS at Utrecht University.

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| --- | --- | --- | --- |
|  | 13C-CH4 [‰] vs. VPDB | D-CH4 [‰] vs VSMOW | CH4 [ppm] (dilution) |
| CG1 | -46.3 ± 0.4 | -243 | 1.860 (1:500) |
| CG2 | -36.2 ± 0.1 | -174 | 1.910 (1:614) |
| Target gas | -48.0 ± 0.2 | -114 | 2.342 ± 0.0002 |

* Preliminary results and conclusions

The CH4 isotopic composition was analyzed over more than two weeks in real-time by laser spectroscopy and off-line by flask or bag sampling in combination with IRMS analysis. At the moment still part of the IRMS data is missing, and therefore interpretation of the data is ongoing. The reproducibility of combined preconcentration QCLAS analysis for repeated target gas measurements was 0.19 ‰ for 13C-CH4 and 1.7 ‰ for D-CH4. The reproducibility of CRDS (G2201-I) and OA-ICOS (MCIA-24e-EP) for 13C-CH4 was 0.26 ‰ and 1.6 ‰, respectively. Preliminary results indicate a good agreement between QCLAS and IRMS (UU) for CH4 mixing ratio, 13C-CH4 and D-CH4 (Figure 2). Results for OA-ICOS were not plotted in Figure 2 due to a poor compatibility with the other techniques; possible reasons include: the much lower precision, the strong dependence of 13C on CH4 mixing ratios, an unknown interference leading to a much stronger nighttime change in 13C-CH4. The IRMS results by Utrecht University and RHUL exhibit a constant offset of 0.3 ‰. After receipt of the final dataset a manuscript will be submitted to a peer reviewed journal for publication.



Figure 2: Compatibility of CH4 isotopic analysis by laser spectroscopy and off-line IRMS.

* Outcome and future studies

Results of the study will be published in a peer-reviewed journal. At present an extended field campaign is ongoing at the Cabauw Tall tower in the Netherlands organized by Utrecht University.

* References

[1] Eyer, S., Stadie, N.P., Borgschulte, A., Emmenegger, L., and Mohn, J. (2014). Methane preconcentration by adsorption: A methodology for materials and conditions selection. Adsorption 20(5-6): 657-666.