



Integrated non-CO<sub>2</sub> Greenhouse gas Observing System

## InGOS TNA 1-2 Activity Report

### INTER-COMPARISON OF N<sub>2</sub>O CHAMBERS USING LASER ABSORPTION SPECTROMETRY: QUANTIFICATION OF SYSTEMATIC ERRORS

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Entry #802

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 and motivation

Chamber based approaches are among the most commonly used to measure greenhouse gas fluxes from soils. Beside carbon dioxide and methane, nitrous oxide (N<sub>2</sub>O) is one of the strongest greenhouse gases emitted from soils. These emissions are characterized by high spatial and temporal variability, issues that can be addressed by a sufficient number of measurement locations and frequency in the measurements. Static chambers have been associated with large systematic errors resulting from chamber disturbances, chamber design, differing flux calculation methods, chamber operation, as well as gas sampling, storage and analysis (Rochette and Eriksen-Hamel 2008; Christiansen *et al.*, 2011; Levy *et al.*, 2011; Pihlatie *et al.*, 2013). Recent developments in laser absorption spectrometry open new possibilities to minimize some of these systematic errors by increasing the accuracy in the gas analysis and improving the resolution in the gas concentration measurements (Savage *et al.*, 2014). Furthermore, the improved accuracy in gas analysis allows for shortening chamber closure times and hence decreasing chamber disturbances. When using laser absorption spectrometers, dynamic chambers (flow-through non-steady-state, FT-NS) are most commonly used. Similar chambers were used in the past to study soil CO<sub>2</sub> fluxes (Pumpanen *et al.*, 2004). Systematic errors related to the use of FT-NS chambers for N<sub>2</sub>O emission measurements are currently poorly quantified. The aim of this study was to quantify systematic errors related to FT-NS chambers measuring N<sub>2</sub>O concentrations using laser absorption spectroscopy. We further investigated the effects of wind, chamber ventilation (vent-tube), collar insertion depth, and manual sampling on chamber N<sub>2</sub>O fluxes measured by a variety of chamber designs.

#### Scientific objectives

The general aim of the campaign was to compare different chambers used for N<sub>2</sub>O flux measurements against known reference fluxes. The main aim was to quantify systematic errors related to chamber measurements, designs and operation, and to assess chamber disturbances to the soil concentration gradient, pressure and the resulting fluxes from the soil.

## Reason for choosing station

Hyytiälä Forestry station has already organized this type of intercomparison campaigns in the past. The site was optimal for the event thanks to the experience of the scientific staff and the availability of the infrastructure specific for the campaign.

## Method and experimental set-up

The chamber inter-comparison campaign was organized at Hyytiälä Forestry Field Station, Southern Finland during June-July 2014. The measurement system presented in Pumpanen *et al.* (2004) and Pihlatie *et al.* (2013) was modified for testing chambers used for measuring N<sub>2</sub>O fluxes using laser absorption spectroscopy. The measurement system comprised of a large gas reservoir (stainless-steel tank, diameter 1.6 m, height 1.0 m, volume 2.6 m<sup>3</sup>) covered with a perforated lid on top of which a layer of quartz sand with particle size of 0.2-0.6 mm was set to act as a porous media. Chamber measurements were conducted on top of the sand bed and these chamber fluxes were compared to simultaneously measured reference fluxes from the tank.

In total 22 chambers of different sizes, shapes and attributes (fan, vent-tube, sampling, seals) from different research groups were tested against the known reference fluxes. The measurements were comprised of 'protocol measurements' and 'extra tests'. In the protocol measurements, each chamber measured fluxes repeatedly with and without external wind (1.5 m/s) from the sand of two different depths (0.2 m and 0.1 m). On average 6 replicate flux measurements per wind speed and sand depth were conducted. In the extra tests, the following tests were made in 3 replicates with selected chambers: vent-tube design and position, collar insertion depth, sealing material (rubber, water), manual sampling and headspace mixing.

At the start of the measurements, a high concentration of N<sub>2</sub>O (1000 ppb) was injected into the tank, and the system was let to stabilize for 20 minutes to reach a steady-state condition. After the stabilization, chamber fluxes from the sand bed were measured together with measurements of the tank N<sub>2</sub>O concentration, and the resulting reference fluxes. The fluxes measured from the tank ranged between 20 and 120 µg N<sub>2</sub>O-N m<sup>-2</sup> h<sup>-1</sup>. Chamber measurements were made in 3 replicates: each chamber closure being 10 minutes with a 20-min stabilization period between the chamber closures. N<sub>2</sub>O concentrations in chamber headspace and in sand profile were measured with two Quantum Cascade Lasers (QCL, Model CW-QC-TILDAS-76-CS, Aerodyne, Research Inc., Billerica, MA, USA), and the concentration in the calibration tank was measured by an LGR N<sub>2</sub>O/CO Analyzer (Model N<sub>2</sub>O/CO-23d, Los Gatos Research, LGR, Mountain View, CA, USA). Leak rates of each chamber were measured by placing the chamber with collar into a water bath, injecting 1000 ppb N<sub>2</sub>O in the chamber headspace, and following the N<sub>2</sub>O concentration in chamber headspace over one hour.

Chamber fluxes were calculated by linear and non-linear fits to the concentration data as described in Pihlatie *et al.* (2013). Flux data was quality checked by goodness-of-fit analysis, and bad data was rejected on the base of normalized root-mean-square-error limit of 3%. Reference fluxes were calculated by a time-discrete exponential function as described in Pumpanen *et al.* (2004). All the fluxes were expressed as µg N<sub>2</sub>O-N m<sup>-2</sup> h<sup>-1</sup>, and were calculated by Matlab-R2012a software (The MathWorks, Inc., Natick, MA, USA).

## Preliminary results and conclusions

The tested flow-through non-steady-state (FT-NS) N<sub>2</sub>O chambers tended to slightly underestimate the reference fluxes with linear flux calculation method (13%), whereas the chamber fluxes calculated by non-linear (exponential) flux calculation method did not differ from the reference fluxes (Table 1). The underestimations of the tested FT-NS chambers were smaller than those observed for non-flow-through non-steady-state (NF-NS) chambers tested in the campaigns for CO<sub>2</sub> and CH<sub>4</sub> (Pumpanen *et al.*, 2004; Pihlatie *et al.*, 2013). Wind outside the chamber as well as different depths of collar insertion did not significantly influence the calculated chamber fluxes (Table 1).

Table 1. Mean ratio of chamber N<sub>2</sub>O fluxes against reference fluxes calculated by linear and exponential fits, and their 95% confidence intervals from all the 22 chambers. Measurements conducted with sand depths of 20 cm and 10 cm, and mean of both sand depths.

	Linear	95% conf. int.	Exponential	95% conf. int.
Sand depth 20cm	0.89	± 0.07	0.98	± 0.09
Sand depth 10cm	0.86	± 0.05	0.94	± 0.10
All sand	0.87	± 0.05	0.96	± 0.07

The high-resolution N<sub>2</sub>O data obtained from the chamber headspace, tank and soil profile by the QCL and LGR lasers provided unique and quantitative information of the short-term disturbances caused by the chambers. Our results strongly support the findings of Christiansen *et al.* (2011) that headspace air mixing improves the data quality, while poorly mixed headspace air created noise to the N<sub>2</sub>O signal, leading to inaccurate estimation of the flux with exponential fitting. Also, the placement of a chamber may disturb both the headspace and soil concentration, and the resultant chamber fluxes. Soil concentrations were most disturbed by chambers, which did not include vent-tubes, and that were either directly pushed into the soil without a collar or chambers that had a water-seal between the collar and the chamber. This disturbance was interpreted to result from a pressure pulse temporarily pushing atmospheric N<sub>2</sub>O into the soil and hence reducing N<sub>2</sub>O gradient in the top of the sand. The decreased concentration gradient in the soil led to flux underestimation. The disturbances caused by chamber placement could be largely avoided when a chamber was equipped with a properly designed vent-tube.

Systematic errors in N<sub>2</sub>O chamber measurements can be quantified in laboratory measurements as shown in the campaign. The application of high accuracy, high-frequency laser absorption spectrometry in N<sub>2</sub>O chambers allows for minimization of some of the systematic errors, leading to improved data quality. Soil N<sub>2</sub>O profile data showed how sensitive the soil concentration gradient is to external disturbances caused by the placement of a chamber, and manual syringe sampling, if the pressure effect is not taken into account. This further underlines the importance of designing chambers so that the disturbance to the soil during a measurement is minimized.

### Outcome and future studies

The study has shown that the chamber used in AGH University and Science and Technology is well designed for the N<sub>2</sub>O flux measurements. The experiment has shown an underestimation (c.a. 20%) of the chamber flux values measured with the laser spectrometer when applying both linear and exponential fit to the measured values.

Additional experiments included also the measurements performed with the additional, small fan inside (for mixing of the headspace volume). The results show that mixing caused no under- or overestimation (within the estimated uncertainty) when using either the exponential or linear fit. The outcome will be the installment of such a fan in the future studies.

Another experiment was performed in order to assess the accuracy of the measurements performed with a GC system at the AGH–UST. 2 series of 5 samples (plastic syringes, 50 ml each, according to the methodology used in *day-to-day* measurements at AGH) were collected during the intercomparison campaign in Hyytiälä. The known value of the flux will be compared to the result obtained at the AGH-UST and possibly used to correct the flux values measured in the recent campaigns.

## References

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