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Comparison of CO_2, CH_4 and N_2O soil-atmosphere exchange measured in static chambers with cavity ring-down spectroscopy and gas chromatography

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ABSTRACT

A laboratory and field experiment compared fluxes of CO_2, CH_4 and N_2O measured with cavity ring-down spectroscopy (CRDS) and gas chromatography (GC). The comparison between CRDS and GC showed that average CO_2 fluxes were significantly higher for CRDS in both the laboratory and field, but the same experimental treatments effects were detected for both techniques. Compared to CRDS, the GC technique was severely limited in detecting CH_4 fluxes in both the laboratory and field. Thus, only 16% of measured GC fluxes were detectable in the laboratory and none in the field whereas CRDS could detect 65% and 97% of the CH_4 fluxes in the laboratory and field. In contrast, N_2O fluxes measured with CRDS and GC were not different for both the laboratory and field. It was observed that a lower proportion of N_2O fluxes could be detected with CRDS (73%) than GC (92%) in the laboratory and similar recovery (65% and 68%) for the field. Thus, the same treatment effects were observed for both CRDS and GC. Furthermore, the comparison between CRDS and GC showed that enclosure times as short as 600 s for our field study site are suitable to estimate the same treatment effects, but not necessarily flux magnitude. We conclude that CRDS and GC can provide the same level of information regarding treatment effects in both laboratory and field experiments for CO_2 and N_2O, but not for CH_4 and it is possible to reduce enclosure time without comprising comparability between the two techniques.

1. Introduction

Soil-atmosphere exchange of the greenhouse gases (GHG) carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) are commonly measured with closed static chambers (Pihlatie et al., 2013) or in laboratory incubations in combination with off-site gas chromatographic (GC) methods. In recent years the development of cavity ring-down spectroscopy (CRDS) and other online techniques for GHGs, such as tunable diode laser (TDL) or quantum cascade laser (QCL) promises to reach an unprecedented level of detail and precision for estimating the exchange of GHGs between the soil and the atmosphere (Cowan et al., 2014; Hensen et al., 2013). Laser technologies like CRDS, TDL or QCL have a superior detection limit and higher precision compared to GC (Christiansen et al., 2015; Hensen et al., 2013). However, these rapid real-time techniques are however expensive, require a stable power supply and can be difficult to transport which constrains their use for many research groups and limits their utility for analysis in remote areas. Also, CRDS instruments are currently limited by only one inlet line. This implies that the same machine has to be used for each chamber or incubation vessel individually either by manually moving the machine around between chambers or having it connected in an automated chamber setup with a distribution manifold (Jassal et al., 2005). State-of-the-art autochamber systems have been developed that can measure GHG fluxes from up to sixteen chambers using the CRDS technology (Picarro Inc., 2013). However, this level of replication still severely limits the capabilities to capture the spatial variability of GHG fluxes within an ecosystem. It was recently shown that CO_2, CH_4 and N_2O fluxes measured with automatic chamber with CRDS and mobile chambers with GC were comparable and that spatial variability could surpass the differences in measurement techniques (Ruan et al., 2014). Thus, it was suggested

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that using a GC based static chambers to capture spatial variability in combination with an automated CRDS system working at high temporal resolution would result in a more accurate spatiotemporal assessment of the GHG exchange within an ecosystem, field or experimental unit (Ruan et al., 2014) than using either technique in isolation.

However, even if a distribution manifold enables automated sampling of chambers (Jassal et al., 2005) in the field or incubation chambers in the laboratory, sample numbers can still be limited by enclosure times. As sampling is done sequentially, long enclosure times that are usually employed in studies of CH_4 and N_2O subject treatments to large temporal variability (e.g., 30 min would only enable 2 samples per hour per chamber). Alternatively, sampling using the GC method, simultaneous or near simultaneous sampling can be achieved with discrete sampling points (e.g., taking multiple samples sequentially or simultaneously using multiple people). Thus, despite often needing enclosure times of ≥30 min (depending on chamber design) to achieve accurate quantification of GHG fluxes there are strategies to use GC sampling methods to capture spatial variability while minimizing the time between samplings within a specific treatment. Alternatively, if the CRDS were made mobile (i.e., no manifold) to capture spatially variability in the field by sampling chambers similar to those used for GC measurements sample numbers would still be limited by enclosure times. The higher frequency and higher precision of concentration measurement achieved by CRDS could however substantially shorten enclosure time and help to avoid or minimize the negative impact of the closed static chamber on the soil-atmosphere gas gradient that can lead to considerable underestimation of the pre-deployment flux (Creelman et al., 2013). Despite the superior analytic capabilities of modern techniques, such as CRDS and other fast methodologies, there is a lack of quantitative information of the relative performance of laser based and GC based techniques to measure GHG fluxes under the same experimental conditions (see Cowan et al. (2014) and Grossel et al. (2014) for recent comparisons between GC and QCL).

Our objectives of this study were therefore, (1) to compare the magnitude and temporal variability of CO_2, CH_4 and N_2O flux rates estimated with CRDS and GC techniques in laboratory and field experiments and (2) compare the flux rate of CO_2, CH_4 and N_2O and relative error measured with CRDS and GC techniques to identify optimal enclosure time for field experiments combining CRDS and GC techniques. The study was conducted using state-of-the-art CRDS and GC systems. The CO_2, CH_4 and N_2O fluxes measured with the two techniques were compared in a laboratory setup where soil moisture and nitrogen (N) levels were manipulated for intact cores from three different land use types as well as in a field experiment where the effect on GHG was evaluated at two levels of aboveground biomass incorporation in to the soil to mimic two N addition levels.

2. Materials and methods

2.1. Laboratory experiment

Twelve 316 cm^3 intact core soil samples were collected from a 2 m^2 permanent plot within each of the three land uses (forest, agriculture and wetland) at the University of British Columbia (UBC) Farm in Vancouver, Canada in February 2014. Before collection, soil moisture was examined using a decagon 5TM moisture meter (Decagon Devices, Pullman, WA, USA) to ensure treatment samples varied by no more than 5% moisture by volume. Because of the small plot size and limited moisture variation, soil physical and chemical properties were assumed to have a high degree of similarity within treatments. Cores were stored under refrigeration before moisture and N application. The incubation was divided into two 2-week experiments to test the effect of two levels of soil moisture (water filled pore space (WFPS)) (called "75% WFPS" and "35% WFPS"). It was assumed that at sampling the water content of the cores were equal to the field capacity of the cores to be used in the second round of testing at the lower moisture level. The cores were stored at 3 °C refrigeration with no manipulation to moisture or nitrogen content.

2.1.1. Treatment manipulation

The porosity of each habitat's soil was first determined by destructively oven drying five excess, fully saturated soil cores at 105 °C for 48 h for each habitat type. Averages of these values were then assumed to represent the overall habitat soil porosity to estimate water additions/removal required to establish two discrete target moisture treatments of 35 and 75% WFPS. Following the two weeks of emissions analysis, actual moisture levels were determined again by oven drying. Agricultural treatments were found to range from 69 to 82% WFPS in treatment one and 36–38% WFPS in treatment two; forest habitat treatments ranged from 22 to 28% and 26–41% WFPS in treatments one and two, respectively; and wetland habitat treatments ranged from 73 to 94% and 32–44% WFPS in the two respective treatments.

To achieve the high moisture level treatment deionized water was added to soils by syringe, ensuring even distribution. Before moisture levels were adjusted, KNO_3 solutions were applied to N-amended treatments, again by syringe. Nitrogen treatment levels were set at 100 kg KNO_3–N ha^{-1}, therefore stock solutions of 100 mL deionized water to 1.88 g KNO_3 were created, and 15 mL of solution added to each core sample. For some cores water needed to be removed to achieve the lower moisture content. After N addition these cores were air dried to the correct weight. After soil moisture manipulation the levels were held constant throughout the two weeks of experimentation by adding deionized water with a syringe to compensate for water loss through evaporation. Following moisture and KNO_3 addition, samples were left to pre-incubate for 48 h in lightly covered containers at room temperature prior to flux measurements.

To measure the fluxes of CO_2, CH_4 and N_2O the cores were placed in a 1 L jar and closed with a screw lid for 30 min. The threading of the jar was covered by layers of teflon tape to achieve a gas tight seal between the jar and the lid. The CRDS was connected to the jar through a combined inlet and outlet, where the outlet tube extended to the bottom of the jar and the inlet tube only extended a couple of centimeters in to the jar from the lid. The CRDS measured continuously for the closure time of the jar by recirculating the air between the jar and the analyzer. Four headspace samples for GC analysis, each of 10 mL of headspace (less than 4% of total headspace of jar + CRDS tubes, pump and cavity), were manually sampled at 0, 10, 20 and 30 min through a butyl rubber septum in the lid and transferred to an evacuated 6 mL Labco exetainer (Labco Limited, Ceredigion, UK) for subsequent GC analyses.

2.2. Field experiment

The field experiment was performed at the UBC Farm. The field experiment started May 14th, 2014 and ended June 2nd, 2014 and the fluxes were measured from eight chamber on four occasions giving a total of 32 chamber enclosures.

Two treatments were compared in the experiment, cover crop (CC) and no cover crop (No CC), to mimic different levels of carbon (C) and N additions to the soil. Two rates of C and N inputs were intended to stimulate the microbial community variably and result in broad differences in fluxes of CO_2, CH_4 and N_2O thus providing a better dataset on which to compare the performance of CRDS and GC.