Simultaneous Measurement of Nitrous Oxide, Carbon Dioxide and Methane Using a Closed-Path Fourier Transform Infra-Red (FTIR) Multi-Component Gas Analyzer

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Introduction

- Measuring GHG (N_2O, CH_4, and CO_2) emissions from soils often involves the collection of discrete gas samples from chamber-based sampling systems, with the samples subsequently analyzed in a laboratory setting using gas chromatography.
- There is a need to deploy gas analysis systems in the field, especially in remote locations.
- Field-based measurements include micrometeorological techniques (e.g., Eddy covariance) and *in-situ* chamber-based systems that employ infrared gas analysis (IRGA), photoacoustic spectroscopy (PAS) or Fourier transform infrared (FTIR) spectroscopy.
  - IRGA systems are well established for the quantification of CO_2 fluxes from soils.
  - PAS and FTIR analyzers are capable of the simultaneous measurement of N_2O, CH_4, and CO_2.
- Whereas performance of PAS has been demonstrated, the performance of FTIR methods of measuring near-ambient GHG concentrations has yet to be validated under either controlled or field conditions.

Objectives

- Evaluate the performance of a FTIR-multi-gas analyzer in terms of its response (including accuracy, precision, and linearity) to N_2O, CH_4, and CO_2; the effects of water vapor on gas concentration measurements; and comparison of gas fluxes measured using FTIR and GC techniques.

FTIR multi-gas analyzer

- Gasmet DX-4015 multi-component gas analyzer (FTIR-MGA; Gasmet Technologies Inc. Helsinki, Finland)
  - FTIR spectrometer (resolution = 8 cm^{-1}; scan frequency = 10 scans s^{-1}; wave number range = 900–4200 cm^{-1})
  - rhodium-gold coated sample cell (multi-pass with a fixed path length of 9.8 m and a volume of 0.45 L)
  - built-in sample pump (2.8 L min^{-1})
  - sample processing electronics and Calcmet™ software
  - rugged, field portable aluminum case

Automated GHG Flux Measurements

- The automated soil greenhouse gas flux measurement system consisted of:
  ① Gasmet DX-4015 FTIR-MGA
  ② Li-Cor LI-8150-16 multiplexer (operating 16 Li-Cor LI-8150-104 long-term flux chambers)
  ③ Custom-built zero-air and calibration gas valve
  ④ Laptop computer running the Calcmet™ software and custom control software to operate the multiplexer and zero-air/calibration gas valve
  ⑤ Custom-built communications interface for the PC/multiplexer
  ⑥ Trailer to house system in the field

FTIR Performance

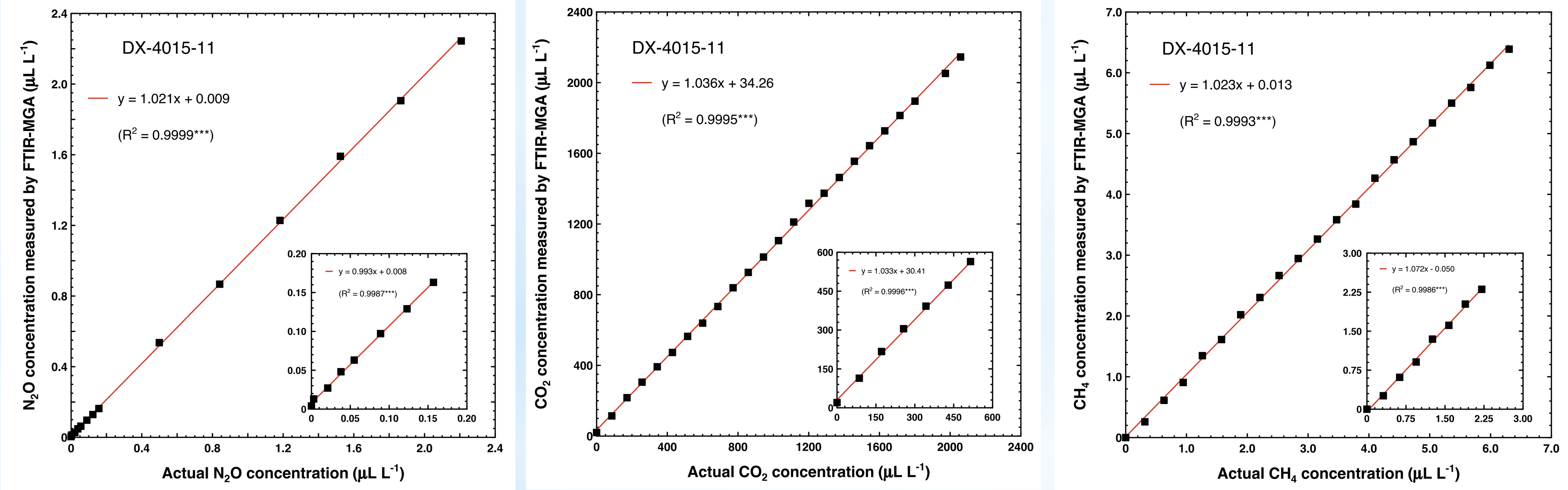

Fig 1. Nitrous oxide (N_2O), carbon dioxide (CO_2) and methane (CH_4) concentrations measured using a Gasmet DX-4015 FTIR-MGA *vs.* the calculated gas concentration. Gas concentration was measured continuously from a chamber into which the gases were injected. Note: only the response in the near-ambient range is shown.

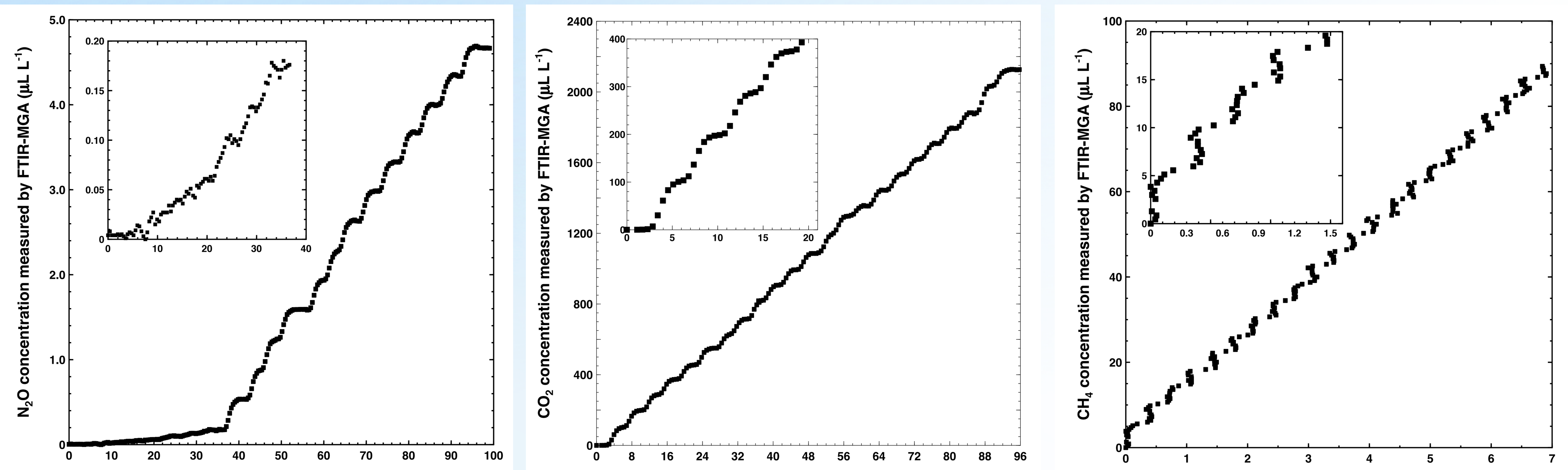

Fig 2. Response of the Gasmet DX-4015 FTIR-MGA to increasing concentrations of nitrous oxide (N_2O), carbon dioxide (CO_2) and methane (CH_4). Complete infrared spectra were collected continuously (at 100 ms intervals) and averaged over 20-s measurement intervals.

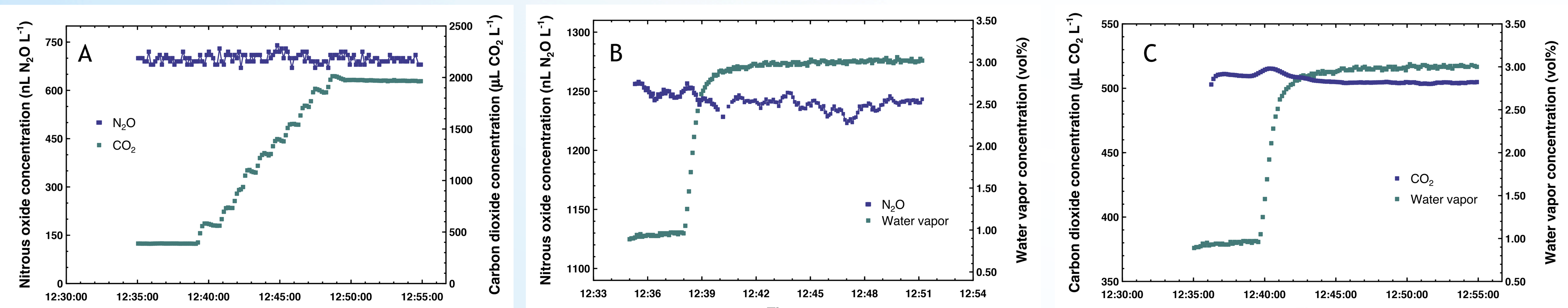

Fig 3. Effect of increasing CO_2 concentration on stability of the N_2O measurement (A); effect of increasing water vapor concentration on stability of the N_2O measurement (B) or CO_2 measurement (C).

Automated GHG Flux Measurements

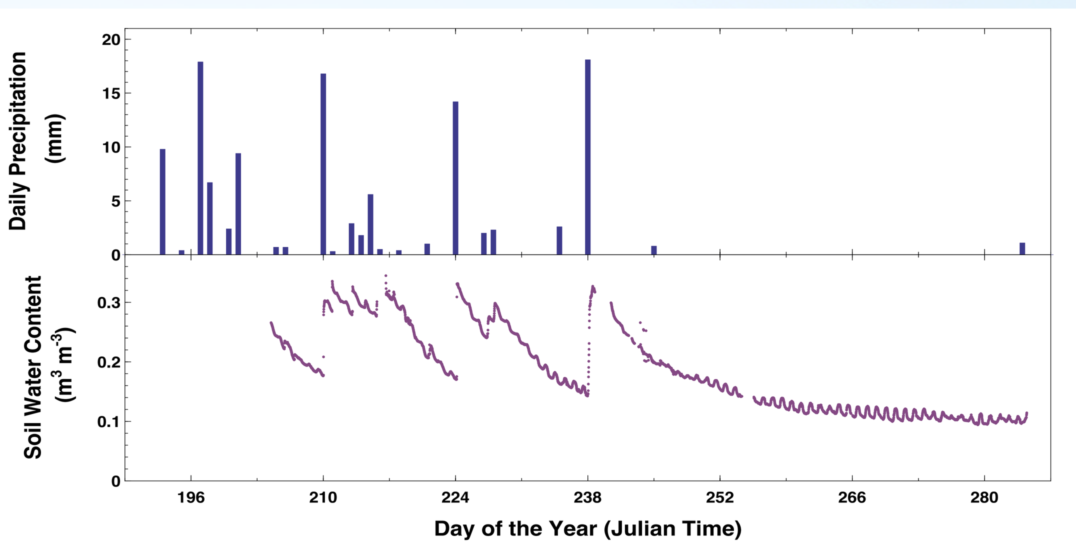

Fig 4. Daily precipitation and soil water content (@ 5 cm) were measured throughout the automated flux chamber deployment period .

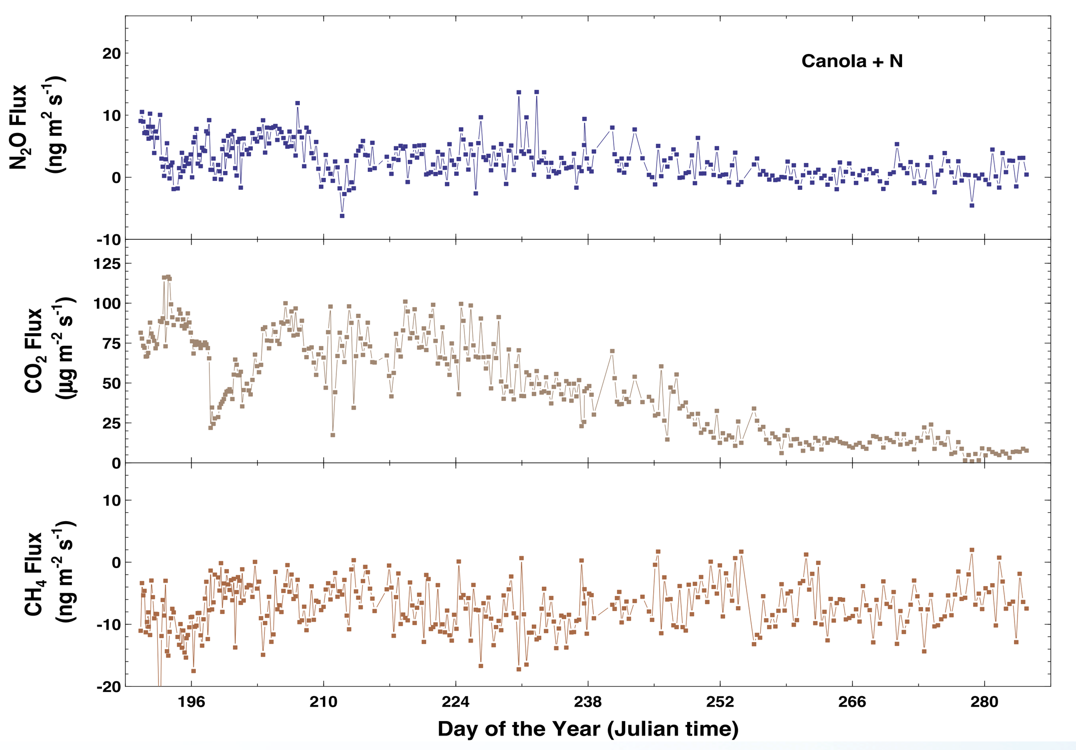

Fig 5. Greenhouse gas (N_2O, CO_2 & CH_4) emissions measured with the Gasmet DX-4015 FTIR-multigas analyzer connected to a Li-Cor 8100-104 long-term flux chamber via a LI-8150-16 multiplexer.

- N_2O emissions were generally quite low, but were in the range normally encountered in Saskatchewan agricultural soils.
- CO_2 emissions exhibited a diurnal pattern (except during and immediately following a precipitation event) and decreased as both the soil temperature and water content decreased.
- CH_4 emissions generally were not observed; rather, the soil acted as a small sink for CH_4.

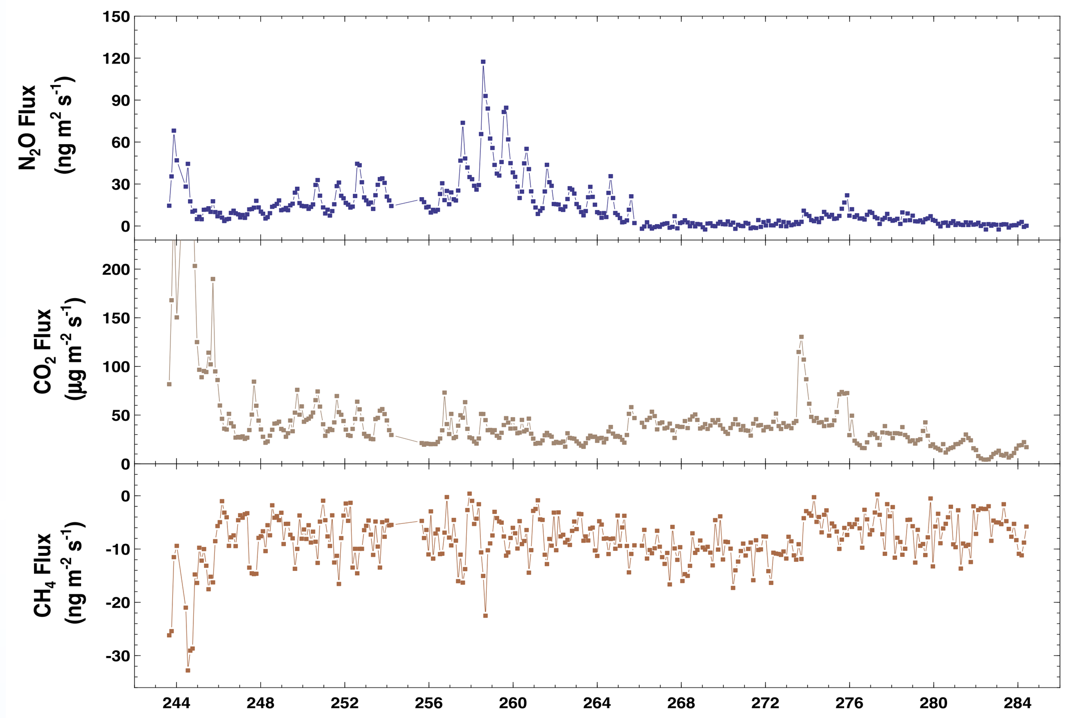

Fig 6. Greenhouse gas (N_2O, CO_2 & CH_4) emissions measured following a late-season fertilizer application.

- Soil disturbance and the application of fertilizer-N resulted in a short burst of activity, during which N_2O and CO_2 emission were significantly greater than background levels (see Fig. 5; days 242 – 284).
- Evidence of a diurnal pattern was present during periods of peak N_2O emission.

Conclusions

- The Gasmet DX-4015 FTIR multi-component gas analyzer is capable of making accurate measurements of N_2O, CO_2 and CH_4 at near-ambient concentrations.
- The accuracy and precision of the FTIR-MGA was comparable to that attainable using conventional gas chromatography.
- Increases in CO_2 concentration, from ambient to about 5-times ambient, had no significant effect on N_2O measurements over the range of N_2O concentrations normally encountered when measuring emissions from Saskatchewan agricultural soils.
- Water vapor interferences with N_2O and CO_2 measurements were generally small (i.e., <4%).
- Simultaneous measurements of N_2O, CO_2 and CH_4 emissions from soils in the field can be automated by interfacing the Gasmet FTIR-MGA with a Li-Cor multiplexer and long-term flux chambers.
- Operational and maintenance requirements of the automated soil greenhouse gas system are comparable to those of a conventional automated soil CO_2 flux measurement system.

Acknowledgements

Saskatchewan Ministry of Agriculture
Agriculture and Agri-Food Canada / Agriculture et Agroalimentaire Canada