Bringing a Needle to a Laser Fight: Comparing Greenhouse Gas Sampling Methods with Gas Chromatography and Fourier Transform Infrared Spectroscopy

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Objectives

- Compare GHG concentrations from closed static chambers over time across a variety of cropping systems and emission levels by sampling technique.
- Determine the best flux regression models for comparability between sampling techniques.

Justification

- Current GHG sampling practices allow for a variety of sampling and analytical techniques including:
  - Syringe sample collection followed by gas chromatography (GC) in the laboratory
  - In-field Fourier transform infrared spectroscopy (FTIR).
- Large databases used in climate modeling will be populated by multiple data streams possibly derived through varying techniques.
- Few studies have compared GHG techniques in the same chamber and with both measurements occurring simultaneously.

Methods

Experimental Design

Field comparisons were conducted at two sites in south-central Wisconsin, in Prairie du Sac, WI on St. Charles Silt Loam and Arlington, WI on Plano Silt Loam. Samples were collected in continuous corn; alfalfa; and dairy cow barn yards with soil, sand, and mulch bedding materials. Specially fitted closed static chambers were used to measure gas concentrations from both systems simultaneously (Figure 1).

Gas Chromatography (GC)

GC sampling used a standard syringe collection and vial storage approach. Normal sampling procedure samples from the chamber headspace every 12 minutes for a 36 minute deployment period. Samples were stored in vials at room temperature and analyzed within two weeks of collection.

Fourier Transform Infrared Spectroscopy (FTIR)

A GasMet® 4040 portable FTIR spectroscopy unit circulates gas between the chamber headspace and the FTIR, analyzing gases with instant results every 30-45 seconds over a 7 minute chamber deployment.

Timing

Two sampling strategies were used to determine a comparison of concentration and flux . For concentration measurements, the FTIR was run continuously for 20 minutes, with GC syringe samples taken from the chamber headspace every 5 minutes. For flux comparison samples taken every 10 minutes for GC samples (Table 1), and only for the first seven minutes of chamber deployment of each chamber lid.

Figure 1. Greenhouse gas chambers, constructed of stainless steel, were used consistently at all sites. Chamber anchors were deployed at least 24 hours in advance of measurements. Chamber lids for this experiment were outfitted with a rubber gas sampling septa for syringe based sampling and two Teflon tubing fittings for FTIR tubing to attach to the chamber.

Table 1. Timing (T) for flux sampling using normal GC and FTIR methods.

	GC							FTIR
	T0	T1	T2	T3	T4	T5	T6	T0
Anchor	*Minutes*							
1	0	10	20	30	40	50	60	0-7
2	8	18	28	38	48	58	68	8-15
3	16	26	36	46	56	66	76	16-23

Concentration Comparison

Statistical Approach: GC and FTIR gas concentrations were compared using a Proc Reg model in SAS to determine if the slope of the concentration comparisons from paired sampling points was significantly different from 1.

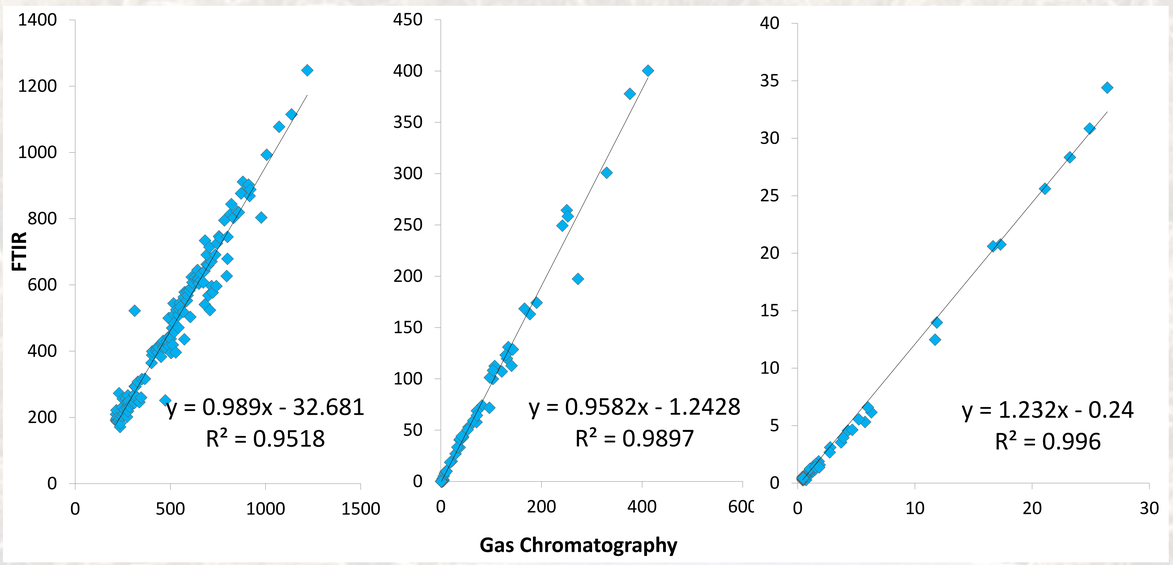

Figure 2. CO_2, CH_4, and N_2O concentration comparisons from 133 paired GHG measurements from FTIR (y-axis) and GC (x-axis).

CO_2	CH_4	N_2O
CO_2 concentrations were not significantly different from a 1:1 relationship (P<0.1) , and are considered comparable between GC and FTIR.	CH_4 concentrations for GC and FTIR were significantly different from a 1:1 relationship, with higher CH_4 concentrations reported from GC sampling.	N_2O concentrations were significantly different from a 1:1 relationship, with higher N_2O emissions measured by FTIR sampling.

Flux Comparison

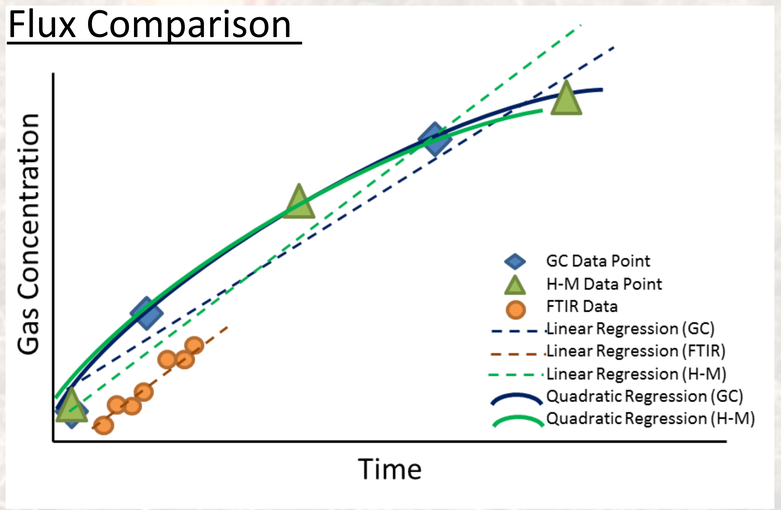

Figure 3. This schematic shows how variable flux regressions can be, from FTIR and GC collection (H-M is considered a subset of GC points, with only three data points used to determine flux) and between regression models from linear to quadratic and H-M calculations. .

Statistical Approach: GC and FTIR flux models were compared using a Proc Reg model in SAS to determine if the slope from paired flux measurements was significantly different from 1.

- Flux was variable between regression models, with the fit of GC data improving from linear (L) to quadratic (Q) to Hutchinson-Mosier (H-M) with the opposite trend in FTIR, suggesting that the best fit for GC was H-M, and the best fit for FTIR was L (fluxes not significantly different from each other shown in **bold**).
- The largest R^2 was between linear FTIR and quadratic GC for all GHGs (best R^2 show in *italics*).

CO_2		FTIR		
		L	Q	H-M
GC	L	0.67 (0.87)	0.39 (0.45)	0.55 (0.58)
	Q	**0.92** ***(0.87)***	0.58 (0.53)	0.75 (0.62)
	H-M	**1.09 (0.82)**	0.68 (0.52)	**0.94 (0.62)**

CH_4		FTIR		
		L	Q	H-M
GC	L	0.51 (0.87)	0.29 (0.81)	0.25 (0.72)
	Q	0.91 *(0.96)*	0.51 (0.87)	0.45 (0.79)
	H-M	**0.94 (0.58)**	0.50 (0.67)	0.46 (0.87)

N_2O		FTIR		
		L	Q	H-M
GC	L	0.84 (0.95)	0.77 (0.98)	0.81 (0.98)
	Q	0.90 *(0.99)*	0.86 (0.94)	**0.90 (0.95)**
	H-M	**1.04 (0.96)**	**0.90 (0.87)**	**0.94 (0.87)**

Table 2. GC (x-axis) and FTIR (y-axis) calculated slopes from linear (L), quadratic (Q) , and Hutchinson-Mosier (H-M) regression models for CO_2, CH_4, and N_2O gas flux measurements (R^2 shown in parentheses). GC and FTIR were considered the most comparable with a slope of 1.

Conclusions

- Gas concentrations from GC and FTIR data were significantly similar for CO_2 data, however, CH_4 and N_2O concentrations were significantly different, and therefore a data transformation is necessary to effectively compare gas concentrations.
- Significant variability was observed when comparing GC and FTIR data with linear, quadratic, and Hutchinson-Mosier models.
- GHG sampling techniques and flux regression models have significant impacts on the outcome of calculated concentrations and flux, which can have significant implications on climate modeling from multiple data streams.