Automated Near-Continuous Measurement of Carbon Dioxide and Nitrous Oxide Fluxes from Soil

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ABSTRACT
Trace gas fluxes often show temporal variability on the order of hours and accurate quantification may be difficult without continuous or near-continuous measurements. We developed an automated near-continuous trace gas analysis system (NCTGAS) to measure soil-atmosphere gas fluxes on a several-times-per-day basis. In this system, air is circulated in a closed sample loop between fully automated flow-through chambers and a photoacoustic infrared trace gas analyzer (TGA). The TGA quantifies infrared active gases at ambient levels within 2 to 3 min. We tested sensitivity, stability, and calibration of the TGA, and the ability of the NCTGAS to measure fluxes of CO₂ and N₂O. In addition to static tests, fluxes of CO₂ and N₂O were simulated by bleeding known quantities of these gases into a test chamber. Gas samples were simultaneously analyzed by TGA and removed for independent analysis of CO₂ by conventional infrared gas analysis and for N₂O by gas chromatography. The TGA-based flux measurements were statistically identical to the independent measurements of both CO₂ and N₂O. In situ fluxes of CO₂ and N₂O measured by the NCTGAS were 105 ± 6 and 93 ± 10%, respectively, of those measured from hand-drawn samples. The TGA was as or more stable than conventional means for measuring CO₂ and N₂O in air at ambient concentrations, and was equally sensitive across the range of concentrations normally encountered in field measurements. Fast response time and ease of use offers significant advantages over conventional gas chromatography.

C O N C E R N about increasing atmospheric concentrations of the radiatively important biogenic gases CO₂ and N₂O has stimulated much recent research concerning their fluxes from soils (e.g., Keller et al., 1986, 1993; Bowden et al., 1990; Mosier et al., 1991; Skiba et al., 1992; Sommerfeld et al., 1993; Castro et al., 1994). Despite much effort, global source and sink strengths of several biogenic trace gases are still obscure (Robertson, 1993; Intergovernmental Panel on Climate Change, 1996) in part because soil fluxes, in particular fluxes of N₂O, have a high temporal and spatial variability. Until now most knowledge of N₂O fluxes has been based on data obtained by conventional chamber methods (e.g., Ambus et al., 1993; Clayton et al., 1994; Livingston and Hutchinson, 1995; Smith et al., 1995), which at best provide a continuous temporal resolution on the order of days, and typically on the order of weeks or months due to sampling and analysis limitations (Mosier, 1989). Because N₂O often shows temporal variability on the order of hours (e.g., Blackmer et al., 1982; Christensen, 1983a; Sexton et al., 1985), the accurate quantification of fluxes in many habitats may be difficult without continuous or near-continuous measurement. Although such measurements cannot be taken at all sites, continuous time series measurements at selected sites can be used to parameterize and test process-level models operating at appropriate time scales, and these models can then be used to accurately estimate fluxes for sites where gas fluxes are less intensively monitored. The uncertainty associated with regional and habitat-specific contributions to global fluxes can then be narrowed.

Micrometeorological techniques (Smith et al., 1994; Christensen et al., 1996) provide one means for obtaining continuous data at the field scale. However, these systems operate only under certain climatic conditions, and require large uniform areas and substantial logistical and technical resources that limit their implementation (Smith et al., 1994). Automated or semi-automated systems designed for gas sampling from in situ enclosures (Denmead, 1979; Christensen, 1983b; International Atomic Energy Agency, 1992; Loftfield et al., 1992) offer a useful and less expensive opportunity to obtain continuous or near-continuous flux data. The analytical units in such systems, however, are usually based on gas chromatography and require complex split-stream detectors in order to monitor two or more gas components simultaneously.

We present here the description and test results of an automated system for near-continuous measurement of CO₂ and N₂O fluxes from soil chambers. The analytical unit is based on a photoacoustic infrared spectrometer that analyzes H₂O vapor, CO₂, and N₂O within 2 to 3 min without the need for subsampling and chromatographic separation.

MATERIALS AND METHODS
System Setup
The overall system is comprised of a closable sampling chamber that sits on the soil surface, a headspace delivery system that circulates headspace between the chamber and the analytical unit, and an infrared spectrometer that analyzes gas for H₂O vapor, CO₂, and N₂O.

The construction and operating condition of the fully automated chambers (Fig. 1) is based on a vented, non-steady state flow-through design (see Livingston and Hutchinson, 1995). Each chamber has a stainless steel base (30 by 58 by 30 cm height) and a Plexiglas lid that slides closed during at least 60-min analysis periods by means of a linear actuator (von Weise Gear Co., St. Clair, MO) mounted at one end of the chamber (Fig. 1a). We used white opaque lids to prevent temperature increases during the short incubation times (data not shown). As the lid slides across the top of the base, it encounters a fixed cam (Fig. 1b) that forces it onto a weatherstrip, forming an airtight seal. The chamber vent is a 1-m coiled 3.2-mm copper tubing that penetrates the chamber base.

Abbreviations: ECD, electron-capture detector; GC—ECD, gas chromatograph with electron-capture detector; IRGA, infrared gas analyzer; NCTGAS, near-continuous trace gas analysis system; SE, standard error; TGA, trace gas analyzer.

Fig. 1. Automated field chamber for measurement of gas fluxes from the soil. The chamber has a stainless steel base (30 by 58 by 30 cm height) and a weighted and painted Plexiglas lid that slides closed during 60-min analysis periods by means of a linear actuator mounted at one end of the chamber (Fig. 1A). As the lid slides across the top of the base, it encounters a fixed cam (Fig. 1B) that forces it onto a weatherstrip, forming an airtight seal.

at one end. The chamber base is pushed 5 cm into the soil when used in the field.

A general schematic of the sample loop is shown in Fig. 2. Two diaphragm pumps (Cole-Parmer Instrument Co., Chicago, IL) recirculate chamber atmosphere at 16 mL through 50 m of 3.2-mm o.d. copper tubing, delivering chamber air to a 200-mL sample tube. Chamber outlet and inlet lines are connected to two multiposition rotary valves (Valco Instruments Co., Houston, TX). Analyzed samples are returned to the sample loop through a three-way solenoid valve, which also prevents the sample from reentering the sample tube (Fig. 2). Presently the system is equipped with eight chambers but the configuration provides for the simultaneous operation of 16 chambers.

Air in the sample tube is analyzed for H2O vapor, CO2, and N2O by a recently introduced TGA (Innova Airtech, Ballerup, Denmark), which quantifies infrared-active trace gases at ambient levels based on photoacoustic infrared detection (Bruel and Kjær. 1990). Briefly, a 3-mL analysis cell in the TGA is purged for 30 s at 5 mL s−1 with air from the 200-mL recirculating system sample tube via 3.2-mm i.d. tubing using an internal pump in the TGA, and the cell is hermetically sealed. Light from an infrared source is pulsed mechanically and then filtered through an optical filter, unique to the gas being analyzed, before entering the analysis cell. The repetitive heating and cooling of the gas, due to its absorption of the pulsed light, causes an equivalent increase and decrease in pressure that is detected by two microphones and converted into a voltage differential, proportional to the concentration of the monitored gas present in the cell. The TGA holds up to six different optical filters in a rotating filter carousel, and is thus capable of measuring six gases including H2O vapor in about 2 min. Because H2O vapor absorbs infrared light at nearly all wavelengths, each optical filter is calibrated for humidity interference, i.e., the ratio of the signal measured with any one filter and the H2O filter measured in a zero gas with constant concentration of H2O vapor. This humidity gain factor for any one optical filter is independent of the H2O vapor concentration. Compensation for cross interference by nontarget gases (e.g., CO2 in N2O) is also necessary. A cross compen-
Fig. 2. General schematic of the sample loop of the near-continuous trace gas analysis system. During the pumping period, two pumps (Pump 1 and 2) recirculate gas throughout a closed chamber and a 200-mL sample tube via two multiposition rotary valves (MPRV 1 and 2). During the sampling period, the sample loop pumps are turned off and the trace gas analysis (TGA) pump draws a sample of gas from the sampling tube for analysis of $\text{H}_2\text{O}$ vapor, $\text{CO}_2$, and $\text{N}_2\text{O}$. The analyzed sample is returned to the sample loop via the three-way solenoid valve, forming a completely closed system.

System Testing

We tested sensitivity, stability, and calibration of the TGA at near-ambient ranges of $\text{CO}_2$ and $\text{N}_2\text{O}$ concentrations, and also tested the ability of the instrument to measure simulated and in situ $\text{CO}_2$ and $\text{N}_2\text{O}$ fluxes. The TGA was calibrated and the humidity gain and cross compensation factors were provided by the manufacturer in early 1994. We performed the test experiments beginning February 1995 through September 1996 and did not recalibrate the TGA. Tests were first conducted in the field with a chamber on a water-filled tray to provide a sealed test system. We then conducted tests under field conditions with chambers situated in different cropping systems at the W.K. Kellogg Biological Station in southwest Michigan. Twenty-five-meter lengths of 3.2-mm o.d. copper tubing connected the chamber input and output ports to the TGA (see Fig. 2). Each chamber lid was also equipped with a rubber septum for manually injecting and removing gases from the chamber during tests. The volume of the entire sample loop (including chamber) was 49 L.

In the first set of experiments we increased $\text{CO}_2$ concentrations within the sealed chamber stepwise from ambient to 1.5 times ambient during a 2-h analysis period. At 20-min intervals during this period, we injected 60-mL aliquots of a 7.1% $\text{CO}_2$ in $\text{N}_2$ mixture into the chamber. This experiment allowed us to evaluate the time required by the system for equilibration. Using a similar protocol, 70-mL aliquots of 52.5 pi L$^{-1}$ $\text{N}_2\text{O}$ in $\text{N}_2$ were injected into the chamber to increase $\text{N}_2\text{O}$ concentrations.

In a second set of experiments, we simulated a variety of steady-state $\text{CO}_2$ fluxes within a sealed chamber by bleeding into the chamber a 3.03% $\text{CO}_2$ in $\text{N}_2$ mixture at flow rates...
Fig. 3. Near-continuous trace gas analysis system (NCTGAS) measurements of H$_2$O vapor, CO$_2$, and N$_2$O concentrations in a sealed chamber in response to repetitive injections (arrows) of known concentrations of (A) CO$_2$ and (B) N$_2$O standards. The horizontal line segments represent average readings assuming equilibrium 12 min following each injection. Note that (A) N$_2$O in the presence of increasing CO$_2$ and H$_2$O is stable, and that (B) CO$_2$ in the presence of increasing N$_2$O and H$_2$O is stable.

varying from 14 to 100 mL min$^{-1}$ during a 60- to 100-min analysis period. We took subsamples every 15 to 25 min by syringe for independent analysis in the laboratory on an infrared gas analyzer (IRGA; Model 865, Beckman Instruments, Fullerton, CA). The IRGA was calibrated using a 7.1% CO$_2$ gas analyzer (IRGA; Model 865, Beckman Instruments, Fullerton, CA). The IRGA was calibrated using a 7.1% CO$_2$ in N$_2$ mixture. Samples were stored in crimped-seal vials prior to IRGA analysis, which occurred within 24 h. Carbon dioxide fluxes were calculated as the slopes of the linear regressions of CO$_2$ concentrations vs. time for both TGA and IRGA measurements. Nitrous oxide fluxes were tested in a similar manner by bleeding 0.5, 4.24, and 52.5 N$_2$O in N$_2$ gas mixtures at flow rates varying from 14 to 100 mL min$^{-1}$. Hand-drawn N$_2$O samples were measured in the laboratory on a Hewlett Packard 5890 gas chromatograph equipped with an electron-capture detector (ECD). The ECD was calibrated using 500 and 740 nL L$^{-1}$ N$_2$O in N$_2$ standards.

In a final set of experiments, we measured in situ CO$_2$ and N$_2$O fluxes in chambers situated in different cropping systems. In these experiments we also compared TGA-measured fluxes to hand-drawn IRGA- and ECD-measured fluxes. Concentrations of CO$_2$ and N$_2$O in the chambers were measured for 1 h, with hand-drawn subsamples removed every 15 min and analyzed as described for the earlier experiment.

**RESULTS AND DISCUSSION**

**Experiment 1: Equilibration Time and Cross-Gas Interference**

The NCTGAS appears to accurately reflect the stepwise aliquots of known-concentration CO$_2$ injected into the system during the first set of experiments (Fig. 3). Preliminary experiments showed that 12 min are required by our system to completely disperse the injected aliquot through the entire sample loop. The difference between adjacent steady-state concentrations ("stair steps" in Fig. 3) was determined by assuming this 12-min period, as indicated by arrows on Fig. 3. The increase in CO$_3$, which is the difference between two adjacent steady-state values, averaged 86 ± 7 IL L$^{-1}$ (± standard error [SE]), not different from the calculated increase of 87 μL L$^{-1}$. Similar results were obtained for N$_2$O (Fig. 3), which gave an average stepwise increase of 85 ± 15 nL (± SE), also not different from the anticipated 75 nL L$^{-1}$ N$_2$O. Data from these experiments also demonstrate that humidity gain and cross-compensation factors were correct. The increase in H$_2$O vapor due to the H$_2$O in the bottom of the water-sealed chamber, concomitant with an increase in CO$_2$, did not affect the N$_2$O signal for the period during which H$_2$O vapor and CO$_2$ increased (Fig. 3A). Likewise, H$_2$O vapor and N$_2$O did not affect the CO$_2$ signal for the period during which H$_2$O vapor and N$_2$O increased (Fig. 3B).

Increments of 86 μL L$^{-1}$ of CO$_2$ and 85 nL L$^{-1}$ of N$_2$O correspond to changes of about 25% relative to ambient concentrations of these gases, and were clearly identified from the TGA signal. A change in CO$_2$ of 25% h$^{-1}$ corresponds to a flux of 1.1 μg C cm$^{-2}$ h$^{-1}$ using our chamber design, and is in the very low range of field CO$_2$ fluxes. A change in N$_2$O of 25% h$^{-1}$ corresponds to a flux of 2.7 nG N cm$^{-2}$ h$^{-1}$, which also is in the low range of field fluxes. Under steady-state conditions with ambient concentrations in the sample loop, the CO$_2$ signal typically fluctuates ±7 μL L$^{-1}$ (2%) and the N$_2$O signal fluctuates ±19 nL L$^{-1}$ (6%) (not shown). This variability compares favorably with that encountered with automated repetitive N$_2$O analysis on a gas chromatograph (e.g., Parkin, 1985), and suggests that even smaller differences in concentrations can be effectively resolved.

**Experiment 2: Simulated Field Test**

Bleeding CO$_2$ or N$_2$O into a sealed chamber provided a constant increase in the measured concentration of either gas both with the NCTGAS and via hand-drawn samples analyzed in the laboratory (Fig. 4). The series of simulated CO$_2$ fluxes measured by the NCTGAS were statistically identical ($P < 0.05$) to the fluxes ob-
The relationship between the two measures can be described by the linear regression \( \text{CO}_2(TGA) = 1.07 \pm 0.02 \times \text{CO}_2(IRGA) - 26 \pm 29 \) \( (R^2 = 0.999) \). The rates varied from 380 to 2066 \( \mu L \text{ L}^{-1} \text{h}^{-1} \), which covers the range typically observed in field work. A similar relationship was also found for \( \text{N}_2\text{O} \) fluxes (Fig. 6), with the relationship described by the linear regression \( \text{N}_2\text{O}(TGA) = 1.04 \pm 0.03 \times \text{N}_2\text{O}(ECD) - 6 \pm 15 \) \( (R^2 = 0.997) \). We varied \( \text{N}_2\text{O} \) rates from 29 to 1212 \( n \text{ L} \text{L}^{-1} \text{h}^{-1} \), which is also typical for field fluxes, and demonstrates that changes as low as 9\% in \( \text{N}_2\text{O} \) (29 \( n \text{ L} \text{L}^{-1} \text{h}^{-1} \)) could be resolved by the NCTGAS.

Although a highly accurate calibration of the analytical unit is not necessary for measuring gas fluxes (as opposed to concentrations), data in Fig. 4 suggest good agreement between the concentrations observed with the TGA relative to those measured with the IRGA and gas chromatograph with electron capture detector (GC-ECD). Further evidence for a reliable calibration of the TGA was achieved by comparing multiple sets of the TGA measurements with independent measurements (IRGA and GC-ECD) on hand-drawn samples (Fig. 7 and 8). Data were used from both the sealed-chamber experiments and from field chambers. For both gases, the two methods gave essentially identical concentrations as indicated by intercepts through the origin of the regression lines, with \( \text{CO}_2(TGA) = 0.98 \pm 0.01 \times \text{CO}_2(IRGA) - 22 \pm 19 \) \( (R^2 = 0.994) \) and \( \text{N}_2\text{O}(TGA) = 1.05 \pm 0.05 \times \text{N}_2\text{O}(ECD) - 4 \pm 39 \) \( (R^2 = 0.922) \), respectively.

De Klein et al. (1996) also found good agreement between known concentrations of \( \text{N}_2\text{O} \) and photoacoustic infrared detection throughout the 0 to 100 \( \mu L \text{ L}^{-1} \) range using an identical analytical unit.

**Experiment 3: In Situ Flux Tests**

We compared NCTGAS measured fluxes of \( \text{CO}_2 \) and \( \text{N}_2\text{O} \) in different cropping systems with those measured by the independent laboratory analysis (Table 1). As for the simulated fluxes, in situ measurements with the NCTGAS across a wide range of fluxes compared very well with those obtained by conventional methods. On...
Table 1. Fluxes of CO₂ and N₂O measured from different cropping systems with the near-continuous trace gas analysis system (NCTGAS) and from hand-drawn samples analyzed independently in the laboratory on an infrared gas analyzer (IRGA) and a gas chromatograph with electron-capture detector (GC-ECD). Rates are calculated from the slope (± standard error) of the regression of gas concentrations inside a 50-L flux chamber vs. time during 1 h (n = 24 samples for NCTGAS; n = 5 for IRGA and GC-ECD).

<table>
<thead>
<tr>
<th>Cropping system and date</th>
<th>CO₂-C</th>
<th>N₂O-N</th>
<th>NCTGAS</th>
<th>IRGA</th>
<th>GC-ECD</th>
</tr>
</thead>
<tbody>
<tr>
<td>No-till corn, 11 June 1996</td>
<td>14.0 ± 0.2</td>
<td>2.5 ± 0.2</td>
<td>0.3</td>
<td>0.8</td>
<td>0.1</td>
</tr>
<tr>
<td>Organic corn, 18 June 1996</td>
<td>11.7 ± 0.2</td>
<td>2.5 ± 0.2</td>
<td>0.3</td>
<td>0.8</td>
<td>0.1</td>
</tr>
<tr>
<td>Organic corn, 5 Aug 1996</td>
<td>3.5 ± 0.2</td>
<td>2.5 ± 0.2</td>
<td>0.3</td>
<td>0.8</td>
<td>0.1</td>
</tr>
<tr>
<td>Alfalfa, 21 Aug 1996</td>
<td>14.0 ± 0.4</td>
<td>15.6 ± 0.9</td>
<td>0.9</td>
<td>0.8</td>
<td>1.0 ± 0.8</td>
</tr>
<tr>
<td>Alfalfa, 21 Aug 1996</td>
<td>9.6 ± 0.5</td>
<td>9.4 ± 0.7</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>No-till corn, 3 Sept. 1996</td>
<td>30.0 ± 0.2</td>
<td>30.7 ± 0.6</td>
<td>0.9 ± 0.0</td>
<td>0.0 ± 0.0</td>
<td>0.0 ± 0.8</td>
</tr>
<tr>
<td>No-till corn, 4 Sept. 1996</td>
<td>32.4 ± 0.4</td>
<td>32.3 ± 1.4</td>
<td>1.0 ± 0.6</td>
<td>1.5 ± 0.6</td>
<td>1.5 ± 0.6</td>
</tr>
<tr>
<td>No-till corn, 5 Sept. 1996</td>
<td>51.5 ± 1.0</td>
<td>46.6 ± 2.1</td>
<td>1.9 ± 0.6</td>
<td>2.2 ± 0.6</td>
<td>2.2 ± 0.6</td>
</tr>
</tbody>
</table>

† n.d. = no data. ‡ Measured from microplot amended with NH₄NO₃ and glucose.

average, TGA-based CO₂ fluxes were 105 ± 6% relative to the IRGA-based measurements, and TGA-based N₂O fluxes were 93 ± 10% relative to the GC-ECD measurements. The accuracy of NCTGAS-derived fluxes were generally higher (lower SE) than that for both IRGA and GC-ECD derived fluxes due to the much higher number of measurements obtained with the NCTGAS.

During these in situ measurements H₂O vapor concentrations inside the chamber typically increased from 2 ± 0.2 to 3 ± 0.2% without affecting TGA readings of CO₂ and N₂O, in agreement with the findings using a sealed chamber (Fig. 3). The measured CO₂ efflux is total soil and root respiration; we assumed no photosynthesis occurred inside the dark chambers.

Experiment 4: Actual Fluxes

Preliminary measurements in the field were made during a 3-d period from one chamber installed in a soybean [Glycine max (L.) Mem] cropping system (Fig. 9). The chamber was activated every 8 h and CO₂ and N₂O in the chamber measured about 24 times during a 1-h period (see inset in Fig. 9). The results show a very high diurnal variability in N₂O fluxes, with a temporal coefficient of variation (CV) of 78%; the CO₂ fluxes had a lower temporal CV of 13%. The increase in activity was preceded by a rainfall (6.8 mm) on Day 181. A temporal high resolution of trace gas fluxes in the field, at a cost comparable to conventional gas chromatography. The advantage of this instrument is its simplicity; the gases in the sample loop are monitored continuously without a need for subsampling, chromatographic separation, and integration of detector signals, and the instrument is portable and operated without the need for pressurized carrier gases. Users should be careful to check the calibration and stability of any given unit in the field, but this is easily done and would need to be performed for standard gas chromatography and infrared spectrometry in any case. Overall, this instrument offers promise for substantially improving the measurement of trace gas fluxes in the field, at a cost comparable to conventional gas chromatography.

CONCLUSIONS

We found that the sensitivity and stability of an infrared photoacoustic TGA is sufficiently high for measuring ambient fluxes of CO₂ and N₂O. We have also demonstrated that fluxes measured by the TGA compare with those obtained by conventional infrared spectrometry and gas chromatography. The advantage of this instrument is its simplicity; the gases in the sample loop are monitored continuously without a need for subsampling, chromatographic separation, and integration of detector signals, and the instrument is portable and operated without the need for pressurized carrier gases. Users should be careful to check the calibration and stability of any given unit in the field, but this is easily done and would need to be performed for standard gas chromatography and infrared spectrometry in any case. Overall, this instrument offers promise for substantially improving the measurement of trace gas fluxes in the field, at a cost comparable to conventional gas chromatography.

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