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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 ana lyzer (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 CO_2 and N_2O. In addition to static tests, fluxes of CO_2 and N_2O 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 CO_2 by conventional infrared gas analysis and for N_2O by gas chromatography. The TGA-based flux measurements were statistically identical to the independent measurements of both CO_2 and N_2O. In situ fluxes of CO_2 and N_2O 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 CO_2 and N_2O 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.

CONCERN about increasing atmospheric concentrations of the radiatively important biogenic gases CO_2 and N_20 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 obscured (Robertson, 1993; Intergovernmental Panel on Climate Change, 1996) in part because soil fluxes, in particular fluxes of N_2O, have a high temporal and spatial variability. Until now most knowledge of N_2O 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 N_2O often shows temporal variability on the order of hours (e.g., Blackmer et al., 1982; Christensen, 1983a; Sexstone 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 designs and multiple 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 CO_2 and N_20 fluxes from soil chambers. The analytical unit is based on a photoacoustic infrared spectrometer that analyzes H_2O vapor, CO_2, and N_2O 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 circulated gas for H_2O vapor, CO_2, and N_2O.

The construction and operating condition of the fully automated chambers (Fig. 1) is based on a vented, non-steadystate 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. la). 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. lb) 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

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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.

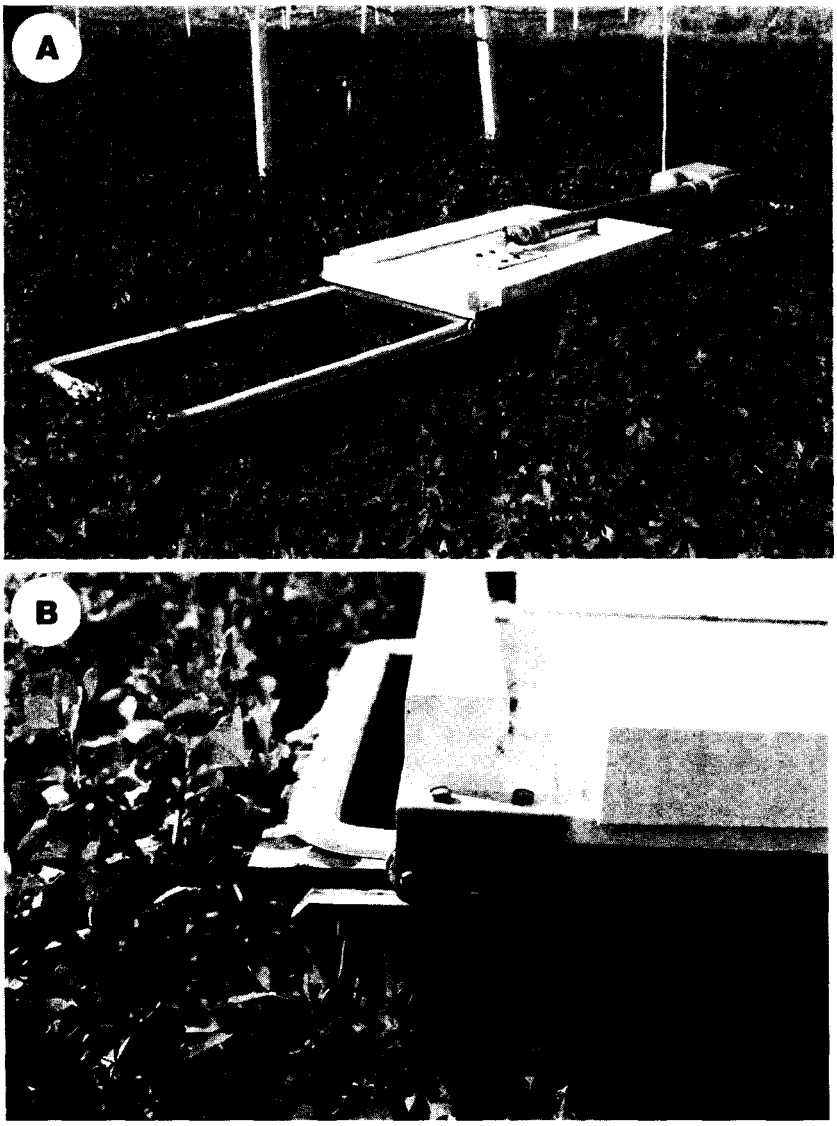

Fig. 1. Automated field chamber for measurement of gas fluxes from the soil. The chamber has a stainless steel base (30 by 58 by 30 cm height) and a weighted and painted Plexiglas lid that slides closed during 60-min analysis periods by means of a linear actuator mounted at one end of the chamber (Fig. 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 H_2O vapor, CO_2, and N_2O by a recently introduced TGA (Innova Airtech, Ballerup, Denmark), which quantifies infrared-active trace gases at ambient levels based on photoacoustic infrared detection (Brüel 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 pulsated 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 pulsated 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 H_2O vapor in about 2 min. Because H_2O 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 H_2O filter measured in a zero gas with constant concentration of H_2O vapor. This humidity gain factor for any one optical filter is independent of the H,0 vapor concentration. Compensation for cross interference by nontarget gases (e.g., CO_2 in N_2O) is also necessary. A cross compen-

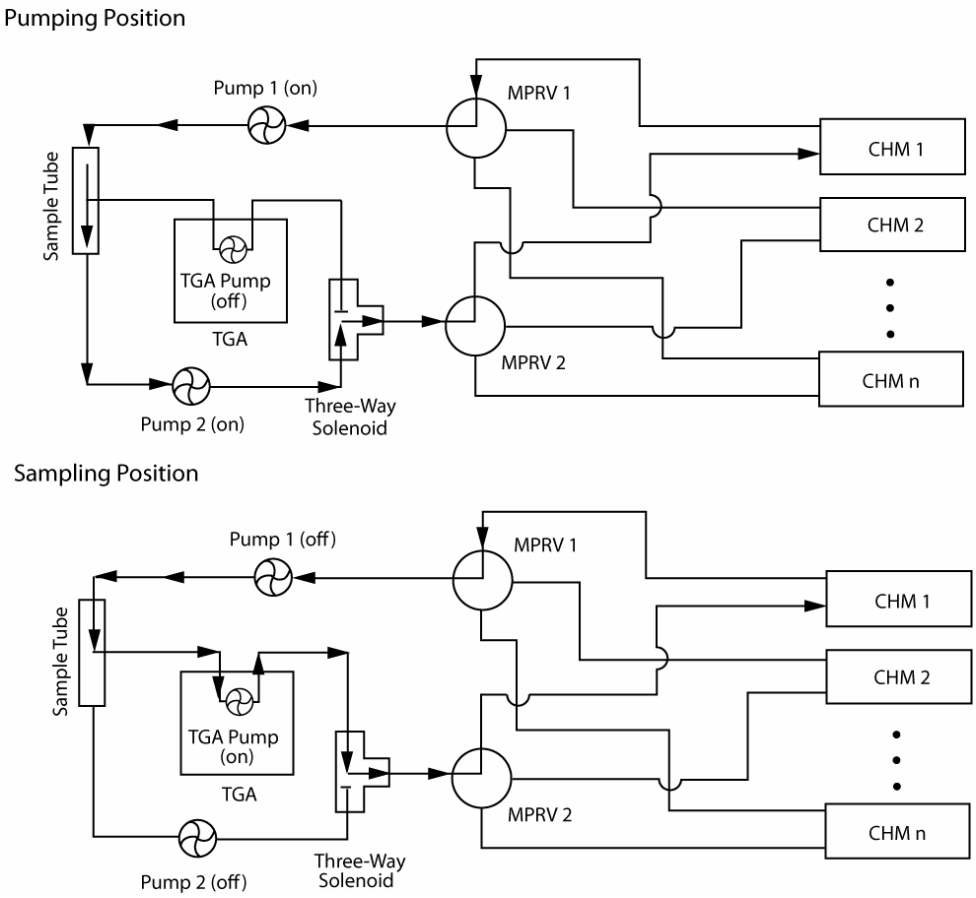

Fig. 2. General schematic of the sample loop of the near-continuous trace gas analysis system. During the pumping period, two pumps (Pump 1 and 2) recirculate gas throughout a closed chamber and a 200-mL sample tube via two multiposition rotary valves (MPRV 1 and 2). During the sampling period, the sample loop pumps are turned off and the trace gas analysis (TGA) pump draws a sample of gas from the sampling tube for analysis of H_2O vapor, CO_2, and N_2O. The analyzed sample is returned to the sample loop via the three-way solenoid valve, forming a completely closed system.

sation factor was obtained by measuring the signal with the N_2O filter in a constant-N_2O gas with different CO_2 concentrations.

An IBM-compatible PC equipped with analog–digital I/O lines controls the chambers, pumps, and valving described in Fig. 2. Each of the eight sample chambers in our current implementation can be activated three times daily and analyzed for N_20 and CO_2 every 2.5 min during a 60-min analysis period. The TGA is controlled by the computer through a serial interface that allows reading and writing data both to and from the TGA. Data received by the computer from the TGA is processed and downloaded to printer and disk. The entire system is controlled by a program written and compiled in QBasic. Although the TGA is portable, it requires 110/220 V alternating current. It is operated without the need of pressurized gases. In our setup, the analytical unit, computer, and pumps were located inside an all-weather shed adjacent to our field plots in order to protect the electronics controlling the automation.

System Testing

We tested sensitivity, stability, and calibration of the TGA at near-ambient ranges of CO_2 and N_2O concentrations, and also tested the ability of the instrument to measure simulated and in situ CO_2 and N_2O 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 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% CO2 in N2 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 $L^{-'}$ N2O in N2 were injected into the chamber to increase N_2O concentrations.

In a second set of experiments, we simulated a variety of steady-state CO_2 fluxes within a sealed chamber by bleeding into the chamber a 3.03% CO_2 in N_2 mixture at flow rates

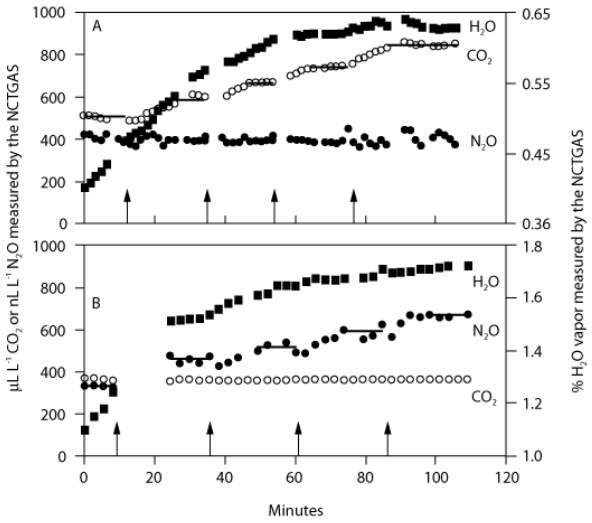

Fig. 3. Near-*continuous* trace gas analysis system (NCTGAS) measurements of H_2O vapor, CO_2, and N_2O concentrations in a sealed chamber in response to repetitive injections (arrows) of known concentrations of (A) CO_2 and (B) N_2O standards. The horizontal line segments represent average readings assuming equilibrium 12 min following each injection. Note that (A) N_2O in the presence of increasing CO_2 and H_2O is stable, and that (B) CO_2 in the presence of increasing N_2O and H_2O 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 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_2O in N_2 gas mixtures at flow rates varying from 6 to 1000 mL min^{-1}. Hand-drawn N_2O 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_2O in N_2 standards.

In a final set of experiments, we measured in situ CO_2 and N_2O 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_2O 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 step wise 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

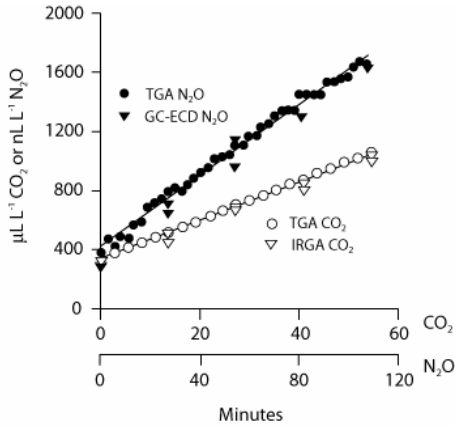

Fig. 4. Carbon dioxide and N_2O concentrations measured with the near-continuous trace gas analysis system (TGA) and with an infrared gas analyzer (IRGA) and a gas chromatograph with an electron-capture detector (GC-ECD) in the laboratory. Samples were taken from a sealed chamber into which either CO_2 or N_20 was bled at a constant rate. The lines indicate the results of regression analysis.

CO_2, 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^{-1} L. Similar results were obtained for N_2O (Fig. 3), which gave an average stepwise increase of 85 ± 15 nL (± SE), also not different from the anticipated 75 nL L^{-1} N_2O. Data from these experiments also demonstrate that humidity gain and cross-compensation factors were correct. The increase in H_20 vapor due to the H_2O in the bottom of the water-sealed chamber, concomitant with an increase in CO_2, did not affect the N_20 signal for the period during which H_20 vapor and CO_2 increased (Fig. 3A). Likewise, H_20 vapor and N_20 did not affect the CO_2 signal for the period during which H_20 vapor and N_2O increased (Fig. 3B).

Increments of 86 µL L^{-1} of CO_2 and 85 nL L^{-1} of N_2O 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_2O of 25% h^{-1} corre sponds 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_2O signal fluctuates ±19 nL L^{-1} (6%) (not shown). This variability compares favorably with that encoun tered with automated repetitive N_2O 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_20 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-

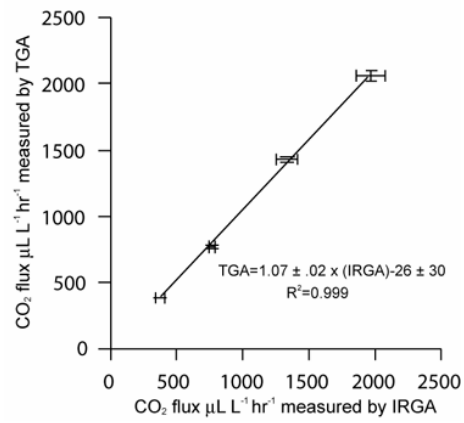

Fig. 5. Relationship between simulated CO_2 fluxes in a sealed chamber measured with the near-continuous trace gas analysis system (TGA) vs. hand-drawn samples measured with an infrared gas analyzer (IRGA). The line indicates the results of a regression analysis. Bars are ± one standard error of the slopes used to calculate single rates.

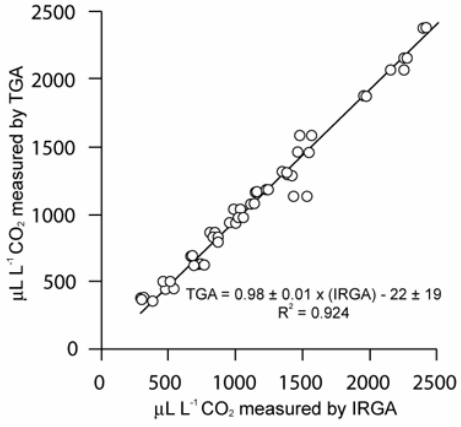

Fig. 7. Relationship between chamber CO2 concentrations measured with the near-continuous trace gas analysis system (TGA) vs. hand-drawn samples measured with an infrared gas analyzer (IRGA). The line indicates the results of a regression analysis.

tained from the hand-drawn samples (Fig. 5). The relationship between the two measures can be described by the linear regression $CO_{2(TGA)}$=1.07±0.02 X $CO_{2(IRGA)}$ − 26 ± 29 (R^2=0.999). The rates varied from 380 to 2066 µL $L^{-1}h^{-1}$, which covers the range typically observed in field work. A similar relationship was also found for N_2O fluxes (Fig. 6), with the relationship described by the linear regression $N_2O_{(TGA)}$ = 1.04 ± 0.03 X $N_2O_{(ECD)}$ − 6 ± 15 (R^2 = 0.997). We varied N_2O rates from 29 to 1212 n L $L^{-1}h^{-1}$, which is also typical for field fluxes, and demonstrates that changes as low as 9% in N_2O (29 nL $L^{-1}h^{-1}$) 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 chomatograph 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 $CO_{2(TGA)}$ = 0.98 ± 0.01 X $CO_{2(IRGA)}$ − 22 ± 19 (R^2 = 0.994) and $N_2O_{(TGA)}$ 1.05 ± 0.05 x $N_2O_{(ECD)}$ 4 ± 39 (R^2 = 0.922), respectively. De Klein et al. (1996) also found good agreement between known concentrations of N_2O and photoacoustic infrared detection throughout the 0 to 100 µL L^{-1} range using an identical analytical unit.

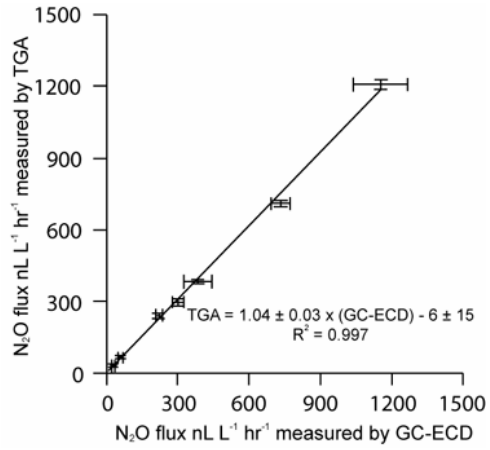

Fig. 6. Relationship between simulated N20 fluxes in a sealed chamber measured with the near-continuous trace gas analysis system (TGA) vs. hand-drawn samples measured with a gas chromatograph with electron-capture detector (GC-ECD). The line indicates the results of a regression analysis. Bars are ± one standard error of the slopes used to calculate single rates.

Experiment 3: In Situ Flux Tests

We compared NCTGAS measured fluxes of CO_2 and N_2O 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

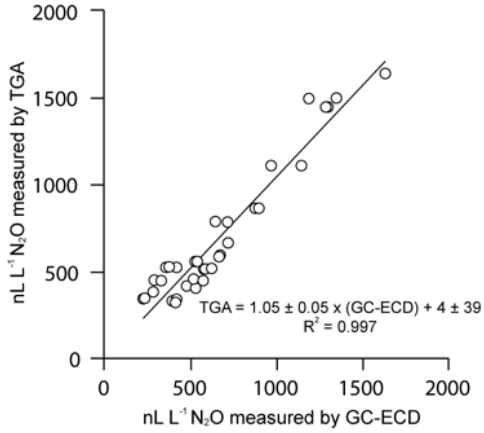

Fig. 8. Relationship between chamber N_20 concentrations measured with the near-continuous trace gas analysis system (TGA) vs. hand-drawn samples measured with a gas chromatograph with electron-capture detector (GC-ECD). The line indicates the results of a regression analysis.

Table 1. Fluxes of CO_2 and N_2O 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 (GCECD). 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).

	CO_2-C		N_2O-N	
Cropping system and date	NCTGAS	IRGA	NCTGAS	GC-ECD
	— μg cm^{-2} h^{-1} —		— ng cm^{-2} h^{-1} —	
No-till corn, 11 June 1996	14.0 ± 0.2	12.9 ± 0.3	3.7 ± 0.2	3.5 ± 1.0
Organic corn, 18 June 1996	11.7 ± 0.2	12.5 ± 0.3	35.3 ± 0.8	42.8 ± 1.6
Organic corn, 5 Aug 1996	3.5 ± 0.2	2.5 ± 0.2	1.3 ± 0.6	0.9 ± 0.1
Alfalfa, 21 Aug 1996	14.0 ± 0.4	15.6 ± 0.9	0.9 ± 0.8	1.0 ± 0.8
Alfalfa, 21 Aug 1996	9.6 ± 0.5	9.4 ± 0.7	n.d.†	n.d.
No-till corn‡, 3 Sept. 1996	30.0 ± 0.2	30.7 ± 0.6	0.0 ± 0.8	0.0 ± 0.8
No-till corn‡, 4 Sept. 1996	32.4 ± 0.4	32.3 ± 1.4	1.0 ± 0.6	1.5 ± 0.6
No-till corn‡, 5 Sept. 1996	51.5 ± 1.0	46.6 ± 2.1	1.9 ± 0.6	2.2 ± 0.6

† n.d. = no data.

‡ Measured from microplot amended with NH_4NO_3 and glucose.

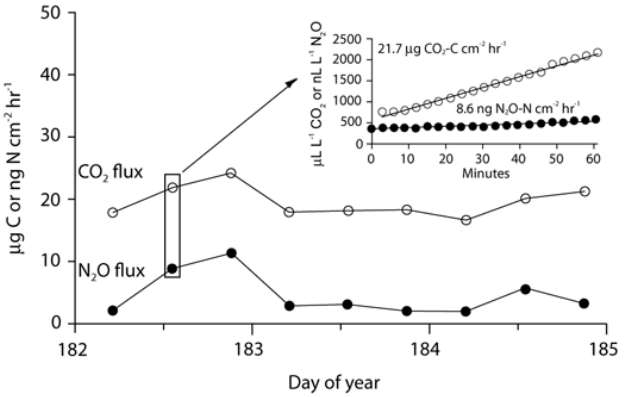

Fig. 9. Fluxes of CO_2 and N_2O during a 3-d period from one chamber installed in a soybean cropping system. Each value is a rate calculated from about 24 samples taken during a 1-h period while the chamber was closed. The graph inset is the CO_2 and N_2O concentrations in the chamber for the Day 182 noontime sample event.

average, TGA-based CO_2 fluxes were 105 ± 6% relative to the IRGA-based measurements, and TGA-based N_2O 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 H_2O vapor concentrations inside the chamber typically increased from 2 ± 0.2 to 3 ± 0.2% without affecting TGA readings of CO_2 and N_2O, in agreement with the findings using a sealed chamber (Fig. 3). The measured CO_2 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 CO_2 and N_2O 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 N_2O fluxes, with a temporal coefficient of variation (CV) of 78%; the CO_2 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 combination with monitoring of important driving factors, e.g., soil moisture and temperature, should provide significant information for model parameterization and add to the understanding of the processes underlying the in situ fluxes of these important gases.

CONCLUSIONS

We found that the sensitivity and stability of an infrared photoacoustic TGAis sufficiently high for measureing ambient fluxes of CO_2 and N_2O. 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.

ACKNOWLEDGMENTS

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REFERENCES

Ambus, P., H. Clayton, J.R.M. Arah, K.A. Smith, and S. Christensen. 1993. Similar N_2O flux from soil measured with different chamber techniques. Atmos. Environ. 27A:121-123.

Blackmer, A.M., S.G. Robbins, and J.M. Bremner. 1982. Diurnal variability in rate of emission of nitrous oxide from soils. Soil Sci. Soc. Am. J. 46:937-942.

Bowden, R.D., P.A. Steudler, and J.M. Melillo. 1990. Annual nitrous oxide fluxes from temperate forest in the northeastern United States. J. Geophys. Res. 95:13997-14005.

Brtiel and Kjxr. 1990. Multi-gas monitor type 1302. Instruction manual. Publ. no. BE 1066-11. Billet and Kjxr, Nzerum, Denmark.

Castro, M.S., W.T. Peterjohn, J.M. Melillo, P.A. Steudler, H.L. Gholz, and D. Lewis. 1994. Effects of nitrogen fertilization on the fluxes of N_2O, CH_4, and CO_2 from soils in a Florida slash pine plantation. Can. J. For. Res. 24:9-13.

Christensen, S. 1983a. Nitrous oxide emission from a soil under permanent grass: Seasonal and diurnal fluctuations as influenced by manuring and fertilization. Soil Biol. Biochem. 15:531-535.

Christensen, S. 1983b. Nitrous oxide emission from the soil surface:

Continuous measurement by gas chromatography. Soil Biol. Biochem. 15:481-483.

Christensen, S., P. Ambus, J.R.M. Arah, H. Clayton, B. Galle. D.W.T. Griffith, K.J. Hargreaves, L. Klemedtsson, A.-M. Lind, M. Maag, A. Scott, U. Skiba, K.A. Smith, M. Welling, and F.G. Wienhold. 1996. Nitrous oxide emission from an agricultural field: Comparison between measurements by flux chamber and micrometeorological techniques. Atmos. Environ. 30:4183-4190.

Clayton, H., J.R.M. Arah, and K.A. Smith. 1994. Measurement of nitrous oxide emissions from fertilized grassland using closed chambers. J. Geophys. Res. 99:16599-16607.

De Klein. C.A.M., R. Harrison, and E.I. Lord. 1996. Comparison of N2O flux measurements using gas chromatography and photo-acoustic infra-red spectroscopy. Dev. Plant Soil Sci. 68:235-258.

Denmead. O.T. 1979. Chamber systems for measuring nitrous oxide emission from soils in the field. Soil Sci. Soc. Am. J. 43:89-95.

International Atomic Energy Agency. 1992. Manual on measurement of methane and nitrous oxide emissions from agriculture. IAEA-TECDOC-674. IAEA,Vienna.

Intergovernmental Panel on Climate Change. 1996. Climate change 1995: The science of climate change. Cambridge Univ. Press, Cambridge, England.

Keller, M., W.A. Kaplan, and S.C. Wofsy. 1986. Emissions of N_2O, CH, and CO_2 from tropical forest soils. J. Geophys. Res. 91:11791-11802.

Keller, M., E. Veldkamp, A. Weitz, and W. Reiners. 1993. Effect of pasture age on soil trace-gas emissions from a deforested area of Costa Rica. Nature (London) 365:244-246.

Livingston, G.P., and G.L. Hutchinson. 1995. Enclosure-based measurement of trace gas exchange: Applications and sources of error. p. 14-51. *In* P.A. Matson and R.C. Harriss (ed.) Methods in ecology - Biogenic trace gases: Measuring emissions from soil and water. Blackwell Science, Oxford, England.

Loftfield, N.S., R. Brumme, and F. Beese. 1992. Automated monitoring of nitrous oxide and carbon dioxide flux from forest soils. Soil Sci. Soc. Am. J. 56:1147-1150.

Mosier, A.R. 1989. Chamber and isotope techniques. p. 175-187. *In* M.O. Andreae and D.S. Schimel (ed.) Exchange of trace gases between terrestrial ecosystems and the atmosphere. John Wiley & Sons, New York.

Mosier, A., D. Schimel, D. Valentine, K. Bronson, and W. Parton. 1991. Methane and nitrous oxide fluxes in native, fertilized and cultivated grasslands. Nature (London) 350:330-332.

Parkin, T.B. 1985. Automated analysis of nitrous oxide. Soil Sci. Soc. Am. J. 49:273-276.

Robertson, G.P. 1993. Fluxes of nitrous oxide and other nitrogen trace gases from intensively managed landscapes: A global perspective. p. 95-108. *In* D.E. Rolston et al. (ed.) Agricultural ecosystems effects on trace gases and global climate change. ASA, CSSA. and SSSA, Madison, WI.

Sexstone, A.J., T.B. Parkin, and J.M. Tiedje. 1985. Temporal response of soil denitrification rates to rainfall and irrigation. Soil Sci. Soc. Am. J. 49:99-103.

Skiba, U., K.J. Hargreaves, D. Fowler, and K.A. Smith. 1992. Fluxes of nitric and nitrous oxides from agricultural soils in a cool temperate climate. Atmos. Environ. 26A:2477-2488.

Smith, K.A., H. Clayton, J.R.M. Arah, S. Christensen, P. Ambus, D. Fowler, K.J. Hargreaves, U. Skiba, G.W. Harris, F.G. Wienhold, L. Klemedtsson, and B. Galle. 1994. Micrometeorological and chamber methods for measurement of nitrous oxide fluxes between soils and the atmosphere: Overview and conclusions. J. Geophys. Res. 99:16541-16548.

Smith, K.A., H. Clayton, I.P. McTaggert, P.E. Thomson, J.R.M. Arah, and A. Scott. 1995. The measurements of nitrous oxide emissions from soil by using chambers. Phil. Trans. R. Soc. Lond. 351:327-338.

Sommerfeld, R.A., A.R. Mosier, and R.C. Musselman. 1993. CO_2, CH_4 and N20 flux through a Wyoming snowpack and implications for global budgets. Nature (London) 361:140-142.