

Rothamsted Repository Download

A - Papers appearing in refereed journals

Yamulki, S. and Jarvis, S. C. 1999. Automated chamber technique for gaseous flux measurements: evaluation of a photoacoustic infrared spectrometer-trace gas analyzer. *Journal Of Geophysical Research-Atmospheres*. 104 (D5), pp. 5463-5469.

The publisher's version can be accessed at:

- <https://dx.doi.org/10.1029/1998JD100082>

The output can be accessed at:

<https://repository.rothamsted.ac.uk/item/8528x/automated-chamber-technique-for-gaseous-flux-measurements-evaluation-of-a-photoacoustic-infrared-spectrometer-trace-gas-analyzer>.

© Please contact library@rothamsted.ac.uk for copyright queries.

Automated chamber technique for gaseous flux measurements: Evaluation of a photoacoustic infrared spectrometer–trace gas analyzer

S. Yamulki and S. C. Jarvis

Institute of Grassland and Environmental Research, North Wyke, Okehampton, Devon, England

Abstract. Experiments were made in order to evaluate the accuracy and sensitivity of a photoacoustic infrared trace gas analyzer (TGA) in conjunction with an automatic opening and closing chamber system developed for near-continuous (2 min intervals) soil gaseous flux measurements. Humidity interference tests on N₂O, CH₄, and CO₂ concentrations measured by the TGA were carried out, and the results showed a linear interference, with correction factors of $3 \times 10^{-5}x$, $1.9 \times 10^{-3}x$ and $4.4 \times 10^{-3}x$ ($x = \text{H}_2\text{O}$ vapor ppm), respectively. CO₂ interference on N₂O and CH₄ signals were also linear, with average correction factors of $2.8 \times 10^{-4}x$ and $6 \times 10^{-5}x$ ($x = \text{CO}_2$ ppm), respectively. Laboratory intercomparisons between the TGA and GC measurements of N₂O and CH₄ standards showed good agreement ($R^2 > 0.993$), indicating the accuracy of the TGA for measurement of these gases at concentrations up to 100 and 40 ppm N₂O and CH₄, respectively. The relatively rapid measurement time for up to five gases simultaneously in 2 min, linearity, and ease of operation of the TGA represent major advantages compared to gas chromatography (GC). The automated chamber system provides a continuous measurement of fluxes with minimum disturbance to the soil environment enclosed by the chamber and provides the means, for example, of quantifying diurnal variability. In situ measurements of N₂O-N and CH₄-C fluxes with a sensitivity $<10 \text{ g ha}^{-1} \text{ d}^{-1}$ ($11.6 \text{ ng m}^{-2} \text{ s}^{-1}$), as well as of CO₂ and water vapor (H₂O), can be measured by the TGA when used with the automated system, and fluxes at background levels (i.e., from unfertilized soils) can be determined.

1. Introduction

The major uncertainty in the estimation of soil/atmosphere gaseous exchange is due to the continuously changing nature of the environmental conditions which act on the soil biological processes which are largely responsible for the fluxes [Jarvis, 1998]. Many studies have been carried out to quantify the influence of soils, management practices, and climatic conditions on trace gas fluxes, especially those of nitrous oxide (N₂O), methane (CH₄), and carbon dioxide (CO₂). However, the major factor controlling the uncertainty of the flux measurements is the influence of the spatial and temporal/diurnal variations. Micrometeorological methods [e.g., Huchinson and Mosier, 1979; Arah *et al.*, 1994] integrate fluxes over larger areas and thus could be deployed to overcome some of the uncertainties in flux measurements associated with the spatial variability. However, these methods are expensive and are still restricted in their application [Smith *et al.*, 1994]. Several automated methods [e.g., Conrad *et al.*, 1983; Loftfield *et al.*, 1992] have been developed to provide continuous measurements of N₂O fluxes with minimal disturbance to the environment, which is a feature of many other chamber methods [Jarvis, 1998]. Automatic chambers provide more data during the observation period and give better information on the diurnal variation and relationships with soil temperature and moisture [Conrad *et al.*, 1983].

In most of the previous studies, fluxes of trace gases such as N₂O were measured using chamber methods and involved gas chromatographic analysis. However, in a number of recent studies [De Klein *et al.*, 1994; Velthof and Oenema, 1995; Velthof *et al.*, 1996], a trace gas analyzer (TGA), which is based on a photoacoustic infrared (IR) spectrometry technique, has been used in conjunction with chamber methods for flux measurements. In this technique, a gas sample is contained in a sealed cell and is irradiated with pulsed IR light at a wavelength at which the gas will absorb (using a specific filter for each gas). The absorbed energy leads to an increase in the temperature and thus the pressure of the gas in the cell. The radiation is modulated by a rotating chopper causing a series of pressure pulses, which are detected by microphones placed in the wall of the cell. The signal from the microphones is converted into voltage differential, proportional to the concentration of the gas in the cell. The instrument can measure up to five gases and water vapor by selection of appropriate filters in 2 min (90 s for three gases and water vapor). The TGA used in this study (Europa Scientific, Gas Monitor Type 1302) was equipped with the following optical filters: UA0985, UA0987, UA0983, and SB0527 (Bruel and Kjaer) for measurements of N₂O, CH₄, CO₂, and water vapor, respectively. Both water vapor absorption wavelengths (6.25, 10, 20 μm) and CO₂ (15 μm) are close to those of N₂O (7.78, 17, 4.5 μm) and CH₄ (7.66 μm) [e.g., Wang *et al.*, 1976], and it is expected that interference will occur. Therefore each optical filter must be calibrated for humidity and CO₂ interference in order to achieve accurate and reliable measurements. This is particularly important

Copyright 1999 by the American Geophysical Union.

Paper number 1998JD100082.
0148-0227/99/1998JD100082\$9.00

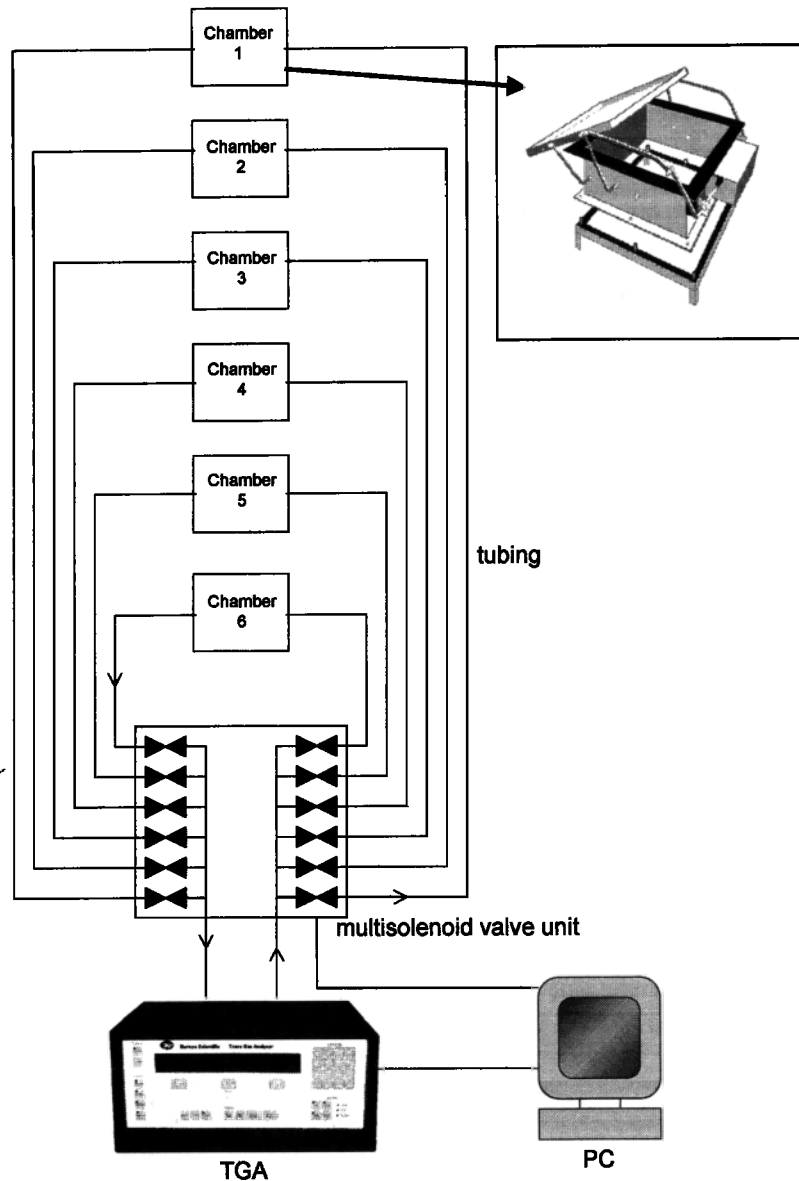


Figure 1. Schematic setup and plumbing of the automated chamber system and the TGA connection to the chambers in a closed loop air circulation system.

when making frequent measurements in the field under conditions, which generate ranging fluxes.

In this paper, we present a detailed evaluation of (1) an automatic opening and closing chamber system for accurate and simultaneous flux measurements of N_2O , CO_2 , and CH_4 and (2) the TGA interference and accuracy for the flux measurements of N_2O , CH_4 , and CO_2 in conjunction with the automated system.

2. Material and Methods

2.1. Design and Test of the Automated Chamber System

The chambers ($400 \times 400 \times 200$ mm high) were constructed from aluminum to prevent internal pressure and temperature fluctuations [Velthof and Oenema, 1995]. Each chamber consisted of three separate parts, a box with top and bottom open, a lid, and a frame which can be inserted into the soil (Figure 1). The box had two air sampling ports and a 3 cm flange at both

ends, each of which was covered with a 4 mm thickness rubber foam which provides a gas tight fit with both the lid and the frame. The lid was opened and closed automatically by a motor that was controlled by a computer. The end position for opening and closing was controlled mechanically by two limiting switches, which were also used to operate a small fan (12 V dc) with a flow rate of 78 L min^{-1} for mixing the air within the chamber when the lid was closed during the flux measurements. The frames for each chamber were inserted 5 cm into the soil, at least 1 day before the start of the experiment, and were fixed tightly to the chamber. All the chambers were visually tested for leakage using Fumite smoke cones.

The schematic arrangement for the gas sampling, plumbing, and valving for the whole system is shown in Figure 1. During the flux measurements, up to six chambers (two were used in the present study) can be attached to the TGA analyzer via a multisolenoid valve unit with a 15 m length polytetrafluoroethylene (PTFE) tubing (2 mm ID) in a closed loop air

circulation. After closing each chamber, concentrations of the gases in the headspace were determined in the field by the TGA at 10 min intervals for a period of up to 60 min. Both the TGA sampling time and the time selected for the enclosure can be reduced (to 90 s and 10 min, respectively). However, the times selected are a trade-off between measurement sensitivity and environmental disturbance. This capacity for optimization for a given flux level can be considered as an important advantage of the automated system. The fluxes were calculated from the slope of the linear gas concentration increase inside the chamber versus time. Air circulation between the chambers and the analyzer (1.4 L min^{-1} for 35 s) was achieved by the internal pump of the TGA. All the chambers, the TGA analyzer, and the multivalve unit were controlled by a PC equipped with a digital-analog I/O converter with software written in Visual Basic: the PC was also used for data acquisition. The software allowed one of the following two options to be selected: (1) each chamber closed consecutively for a period of time, during which the concentration of the gas within the headspace of the closed chamber was measured (i.e., as used in this study), (2) all chambers closed together for a period of time, during which the concentrations of the gas within the headspace of all the chambers was measured sequentially. In both options the measurement could be repeated a number of times to allow accurate flux measurements to be made.

In order to test the automated chamber in conjunction with the TGA analyzer, fluxes of N_2O , CH_4 , and CO_2 were measured during three periods, each of ~ 3 days from December 11, 1996, to January 10, 1997. The flux measurements were carried out on long-term managed grassland at the Institute of Grassland and Environmental Research, Devon, England. The sward, which was largely of ryegrass (*Lolium perenne* L.), was fertilized with 120 kg N ha^{-1} as NH_4NO_3 , 8 hours after the start of the experiment. Fluxes of N_2O and CH_4 were also determined from the same chambers on occasion by taking grab samples and measuring with a gas chromatograph (GC) to allow comparisons between the TGA and an alternative, conventional method.

2.2. TGA Humidity and CO_2 Interference Test

To investigate the humidity interference with the TGA signals for N_2O , CO_2 , and CH_4 , the corrections for humidity and CO_2 interference were set to zero, i.e., no correction, and the TGA inlet was connected to a source of pure N_2 via a thermostatically controlled water bath in the laboratory. Various concentrations of water vapor were achieved by changing the temperature of the water bath. Measurements of the TGA signals for N_2O , CH_4 , and CO_2 produced at the various water vapor concentrations (ranging between 0 and 30000 ppm water vapor) were then made (Figure 2). Water vapor concentrations were not determined independently of the TGA, as the aim was to see the effect of increasing H_2O concentration on the gases measured and not absolute concentrations. However, no interference was expected or has been documented for the TGA H_2O -optical-filter.

For CO_2 interference the TGA was set to correct only for the humidity interference, and the TGA inlet and outlet were connected to a PTFE gas-sampling bag (10 L) with pure N_2 in a closed loop circulation flow. The water vapor concentration within the bag was approximately 12,000 ppm. The bag had a septum to allow CO_2 , N_2O , and CH_4 standards to be injected to achieve a combination of CO_2 concentrations ranging between 0 and 4500 ppm, each at three concentrations of N_2O (0,

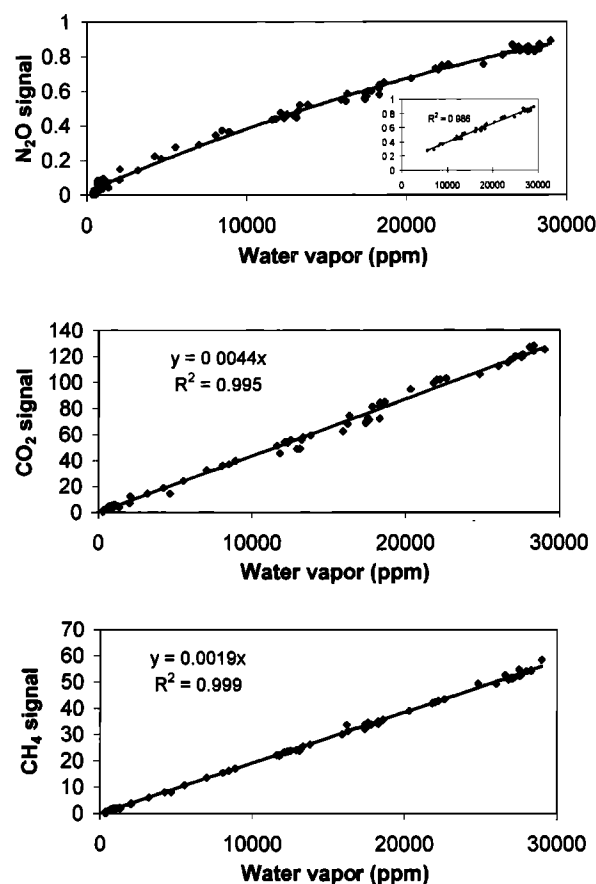


Figure 2. TGA signals (ppm) of N_2O , CH_4 , and CO_2 measured at different concentrations of water vapor in pure N_2 . The inserted graph shows the N_2O linear response at water vapor concentration > 5000 ppm.

0.5, and 2 ppm) and CH_4 (0, 4, and 6 ppm). The effects of increasing CO_2 on N_2O and CH_4 analysis by the TGA (Figures 3a and 3b) were then monitored at each N_2O and CH_4 concentration.

2.3. TGA-GC Intercomparison

Both field and laboratory intercomparisons were made between the TGA and a GC (ATI-Unicam 610). The GC was equipped with a headspace autosampler (HP type 19395A) and had electron capture detectors (ECD) and flame ionization (FID) detectors to allow measurements of N_2O and CH_4 to be carried out simultaneously. The precision of the GC was determined from repeated analysis of N_2O and CH_4 at ambient background concentrations, with a relative standard deviation of 1.5% and 1%, respectively. In the laboratory trial the TGA was connected to a PTFE gas-sampling bag containing pure N_2 with a closed loop circulation flow as indicated earlier. Various concentrations of N_2O and CH_4 were obtained by injecting small volumes of 1000 ppm N_2O and 100 ppm CH_4 (Linde Gas UK Ltd.) into the bag to achieve the following: N_2O at 0, 0.25, 0.50, 1, 5, and 10 ppm and CH_4 at 0, 5, 10, 20, 25, and 40 ppm. At each of these concentrations, duplicate gas samples were also analyzed simultaneously by the GC (Figure 4). Gas samples were transferred by polypropylene syringes into 20 mL vials and were injected into the GC using the headspace autosampler.

Field intercomparisons between the TGA and the GC dur-

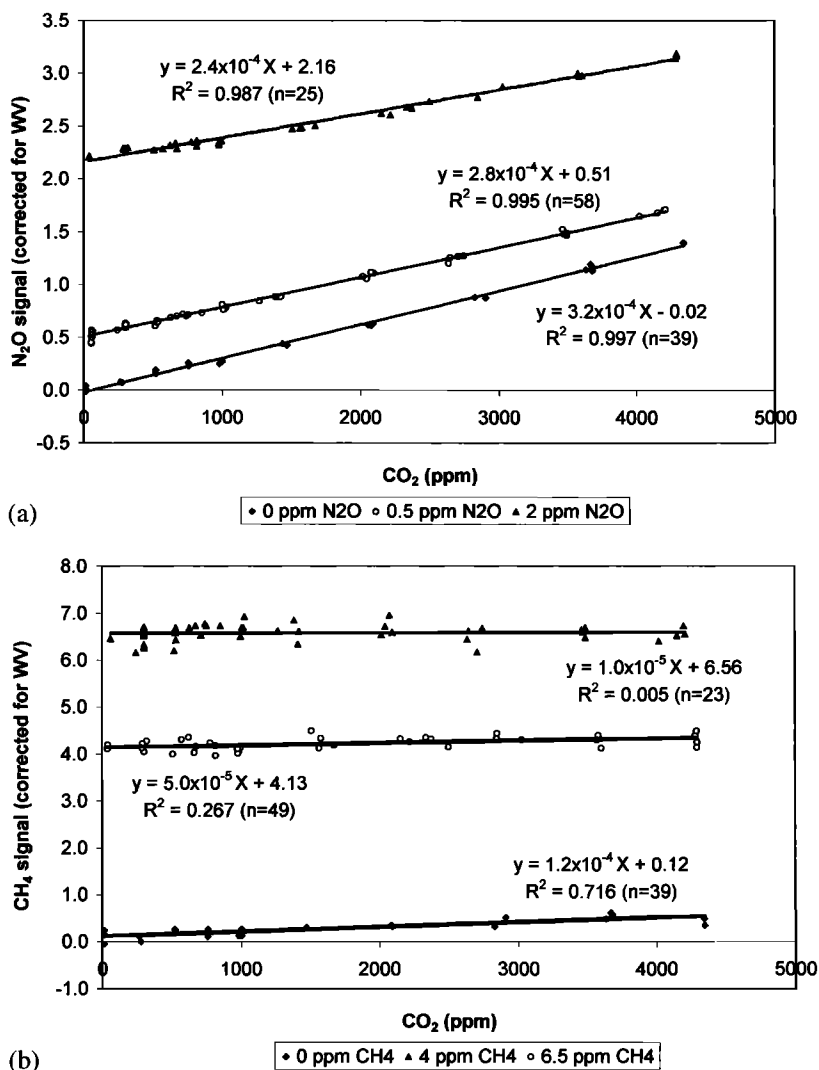


Figure 3. TGA signals (ppm) of (a) N₂O and (b) CH₄ response to various concentrations of CO₂ each at three levels of N₂O and CH₄ concentration in pure N₂.

ing the flux measurements by the automated chamber were carried out by taking duplicate gas samples within the headspace of each automated chamber at 0, 20, 40, and 60 min intervals after closing each chamber prior to analysis by the GC as before. The corresponding N₂O and CH₄ concentrations were calculated from the peak area compared against N₂O and CH₄ standards. The calculated fluxes measured by the GC were then compared to those of the TGA.

3. Results and Discussion

3.1. Evaluation of the TGA

The major interference with the TGA signals for N₂O, CH₄, and CO₂ comes from water vapor. The results showed that CH₄ and CO₂ signals (ppm) increased linearly with water vapor concentrations ranging between 0 and 30000 ppm (Figure 2). For N₂O, the signal (ppm) increased linearly between 5000 and 30,000 ppm water vapor, but at lower concentrations (<5000 ppm), the increase in N₂O signal was not linear. The interference was described by linear regression equations, which were then used to correct the N₂O, CH₄, and CO₂ signals, i.e.,

$$X_{ci} = X_{TGAi} - (a \times WV_{TGA} - y) \quad (1)$$

Where X_{ci} is the corrected N₂O, CH₄, or CO₂ reading; X_{TGAi} is the TGA signal for N₂O, CH₄, or CO₂; a is the slope of the linear regression line; WV_{TGA} is the TGA reading for water vapor concentration; and y is the intercept ($y = 0$ for CH₄ and CO₂). For N₂O, a polynomial (quadratic) equation was used to correct for water vapor interference in the range 0–30,000 ppm. However, apart from extreme dry weather conditions, i.e., <5000 ppm water vapor, the interference was linear, and therefore the above equation was valid. The slope of the linear regression line, which could be considered as a factor for the WV correction, increased in the order N₂O (3×10^{-5}) < CH₄ (1.9×10^{-3}) < CO₂ (4.4×10^{-3}). This means that a small divergence from the above linearity will have more effect on CO₂ correction than, for example, on N₂O.

After correction for water vapor, the CO₂ interference (i.e., a cross interference) on the TGA N₂O and CH₄ signals was investigated at the three different concentrations of N₂O and CH₄. The CO₂ interference was then determined from the linear regression equation (Figure 3), and the TGA signals of

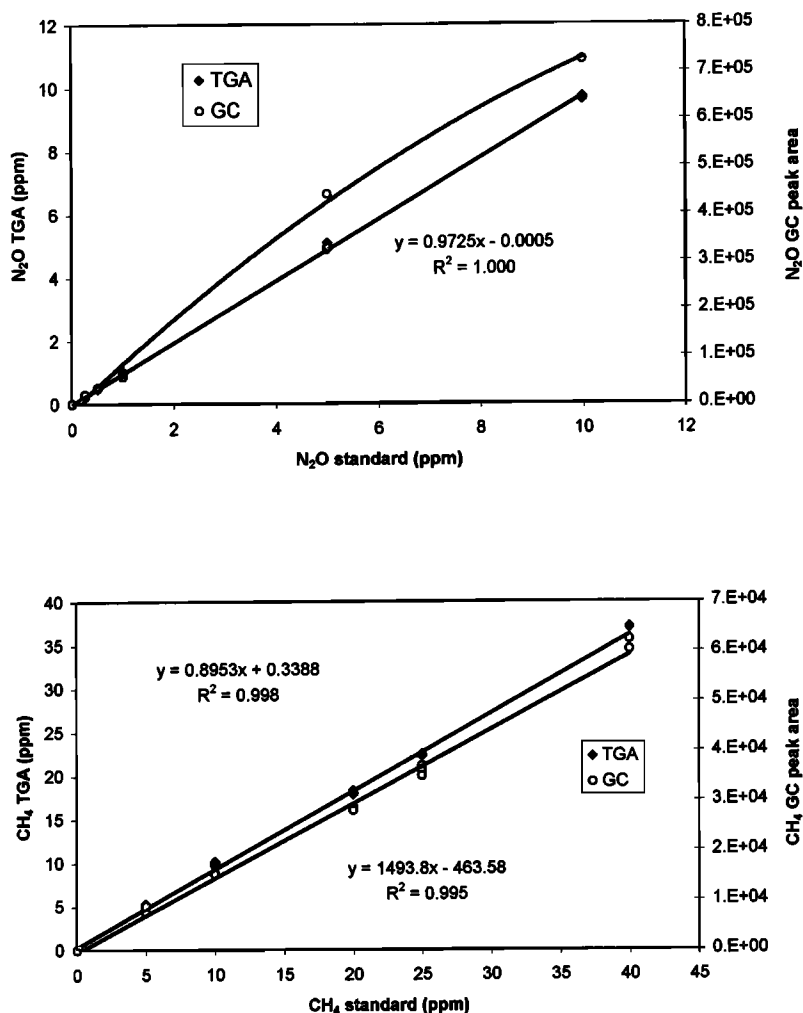


Figure 4. Laboratory intercomparisons between the TGA and GC (ECD) measurements of standards of N_2O and CH_4 gases.

N_2O and CH_4 were corrected, similarly to that of the water vapor, by the following equation:

$$X_{c2} = X_{\text{TGA}2} - (a \times \text{CO}_{2\text{TGA}} - y) \quad (2)$$

where X_{c2} is the N_2O or CH_4 concentration, $X_{\text{TGA}2}$ is the TGA N_2O or CH_4 signal (corrected for water vapor), a is the slope of the linear regression line, $\text{CO}_{2\text{TGA}}$ is the CO_2 concentration measured by the TGA, and y is the intercept (i.e., = N_2O or CH_4 concentration signal in the absence of interference). For N_2O the TGA signal at each of the N_2O levels increased linearly ($p < 0.001$) with CO_2 concentrations between 0 and 4500 ppm (Figure 3a). The slope of the line (i.e., the N_2O correction factor) at 0, 0.5, and 2 ppm N_2O levels was 3.2×10^{-4} , 2.8×10^{-4} , and 2.4×10^{-4} , respectively. *De Klein et al.* [1994] have also investigated CO_2 interference on the N_2O signals measured by the TGA at N_2O concentration levels ranging between 0 and 2.25 ppm. Their results showed a similar linear increase in the TGA N_2O signal with CO_2 concentration at any given N_2O concentration, with slopes ranging between 3.4×10^{-4} and 5.5×10^{-4} , with an average of 4.2×10^{-4} . Our results indicate that corrections for CO_2 interference can be valid for a range of N_2O concentrations. For CH_4 , however, the CO_2 interference was minimal, with correction

factors (slopes of linear regression lines) of 1.2×10^{-4} , 5×10^{-5} , and 1×10^{-5} at 0, 4, and 6 ppm CH_4 , respectively (Figure 3b). Statistical analysis showed that although correction factors for CH_4 were minimal, the corrections were highly significant ($p < 0.001$) for CH_4 levels of zero and 4 ppm but insignificant at 6.5 ppm. It is important to mention here that all the above measurements were made at H_2O concentrations ranging between 12,000 and 15,000 ppm in the linear part of the response, as indicated previously.

To evaluate the accuracy of the TGA, a laboratory inter-comparison was made between the TGA and the GC measurements of N_2O and CH_4 standards (Figure 4). For N_2O the TGA showed a linear response close to unity for the range of N_2O concentrations between 0 and 10 ppm. However, the GC response was not linear. A linear response from TGA, in contrast to the GC, can be observed for much wider ranges of N_2O concentrations of up to 103 ppm [*De Klein et al.*, 1994]. The detection limit of the TGA (3δ) was ~ 50 ppb N_2O , with a relative standard deviation (RSD) of 5% for repeated analysis at ambient concentrations. For CH_4 both the TGA and the GC showed a linear response between 0 and 40 ppm but with a small divergence from unity for concentrations > 10 ppm. The TGA detection limit for CH_4 was < 600 ppb with RSD of 7.

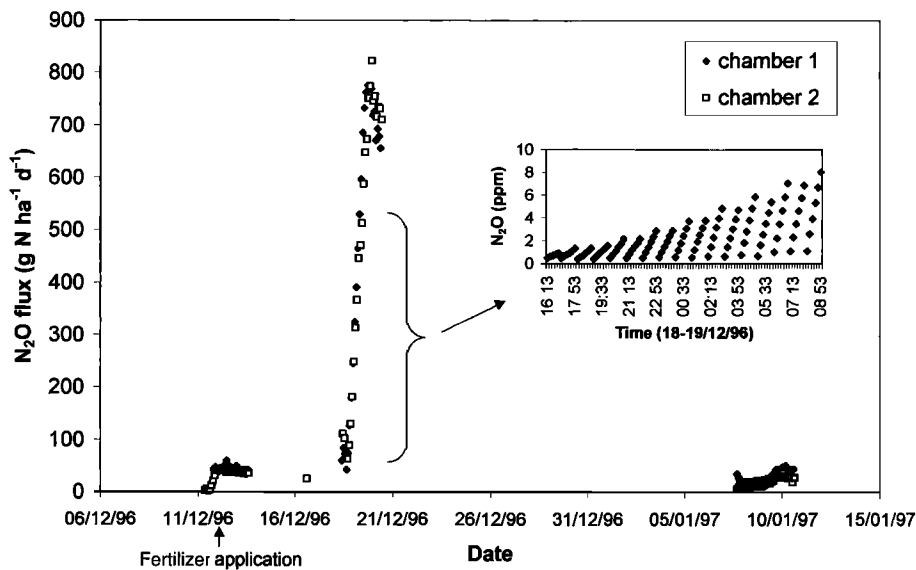


Figure 5. Fluxes of N_2O measured at three periods after fertilizer application from two automated chambers by TGA. The inserted graph shows examples of the hourly N_2O concentration increase inside the each chamber consecutively at 10 min intervals.

3.2. Evaluation of the Automated Flux Measurement

Figure 5 shows an example of the hourly flux measurements for N_2O carried out in the field using two automated chambers. During the first period, fluxes were low, and the effect of fertilizer was minimal because of a period of dry (0.7 mm rain) and cold (-0.4 – 3°C) conditions. However, during the second period (~ 8 days after fertilizer application), fluxes of up to $822 \text{ g N ha}^{-1} \text{ d}^{-1}$ were observed following $\sim 16 \text{ mm}$ cumulative rainfall and a higher temperature of up to 12°C . Diurnal variation in N_2O fluxes was not observed, which could be because of the overriding effect of fertilizer application. The increases in N_2O concentrations within the headspace of the automated chamber were generally linear with time (Figure 5). Fluxes of CH_4 indicated both emission and uptake by the soil. However, the overall flux was minimal, as expected, compared with that for N_2O and ranged between -20 and $+20 \text{ g C ha}^{-1} \text{ d}^{-1}$. For CO_2 , fluxes ranged between 7.3 and $39.9 \text{ kg C ha}^{-1} \text{ d}^{-1}$.

The sensitivity of the flux measurements for N_2O , CH_4 , and CO_2 was determined as described by Velthof and Oenema [1995] from the relationship between the calculated flux and the R^2 for the concentration increase within the chamber versus time, for all the fluxes (Figure 6). Generally, fluxes of N_2O -N and CH_4 -C greater than $10 \text{ g ha}^{-1} \text{ d}^{-1}$ had an R^2 value of >0.9 . Taking the R^2 value as a criterion for the sensitivity of the method for the flux measurements, and assuming that fluxes with an R^2 value >0.7 would still be acceptable, the sensitivity of the method can be considered to be significantly lower than $10 \text{ g ha}^{-1} \text{ d}^{-1}$ of N_2O -N and CH_4 -C fluxes (Figure 6).

A comparison between fluxes measured using the TGA and the GC from the same chambers generally showed good agreement and can best be described by the linear regression $\text{N}_2\text{O}_{(\text{TGA})} = 0.91 \times \text{N}_2\text{O}_{(\text{GC})} + 11.8$. Although a significant correlation ($p < 0.001$) was observed between the TGA and the GC ($R^2 = 0.878$), N_2O fluxes were higher by a factor of ~ 1.4 when measured using the TGA. De Klein et al. [1994] also found some discrepancy between methods, but in contrast, their results showed up to $2.5 \times$ higher fluxes when based on

a GC analysis. The discrepancy between the TGA and GC flux measurements was not very clear. The GC/ECD is generally subject to nonlinearity, particularly at high concentrations of N_2O , because of detector saturation, which could affect the discrepancy. In this study, however, the GC was calibrated over

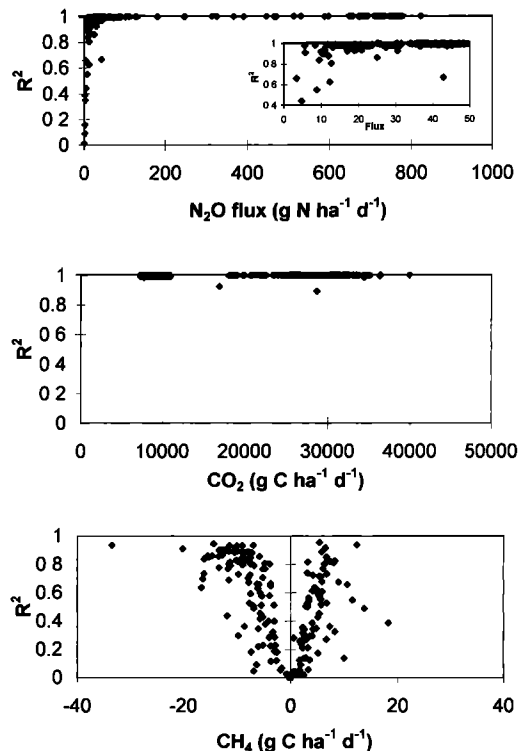


Figure 6. Relationship between calculated fluxes of N_2O , CH_4 , and CO_2 and the R^2 determined from the linear regression of the gas concentration increase with time, for all the fluxes. The inserted graph is a larger scale for N_2O fluxes up to $50 \text{ g N ha}^{-1} \text{ d}^{-1}$ versus the corresponding R^2 .

a range of N₂O concentrations (e.g., Figure 4), and fluxes were generally in the linear part of the GC calibration curve. Therefore the discrepancy could not be related to the GC nonlinearity. Discrepancy may also arise from cross contamination when air from the headspace of one flux chamber is pumped (mixed) with the headspace of the next flux chamber [King and Harrison, 1995; Velthof and Oenema, 1995]. In our study this "dead volume," i.e., the volume between the TGA and the automated system manifold, represented about only 1% of the chamber plus tubing headspace. The problem associated with the cross contamination is therefore expected to be negligible; furthermore, fluxes were measured from each chamber consecutively, and any such contamination would only occur at the start of closing of each flux chamber. The discrepancy between the TGA and GC flux measurements, albeit small, could easily be accounted for by a simple instrument cross calibration, since low and high flux levels contributed equally to the discrepancy in our study. For example, the discrepancy factor increased by only 1.2% when the average N₂O flux increased from 39 to 680 g N ha⁻¹ d⁻¹.

For CH₄, however, a comparison could not be made accurately in our study because fluxes measured were close to or below the limits of the sensitivity of the method (Figure 6). Comparison between the TGA and the GC with regard to CO₂ flux measurements was not carried out during this study.

4. Conclusions

Our results showed that we were able to detect fluxes of <10 g ha⁻¹ d⁻¹ (11.6 ng m⁻² s⁻¹) of N₂O-N and CH₄-C, using the photoacoustic infrared trace gas analyzer (TGA) with the automated flux chamber system for in situ flux measurements of N₂O-N and CH₄-C as well as CO₂-C. The TGA signals for N₂O, CH₄, and CO₂ were tested for interference with water vapor, and those for N₂O and CH₄ were tested for CO₂ interference. Both water vapor and CO₂ concentrations of up to 30,000 and 4500 ppm, respectively, had a linear interference on the TGA signals. CO₂ interference on N₂O and CH₄ signals was also linear at various concentrations of N₂O and CH₄. The accuracy of the TGA was tested by laboratory intercomparisons between the TGA and GC measurements of N₂O and CH₄ standards. The results showed good agreement ($R^2 = 0.993$) up to 100 and 40 ppm N₂O and CH₄, respectively. The main advantages of the TGA are its linearity, rapid measurement time (up to five gases simultaneously in 2 min), and portability as compared to conventional GC, and ease of operation, instrumental complexity, and cost effectiveness as compared to other instruments, such as laser spectroscopy. The complete system provides automatic chamber opening and closing over times necessary to obtain sufficient sensitivity required for a given flux level, as well as data acquisition. Thereby, fluxes of trace gases can be measured accurately and with minimum disturbance to the soil environment enclosed by the chamber.

Acknowledgments. We thank J. Birch and C. Lethbridge for their technical assistance and Ken Ellis for help with the computer software. This research was financially supported by the Ministry of Agriculture, Fisheries and Food (MAFF), London. The research was also part of the EU funded FAIR3-CT96 COGANOG project. IGER is supported by the Biotechnology and Biological Science Research Council (BBSRC), Swindon, England.

References

- Arah, J. R. M., I. J. Crichton, K. A. Smith, H. Clayton, and U. Skiba, Automated gas chromatographic analysis system for micrometeorological measurements of trace gas fluxes, *J. Geophys. Res.*, **99**, 16,593–16,598, 1994.
- Conrad, R., W. Seiler, and G. Bunse, Factor influencing the loss of fertilizer nitrogen into the atmosphere as N₂O, *J. Geophys. Res.*, **88**, 6709–6718, 1983.
- De Klein, C. A. M., R. Harrison, and E. I. Lord, Comparison of N₂O flux measurements using gas chromatography and photoacoustic infrared spectroscopy, in *Progress in Nitrogen Cycling Studies, Proceedings of the 8th Nitrogen Workshop, University of Ghent, Development in Plant and Soil Sciences*, vol. 68, edited by O. van Cleemput, G. Hofman, and A. Vermoesen, pp. 533–536, Kluwer Acad., Norwell, Mass., 1994.
- Hutchinson, G. L., and A. R. Mosier, Nitrous oxide emissions from an irrigated cornfield, *Science*, **205**, 1125–1127, 1979.
- Jarvis, S. C., Sampling for greenhouse gases at the small scale: Enclosure techniques, in *Biogenic Emissions of Greenhouse Gases Caused by Arable and Agriculture-Measurement Technologies and Emission Factors, Proceedings of the EU Concerted Action FAIR3-CT96-1877 Workshop at ECN Petten, Netherlands*, edited by A. Freibauer and M. Kaltschmitt, pp. 45–60, Inst. für Energiewirt. und Rationelle Energieanwendung, Stuttgart, March 1998.
- King, J. A., and R. Harrison, An automated chamber system to measure soil respiration, in *Field Experiments Techniques*, pp. 87–94, Assoc. of Appl. Biol., Churchill College, Cambridge, England, 1995.
- Loffield, N. S., R. Brumme, and F. Beese, Automated monitoring of nitrous oxide and carbon dioxide flux from forest soils, *Soil Sci. Soc. Am. J.*, **56**, 1147–1150, 1992.
- Smith, K. A., et al., Micrometeorological and chamber methods for measurements of nitrous oxide fluxes between soils and the atmosphere: Overview and conclusions, *J. Geophys. Res.*, **99**, 16,541–16,548, 1994.
- Velthof, G. L., and O. Oenema, Nitrous oxide fluxes from grassland in the Netherlands, 1, Statistical analysis of flux-chamber measurements, *Eur. J. Soil Sci.*, **46**, 533–540, 1995.
- Velthof, G. L., S. C. Jarvis, A. Stein, A. G. Allen, and O. Oenema, Spatial variability of nitrous oxide fluxes in mown and grazed grasslands on a poorly drained clay soil, *Soil Biol. Biochem.*, **28**, 1215–1225, 1996.
- Wang, W. C., Y. L. Yung, A. A. Lacis, T. Mo, and J. E. Hansen, Greenhouse effects due to man-made perturbations of trace gases, *Science*, **194**, 685–690, 1976.

S. C. Jarvis and S. Yamulki, Institute of Grassland and Environmental Research, North Wyke, Okehampton, Devon, England EX20 2SB. (sirwan.yamulki@bbsrc.ac.uk)

(Received June 16, 1998; revised November 10, 1998; accepted November 17, 1998.)