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Assessing the performance of the photo-acoustic infrared gas monitor for measuring CO_2, N_2O, and CH_4 fluxes in two major cereal rotations

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Abstract

Rapid, precise, and globally comparable methods for monitoring greenhouse gas (GHG) fluxes are required for accurate GHG inventories from different cropping systems and management practices. Manual gas sampling followed by gas chromatography (GC) is widely used for measuring GHG fluxes in agricultural fields, but is laborious and time-consuming. The photo-acoustic infrared gas monitoring system (PAS) with on-line gas sampling is an attractive option, although it has not been evaluated for measuring GHG fluxes in cereals in general and rice in particular. We compared N_2O, CO_2, and CH_4 fluxes measured by GC and PAS from agricultural fields under the rice–wheat and maize–wheat systems during the wheat (winter), and maize/rice (monsoon) seasons in Haryana, India. All the PAS readings were corrected for baseline drifts over time and PAS-CH_4 (PCH_4) readings in flooded rice were corrected for water vapor interferences. The PCH_4 readings in ambient air increased by 2.3 ppm for every 1000 mg cm^{-3} increase in water vapor. The daily CO_2, N_2O, and CH_4 fluxes measured by GC and PAS from the same chamber were not different in 93–98% of all the measurements made but the PAS exhibited greater precision for estimates of CO_2 and N_2O fluxes in wheat and maize, and lower precision for CH_4 flux in rice, than GC. The seasonal GC- and PAS-N_2O (PN_2O) fluxes in wheat and maize were not different but the PAS-CO_2 (PCO_2) flux in wheat was 14–39% higher than that of GC. In flooded rice, the seasonal PCH_4 and PN_2O fluxes across N levels were higher than those of GC-CH_4 and GC-N_2O fluxes by about 2- and 4fold, respectively. The PAS (i) proved to be a suitable alternative to GC for N_2O and CO_2 flux measurements in wheat, and (ii) showed potential for obtaining accurate measurements of CH_4 fluxes in flooded rice after making correction for changes in humidity.

Keywords: Agriculture, carbon dioxide, greenhouse gas emission, methane, nitrous oxide, photo-acoustic infrared gas analyzer

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Introduction

Current changes in soil, crop, and fertilizer management practices have been reported to play major roles in regulating greenhouse gas (GHG) emissions (Cai *et al.*, 1997; McSwiney & Robertson, 2005; Roelandt *et al.*, 2005; Venterea *et al.*, 2005; Ma *et al.*, 2007; Malhi & Lemke, 2007; Almaraz *et al.*, 2009; Johnson *et al.*, 2010). However, most GHG inventories from agricultural fields are calculated based on IPCC emission factors (IPCC Guidelines for National Greenhouse Gas Inventories, 2006), which are quite generalized and do not take into account variations brought about by different management scenarios and cropping systems. Actual measurements of GHG fluxes from various cropping systems and current management, including conservation agriculture practices, need to be made to obtain crop and soil management-specific emission factors that would increase the precision of GHG inventories and serve as a basis for future strategies to reduce emissions. Accurate, precise, and globally comparable data on GHG emissions are crucial for the improvement of GHG mitigation strategies and eventually for the development of policies for mitigating climate change (UNFCCC, 2012). A full accounting of the GHG contributions of agricultural soils is imperative for determining the true mitigation potential of management practices (Gregorich *et al.*, 2005). To achieve this, a quick but reliable and inexpensive methodology is needed for estimating GHG fluxes.

Continuous monitoring of GHG fluxes on a field or landscape scale is achieved by micrometeorological

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methods that significantly reduce spatial and temporal variability as they integrate emissions over large areas, and assess the effect of rainfall, temperature, and wind speed on emissions (Fowler & Duyzer, 1989; Mosier, 1990; Hargreaves *et al.*,1994; Ausma *et al.*, 1995; Rinne *et al.*, 2007). But, micrometeorology requires expensive instruments and large homogeneous field trials (Fowler *et al.*, 1997). The most widely used and least expensive method for measuring GHG fluxes in agricultural fields involves periodic gas samplings from static flux-chambers followed by gas chromatography (GC) (Parkin & Venterea, 2010). The GC method, which involves (i) manual gas sampling, (ii) storage in glass vials under positive pressure, and (iii) gas analysis, is laborious and time-consuming and may result in large variations in measurements due to many possible sources of mechanical error. A more practical alternative to the GC methodology that can produce results in less time but with high precision is needed for routine measurements of GHG emissions under different cropping scenarios and soil management practices.

The photo-acoustic infrared multi-gas monitoring system (PAS) has been used recently in agricultural air monitoring studies (Lawrence *et al.*, 2009; Ni *et al.*, 2009; Stackhouse *et al.*, 2011; US Environmental Protection Agency, 2011) and for accurate and rapid measurements of N_2O (Velthof & Oenema, 1993, 1995; Van Groenigen *et al.*, 2004; Adviento-Borbe *et al.*, 2007, 2010), CO_2 (Adviento-Borbe *et al.*, 2007), and NH_3 (Adviento-Borbe *et al.*, 2010) emissions in maize and grasslands. The PAS, a semi-automated system, based on a photo-acoustic infrared detection method, appears to be an attractive alternative to GC. The principle of photo-acoustic infrared technology was discussed by Christensen (1990a,b). A built-in pump circulates gas from the static chamber to the PAS up to 50 m away, as GHG concentrations are automatically recorded at selected time intervals. Thus, the PAS avoids large variations involved in manual gas sampling, storage, and analysis in the GC method. Neftel *et al.* (2006) compared different commercially available trace-gas analysis systems, including the PAS and GC, based on detection principle, sensitivity, time resolution, gases analyzed, costs, and field compatibility, but no simultaneous comparisons were made. Yamulki & Jarvis (1999) found a significant correlation between N_2O fluxes measured by GC and PAS from a long-term managed grassland, although the latter were higher by a factor of 1.4. On the contrary, De Klein *et al.* (1999), also in grasslands, did not find significant differences between N_2O measurements by the two methods. More recently, Iqbal *et al.* (2013) reported similar accuracy and precision of N_2O and CO_2 measurements by PAS and GC using standard gases. Iqbal *et al.* (2013) conducted simultaneous N_2O flux measurements only from one chamber base inserted into soil collected from the soybean phase of a soybean–corn experimental field (measurement was not done in the actual soybean–corn field), using six PAS and two GC units, and found that the average N_2O fluxes were not significantly different from each other. The PAS has not been evaluated relative to the GC method for the measurement of CO_2, N_2O and CH_4 emissions in different cereal cropping systems under different field and weather conditions.

This study evaluated the PAS relative to the GC in terms of their measured daily and cumulative N_2O, and CO_2 fluxes in wheat fields during the winter season, CH_4 and N_2O fluxes in flooded rice fields during the monsoon season, and N_2O flux in maize fields during the summer months in northwestern India. Our study also compared the two methods in terms of simplicity, precision, cost, and efficiency of gas flux measurements in the field.

Materials and methods

Site description, treatments, and field layout

Flux measurements were made in the Central Soil Salinity Research Institute (CSSRI) experimental field (loam, pH 8.6, bulk density 1.39, total organic C 0.59%, and total N 0.056%) in Karnal, Haryana, India, in 2010 and 2011. The GHG measurements were made under two crop rotations and management scenarios: S1 = rice–wheat with typical farmers' management practices, and S2 = maize–wheat–mungbean rotation with best management together with key conservation agriculture components (zero tillage and residue mulch). The daily flood water levels recorded during the rice season indicate that the water regime in the area may be classified as intermittently flooded with multiple aeration (2006 IPCC Guidelines for National Greenhouse Gas Inventories), rather than continuous flooding. In addition, four rates of N were superimposed on each of the two scenarios [0 (N1), 75 (N2), 150 (N3), and 300 (N4) kg N ha^{-1}]. Rice–maize was grown from July to October, wheat from November to April, and mungbean from April to June. The field was laid out in a randomized complete block design (60 m^2 plot size) with four replicates (R). Nitrous oxide and CO_2 fluxes were measured in wheat and maize, and N_2O and CH_4 in rice during 2010–2011. The measurements in wheat involved 32 plots (2S × 4N × 4R) on 23 sampling dates, maize involved 16 plots (1S × 4N × 4R) on 12 sampling dates, and rice involved 16 plots (1S × 4N × 4R) on 15 sampling dates.

Description of the gas chamber

The static gas chamber consisted of (i) a permanent round base (43 cm diameter), made of galvanized steel, inserted 8–10 cm below the soil surface, and (ii) a portable chamber top, 100-L plastic bucket. Each base had a hole just above the soil level to allow irrigation water to flow in and out of the base. The hole was plugged with a rubber stopper during flux measurement. Each chamber had (i) a digital thermometer to measure the inside air temperature, (ii) a fan for mixing the air inside the chamber, and (iii) a sampling port, with a sleeve-type rubber septum through which gas samples for GC analyses were withdrawn. The chamber for PAS measurements had an inlet and outlet port to allow gas circulation from the chamber to the PAS and back to the chamber. The portable chamber was placed on top of a permanently fixed chamber base in the field, over a water channel that sealed the connection of the base to the chamber. Weights were placed on top of the chamber during flux measurement to prevent movement.

Gas sampling for GC analysis and PAS recording of CO_2, N_2O, and CH_4 fluxes

Gas samplings were done between 09:00 and 13:00 h, replicate-wise to account for diurnal variations, if any. Fifty milliliter gas samples were collected for GC analyses from the chamber at 0, 10, 20, and 30 min in each plot using a 50-mL Terumo® (Terumo Corporation, Shibuya-ku, Tokyo, Japan) Luer lock tip disposable syringe. The 50-mL gas samples were immediately transferred and stored in 30-mL pre-evacuated, crimped glass vials with butyl rubber stoppers (under positive pressure) until the GC analyses.

For PAS measurements, 50-m plastic tubing of 3 mm diameter was connected to the inlet and outlet ports of the gas chamber and the PAS. A moisture trap (Genie® membrane separator™; A+ Corporation, Gonzales, LA, USA) was attached to the tubing between the chamber and the PAS. Before the actual flux measurements, the PAS was allowed to suck ambient air for about 15–30 min, until readings for CO_2, N_2O, and CH_4 were stabilized. For each flux measurement, there was a chamber flushing time of 8 s, tube flushing time of 3 s, and 710 s for the 10 automatic PAS readings (each for CO_2, N_2O, and CH_4) – totaling to 721 s or 12 min. Two additional readings of ambient air were taken after the chamber was opened, in between flux measurements for an additional 142 s or 2.4 min. Therefore, the total time required per plot was 14.4 min excluding the time required to move from one plot to the next. The air pressure inside the chamber was also recorded by the PAS during the 12-min chamber deployment time and no change in air pressure was found indicating no significant gas volume change inside the chamber.

The GC and PAS measurements were taken from the same location (same base per plot) on the same day. Chamber deployment time for GC sampling was 30 min while that for PAS was only 12 min. For GC, sampling for one replicate block (four plots) was done within 36 min with a time interval of 2 min between plots (i.e., 0-time samples from four plots were taken at 0–6 min, followed by 10-min samples at 10–16 min, 20-min samples at 20–26 min, and, lastly, 30-min samples at 30–36 min). On the other hand, PAS measurements for four plots were completed in 1 h since measurement could be made for only one plot at a time. PAS and GC measurements were made in a random order per block and the maximum time difference between PAS and GC measurements was 2 h. Greenhouse gas fluxes measured by PAS were referred to as PN_2O, PCH_4, and PCO_2, and those by GC as GC-N_2O, GC-CH_4, and GC-CO_2.

GC specifications

A gas chromatograph Varian 450 equipped with three detectors was used for analysis of CH_4, N_2O, and CO_2. A thermal conductivity detector (TCD) was used for analysis of CO_2, an electron capture detector (ECD) for N_2O, and a flame ionization detector (FID) for CH_4. The carrier gases used were helium with a flow rate of 60 mL min^{-1}, for the TCD and FID, and argon + 5% methane with a flow rate of 60 mL min^{-1} for the ECD. The columns used for CO_2 and CH_4 analyses were Hayesep N 80/100 and Porapak QS 80/100, while that for N_2O was Hayesep N 80/100 and Hayesep D 80/100. Detector temperature settings were 200 °C for the TCD, 300 °C for the FID, and 350 °C for the ECD.

The GC was calibrated at the start of each analysis using NIST (National Institute of Standards and Technology) traceable calibration gases from Portagas Inc. (S. Pasadina, TX, USA) and Spectragas Inc. (Linde North America Inc.), Alpha, NJ, USA. The GC was calibrated for CH_4 using standard gas concentrations of 2, 10 and 50 ppm; for N_2O using 0.5, 1.0 and 10 ppm; and for CO_2 using 500, 1000, and 10 000 ppm. The detection limits were 36, 0.01, and 0.26 ppm for CO_2, N_2O, and CH_4, respectively. The detection limits of the flux measurements based on the chambers used (100 L volume, 0.145 m^2 area and 12 min chamber deployment time) were 2175, 0.58, and 5.7 mg m^{-2} d^{-1} for CO_2, N_2O, and CH_4, respectively.

PAS specifications

The INNOVA 1412 Photoacoustic Infrared Field Gas Monitoring System was manufactured by INNOVA Air Tech Instruments, Ballerup, Denmark. The following filters were installed: UA0982 for CO_2, UA0969 for CH_4, UA0985 for N_2O, and SB0527 for water vapor. The CO_2, N_2O, and CH_4 filters were in positions A, B, and C of the filter carousel, respectively. Positions D and E were vacant, and the water vapor filter was next to the CO_2 filter. The INNOVA 1412 was precalibrated by the manufacturer using NIST traceable calibration gases. A full calibration of the optical filters for CO_2, N_2O, and CH_4, involving zero point calibration (using zero gas or pure nitrogen), humidity-interference calibration (using water vapor), span calibration, using a known concentration of CO_2 [3500 ppm ± 70 ppm], N_2O [5.0 ppm ± 2%], and CH_4 [45.0 ppm ± 2%]), and cross-interference calibration, was done (INNOVA Air Tech Instruments, 2007). The detection limits for PCO_2, PN_2O, and PCH_4 estimated as 2 × the standard deviation of the measured concentrations of the respective gases in ambient air, at constant water vapor below 7000 mg m^{-3}, were 10.6, 0.03, and 0.16 ppm, respectively, and the detection limits of flux measurements based on the chambers used (100 L volume, 0.145 m^2 area and 12 min chamber deployment time) were 1606, 4.5, and 8.8 mg m^{-2} d^{-1} for CO_2, N_2O and CH_4, respectively.

Calculation of emission rates

For both GC and PAS, emission rates were calculated from the change in GHG concentration over time (slope in ppm min^{-1}), and their 95% confidence limits (CL) were determined by linear regression analysis. Four GC data points collected over a 30-min period and 10 PAS data points generated over a 12-min period were used for determining the slopes and regression analysis. An emission was considered positive when the slope was significantly different from 0 at $P < 0.10$ for GC and at $P < 0.05$ for PAS by regression analysis. Otherwise, the emission was considered as 0. Emission rates in ppm min^{-1} were converted to μmol L^{-1} min^{-1} and mg m^{-2} d^{-1} as follows:

$$\mu\text{mol GHG L}^{-1}\,\text{min}^{-1} = \frac{\text{ppm GHG}\,\text{min}^{-1}}{[0.08206 \times (273 + \text{T})^{\circ}\text{K}]} \tag{1}$$

$$\begin{aligned}\text{mg GHG m}^{-2}\,\text{d}^{-1} &= \mu\text{mol GHG L}^{-1}\text{min}^{-1} \times \text{V} \\ &\quad \times \text{MW} \times 60 \times 24 \times \frac{10}{\text{A}},\end{aligned} \tag{2}$$

where

0.08206 is the gas law constant in L atm mol^{-1}°K^{-1}
T is the temperature inside the chamber in °C.
V is the total headspace volume in liters (L).
MW is the molecular weight of the GHG in μg μmol^{-1}
A is the surface area covered by the chamber in cm$^{2.}$

Estimation of seasonal GHG emissions

Seasonal N_2O emissions in wheat and maize, where distinct peaks or trends in daily emissions were observed, were estimated from the sum of daily emission rates. Daily emissions in between weekly measurements were estimated from linear interpolation of two consecutive weekly measurements. In rice, where CH_4, N_2O, and CO_2 had no distinct trends, values were calculated by multiplying average daily emission rates with the crop duration. When rice fields are kept continuously flooded, peaks of CH_4 emissions generally appear at the early tillering stage, in soil with inherently high organic matter or where rice straw has been incorporated (Neue *et al.*, 1997); and at the flowering or reproductive stage (Yang & Chang, 1999) due to increased supply of plant-borne C through root exudates and decaying tissues (Neue *et al.*, 1997). However, these peaks were not observed in our experimental sites where low CH_4 emissions were observed, due to intermittent flooding and multiple aeration resulting from the high-percolating nature of the soil.

Correction of PCH_4 readings for water vapor interference

Although the PAS was equipped with a moisture trap and was calibrated to compensate for water vapor (WV) and cross-interferences, it was observed that CH_4 readings from ambient air in the experimental fields from Nov 2010 to Oct 2011 increased with increasing WV ($R^2 = 0.84$) from 8000 to 31 000 mg cm^{-3} (Fig. 1a). The moving averages technique (Wikipedia, 2013) was used to reduce the spread of the points and increase the regression coefficient (Fig. 1b). The paired data points (water vapor and PCH_4 readings) were sorted according to increasing water vapor, then moving averages in groups of 5 were calculated for both PCH_4 and water vapor. The moving averages of PCH_4 and water vapor were plotted and linear regression was done on these values. The PCH_4 readings were stable at water vapor below 8000 mg cm^{-3} (Fig. 1c). The same trend was observed during the following year (data not shown).

From the slope of linear regression, PCH_4 readings were estimated to increase by 0.0023 ppm for every 1 mg m^{-3} increase in water vapor (at WV 8000–31 000 mg cm^{-3}) (Fig 1b). Therefore, a correction factor equal to 0.0023 × the change in water vapor relative to that recorded at the start of chamber deployment was subtracted from each observed PCH_4 reading. Since PCH_4 readings from ambient air were stable at WV less than 8000 mg m^{-3}, a mathematical correction was not applied when the WV was less than 8000 mg m^{-3}.

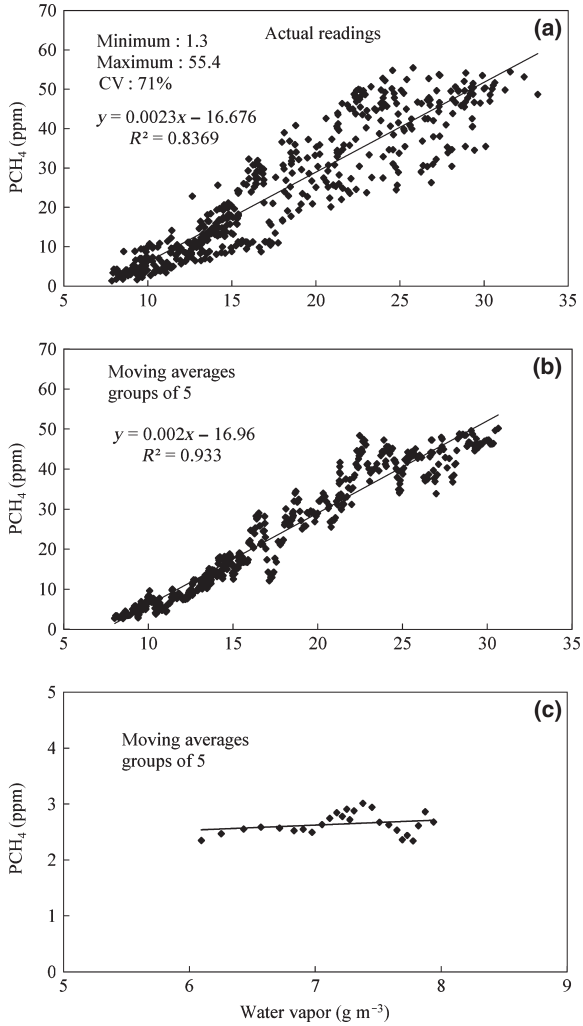

Fig. 1 Relationship between PAS-CH4 (PCH4)measured from ambient air across seasons and water vapor at 6000–30 000 mg m^{-3} using (a) actual values, (b) moving averages, and (c) PAS-CH4 and water vapor at 6000–8000 mg m$-^{3}$ water vapor using moving averages (Nov 2010 to Oct 2011).

For CH_4 flux measurements during the monsoon season, the change in PCH_4 due to a WV interference was estimated as follows:

$$\Delta PCH_{4WVt} = (WV_t - WV_0) \times 0.0023 \tag{3}$$

where

ΔPCH_{4WVt} is the change in PCH_4 due to a change in WV at time t.

WV_t = WV at time t after chamber deployment.

WV_0 = WV at time 0 of chamber deployment.

0.0023 is the increase (slope) in PCH_4 per 1 mg m^{-3} increase in WV.

Relationship between PN_2O readings and water vapor

There was no significant relationship between PN_2O and WV, ranging from 6000 to 18 000 mg m^{-3}, in ambient air measured during the wheat season (November to April) (Fig. 2). Since the coefficient of variation of PN_2O in ambient air (5.7% with a standard deviation of 0.018) was close to the measured detection limit, no further correction was required. Whereas during the rice and maize season (May to October) when WV ranged from 18 000 to 30 000, the PN_2O average from ambient air increased to 0.6 with a standard deviation of 0.081 which is much higher than the measured detection limit of PAS for N_2O. Nevertheless, since the regression coefficient between PN_2O and water vapor was low, the PN_2O readings were likewise not corrected for variations in water vapor during the rice and maize season (Fig. 2). Similarly, no significant relationship was obtained between PCO_2 and water vapor.

Correction of PN_2O, PCO_2, and PCH_4 readings for baseline drifts not related with water vapor

The PN_2O, PCO_2, and PCH_4 readings were corrected for baseline drifts over time that were not correlated with WV. The reason is unclear but this leads to very high or very low fluxes, if not corrected. Corrections were applied when baseline drifts exceeded the detection limits (11 ppm for CO_2, 0.03 ppm for N_2O, and 0.16 ppm for CH_4). In wheat and maize, baseline drifts greater than the detection limits occurred occasionally. More frequent baseline drifts in PN_2O (higher than the detection limit) were observed for rice. High PCH_4 readings were usually related to increased WV but occasional baseline drifts in PCH_4 readings also occurred without an increase in WV. A change in baseline reading for PX (X is N_2O, CO_2, or CH_4) was calculated at each sampling time (t) during chamber deployment as follows:

$$\Delta PX_{Bt} = (PX_{B2} - PX_{B1}) \times \frac{t}{(t_2 - t_1)}, \tag{4}$$

where

ΔPX_{Bt} is the change in PX baseline reading at time t.

PX_{B1} and PX_{B2} are baseline (0-time) readings for CH_4 from two successive plots.

t_1 = time when PX_{B1} was recorded from the first plot.

t_2 = time when PX_{B2} was recorded from the second plot.

t = time interval after chamber deployment in the first plot.

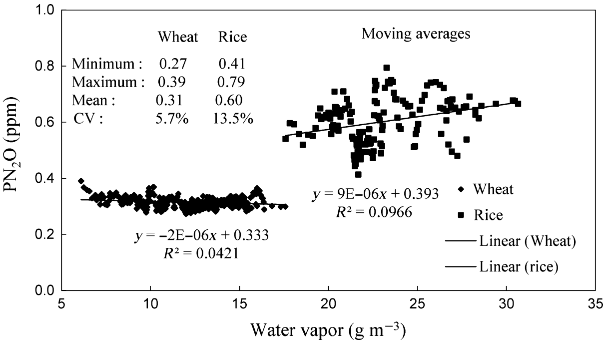

Fig. 2 Relationship between water vapor and PAS-N2O (PN2O) measured from ambient air during the wheat (6000–18 000 mg m^{-3} water vapor) and rice (18 000–30 000 mg m^{-3} water vapor) seasons.

The PAS readings for CH_4, N_2O, and CO_2 were corrected as follows:

$$PCH_{4c} = PCH_{4t} - PCH_{4t0} - \Delta PCH_{4WVt} - \Delta PCH_{4Bt} \tag{5}$$

$$PN_2O_c = PN_2O_t - PN_2O_{t0} - \Delta PN_2O_{Bt} \tag{6}$$

$$PCO_{2c} = PCO_{2t} - PCO_{2t0} - \Delta PCO_{2Bt}, \tag{7}$$

where

PCH_{4c}, PN_2O_c, and PCO_{2c} are the corrected PAS readings for CH_4, N_2O, and CO_2, respectively.

PCH_{4t}, PN_2O_t, and PCO_{2t} are the actual PAS readings for CH_4, N_2O, and CO_2 at time t, respectively.

PCH_{4t0}, PN_2O_{t0}, and PCO_{2t0} are the actual PAS readings for CH_4, N_2O, and CO_2 at time 0, respectively.

ΔPCH_{4WVt} is the change in PCH_4 due to a change in WV at time t.

ΔPCH_{4Bt}, ΔPN_2O_{Bt}, and ΔPCO_{2Bt} are changes in the baseline readings for CH_4, N_2O, and CO_2 at time t, respectively.

The corrected readings were used in regression analysis for determining the flux rates (slopes, change over time) and their 95% confidence limits (CL).

Statistical analyses

Comparisons of GC- and PAS-measured emission rates within each plot, on the same date, were made based on the 95% CL of the slopes obtained from regression analysis. The combined analysis of GC and PAS data on different days after sowing (DAS) and N rates were done by the SAS mixed procedure (SAS Institute, 2001) with repeated/group effect (group = method, PAS vs. GC) at alpha = 0.05.

Results

GC- and PAS-measured N_2O and CO_2 fluxes during the wheat season

Comparisons of GC- and PAS-measured CO_2 and N_2O emissions, from each plot, on 23 sampling dates, were made based on the 95% CL of the slopes (change in CO_2 and N_2O concentrations over time) calculated by linear regression analysis. The N_2O and CO_2 fluxes measured from each plot on the same day by GC and PAS were not different from each other in 93–94% (684–689) of the total of 736 measurements. On average, significant differences between PAS and GC results were observed in only 1–2 plots per sampling day. The GC-N_2O and PN_2O measurements on January 13, when the average N_2O was highest showed greater values of GC-N_2O in 3 out of 32 plots than PN_2O (Fig. 3). All of these plots had 300 kg N ha^{-1} fertilizer. Generally, PN_2O exhibited greater precision than GC-N_2O as shown by their 95% CL. Likewise, PAS had better precision than GC for measuring CO_2 (Fig. 4). The daily time trends of N_2O and CO_2 fluxes measured by GC and PAS during crop duration were similar. The daily averages of GC-N_2O and PN_2O were not different from each other but PCO_2 was higher than GC-CO_2 on three sampling dates (Figs. 5 and 6). No N_2O was detected by both GC and PAS after basal N application on November 25, but it was higher after the first topdressing than that after the second by both GC and PAS (Fig. 6).

The SAS test of fixed effects showed that method of measurement (GC vs. PAS) had no significant effect on N_2O fluxes. Likewise, the method × N and method × N × day interactions were not significant (Table 1), which indicates that PAS and GC flux means did not

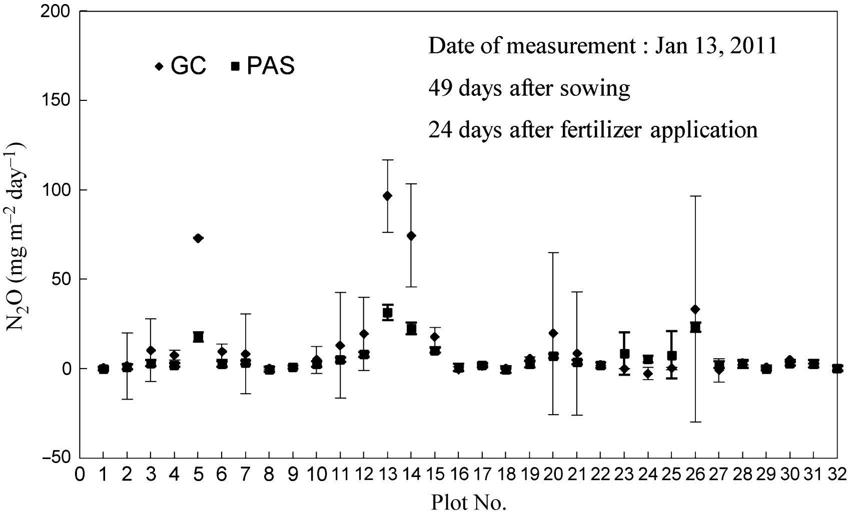

Fig. 3 Plot-wise N_2O emission rates measured by GC and PAS in a wheat field, with their 12 95% confidence limits (shown by error bars).

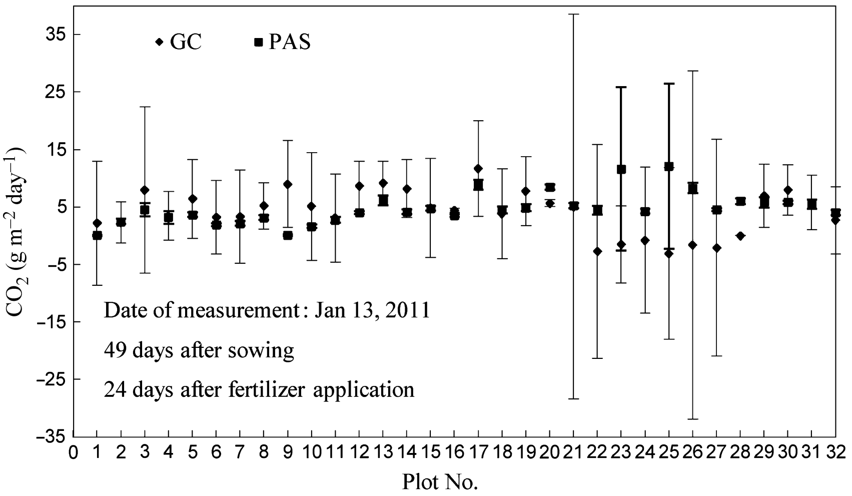

Fig. 4 Plot-wise CO_2 emission rates measured by GC and PAS in a wheat field, with their 15 95% confidence limits (shown by error bars).

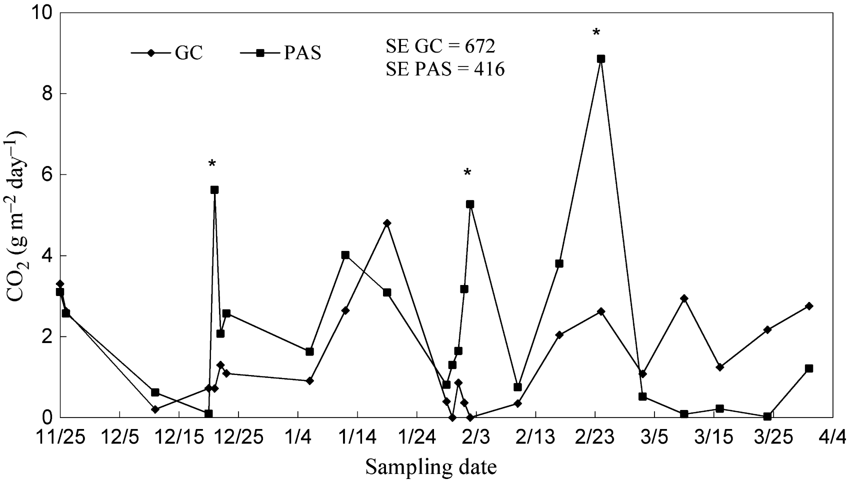

Fig. 5 Daily average CO_2 fluxes measured by PAS and GC in a wheat field (2010–11). (*GC and PAS significantly different at $P < 0.05$).

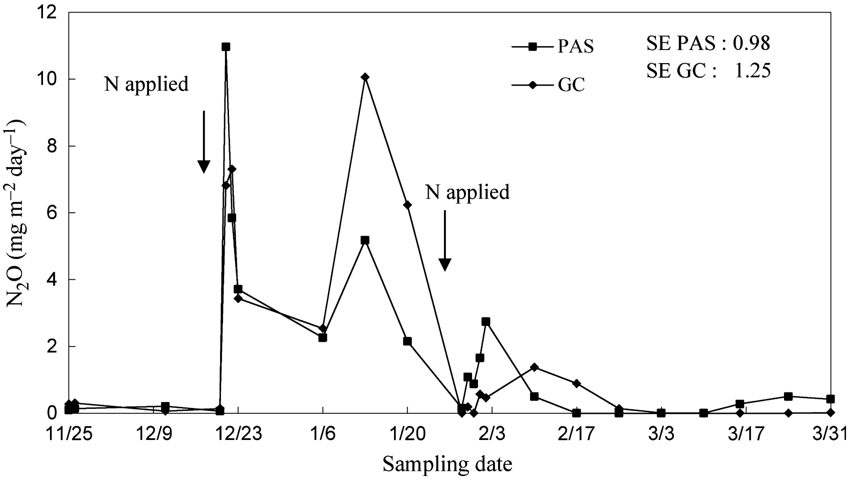

Fig. 6 Daily average N_2O fluxes measured by PAS and GC in a wheat field (2010–11).

differ within each N and N × DAS and that the same response to fertilizer N rate in terms of N_2O flux was determined by both methods.

On the other hand, the GC and PAS methods varied significantly in terms of CO_2 fluxes (Table 1). The cumulative CO_2 emissions were 14–39% higher by PAS than by GC (Table 2). The M × DAS interaction was also significant for CO_2 fluxes, indicating that, on some days, PCO_2 and GC-CO_2 means varied significantly from each other (Fig. 5). However, the M × N and M × N × DAS interactions in CO_2 fluxes were not significant (Table 1), which indicates that PAS and GC flux means did not differ within each N and N × DAS and that the same response to N application in terms of CO_2 flux was determined by both methods.

The seasonal (cumulative) N_2O flux measured by GC and PAS in the wheat field were not different within each N rate except with 300 kg N ha^{-1}, in which GC value was higher than that of PAS by about threefold (Table 2). This difference was due mainly to high GC-N_2O fluxes as compared to those of PAS on 2 sampling days (Fig. 6). However, the seasonal N_2O and CO_2 flux increased with increasing fertilizer N rate by the two methods (Tables 2 and 3). The relative standard error of the seasonal GC-N_2O flux was lower (18%) as compared to that of the seasonal PN_2O flux (25%). On the other hand, the relative standard error of the seasonal GC-CO_2 flux was 2-folds higher (9%) as compared to that of the seasonal PCO_2 flux (4.5%) (Tables 2 and 3).

GC- and PAS-measured N_2O fluxes during the maize season

The SAS test of fixed effects showed that method (GC vs. PAS) had no significant effect on N_2O fluxes in maize fields (Table 4). The M × N and M × N × DAS

Table 1 Test of fixed effects on N_2O and CO_2 emissions in wheat by SAS mixed procedure with repeated/group effect

	N_2O		CO_2	
Effect*	*F* value	$P > F$	*F* value	$P > F$
Method (PAS vs. GC) (M)	0.07	0.789	22.70	<0.0001
N	11.71	<0.0001	11.00	<0.0001
M × N	1.51	0.21	0.53	0.66
D	11.04	<0.0001	11.70	<0.0001
M × D	1.26	0.19	8.41	<0.0001
N × D	1.98	<0.0001	1.34	0.04
M × N × D	0.47	1.00	1.16	0.19

*M, method, N, fertilizer N rate; D, sampling date.

Table 2 Cumulative N_2O emissions measured by PAS and GC in wheat at four N rates

N applied ($kg\ ha^{-1}$)	PAS	GC
	($kg\ N_2O\ ha^{-1}$)	
0	0.26	0.16
75	0.86	1.06
150	1.48	2.40
300	2.23	6.81
Standard error	0.30	0.48

Table 3 Cumulative CO_2 emissions measured by PAS and GC in wheat at four N rates

N applied ($kg\ ha^{-1}$)	PAS	GC
	($kg\ N_2O\ ha^{-1}$)	
0	1.847	1.133
75	3.036	2.613
150	2.868	1.938
300	3.885	3.130
Standard error	132	200

interactions were also not significant. However, there was a significant M × DAS interaction, which was mainly due to the difference between the average PN_2O and GC-N_2O on one sampling date (Fig. 7). The time trends of N_2O fluxes measured by GC and PAS in maize fields were similar (Fig. 7). Likewise, the seasonal (cumulative) N_2O fluxes in maize were not different by GC and PAS at each N level and increases in N_2O fluxes with high N were observed by both methods (Table 5). Higher variability in terms of relative standard error was exhibited by GC (24%) than by PAS (18%) for the measured N_2O fluxes in maize (Table 5, Fig. 7).

Table 4 Test of fixed effects on N_2O emissions in maize by SAS mixed procedure with repeated/group effect

Effect*	*F* value	$P > F$
Method (PAS vs GC) (M)	0.19	0.659
N	30.35	<0.0001
M × N	1.54	0.205
D	9.46	<0.0001
M × D	2.19	0.015
M × N × D	0.84	0.726

*M, method; N, fertilizer N rate; D, sampling date.

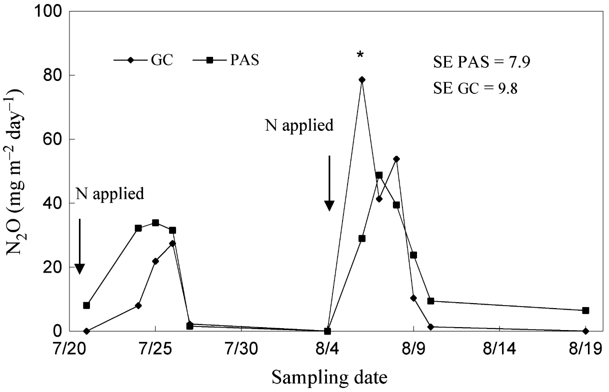

Fig. 7 Daily average N_2O fluxes measured by PAS and GC in a maize field (2011) (* GC and PAS significantly different at $P < 0.05$).

Table 5 Cumulative N_2O emissions as measured by PAS and GC in maize at four N rates

	PAS	GC
N applied ($kg\ ha^{-1}$)	($kg\ N_2O\ ha^{-1}$)	
0	0.45	0.33
75	7.83	6.23
150	6.73	7.53
300	17.31	13.58
Standard error	1.43	1.70

GC- and PAS-measured CH_4 and N_2O fluxes during the rice season

Of the total 240 measurements of CH_4 and N_2O fluxes on 15 sampling dates, the pair-wise comparison of results from GC and PAS within the same plot showed differences in only 5 cases for CH_4 and 14 cases for N_2O (data not shown), indicating a large agreement between the two methods. The GC-CH_4 and PCH_4 fluxes from each plot on August 01, when the highest average CH_4 flux was observed, are shown in Fig. 8. The PCH_4 flux was significantly higher than that by

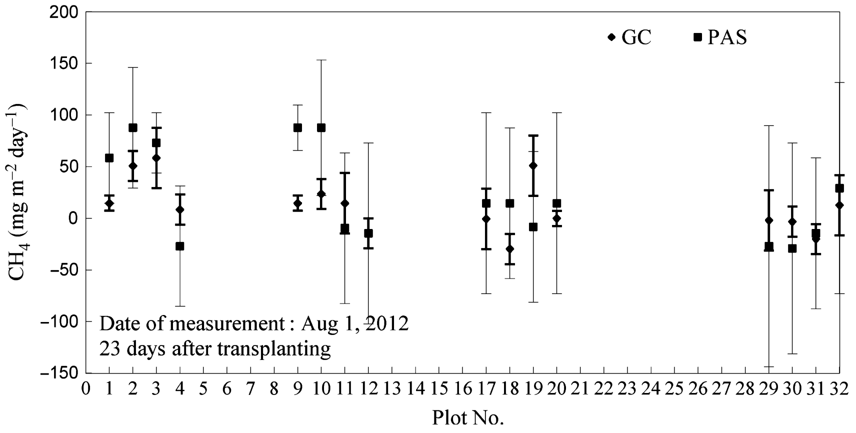

Fig. 8 Plot-wise CH_4 emission rates measured by GC and PAS in a rice 1 field, with their 95% confidence limits (shown by error bars).

Table 6 Test of fixed effects on CH_4 and N_2O emissions in rice by SAS mixed procedure with repeated/group effect

Effect*	CH_4 *F* value	*P* > F	N_2O *F* value	*P* > *F*
Method (PAS vs GC) (M)	7.29	0.007	7.96	0.005
N	0.50	0.71	1.30	0.27
M × N	0.05	0.96	0.42	0.74
D	1.78	0.04	2.19	0.009
M × D	1.33	0.19	0.82	0.65
N × D	0.75	0.87	1.01	0.46
M × N × D	1.10	0.33	0.58	0.98

*M, method; N, fertilizer N rate; D, sampling date.

Table 7 Cumulative CH_4 and N_2O emissions as measured by GC and PAS in rice at four N rates

	CH_4 (kg ha^{-1})			N_2O (kg ha^{-1})		
N applied (kg ha^{-1})	PAS corrected	PAS actual	GC	PAS corrected	PAS actual	GC
0	12.1	38.9	4.5	1.55	2.19	0
75	13.1	71.0	6.4	2.54	2.73	0.12
150	14.0	95.0	7.8	3.94	5.85	0.89
300	8.2	87.3	4.1	2.86	7.79	1.89
Standard error	5.4	33.6	2.3	1.28	1.68	0.6

GC-CH4 in only 1 of the 16 plots. However, the precision shown by PCH_4 fluxes were lower than the GC-CH_4 fluxes. The test of fixed effects by the SAS mixed procedure showed that method (M, PAS vs. GC) had a significant effect on CH_4 and N_2O fluxes. However, the M × N, M × DAS, and M × N DAS interactions were not significant, showing that within each N, DAS, and N × DAS treatment, CH_4 and N_2O fluxes measured by PAS and GC were not significantly different from each other (Table 6).

The methane fluxes measured in rice were relatively low (averaging 12 and 6 kg CH_4 ha^{-1} across N levels by PAS and GC, respectively: Table 7), as has also been observed earlier by Jain *et al.* (2000) in rice fields in Northern India. This is most likely due to multiple aeration, resulting from the high-percolating nature of the soil. Yagi *et al.* (1990) and Inubushi *et al.* (1992) have reported that high percolation rates resulted in an inflow of oxygen into the soil and downward discharge of methanogenic substrates leading to low emission rates. Under continuous flooding with no organic fertilizers, CH_4 emission rates have been reported to vary from 15 to 200 kg CH_4 ha^{-1} in Asian countries (Wassmann *et al.*, 2000).

The cumulative corrected PCH_4 and PN_2O fluxes averaged over N levels were higher than those of GC-CH_4 and GC-N_2O fluxes by about two- and four-folds, respectively, while the uncorrected PAS values were 12 and 6 times higher than the GC values for CH_4 and N_2O fluxes, respectively (Table 7). The average daily CH_4 fluxes recorded during the rice season over four N levels by GC and PAS showed similar trends but PAS generally had higher fluxes than GC (Fig. 9). The uncorrected daily average PCH_4 readings were 8–45 times higher than the corrected ones showing the large effect of water vapor on the PCH_4 readings.

Fertilizer N level had no effect on the cumulative CH_4 and N_2O emissions as measured by the two methods and fluxes were not different from each other within each N level (Table 7). Based on relative standard errors, the PAS showed greater variability (46%) than GC (40%) in the seasonal CH_4 flux while GC showed greater variability (83%) than PAS (47%) in the seasonal N_2O flux.

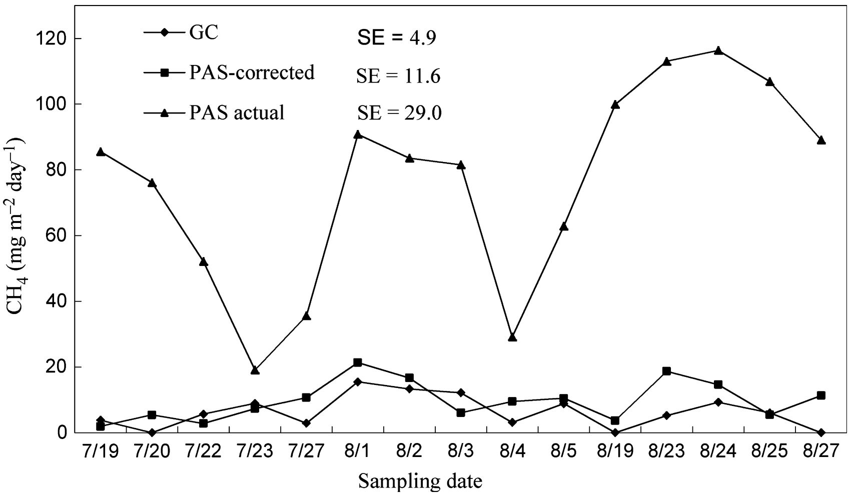

Fig. 9 Daily average CH_4 fluxes measured by PAS and GC in a rice field (2011).

Discussion

Our field study with numerous measurements of CO_2, N_2O, and CH_4 made throughout the crop duration is the first systematic comparison of GC and PAS in cereal-based crop rotations under different field and weather conditions. Also, to date, there has been no published report of CH_4 measurements in a rice system using a PAS. Earlier studies are limited to a comparison of GC-N_2O and PN_2O fluxes in grasslands (De Klein *et al.*, 1999; Yamulki & Jarvis, 1999) and in incubated soil collected from a soybean–corn experimental field (Iqbal *et al.*, 2013).

Comparisons of N_2O, CO_2 and CH_4 fluxes measured by GC and PAS

Our results demonstrated that the cumulative N_2O and CO_2 flux measurements within each N level, by PAS and GC in wheat and maize fields were comparable (Tables 2, 3 and 5) and PN_2O and PCO_2 readings were not affected by water vapor (Fig. 2). Further, the precision of daily emission rates exhibited by PAS for N_2O and CO_2 in wheat and maize were higher and more consistent as compared to that by GC (Figs. 3 and 4). The PAS method eliminated several sources of mechanical/manual errors from gas sampling and storage by the GC method, for example, incomplete evacuation and leakage of gas storage vials, moisture in gas storage vials which may dilute gas samples, inaccurate timings of gas samplings, and extended storage time. The use of a more efficient vacuum system, for example, a lyophilizer (as compared to the vacuum pump used in our study), could eliminate dilution errors in the GC method. But due to its high cost, this equipment would not be readily available in most laboratories. Storage time may also not be a problem if only a few gas samples are to be analyzed. Moreover, continuous gas sampling by PAS generates more data points as compared to manual sampling by the GC, and statistically, increasing the number of data points increases the confidence level. Linquist *et al.* (2012) conducted a literature survey on ranges of global warming potentials (GWP) for GHG fluxes in major cereal crops. For wheat and maize applied with 0–300 and 0–310 kg N ha^{-1}, respectively, the reported ranges in GWP were equivalent to emissions of 0.11–14.59 kg N_2O ha^{-1} in wheat and 0.20–18.08 kg N_2O ha^{-1} in maize. The N_2O fluxes, measured from our study, by PAS in wheat (0.26–2.23 kg N_2O ha^{-1}) and maize (0.45–17.31 kg N_2O ha^{-1}) are within these reported ranges.

Compared to maize and wheat grown in uplands, rice which is normally grown in lowlands had lower precision of PN_2O due to frequent baseline drifts over time of up to 0.013 ppm N_2O min^{-1}. This is most likely associated with the combined effects of high temperature, humidity, and water vapor which commonly prevail in lowland rice. The cumulative N_2O flux across 4 N levels as measured by PAS was 4 times higher than that of the GC although the difference was not significant ($P < 0.05$) within each N level (Table 7). The measured N_2O fluxes in rice expressed as a percentage of the N applied averaged 0.3% by GC and 0.7% by PAS. The IPCC default value for N_2O-N emissions in irrigated lowland rice is 0.3% (0–0.6%) of the N applied (IPCC Guidelines for National Greenhouse Gas Inventories, 2006). This was based on measurements by Akiyama *et al.* (2005) in Japanese rice paddy fields which were continuously flooded. With intermittent flooding or multiple aeration, the N_2O-flux in N fertilized fields may increase due to greater chances for the nitrification–denitrification processes to occur.

Water vapor in humid rice environment is a major constraint in PCH_4 measurements causing interference by the overlapping absorption spectra of the different gases and WV together with confounding temperature effect (Neftel *et al.*, 2006). Because the IR spectra of water vapor cover a wide spectral range, water vapor interferes with most gases unless the air sample is dry (Zhao *et al.*, 2012). Therefore, rice poses a special challenge for measurements of CH_4 by the PAS. Using enclosed climate chambers, Neftel *et al.* (2006) tried to develop a correction algorithm for N_2O, CO_2, CH_4, and H_2O against a range of water vapor and temperatures but failed due to the associated complexities. Zhao *et al.* (2012) reviewed issues related to cross interferences in PAS measurements and have proposed two methods for measuring interferences in multi-gas measurements. The high correlation that we obtained between WV and PCH_4 in ambient air is an indication that WV interference was not fully addressed by the instrument's (INNOVA 1412) internal cross-compensation. There was an increase of 2.3 ppm in the PCH_4 reading with 1000 mg m^{-3} increase in water vapor when water vapor was above 8000 mg m^{-3} (Fig. 1). Normally, the humidity during the rice season ranged from 20 000 to 33 000 mg m^{-3} and therefore the PCH_4 readings warranted correction. However, at water vapor below 8000 mg m^{-3}, the instrument's internal compensation for WV was adequate (Fig. 1c). We eliminated the interference of WV on PCH_4 measurements using a simple mathematical calculation based on a linear relationship between CH_4 and WV in ambient air. The estimated PCH_4 fluxes, after correcting for baseline drifts and water vapor interference, were in good agreement with the GC-CH_4 fluxes (Fig. 9). The cumulative PCH_4 flux was 8–21 times higher than the GC-CH_4 flux before correction. After correction, the difference was reduced by 78–95% (Table 7). The lower CH_4 flux measured by GC could be due to dilution in the storage vials arising from either incomplete evacuation of the storage vials or due to entry of ambient air into the vials prior to filling of the gas samples. However, we avoided this problem by evacuating the vials just a few hours prior to sampling and by injecting standard gases for calibration in the same evacuated vials prior to GC analysis. The average CH_4 flux measured by PAS over 4 N levels (12 kg ha^{-1}) was within the range obtained by Jain

Table 8 Comparison of GC and PAS methods

Criteria	GC	PAS
Simplicity and ease of use	Requires more training for gas sampling to ensure precise timing, and skill for GC analysis, including calibration	Procedure for running the PAS is straightforward and calibration of the instrument can be done only once a year
Time required for gas sampling and analysis	40 min per plot for gas sampling and GC analysis, using the protocol described in this article	15 min per plot for automatic gas sampling and recording of GHG concentrations including time required to move from 1 plot to the next
Chamber deployment time	30 min to obtain four data points at 10-min intervals	12 min to obtain 10 data points at 1.2-min intervals
Precision	Lower precision for N_2O and CO_2 measurements in wheat and maize but higher precision for CH_4 in rice	Higher precision for N_2O and CO_2 measurements in wheat and maize but lower precision for CH_4 in rice
Diurnal variation	Gas samplings for all plots can be done within a shorter period of time, especially if more people can take gas samples simultaneously from different plots, thus reducing the effect of any diurnal variation.	If only one instrument is used, we recommend a maximum of 16 measurements per day, which may take 4 h. Diurnal variations can be taken into account by doing measurements replicate-wise.
Equipment cost in USD	24 000	60 000
Cost of Consumables in USD/plot/day	0.50 – Carrier gases 1.15 – Calibration gases (3 concentrations each of CH_4, N_2O and CO_2) 0.64 – Storage vials 0.40 – Syringes for sampling 2.69 – Total	0.24 – Calibration gases (2 concentrations each of CH_4, N_2O and CO_2)
Labor cost in USD/plot/day	3.31 – 1 researcher + 2 skilled labor for gas sampling and 1 researcher for GC analyses	2.25 – 1 researcher + 1 skilled labor

et al. (2000) for rice fields under intermittent irrigation in Northern India (10–32 kg ha^{-1}), but the average CH_4 flux we measured by GC was lower (6 kg ha^{-1}). The precision of PCH_4 fluxes in flooded rice fields were lower than the GC-CH_4 fluxes. The correction factors used for humidity interferences and baseline drifts have associated error terms that may lower the precision of PCH_4 as compared to GC-CH_4. Moreover, correction of PAS data, increases the time required for data processing and tends to lose the simplicity of the PAS method. The extent of humidity interference in PCH_4 readings may vary with the field and weather conditions. Thus, it is important to check the correlations of WV with CH_4, N_2O, and CO_2 readings in *in situ* ambient air before proceeding with actual flux measurements.

Comparison of GC and PAS as an analytical tool for measuring GHG emissions in agricultural fields

An overall assessment of GC and PAS as analytical tools for measuring GHG emissions in agricultural fields was made based on several criteria (Table 8). In terms of simplicity and ease of use, total time required for measurement, chamber deployment time, cost of consumables, and labor cost, the PAS is a better choice than the GC for routine GHG flux measurements. However, not considering the time required for GC analysis (7 min per sample or 28 min per plot), manual gas sampling by GC requires less time (36 min for four plots) than automatic recording of CO_2, N_2O, and CH_4 by PAS (1 h for four plots) following the protocol described earlier. Thus, for GHG estimations using PAS, we recommend taking readings from a maximum of only 16 plots per day, which will take around 4 h, from 9AM to 1PM, to minimize diurnal variation, if any.

The main disadvantage of the PAS over the GC is its higher (2.5 times) cost than the GC. However, this is offset by the lower (2.4 times) cost of consumables and labor required by the PAS (Table 8). The PAS requires calibration gases for only 1–2 calibrations per year while the GC requires a continuous supply of carrier gases and calibration gases for daily calibration. The GC also requires storage vials and syringes which are not required by PAS.

In conclusions, compared to GC, the overall performance of PAS is superior for CO_2 and N_2O measurements in upland crops such as maize and wheat. Water vapor in rice poses a challenge for CH_4 and N_2O measurements. However, a careful examination of baseline drifts and changes in water vapor during chamber deployment, and making subsequent corrections, have potential to make accurate measurements by the PAS. Further studies should be designed and carried out under flooded field conditions to trap the water vapor in the gas sample before reaching the infrared detector of the PAS to minimize the interferences.

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