Accuracy and precision of no instrument is guaranteed

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Abstract
Photoacoustic infrared spectroscopy (PAS) is increasingly used for measurement of N₂O and CO₂ fluxes at the soil surface. However, PAS calibration is complex. Water vapor, CO₂, and temperature interfere with accurate N₂O measurement. To accurately measure N₂O, PAS calibrations must compensate for these interferences. Our article, ‘Evaluation of photoacoustic infrared spectroscopy for the simultaneous measurement of N₂O and CO₂ gas concentrations and fluxes at the soil surface’ (Iqbal et al., 2013), compared PAS and gas chromatography (GC) analytical procedures. Results demonstrated that PAS can measure N₂O concentrations (ca. 0.5–3.0 ppm) and fluxes (ca. 0.5–5.0 ppm min⁻¹) with accuracy and precision similar to GC without interferences from H₂O vapor or CO₂ concentrations typically encountered in static flux chambers at the soil surface.

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Comments

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LETTER

Accuracy and precision of no instrument is guaranteed: a reply to Rosenstock et al.

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Photoacoustic infrared spectroscopy (PAS) is increasingly used for measurement of N₂O and CO₂ fluxes at the soil surface. However, PAS calibration is complex. Water vapor, CO₂, and temperature interfere with accurate N₂O measurement. To accurately measure N₂O, PAS calibrations must compensate for these interferences. Our article, ‘Evaluation of photoacoustic infrared spectroscopy for the simultaneous measurement of N₂O and CO₂ gas concentrations and fluxes at the soil surface’ (Iqbal et al., 2013), compared PAS and gas chromatography (GC) analytical procedures. Results demonstrated that PAS can measure N₂O concentrations (ca. 0.5–3.0 ppm) and fluxes (ca. 0.5–5.0 ppm min⁻¹) with accuracy and precision similar to GC without interferences from H₂O vapor or CO₂ concentrations typically encountered in static flux chambers at the soil surface.

In response, Rosenstock et al. (2013) initiated a valuable dialogue by reminding readers that analytical instrument accuracy and precision are not guaranteed. Although we agree with this primary assertion, several other assertions in the authors’ letter are flawed. Based on two PAS evaluations that produced inaccurate N₂O measurements at low concentrations (ca. 0.0–0.7 ppm), Rosenstock et al. (2013) suggested that the results of Iqbal et al. (2013) were limited to unique experimental conditions including relatively high N₂O concentrations and fluxes. Ultimately, the authors questioned the ability of PAS to be calibrated for accurate measurement of N₂O concentrations and fluxes across the ranges encountered during standard operating conditions.

We highlight published data, new experimental results, and differences in calibration procedures that indicate Rosenstock et al. (2013) evaluated improperly calibrated instruments. We extend the experiments of Iqbal et al. (2013) to low N₂O concentrations and clarify the importance of evaluating high N₂O concentrations and fluxes. Finally, we suggest procedures to avoid faulty PAS calibrations.

The PAS evaluations conducted by Rosenstock et al. (2013) demonstrated: (i) two PAS units did not accurately measure three N₂O concentrations in analytical standards (hereafter PAS 1 and PAS 2); and (ii) measurements of N₂O concentrations with a third PAS unit experienced significant interferences from H₂O vapor and/or temperature (hereafter PAS 3). Relative to our evaluations, they stated:

‘The most parsimonious explanations for variation among instrument performance are differences in experimental conditions or calibration algorithms that account for interference among gas and water vapor absorption spectra and for cross-interferences among the targeted molecules. However, differences may also be attributable to the gas concentrations tested.’

Although the authors identified three potential causes for the differences among instrument performance, they devoted discussion to two of the three possibilities: experimental conditions and tested N₂O concentrations. They did not describe calibration procedures or discuss the potential for improper calibration. Nevertheless, the authors extended results from one experiment with one PAS unit to suggest PAS cannot be calibrated to produce accurate N₂O measurements due to uncorrectable interferences from nontarget gases and temperature.

We present three lines of evidence that indicate the authors evaluated improperly calibrated instruments:

First, Rosenstock et al. (2013) incorrectly asserted that ‘Data from our experiments suggest PAS is less accurate and precise than Iqbal et al. (2013) suggest.’ Both assertions in this statement are false: Although a quantum cascade laser was used to verify N₂O concentrations used in evaluations of PAS 3, the accuracy of ‘known gas concentrations’ used in evaluations of PAS 1 and PAS 2 is not reported nor independently verified with a different analytical technique; thus it is impossible to determine accuracy. Communications with the authors indicated that the 0.331 PPM and 0.649 ppm N₂O standards used in evaluations of PAS 1 and PAS 2 were accurate at ±10% (T. Rosenstock, personal communication). Also, PAS calibration is typically accurate only within ±5% of an
independent standard (subject to ±5–10% error) used by
the vendor to test the calibration. Regardless, the most
parsimonious explanation for inaccurate standard mea-
surement with an analytical instrument that has been
demonstrated to be accurate is: calibration error.

Moreover, PAS precision reported by Rosenstock et al.
(2013) and Iqbal et al. (2013) did not differ. Precision
reported by Iqbal et al. (2013) ranged from 1.2 to 2.5%
while precision reported by Rosenstock et al. (2013) ran-
ged from 1.2 to 5.4%. Both ranges favorably compare to
GC (Iqbal et al., 2013; Tirol-Padre et al., 2013).

Second, we conducted a new experiment similar to
the authors’ evaluation of PAS 3. This experiment
tested for interactive effects of H₂O vapor and tempera-
ture on low-concentration N₂O measurements. In con-
trast to data presented by Rosenstock et al. (2013), we
observed no H₂O vapor or temperature interferences
with measurements of atmospheric and NIST-certified
N₂O concentrations (Figure 1).

Third, Zhao et al. (2012) demonstrated that internal
or external PAS calibration algorithms can be devel-
oped to produce accurate N₂O measurements at con-
centrations >0.03 PPM if cross-interfering gases (i.e.
H₂O vapor and CO₂) are measured and accounted for
in calibration algorithms. If environmental conditions
produce inaccurate measurements, it is not because
calibrations cannot account for interferences (assuming
H₂O vapor and CO₂ are the only interfering gases); it is
because the calibration algorithms are insufficient or
cross-interfering gases are unaccounted for. Other than
H₂O vapor and CO₂, we know of no gases that interfere
with N₂O.

Rosenstock et al. (2013) further suggested that our
evaluations were limited because we worked at high
N₂O fluxes:

‘Iqbal et al. (2013) report changes in headspace
concentrations of 50–600 ppb N₂O min⁻¹, roughly
equivalent to 600–7000 g N₂O-N m⁻² h⁻¹ (or 50–
600 kg N ha⁻¹ yr⁻¹) when assuming a 15 cm high
chamber. Soil fluxes of that magnitude are rarely
found and only occur under high emission condi-
tions.’

Although evaluations in Iqbal et al. (2013) were con-
ducted at high fluxes, the minimum flux detection limit
was calculated and reported as 0.0033 ppm min⁻¹
(assuming five gas concentration measurements during
an 8 min chamber closure). This was compared to the
GC N₂O minimum flux detection limit calculated as
0.0007 ppm min⁻¹ (assuming three gas concentration
measurements during a 45 min chamber closure).
Additionally, Iqbal et al. (2013) explicitly identified two
reasons for working at high N₂O concentrations: First,
Ambus & Robertson (1998) previously determined that
PAS and GC produce ‘statistically identical’ N₂O flux
estimates at extremely low fluxes. Given that we stated
‘Ambus & Robertson (1998) demonstrated similar N₂O

Fig. 1 Photoacoustic infrared spectroscopy (PAS; black bars) and gas chromatography (GC; gray bars) measurements of ambient air (a,
b, c) and a National Institute of Science and Technology-certified (NIST) concentration of N₂O (0.718 ± 0.0017 ppm) (d, e, f) at three
temperatures (10 °C, 22 °C, 40 °C) at variable humidity. The reference line (panels d, e, f) is the NIST-certified N₂O concentration.
Percent values displayed above paired PAS and GC bars are the humidity values in each gas bag at each run. Each PAS bar represents
the average of three consecutive measurements. Each GC bar indicates average of three samples withdrawn from each gas bag during
PAS measurement. To facilitate comparison among methods, error bars indicate ±5% of each column (i.e. the average of replicate
measurements with each instrument).
flux measurements among PAS and GC at low fluxes from 0.0005 to 0.0202 ppm min⁻¹ (ca. 0.46–18 kg N₂O-N ha⁻¹ yr⁻¹) we are surprised that the authors did not address this report. Second, the primary objective of Iqbal et al. (2013) was to test for H₂O vapor and CO₂ interferences with N₂O measurements because such interferences have been suggested to explain inaccurate N₂O measurements with PAS (Akdeniz et al. 2009). Water vapor and CO₂ concentrations are expected to produce the most interference with N₂O detection at high concentrations (Zhao et al., 2012) and concentrations of these gases in static chambers are positively correlated (Xu et al., 2008).

Further, the idea that N₂O fluxes of 0.05 PPM min⁻¹ are ‘rarely found’ is ambiguous. Such fluxes are not uncommon in N-fertilized agroecosystems, the largest anthropogenic source of N₂O and the focus of most N₂O measurements. Short periods of high emissions account for a disproportionate amount of cumulative annual emissions. In our data collected with GC from conventionally managed corn-soybean systems in Iowa, USA fluxes ≥0.5 PPM min⁻¹ accounted for ca. 40% of annual emissions, and a recent comparison of PAS and GC demonstrated that accurate measurement of high N₂O fluxes is the most important factor affecting variations in annual flux estimations (Tirol-Padre et al., 2013).

We maintain that PAS can be calibrated to provide accurate N₂O measurements across ranges of CO₂, H₂O vapor and temperature that are encountered in static chambers at the soil surface. In summary: (i) four independent studies have reported positive evaluations of PAS across the range of N₂O fluxes encountered at the soil surface (<0.01 to >5.7 mg N₂O-N m⁻² h⁻¹) without interferences from H₂O vapor or CO₂ (Ambus & Robertson, 1998; Yamulki & Jarvis, 1999; Iqbal et al., 2013; Tirol-Padre et al., 2013); (ii) analytical simulations and experimental evaluations demonstrated that internal PAS calibration algorithms can eliminate cross-interferences from H₂O vapor and CO₂ (Zhao et al., 2012); and (iii) the only data Rosenstock et al. (2013) presented regarding temperature and H₂O interferences are derived from a single experiment with N = 1.

Our PAS units were calibrated by California Analytical Instruments (Orange, CA, USA) whereas the authors’ were calibrated by Lumasense Technologies (Santa Clara, CA, USA). A major difference in calibration procedures was the number of calibration points for CO₂: our machines used a two-point CO₂ calibration whereas the authors’ used a one-point CO₂ calibration (T. Rosenstock, personal communication). This may be one factor contributing to inaccurate N₂O measurements (improper CO₂ interference calibrations will produce inaccurate calibration algorithms for N₂O; Zhao et al., 2012). To avoid performance issues, PAS users should request confirmation of accurate measurement of a low N₂O concentration at high H₂O vapor and CO₂ concentrations. Users can also remove H₂O vapor and/ or CO₂ during gas intake. As with all analytical equipment that is calibrated by a vendor, users must independently verify performance. Tests of PAS calibration accuracy should not be limited to gas standards in a N₂ balance with high potential error (e.g., ±5–10%).

Several manufacturers and manufacturer representatives market PAS units. Significant variation in calibration accuracy is probable. We highlight that Iqbal et al. (2013), and other reports cited herein, demonstrated that PAS can accurately measure a range of N₂O concentrations encountered in static chambers at the soil surface. This does not guarantee accuracy of PAS calibration.

We agree with Rosenstock et al. (2013): ‘a better understanding of the mechanisms driving variation in PAS performance’ is needed, and ‘one should be careful when considering using PAS for measurements of greenhouse gases’. However, the data presented by Rosenstock et al. (2013) fall far short of suggesting that PAS cannot be calibrated for accurate measurement of N₂O concentrations encountered in static chambers at the soil surface.

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References


