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ORIGINAL ARTICLE

Improving process-based estimates of N_2O emissions from soil using temporally extensive chamber techniques and stable isotopes

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Abstract Nitrous oxide (N_2O) is an important greenhouse gas that is emitted from soil, but obtaining precise N_2O source and sink strength estimates has been difficult due to high spatial and temporal flux variability and a poor understanding of the mechanisms controlling fluxes. Tools that improve our ability to quantify trace gas fluxes from soil and constrain annual budgets are therefore needed. Here we describe an improved chamber-based sampling system that continuously traps evolving soil gases onto molecular sieve thereby obtaining a single sample that integrates fluxes over extended periods (several weeks or more) and the use of stable isotopic methods to study microbial origins of N_2O. We demonstrate that N_2O can be trapped on molecular sieve within our chamber system with near 100% recovery and without isotopic fractionation. In field trials the site preference of N_2O (the difference in $\delta^{15}N$ between the central and outer N atoms) varied between −6 and 14.4‰, indicating that the majority of flux was derived from bacterial denitrification. Further development with automation would improve flux estimates by providing a system capable of capturing episodic flux events owing to long-term deployment. Further, an automated trapping chamber approach will also provide process-based understanding of N_2O dynamics via stable isotopes and a new and affordable tool for evaluating the response of trace gas fluxes to land management practices.

Keywords Soil trace gas flux · Nitrous oxide (N_2O) · Stable isotopes · Soil management · Climate change

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Introduction

Many greenhouse gases, particularly carbon dioxide (CO_2) and nitrous oxide (N_2O), are rapidly increasing in the atmosphere (Forster et al. 2007), and the processes controlling their dynamics are greatly influenced by human activities such as land conversion to agriculture (Grandy et al. 2006; Grandy and

Robertson 2006) and alteration of the global nitrogen cycle (Ambus and Robertson 2006; Vitousek et al. 1997). Soils can serve as either sources or sinks for CO_2 and N_2O (Chapuis-Lardy et al. 2007) and soil microbial N cycling, in association with N fertilization, represents the single largest source of anthropogenic N_2O to the atmosphere (Barton et al. 2008; Davidson et al. 2004). Nevertheless, the exact mechanisms controlling CO_2 and N_2O fluxes are poorly understood and precise estimates of terrestrial sources and sinks for these gases remain uncertain (Forster et al. 2007; Robertson 1993).

Much of our current knowledge of CO_2 and N_2O fluxes comes from flux chambers (e.g. Ambus and Robertson 2006), micrometeorological approaches (e.g. Valentini et al. 2000), and stable isotope techniques (e.g. Bergsma et al. 2001; Opdyke et al. 2009; Powers et al. 2010). Traditional chamber techniques, such as closed or continuously circulated chambers placed over the soil, provide good flux estimates but are spatially limited, labor intensive, can miss short-term flux events when only deployed for brief time periods. For example, soils often experience short-term environmental perturbations, such as rain events. Such events are often associated with marked changes in flux (Bergsma et al. 2002; Christensen et al. 1990b; Li et al. 1992) that are not often captured by weekly monitoring programs. The quantity of N_2O from flux chamber samples is often not sufficient for the application of new techniques such as N_2O isotopomer analysis (Sutka et al. 2006) and lengthy trapping intervals (e.g. 24–48 h) required to obtain sufficient gas quantities can result in a variety of chamber artifacts (e.g. high humidity, leakage, and alteration of flux (Jury et al. 1982)). Micrometeorological techniques, in contrast, provide continuous data at the landscape scale and capture event-driven fluxes (Pattey et al. 2007) and recent developments in laser-based isotope techniques enable rapid and precise measurements of the C and O isotope composition of atmospheric CO_2. However, these techniques are expensive and therefore impractical for deployments in multiple field sites.

Variation in the stable isotopic composition of trace gases can provide insight into the biological and physical processes that control fluxes. In particular, the ^{13}C and ^{14}C isotopic composition of atmospheric CO_2 has provided constraints on the global CO_2 budget by associating changes in CO_2 concentration in the past century with fossil fuel burning and the release of CO_2 from native soils following cultivation (Trumbore 1997). The relative abundance of N_2O isotopomers ($^{15}N^{14}NO$ vs. $^{14}N^{15}NO$) provides the basis for determining the proportion of N_2O derived from oxic nitrifying versus anoxic denitrifying bacteria (Ostrom et al. 2007; Sutka et al. 2006, 2008; Pérez et al. 2000). However, the low abundance of atmospheric N_2O has greatly limited the ability of tower-based micrometeorological approaches to quantify microbial origins based on isotopomers. Understanding the sources, controls, and response of trace gases to environmental change is essential for assessing the impacts of management and unplanned disturbances on greenhouse gas dynamics, which could be resolved by using techniques that combine temporally extensive concentration data and isotope measurements by providing sufficient quantities of trace gases.

Here we describe a prototype Soil-derived Trace Gas Trapping System (STGTS) intended to offer integrated estimates of trace gas flux and isotopomer measurement by trapping gases evolved from soils over periods of days to weeks or months and thereby capturing episodic flux events. Chambers using similar methodological approaches have been developed in the past to capture trace gases and estimate emissions (e.g. Ryden et al. 1978, 1979; Egginton and Smith 1986; Pérez et al. 2000; Skiba et al. 1992). However, such efforts were limited in terms of temporal scope and did not provide cumulative fluxes that could be used for broad process-based examinations of emission sources over time and responses to environmental drivers and episodic events. Our approach is to use molecular sieve traps to enable continuous sampling of trace gases accumulating within the flux chamber. Our objective is not to capture variability in trace gas fluxes, which would require continuous data measurement; rather our objective is to continuously trap evolving soil gases onto molecular sieve thereby obtaining a single sample that integrates fluxes over extended time periods. We envision long term deployment to be facilitated by the use of subchambers that reduce the amount of gas trapped onto the molecular sieve at each sampling interval and thereby extend the length of deployment before saturating the molecular sieve. We present proof-of-concept data from a prototype system demonstrating CO_2 and N_2O capture, with a particular focus on quantitative recovery of N_2O and demonstration of isotopic fidelity during molecular sieve

trapping, storage, and extraction. Moreover, we demonstrate and discuss the potential for automation that will allow the STGTS to be powered by battery and solar panel, operated autonomously, readily deployed and operated, and inexpensive to manufacture relative to other trace gas monitoring systems (i.e. micrometeorological and laser spectroscopic). Our ultimate goal is to provide an inexpensive system that can be widely used by researchers and land managers in a variety of managed and natural ecosystems to quantify fluxes for greenhouse gas accounting protocols, as well as to provide process level information via stable isotope analysis.

Methods

STGTS concept

Our vision of a field deployable STGTS for long-term sampling encompasses the following objectives and design criteria: (1) provide flux data from continuous sampling over extended time periods to facilitate capture of episodic flux events, (2) enable quantitative recovery of trapped CO_2 and N_2O for isotopologue analysis without fractionation, and (3) is fully automated, portable, easy to use, and inexpensive to manufacture. Our STGTS concept uses zeolite molecular sieve 5A to quantitatively trap N_2O and CO_2, similar to past trace gas trapping approaches (Ryden et al. 1978, 1979; Duxbury and Voghel 1982; Egginton and Smith 1986; Godbout et al. 2006a, b; Kumagai and Koda 1999; Pérez et al. 2000; Skiba et al. 1992; Yoshida and Matsuo 1983); however, continuous sampling for extended time periods using such approaches would result in trap saturation. Further, as water interferes with the retention of trace gases on molecular sieve, large quantities of water vapor would need to be removed. For these reasons, we envision the use of low volume sub-chambers to enable long-term sampling by reducing the risk of trap saturation. Because accumulation of CO_2 and N_2O in the chamber may decrease the rate of microbial trace gas production and slow diffusional processes (Jury et al. 1982), an STGTS should cycle at regular intervals (e.g. 2–4 h) followed by flushing with atmospheric air that then prevents excessive gas build-up in the chamber and avoiding flux underestimates due to gas accumulation (Jury et al. 1982).

We developed a manually operated STGTS prototype to perform proof-of-concept experiments. Figure 1 provides an illustration of the basic flow diagram and components of the prototype system. The prototype system was used both in the laboratory and as a portable field-based system, is the basis for much of the data presented in this paper, and provides a foundation for the design of the proposed automated system. The general approach of circulating the headspace of a static chamber through chemical traps and gas adsorbents (e.g. Egginton and Smith 1986; Skiba et al. 1992) and using stable isotopes (e.g. Pérez et al. 2000; Ryden et al. 1978, 1979) has been used previously, but isotopic integrity of N_2O adsorbed and extracted from molecular sieve has not been demonstrated.

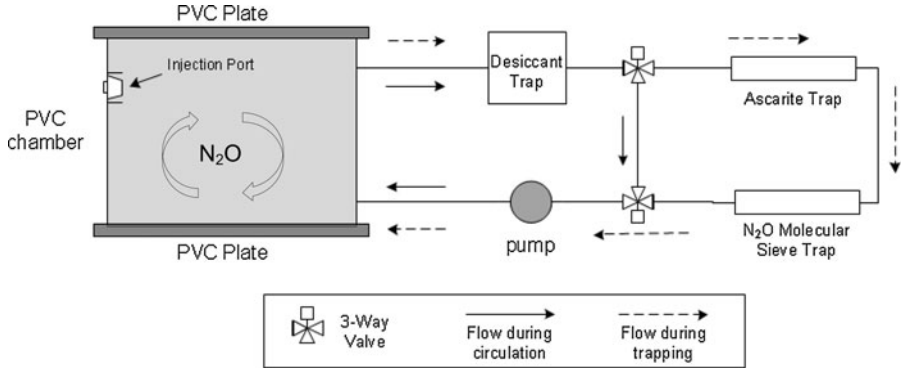

Fig. 1 Flow diagram and components of the trapping system used for evaluation of N_2O recovery and isotopologue fractionation. For the laboratory experiments, we used a metal bellows pump and N_2O was injected through the injection (septum) port in the side of the chamber. For field deployment, we used a battery operated 6 V diaphragm pump, the bottom PVC plate was removed for placement over the soil, and chamber headspace gas samples were extracted using the injection port

Gas trapping

We tested the adsorption efficiency of molecular sieve 5A with pure (>99.9%) N_2O of known isotopic composition and pure CO_2. A 4 L PVC gas chamber was sealed with PVC plates on the top and bottom (Fig. 1). CO_2 and N_2O traps were made from a 30 cm × 1.27 cm O.D. quartz tubing, filled with either Ascarite for CO_2 removal or molecular sieve for collection of N_2O and sealed with Swage-lock toggle valves and Cajon Ultra-torr unions. The molecular sieve traps were pre-conditioned at 180°C for 24 h under high vacuum (<1 torr) using flexible heating tape. A Nafion© membrane gas drier coiled through 2 L of pre-conditioned (24 h at 300°C) molecular sieve 4A was used as a desiccant trap. A stainless steel bellows pump (Senior Aerospace Metal Bellows, Sharon, MA) circulated high purity N_2 gas between the chamber and chemical traps. Once the chamber was completely purged and dry, the system was closed, 0.42 μmol of N_2O and 61.76 μmol of CO_2 were injected into the chamber using a gas-tight syringe, and the chamber circulated for 5 min. Headspace gas samples were taken every minute and injected into a Hewlett Packard 5890 gas chromatograph with ECD and infra red gas analyzers for analysis of N_2O and CO_2 concentrations, respectively. Flow was diverted to the CO_2 trap (5 min) and N_2O trap (15 min) sequentially. After 25 min, flow was diverted away from the CO_2 trap and pure CO_2 (82.34 μmol) was injected into the system to test for the potential loss of N_2O from the molecular sieve owing to the presence of CO_2. This experiment was conducted in triplicate on three different dates.

Sample recovery and analysis of isotopomers

Using molecular sieve traps similar to those used in the prototype system (Fig. 1), we evaluated recovery and maintenance of isotopic integrity of N_2O during collection and storage on molecular sieve. This was accomplished by injecting 100, 150, or 200 μL (4.12, 6.18, or 8.23 μmol) of pure N_2O onto three different conditioned molecular sieve traps through a rubber septum and storing them at ambient laboratory conditions. After 1 week, N_2O was removed from the molecular sieve by heating the trap to 180°C under high vacuum followed by cryogenic collection and purification. During cryogenic purification, residual H_2O was condensed under vacuum in a cold finger submerged in −90°C isopropanol. Recovery was quantified by releasing the N_2O sample back into a high-vacuum gas manifold, cryogenically focusing the gas into a calibrated cold-finger within the vacuum line and recording the change in pressure on a calibrated Baratron pressure sensor upon warming the gas to room temperature (MKS Instruments, Andover, MA).

The prototype system (Fig. 1) was further used to evaluate recovery of N_2O within the headspace and maintenance of isotopic integrity during adsorption to and recovery from molecular sieve in the laboratory. After purging the system with pure N_2 gas and circulating the headspace gases through the desiccant and CO_2 traps, we added 20.58 μmol or 41.16 μmol of a pure N_2O standard previously characterized for $\delta^{18}O$, $\delta^{15}N$ and site preference (SP; Sutka et al. 2006), allowed the N_2O circulate and mix for 30 min, and then directed the gas flow through a pre-conditioned molecular sieve trap. After 5 min, the chamber headspace was tested for the presence of N_2O to evaluate uptake efficiency. Molecular sieve traps were then removed from the system and stored at laboratory conditions for 1 week prior to further analysis.

N_2O recovery and isotopic integrity were evaluated via desorption of N_2O from molecular sieve at 180°C under high vacuum followed by cryogenic separation and collection as described above. N_2O was condensed into a cold finger submerged in liquid N_2, and then cryogenically transferred to a glass sample bottle with a high-vacuum stopcock and sideport butyl rubber septum (GeoMicrobial Technologies, Ochelata, OK) and removed from the vacuum line. Each sample bottle was brought to atmospheric pressure by equilibrating the sample bottle with a tedlar gas bag containing pure N_2 (>99.99%).

Using a gas-tight syringe, aliquots of gas were introduced from the glass sample bottle to a multi-collector IsoPrime stable isotope mass spectrometer (Elementar, UK) interfaced with a Trace Gas System for isotopic analysis (Sutka et al. 2006). The concentration of N_2O was determined based on the peak height of the mass 44 trace corresponding to the N_2O peak. As described in Sutka et al. (2003), our stable isotope mass spectrometer simultaneously monitors five masses for N_2O isotopomers: 30, 31,

44, 45 and 46. Masses 30 and 31 are the NO^+ fragment ions, which allow determination of the $\delta^{15}N$ of the central (α) and outer (β) N atoms, as the NO^+ fragment ion contains the α atom (Toyoda and Yoshida 1999). The isotopic composition of $\delta^{15}N$ and $\delta^{18}O$ in N_2O are expressed with respect to Air and Vienna Standard Ocean Water (VSMOW) international standards, respectively, and isotope ratios are expressed in per mil notation:

$$\delta^{15}N \text{ and } \delta^{18}O\ (‰) = \left[\left(R_{sample}/R_{standard}\right) - 1\right] \times 1000, \quad (1)$$

where R is the abundance ratio ^{15}N to ^{14}N or ^{18}O to ^{16}O. Isotope values were corrected for the contribution of ^{17}O to masses 31 and 45 and rearrangement of ^{15}N between the α and β positions using the approach outlined in Toyoda and Yoshida (1999). The reproducibility of replicate samples was 0.5 ($\delta^{15}N$) and 0.7 ($\delta^{18}O$) ‰. The difference in $\delta^{15}N$ between the α and β atoms in N_2O is expressed as site preference ($SP = \delta^{15}N^{\alpha} - \delta^{15}N^{\beta}$).

Field testing

Field trials of a prototype STSGS were conducted in the no-till soybean treatment of the Kellogg Biological Station Long-Term Ecological Research (KBS-LTER) site during July. We used a modified configuration of the STGTS design in Fig. 1 that included a 6 volt battery and, in place of the metal bellows pump, a 6 volt DC mini-diaphragm pump (KNF-Neuberger, Freiburg, Germany) with a flow rate of ~500 mL/min. The chamber was isolated from the trapping system via three-way valves and allowed to collect soil gas flux for 4 h. After the 4 h period, a gas sample (3.5 mL) was collected through a side-port septum to quantify the concentration of N_2O and CO_2 in the headspace, and then the entire headspace volume was circulated through the gas trapping system for 10 min. A second gas sample was taken from the chamber headspace at the end of the trapping cycle to quantify uptake efficiency, and finally the chamber headspace was flushed with ambient air for 10 min. This process was repeated for a period ranging from 36 to 52 h, and the complete experiment was repeated in triplicate. The concentrations of CO_2 and N_2O before and after trapping were determined via gas chromatography. The N_2O molecular sieve trap was removed at the end of the measurement period and gases extracted and analyzed for the concentration and isotopic composition of N_2O as described previously.

In the field validation experiments, the initial chamber headspace contained ambient air and, therefore, N_2O with a known abundance and isotopologue composition (Toyoda and Yoshida 1999). Isotopologue values measured after chamber deployment are a mixture of soil-derived and atmospheric N_2O. The isotopologue composition of soil-derived N_2O was determined by correcting for the addition of N_2O from the atmosphere using the following mass balance equation:

$$\delta_m Q_m = \delta_a Q_a + \delta_b Q_b \quad (2)$$

where, Q_m is total number of moles of N_2O in the chamber headspace (determined from concentration and chamber volume), Q_a is moles of N_2O contributed from the atmosphere (determined from the atmospheric N_2O concentration and chamber volume), Q_b is moles of N_2O that are soil-derived ($Q_m - Q_a$), δ_m is $\delta^{15}N$, $\delta^{18}O$, or SP of the mixture (measured), δ_a is $\delta^{15}N$, $\delta^{18}O$, or SP of atmospheric N_2O (known) and δ_b is $\delta^{15}N$, $\delta^{18}O$, or SP of soil-derived N_2O (determined).

Results and discussion

Laboratory adsorption and recovery of N_2O from molecular sieve

We demonstrated quantitative adsorption of N_2O onto molecular sieve after circulation of the chamber headspace. Experiments using known quantities of gas showed that concentrations of both headspace CO_2 and N_2O declined to undetectable levels within 2 min (Fig. 2). Recovery of N_2O from molecular sieve traps was nearly 100% after 1 week of storage (Table 1); much higher than recovery rates from past studies (Godbout et al. 2006a, b) but similar to those reported by Ryden et al. (1978) using a water extraction method. Moreover, injection and absorption of pure CO_2 did not result in the release of N_2O from molecular sieve (Fig. 2) suggesting that N_2O is stable on molecular sieve despite the presence of gases that can compete for adsorption sites.

Quantitative recovery in our experiments is most likely due to the use of a higher temperature of

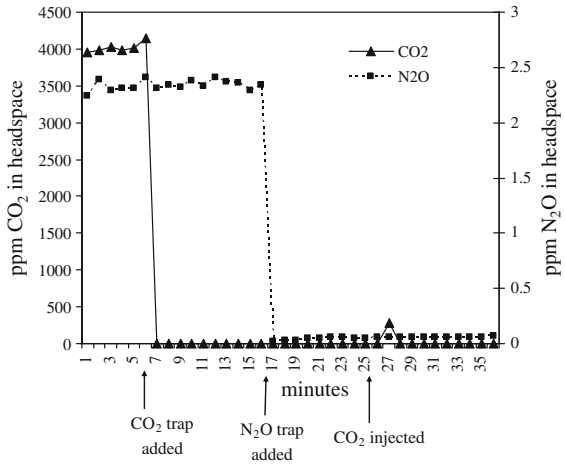

Fig. 2 Sequential additions of Ascarite (for removal of CO_2) and molecular sieve 5A (for adsorption of N_2O) traps to a static chamber with a dry circulating N_2 atmosphere and additions of CO_2 and N_2O. Arrows at bottom indicate the time (min) at which each trap was added and when CO_2 was injected into the system

Table 1 Recovery of N_2O injected onto pre-conditioned molecular sieve 5A traps after 1 week of storage

Volume of N_2O injected (μL)	Amount of N_2O injected (μmol)	Amount of N_2O recovered (μmol)	% recovery
100	4.12	4.07	98.8
150	6.18	6.13	99.2
200	8.23	8.39	101.9

N_2O recovery was calculated following extraction from molecular sieve and cryogenic purification *in vacuo*

extraction than in prior studies (Godbout et al. 2006a, b) and extraction into vacuum with cryogenic trapping. A similar system and extraction temperature was used by Pérez et al. (2000), but they did not present data on recovery or isotopic integrity. Alternative extraction methods, such as the H_2O method employed in past studies (e.g. Egginton and Smith 1986; Skiba et al. 1992; Ryden et al. 1978, 1979) would require removal of N_2O from the water and also have not been tested for maintenance of isotopic integrity. We found no appreciable isotopic fractionation for N_2O isotopomer and SP values during the adsorption, removal, and trapping process (Table 2). The observation that all isotopologue values for N_2O extracted from molecular sieve were within the range of instrument analytical precision (instrument precision for SP was 1.2‰) indicates that isotope effects associated with trapping and extraction are negligible. While we have not tested our procedure for maintenance of the isotopic composition of CO_2 or CH_4, other studies have observed quantitative recovery of CH_4 from molecular sieve (Godbout et al. 2006a, b) and integrity and stability of CO_2 on molecular sieve (Mayinger and Eggertsteger 1992). This suggests that isotopolgue fractionation during trapping and extraction of these gases will also be negligible with quantitative recovery.

Adsorption and recovery of N_2O during field deployment

Using our field-deployed chamber system, we found that after each trapping event the soil-derived N_2O in the chamber headspace was reduced to levels below detection limits (Fig. 3). Concentration and data from the molecular sieve traps suggest that this method is suitable for trapping N_2O over at least a 2–3 day period and provides isotopologue measurements (Table 3) similar to values obtained elsewhere at KBS using a static-chamber method (Opdyke et al. 2009). At the end of a trapping cycle CO_2 was always below atmospheric concentrations but was not entirely absent from the headspace. This likely resulted from the high CO_2 flux rate relative to the residence time of the chamber headspace during the trapping interval. While past approaches have had similar success at trapping soil gas flux, those fluxes and sources were estimated over a much shorter time period ($\sim$2.5 h) (Pérez et al. 2000).

Our data also indicate that the flux and microbial origin of the N_2O varied with changing environmental conditions (Table 3). Our first field trial was conducted over a 36 h period that included several periods of intense rainfall. N_2O production was highest during this trial and the low N_2O SP values (SP = −0.6‰; Table 3) indicate that most of the N_2O was derived from bacterial denitrification (SP = $\sim$0 to −10‰; (Frame and Casciotti 2010; Sutka et al. 2006)). This finding is consistent with the expectation that N_2O fluxes will be highest and denitrification will dominate fluxes relative to nitrification when soils are saturated (e.g. Bergsma et al. 2002; Christensen et al. 1990a, b; Drury et al. 1992; Li et al. 1992; Sexstone et al. 1985; Pérez et al. 2000),

Table 2 Comparison of expected N_2O standard isotopologue values with observed values after three experiments where N_2O was injected into an 8 L enclosed chamber and recovered from a molecular sieve 5A trap (all values are per mil (‰)). Differences between expected and observed values are less than or near the precision of the mass spectrometer. Site Preference (SP) is the difference in $\delta^{15}N$ between the α (central N atom) and β (outer N atom) positions in the N_2O molecule. Values in parentheses are standard errors from three analytical replicates of the same sample. $N = 3$ analytical reps for Experiments 1 and 3. Only one injection was performed in the second experiment

	$\delta^{15}N\text{-}N_2O_{air}$	$\delta^{15}N_\alpha$	$\delta^{15}N_\beta$	$\delta^{18}O\text{-}N_2O_{VSMOW}$	SP
Expected	−0.9	0.7	−2.6	38.5	3.4
Observed[a]	−1.0 (0.1)	1.6 (0.1)	−3.7 (0.4)	38.4 (0.04)	5.3 (0.6)
Observed[b]	−0.2	2.5	−2.8	40.3	5.3
Observed[b]	−0.5 (0.04)	1.4 (0.6)	−2.4 (0.5)	38.5 (0.2)	2.1 (1.1)
Average observed	−0.6	1.8	−3	39.1	4.2

[a] 1 mL of N_2O standard injected into chamber at 25°C

[b] 0.5 mL of N_2O at 25°C injected into chamber

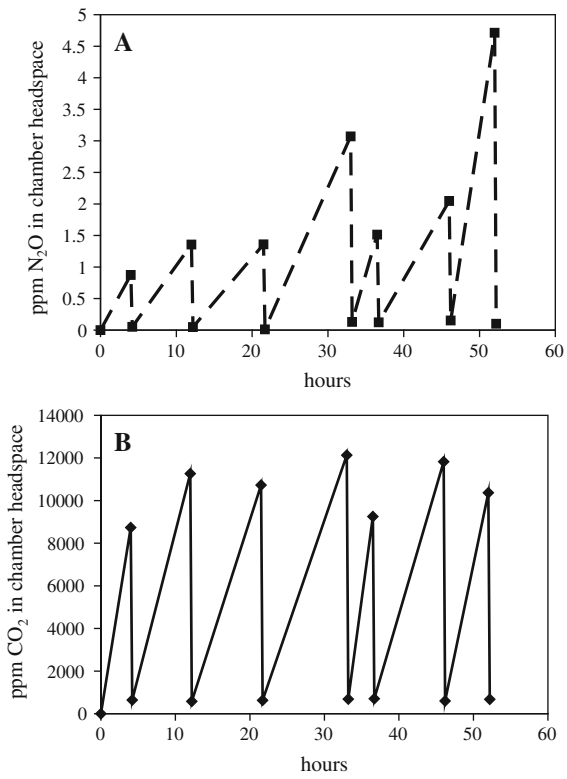

Fig. 3 Concentrations of N_2O (**a**) and CO_2 (**b**) in the headspace of a field-deployed chamber before and after gas trapping events

and consistent with prior research at KBS that found the majority of N_2O originates from denitrification (Opdyke et al. 2009). The next two trials were conducted for longer periods (48–52 h) characterized by no rain (trial 2) and brief periods of light rain showers (trial 3). Total N_2O production in these trails was less than trial 1 and smallest in trial 2. SP values (trial 2 = 14.4‰; trial 3 = 12.6‰) were intermediate between those indicative of production from bacterial denitrification (~0 to −10‰) and those expected for nitrification (SP = ~33‰; (Frame and Casciotti 2010; Sutka et al. 2006)). Because SP is not affected by the availability and isotopic composition of inorganic nitrogen substrates (Sutka et al. 2006), it is a robust indicator of the microbial origin of N_2O flux. These results are consistent with those of Ostrom et al. (2010) that, on the basis of SP, flux was derived predominantly from bacterial denitrification during a period of high flux and a mixture of both nitrification and denitrification during a period of low flux. Overall, these trials demonstrate that our system can quantitatively adsorb N_2O and isotopologue analyses of the resulting gases can provide accurate estimates of the flux and processes contributing to N_2O production over a period of several days or longer. We therefore can capture short-term and discreet events that influence N_2O production pathways, concentration, and flux, something that has not been done previously.

Based on these results, we are currently developing a fully automated and field-deployable STGTS where headspace gases repeatedly accumulate in a large chamber and equilibrate with smaller subchambers that are cycled and trapped separately. In this manner, the cumulative trace gas subsamples represent the entire flux from the soil during a collection period of days to weeks. Trapping from subchambers will enable longer deployments before the molecular

Table 3 N_2O emission and isotope values from experiments conducted in June 2006 at the KBS-LTER site with a field-deployed prototype STGTS

	Deployment time (h)	nmol of N_2O from soil	Soil-derived values				
			$\delta^{15}N_{Bulk}$	$\delta^{15}N_{\alpha}$	$\delta^{15}N_{\beta}$	$\delta^{18}O$	SP
Field test 1	36	5115.5	−15.0	−15.3	−14.7	37.3	−0.6
Field test 2	42	714.3	2.1	9.3	−5.1	43.1	14.4
Field test 3	52	2417.4	−3.7	2.6	−9.9	48.6	12.6

The reported isotopologue values (all values are per mil (‰)) are for N_2O extracted from molecular sieve traps and corrected for the contribution of N_2O from the atmosphere using Eq. 2

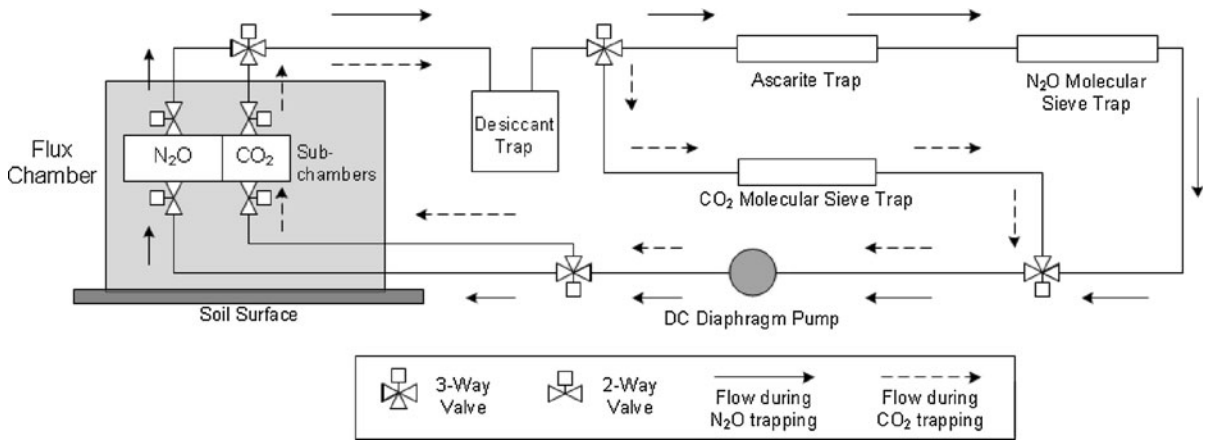

Fig. 4 Flow diagram and trapping components for an idealized STGTS in which gases collected in the main chamber are equilibrated in smaller sub-chambers, pumped through a series of chemical and molecular sieve traps, and then analyzed ex situ for concentration and isotopomers. Valve opening and event timing is controlled by a microprocessor and a pressure sensor (not depicted in illustration)

sieve is saturated with trace gases. Figure 4 depicts the flow and trapping components of an idealized STGTS that utilizes much of our prototype design. We anticipate this automated STGTS will function for ~1 month or more with little to no user input.

Implications and applications

Awareness of the need to slow or mitigate climate change has increased in the past decade and controlling emission of CO_2, CH_4 and N_2O from soils, with verification, is central to this effort (Forster et al. 2007). Agricultural lands and other ecosystems can be managed to enhance carbon sequestration and reduce overall greenhouse gas emissions (Robertson et al. 2000). Moreover, practices such as alternative tillage techniques, winter cover cropping, continuous cover cropping, reductions in nitrogen fertilizer use, and changes in animal and manure management are effective means to mitigate emissions and represent carbon offsets. However, any future greenhouse gas reduction legislation that incorporates such practices will likely require monitoring and the use of standardized methodologies.

Beyond providing important scientific data relating to greenhouse gas fluxes, the automated STGTS could be an effective and cost-efficient tool for meeting legislative mandates focused on greenhouse gas mitigation. Because the STGTS will be an autonomous relatively simple and inexpensive instrument capable of capturing soil-derived greenhouse gases over long time periods (ca. 1 month) for subsequent analysis, it could be utilized by inexperienced users and readily deployed in remote locations and in large numbers. Sample extraction from

molecular sieve and subsequent chromatographic and isotopic analyses, however, will require more specialized facilities and remains an area that could be simplified with further research. Nevertheless, the data provided by such an instrument would allow farmers, researchers and regulators to evaluate the relative importance of different ecosystem processes (e.g. photosynthesis, respiration, nitrification and denitrification) as well as management activities (e.g. till vs. no-till) in controlling greenhouse gas fluxes and other factors that ultimately determine net C sequestration.

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References

Ambus P, Robertson GP (2006) The effect of increased n deposition on nitrous oxide, methane and carbon dioxide fluxes from unmanaged forest and grassland communities in Michigan. Biogeochemistry 79(3):315–337

Barton L, Kiese R, Gatter D, Butterbach-Bahl K, Buck R, Hinz C, Murphy DV (2008) Nitrous oxide emissions from a cropped soil in a semi-arid climate. Global Change Biol 14(1):177–192. doi:10.1111/j.1365-2486.2007.01474.x

Bergsma TT, Ostrom NE, Emmons M, Robertson GP (2001) Measuring simultaneous fluxes from soil of N_2O and N-2 in the field using the N-15-gas "nonequilihrium" technique. Environ Sci Technol 35(21):4307–4312

Bergsma TT, Robertson GP, Ostrom NE (2002) Influence of soil moisture and land use history on denitrification end-products. J Environ Qual 31(3):711–717

Chapuis-Lardy L, Wrage N, Metay A, Chotte JL, Bernoux M (2007) Soils, a sink for N_2O? A review. Global Change Biol 13(1):1–17. doi:10.1111/j.1365-2486.2006.01280.x

Christensen S, Simkins S, Tiedje JM (1990a) Spatial variation in denitrification- dependency of activity centers on the soil environment. Soil Sci Soc Am J 54(6):1608–1613

Christensen S, Simkins S, Tiedje JM (1990b) Temporal patterns of soil denitrification- their stability and causes. Soil Sci Soc Am J 54(6):1614–1618

Davidson EA, Ishida FY, Nepstad DC (2004) Effects of an experimental drought on soil emissions of carbon dioxide, methane, nitrous oxide, and nitric oxide in a moist tropical forest. Global Change Biol 10(5):718–730

Drury CF, McKenney DJ, Findlay WI (1992) Nitric oxide and nitrous oxide production from soil- water and oxygen effects. Soil Sci Soc Am J 56(3):766–770

Duxbury JM, Voghel S (1982) Storage of nitrous-oxide on molecular sieves. Soil Sci Soc Am J 46(6):1336–1338

Egginton GM, Smith KA (1986) Losses of nitrogen by denitrification from a grassland soil fertilized with cattle slurry and calcium nitrate. J Soil Sci 37(1):69–80

Forster VRP, Artaxo P, Berntsen T, Betts R, Fahey DW, Haywood J, Lean J, Lowe DC, Myhre G, Nganga J, Prinn R, Raga G, Schulz M, Van Dorland R (2007) Changes in atmospheric constituents and in radiative forcing. In: Solomon SDQ, Manning M, Chen Z, Marquis M, Averyt KB, Tignor M, Miller HL (eds) Climate change 2007: the physical science basis. Contribution of working group i to the fourth assessment report of the intergovernmental panel on climate change. Cambridge University\Press, Cambridge

Frame CH, Casciotti KL (2010) Biogeochemical controls and isotopic signatures of nitrous oxide production by a marine ammonia-oxidizing bacterium. Biogeosciences 7(9):2695–2709. doi:10.5194/bg-7-2695-2010

Godbout S, Phillips VR, Sneath RW (2006a) Passive flux samplers to measure nitrous oxide and methane emissions from agricultural sources, part 1: adsorbent selection. Biosys Eng 94(4):587–596

Godbout S, Phillips VR, Sneath RW (2006b) Passive flux samplers to measure nitrous oxide and methane emissions from agricultural sources, part 2: desorption improvements. Biosys Eng 95(1):1–6

Grandy AS, Robertson GP (2006) Initial cultivation of a temperate-region soil immediately accelerates aggregate turnover and CO_2 and N_2O fluxes. Global Change Biol 12(8):1507–1520

Grandy AS, Loecke TD, Parr S, Robertson GP (2006) Long-term trends in nitrous oxide emissions, soil nitrogen, and crop yields of till and no-till cropping systems. J Environ Qual 35(4):1487–1495

Jury WA, Letey J, Collins T (1982) Analysis of chamber methods used for measuring nitrous-oxide production in the field. Soil Sci Soc Am J 46(2):250–256

Kumagai S, Koda S (1999) Passive sampling and head space analysis for quantitative determination of nitrous oxide exposure. Am Ind Hyg Assoc J 60(4):458–462

Li CS, Frolking S, Frolking TA (1992) A model of nitrous oxide evolution from soil driven by rainfall events- 1. Model structure and sensitivity. J Geophys Res-Atmos 97(D9):9759–9776

Mayinger F, Eggertsteger R (1992) Experimental and theoretical investigations concerning coadsorption of CO_2 and N_2O on Molecular Sieve-5A. Warme Und Stoffubertragung-Thermo and Fluid Dynamics 27(7):405–412

Opdyke MR, Ostrom NE, Ostrom PH (2009) Evidence for the predominance of denitrification as a source of N_2O in temperate agricultural soils based on isotopologue measurements. Gobal Biogeochem Cy 23:10. doi:Gb401810.1029/2009gb003523

Ostrom NE, Pitt A, Sutka R, Ostrom PH, Grandy AS, Huizinga KM, Robertson GP (2007) Isotopologue effects during N_2O reduction in soils and in pure cultures of denitrifiers. J Geophys Res-Biogeosciences 112:G02005. doi:10.1029/2006JG000287

Ostrom NE, Ostrom PH, Gandhi H, Millar N, Robertson GP (2010) Isotopologue data reveal denitrification as the primary source of nitrous oxide at nitrogen fertilization

gradient in a temperate agricultural field. Geochim Cosmochim Acta 74(12):A780–A780

Pattey E, Edwards GC, Desjardins RL, Pennock DJ, Smith W, Grant B, MacPherson JI (2007) Tools for quantifying N_2O emissions from agroecosystems. Agr Forest Meteorol 142(2–4):103–119

Pérez T, Trumbore SE, Tyler SC, Davidson EA, Keller M, de Camargo PB (2000) Isotopic variability of N_2O emissions from tropical forest soils. Gobal Biogeochem Cy 14(2):525–535

Powers HH, Hunt JE, Hanson DT, McDowell NG (2010) A dynamic soil chamber system coupled with a tunable diode laser for online measurements of delta C-13, delta O-18, and efflux rate of soil-respired CO_2. Rapid Commun Mass Sp 24(3):243–253. doi:10.1002/rcm.4380

Robertson GP (1993) Fluxes of nitrous oxide and other nitrogen trace gases from intensively managed landscapes: a global perspective. In: al. LAHe (ed) Agricultural ecosystem effects on trace gases and global climate change. American Society of Agronomy, Madison, pp 95–108

Robertson GP, Paul EA, Harwood RR (2000) Greenhouse gases in intensive agriculture: contributions of individual gases to the radiative forcing of the atmosphere. Science 289(5486):1922–1925

Ryden JC, Lund LJ, Focht DD (1978) Direct in-field measurement of nitrous-oxide flux from soils. Soil Sci Soc Am J 42(5):731–737

Ryden JC, Lund LJ, Letey J, Focht DD (1979) Direct measurement of denitrification loss from soils: 2. Development and application of field methods. Soil Sci Soc Am 43(1):110–118

Sexstone AJ, Parkin TB, Tiedje JM (1985) Temporal response of soil denitrification rates to rainfall and irrigation. Soil Sci Soc Am J 49(1):99–103

Skiba U, Hargreaves KJ, Fowler D, Smith KA (1992) Fluxes of nitric and nitrous oxides from agricultural soils in a cool temperate climate. Atmospheric Environ Part A-General Topics 26(14):2477–2488

Sutka RL, Ostrom NE, Ostrom PH, Gandhi H, Breznak JA (2003) Nitrogen isotopomer site preference of N_2O produced by *Nitrosomonas europaea* and *Methylococcus capsulatus* Bath. Rapid Commun Mass Sp 17(7):738–745. doi:10.1002/rcm.968

Sutka RL, Ostrom NE, Ostrom PH, Breznak JA, Gandhi H, Pitt AJ, Li F (2006) Distinguishing nitrous oxide production from nitrification and denitrification on the basis of isotopomer abundances. Appl Environ Microbiol 72(1):638–644. doi:10.1128/aem.72.1.638-644.2006

Sutka RL, Adams GC, Ostrom NE, Ostrom PH (2008) Isotopologue fractionation during N_2O production by fungal denitrification. Rapid Commun Mass Sp 22(24):3989–3996. doi:10.1002/rcm.3820

Toyoda S, Yoshida N (1999) Determination of nitrogen isotopomers of nitrous oxide on a modified isotope ratio mass spectrometer. Anal Chem 71(20):4711–4718

Trumbore S (1997) Potential responses of soil organic carbon to global environmental change. Proc Natl Acad Sci USA 94:8284–8291

Valentini R, Matteucci G, Dolman AJ, Schulze ED, Rebmann C, Moors EJ, Granier A, Gross P, Jensen NO, Pilegaard K, Lindroth A, Grelle A, Bernhofer C, Grunwald T, Aubinet M, Ceulemans R, Kowalski AS, Vesala T, Rannik U, Berbigier P, Loustau D, Guomundsson J, Thorgeirsson H, Ibrom A, Morgenstern K, Clement R, Moncrieff J, Montagnani L, Minerbi S, Jarvis PG (2000) Respiration as the main determinant of carbon balance in European forests. Nature 404(6780):861–865

Vitousek PM, Aber JD, Howarth RW, Likens GE, Matson PA, Schindler DW, Schlesinger WH, Tilman DG (1997) Human alteration of the global nitrogen cycle: sources and consequences. Ecol Appl 7(3):737–750

Yoshida N, Matsuo S (1983) Nitrogen isotope ratio of atmospheric N_2O as a key to the global cycle of N_2O. Geochem J 17:231–239