Continuous Measurements of Belowground Nitrous Oxide Concentrations

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Nitrous oxide released from soil is a concern since it can act as a potential atmospheric pollutant and it represents a loss of N from the soil. To better understand the factors controlling N_2O production and transport, we developed a system to obtain continuous measurements from below the soil surface. The sampling system pulls small volumes of soil gas from buried sample probes through a tunable diode laser trace gas analyzer. The advantage of this system is that it measures concentrations spectroscopically, allowing regular, continuous measurements. This provides it with the distinct advantage of being able to capture short-term changes in gas concentrations that may be important for nutrient and greenhouse gas budgeting. Furthermore, the system is relatively simple to install and could be integrated into existing field measurements of trace gas flux. Measurements of belowground N_2O concentrations were obtained during the spring thaw from buried probes in a conventionally tilled field that was planted in soybean [*Glycine max* (L.) Merr.] the previous summer. Measurements showed that belowground N_2O concentrations at the 25-cm depth varied between 65 and 85 $\mu\text{mol mol}^{-1}$ before snowmelt. After melting of the snow and the beginning of the soil thawing, N_2O concentrations decreased to a value generally $<1 \mu\text{mol mol}^{-1}$. During this period when belowground N_2O concentrations were near atmospheric values, wind speed influenced concentrations, possibly through a pressure pumping effect.

Abbreviations: TDLTGA, tunable diode laser trace gas analyzer.

Nitrous oxide is produced in soils during the biological processes of nitrification and denitrification. A comprehensive review of these processes can be found in Firestone and Davidson (1989). Current estimates of global N_2O fluxes suggest that human activities are primarily responsible for the recent increases in measured N_2O atmospheric concentrations (Ehhalt et al., 2001). In particular, the addition of N fertilizer to soils has increased the available N in the soil, which then feeds the various reactions leading to emissions of N_2O . The measured increase in N_2O concentration in the atmosphere has important implications for stratospheric ozone depletion and climate change (Badr and Probert, 1993). Additionally, since emissions of N_2O represent a loss of N from the soil, it is an important consideration for soil nutrient management in agricultural ecosystems (Mosier, 2001). For these reasons, there is a concerted effort to understand the magnitude of the global pools and fluxes of N_2O and to investigate possible management strategies that can reduce anthropogenic emissions from agricultural ecosystems.

Emissions of N_2O are controlled by a number of physical, chemical, and biological factors, which affect both its production in the soil and transport through the soil-atmosphere system (Grant and Pattey, 2003). Many of these factors can be very heterogeneous on a scale of meters in typical agricultural settings (Yanai et al., 2003), making it difficult to generalize about the larger scale spatial and temporal behavior of fluxes. Many studies have reported emission "hot spots", which are

localized zones that temporarily experience high emissions (Kaiser et al., 1998; Röver et al., 1999). Researchers have also reported a springtime flush of N_2O from soils, which appears to be related to the thawing of the soil (Nyborg et al., 1997; Koponen and Martikainen, 2004). This flush is probably a combination of increased production due to saturated conditions, increased organic substrate availability from microbial biomass, and sudden changes in soil moisture resulting in changes in the transport and release of N_2O from soil water. To gain a better understanding of the magnitude of N_2O emissions and potential best management practices to minimize these emissions, it is critical to develop our suite of tools and techniques to quantify the magnitude of N_2O produced and stored in soils. Measurements and observations of N_2O concentrations can, in turn, be used to infer fluxes, which will lead to improved management strategies.

A common method used to investigate N_2O under field conditions has been the direct measurement of concentrations in the soil, such as those obtained by Colborne et al. (1984) and Kammann et al. (2001). This equipment usually has a buried porous sample tube, which is linked to the soil surface to allow the withdrawal of discrete gas samples. These samples are then analyzed using standard analytical methods such as gas chromatography (e.g., Farrell et al., 1993). Unfortunately, the manual sampling required is quite difficult to continue for long periods of time at high temporal resolution. Højberg et al. (1994) used an electrochemical technique to measure N_2O in soil aggregates, but this method may be difficult to apply to larger spatial areas and could be problematic under field conditions. Other gases that have been measured directly in the soil using advances in sensor technology include CO_2 (Tang et al., 2003) and O_2 (Wolfbeis, 2004).

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We have developed a method to obtain near-continuous field measurements of N_2O in the soil using a gas analyzer. These measurements are useful for observing short-term changes in belowground concentrations, allowing better temporal resolution of processes influencing N_2O production and transport. Since the flux of N_2O at the surface is ultimately related to the gradient of N_2O in the soil, these measurements could be valuable in better understanding the processes controlling N_2O flux into the atmosphere. This system also has the advantage of being able to measure across a relatively large area, thereby providing a degree of spatial integration and eliminating the effects of localized zones of high production. Although the focus of this study was on the measurement of N_2O , the system could easily be adapted to measure other trace gases of interest such as CH_4 and potentially even the ^{12}C and ^{13}C isotopes of CO_2 (Griffis et al., 2004). Finally, this system is relatively simple and could be integrated into existing micrometeorological flux-gradient measurements of trace gas exchange across agricultural surfaces.

MATERIALS AND METHODS

Site Description and General Measurements

Measurements were obtained at the Elora Research Station located in southern Ontario, Canada ($43^\circ 30' \text{ N}$, $80^\circ 15' \text{ W}$, 340 m above sea level). The soil is classified as a Woolwich silt loam (29% sand, 52% silt, and 19% clay) with a pH of 7.7, 2.7% by mass organic C and 0.24% by mass organic N. The field used in this study was conventionally tilled, 150 by 100 m, and has been used as one of two control plots in an investigation into no-till agriculture since 1999 (McCoy et al., 2006). Measurements of belowground N_2O concentration were obtained from 15 Mar. to 13 Apr. 2005. The crop rotation for this type of farm management system was wheat (*Triticum aestivum* L.) in 2002, corn (*Zea mays* L.) in 2003, and soybean in 2004, with all stubble incorporated into the soil during fall plowing. The field is tile drained at a depth of 75 cm with a spacing of approximately 15 m between tiles. The terrain slopes $<3\%$ toward the northeast. At the center of the four plots (two no-till, two control) is a small trailer housing instruments and datalogging equipment.

Soil volumetric water content, θ_v , was measured with reflectometers (Model CS615, Campbell Scientific, Logan, UT) inserted at an angle to obtain an integrated measurement in four soil layers (0–10-, 10–40-, 40–70-, and 70–100-cm depths). These reflectometer measurements were calibrated in situ with manual time domain reflectometry measurements throughout the year. Soil temperature was also measured

with custom-manufactured direct burial Cu-constantan thermocouples placed at the midpoints of the reflectometer measurement layers. These measurements were obtained at a site approximately 20 m away from the soil gas sampling probe but in the same field treatment (conventionally tilled). Hourly measurements of precipitation were obtained with a weighing-type rain gauge (Belfort Model 5-780, Belfort Instruments, Baltimore, MD). Air temperature was measured with a Vaisala Model HMP45C-L temperature–humidity sensor (Vaisala Oyj, Helsinki, Finland), and wind velocity measured with a propeller anemometer (Model 05103, R.M. Young Co., Traverse City, MI).

Tunable Diode Laser Trace Gas Analyzer Setup

The gas analyzer used in this study was a Campbell Scientific tunable diode laser trace gas analyzer (TDLTGA) of which a detailed description is available in Edwards et al. (2003). The advantage of this system is the high sensitivity and the ability to resolve absorption lines of various simple trace gas molecules, including greenhouse gases such as CO_2 , N_2O , and CH_4 (Edwards et al., 2003). The laser was tuned to a wavenumber of 2219.5 cm^{-1} , corresponding to a relatively strong N_2O absorption line with minimal interference from other gases (Rothman et al., 2003). The reference gas used in this study had a concentration of $2498 \mu\text{mol mol}^{-1}$. The entire system was maintained at a pressure of approximately 1500 Pa during the measurements, with the soil gas being drawn directly into the 1.53-m sample cell. Since the measurements in this study do not strictly require the 10-Hz sampling capability of the TDLTGA, data were averaged and sampled at 0.2 Hz via the instrument software settings.

Soil gas was drawn directly from the buried probe (described below) using a single-stage rotary vane vacuum pump (Model RC0021, Busch Inc., Virginia Beach, VA) into the gas analyzer. A single, two-way alternating current (AC) solenoid valve (Model 8263A35, Ascoelectric Ltd., Brantford, ON) was used to switch flow into the TDLTGA for 20 min every 2 h. The remaining time, the TDLTGA was sampling room air through a second critical flow orifice and filter assembly. The solenoid valve was controlled by a 21X datalogger (Campbell Scientific) connected to a custom-built relay board. The sample tubing from the probes to the TDLTGA was 6.4-mm o.d., 4.2-mm i.d. tubing (Synflex 1300, Saint-Gobain Performance Plastics, Wayne, NJ). This tubing from the buried probe to the TDLTGA was heated with 15 W m^{-1} electrical heating tape and bundled into closed-cell pipe insulation to prevent the relatively warm humid air from below the soil surface condensing and freezing inside the sample tubing.

Soil Gas Sampling Apparatus

The probe used in this study, shown in Fig. 1, was manufactured from plumbing-grade polyvinyl chloride tubing. The probe had a horizontal length of 3.2 m, a diameter of 9.5 cm and a 1-m-long connected vertical access tube. The bottom of the horizontal tube was perforated with 1.25-cm-diameter holes, each separated by a distance of approximately 1 cm. The flange of the top cap was attached to the body flange with bolts and was sealed with a 1-cm-thick closed-cell foam circular gasket. The probe was buried so the bottom perforations were, on average, 25 cm below the soil surface and the upper access tube protruded above the soil surface. Two 6.35-mm ($\frac{1}{4}$ -inch) male National pipe thread (NPT) connectors (Swagelok Corp., Solon, OH) were attached to the top cap. One of them was used for the gas sampling while the second was sealed with an epoxy-filled male connector containing wires for a liquid level sensor and thermocouple cables. A 0 to 50 mL min^{-1} flow meter (Model U003(A), Matheson

Fig. 1. Schematic of the buried sampling probe used to obtain measurements of belowground N_2O concentration. Liquid level sensor, thermocouples, and gas sampling tubing extended to the base of the vertical access tube. TDLTGA = tunable diode laser trace gas analyzer.

Corp., Whitby, ON) was attached to the exterior of the top cap. Downstream of the flow meter was a 0.2- μm , 25-mm-diameter Teflon filter (Versapor-200, Gelman Sciences, Ann Arbor, MI) to eliminate contamination of the sample lines or the TDLTGA and to prevent the incursion of liquid water. In laboratory testing, we found that with the sample pump set to the lowest possible pressure (~ 1000 Pa), water did not break through the filter. This provided a means of ensuring that the TDLTGA did not draw in water.

An additional water protection feature was a simple, home-made liquid water detector that compared the voltage drop across the second of two resistors in series and a small two-wire probe across the first resistor. When the probe is immersed in conductive liquid water, the short circuit is completed and the measured voltage changes. This device was connected to the 21X datalogger and provided a relatively crude but reliable method to determine the presence of liquid water in the buried sample tube. The datalogger was programmed to conditionally sample only if water was not present in the sample tube. After installation, the vertical access tube protruding from the soil was heated with a 20-W heater and wrapped in insulation to prevent ice formation from warm humid air from the sampling probe depth.

The sample tube used to draw soil air from the probe to the gas analyzer had an internal radius of 2.1 mm and a length of approximately 20 m. Laboratory testing showed that the 0.2- μm filter was responsible for approximately 75% of the pressure drop between the intake and the TDLTGA. The low pressure in the sample line provides additional protection against condensation and ice formation. Flow rate at the sample probe was set to approximately $10\text{ cm}^3\text{ min}^{-1}$ at 20°C and 101 kPa of pressure. This combination of pressure drop and flow rate produced an average flow velocity inside the sample tube of approximately 0.4 m s^{-1} , requiring 50 s for the sample to travel from the buried probe to the TDLTGA.

For this prototype version of the plumbing system, the 20-min sampling was determined to be sufficient to measure the average concentration inside the buried probe. It was noted that the concentration did not stabilize as quickly as expected during the sampling, which could be attributed to a combination of pressure fluctuations in the TDLTGA, adsorption or desorption of N_2O inside the plumbing system, or a change in the performance of the sample solenoid between laboratory testing and installation in the field. If the flow resistance of the solenoid was higher than expected, the amount of time for the pressure of the TDLTGA to stabilize would be greater than anticipated and could account for the long period of time for the concentration to stabilize.

The response of the entire flow system was verified by removing the top cap and intake assembly and sampling directly from a tank of $65\text{ }\mu\text{mol mol}^{-1}$ N_2O in air mixture. This was performed at the beginning and end of the month-long measurement period. During both of these calibrations, the system was able to measure the calibration gas concentration to within $1\text{ }\mu\text{mol mol}^{-1}$ in <10 min. This calibration provided an effective means of verifying the gas measurements before and after the soil gas measurements.

The total volume of the buried sample probe was approximately 20.36 L, not including the vertical access tube (Fig. 1). With a sample flow rate of $10\text{ cm}^3\text{ min}^{-1}$ and a sample extraction duration of 20 min, only 200 cm^3 , or $<1\%$ of the probe volume, was withdrawn during any half-hour period. If it can be assumed that N_2O concentrations in the soil equilibrate in a matter of minutes to hours to the production or consumption of N_2O in the soil, then withdrawing such a sample volume should not induce driving gradients or mass flow of N_2O -depleted air from the soil surface. Other researchers have demonstrated the utility of soil gas measurement systems that replace withdrawn soil air with an

on-line gas mixing apparatus (Gut et al., 1998). Although the system proposed here does not replace the withdrawn gas, the small sample volume relative to the soil probe combined with the relative simplicity of the plumbing makes it a potentially attractive system for belowground concentration measurements.

We recognize that the insertion of a buried probe and withdrawing soil gas may disturb the soil and influence processes in the surrounding soil thereafter. While insertion of a probe in the soil requires extreme care, it is very difficult to determine if there is negligible effect due to the fact that controlled comparison measurements in the field are very difficult in practice. If processes in the soil are assumed to occur mainly in the vertical direction (e.g., water and gas flow), then minimizing the projected area of the probe will reduce the influence on these exchanges; however, increasing the length of the probe will have the desirable effect of sampling from a larger area, thereby providing a degree of spatial averaging. Ultimately the dimensions of a probe such as the one in this study must consider these various factors and the ultimate goals of the measurement campaign.

The probe was installed in October 2004 after the field was harvested and plowed to incorporate the soybean stubble. The probe was installed at the bottom of the plow layer at a depth of approximately 25 cm below the soil surface. The probe was installed so that it was positioned directly above and parallel to the tile drain nearest the instrument trailer housing the TDLTGA. Placing it in this manner provided an additional degree of safety against drawing water into the system. The plumbing system and gas analyzer were installed in early March 2005 and measurements began on 16 March. When the sample tube was removed in May 2005 before planting, no evidence of water incursion into the vertical sample tube could be seen.

RESULTS AND DISCUSSION

Tunable Diode Laser Trace Gas Analyzer Measurements

An example of the TDLTGA response to one soil gas sampling event is shown in Fig. 2. At 21:40 h, the three-way sampling solenoid switched to pull air from the sample probes. This immediately caused a fluctuation in the concentration, probably due to a pressure difference between the sample and reference cells of the

Fig. 2. Time series of 0.2 Hz N_2O concentrations measured by the tunable diode laser trace gas analyzer during soil gas sampling on 27 Mar. 2005.

gas analyzer. The concentration gradually equilibrated as the previous sample was flushed through the sample tubing between the buried probe and the three-way valve (from 2140 to 2200 h) until the concentration stabilized. At this point the 5-s N_2O concentration measurements were averaged to give a single average concentration measurement. The sampling cycle was repeated every 2 h to provide 12 measurements of belowground soil N_2O concentration every 24 h. When the three-way solenoid was switched at 2200 h, room air was drawn through a critical flow orifice and series of filters, which gradually removed N_2O from the TDLTA sample tube until the next sampling cycle 2 h later.

Measurements of Environmental Variables

Air temperatures, soil temperatures, and soil volumetric water content measured during the period of soil gas sampling

Fig. 3. Time series of measurements during soil gas sampling in March and April 2005: (A) snow depth (thick line) and cumulative precipitation in units of millimeter liquid equivalent (thin line), (B) wind velocity measured at 10 m above the ground, (C) air temperature measured at 1.5 m above the ground, (D) soil temperature measured at 5- (thin line) and 25-cm (thick line) depths, (E) soil volumetric water content measured at 5- (thin line) and 25-cm (thick line) depths, and (F) N_2O concentrations at the 25-cm depth.

are shown in Fig. 3. Also shown are the precipitation (water equivalent), snow depth, and wind velocity measured at 10 m above the ground, all of which could potentially influence gas transport through soil. During the period shown in Fig. 3, all precipitation fell as snow except for the final event on 2 Apr. 2005, which was a mixture of snow and rain. During this period, the air temperature showed a relatively strong diurnal trend with a gradual increase over the duration of the period. Soil temperatures showed little diurnal change until approximately 29 March, when the 5-cm depth became ice free, resulting in large diurnal fluctuations. Subsequently, the 10- to 30-cm layer soil temperature increased, although with the typical lower amplitude and phase lag compared with the temperature measured in the shallower layer.

Soil water content, θ_v , showed a gradual increase during the period around 26 March onward, which is probably due to a gradual decrease in ice content and increase in liquid water content during the thawing process. Additionally, water from the melting snow would probably penetrate the soil, resulting in the observed increase in θ_v . During the month-long period of these measurements, θ_v in the 10- to 40-cm depth layer was higher than the surface measurements but generally followed the same pattern as the surface measurements of θ_v with a slight temporal lag. These water content measurements were obtained at a distance of 20 m from the buried gas-sampling probe and were not located near a tile drain. Although these measurements can illustrate the general behavior of θ_v in the soil, the absolute values at the soil gas probe were probably different from these measurements.

Temporal Behavior of Belowground Nitrous Oxide

Concentrations of N_2O measured every 2 h at the 25-cm depth are shown in Fig. 3f. During the period from approximately 15 to 24 March, concentrations measured in the soil averaged $78.1 \mu\text{mol mol}^{-1}$, with a standard deviation of $7.9 \mu\text{mol mol}^{-1}$. During this period, the concentrations fluctuated from a minimum of 64.5 to a maximum of $96.4 \mu\text{mol mol}^{-1}$. Some of these fluctuations occurred during a short time period, such as the increase in the morning of 18 March, when concentration rose by approximately $25 \mu\text{mol mol}^{-1}$ in a 2-h period. Between 0800 h, 23 March, and 1400 h, 24 March, the data acquisition system failed, resulting in a data gap. Following the system restart, N_2O concentration began a precipitous decline during the next 6 d until the concentrations stabilized to just slightly less than $1 \mu\text{mol mol}^{-1}$.

The presence of snow on the ground will pose an additional resistance for the diffusion of gases from the soil to the atmosphere. During the period when the snow was melting, there was a coincident decrease in N_2O concentrations (Fig. 3a and 3f). During the period before 30 March, there was probably significant melting of ice in the soil, resulting in little temperature change during the ice–water phase change. This physical change from solid to liquid could possibly allow for greater diffusion of trace gases from the soil. Furthermore, it cannot be ruled out that there was a concomitant change in production due to factors influencing microbial N_2O production, such as the thawing of frozen organic substrate.

Fig. 4. Time series of (A) wind velocity and (B) N_2O measurements obtained at the 25-cm soil depth in a conventionally tilled agricultural field between 15 and 24 Mar. 2005.

One factor that does show an influence on N_2O concentrations in the soil is the wind velocity (Fig. 4 and 5). During the belowground measurements when concentrations were high (15–23 March), there was a general inverse relationship between wind velocity and concentrations. During this period, however, the melting of snow and ice above and within the soil confounds the relationship between soil N_2O concentrations and the effect of wind. Figure 6a shows that during this period, the concentrations at high wind speed were slightly lower and less variable than at low wind speeds; however, it is apparent that the relationship is quite noisy due to other factors.

During the period of 31 March to the end of the measurements on 20 April, N_2O concentrations were relatively low but show a more distinct relationship with wind velocity (Fig. 5 and 6b). Generally, during periods of low wind velocity, concentrations showed more variability, and in some cases were higher by almost a factor of three. Conversely, during periods of high wind velocity, soil N_2O concentrations fell to typical atmospheric concentrations near $0.3 \mu\text{mol mol}^{-1}$. We hypothesize that these changes in concentration are similar to those discussed in Massman et al. (1997) and more recently in Takle et al. (2004). The increase in turbulence near the surface results in a pressure pumping effect, which increases the rate of gas movement from the soil pores to the atmosphere. Although a plausible physical mechanism for increasing the rate of gas transport through the soil can help explain sudden changes in concentrations, other factors related to atmospheric turbulence would probably have to be considered as well. The duration and relative frequency of high-wind-speed events could also be important factors in determining concentrations below the soil surface, as would the temporal lag between turbulent conditions and concentration changes.

Relating concentration gradients to surface fluxes could provide insight into the biological and physical processes controlling the production and transport of trace gases in the soil. In this study, only one probe was used to determine the feasibility of this system

Fig. 5. Time series of (A) wind velocity and (B) N_2O measurements obtained at the 25-cm soil depth in a conventionally tilled agricultural field between 31 Mar. and 14 Apr. 2005.

for concentration measurements; however, the large concentration change observed during the period of 25 to 31 March (inclusive) represents a change in soil N_2O storage, which may explain a portion of the surface fluxes. Total porosity of the conventionally tilled fields at the Elora research station is typically $0.5 \text{ m}^3 \text{ m}^{-3}$. Water content during this period was approximately $0.15 \text{ m}^3 \text{ m}^{-3}$, resulting in a maximum possible air-filled porosity of $0.35 \text{ m}^3 \text{ m}^{-3}$. During this period, the soil N_2O concentration at the 0.25-m depth changed by approximately $80 \mu\text{mol mol}^{-1}$. Assuming a linear increase in concentration with depth from the surface to the bottom of the plowed layer, a constant soil temperature of 0°C and atmospheric pressure

Fig. 6. Relationship of 25-cm-depth soil N_2O concentration and wind speed measured at 10 m above the surface between (A) 15 and 24 Mar. 2005 and (B) 30 Mar. and 14 Apr. 2005.

at the site of 98 kPa, an average flux of $7 \text{ ng m}^{-2} \text{ s}^{-1}$ of N during the 7-d period is calculated assuming soil air behaves as an ideal gas. Concurrent micrometeorological measurements during the same period over the conventionally tilled plots show an average flux during this period of $46 \text{ ng m}^{-2} \text{ s}^{-1}$ N. This result strongly suggests that this single-depth measurement of soil gas storage changes is insufficient to explain the large flux of N_2O commonly observed during spring thaw conditions (e.g., Maggiotto and Wagner-Riddle, 2000; Teepe et al., 2000).

System Performance and Potential Improvements

As this was a prototype system, there are various suggested improvements that could easily be implemented in future versions. One possible modification would be to regulate the flow rate from the buried sample probe using a low-flow-rate mass flow controller. Commercial versions of these devices that operate from 1 to $10 \text{ cm}^3 \text{ min}^{-1}$ are available and would probably be helpful in maintaining a consistent flow rate from the buried probe. While it would be most appropriate to maintain such a flow-control device indoors near the TDLTGA, it may require additional modifications to maintain a low system pressure inside the sample tubing to prevent condensation and ice formation. Related to this suggested improvement would be to use smaller internal diameter sample tubing from the buried probe to the TDLTGA. This would have the advantage of lower pressures, faster flow velocity, and lower volume, which would minimize the time for the TDLTGA to equilibrate to any pressure changes and further reduce the volume of sample required.

A second improvement would be the addition of an automated multiplexing plumbing system to allow the sampling of multiple buried probes. This would allow the measurement of horizontal and vertical gradients of N_2O in the soil, which would be extremely useful to relate to the surface flux. Computer-controlled relay and solenoid valve systems are available that can be configured for almost any conceivable sampling schedule. The multiple soil probes could be located at various depths and horizontal positions to measure vertical gradients and examine questions of spatial variability of trace gases in soils. Such a system would facilitate direct manipulation studies to address questions such as fertilization and management strategies.

A third modification would be changes to the dimensions of the buried probe. In this study, the probes were fabricated to allow relatively easy installation and burial. It would be feasible, however, to make the probes much longer with a smaller diameter. This would have the desirable effect of reducing any influence of the probe on vertical transport of water or trace gases. Making the probes longer would provide more spatial averaging and allow larger volumes of soil gas to be withdrawn without pulling air from other depths. In this study, the probes were installed approximately 10 d after plowing in the fall and measurements began in early spring the following year. Although the insertion of any probe into the soil will probably cause some disturbance, careful scheduling of probe insertion can take advantage of agricultural operations to minimize additional disturbance.

CONCLUSIONS

We developed a relatively simple method to measure trace gas concentrations below ground. The advantages of this method are the ability to obtain nearly continuous measure-

ments, thereby removing the need for manual sampling and site visits by skilled personnel. This method provides high temporal resolution measurements, which can capture short-term changes in concentration. This preliminary version of the sampling system could be integrated into the sampling schedule of an existing micrometeorological (flux-gradient) measurement system using a TDLTGA. These measurements could be an important component of trace gas budgeting and monitoring and would complement micrometeorological or chamber studies of ecosystem-atmosphere trace gas exchange. These measurements could ultimately be used to calibrate or validate models of N cycling in soils. As with many soil measurement procedures, this system requires the insertion of probes, which can cause disturbance of the nearby soil, which makes its utility for measurements in non-agricultural soils questionable. Additionally, the system must be protected against the ingress of water during wet conditions by a membrane barrier or by conditional sampling logic.

Preliminary measurements obtained by this system show that soil N_2O concentration varied by up to $25 \text{ } \mu\text{mol mol}^{-1}$ during a period of hours. Additionally, a large drop in concentration was observed coincident with snow melting and soil warming. This drop in concentration was on the order of $80 \text{ } \mu\text{mol mol}^{-1}$ and occurred during a period of approximately 6 d. Analysis shows, however, that this concentration change is insufficient to explain the large flux of N_2O measured at the site using micrometeorological techniques. During the snow-free period, the concentration of N_2O in the soil showed a slight inverse relationship with wind velocity, suggesting a pressure-pumping mechanism responsible for trace gas movement from the soil. This system provides a method to obtain N_2O measurements at a temporal resolution and has the potential to complement standard micrometeorological measurements used to investigate the exchange of other trace gases at the soil surface.

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