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Real-Time, High-Resolution Quantitative Measurement of Multiple Soil Gas Emissions: Selected Ion Flow Tube Mass Spectrometry

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ABSTRACT

A new technique is presented for the rapid, high-resolution identification and quantification of multiple trace gases above soils, at concentrations down to 0.01 μL L^{-1} (10 ppb). The technique, selected ion flow tube mass spectrometry (SIFT–MS), utilizes chemical ionization reagent ions that react with trace gases but not with the major air components (N_2, O_2, Ar, CO_2). This allows the real-time measurement of multiple trace gases without the need for preconcentration, trapping, or chromatographic separation. The technique is demonstrated by monitoring the emission of ammonia and nitric oxide, and the search for volatile organics, above containerized soil samples treated with synthetic cattle urine. In this model system, NH_3 emissions peaked after 24 h at 2000 nmol m^{-2} s^{-1} and integrated to approximately 7% of the urea N applied, while NO emissions peaked about 25 d after urine addition at approximately 140 nmol m^{-2} s^{-1} and integrated to approximately 10% of the applied urea N. The monitoring of organics along with NH_3 and NO was demonstrated in soils treated with synthetic urine, pyridine, and dimethylamine. No emission of volatile nitrogen organics from the urine treatments was observed at levels >0.01% of the applied nitrogen. The SIFT method allows the simultaneous in situ measurement of multiple gas components with a high spatial resolution of <10 cm and time resolution <20 s. These capabilities allow, for example, identification of emission hotspots, and measurement of localized and rapid variations above agricultural and contaminated soils, as well as integrated emissions over longer periods.

T$_{\text{HE MEASUREMENT OF}}$ trace gases in an air sample (e.g., environmental air, breath samples, the headspace volumes above liquids and solids) often requires laborious sample preprocessing, and sample storage and transport that may compromise sample integrity. However, a new mass spectrometric technique SIFT–MS has been developed recently that allows the detection and quantification of multiple trace gases at concentrations down to 0.01 μL L^{-1} (10 ppb) in real time without any sample manipulation (Španel and Smith, 1996, 1999a). This method combines soft, nonfragmenting chemical ionization (Harrison, 1982) with the sensitivity and quantitative capability of a selected ion flow tube (SIFT) (Adams and Smith, 1976; Smith and Adams, 1987), as explained below.

Chemical ionization is achieved in SIFT–MS through the reactions of three chemi-ionization reagent ions, H_3O^+, NO^+, or O_2^+. These reagent ions are chosen as they do not react rapidly with any of the major components of air (see Eq. [2]–[4] for examples with O_2^+) but do have high reaction rate coefficients with most of the trace gases in air. The reactions occur through low-energy proton transfer or charge transfer reactions that generate the ionized molecular ions, facilitating the identification of the corresponding parent molecules. Chemical ionization avoids fragmentation that occurs by electron impact ionization of organic molecules, which can make identification and especially quantitative measurements difficult. Unknown species can be identified by a combination of several reagent ions and observing the masses of the ionic products formed. Even isobaric species (species with the same molecular mass) can often be resolved, as their reactivity with the various reagent ions may be quite different. Quantification is achieved by measuring the amount of reagent ions lost and product ions formed during a known reaction time in the SIFT flow tube (Španel and Smith, 1996).
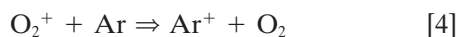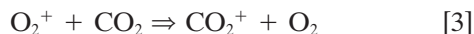
In the present study we use O_2^+ as the reagent ion. This ion reacts rapidly by exothermic charge transfer with molecules that have lower ionization potentials than oxygen, but does not react with molecules that have higher ionization potentials. In the present reactions the flow tube contains air with trace amounts of ammonia (NH_3) or nitric oxide (NO). When we inject O_2^+ ions, the reaction illustrated in Eq. [1] generates the NH_3^+ ion, which is detected by the mass spectrometer:

$$O_2{}^+ + NH_3 \Rightarrow NH_3{}^+ + O_2 \qquad [1]$$
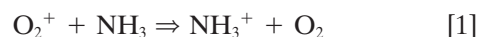
The reaction shown in Eq. [1] is exothermic ($\Delta H^\circ = -185$ kJ mol^{-1}) and fast ($k = 2.6 \times 10^{-9}$ cm^3 s^{-1}), that is, it proceeds with near unit collision efficiency, typical of exothermic ion-molecule reactions. Conversely, the ion-molecule reactions shown in Eq. [2] through [4]

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are endothermic and do not occur at observable rates (Anicich, 1993; Mallard, 2000):

$$O_2^+ + N_2 \Rightarrow N_2^+ + O_2 \qquad [2]$$

$$O_2^+ + CO_2 \Rightarrow CO_2^+ + O_2 \qquad [3]$$

$$O_2^+ + Ar \Rightarrow Ar^+ + O_2 \qquad [4]$$

Therefore, in the present mixtures, O_2^+ does not react with the main air components but reacts selectively with NO, as well as with NH_3, and other gases with lower ionization potentials, including all organics. None of the primary ions used in SIFT–MS react rapidly with water, and so the technique is essentially insensitive to the levels of water vapor in the air sample. Selected ion flow tube mass spectrometry can also be applied to other soil gases such as nitrogen dioxide (NO_2) and nitrous acid (HNO_2) (Španel and Smith, 2000) as well as methane (CH_4), though with less sensitivity due to a lower rate coefficient. Special reagent ions would have to be used for some other important soil emission gases such as carbon dioxide (CO_2) and CH_4, which have high ionization energies. The analysis of nitrous oxide (N_2O) does not appear to be possible using the current precursor ions (Španel and Smith, 2000).

Applications of the SIFT–MS technique have already spanned a wide range of fields. The analysis of the volatile organic compounds in breath has received special emphasis in medical diagnosis. For example, the presence of NH_3 was detected in the breath of patients with renal failure (Davies et al., 1997), and acetone on the breath of certain diabetics and athletes (Senthilmohan et al., 2000, p. 151–153). The odor components of foods, both fresh and spoiled, have also been investigated (Španel and Smith, 1999b). The emission of organic compounds, such as ketones, from wounded or decaying plant materials was also analyzed using the conceptually similar proton transfer mass spectrometry (PTR–MS) technique (Fall et al., 1999; Lindinger et al., 1998). In addition, the SIFT–MS technique has been employed for assessing its role in the diagnostic and physiological monitoring of fecal and urine compounds (Smith et al., 2000).

In the present work we demonstrate the application of SIFT–MS to the monitoring and quantification of soil gas emissions. Conventional methods often involve several steps that are laborious and may introduce cumulative errors. For example, we monitor in this work NH_3, NO, and NO_2, and search for volatile organic compounds. With SIFT–MS, this can be done in real-time by directly sampling from air. In comparison, conventional methods would require separate specific analysis for each component. For example, the sampling of NH_3 from a pasture surface can be achieved using chamber methods and wet trapping of the NH_3 gas in acid for subsequent laboratory analysis (Black et al., 1985) or micrometeorological methods (Sherlock et al., 1989). These methods require prolonged trapping (hours to days) and/or large volumes of air that prevent high-resolution measurements. The NO_x gas sampling and analysis can be performed in situ using chamber methods that employ a portable luminol-based NO_2 detector

(Hutchinson et al., 1999) with detection of NO being dependent on its prior oxidation to NO_2.

The present study involves soils treated with urea. This compound results in the release of gaseous NH_3 from the soil, a process commonly termed *ammonia volatilization*. Urea $[CO(NH_2)_2]$ deposited onto the soil surface in urine or as fertilizer undergoes hydrolysis, catalyzed by the enzyme urease in the presence of water to give ammonium bicarbonate and hydroxide ions (Haynes and Sherlock, 1986; Jarvis and Pain, 1990):

$$CO(NH_2)_2 + 3H_2O \xrightarrow{\text{urease}} 2NH_4^+ + HCO_3^- + OH^- \qquad [5]$$

Through these processes urine patches become localized areas of high pH with subsequent alteration of the equilibrium between ammonium (NH_4^+) and NH_3, in favor of NH_3. At common atmospheric temperatures and pressures gaseous NH_3 is strongly soluble in water and undergoes base hydrolysis to yield NH_4^+ and OH^-. This dissociation and other factors that govern the loss of NH_3 from soils have been previously reviewed (Nelson, 1982; Freney et al., 1983; Haynes and Sherlock, 1986; Jarvis and Pain, 1990). The most influential of these factors is probably the pH of the soil solution containing the NH_3. The amount of NH_3 ultimately volatilized depends on the rate of urea hydrolysis and the complex interaction of the factors mentioned above (Sherlock et al., 1995). Losses of NH_3–N from grazed pasture systems can be substantial and are of economic and environmental concern.

In the soil, NH_3 is converted to the nitrite ion (NO_2^-), which then reacts with hydrogen ions to form HNO_2, and can in turn decompose to form NO. This provides another possible gaseous loss process for nitrogenous compounds added as fertilizers. Normally this nitrite does not accumulate in the soil, but when fertilizers that significantly raise the pH level (e.g., urea) are applied, the oxidation of NO_2^- is strongly inhibited, resulting in higher soil nitrite concentrations. The NO_2^- so formed can diffuse to nearby zones of much lower pH and undergo protonation to form HNO_2:

$$NO_2^- + H^+ \Rightarrow HNO_2 \qquad [6]$$

The HNO_2 may subsequently decompose to form NO and NO_2. The emission of NO_x gas from soils following the application of animal urine or nitrogen fertilizers has been reported (Colbourn et al., 1987; Bronson et al., 1999; Skiba et al., 1997). These gases are of environmental interest due to the environmental effects of their changing concentrations (Williams et al., 1992). The SIFT–MS method offers an efficient new way to simultaneously measure these soil gas emissions.

MATERIALS AND METHODS

Selective Ion Flight Tube Mass Spectrometry

A brief description of SIFT–MS is presented below. Detailed reviews of the technique are available in the literature (Španel and Smith, 1996). In the simplest terms, the precursor ions are generated in a gas mixture subjected to electron impact ionization or a microwave discharge plasma. Ions extracted from the plasma are mass selected and the precursor
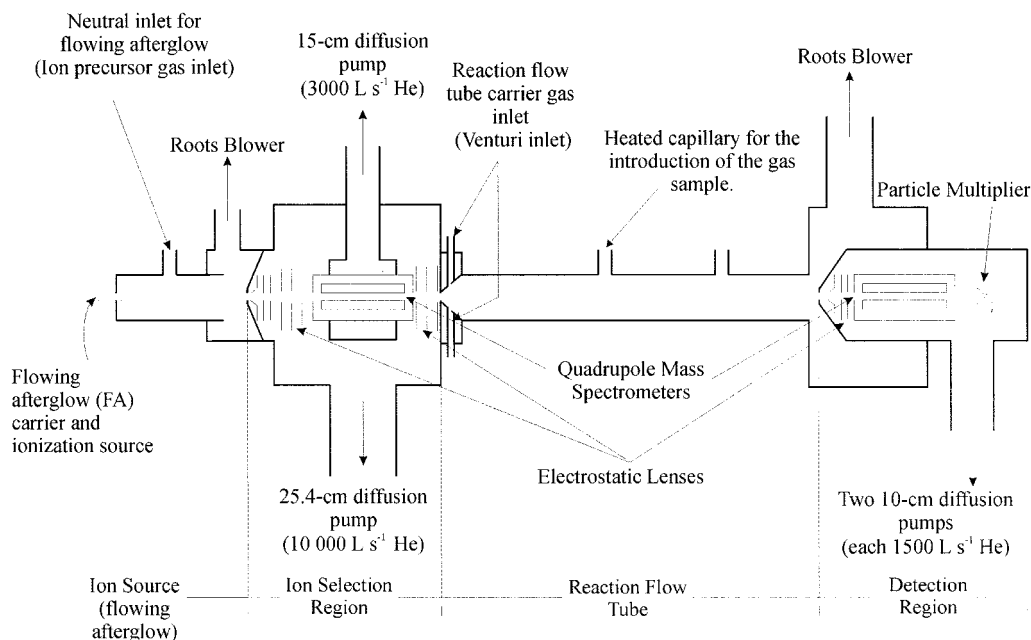
Fig. 1. A schematic diagram of the flowing afterglow–selected ion flow tube mass spectrometry (FA–SIFT) apparatus at the University of Canterbury.

ions (in this case O_2^+ ions, m/z 32) are injected into a flowing stream of helium gas. A small stream of the analyte air sample is introduced into the helium flow through a heated capillary downstream from the ion injection port. In the absence of reactive analytes, a fraction of the injected O_2^+ ions traverse the flow tube and are detected by mass analysis. When reactive analytes are present, reactions such as Eq. [1] above decrease the count of the O_2^+ ions. In turn, the number of counts in all the product channels from one volatile chemical allows the calculation of the amount of this species present in the sample.

At the University of Canterbury the SIFT–MS technique is performed using a modified flowing afterglow/selected ion flow-drift tube, which is shown in Fig. 1 (Milligan et al., 2000). The ions are generated in the flowing afterglow (FA) section, from whence they pass into the ion selection region. The first quadrupole mass filter is housed in this region and it allows ions with only one mass to charge (m/z) ratio to pass. Thus, the ions that enter the flow tube are essentially all a single species with no interference from other ions or the neutral species used to form the precursor ions. This is a significant advantage of the SIFT method over more conventional chemical ionization techniques (Adams and Smith, 1976). The mass selected ions from the FA source then pass through the venturi inlet into the reaction flow tube region. The venturi inlet (Dupeyrat et al., 1982; Fishman and Grabowski, 1998; Milligan et al., 2000) admits the carrier gas (usually helium) into the reaction region in such a way that back-streaming from the high pressure reaction region (0.5 Torr) to the low pressure ion source (approximately 2×10^{-5} Torr) is minimized. Once in the reaction region, the ions are transported along the flow tube by the rapid flow of helium carrier gas, which moves under the influence of the high-speed roots blower pump. Thus, the ions take a reproducible time to transit between the point at which the gas sample is introduced and the exit to the detection region. This is the time available for reaction between the ion and the neutral analyte.

The number of ions in the tube is much less than the number of molecules of trace species introduced and the ionization process follows pseudo–first order kinetics. This means that

the rate of loss of the reagent ions depends only on the neutral concentration as shown in Eq. [7]:

$$\frac{dN_i}{dt} = -N_i k[A] \qquad [7]$$

Here, dN_i is the number of precursor ions lost during reaction, dt is the reaction time, N_i is the initial number of precursor ions, $[A]$ is the concentration of the trace species, and k is the rate coefficient for the reaction between A and the precursor ion. Ion loss by physical mechanisms (e.g., diffusion to the walls of the reaction tube) can be readily accounted for.

Equation [7] shows that using the known rate coefficient k and the reaction time, the concentration of the trace species $[A]$ can be calculated from the loss in reagent ion counts. This loss is accompanied by an equal rise in the total product ion counts whose relative amounts give a direct measure of the relative amounts of the trace species. For this method all the ionic products generated by a particular trace species need to be known and counted, which is easily accomplished. When several analytes are present, their total concentration can be calculated from Eq. [7] and their relative concentrations can be calculated knowing the distribution of product ion intensities and the rate constants of the reactions of the reagent ions leading to the product ions (Španel and Smith, 1996). This information can be easily obtained using the SIFT in its usual kinetic mode, adding known amounts of the analyte trace gases. The rate coefficients for many of the reactions are known or can be assumed equal to the ion-molecule collision rate as calculated for example from parameterized equations (Su and Chesnavich, 1982). The rate coefficients are usually known with an uncertainty of ±15%, which may be the main source of uncertainty in the concentration measurements. Once the number density $[A]$ of a species in the flow tube is determined, its partial pressure in the ambient air can be calculated knowing the flow rate of the carrier gas in the SIFT tube and the flow rate of the sampled air into the SIFT tube through the capillary sampling tube. The overall uncertainty of the concentration measurements was assigned as ±17% using calibrated gas mixtures (Španel et al., 1997).

Selected ion flow tube mass spectrometry methodology has been validated for a range of volatile compounds. Smith et al. (1998) and Španel et al. (1997) used syringe detection methods and permeation tubes to validate SIFT–MS quantification of a number of volatile organic molecules down to 0.01 $\mu L\ L^{-1}$ (10 ppb). We have validated the technique for ethanol on human breath and in the headspace above an aqueous ethanoic solution and blood (Wilson et al., 2001), where the SIFT–MS results were verified using known solution concentrations of ethanol and Henry's Law constant, and also using forensic procedures for ethanol vapor measurements. Also, Španel et al. (1998) have quantified NH_3 on human breath using various ion precursors. Although the optimal sensitivity of the SIFT is 0.01 $\mu L\ L^{-1}$ (10 ppb), in the present work, which used relatively fast sampling times, the reliable detection limit is estimated conservatively as 0.05 $\mu L\ L^{-1}$ (50 ppb).

Data Acquisition

Data acquisition and analysis is performed in real time using computerized control of the downstream quadrupole mass spectrometer and ion counting. The SIFT–MS at Canterbury University can analyze multiple trace components in two different modes: mass scanning and selected ion monitoring modes.

Mass scanning mode is usually used in the early stages of an investigation, when the identity of the major trace species is unknown. In this mode the downstream quadrupole analyzer is scanned linearly through a mass range, effectively generating a mass spectrum of the ions. The identity of the trace gas in a sample can be determined from the spectrum and the ion chemistry. However, this mode is not well suited for quantification, as its temporal resolution is poor (a single scan from $m/z = 10$ to 140 may take 20 s to acquire).

For quantification the selected ion monitoring mode was used. This mode steps the mass analyzer in discrete steps, stopping only on the chosen precursor and product ions of interest. Therefore, an accurate knowledge of the ion chemistry is necessary before the analysis can be performed, and it must be ensured that there is no interference from other trace gases of the same mass, by selecting appropriate precursor ions. The selected ion monitoring mode can generate data points rapidly (the count time on primary ions is usually approximately 0.01 s and that for product ions approximately 0.2 s, allowing a single trace gas component to be quantified <0.5 s). Typically, replicate scans are performed over 20 s to increase the accuracy. This method therefore allows high temporal resolution and can monitor concentration changes over short time scales.

Soil and Synthetic Urine

Silt loam soil (Pallic typic soil, New Zealand soil classification; Hewitt, 1992) was collected from a sheep pasture (0–10 cm), air-dried, and sieved (0.2 cm). The sieved soil (300 g) was then placed into 1-L glass jars, at a depth of 4.5 cm (providing approximately 0.7 L of open headspace above the soil). Synthetic urine (Fraser et al., 1994) and deionized water were applied according to treatments described below so that all jars had the same gravimetric water content. In some samples, four to eight grass plants were also planted to examine biological effects on the urea degradation. However, because of the high urea concentrations, the grass plants did not survive the first planting or a second planting 25 d after the application of the synthetic urine.

Treatments

The soils were watered with 0.1 L of distilled water, followed immediately by the application of the artificial urine solution. The artificial urine was applied at a rate equivalent to 1000 kg N ha^{-1} using 0.04 L and concentration of 0.46 mol L^{-1} of urea, simulating a bovine urination event. Controls were also made consisting of soils to which an additional 0.04 L of water rather than artificial urine were added. Four replicates of the treatment and two blanks were used. Two replicate samples were also prepared to determine whether the timing of the addition of the synthetic urine was important. In these samples the water and artificial urine were either added concurrently or the water was added approximately 10 h beforehand to allow the soil to wet up and the synthetic urine solution added later. The treated soils were kept in the laboratory at a temperature of approximately 25°C and were weighed and watered every 2 to 4 d to maintain a constant water content. The jars were kept open to air except when the lids were sealed to allow sample collection in the headspace. Before each measurement the background air was sampled to correct for any background signal of $m/z = 30$ and also for any NO signal arising from photoionization of nitrogen and oxygen in the reaction flow tube in the absence of NO in the air sample.

Volatile Organic Compounds

The SIFT–MS is also able to observe many other volatile compounds, including nitrogen bases, in the headspace above the soil, down to levels of 1 to $5 \times 10^{-2}\ \mu L\ L^{-1}$, depending on the trace gas and the rate constants for chemical ionization. In the present experiments this corresponds to emission rates of 0.17 to 0.85 nmol m^{-2} s^{-1}. Mass scanning mode searches for these species were made on several occasions. As a test for the detection of these compounds a mixed 1% (v/v) pyridine and 1% (v/v) dimethylamine solution was added to a soil sample to which the artificial urine had been freshly added. This solution was added at two rates either 0.001 or 0.01 L of solution per jar, delivering, for example, 10 μL or 1.2×10^{-5} mol, or 100 μL or 1.2×10^{-4} mol of pyridine, respectively.

Gas Sampling

During the measurements, a small flow of the gas mixture in the headspace above the soil sample is allowed to leak continuously into the SIFT–MS flow tube. The flow is facilitated by the pressure difference between the sample gas, which is at 1 atmosphere, and the mass spectrometer flow tube, which is less than 1 Torr. The flow rate is controlled by a small capillary (0.25 mm internal diameter and 50 mm in length), which meters the flow at 3.4 Torr L s^{-1}. To measure the emission rates from the soil, the emitted gases were collected in the jars for a short period (usually 5 min) before sampling. To this end, each jar was sealed with a cap containing a septum. The measurements were achieved by piercing the septa with a syringe needle attached to the sample inlet line and the headspace gas allowed to flow through the capillary to the flow tube.

Each headspace was sampled from the region of headspace gas approximately 30 mm above the surface of the soil block. The average sampling time for each soil vessel was around 10 s and thus the air pressure inside the vessel was altered by <5% from atmospheric pressure. This fact is significant since the flow through the capillary will alter if the external pressure deviates significantly from atmospheric pressure.

In each sampling, NH_3, NO, and NO_2 were monitored quantitatively using the selected ion monitoring mode. Periodically,

organic emissions were also searched for. The O_2^+ reagent ion was used since it is the most effective at monitoring these trace species (Španel and Smith, 2000). Gas sampling was conducted at intervals appropriate to the total gas emission pattern. During the initial 48-h NH_3 emission period, samples were measured at intervals of several hours. The emission of NO started later and varied more slowly and samples were measured at intervals of several days. The emissions were monitored for 105 d after the artificial urine had been added, by which time all emissions had virtually stopped. As noted above, each sampling was accomplished in a few seconds, with a sample time that is negligible compared with the time scale of changes in the emission rates.

RESULTS AND DISCUSSION
Gas Sampling Procedure

This work illustrates the SIFT method by measuring soil emissions of NH_3, NO, NO_2, and volatile nitrogen organics. Samples of the head space taken in the time leading up to 5 min show that the concentration of the emitted gases in the headspace increases linearly with time, as shown in Fig. 2. This shows that the partial pressures of the emitted gases collected in the headspace in 5 min were controlled by the *emission rate* and not by equilibrium of the emitted gases with the gases adsorbed in the soil or on the glass walls of the container.

Note that an extrapolation of the points in Fig. 2 to zero time intercepts the *y* axis at a nonzero concentration. This may be due to the presence of small amounts of emitted gases in the vessels before they were capped. A small uncertainty of <5% may be introduced in the reported emission rates due to this effect.

The flux of emitted gas, that is, the number of moles emitted per unit area per unit time from the soil sample, can be calculated from the amount accumulated in the headspace sampling volume using Eq. [8]:

$$\text{Flux} = \left[\frac{d(NH_3)}{dt}\right]/A = \left\{\frac{[P(NH_3)]V}{RT}\right\}/At \qquad [8]$$

Here $P(NH_3)$ is the partial pressure of the collected

NH_3 in the sampling volume, *V* is the headspace volume, *R* is the gas constant, *T* the absolute temperature, *t* the collection time, and *A* the soil surface area.

Ammonia Emissions

The NH_3 emission peaked approximately 24 h after the artificial urine was added to the soil (Fig. 3). Several replicates of this system were prepared and the relative rate of ammonia emission with time was reproducible. The NH_3 emission profile over time was very similar to others reported in the literature. The NH_3 volatilization from urine applied to grass swards normally reaches a maximum 2 d after application and declines to negligible levels after 8 to 14 d (Sherlock et al., 1995). However, the exact integrated amount of NH_3 emitted was affected by several variables, such as varying soil agglomeration in the replicate runs, various degrees of packing as a result of the watering, and the method of synthetic urine addition, air temperature, and humidity, resulting in a variation of up to 50% in the integrated emission rates. The integrated emission rates showed that $7 \pm 3\%$ of the nitrogen added as urea was emitted as NH_3.

Samples with constant amounts of liquid but with half or quarter of the artificial urine concentration applied above were also prepared. The results showed that the amount of NH_3 emitted depended on the initial amount of synthetic urine added (Fig. 4), although the relationship was nonlinear. Despite the absolute amounts of NH_3 emitted varying between replicate runs at full and more dilute concentrations, the time profile of the NH_3 fluxes was very similar in all cases.

The NH_3 emission rates were affected by the procedure of sample preparation. As noted above, the method of adding the water and synthetic urine to the soil samples was found to influence the magnitude of the NH_3 emissions. When the water and synthetic urine were added together both the peak levels and the total amount of NH_3 emitted were less than when the water was added prior to the urine. The NH_3 emission rates
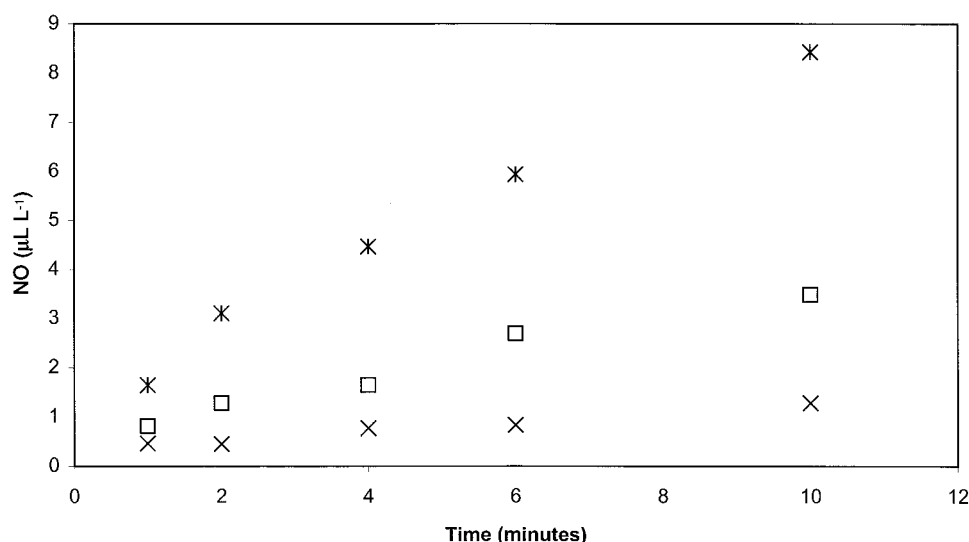

Fig. 2. Gas sampling sequences showing the linear increase of NO headspace concentration with collection time during a 5-min collection time. The symbols represent experiments with different urea soil concentrations and NO emission rates.
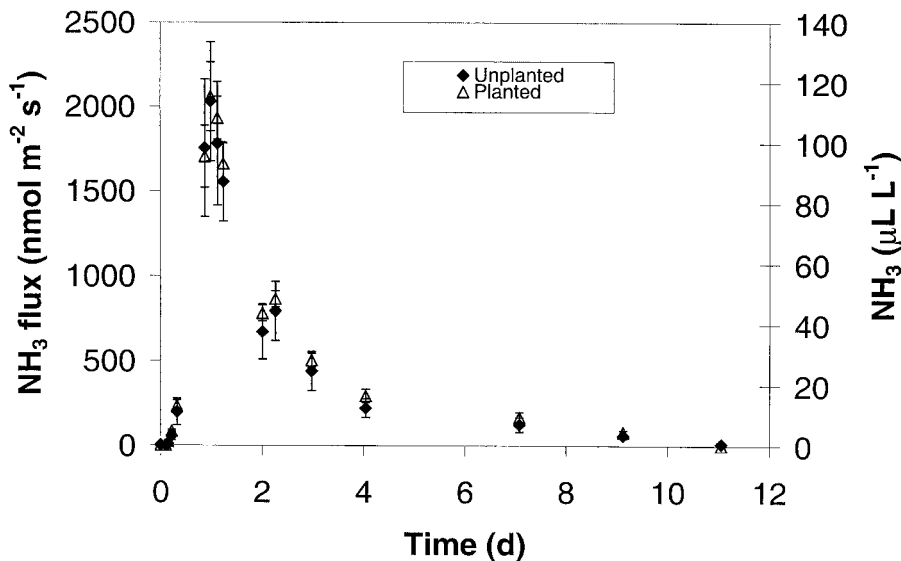
Fig. 3. A plot of the headspace NH₃ concentrations and flux vs. time since urine application. Planted treatments incorporated four to eight mature grass plants. Both planted and unplanted treatments received 0.04 L of the synthetic urine. Data points are means of four replicates and error bars represent 95% confidence intervals.

and the integrated amount emitted were higher by a factor of 1.3 to 2 when the soil was prewatered, although the total amounts of water added were equal. Prewetting the soil may have filled the micropores with water and forced the synthetic urine into macropores from which the NH₃ gas produced is more easily volatilized.

NOₓ Emissions

Detectable NO emission started approximately 15 d after synthetic urine addition, when the headspace concentrations rose above the background ion signal (see above) equivalent to approximately $0.2 \mu L L^{-1}$ observed in the air in the flow tube (Fig. 5). The background was subtracted from the ion signal intensity of the samples.

We noted a dip in the NO emission rates with a

minimum about 45 d after the synthetic urine was added, when we replicated summer drought conditions by raising the temperature to 28 to 30°C and allowing the soils to partially dry out. These conditions can inhibit microbial NO_2^- production. When the soil was restored to the original temperature and water content, NO_2^- production and hence NO emission resumed and increased relative to the emission rate just before the drying, then decreased to the levels extrapolated from the predrying period. The increased emissions after rewetting seemed to compensate for the dry period such that it had little effect on the integrated NO emission. This was verified by a further set of samples that were maintained in a moist state for 56 d during which the emission continued without a similar decrease and increase. All the emissions decreased to negligible levels
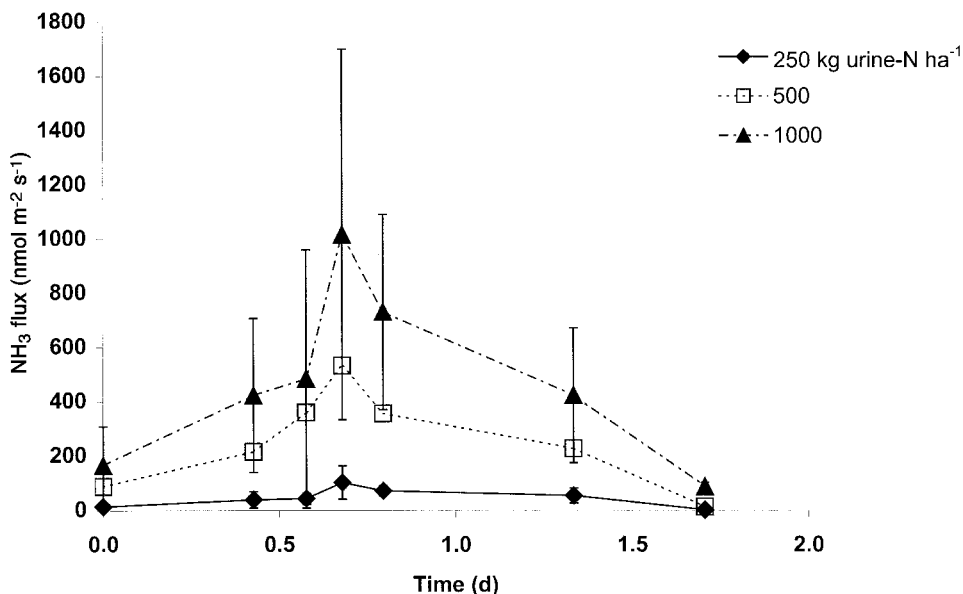

Fig. 4. A plot of headspace NH₃ concentrations and fluxes from soil samples prepared with three different rates of synthetic urine. Points are means of two replicates with error bars showing 95% confidence intervals.
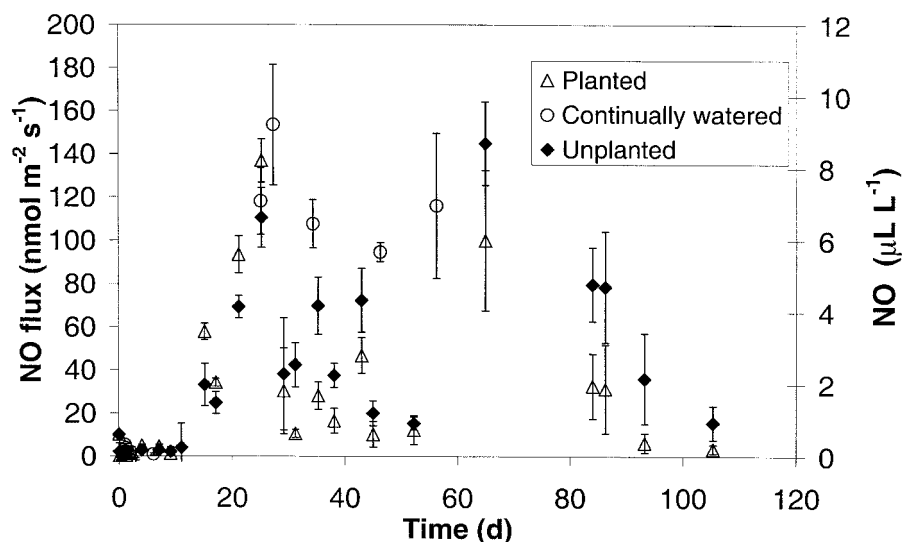
Fig. 5. Flux of NO gas over time, following the application of synthetic urine. The samples with or without grass plants partially dried out at Day 45 to simulate summer drought, and were not fully rehydrated until Day 65. A third treatment, unplanted, remained wet throughout. Points are means of four replicates with error bars showing 95% confidence intervals.

after 100 d. The integrated NO emission represented about $10 \pm 3\%$ of the nitrogen applied.

The headspace concentrations of NO_2 were always $<0.05 \ \mu L \ L^{-1}$, corresponding to an emission flux of <1 nmol m^{-2} s^{-1}. This level was consistent with predictions based on reaction kinetics (Steadman and Niki, 1973).

Organic Nitrogen Species

Selected ion flow tube mass spectrometry can also quantify the concentration of organic compounds in the sample headspace down to levels of approximately 0.05 $\mu L \ L^{-1}$ (50 ppb). In all the samples treated with urea, without the addition of other organics, no evidence for any volatile compounds other than NH_3 and NO_x was seen. This demonstrates that $<0.05 \ \mu L \ L^{-1}$ of any one compound had accumulated during the 5-min collection time. Note that this only indicates the lack of gas emissions, as volatile organics that may have been produced could have remained adsorbed as the soil and container system used had a high affinity for organic species.

As a test for detecting the emission of organic compounds we added a 1% (v/v) pyridine and dimethylamine solution to some of the soil samples. These samples were then analyzed by SIFT–MS using O_2^+ as the reagent ion. After adding 1 mL of this solution, containing 10 μL or 1.2×10^{-4} mol of pyridine, the pyridine signal disappeared in about 10 min, suggesting that all the pyridine was adsorbed into the soil. After adding 10 mL of this solution (containing 100 μL or 1.3×10^{-3} mol of pyridine) a detectable signal remained permanently in the sealed jar, and an ion of $m/z = 79$ corresponding to pyridine was observed in the mass spectrum. A sample mass spectrum (generated in mass scanning mode) is shown in Fig. 6 below. This mass spectrum shows peaks from both pyridine, dimethylamine, and NH_3 after a sample already emitting NH_3 was doped with a solution containing 1% (v/v) of each of these species. Using this as a model for volatile organics, we

may assume that if more than 1.2×10^{-3} mol of volatile organics are present in the soil, they would be detected.

These observations suggest that very little if any nitrogen is emitted from the soil as volatile organics after the addition of urea or synthetic urine. Quantitatively, an upper level on the emissions can be calculated assuming a conservative detection limit of 0.1 $\mu L \ L^{-1}$, that is, 7.6×10^{-5} Torr in 1 L headspace, collected in 2 h. Therefore, the equilibrium vapor pressure of any nitrogen organics over the treated soil is $<7.6 \times 10^{-5}$ Torr. The calculated upper limit for the emission of organics is 3.4×10^{-11} mol min^{-1}. Integrated over the 105 d, the emission is less than 5×10^{-6} mol, compared with the 0.023 mol of urea added (i.e., less than 0.01% of the nitrogen from urea was lost in this form). The losses through conversion to volatile organics are therefore at most very small.

Comparison with Other Methods

The SIFT method may be compared with other methods for measuring soil trace gas emissions. For NH_3, a common method is acid trapping. Quantifying NH_3 fluxes from a soil surface typically involves the measurement of the NH_3 concentration profile in the air 2 to 3 m above the surface of a circular (20 to 30 m diameter) plot of treated ground (Black et al., 1985; Sherlock et al., 1995). The concentrations typically encountered range from 0.1 to 1 $\mu L \ L^{-1}$. To measure such concentrations using acid trapping, high flow rates (e.g., 10 L min^{-1}), relatively small trapping volumes (e.g., 0.05 L), and long aspiration times (e.g., >2 h) are required. In contrast, SIFT allows gas concentration measurements over the same concentration range requiring very small sample volumes of 0.1 L and very short sampling times of about 20 s. For a direct comparison, we conducted an experiment where the NH_3 was measured by both acid trapping and SIFT simultaneously on the same air sample. In this experiment a constant headspace concentration
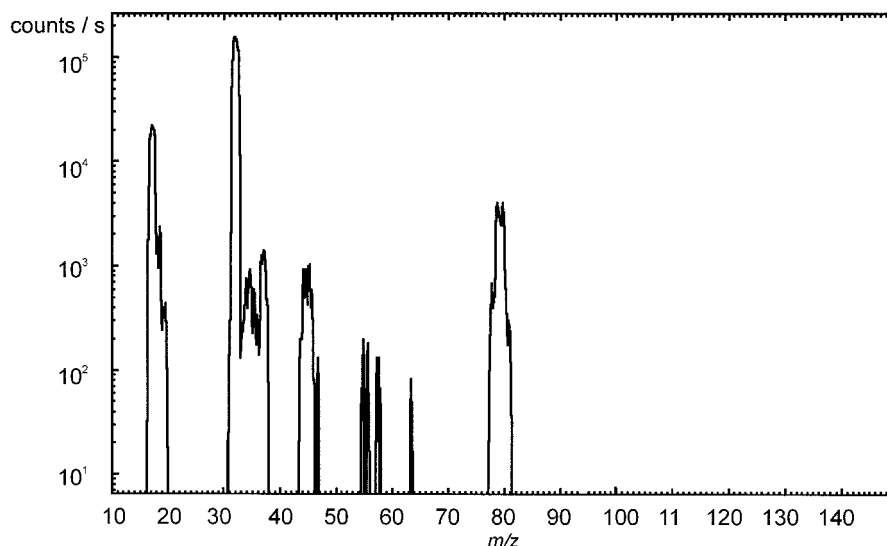
Fig. 6. A sample mass spectrum, generated in mass scanning mode. The primary ion is O_2^+ (32 amu). This sample was emitting NH_3 and had been treated with pyridine and dimethylamine. Consequently, peaks from these species (17 amu-NH_3, 44 and 45 amu-dimethylamine, and 79 amu-pyridine) are also present, demonstrating that multiple emissions can be readily analyzed.

of NH_3 was generated by placing 1 L of solution (3 g L^{-1} of ammonium sulfate at pH 10) in a 5-L jar. Air was pumped through the solution and the resulting air stream containing NH_3 in equilibrium with the solution was pumped through two traps in series each filled with 0.04 L of 1 M H_2SO_4 at a slow flow rate of 0.03 L min^{-1} to ensure complete collection of NH_3 in the traps. This was verified by the lack of detectable NH_3 in the second trap. The concentration of the NH_3 in the air stream was monitored through a branch-off from the flow line coupled to the SIFT. A constant concentration of 28 ± 4 μL L^{-1} (i.e., 0.021 ± 0.003 Torr of NH_3) was measured during the collection period.

Experiments were conducted using 1- and 11-h aspiration times. In the 1-h experiment the amount of NH_4–N collected in the acid trap was too small for accurate determination. In the 11-h experiment the concentration of the NH_3 collected in the trap was 16.9 ± 1.74 μL L^{-1} NH_4^+–N (i.e., a total of 0.82 ± 0.08 mg NH_3 collected). In comparison, the amount expected in the trap as calculated from the SIFT air concentration and flow rate and flow time was 0.94 ± 0.30 mg NH_3, with the uncertainty estimated from the accuracies of the SIFT and flow rate measurements. The agreement between the methods is therefore well within the estimated uncertainty. The advantage of the SIFT determination is of course that the results are obtained in real-time without the need for sample collection (usually for hours or days) and subsequent laboratory analysis.

The main distinction between SIFT and trap collection is that SIFT determines instantaneous trace gas concentrations while trap collection measures integrated concentration and emission rates over long periods. With measuring instantaneous concentrations, the SIFT method allows much enhanced spatial and time resolution. A SIFT measurement using an air sample of 0.1 L allows a corresponding spatial resolution of <10 cm, as the air is sampled from a volume with a radius of about 3 cm about the inlet of the sampling

capillary. This could identify emission hotspots such as individual urine patches or accurate locations of organic soil pollution, and the effects of local soil composition, fertilizer distribution, and plant cover over a 10-cm scale. The time resolution of 20 s allows the analysis of instantaneous responses in emission rates to variations in temperature, light and shade, moisture, and precipitation. These studies can be applied to multiple gases such as NO and NO_2 and organics, and with appropriate reagent ions also other environmentally important gases such as CH_4 and CO_2, all simultaneously. Of course, repeated sampling can be used to integrate cumulative emission rates over longer periods, as in this study.

CONCLUSIONS

Multiple gas emissions from soils can be monitored efficiently by the SIFT–MS method. Selective chemical ionization by specific reagent ions, or combinations of reagent ions, allows qualitative identification, while the known reaction kinetics allows quantitative determination. A major advantage is that real-time monitoring of multiple emissions is possible without the need for sample collection, preconcentration, and preparation. Gas concentrations of <0.05 μL L^{-1} (50 ppb) above the soil are readily detected and quantified, depending on background signals. Several emitted gases can be monitored simultaneously, for gases that may otherwise require laborious separate measurements. For example, Fig. 6 shows that diverse gases such as NH_3 and various organics can be monitored simultaneously and in real time directly from the headspace above soil. Discrete emission rates and cumulative integrated total emissions are measured readily.

In the present measurements, the time profiles of NH_3 and NO emissions agree qualitatively with expectations of the chemical and microbial decomposition of urea in soil. Quantitatively, the integrated emission of more than 10% of the applied nitrogen in the form of NO is

significant, although in these samples leaching and plant uptake of nitrogen were not operating. Chemical formation of NO_2 and the emission of nitrogen organics were not found to be significant. The present measurements account for the NH_3 and NO_x emissions, which constitute about 17% of the added N. The rest of the added N was present as inorganic NH_4^+, NO_2^-, NO_3^-, immobilized organic N, and/or emissions of N_2 and N_2O (data not presented).

The SIFT–MS method for monitoring multiple soil gas emissions has major advantages of speed, specificity, quantification, and high spatial and temporal resolution. The present immobile prototype apparatus can be replaced with cheaper portable equipment, currently under development. This will allow fast real-time quantitative measurements of multiple gas emissions under field conditions. With access to field measurements, the SIFT method can allow the determination of gas emissions with a spatial resolution of 10 cm and time resolution of 20 s, allowing the identification of emission hotspots over agricultural and contaminated soils, and instantaneous responses to environmental conditions, determined real-time for multiple inorganic and organic volatiles. Of course, repeat measurements can be also integrated to measure cumulative emissions. The SIFT capabilities may therefore improve not only the ease of measurements but also allow new types of studies.

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Nitrous Oxide and Ammonia Fluxes in a Soybean Field Irrigated with Swine Effluent

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ABSTRACT

In the United States, swine (*Sus scrofa*) operations produce more than 14 Tg of manure each year. About 30% of this manure is stored in anaerobic lagoons before application to land. While land application of manure supplies nutrients for crop production, it may lead to gaseous emissions of ammonia (NH_3) and nitrous oxide (N_2O). Our objectives were to quantify gaseous fluxes of NH_3 and N_2O from effluent applications under field conditions. Three applications of swine effluent were applied to soybean [*Glycine max* (L.) Merr. 'Brim'] and gaseous fluxes were determined from gas concentration profiles and the flux-gradient gas transport technique. About 12% of ammonium (NH_4–N) in the effluent was lost through drift or secondary volatilization of NH_3 during irrigation. An additional 23% was volatilized within 48 h of application. Under conditions of low windspeed and with the wind blowing from the lagoon to the field, atmospheric concentrations of NH_3 increased and the crop absorbed NH_3 at the rate of 1.2 kg NH_3 ha^{-1} d^{-1}, which was 22 to 33% of the NH_3 emitted from the lagoon during these periods. Nitrous oxide emissions were low before effluent applications (0.016 g N_2O–N ha^{-1} d^{-1}) and increased to 25 to 38 g N_2O–N ha^{-1} d^{-1} after irrigation. Total N_2O emissions during the measurement period were 4.1 kg N_2O–N ha^{-1}, which was about 1.5% of total N applied. The large losses of NH_3 and N_2O illustrate the difficulty of basing effluent irrigation schedules on N concentrations and that NH_3 emissions can significantly contribute to N enrichment of the environment.

In the United States, swine operations produce more than 14 Tg of manure each year (Sweeten, 1992) and much of the manure is generated in relatively small geographic areas. Land application is the preferred method of manure management but high concentrations of animals may lead to excessive applications. Application of organic waste materials on agricultural land has received considerable attention in recent years because of potential environmental problems such as water quality degradation, air pollution through N gas emissions, odors, and dispersal of pathogenic organisms (Dosch and Gutser, 1996; Edwards et al., 1996; Paul and Zebarth, 1997).

Gaseous emissions of N from waste applications generally occur through volatilization of NH_3 and loss of N_2 and N_2O through nitrification–denitrification processes. These emissions are affected by waste characteristics, method of application, climatic conditions, and chemical and physical soil properties (Misselbrook et al., 1996; Lowrance et al., 1998). As much as 13% of applied NH_4 can be volatilized during irrigation before the effluent reaches the soil, with an additional 10 to 70% lost within 48 h after irrigation (Sharpe and Harper, 1997; Schilke-Gartley and Sims, 1993). Large losses of NH_3 can result in insufficient N availability for plant uptake or environmental degradation. Ammonia is the primary neutralizing agent for acid gases in the atmosphere and is a common component of atmospheric aerosols. Volatilization of NH_3 may result in eutrophication of natural ecosystems. Natural ecosystems are thought to be net sinks for NH_3 (Denmead et al., 1976; Hutchinson et al., 1972; Van Hove et al., 1987) and cropping systems have shown significant absorption capacity (Harper et al., 1987). Atmospheric NH_3 from agricultural sources has been implicated in forest decline (McLeod et al., 1990; Nihlgard, 1985) and species changes in European heathlands (Van Hove et al., 1987).

Nitrous oxide is a radiatively active trace gas that contributes to global warming and to the destruction of atmospheric ozone when it is converted to nitric oxide (Crutzen, 1981). Anthropogenic sources account for about 41% of total N_2O emissions, but the strength of individual sources is uncertain (Intergovernmental Panel on Climate Change, 1996). Consequently, better source strength estimates are required for all systems. Atmospheric concentrations of N_2O are increasing at about 1.5 μg m^{-3} yr^{-1} and stabilization of N_2O concentrations at current levels would involve reductions in anthropogenic emissions of more than 50% (Sanhueza and Zhou, 1996). The primary biogenic sources of N_2O are nitrification and denitrification of soil N (Knowles, 1982; Poth and Focht, 1985). Nitrous oxide emissions are favored by low oxygen (O_2) concentrations, high soil organic C, and NO_3 (Payne, 1981).

Several studies have shown that land application of animal waste increases both NH_3 (Lockyer et al., 1989; Whitehead and Raistrick, 1992) and N_2O emissions (Cabrera et al., 1994; Stevens and Cornforth, 1974; Egginton and Smith, 1986). These studies dealt with cattle and poultry manure or slurry applications and there is little information available concerning NH_3 and N_2O emissions associated with application of waste lagoon effluent. Our objectives were to quantify gaseous losses of

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Abbreviations: DOY, day of year.