Ammonia, Methane, and Nitrous Oxide Emission from Pig Slurry Applied to a Pasture in New Zealand

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ABSTRACT

Much animal manure is being applied to small land areas close to animal confinements, resulting in environmental degradation. This paper reports a study on the emissions of ammonia (NH_3), methane (CH_4), and nitrous oxide (N_2O) from a pasture during a 90-d period after pig slurry application ($60 \ m^3 \ ha^{-1}$) to the soil surface. The pig slurry contained 6.1 kg total N m^{-3}, 4.2 kg of total ammoniacal nitrogen (TAN = NH_3 + NH_4) m^{-3}, and 22.1 kg C m^{-3}, and had a pH of 8.14. Ammonia was lost at a fast rate immediately after slurry application (4.7 kg N $ha^{-1} \ h^{-1}$), when the pH and TAN concentration of the surface soil were high, but the loss rate declined quickly thereafter. Total NH_3 losses from the treated pasture were 57 kg N ha^{-1} (22.5% of the TAN applied). Methane emission was highest (39.6 g C $ha^{-1} \ h^{-1}$) immediately after application, as dissolved CH_4 was released from the slurry. Emissions then continued at a low rate for approximately 7 d, presumably due to metabolism of volatile fatty acids in the anaerobic slurry–treated soil. The net CH_4 emission was 1052 g C ha^{-1} (0.08% of the carbon applied). Nitrous oxide emission was low for the first 14 d after slurry application, then showed emission peaks of 7.5 g N $ha^{-1} \ h^{-1}$ on Day 25 and 15.8 g N $ha^{-1} \ h^{-1}$ on Day 67, and decline depending on rainfall and nitrate (NO_3) concentrations. Emission finally reached background levels after approximately 90 d. Nitrous oxide emission was 7.6 kg N ha^{-1} (2.1% of the N applied). It is apparent that of the two major greenhouse gases measured in this study, N_2O is by far the more important tropospheric pollutant.

THE NEED TO increase food production to keep pace with population growth and changing consumer tastes has led to a large increase in animal production (FAOSTAT, 1999), and problems related to disposing massive dung and urine quantities. The problem is exacerbated by disassociation of crop and livestock production (Bouwman and Booij, 1998; Ke, 1998). This has meant that the animal wastes cannot be returned to fields where feed was grown and used to provide nutrients for succeeding crops. Consequently, much animal manure is being applied to small land areas close to animal confinements, resulting in environmental degradation (Burton, 1997).

Applying manure or slurries to agricultural land can lead to ground water contamination by nitrate (NO_3)

after nitrification of the ammonium nitrogen (NH_4–N) present, and emission of NH_3 (European Centre for Ecotoxicology and Toxicology of Chemicals, 1994), CH_4 (Chadwick and Pain, 1997) and N_2O (Jarvis et al., 1994), all of which contribute to climate change. Methane and N_2O are greenhouse gases that contribute directly to climate change (Intergovernmental Panel on Climate Change, 1996). Ammonia, after deposition on land surfaces and water bodies and nitrification, acts as a secondary source of N_2O (Mosier et al., 1998), and may also decrease the capacity of soils to absorb CH_4 and act as a sink for this gas (Mosier et al., 1991, 1996). However, the magnitude of these direct effects and interactions is not known with certainty.

The Intergovernmental Panel on Climate Change (IPCC) has been coordinating the development of inventory methodologies for greenhouse gases (Intergovernmental Panel on Climate Change, 1997) and this has revealed the lack of information required to define appropriate factors for CH_4 and N_2O emission from different sources. For example, there is considerable doubt as to which emission factor should be used for calculating N_2O emission from redeposited NH_3 and the various organic forms of N used in agriculture (Mosier et al., 1998). In addition, the Intergovernmental Panel on Climate Change (1997) protocol assumes there is no CH_4 emission from animal slurry applied in the field, whereas Chadwick and Pain (1997) and Sommer et al. (1996) have shown in laboratory studies that CH_4 is emitted following pig and dairy slurry application to soil.

Developing strategies to reduce CH_4 and N_2O emissions from agricultural land requires an understanding of the production, emission, and consumption of these gases. In particular, studies are required on the interactions between these gases because it is of concern that strategies to reduce emission of one gas may increase emission of the other (Intergovernmental Panel on Climate Change, 1996). Consequently, it is necessary to measure emission of all three gases simultaneously in the system under study. This paper reports a study on NH_3, CH_4, and N_2O emission from a pasture under conditions recommended by the Intergovernmental Panel on Climate Change (1997), after pig (*Sus scrofa*) slurry application, to assist in defining suitable factors to calculate CH_4 and N_2O emissions. Micrometeorological methods are available for accurately measuring NH_3 volatilization in the field (Denmead et al., 1974; Denmead, 1983; Wilson et al., 1983; Schjoerring et al., 1992; Sherlock et al., 1995; Wood et al., 2000). Various chamber procedures for NH_3 have also been implemented in

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the field, but these can introduce experimental artifacts that alter the dynamics and extent of NH_3 volatilization (Freney et al., 1983; Black et al., 1985). Ammonia is very reactive with water compared with CH_4 and N_2O (Liss and Slater, 1974). The elevated NH_3 concentration in a static chamber will, consequently, reduce NH_3 emission from the soil covered by the chamber. The NH_3 emission, therefore, was measured with a micrometeorological mass balance technique (Wilson et al., 1983) that does not affect the NH_3 concentration above the soil amended with slurry. In contrast with NH_3, static chambers are the preferred current method for measuring surface fluxes of both CH_4 and N_2O since these gases are less reactive with water and are much less affected by increases in chamber headspace concentrations (Mosier et al., 1991). Also in contrast to NH_3, it is generally very difficult to detect the small concentration gradients of N_2O and CH_4 above the soil surface when these gases are being emitted. This is necessary for implementing micrometeorological techniques. Nevertheless, when comparisons between methods have been possible, little if any difference is observed between N_2O emissions measured with a micrometeorological technique and static chambers (Fowler et al., 1997). Consequently, we decided to use static chambers to measure N_2O and CH_4 fluxes in this study.

MATERIALS AND METHODS

Study Site

Gas emission was studied at a site 2 km from Lincoln University on the South Island of New Zealand (172°30′ E, 43°38′ S). The study site was a pasture having <1% slope on which sheep-grazing was discontinued two weeks prior to the experiment start. The pasture was a mixture of perennial ryegrass (*Lolium perenne* L.), white clover (*Trifolium repens* L.) and weeds. The pasture covered the soil completely and its height was approximately 5 cm during the course of the experiment. The soil at the site is classified as a Wakanui silt loam (Udic Dystrochrept) (Kear et al., 1967). Pig slurry was applied to a 20-m-radius circular plot at the rate of 60 m³ ha⁻¹ by a tanker fitted with a spreading bar at 1030 h on 9 Aug. 1995. Some properties of the soil and slurry are given in Table 1.

During the initial 10 d of NH_3 emission measurements, wind speed at 0.5 m was measured with a cup anemometer (Sensitive Anemometer T16108/2; Casella London Ltd., London) with a low stalling speed; soil temperatures at a 2.5-cm depth (LM

Table 1. Properties of the pasture soil and slurry used in the study.

Property	Soil	Slurry
Soil classification	Wakanui silt loam	
Clay, %	27	
Silt, %	67	
Sand, %	6	
pH	5.36	8.14
Amount applied, m³ ha⁻¹		60
Density, kg m⁻³		1053
Dry matter, kg m⁻³		43.8
Total C	25.6 g kg⁻¹	22.1 kg m⁻³
Total N	2.8 g kg⁻¹	6.1 kg m⁻³
TAN†	0.84 mg kg⁻¹	4.2 kg m⁻³
Nitrate N	2.9 mg kg⁻¹	0
CEC‡, cmol [Na⁺] kg⁻¹	15.4	

† Total ammoniacal nitrogen.
‡ Cation exchange capacity.

35 CZ; R.S. Components, Corby, UK) were measured and stored as 30-min averages on a datalogger (Campbell Scientific Ltd., Shepshed, UK), and wind direction was determined by a wind vane (Ota Keiki Seisakusho Co. Ltd., Tokyo). During the entire 0- to 90-d period of CH_4 and N_2O emission measurements, air temperature data (2 m), soil temperatures (10 cm), and rain and pan evaporation from a climate station (Crop & Food Research, Lincoln, NZ) within 400 m of the field were used.

Ammonia Emission

Measurements of NH_3 emission from the slurry-treated plot commenced immediately after slurry application on 9 August and continued for 10 d until NH_3 emission returned to background levels. The fluxes were determined by the mass balance micrometeorological method described in Sherlock et al. (1995). The mass balance method equates the average surface flux density of NH_3 from the circular plot amended with pig slurry to the difference between the integrated horizontal flux at a known downwind distance and that at the upwind edge (Wilson et al., 1983). With passive Leuning samplers (Leuning et al., 1985) mounted at several heights z (m), on masts placed at the upwind edge and at the center of the plot (radius 20 m), the net horizontal flux (F, g m⁻² s⁻¹) is derived from:

$$F = \frac{1}{x}\left(\sum_0^z \overline{uc}_{dw} - \overline{uc}_{uw}\Delta z\right) \qquad [1]$$

where x is the radius of the circular plot (20 m), $\overline{uc}$ is the mean horizontal flux (u is wind speed, m s⁻¹ and c is NH_3 concentration, g m⁻³) measured by each sampler at the downwind (dw) or upwind (uw) edge of the treated area. According to Leuning et al. (1985), $\overline{uc}$ is derived from:

$$\overline{uc} = \frac{M}{At} \qquad [2]$$

where M is the mass of NH_3–N collected (g) by oxalic acid coating the interior of the Leuning sampler during the sampling period t (s), and A is the effective cross-sectional area of the sampler (m²) determined in wind-tunnel calibrations. After exposure, the coating was dissolved in 0.040 L deionized water and the NH_4–N concentration (M) determined on a 0.0204 aliquot with an NH_3 specific ion electrode (HNU Systems, Newton, MA). The samplers were mounted on a mast in the center of the field at 0.2, 0.4, 0.8, 1.2, 2.4, and 3.6 m above the soil surface. Background measurements were made with samplers placed at 0.4 m and 1.2 m on a mast located on the upwind side of the treated area. The ammonia samplers were changed three times each day during the first 5 d (0900–1300, 1300–1700, and 1700–0900 h) and once a day (at 1300 h) during the period 6 to 10 d. (Note that on the day of slurry application the first sampling period extended from 1030 to 1300 h only).

As a backup, NH_3 flux was also determined with a second design of passive sampler (Ferm tubes) consisting of two parallel sampler units, each of which had three glass tubes (inner diameter 7 mm and lengths of 100, 100, and 23 mm) joined by silicone tubing (Schjoerring et al., 1992). The interior surface of the two 100-mm tubes was coated with oxalic acid for approximately 70 mm of the tube length. Glued to the end of the 23-mm tube was a stainless steel nozzle with a central hole of 1-mm diameter.

After exposure, the tubes were disconnected and the two 100-mm tubes analyzed separately. The coating was dissolved in 0.003 L deionized water and the NH_4–N content determined

by the indophenol blue colorimetric method with a flow injection analyzer (Tecator [Höganäs, Sweden] FIAstar).

The Ferm tube flux samplers were mounted on four masts at 0.2, 0.6, 1.2, 2.4, and 3.6 m above ground level, positioned at 0, 90, 180, and 270° angles around the circumference of the circular plot. The samplers continuously integrate the horizontal ammonia flux at the various heights. After analysis of the ammonia content in the tubes facing the NH₃ source (exposed tubes) and surroundings (background tubes), the net horizontal flux can be calculated for each measurement height. Knowing the net horizontal ammonia flux, the vertical flux from the experimental plot was obtained by applying mass balance equations.

The average horizontal NH₃ flux (F_{hm}, µg NH₃–N m^{-2} s^{-1}) through two glass tubes facing in the same direction at each measuring height (h) on each mast (m) either away from (background tubes) or toward (exposed tubes) the NH₃ source was calculated by the following equation:

$$F_{hm} = \frac{(C_1 + C_2)V}{2 \times \pi \times r^2 \times K \times \Delta t} \quad [3]$$

where C_1 and C_2 are the concentrations of NH₄ (µg NH₄–N L^{-1}) in either the two exposed tubes or the background tubes, V is the volume of deionized water used to dissolve the NH₄ sorbed in the tubes (0.003 L), r is the radius of the hole in the stainless steel disc (0.0005 m), t is the time (s) between the start and conclusion of the measurement, and K is a correction factor ($K = 0.77$; Schjoerring et al., 1992).

The horizontal net flux ($F_{net,h}$, µg NH₃–N m^{-2} s^{-1}) at each height was calculated by the equation (Schjoerring et al., 1992):

$$F_{net,h} = \sum_{m=1}^{m=4} (F_{hm,s} - F_{hm,b}) \quad [4]$$

where $F_{hm,s}$ is the NH₃ flux from the source measured with the exposed tubes and $F_{hm,b}$ is the flux from the background measured with the background tubes at each measuring height (h) and at each mast (m).

The vertical NH₃ flux from the plot (F_v, µg NH₃–N m^{-2} s^{-1}) was calculated by stepwise summation of the horizontal net flux over the height intervals represented by the flux samplers (Schjoerring et al., 1992):

$$F_v = \frac{1}{x}\sum_{h=1}^{h=5} F_{net,h}\Delta h \quad [5]$$

where Δh is the height interval represented by the flux samplers and x (20 m) is the diameter of the experimental plot.

Methane and Nitrous Oxide Emissions

Measurements of CH₄ and N₂O emission with a closed chamber technique (Hutchinson and Mosier, 1981) commenced immediately following slurry application on 9 August and continued until 7 November. Emission was measured from microplots formed by pushing steel cylinders (24-cm diameter) into the soil. Five cylinders were placed in the slurry-treated plot and four cylinders were located on untreated soil upwind of the plot. Cylindrical gas-tight lids, having a headspace height of 10 cm and fitted with rubber septa for sampling, were attached to the steel cylinders during gas emission measurements, but were left open between measurements. Changes in headspace CH₄ and N₂O concentrations were used for calculating gas fluxes. Gas samples were collected with 50-mL syringes at 0, 10, and 20 min after lid closure. Samples were collected twice a day during the first 5 d, twice every second day during the period 5 to 11 d, once a day during the period 11 to 60 d, and once every second day during 60 to 90 d. Emission was

measured at 1000 and 1600 h when two measurements were taken per day and at 1200 h on the other measurement days.

The gas samples were injected via a 10-port sampling valve into a carrier stream of N₂, and a four port-switching valve directed the carrier gas stream to either of two gas chromatographs for CH₄ or N₂O determination. Methane was determined on an SRI (Torrance, CA) instrument equipped with a flame ionization detector. Nitrous oxide was determined on a Varian (Walnut Creek, CA) Aerograph Series 2800 equipped with a ⁶³Ni electron-capture detector (Pye-Unicam, Cambridge, UK) and a stainless steel column (4-m length, 3-mm internal diameter) packed with Porapak Q (80/100 mesh) (Alltech Associates, Deerfield, IL). Detector and column temperatures were 350 and 20°C, respectively.

In general, CH₄ and N₂O fluxes were calculated with the logarithmic equation described by Hutchinson and Mosier (1981). At times when gas fluxes were small, they were determined with a linear equation.

Soil and Manure Analysis

Pig slurry was sampled from the slurry spreader and stored at 4°C until analysis. Pig slurry dry matter was determined gravimetrically, slurry density by weighing an aliquot of 20 mL in a graduated flask, total N and total C with a mass spectrometer (Tracermass; Europa Scientific, Crewe, UK), and NH₄ and NO₃ on a flow injection analyzer (Tecator FIAstar).

Soil samples (0–5 cm) were collected immediately before slurry application, three times per day for the first 5 d after application, once per day from 6 to 10 d, three times per week during 10 to 20 d, twice per week during 20 to 60 d, and once every second week during 60 to 90 d. Five replicate samples were taken on each occasion. Soil samples were well mixed in a field laboratory at the site and stored at temperatures less than 4°C until analysis. The pH of soil and canopy surfaces was measured with a portable pH meter and a flat surface pH electrode. Soil NO₃, TAN, and volatile fatty acids were extracted with 2 M KCl (2 KCl to 1 soil, w/w). These suspensions were shaken for 30 min and filtered through Whatman (Maidstone, UK) #42 filter paper. Ten milliliters of each sample was used to determine NO₃–N and TAN, with standard colorimetric techniques (Keeney and Nelson, 1982), on a FI-Astar 5010 analyzer (Tecator). Five milliliters of the extract was used to determine volatile fatty acids. To each aliquot, 0.5 mL of 0.3 M oxalic acid and 0.5 mL of pivalic acid (25 000 mg L^{-1} in 0.3 M oxalic acid) as an internal standard were added. The mixture was centrifuged at 16 000 rpm for 10 min, the supernatant was passed through a 0.45-µm filter, and the resulting filtrates were stored at −18°C until analysis. The C₂–C₅ fatty acids in the filtrates were determined on a Shimadzu (Kyoto, Japan) GC-7A gas chromatograph equipped with a flame ionization detector (140°C) and a glass column (1.8-m length, 4-mm internal diameter) packed with Tenax GC (60/80) and FAL-M (Buchem BV, Apeldoorn, the Netherlands). Injector and oven temperatures were maintained at 210 and 136°C, respectively. The carrier gas was N₂ adjusted to a flow rate of 60 mL min^{-1}.

Calculations and Statistics

It has been shown that NH₃ loss from both flooded and nonflooded fields is determined by two main variables, the equilibrium NH₃ concentration and the wind speed (Freney et al., 1985; De Datta et al., 1989; Sherlock et al., 1995). Ammonia is lost from solution at the soil's surface when the NH₃ gas concentration in equilibrium with the solution is greater than that of the atmosphere. Increasing wind speed increases

the volatilization rate by promoting more rapid NH_3 transport away from the surface. Immediately after applying animal slurry, urine, or fertilizer, the equilibrium NH_3 concentration is much greater than that in the ambient atmosphere, thus the latter can be ignored and the relationship between the main variables is described by:

$$F \propto u[NH_3]_{gas} \qquad [6]$$

where F is the vertical flux of NH_3 (μg N m^{-2} s^{-1}), $[NH_3]_{gas}$ is the concentration of NH_3 gas (μg N m^{-3}) in equilibrium with NH_3 dissolved in the soil solution ($[NH_3]_{solution}$, μg N m^{-3}), and u is wind speed (m s^{-1}). The equilibrium ammonia concentration ($[NH_3]_{gas}$) is determined from the TAN concentration, pH, and temperature of the solution at the soil surface (Emerson et al., 1975; Hales and Drewes, 1979; Denmead et al., 1982; Sherlock et al., 1995) as follows:

$$[NH_3]_{gas} = [NH_3]_{solution}/K_H \qquad [7]$$

$$[NH_3]_{solution} = \frac{[TAN]}{1 + ([H_3O^+]/K_N)} \qquad [8]$$

where TAN is $NH_3 + NH_4$ (μg N m^{-3}), K_N is the equilibrium constant for NH_4 dissociation, and K_H is Henry's law constant for the distribution between $[NH_3]_{solution}$ and $[NH_3]_{gas}$. The relationships between these equilibrium constants and temperature (T) in Kelvin (K = 273 + °C) are:

$$\log K_H = -1.69 + 1477.7/T \qquad [9]$$

$$\log K_N = -0.09018 - 2729.92/T \qquad [10]$$

The effect of environment and soil composition on N_2O emission was analyzed by means of linear regression analysis (Stepwise; SAS Institute, 1989).

RESULTS

Manure and Climate

The pig slurry used (Table 1) was similar in composition to slurries studied in Europe (Japenga and Harmsen, 1990; Sommer and Husted, 1995), but contained more dry matter and plant nutrients than the slurry employed in a previous experiment by Sommer and Sherlock (1996). Daily mean air temperature during the course of the study increased from 7 to 18°C with considerable fluctuations of up to 10°C between days (Fig. 1A). During the same period, the mean soil temperature at a 10-cm depth increased from 6 to 17°C, with fluctuations between days of approximately 2°C. Little rain fell during the first 19 d (Fig. 1B), but the next 8 d were reasonably wet with 20 mm of rain on Day 20, 5 mm on Day 24, and 25 mm on Day 28. No rain fell between Days 29 and 46, but there were numerous rainfall events between Days 46 and 90 when between 0.5 and 25 mm rain fell per day (Fig. 1B). Pan evaporation was generally greater than rainfall (Fig. 1C), thus the soil dried between major rainfall events (Fig. 1D).
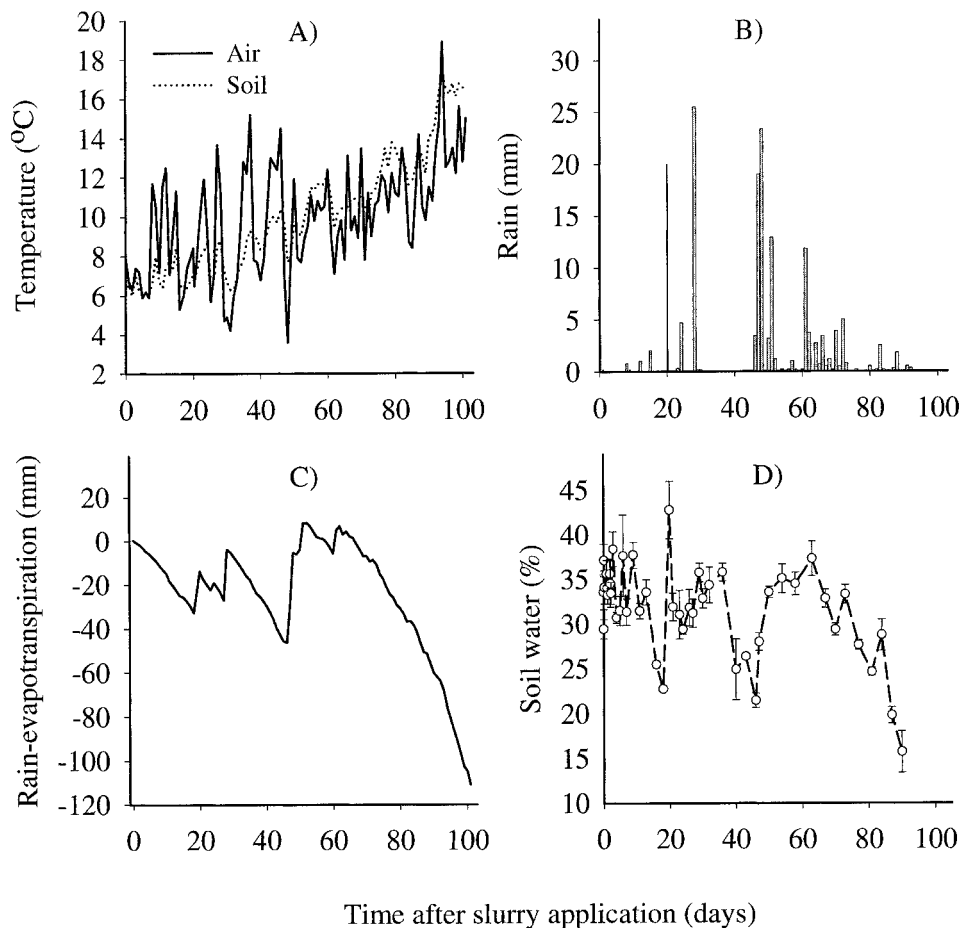

Fig. 1. Daily mean soil temperature at 10 cm and air temperature (*A*), rainfall (*B*), rainfall − evapotranspiration (*C*), and soil water content (*D*) during the duration of the study. Error bars are ±1 SD.

After 65 d, the discrepancy between evaporation and rainfall increased markedly (Fig. 1C) and the soil moisture content fell to approximately 15% (Fig. 1D). The wind speed varied from 0.63 to 2.83 m s^{-1} during the first 3 d after slurry application.

Soil Composition

The surface soil pH increased from 6.3 to 8.1 immediately after slurry application. The pH then rose to 8.3 (probably due to the loss of carbon dioxide; Sommer and Sherlock, 1996), remained at that level for approximately 3 d, and then decreased slowly to 7.7 on Day 16 (Fig. 2A). Immediately after application the NH₄–N
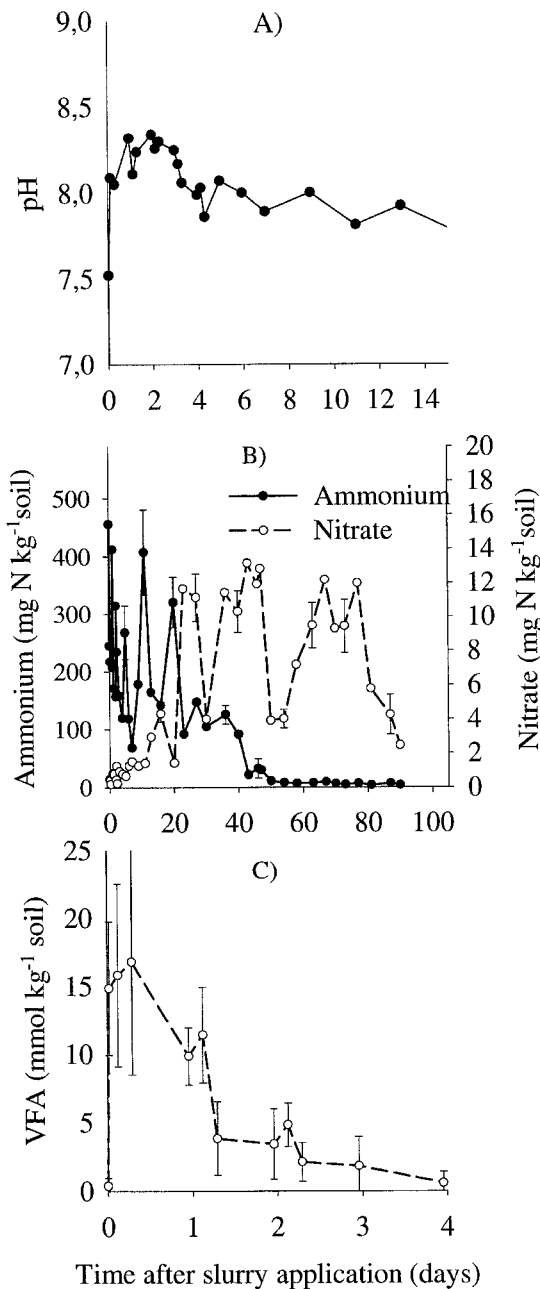
concentration in the 0- to 5-cm surface soil layer was approximately 460 mg kg^{-1} soil. The NH₄–N concentration fluctuated between 400 and 60 mg kg^{-1} soil over the next 22 d, remained around 100 mg kg^{-1} soil until Day 40, and then decreased to background levels on Day 52 (Fig. 2B).

The TAN concentration in the soil solution before slurry application was 20 mg L^{-1}. When the slurry was applied, TAN in the soil solution at the surface was equal to that in the solution applied, 4200 mg L^{-1}. This decreased to 1026 mg L^{-1} 3 h after slurry application and fluctuated around 713 mg L^{-1} for the next 2.5 d. It declined to background values on Day 52 (Fig. 2B).

Pig slurry application decreased the NO₃ concentration in the 0- to 5-cm soil layer from 2.9 to 0.2 mg N kg^{-1} soil. There was little change in the NO₃ concentration of the top 5 cm of soil until Day 10 when approximately 3 mm rain fell. After 20 mm rain fell on Day 20, the NO₃ concentration in the surface soil decreased from 4 to 1.2 mg N kg^{-1} soil and then increased rapidly to approximately 11.4 mg N kg^{-1} soil (Fig. 1B and 2B). The NO₃ concentration fell again after rain on Days 30 and 50 and returned to approximately 12 mg N kg^{-1} soil on each occasion. It finally decreased to the background value around Day 90 (Fig. 2B).

The concentration of volatile fatty acids in the soil solution declined from approximately 15 mM kg^{-1} soil just after slurry application to 4 mM kg^{-1} soil within 1.5 d (Fig. 2C). It then slowly decreased over the next 3 d to 0.8 mM kg^{-1} soil, which was not significantly different from the background concentration of 0.6 mM kg^{-1} soil.

Ammonia Emission

In the first 2.5-h period after slurry application, NH₃ was lost at a rate of 4.7 kg N ha^{-1} h^{-1}. In the next 4-h period, NH₃ was lost at about half the initial rate (2.2 kg N ha^{-1} h^{-1}) and overnight the rate dropped to 0.26 kg N ha^{-1} h^{-1} (Fig. 3A). After Day 1, NH₃ volatilization rates declined markedly to average daytime and nighttime rates over the next 2 d of 0.57 and 0.11 kg N ha^{-1} h^{-1}, respectively (Fig. 3A). Ammonia was lost at faster rates in the morning session (900–1300 h) than in the afternoon session (1300–1700 h) and the overnight rates

Fig. 2. Changes in surface soil pH (*A*), NO₃ and NH₄ concentrations (*B*), and volatile fatty acids (VFA) (*C*) in the pasture soil following slurry application. Error bars are ±1 SD.
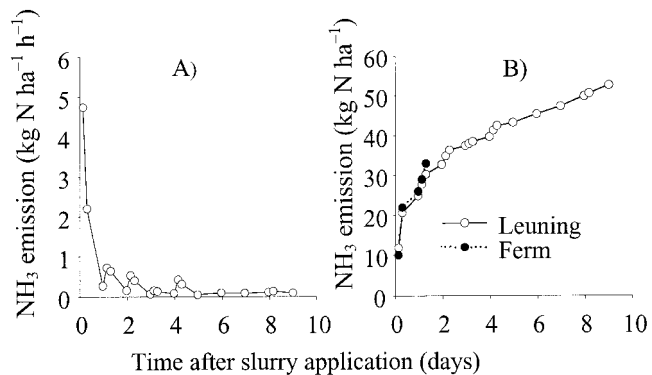

Fig. 3. Ammonia emission from the slurry amended area during the study (*A*) and cumulative NH₃ loss in Leuning samplers and Ferm tubes (*B*).

Table 2. Accumulated flux of gases from a pasture after pig slurry application in late winter and spring.

| | Emission during 12 d after slurry application | | Emission during the experiment | | Net emission |
	Slurry-amended plot	Untreated area	Slurry-amended plot	Untreated area	Slurry-amended plot
			g ha^{-1}		
NH$_3$–N	57 000	0	57 000	0	57 000
CH$_4$–C	1 065	−26†	858‡	−194	1 052
N$_2$O–N	442	534	8 134	534	7 600

† The control area absorbed 26 g C ha^{-1} during the 12 d methane was emitted and 194 g C ha^{-1} overall.
‡ The slurry-treated plot absorbed 207 g C ha^{-1} after methane emission ceased.

were always low (Fig. 3A). As a result of the fast rates of loss, 24.8 kg N ha^{-1} was lost on Day 1 (Fig. 3B; equivalent to 6.8% of the applied N or 9.8% of the TAN). During the next two days, 7.8 and 4.8 kg N ha^{-1} were lost, and thereafter until Day 9, NH$_3$ was lost at the rate of approximately 2.5 kg N ha^{-1} d^{-1}. Little NH$_3$ was volatilized after Day 10. The total NH$_3$ emission was 57 kg N ha^{-1} (Table 2), corresponding to 15.5% of the total nitrogen applied to the field in pig slurry or 22.5% of its original TAN content. It can be seen from Fig. 3B that the results for NH$_3$ loss obtained with the Ferm tubes (Schjoerring et al., 1992) were similar to those obtained with the passive samplers of Leuning et al. (1985).

As the slurry applied had a high TAN concentration (4.2 kg N m^{-3}) and a high pH (8.14), the equilibrium NH$_3$ concentration ([NH$_3$]$_{gas}$) at the beginning of the study was high. Its concentration decreased with time. The product of [NH$_3$]$_{gas}$ and wind speed also decreased with time, and there was a very strong linear relationship between NH$_3$ loss and this product:

$$F = 89 \times 10^{-4}[NH_3]_{gas} \times u - 19.95; r^2 = 0.9423 \quad [11]$$

Methane

Methane emission commenced at the very fast rate of 39.33 g C ha^{-1} h^{-1} immediately after pig slurry application and decreased to 10 g C ha^{-1} h^{-1} within 6 h (Fig. 4A). The CH$_4$ emission rate then decreased, but emission continued at a lower rate for approximately 7 d. Thereafter, CH$_4$ flux measurements indicated net uptake of atmospheric CH$_4$ by the treated plot (Table 2). The control plot absorbed CH$_4$ from the atmosphere at the rate of 9.1 µg C m^{-2} h^{-1} throughout the study period.

Except for the first flux measurement, the CH$_4$ flux (F_{CH4}) from the slurry-amended plot was linearly related to the volatile fatty acids (VFA) concentration in the soil:

$$F_{CH4} = 0.170VFA + 0.026; r^2 = 0.948 \quad [12]$$

during the period 2 h to 11 d after slurry application (Fig. 4B). The emission immediately after slurry application was considerably faster than that after 1 h, which suggested that the first burst of CH$_4$ gas originated from CH$_4$ dissolved in the slurry. The regression between subsequent emissions and the disappearance of volatile fatty acids in the soil suggests that the subsequent CH$_4$ was produced in the soil from organic matter supplied in the slurry. In the 12 d immediately following application, 1065 (SE ± 425) g CH$_4$–C ha^{-1} was emitted from the slurry-amended plot, of which 26% was emitted within 1 h and 46% within 6 h. The subsequent small net sink activity from the treated area over the following 78 d amounted to 207 (±16) g CH$_4$–C ha^{-1}. The net emission from the slurry-amended plot, therefore, was 858 g CH$_4$–C ha^{-1}. During the experiment the control area absorbed 194 g CH$_4$–C ha^{-1}, consequently the net emission from the treated area was 1052 g CH$_4$–C ha^{-1}.

Nitrous Oxide

At all times emissions from the slurry-treated plot were significantly greater than those from the untreated control plots (approximately 0.08 g N ha^{-1} h^{-1}; Fig. 5). Nitrous oxide emissions from the slurry-amended plot were low (1 g N ha^{-1} h^{-1}) for the first 14 d after applica-
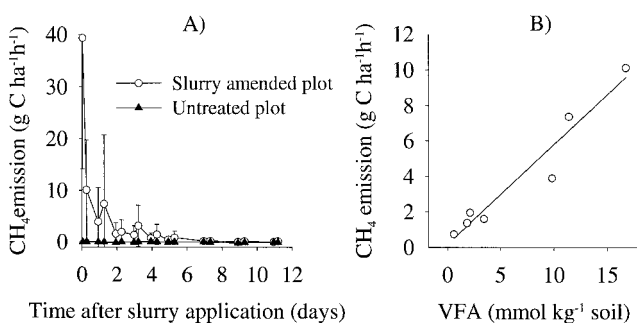
Fig. 4. Methane emission from the slurry amended area, and the control areas during the study (A), and the relationship between CH$_4$ emission and the volatile fatty acid concentration in the 0- to 5-cm surface layer of soil (B). Error bars are ±1 SD.
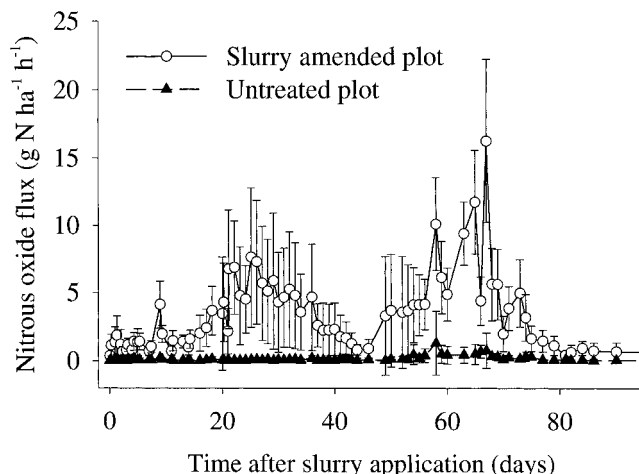
Fig. 5. Nitrous oxide emission from the slurry amended area and the control areas during the study. Error bars are ±1 SD.

tion, when the NO_3 concentration in the 0- to 5-cm surface soil layer was low. In the 11 d that followed, the NO_3 concentration in the surface soil increased (Fig. 2B), and N_2O emissions increased to a peak of 7.5 g N $ha^{-1} h^{-1}$. The emissions then declined to approximately 1 g N $ha^{-1} h^{-1}$ after 20 d of rain-free weather (Fig. 1B). Nitrous oxide fluxes then increased in response to rain to create a second peak flux of 15.8 g N $ha^{-1} h^{-1}$, 67 d after slurry application. The subsequent decline in daily N_2O flux over the next 23 d to background values coincided with low rainfall and low mineral N in the soil layer (Fig. 1B and 2B).

DISCUSSION

Loss Patterns

Pig slurry consists of a mixture of urine, feces, used bedding, waste feed, and other residual organic matter. In stored slurry, urea (added in urine) is hydrolyzed, providing NH_3 and alkalinity, CH_4 is produced through the degradation of organic compounds under anaerobic conditions, and nitrification is inhibited (Husted, 1994). The composition of the pig slurry manure applied in this study is similar to the composition of manures analyzed in Europe (Sommer and Hutchings, 2001).

The fastest rate of NH_3 loss occurred immediately after application, and the loss rate then decreased quickly with time (Fig. 3A). In contrast, when urea or urine is added to the soil surface, little NH_3 is lost initially and the maximum rate of loss does not occur until two or three days after application, and thereafter the loss rates decline slowly (Sherlock et al., 1995). The differing patterns at the beginning seem to be due to the composition of the material added. With fertilizer or urine, urea has to be hydrolyzed to produce NH_3 and a source of alkalinity before any loss could occur, whereas the slurry contained a high TAN concentration and had a high pH, and thus NH_3 could be lost immediately.

As noted above (Eq. [11]), a very strong relationship was found between the vertical flux density of NH_3 and the product of $[NH_3]_{gas}$ and wind speed, following pig slurry application to a pasture soil. In studies on NH_3 losses following urea and urine application to unsaturated soils (Sherlock et al., 1995) the coefficients of inclination (slopes) of the comparable relationships were 0.69×10^{-4} after urea application and 0.9×10^{-4} after urine application. The slope in this current study was higher due to the different approach used to sample the soil, that is, in the study of Sherlock et al. (1995) soil was sampled by scraping off the top few millimeters of the soil surface, while in this current study soil samples were taken from the 0- to 5-cm depth. The TAN concentration will be lower when taking a 0- to 5-cm sample than in a sample from the topsoil of slurry- or urea-amended soil, and therefore the $[NH_3]_{gas} \times u$ product is lower.

The reasons for the low NH_3 emission rates after the initial fast rate are uncertain. In the case of urea or urine the slow decline in loss rates may be due to acidifi-

cation of the soil surface as a result of NH_3 loss, leaching of urea below the soil surface by rainfall, oxidation by nitrifying organisms, reaction with the cation exchange complex, immobilization, and uptake by plants. While many of these factors would have operated to reduce NH_3 loss after slurry application, none of them seems to be responsible for the rapid decline in NH_3 loss rates on Day 1. The pH of the surface soil actually increased slightly during the first 3 d (Fig. 2A), there was little rainfall to leach the slurry into the soil during the first 20 d (Fig. 1B), and little NO_3 was produced until after Day 20. The soil has considerable cation exchange capacity (15.4 cmol $[Na^+] kg^{-1}$), and NH_4 would be adsorbed on the cation exchange complex in the surface soil as the slurry infiltrated. Immobilization would be expected to occur, especially as organic carbon was added in the slurry (Comfort et al., 1988; Kirchmann and Lundvall, 1993), but considerable NH_4 remained in the soil until Day 40, and only 22.5% of the TAN was lost as NH_3. Nitrogen uptake by plants should have been slow and small because the surface cover was small and growth slow because of the low soil and air temperatures. However, Thompson et al. (1990) studied NH_3 loss from slurries in the absence of soil and concluded that the decline in NH_3 loss rates was due to the formation of a crust on the slurry surface. With time, the crust becomes thicker and the slurry more viscous, thereby increasing resistances to diffusion within the slurry. The TAN in the crust surface can then become depleted due to NH_3 volatilization (Sommer and Olesen, 2000).

The changes in the physical nature of the slurry would also restrict oxygen diffusion and ensure that the slurry remained anaerobic for up to 20 d, thus allowing CH_4 formation in situ, and limiting NH_4 nitrification (Fig. 2B). The addition of carbon in the slurry would stimulate microbial activity in the soil, rapidly consume any available oxygen present (Firestone, 1982), and guarantee that the slurry-treated surface soil remained anaerobic. The CH_4 emission from the treated pasture at a rate of 39.6 g C $ha^{-1} h^{-1}$ immediately after slurry application indicates that this CH_4 was formed in the slurry pit prior to application, as there would not have been sufficient time for its formation in soil (Fig. 4A). It is noteworthy that this initial peak CH_4 emission is not high in relation to the likely CO_2 emissions. For example, Dendooven et al. (1998) measured average CO_2 emission rates of 23 kg CO_2–C $ha^{-1} d^{-1}$ (960 g CO_2–C $ha^{-1} h^{-1}$) during the 28 d following pig slurry application (40 000 kg ha^{-1}) to a bare soil. Further, small amounts of CH_4 originating from this initial source may have diffused out from the viscous layer over the next few hours. However, the strong correlation between CH_4 emission and volatile fatty acids (Fig. 4B) suggests that the CH_4 emissions over the next 7 d were more likely to have arisen in the anaerobic soil layer from the metabolism of volatile fatty acids supplied in the slurry. The duration of CH_4 emission was longer than that observed previously (Sommer et al., 1996). The low temperatures may have caused this during the experiment, as it is known that CH_4 production is strongly related to temperature (Zeikus and Winfrey, 1976).

Table 3. Linear regression analysis (stepwise procedure) of nitrous oxide (N_2O) emission (g N ha^{-1} d^{-1}) from a pasture amended with pig slurry (1–90 d). The full model is significant ($P < 0.0001$, df = 30) with an R^2 of 0.6727.

Variable†	df	Estimate	Standard error	T for H_0	$P > |T|$	Partial r^2
Intercept	1	−74.7828	49.42681	−1.5	0.143	
(0) Nitrate	1	4.7094	3.0291	1.55	0.1331	0.1942
(0) Rain*	1	−22.21939	9.80682	−2.27	0.0328	0.0631
(1) Rain**	1	5.78517	1.88698	3.07	0.0053	0.0450
(1) Air temperature*	1	12.69788	5.36952	2.36	0.0265	0.0573
(0) Incident solar radiation**	1	5.97654	2.19186	2.73	0.0118	0.0505
Σ (Rain − evaporation)***	1	4.39803	0.76016	5.79	<0.0001	0.2556

* Significant at the 0.05 probability level.
** Significant at the 0.01 probability level.
*** Significant at the 0.001 probability level.
† The number before the variable denotes whether the variable pertains to the day of flux measurements (0) or the day before (1).

As discussed above, slurry addition appeared to restrict oxygen diffusion and the surface soil remained anaerobic for a lengthy period. While this limited nitrification for the first 14 d after application, it did not completely prevent it, as some NO_3 was formed (Fig. 2B) and some N_2O was emitted (Fig. 5). The likely sequence of reactions responsible for the small NO_3 and N_2O production seems to be the same as those operating in flooded soils, namely (i) NH_4 in the slurry diffused to a zone in the soil containing residual oxygen, (ii) this NH_4 was oxidized to NO_3 by nitrifying organisms, (iii) the NO_3 formed diffused back to the anaerobic zone, (iv) denitrification occurred with N_2O and N_2 production, and (v) the gaseous products diffused through the anaerobic layer to the atmosphere. During the diffusion through the anaerobic layer, N_2O may have been further reduced to N_2, resulting in little N_2O emission (Patrick, 1982; Petersen et al., 1992).

The initial peak in N_2O emission occurred during a period of active nitrification (Fig. 2B) and may have resulted from nitrification as well as by denitrification of the resulting NO_3 (Jarvis et al., 1994; Lessard et al., 1996). However, the second peak occurred when NH_4 concentrations were low (Fig. 2B), and NO_3 concentrations (Fig. 2B) and soil moisture contents (Fig. 1D) were high, and thus appears to be mainly the result of denitrification. Lessard et al. (1996) have shown that both nitrification and denitrification may be sources of N_2O within soils amended with manure N but that the relative contribution of the two processes could not be quantified. In this study the pool of NH_4 was significantly higher than the NO_3 pool during 0 to approximately 30 d after slurry application (Fig. 2B). Consequently, NH_4 oxidation may have been the most prominent source of N_2O emission in this period (Jarvis et al., 1994). After 30 d the NH_4 pool was nearly depleted while the pool of NO_3 was significantly higher. Thus, NO_3 may have been the major N_2O source from 30 d until the conclusion of the experiment at 90 d.

The N_2O emission was slightly greater at 1600 than at 1000 h during days when emissions were measured twice daily, indicating a diurnal variation. Therefore, estimates of accumulated N_2O emissions may be influenced by the sampling times selected, for example, estimated emissions would be higher from measurements performed at 1600 than at 1000 h (Brumme and Beese, 1992; Granli and Bøckman, 1994; Thornton et al., 1996). The diurnal variation was largely related to warming of

soil during the day. We therefore assumed that N_2O fluxes measured around noon would represent the average diurnal flux, and statistical analysis was performed with N_2O emission rates and average daily climate data. Nitrous oxide emission was correlated ($P < 0.15\%$) to the NO_3 concentration in the topsoil (Table 3), confirming that most of the N_2O emitted originated from NO_3. Cumulative net precipitation and rain the day before a measurement had a significant positive effect on N_2O fluxes ($P < 0.01$). This is consistent with stimulation of NO_3 denitrification due to water saturation, which induces anoxic conditions in the soil. Rain on the day of measurement had a negative significant effect ($P < 0.05$) on N_2O emission. Rain causes an immediate increase in soil water content to above field capacity in the topsoil and air-filled porosity will be very low under this condition. Consequently, N_2O gas has to be transported by slow diffusion through water instead of a faster combination of diffusion and convection in soil air. This change in transport mechanism reduces the N_2O flux until the soil water is again less than or equal to field capacity. Air temperature and incident solar radiation has a positive significant effect on N_2O emission (Table 3). The increase with air temperature and incident solar radiation may be due to a reduced solubility of N_2O in soil solution at increasing temperatures or an increase in N_2O production with temperature (Müller et al., 1997).

Amounts Lost

The ammonia amounts lost from pig slurry in this study were within the range found in other studies (e.g., Bless et al., 1991; Moal et al., 1995; Sommer and Olesen, 2000) where losses of up to 67% of TAN contained in the slurry were reported. The relatively low loss in the current study (22.5% of the TAN) is most likely due to the lower air and soil temperatures.

It is considered that animal slurries applied to soil do not constitute an important source of CH_4 (Intergovernmental Panel on Climate Change, 1996), but very few studies appear to have been made on the amounts lost from pig slurry after surface application to field soils. Chadwick and Pain (1997) investigated the effect of soil and slurry type on CH_4 emissions under laboratory conditions and showed that most of the CH_4 emitted was derived from the slurry, that emissions declined to background levels after 48 h, and that more CH_4 was

emitted from pig slurry than cattle slurry when applied to a clay soil. In another laboratory study, Sommer et al. (1996) found that 30 g were emitted from a silt loam after applying the equivalent of 50 000 kg slurry per hectare. In that study the bulk of the CH$_4$ (90%) was emitted within 4 h of slurry application. In the current study, the net CH$_4$ emission was 0.07% of the carbon applied, and 46% of the total was lost within 6 h.

Simple integration and extrapolation of the daily emissions gives a total emission of 7.6 kg N$_2$O-N ha^{-1} during the course of this study (2.1% of slurry N applied). Petersen (1999) reported accumulated N$_2$O emissions between 0.14 and 0.64% of total N during a period of 6 to 8 weeks between slurry application and when crop uptake had depleted the inorganic N pools in the soil. Higher emissions reported in this study may be due to lower crop uptake of the mineral N applied in the manure. Based on data from long-term experiments with a variety of mineral and organic fertilizers, Mosier et al. (1998) recommend that only one factor should be used for calculating the N$_2$O emission from different fertilizer types:

$$N_2O \text{ emitted} = 1.25\% \text{ of N applied (kg N ha}^{-1})$$

although it is acknowledged that more data are required before final emission factors can be allocated. The results of our study may assist in assigning a suitable factor for calculating N$_2$O emission following animal slurry application to agricultural land. In the current study, N$_2$O emission was 2.1% of the total N applied in the slurry, which is much greater than the emission factor proposed for inorganic and organic fertilizers.

Interactions

Aerobic soils constitute one of the most important sinks for atmospheric CH$_4$ (Intergovernmental Panel on Climate Change, 1996). However, the capacity of soils to absorb CH$_4$ and oxidize it to CO$_2$ (Knowles, 1993) is reduced by agricultural practices that affect N cycling. This occurs because of the close relationships between pathways for NH$_3$ and CH$_4$ oxidation (Steudler et al., 1989; Mosier et al., 1991). There have been a number of studies on the effects of fertilizer N and cultivation on CH$_4$ uptake, and the effect is greater in some soils than in others and in general NH$_4$ addition has a greater effect than NO$_3$ addition (e.g., Adamsen and King, 1993; Delgardo et al., 1996; Hütsch et al., 1994; Mosier et al., 1991, 1997; Willison et al., 1995). However, there have been few studies on the effect of slurry application on CH$_4$ uptake (e.g., Hansen et al., 1993).

Two effects would be expected, a direct effect of the TAN from the slurry on the treated area and an indirect effect due to deposition of volatilized NH$_3$ on the surrounding countryside. When NH$_3$ is emitted into the atmosphere, some is absorbed by vegetation, some is dissolved in atmospheric water, converted to aerosols, and transported long distances (1000 + km), and some is deposited nearby (Ferm, 1998). Model estimates indicate that about 50% of the emitted NH$_3$ is deposited on land or water surfaces within 50 km of the source

(Ferm, 1998). When NH$_3$ or NH$_4$ is deposited back onto soil the capacity of the soil to take up atmospheric CH$_4$ may be affected.

After 12 d when CH$_4$ contained in the slurry had been emitted and production in the soil had ceased, atmospheric CH$_4$ was absorbed by the treated area. During the next 78 d, 207 (SE $\pm$ 16) g CH$_4$–C ha^{-1} (9.7 μg C m^{-2} h^{-1}) were absorbed by the treated area. Thus, the slurry treatment did not reduce the capacity of the soil to absorb CH$_4$. In the control plots, CH$_4$ absorption during the same time period amounted to 194 (SE $\pm$ 9) g CH$_4$–C ha^{-1} (9.1 μg C m^{-2} h^{-1}). Thus, the addition of the slurry had essentially no effect on CH$_4$ uptake. The CH$_4$ uptake in the slurry-treated area was similar to that on the unfertilized area of Hansen et al. (1993) in Norway (9.7 μg C m^{-2} h^{-1}) and almost twice that in the area they had treated with cattle slurry (5.9 μg C m^{-2} h^{-1}).

Total ammoniacal nitrogen added in the slurry would be expected to contribute to the burden of N$_2$O in the atmosphere in two ways, directly by nitrification and denitrification on the treated area, and indirectly by metabolism of deposited NH$_3$ on the surrounding countryside (Mosier et al., 1998). As noted above, the direct emission was 7.6 kg N ha^{-1}, and the indirect effect is 0.6 kg N ha^{-1} (calculated from the emission factor proposed by Intergovernmental Panel on Climate Change [1997] and Mosier et al. [1998], namely 0.01 times the amount of NH$_3$ emitted, 57 kg N ha^{-1}), giving a total of 8.2 kg N$_2$O-N ha^{-1}.

CONCLUSIONS

This work has clearly shown that, of the two major greenhouse gases measured following the slurry application, N$_2$O is by far the more important tropospheric pollutant. The quantity of N$_2$O emitted was more than seven times that of the CH$_4$. Furthermore, when scaled according to their global warming potentials and expressed in CO$_2$ equivalents, the N$_2$O emission equates to 3700 kg CO$_2$ while the CH$_4$ emitted equates to only 29 kg CO$_2$. This direct comparison does not include the indirect N$_2$O emissions from the volatilized NH$_3$ that has been deposited on land or water bodies. The current IPCC default emission factor for N$_2$O released from volatilized NH$_3$ after deposition is 0.01 (Intergovernmental Panel on Climate Change, 1997). Thus, the N$_2$O from that additional source could be expected to contribute a further 277 kg of CO$_2$ equivalents as a consequence of this slurry application.

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