Effects of slurry pre-treatment and application technique on short-term N_2O emissions as determined by a new non-linear approach

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ABSTRACT

Direct injection of slurry is increasingly used to mitigate odour and ammonia emissions, but this may be at the expense of higher denitrification and N_2O emission rates. This study investigated how injection technique and slurry pre-treatment influence distribution and turnover of slurry nitrogen, and losses via N_2O. Two field experiments were carried out on a loamy sand. Pig slurry was applied to established crops, i.e., to spring barley (*Hordeum vulgare* L.) in May 2007, and to winter wheat (*Triticum aestivum* L.) in April 2008. In 2007 the slurry was applied by direct injection using either winged or straight tines. In 2008, three slurry types (digested, separated or untreated) were applied by straight tine injection. In both years band spreading of the slurries by trail-hose application was included as reference. Nitrous oxide emissions were quantified using static chambers for up to 44 days after slurry application. A new flux calculation method (HMR) was applied. With HMR, flux estimation is based on non-linear regression using a single-parameter criterion. In connection with gas samplings, soil cores were collected to 20-cm depth within and between bands for analysis of mineral N. Short-term emissions of N_2O corresponded to 0.3–1.5% of the N applied in 2007, and to 0.3–0.7% in 2008. In 2007 N_2O emissions were higher with injection than with surface application of slurry, while there was no consistent difference between the two injection techniques. In 2008 there was no effect of application method, and N_2O emissions from untreated, digested and separated slurry were similar, although higher N_2O emissions from treated slurry were indicated. A conceptual model to explain the observed patterns of N_2O is discussed. Accounting for the indirect emissions of N_2O associated with NH_3 volatilization, production of synthetic fertilizer N and energy used for slurry injection, the overall greenhouse gas emissions associated with trail-hose application, winged tine injection and straight tine injection of slurry corresponded to 830, 997 and 1482 kg CO_2 eq ha^{-1}, respectively. Provided plant damage can be minimized, this moderate increase in greenhouse gas emissions compared to surface application appears to be an acceptable trade-off for the reduction in NH_3 losses achievable with direct injection of slurry to established crops.

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1. Introduction

The environmental pressure from intensive livestock production on air, soil and water resources has stimulated the development of technologies for processing and handling of livestock manure. In the field, slurry injection is increasingly used to mitigate odour and ammonia emissions during fertilization of growing crops such as winter cereals or grassland, where subsequent incorporation by tillage is not possible. However, this may be at the expense of higher denitrification and N_2O emission rates, since the C and N rich injection slit environment is temporally stable (e.g., Comfort et al., 1988; Petersen et al., 2003).

Nitrous oxide (N_2O) is involved in global warming and stratospheric ozone depletion (Williams et al., 1992), and agriculture is estimated to contribute more than two-thirds of total anthropogenic N_2O emissions (Pattey et al., 2007), particularly through land application of manure and fertilizers (Smith et al., 2007). As the global warming potential of N_2O is 298 times as strong as that of carbon dioxide (CO_2), N_2O emissions from soils thereby exert an important impact on the environment (Wrage et al., 2001).

N_2O emissions from agricultural soils are largely proportional to the additions of N in organic and synthetic fertilizers (Bouwman et al., 2002; IPCC, 2006), but in any given situation this relationship is moderated by effects of soil type, climate, application practice and slurry properties. The relative contributions of nitrification and denitrification to N_2O emissions from soil depend on environmental conditions and substrate availability (Bollmann and Conrad, 1998; Wrage et al., 2001). Liquid manure (slurry)

provides nitrogen, moisture and a source of easily degradable C to the soil, and the increase in heterotrophic activity due to C turnover may provide oxygen-deficient conditions stimulating N_2O emissions for extended periods (Petersen et al., 1996, 2003; Chadwick et al., 2000). Accordingly, slurry treatment technologies which remove degradable C and/or promote the infiltration of slurry liquids should reduce the potential for oxygen limitation and N_2O emissions.

Anaerobic digestion of slurry is traditionally considered for energy production, but the removal of degradable organic matter during digestion has also been found to reduce denitrification following application to soil (Petersen et al., 1996). A reduction of N_2O emissions from digested slurry has been observed under field conditions (Petersen, 1999; Bhandral et al., 2009). Mechanical separation of slurry concentrates a fraction of nutrients and organic matter in a solid fraction that may be exported from the farm or further processed (Burton, 2007). In comparison with anaerobic digestion, separation is less selective in the removal of organic matter and could therefore be less effective in mitigating denitrification and N_2O emissions (Bertora et al., 2008).

The present study evaluated effects of application method and slurry pre-treatment on N_2O emissions from a loamy sand; NH_3 losses were also determined, but details of these measurements are published elsewhere. We hypothesized that a more concentrated sub-surface placement of slurry by injection would stimulate N_2O emissions compared to surface application. Secondly, it was hypothesized that slurry pre-treatment processes removing organic matter would reduce the potential for N_2O emissions with a given application practice.

2. Materials and methods

2.1. Soil and site

The experiments were carried out in the spring of 2007 and 2008 in a field at Research Centre Bygholm (55°52′N, 9°49′E). The soil is a loamy sand (Glossic Phaeozem) with 12% clay, 15% silt and 70% sand. Total C in the soil was 1.9%. In 2007 the field site was grown with spring barley (*Hordeum vulgare* L.), and in 2008 with winter wheat (*Triticum aestivum* L.). Temperature and precipitation in the two experimental periods are presented in Fig. 1.

2.2. Experimental design

The intention of this study was to evaluate NH_3 and N_2O losses after slurry application under realistic conditions. In practice
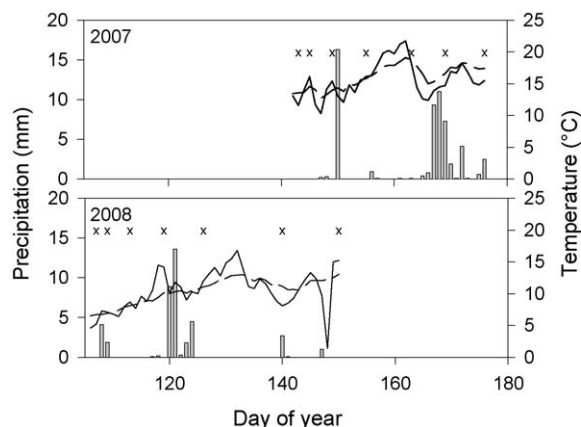

Fig. 1. Air temperature (solid line), soil temperature in 10-cm depth (dotted line) and precipitation (columns) during the two periods of the experiments in 2007 and 2008. Dates of gas measurements and soil sampling are indicated by "x". In both years the application of slurry took place the day before the first gas measurement.

application occurred within the same field in largely parallel stretches, each with six bands of slurry, that were separated by around 30 m. The direction of slurry application in each year was chosen to minimize wind-borne cross-contamination between treatments. Relatively long stretches were required to achieve constant slurry dosage rates. In the 2008 experiment, trail-hose application and direct injection were combined in one stretch by lowering the cross bar with injection tines (see below) half-way through a run. Another important restriction on the experimental design was the power demand for wind tunnels used to determine NH_3 losses. These practical considerations made it necessary to allocate experimental treatments to different sections of the field, and differences between treatments were thus confounded by potential differences in soil conditions between these sections, making the replicated sampling points within the individual stretches of slurry application pseudo-replicates (Hurlbert, 1984, 2004). Hence, treating them as genuine replicates in comparisons between application methods would only be valid to the extent that homogeneity of soil conditions across the field could be assumed. This assumption was not needed in comparisons of soil sampled between and within bands (see below) which were replicated within each experimental treatment.

2.3. Treatments

In both years pig slurry was applied in the spring to a growing cereal crop. An overview of the experimental treatments is given in Table 1.

In 2007, where the effect of application technique on N_2O emissions was investigated, the same batch of slurry from fattening pigs was used in all treatments. The pig slurry (162 kg total N ha^{-1}) was injected with either straight or winged tines using an experimental plot slurry spreader (Petersen, 1994) equipped with a 3-m wide injection boom on which six tines were mounted. The straight tine was 600-mm long with a rectangular cross section of 10 mm × 40 mm. The straight and winged tines were identical, except that metal wings (50-mm wide and 80-mm long) had been fixed to the bottom of the winged tine. The resulting depth of the injection slit was determined to be 12 cm with the straight tine, and 6–7 cm with the winged tine. A third section of the field was supplied with the same amount of pig slurry by trail-hose application of slurry at the soil surface. Trail-hose application was simulated by lifting the tines from the ground to give surface bands as with regular trail-hose equipment. The distance between injection tines and slurry bands was 0.30 m. Slurry was applied on 22 May in 2007.

In the 2008 experiment, effects of slurry pre-treatment were examined using three slurries derived from the same batch of pig slurry, i.e., the slurry was either untreated, anaerobically digested, or slurry solids had been removed by separation. Anaerobic digestion took place in a 30-m³ experimental reactor operated at

Table 1
Overview of the experimental treatments in spring 2007 and 2008.

Year	Date	Slurry type	Application method	Depth of application (cm)
2007	22 May	Untreated	Straight tine	12
			Winged tine	6–7
			Trail hose	Surface
2008	15 April	Untreated	Straight tine	8
			Trail hose	Surface
		Digested	Straight tine	8
			Trail hose	Surface
		Separated	Straight tine	8
			Trail hose	Surface

Table 2
Some characteristics of the pig slurries applied in spring 2007 and 2008.

Year	Slurry type	Dry matter (%)	Total N (g L^{-1})	NH$_4$-N	pH
2007	Untreated	3.8	5.4	4.7	7.9
2008	Untreated	4.7a[§]	4.5a	2.9b	8.0
	Digested	2.5b	4.3a	3.0a	8.6
	Separated	1.9c	3.6b	2.7c	7.9

[§] Values followed by different letters were significantly different ($n = 2$; $P < 0.05$).

approximately 52 °C and with a retention time of 16 days. Pig slurry was co-digested with 4% (w/w) maize silage to keep the fermentation process stabile. Slurry separation was performed using an experimental belt separator (Hjorth et al., 2009) with a mesh size of 1.2 mm following addition of polyacrylamide (Optifloc c2364; Kemira Water, Esbjerg, Denmark) as flocculants to increase the separation efficiency. All slurries were applied by direct soil injection (straight tine) and by trail hoses in adjacent sections of the field on 15 April 2008. The amounts of N applied were 127 kg N ha^{-1} (untreated and separated slurry) and 132 kg N ha^{-1} (digested slurry). The depth of injection was 8 cm below soil surface for all slurries. Trail-hose application was conducted as in 2007. Details on the slurries used in 2007 and 2008 are presented in Table 2.

2.4. N$_2$O flux measurements

Fluxes of N$_2$O were measured using vented static chambers ($l \times w \times h$, 35 cm × 25 cm × 25 cm) covered with a 13-mm insulating material (Thermaflex, Alu Stucco, Waalwijk, NL). Permanently installed collars for N$_2$O flux measurements were randomly distributed on top of individual slits or bands of slurry next to the wind tunnels, avoiding the outmost slits/bands to either side. The collars of galvanized iron (20-cm depth) were placed on top of three (2007) or two (2008) separate injection slits or slurry bands immediately after slurry application, with the 35-cm side of the collar parallel with the slit or band. In 2007, gas measurements took place 1, 3, 7, 13, 21, 27 and 34 days after slurry application corresponding to Julian days of the year 143, 145, 149, 155, 163, 169 and 176. In 2008 measurements were carried out 1, 3, 7, 13, 20, 34 and 44 after application of slurry corresponding to days of the year 107, 109, 113, 119, 126, 140 and 150. Chambers installed in an unmanured section of the field served as reference. In 2007 three chambers were included; due to shortage of chamber systems in 2008 it was necessary to use a single unit which, however, covered an area corresponding to 6.4 of the smaller chambers.

At each sampling, the top covers were mounted on the collars. Using a 10-mL air-tight polypropylene syringe equipped with a 0.6 mm × 25 mm hypodermic needle (Terumo, Leuven, Belgium), 7-mL gas samples were drawn from each chamber at the time of chamber deployment (0 min), and then after approximately 30, 60 and 120 min via a butyl rubber septum located at the centre of the chamber top; the syringe was purged three times with headspace air before taking the sample. Gas samples were transferred to 3-mL pre-evacuated Venoject vacutainers (Terumo, Leuven, Belgium) with butyl rubber stoppers. Gas sampling always started between 10:00 and 10:20.

2.5. Soil sampling

On each day of gas measurement, soil cores (20-cm depth, 2-cm diameter) were taken except for day 169 in 2007. Three separate soil cores were taken in the centre of the injection slits/bands and between adjacent injection slits/bands, respectively. Each soil sample consisted of three soil cores. The soil samples were stored at 2 °C until further processing.

In 2008 the distribution of ammonium in the soil around and below injection slits was determined 24 h after slurry application. Blocks of soil 20 × 4 × 15 ($l \times w \times h$) were taken with a rectangular steel corer centred on the injection slit. The soil was sectioned into eight fractions as described by Petersen et al. (2003). The height of the upper layer was defined from the bottom of the injection slit; the lower layer constituted 4 cm of soil below this depth. Soil below this depth was discarded. Corresponding sections on either side of the slit were pooled. Two replicate profiles were sectioned for each treatment; the results shown represent average concentrations.

2.6. Analytical methods

Nitrous oxide concentrations were determined within 24 h after sampling using a Chrompack 9001 gas chromatograph with ^{63}Ni electron capture detector and two serially connected 3-m packed columns (Porapak Q) operated with backflush on column 1. The column temperature was 100 °C, and detector temperature 325 °C. Carrier gas was argon/methane (95%/5%), with 99.999% N$_2$ as make-up gas; argon/methane passed filters (CP17970 and CP17971, Analytical Instr., Copenhagen, Denmark) to remove oxygen and moisture, respectively. Sample introduction occurred via an autosampler (Mikrolab, Højbjerg, Denmark), the overpressure of the sample filling a 250-μL sample loop. Routine analytical runs involved a two-point calibration with atmospheric air and a 1.06-ppmv N$_2$O in N$_2$ reference gas mixture (AGA A/S, Fredericia, Denmark) at the beginning of each run and after every 10 samples. Linearity of the detector response in this concentration range was assured.

The soil samples collected were sieved (8 mm) and portions of moist soil (ca. 10 g) extracted with 40 mL 1 M KCl in 30 min for inorganic N determination. Nitrate (NO$_3$) and ammonium (NH$_4$) in the KCl extracts were determined colorimetrically on a Technicon Autoanalyser II. Nitrite (NO$_2$) was quantified manually using the colorimetric procedure of Mulvaney and Bremner (1979). Soil moisture was determined after drying at 105 °C for 24 h.

Ammonium concentrations in soil profiles around slurry injection slits were used to prepare contour plots using Surfer 8.02 (Golden Software Inc., Golden, CO, USA)

2.7. N$_2$O flux calculations

The accumulation of N$_2$O was frequently non-linear, in particular during the late-spring experiment of 2007. For the flux calculations a new method (HMR), derived from a model originally presented by Hutchinson and Mosier (1981), was therefore adopted. In this model (HM), the headspace concentration, C_t, at time t after deployment ($t = 0$) is defined by

$$\frac{dC_t}{dt} = \kappa(\varphi - C_t)$$

where κ is a positive model parameter related to chamber design and soil characteristics, and φ denotes the (assumed constant) source concentration at some unknown depth. The solution to the differential equation is given by

$$C_t = \varphi + f_0 \frac{\exp(-\kappa t)}{-\kappa} \frac{A}{V}$$

where A and V denote, respectively, the cross-sectional area and volume of the chamber, and f_0 denotes the initial flux. The model parameters φ, κ, and, in particular, f_0 can be estimated from headspace concentration measurements by minimizing the least squares criterion (standard non-linear regression; Seber and Wild,

1989). Moreover, in order to avoid the usual problems with multi-parameter estimation the HMR method utilizes the fact that the least squares estimates of φ and f_0 for any given value of κ can be calculated by linear regression of the headspace concentration measurements, C_{t_i}, against the independent variable

$$x_{t_i} = \frac{\exp(-\kappa t_i)}{-\kappa} \frac{A}{V}$$

Denoting these estimation functions by $\hat{\varphi}(\kappa)$ and $\hat{f}_0(\kappa)$, respectively, the least squares criterion function reduces to a single-parameter criterion

$$LS(\kappa) = \sum_{i=1}^{n} \left(C_{t_i} - \hat{\varphi}(\kappa) - \hat{f}_0(\kappa) \frac{\exp(-\kappa t_i)}{-\kappa} \frac{A}{V} \right)^2$$

which is easily minimized and monitored for a globally optimized estimate, $\hat{\kappa}$, of κ. Then, finally, the estimates of φ and f_0 are given by $\hat{\varphi}(\hat{\kappa})$ and $\hat{f}_0(\hat{\kappa})$, respectively.

The HMR method leads to a simple and efficient test of linearity. With approximately linear concentration data the HM model will be overparametrized, and $LS(\kappa)$ will not possess a minimum value but rather continue to decrease for ever decreasing values of κ. In such cases, the HMR method applies linear regression. For non-linear data the HMR method is very similar to exponential regression, but the two methods differ in two respects. Firstly, the profiling of φ and f_0 provides a safe way to ensure that the parameter estimates are really at the global minimum of the least squares criterion. Secondly, during optimization the HMR method ensures that the estimated values of κ, φ and C_0 do not become negative. The HMR method is available as a free add-on package to the free software program R version 2.9.2 or later (http://www.r-project.org).

2.8. Statistical analyses

As explained above, slurry had to be applied to single, adjacent sections of the field for practical reasons, and the measurements of gaseous losses were therefore not replicated, but rather pseudo-replicated within each of the experimental treatments. Soil sampling positions, i.e., within and between slurry application bands, were, however, replicated within the individual section used for each application method. Hence, between- and within-band samples could be compared by sampling day using 2- (2007) or 3-way (2008) ANOVA. Effects of slurry type and application method were in fact tested by similar ANOVA analyses, although the statistical test results are only valid to the extent that homogeneity between experimental fields is assumed.

In this study the significance of N$_2$O fluxes was evaluated using the 95% confidence interval of the slope estimated by linear regression. Fluxes were deemed significant if the 95% confidence interval did not include zero (Chan et al., 1998). Non-significant fluxes were set to zero, whereas significant fluxes were then processed using the HMR method.

3. Results

3.1. Experiment 1: effect of application technique

The application of slurry in 2007 took place in late May. Soil temperature at the time of application was 13.1 °C increasing to 15.5 °C when the experiment was terminated (Fig. 1). Soil moisture gradually declined during the first three weeks of the experiment in 2007, with WFPS decreasing from 42% to a minimum of 22% after 20 days (Fig. 2e). At the last sampling, 34 days after slurry application, WFPS had increased to 39% after several days with rain.
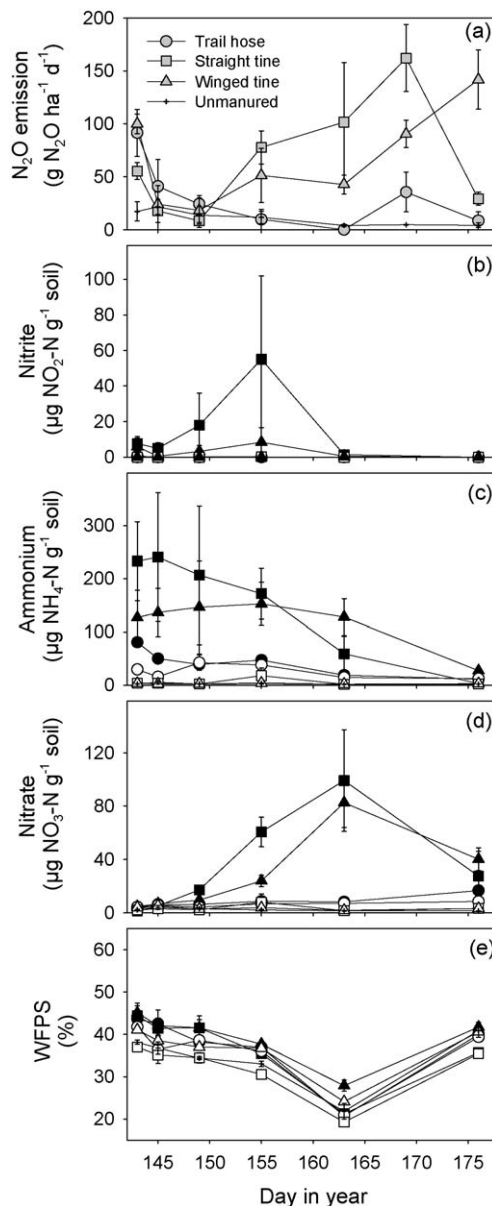
Fig. 2. In 2007 untreated pig slurry was applied with trail hoses or injected with straight or winged tines. Sub-plots show (a) N$_2$O emissions, (b) NO$_2$, (c) NH$_4$, (d) NO$_3$ and (e) WFPS. Open and closed symbols (b–e) represent samples taken between and within slurry application bands, respectively. Error bars represent standard errors ($n = 3$).

Concentrations of NH$_4$ in soil sampled within injection slits, both straight and winged tine, were higher than in soil sampled between slits except for the last sampling day ($P < 0.01$) (Fig. 2c). With trail-hose application the difference was only significant ($P < 0.05$) at the first two samplings. After the first week NH$_4$ concentrations within and between trail-hose application bands were similar, and elevated compared to between-band levels in the injected treatments.

NO$_3$ concentrations in soil sampled within injection slits increased to a maximum after 21 days (Fig. 2d) after which time NO$_3$ uptake by the winter wheat crop was probably a major sink. Nitrate accumulation in/around the injection slits coincided with the decline in WFPS and increase in soil temperature, both of which probably stimulated nitrification activity. NO$_3$ level within trail-hose application bands remained at the level of within-band soil samples throughout the experiment.

Nitrite concentrations were generally at or below the detection limit (Fig. 2b), although local high concentrations could have been missed as the soil samples analyzed represented mixed samples from 0- to 20-cm depth. However, at the samplings 7 and 13 days after slurry application a slight (winged tine) or stronger (straight tine) accumulation of NO_2 was observed.

One day after slurry application N_2O fluxes ranged from 55 to 100 g N_2O ha^{-1} day^{-1}, and then declined to a minimum after one week (Fig. 2a). This was followed by a consistent increase in N_2O emissions from the treatments with injected slurry, which coincided with the accumulation of soil NO_3 (Fig. 2d). N_2O fluxes reached maxima of 162 and 142 g N_2O ha^{-1} day^{-1} for slurry injected with straight tine and winged tine, respectively. Presumably N_2O emissions from the winged tine treatment would have declined shortly after the last sampling due to a depletion of soil mineral N (Fig. 2b–d). N_2O emissions from surface applied slurry was initially in the same range as from injected slurry with a winged tine, but then gradually declined except for a temporary increase after four weeks following a period with precipitation.

3.2. Experiment 2: effect of slurry pre-treatment and application technique

The pre-treatment of slurry by anaerobic digestion or chemical–mechanical separation in 2008 resulted in three materials differing especially in dry matter (DM) content (Table 2). Both separation and digestion reduced slurry DM compared with untreated slurry. Total ammoniacal N (TAN) accounted for 64% of total N in untreated slurry and slightly higher proportions (70% and 75%) in digested and separated slurry, respectively. Finally, the pH of digested slurry was somewhat higher than that of untreated and separated slurry.

In 2008 slurry application took place earlier in the year than in 2007, and soil temperature was lower (Fig. 1) and WFPS (Figs. 3d and 4d) higher at the time of application. For injected slurry (Fig. 3) there was a steady decline in NH_4 concentrations in the slits, reaching the concentration level between slits after about three weeks (Fig. 3d). NO_3 accumulation commenced after one week and reached a temporary maximum after 13 days. After this time the NO_3 concentration in slits with untreated slurry remained at a level of 7–8 μg N g^{-1}, whereas NO_3 concentrations increased to 15–20 μg N g^{-1} with injection of digested and separated slurry. For soil sampled between slits, NO_3 concentrations were generally low throughout the experimental period. NO_2 concentrations in 2008 were at or below the detection limit in all treatments and are not presented.

N_2O emissions from injected slurry peaked after around three weeks (Fig. 3a), which was earlier in the year than in 2007, but fluxes at this time after application were similar in the two years. The fluxes were generally lower in 2008, but no distinct differences between the three slurries were found.

When slurry was applied to the surface by trail-hose application, concentrations of NO_3 and NH_4 were generally low throughout the experimental period, and similar for soil sampled within and between application bands (Fig. 4c and d). Fluxes of N_2O from surface applied digested and separated slurry peaked at different times, whereas N_2O from untreated slurry remained low, though still elevated compared to the reference soil (Fig. 4a).

The infiltration capacity of the three slurries applied in 2008 differed. This is illustrated in Fig. 5 showing contour plots based on NH_4 concentrations in eight soil fractions obtained 24 h after slurry application. It should be stressed that corresponding layers on either side of the injection slits were pooled prior to analysis, hence the contour plots are symmetrical. The infiltration in soil apparently reflected the slurry dry matter contents of 4.7% for
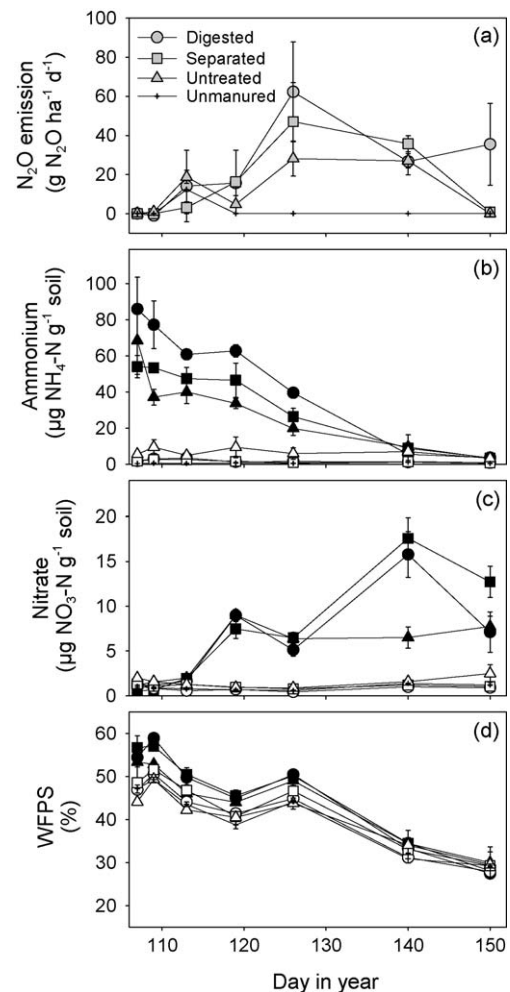
Fig. 3. Results from direct injection of untreated, digested and separated pig slurry in 2008. Sub-plots show (a) N_2O emissions, (b) NH_4, (c) NO_3 and (d) WFPS. Open and closed symbols (b–d) represent samples taken between and within slurry application bands, respectively. Error bars represent standard errors ($n = 2$).

untreated slurry, 2.5% for digested slurry, and 1.9% for separated slurry (Table 2).

3.3. Cumulated N_2O emission in 2007 and 2008

In 2007 the cumulated N_2O emissions from directly injected pig slurry ranged from 1.2% to 1.5% of total N applied, whereas emissions from trail-hose applied slurry constituted 0.3% of N applied (Table 3). When adjusted for gaseous NH_3 losses (T. Nyord et al., unpublished results), the difference between N_2O emissions from slurry applied with straight and winged tines increased. Emissions from injected slurry were significantly higher than from trail-hose applied slurry, although it must be re-emphasized that the experiment contained no true replication of application methods.

In 2008 gaseous NH_3 losses were only determined for surface applied slurry, and N_2O emissions from injected slurry materials could therefore not be adjusted. The unadjusted cumulated N_2O emissions from injected slurry were lower than in 2007 (Table 3). Both adjusted and non-adjusted N_2O emissions after trail-hose application of untreated slurry were at the same level in the two years. There were no strong differences between untreated, digested and separated slurry with either application method. Emissions of N_2O tended to be higher from treated slurry.
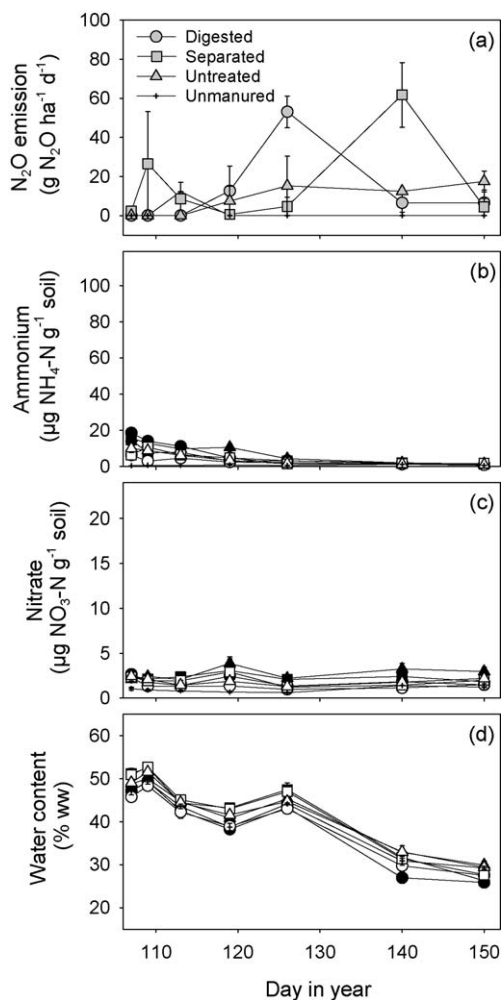
Fig. 4. Results from trail-hose application of untreated, digested and separated pig slurry in 2008. Sub-plots show (a) N_2O emissions, (b) NH_4, (c) NO_3 and (d) WFPS. Open and closed symbols (b–d) represent samples taken between and within slurry application bands, respectively. Error bars represent standard errors ($n = 2$).
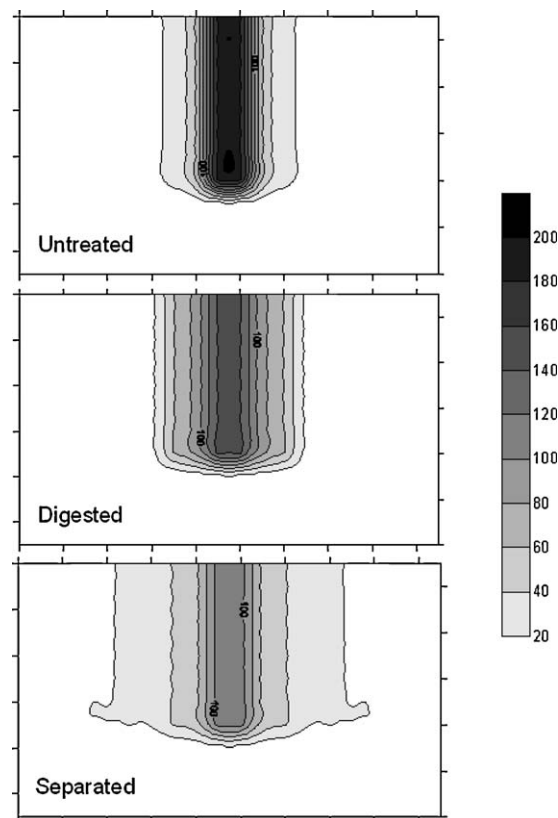

Fig. 5. Distribution of ammoniacal N 24 h after injection of untreated, digested and separated slurry in 2008. Intact blocks of soil ($n = 3$) taken across the injection slit or trail-hose application band were sectioned as described in the text, pooling corresponding sections on either side of the slurry band. The contour plots were simulated based on average concentrations (see text).

4. Discussion

4.1. Flux calculations

Non-linear trace gas accumulation has been addressed by several different models, each of which has strengths and limitations (e.g., Hutchinson and Mosier, 1981; Pedersen et al., 2001; Livingston et al., 2006; Kroon et al., 2008). In this study N_2O flux rates were calculated using a new method, HMR, which is based on the model originally proposed by Hutchinson and Mosier (1981). HMR has been programmed in the free software R and is available in a user-friendly version as a so-called package from within R. An important aspect of HMR is the fact that only one parameter, κ, must be optimized, and the method ensures that the best solution is identified (Pedersen et al., submitted for publication). Moreover, HMR will automatically calculate flux estimates by linear regression if the trace gas accumulation is linear.

Four observations were available from each chamber, which is at the lower limit for reliable flux estimation. However, a pre-screening was conducted based on linear regression, and only statistically significant fluxes were processed by HMR. A standard error and confidence limits are calculated for each flux estimate; the relative error of flux estimates in 2007 and 2008 averaged 6.6% and 8.8%, respectively.

The proportion of fluxes showing non-linearity ranged from 31% to 76% in the different experimental treatments (data not shown). There were no clear trends in the occurrence of non-linearity among treatments, and non-linearity was observed with both high and low fluxes. Accounting for non-linearity increased N_2O flux estimates by 25% to 65%.

4.2. Effects of application method

In 2007 two injection techniques and trail-hose application at the soil surface were compared with respect to N_2O emissions using untreated pig slurry. All treatments showed an initial peak in N_2O emissions, and injected slurry furthermore showed a prolonged increase during the second and third week of the experiment. Average WFPS in the soil samples taken to 20-cm depth never exceeded 42% and was thus always lower than the threshold of around 60% often found to trigger high N_2O emission rates (Dobbie and Smith, 2003; Saggar et al., 2004). However, the soil moisture content was significantly higher in soil samples taken in the slits compared to between-slit positions, except at the last sampling, and this indicates that wet conditions were maintained in a restricted volume around the injected slurry which may have supported N_2O emissions during several weeks. Temporal stability of moisture gradients around slurry injection slits has previously been observed on a different sandy loam soil (Petersen et al., 2003).

N_2O emissions were lower with trail-hose application than with direct injection (Table 3), although this was also coupled with significantly higher NH_3 losses, i.e., 20% vs. 10 and 4% for straight and winged tine, respectively (T. Nyord et al., unpublished data). The winged tine improved the distribution of slurry in the soil as indicated by NH_4 patterns, the lower NO_2 accumulation, and the

Table 3
Total and ammoniacal N (TAN) supplied, accumulated N_2O emissions, and N_2O emission factors (EF) with and without adjustment for NH_3 losses.

Year	Slurry type	Application method	Total N supplied (kg total N ha^{-1})	TAN supplied (kg NH_4-N ha^{-1})	N_2O emissions (kg N ha^{-1})	N_2O emission factor (in parentheses EF adjusted for NH_3 losses[a])
2007	Untreated	Straight tine	162	140	2.51	0.015 (0.017)
	Untreated	Winged tine	162	140	1.86	0.012 (0.012)
	Untreated	Trail hose	162	140	0.49	0.003 (0.004)
2008	Untreated	Straight tine	127	81	0.70	0.006
	Digested	Straight tine	132	94	1.27	0.010
	Separated	Straight tine	127	95	1.00	0.008
	Untreated	Trail hose	127	81	0.40	0.003 (0.004)
	Digested	Trail hose	132	94	0.70	0.005 (0.008)
	Separated	Trail hose	127	95	0.90	0.007 (0.007)

[a] T. Nyord et al. (personal communication).

different time course of N_2O emissions (Fig. 2). The transient accumulation of NO_2 observed with straight tine injection reflected an imbalance between NH_4 oxidation and NO_2 oxidation, probably as a result of low-oxygen conditions, and this environment would be expected to stimulate N_2O emissions via nitrifier denitrification (Venterea, 2007). Higher rates from straight tine injection were indicated during the third and fourth week of the experiment, but accumulated N_2O losses were similar with both injection techniques.

4.3. Manure management and soil mineral N

The profiles of NH_4 around slurry injection slits (straight tine) amended with untreated, digested and separated slurry (liquid fraction) indicated clear differences in the infiltration corresponding to the dry matter content of the three materials (Fig. 5). This is in accordance with the observations of Petersen et al. (2003), who observed a consistent relationship between slurry organic dry matter content and water retention for 22 different slurry materials. A better infiltration will improve the supply of oxygen during turnover of slurry C and N, which should reduce the potential for denitrification; whether this results in more or less N_2O accumulation and release, however, will also depend on soil aeration status (see Section 4.5).

In 2008 the NO_3 concentrations in bands with injected slurry were lower than in 2007. This could be due to the lower amounts of NH_4 applied (Table 3) or to the earlier application in 2008, where the well-established crop of winter wheat may have been an important sink for inorganic N. N_2O fluxes were correspondingly lower in 2008, and differences between N_2O fluxes from injected and surface applied slurry were smaller than in 2007 (Figs. 3 and 4).

4.4. Manure management and N_2O emissions

The N_2O emission factors calculated (Table 3) represented emissions during 34 or 44 days after application in the two experimental years. They should thus not be confused with annual emission factors as defined in the IPCC methodology (IPCC, 2006), although 60–90% of N_2O emitted during the first 6 months may occur within this initial phase (Lessard et al., 1996; Rochette et al., 2008).

In 2007, but not in 2008, there was an increase in short-term N_2O emissions by direct injection compared to trail-hose application. Soil WFPS was higher in 2008 than in 2007, and the higher soil water content could have delayed the exchange of gases between sites of N transformations and the atmosphere, shifting the balance between processes towards complete denitrification to N_2 (Focht, 1974). Velthof et al. (2003) found that simulated injection of pig slurry to a sandy soil increased N_2O emissions compared to surface application or more complete mixing. Similarly, Wulf et al. (2002)

recorded a twofold increase in short-term N_2O emissions after direct injection of cattle slurry and fermentation products to a well-drained Luvisol compared to surface application. In contrast, Clemens et al. (2006) did not find effects of either application technique (broadcasting, band application or injection) or separation of cattle slurry on N_2O emissions due to large variability. Hence, it appears that the potential for N_2O emissions is higher after direct injection as opposed to surface application, but interactions with soil type and climatic conditions at the time of application may obscure or eliminate these effects.

No effects of slurry pre-treatment on N_2O emissions were observed in the 2008 experiment, in fact there was a tendency for lower emissions from untreated slurry. Effects of anaerobic digestion and separation on N_2O emissions have been investigated in numerous laboratory and field experiments. A Danish field study during two cropping seasons of spring barley indicated that anaerobic digestion could reduce N_2O emissions from field-applied slurry (mixture of cattle and pig slurry) by 20–40% (Petersen, 1999). A consistent reduction of N_2O emissions after digestion was achieved in an incubation study with 10 pig slurries on a sandy soil, but not on clay (Oenema et al., 2005). Clemens et al. (2006) observed a significant effect of cattle slurry digestion on CH_4 and NH_3 emission during storage, but no effects on N_2O after field application to a poorly drained pasture (Clemens et al., 2006). Finally, Bertora et al. (2008) observed N_2O emission factors during a 58-day mesocosm experiment of 4.8%, 2.6% and 1.2% for untreated pig slurry, the thin fraction of separated pig slurry, and digested slurry, respectively. The conflicting evidence on the effects of application method and slurry pre-treatment in the present study, as well as in the studies mentioned above, points to a complex interaction of the liquid manure with soil type and moisture content.

4.5. Manure–soil interactions and N_2O

Davidson (1991) presented a conceptual model of the effect of soil water-filled pore space on the balance between N_2O and N_2, which has been widely accepted. Replacing WFPS with a more general term expressing the balance between supply and demand of oxygen may be helpful in understanding the effects of application method and slurry treatment on the N_2O emission potential after field application. Fig. 6 illustrates the relationship between the O_2 demand:O_2 supply ratio and denitrification products from heterotrophic and nitrifier denitrification. Assuming the O_2 demand from substrates in soil and slurry is constant, a wet soil (high WFPS) would lower the denominator, shifting the balance to the right. Similarly, at constant soil moisture, removing degradable carbon by slurry treatment, would lower the O_2 demand and shift the balance to the left. Situation 1 in Fig. 6 could exemplify slurry application to a moderately dry soil. Injection of
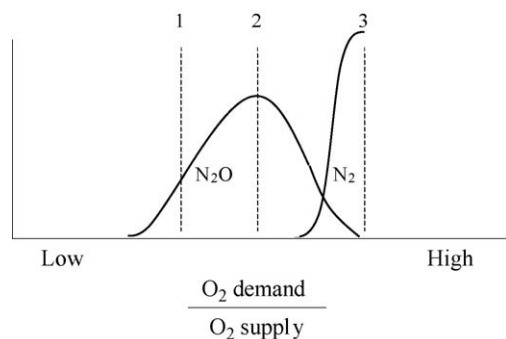
Fig. 6. A conceptual model of the relationship between N_2O/N_2 emissions and the supply and demand of O_2 in the soil. The three dotted lines represent three situations that would differ in the response of N_2O emissions to application method and/or slurry treatment to remove degradable carbon (see text).

slurry (lower O_2 supply) would shift the balance towards increased N_2O emissions compared to surface application (or mineral fertilizers), while slurry treatment (lower O_2 demand) would be expected to reduce N_2O emissions. In situation 2 the effect of slurry treatment would still be a reduction of N_2O, whereas injection (or slurry application at high soil moisture content) would shift the balance towards N_2, i.e., N_2O emissions would be lower after direct injection. Finally, in situation 3 there would be an *increase* in N_2O emissions following slurry treatment to remove degradable C, but little or no effect of reducing the O_2 supply. Referring to Figs. 2e and 3d, the WFPS of the bulk soil was higher in 2008 than in 2007, and presumably even higher in and around the injection slit. This may have shifted the balance beyond the point of maximum emissions in 2008, lowering N_2O emissions after direct injection compared to the previous year. Also, a reduced O_2 demand:O_2 supply ratio would explain the trend towards higher N_2O emissions from treated slurry.

4.6. The trade-off between NH_3 and greenhouse gas emissions

Besides N_2O emissions, the reduced NH_3 emission potential with direct injection must be taken into account when evaluating management effects on the overall greenhouse gas balance of manure application. NH_3 losses must be replaced by a different source of N, and an overall evaluation of application method for the GHG balance of slurry application should therefore take the cost of N substitution into account. With the observed NH_3 losses (see Section 4.1) and N_2O emission factors (Table 3) it was calculated that summed direct and indirect N_2O emissions from the field-applied slurry, the production and transport of synthetic N, and the turnover of synthetic N in soil amounted to 830, 997 and 1482 kg CO_2 eq ha^{-1} with trail-hose application, winged tine injection and straight tine injection, respectively. Here it was assumed that the cost of synthetic N was 9.2 kg CO_2 eq kg^{-1} (Nielsen et al., 2003), that the extra energy required for injection was 5.6 kg CO_2 eq ha^{-1} (Hansen et al., 2003), and that the N_2O emission factor for synthetic N was 0.01 (IPCC, 2006). The winged tine treatment with 4% NH_3 loss had total GHG emissions in the same order as trail-hose applied slurry, but 91% of emissions from injected slurry were due to N_2O emissions from the slurry, while only 34% of GHG emissions from trail-hose applied slurry were from this source and the rest linked to the substitution of fertilizer N.

5. Conclusion

Both application technique and pre-treatment influence the distribution of slurry in the soil upon field application. Under relatively warm and dry conditions direct injection increased N_2O emissions relative to trail-hose application, but not under more wet soil conditions. Dry matter removal by separation and anaerobic digestion promoted slurry infiltration, but there was no indication of reduced N_2O emissions, rather an increase was suggested, which was related to the balance between O_2 demand and O_2 supply. The overall increase in GHG emissions by direct injection of slurry was moderate, and therefore, considering the agronomic and environmental benefits of minimizing NH_3 volatilization, it is concluded that direct injection offers an acceptable alternative to surface application of slurry.

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