



## Nitrogen Transformations and Losses following Pig Slurry Applications to a Natural Soil Filter System (Solepur Process) in Brittany, France

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The soil filter system, Solepur, has been shown to be highly successful at removing organic matter and nitrogen (N) from pig slurry during its first five years of operation. The system involves three operations; application of large volumes of pig slurry to a managed field; collection and treatment of the nitrate-rich leachate; and irrigation of the treated water over other fields. The purpose of this study was to determine the environmental implications of applying excessive volumes of slurry to the managed field and to improve the understanding of the N cycle in the soil filter system. Nitrous oxide (N<sub>2</sub>O) and ammonia (NH<sub>3</sub>) emissions were measured from the managed field following two slurry applications under different soil conditions. Denitrification losses, nitrate leaching, N uptake by plants and soil immobilization of N were determined and methane (CH<sub>4</sub>) emissions were measured.

Emissions were monitored following slurry applications in June and in the following October. Losses of nitrogen (expressed as a percentage of that applied), following the October application, were measured as 6% (ammonia), 23% (as nitrous oxide) and 12% (as dinitrogen gas). Losses as ammonia following the previous June application were greater (31%) but losses as nitrous oxide were less (<1%) coinciding with lower emissions of methane.

Measured losses and transformation of N were in agreement with the estimated N balance made in earlier work. Methods for reducing NH<sub>3</sub> and denitrification losses from the system are discussed, e.g. shallow injection of slurry to reduce ammonia losses and the addition of nitrification inhibitors to slurry to reduce the production of a suitable nitrogen source at times when conditions are favourable for denitrification.

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### 1. Introduction

Intensification of livestock production systems has resulted in large quantities of slurries being produced in limited geographical areas<sup>1</sup> with insufficient land area to utilize the slurry efficiently. In France, 55% of pig production, 46% of the poultry production and 21% of the dairy production is located in Brittany.<sup>2</sup> Approximately 75% of the excreta collected from these animal production systems is as slurry. Annually this material is estimated to contain  $2 \times 10^5$  t of nitrogen (N), with 57, 25 and 13% of the total N being derived from the cattle, pig and poultry systems, respectively.<sup>3</sup> The intensive livestock systems in Brittany tend to be situated on freely draining soils, so the safe disposal of this waste with minimum risk of polluting the watercourses with high nitrate (NO<sub>3</sub><sup>-</sup>) concentrations, is of greater concern than fully exploiting its value as a fertilizer.

In order to reduce the risk of NO<sub>3</sub><sup>-</sup> pollution, the period of the year in which spreading of slurries onto land is permitted is controlled by legislation in Brittany.<sup>4</sup> The conventional treatment system available for removing N from slurry prior to spreading is aerobic digestion<sup>5</sup> but the process requires sophisticated, expensive equipment and skillful operation. The Solepur process which was designed to treat slurry using biological processes only, offers a potentially simpler, less expensive alternative.

The Solepur pilot experiment has been described elsewhere.<sup>6,7</sup> Briefly, it is a pilot-scale system for treating pig slurry using natural soil processes. There are three main stages (a) a managed field (grass or arable) to which slurry is applied and all drainage is recovered by means of an impermeable layer 80 cm below the surface, (b) a system of storage lagoons or "reactors" for promoting denitrification of drainage water and (c) a non-managed field (grass) for irrigating the denitrified drainage water. The Solepur process involves applying large volumes of slurry onto the managed site and collecting and treating

the  $\text{NO}_3^-$ -rich leachate in the reactors, which is then irrigated onto the non-managed field. The system was run between December 1990 and March 1996 with pig slurry applied to the managed field once a month between March and November of each year. This resulted in an average annual loading of slurry N of approximately 5000 kg N/ha.

Although the process has been successful at removing  $\text{NO}_3^-$  from the drainage water<sup>8</sup> N loss from the system through other pathways, such as  $\text{NH}_3$  volatilization and denitrification have not been evaluated to date. Both of these processes can lead to significant N loss following slurry applications to land.<sup>9,10</sup> Applications of livestock wastes to land also enhance soil conditions for  $\text{N}_2\text{O}$  (Ref. 11) and  $\text{CH}_4$  (Ref. 12) production.

In the present study,  $\text{NH}_3$ ,  $\text{N}_2\text{O}$  and  $\text{CH}_4$  emissions and  $\text{NO}_3^-$  leaching were measured following two applications of slurry to the Solepur system in June and the following October to determine the significance of each of the N loss pathways. During the first application,  $^{15}\text{N}$ -enriched slurry was applied to micro-plots on the managed field to quantify N uptake by the sward and N immobilization by the soil which enabled a N balance of this application to be calculated. Dinitrogen losses were evaluated following the October slurry application when conditions were thought to be favourable for this denitrification.

## 2. Materials and methods

### 2.1. Site

The Solepur site, near Plouvorn in Northern Brittany, France, is 50–55 m above sea level and had a mean annual rainfall of 1000 mm and a mean annual air temperature of 11°C (for the years between 1986 and 1995). The soil is a freely draining silty loam with a soil texture of, clay 14%, silt 63% and sand 23%. The total carbon (C) and N contents for the soil were 1.8 and 0.18%, respectively. Soil pH was 7.2 at a depth between 0 and 20 cm.

### 2.2. Slurry applications

Pig slurry from a nearby intensive sow house was applied at the rates of 95 m<sup>3</sup>/ha in summer (June 1995) and 227 m<sup>3</sup>/ha in autumn (October 1995) to areas of 0.22 ha (80 m × 28 m) and 0.32 ha (80 m × 40 m) on the managed field, respectively. Slurry was applied using an umbilical system connected to a 40 m wide spray boom which ensured a uniform application across the field. The slurries, described in Table 1, had contrasting characteristics with the slurry used for the summer application having a much greater total solids content than the slurry used for the autumn application. The summer application was made to a ryegrass sward (with a sward height of 15 cm), whilst the autumn application was made to ploughed soil.

#### 2.2.1. Measurement of $\text{NH}_3$ emissions

The micro-meteorological mass balance technique was used to measure  $\text{NH}_3$  emissions following slurry application.<sup>13,14</sup> A mast positioned in the centre of the treated field supported an array of  $\text{NH}_3$  passive samplers<sup>15</sup> or “shuttles” which gave a measure of the horizontal  $\text{NH}_3$  flux at each height. The shuttles were mounted at 0.2, 0.4, 0.7, 1.2, 2.0 and 3.0 m above the soil surface thus producing a horizontal flux profile. The vertical  $\text{NH}_3$  flux from the treated field was calculated by vertically integrating the horizontal flux profile, which was then divided by the distance from the mast to the edge of the field, or the “fetch”. Because the field was rectangular, wind direction was logged so that the fetch could be calculated for each sampling period. Background  $\text{NH}_3$  was measured by placing an additional mast, supporting three shuttles mounted at 0.4, 1.2 and 3.0 m above the soil surface, upwind of the treated field.

To trap the  $\text{NH}_3$ , the shuttles were charged prior to use with 30 ml of 3% oxalic acid in acetone (w/v) to coat the interior surfaces with oxalic acid crystals. At the end of a sampling period, the sampler contents were washed out with 40 ml of deionized water. Sampling periods varied in length with shorter sampling periods immediately following slurry application to avoid saturation of the oxalic acid with  $\text{NH}_3$  and longer sampling periods

**Table 1**  
Slurry analyses and rates of application

	TAN* content (kg/m <sup>3</sup> )	Total N content (kg/m <sup>3</sup> )	Total solids (%)	Total C content (kg/m <sup>3</sup> )	TAN applied (kg N/ha)	Total N applied (kg N/ha)	Total C applied (kg N/ha)
Summer	4.2	6.9	10.4	43	399	656	4085
Autumn	3.5	5.2	4.5	15	794	1180	3405

\*TAN = Total ammonical nitrogen.

towards the end of the experiment. Measurement of emissions continued for 8 and 4 d following slurry application in summer and autumn, respectively, by which time the volatilization process was virtually complete. Measurements were also made during the two days prior to the slurry applications to establish emission levels from the site without the influence of the applied slurry.

### 2.2.2. Measurement of $N_2O$ and $CH_4$ emissions

Greenhouse gases were trapped using static cover boxes.<sup>16</sup> Open steel boxes, 20 cm high  $\times$  15 cm wide  $\times$  50 cm long, were either pushed or lightly hammered into the soil to a depth of 2 cm. The boxes had a 1.5 cm flange around the upper edge to allow a clear perspex lid to be tightly clamped to the box. The contact between lid and box was made air tight by the use of a rubber seal glued to the lid. Each lid had a port fitted with a silicone rubber septum to allow gas samples to be taken with a syringe.

At each sampling period, the lids were clamped to the boxes and gas samples (20 ml) were taken over a period of 40 min and stored in evacuated glass storage vials. Ambient air samples were also taken as the lids were clamped to the box. Appropriate  $N_2O$  and  $CH_4$  standards were stored in a similar way. After each sampling period the lids were removed but the boxes remained *in situ*. Nitrous oxide and  $CH_4$  emissions were measured for the first 9 d following the June application and for 111 d following the October application.

Nitrous oxide and  $CH_4$  were measured on an HP 5890 series II gas chromatograph fitted with an electron capture detector (operating at 300°C) and a flame ionization detector (operating at 250°C). The column was operated at 60°C with a backflush system.

### 2.2.3. Denitrification measurements

Denitrification losses were determined following the October slurry application using a modified acetylene inhibition technique.<sup>17</sup> After the extremely high application rate of slurry in October, it became impossible to sample intact soil cores using the conventional corer. The method was adapted so that instead of taking eight separate cores (2.5 cm diameter  $\times$  10 cm long) per Kilner jar of 1 l capacity, one large intact soil core (7 cm diameter  $\times$  10 cm long) was taken per Kilner jar. Sampling was performed so that two Kilner jars were filled with soil sampled from the same area of the field. Five representative areas of the field were sampled on each occasion.

The jars were then closed and 60 ml of air removed from each through a silicon rubber septum in the lid using a syringe. To one of each pair of Kilner jars, 60 ml of acetylene was added (resulting in an atmosphere of 10% acetylene), 60 ml of air was returned to the other

Kilner jar. The jars were then placed in holes in the ground, to maintain the soil cores at ambient temperature, for a period of 24 h. Gas samples of 20 ml were then removed from each Kilner jar and stored in evacuated glass storage vials. Nitrous oxide standards were stored at the same time. The difference in  $N_2O$  measured from the jars that received acetylene and those that did not was assumed to be the additional  $N_2O$  that would normally be lost as dinitrogen ( $N_2$ ) following complete denitrification.

Soil was emptied out of the Kilner jars and the fresh weight determined. After crumbling, 50 g sub-samples were taken and dried at 80°C to constant weight to determine the moisture content.

### 2.2.4. Extractable soil $NH_4^+-N$ and $NO_3^- -N$ concentrations

Soil samples (0–10 cm) taken daily during the June experiment and those from the control Kilner jars following the October application (those without acetylene addition) were crumbled and 100 g (fresh weight) extracted with 1 molar KCl in an end-over shaker for 1 h. After filtering through Whatman No. 42 filter paper, the  $NH_4^+-N$  and  $NO_3^- -N$  concentrations of the KCl extract were determined by distillation of an aliquot with MgO and Devardo's alloy.<sup>18</sup>

### 2.2.5. N uptake by the grass and N immobilization in the soil

Three replicate micro-plots (2 m  $\times$  1 m), were covered with plastic sheeting during the slurry application in June and some pig slurry retained for enrichment with  $^{15}N$ . The labelled slurry was prepared from the addition of enriched ammonium sulphate (60% atom percent excess) to reach an atom percent excess of 0.61% within the slurry total N and an atom percent excess of 0.88% within the total ammoniacal-N. The labelled slurry was applied to the micro-plots at the rate of 100 m<sup>3</sup>/ha using an adapted watering can. This resulted in a total ammoniacal-N application of 450 kg/ha and a total N application of 728 kg/ha to each micro-plot, a similar application rate to that applied to the main experimental field.

One month after the slurry application the central 0.5 m<sup>2</sup> of each micro-plot was cut and separated into above ground (shoots) and below ground (roots) biomass. Eight soil cores were also sampled to a depth of 30 cm. Soil samples were sieved through a 5 mm mesh before being prepared for analysis. All samples were analysed in duplicate for their total N content by the Kjeldahl–Olsen method.<sup>19</sup> The titrated distillates of plant and soil digestions were acidified with a few drops of 1 molar  $H_2SO_4$  and were evaporated until dry. The  $^{15}N$  content of these samples was determined<sup>20</sup> by mass spectrometer (Micromass VG G22).

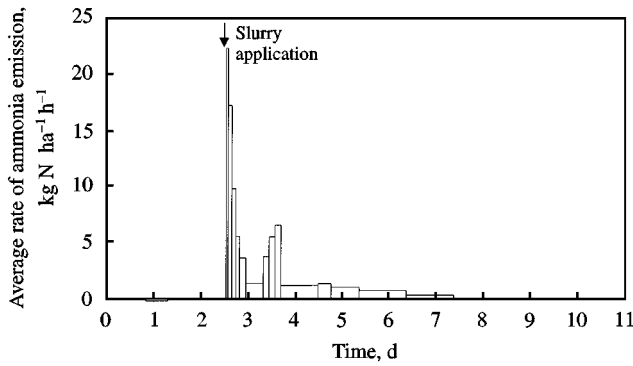


Fig. 1. Rate of ammonia emission from the managed field following slurry application in June

### 3. Results

#### 3.1. $\text{NH}_3$ emissions

Background emissions were very low for the first 2 d prior to the slurry application in both experiments, but immediately following the application,  $\text{NH}_3$  emissions increased significantly. Large  $\text{NH}_3$  emissions were measured following the summer application (Fig. 1). At the end of 8 d, a total emission of 205 kg/ha of ammonia had been recorded representing 51% of the TAN and 31% of the total N applied. Nearly 95% of this emission occurred in the first 4 d following application and 59% in the first 24 h. The rate of volatilization was greatest immediately following the application when 22.4 kg  $\text{NH}_3\text{-N/ha h}$  was measured.

The  $\text{NH}_3$  emission from the autumn application is shown in Fig. 2 and totalled 66 kg  $\text{NH}_3\text{-N/ha}$  over 4.25 d following application, which represented 8 and 6% of the TAN and total N applied, respectively. As with the summer application, nearly 95% of the total loss occurred in the first 4 d after application, whilst 47 kg  $\text{NH}_3\text{-N/ha}$

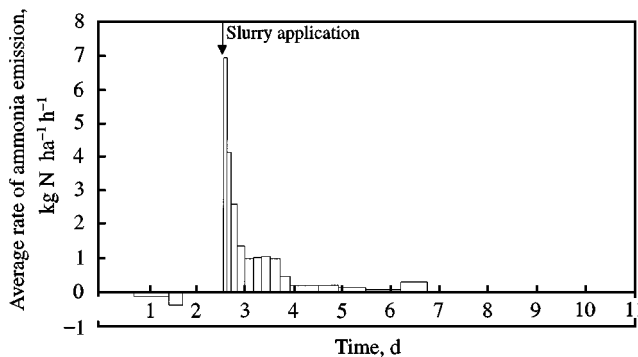


Fig. 2. Rate of ammonia emission from the managed field following slurry application in October

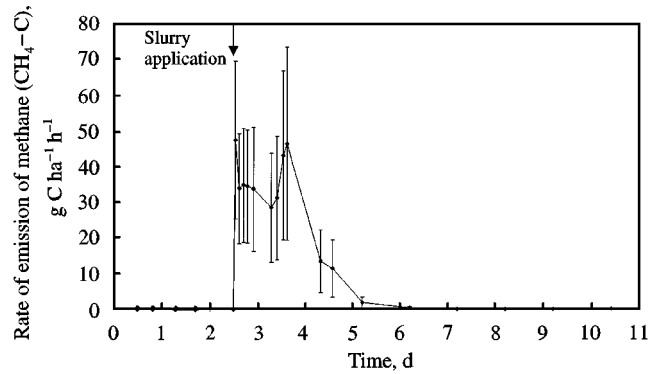


Fig. 3. Rate of methane emission from the managed field following slurry application in June. Vertical line =  $\pm$  standard error.  $N = 5$

was lost in the first 24 h, equivalent to 71% of the total loss. Immediately following the application, a volatilization rate of 7 kg  $\text{NH}_3\text{-N/ha h}$  was measured.

#### 3.2. $\text{CH}_4$ emissions

Methane emissions were negligible prior to the slurry application but increased significantly immediately after application. The summer application resulted in a total emission of 1.77 kg  $\text{CH}_4\text{-C/ha}$  after 11 d. This represented 0.04% of the total C applied in the slurry. Over 98% of the loss occurred in the first 4 d (Fig. 3). Methane emissions following the autumn application totalled 4.15 kg  $\text{CH}_4\text{-C/ha}$  111 d after application. This loss represented 0.12% of the C added in the slurry. After the initial peak of  $\text{CH}_4$  emission that followed the application of slurry the emission rate rapidly decreased to a relatively low and constant level (Fig. 4).

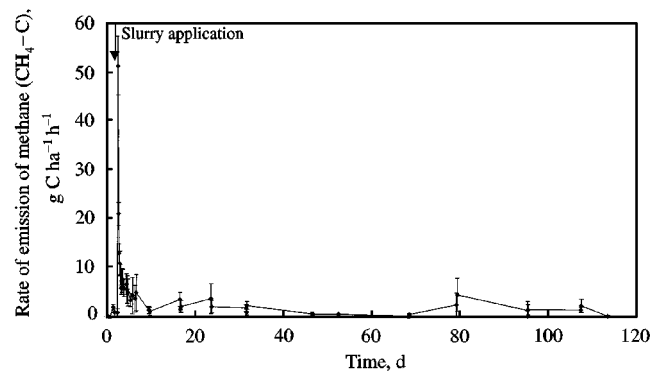


Fig. 4. Rate of methane emission from the managed field following slurry application in October. Vertical line =  $\pm$  standard error.  $N = 5$

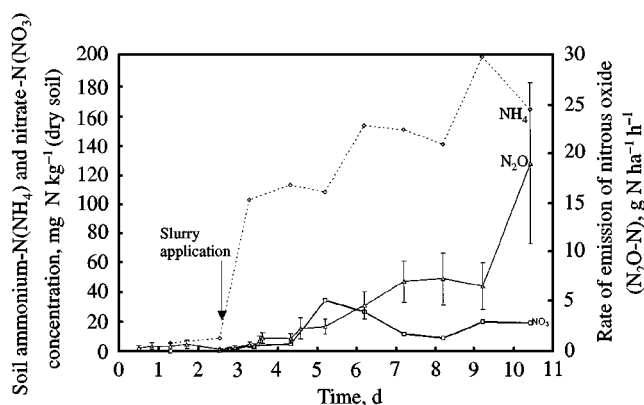


Fig. 5. Rate of nitrous oxide emission and soil ammonium-N and nitrate-N concentrations following slurry application in June

3.3. N<sub>2</sub>O emissions

Figures 5 and 6 show N<sub>2</sub>O emissions and soil ammonium-N and nitrate-N concentrations following the slurry applications. (Error bars are not shown to ensure clarity of the presentation. However, the cumulative N<sub>2</sub>O emissions are given in the text with associated standard errors). Nitrous oxide emission rates were very low during the first 2 d before the slurry application in summer, gradually increased following the application and were still increasing when measurements ceased. Figure 5 shows that there was a peak in soil NO<sub>3</sub><sup>-</sup> concentration 3 d after slurry application but this was not accompanied by a peak in N<sub>2</sub>O flux. After this time the soil NO<sub>3</sub><sup>-</sup> concentration gradually decreased as the N<sub>2</sub>O emission rate continued to increase.

The NH<sub>4</sub><sup>+</sup> concentration in the soil increased significantly following the slurry application in June (*P* < 0.05)

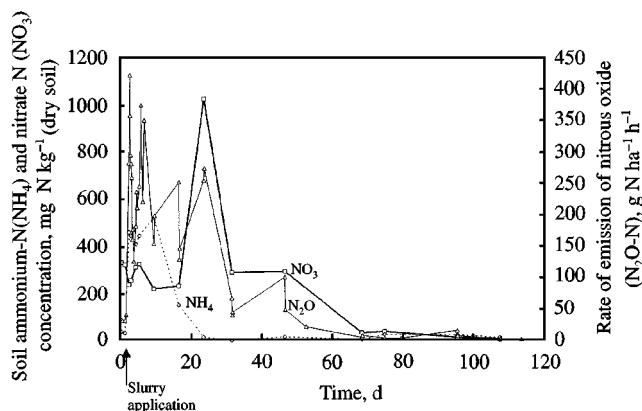
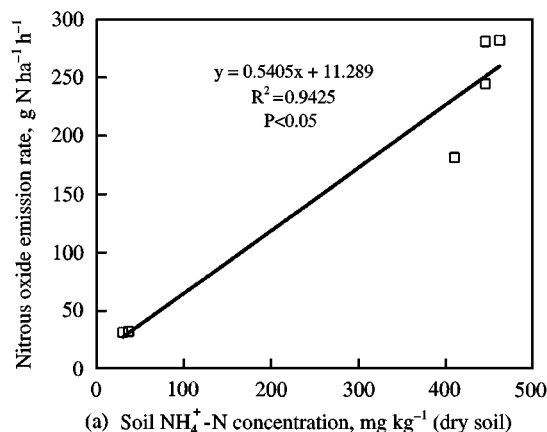


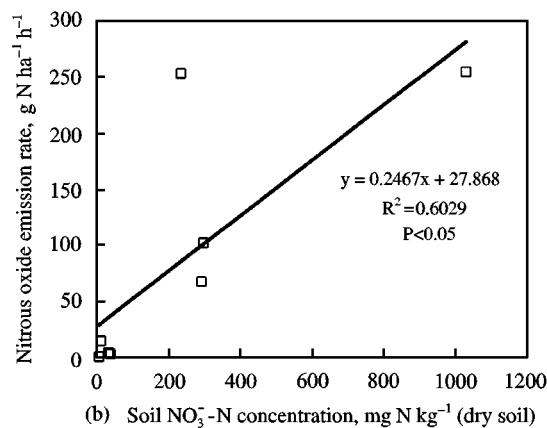
Fig. 6. Rate of nitrous oxide emission and soil ammonium-N and nitrate-N concentrations following slurry application in October

and, although Fig. 5 shows an upward trend in NH<sub>4</sub><sup>+</sup> concentration following the slurry application, this was not significant (*P* > 0.05) except for that on day nine which was probably the result of mineralization of slurry N. The cumulative loss of N<sub>2</sub>O-N during the 8 d following application was 1.1 kg/ha (± 0.3) representing 0.17% of the applied N.

In the autumn, N<sub>2</sub>O emission rates were already high during the 2 d prior to slurry application, as was the soil NO<sub>3</sub><sup>-</sup> concentration (Fig. 6), but emission rates increased significantly following the addition of slurry and remained high for the next 14 d. A further peak in N<sub>2</sub>O emission rate 21 d after application was accompanied by a similar peak in soil NO<sub>3</sub><sup>-</sup> concentration. After this time, the soil NO<sub>3</sub><sup>-</sup> concentration and N<sub>2</sub>O emission rates gradually decreased. Emission rates of N<sub>2</sub>O showed a linear relationship with the soil NH<sub>4</sub><sup>+</sup>-N concentration for the first 6 d of monitoring (*r*<sup>2</sup> = 0.94, *P* < 0.05), whereas after day ten the rate of N<sub>2</sub>O emission was related to the soil NO<sub>3</sub><sup>-</sup>-N concentration (*r*<sup>2</sup> = 0.60, *P* < 0.05) (see Fig. 7).



(a) Soil NH<sub>4</sub><sup>+</sup>-N concentration, mg kg<sup>-1</sup> (dry soil)



(b) Soil NO<sub>3</sub><sup>-</sup>-N concentration, mg N kg<sup>-1</sup> (dry soil)

Fig. 7. Relationship between nitrous oxide emission rate and (a) soil ammonium concentration during the first six days of monitoring (*N* = 6) and (b) soil nitrate concentration from day ten (*N* = 7)

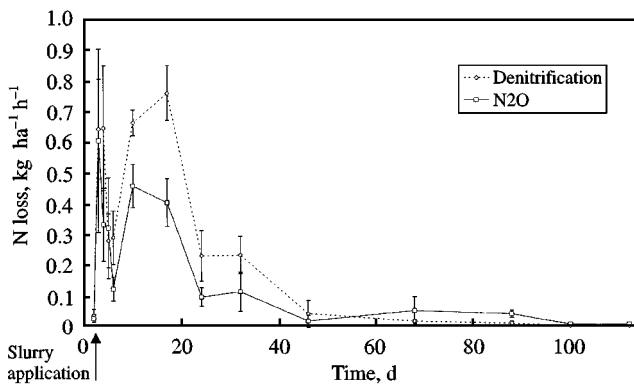


Fig. 8. Denitrification losses and nitrous oxide emissions following the October application of slurry using the Kilner jar technique. Vertical lines =  $\pm$  standard error  $N = 5$

The cumulative  $N_2O-N$  emission for the 113 d measurement period was  $272 \pm 60$  kg/ha representing 23% of the 1179 kg N applied in the slurry. The Kilner jar method of measuring  $N_2O$  emission (i.e. soil not treated with acetylene) gave a similar total of  $268 \pm 24$  kg/ $N_2O-N$  ha.

### 3.4. Denitrification losses

Figure 8 compares the total denitrification loss ( $N_2O + N_2$ ) and  $N_2O$  loss following the autumn slurry application measured with the Kilner jar technique. The cumulative denitrification loss during the 111 d following application was  $407 \pm 53$  kg N/ha, representing 34% of the slurry N applied. The difference between this total denitrification loss (407 kg N/ha) and the total  $N_2O$  loss (268 kg N/ha) can be assumed to be that lost as  $N_2$ , i.e. 139 kg N/ha.

**Table 2**  
Recovery of  $^{15}N$ -labelled pig slurry in the soil-plant system (percent)

Micro-plot number	Soil	Plant			Total
		Shoots	Roots	Total	
1	25	9.8	8.3	18.1	43.1
2	29	10.7	6.7	17.4	46.4
3	39	7.4	3.9	11.3	50.3
Mean	31	9.3	6.3	15.6	46.6

### 3.5. Plant uptake and soil immobilization of slurry N

Table 2 shows the results from the micro-plots that received  $^{15}N$  labelled slurry in June. A mean of 31% of slurry N was immobilized in the soil and 15.6% was taken up by the grass, representing a total of 46.6% of slurry N.

### 3.6. Nitrogen balance

A nitrogen balance was constructed for the slurry-N losses and transformations following the June application. This application was the first of the 1995 season therefore the soil nitrate content was low (Fig. 5) following drainage and denitrification during winter 1994 and spring 1995. Previous work has demonstrated that approximately one-fifth of the total  $N_2O$  loss occurs within the first 10 d following slurry application and that levels of  $N_2O$  emissions from slurry treated plots return to control levels within four weeks.<sup>21</sup> Therefore, to extrapolate from the cumulative  $N_2O$  loss from the nine day measurement period to one month following the slurry application in summer, which is when the  $^{15}N$

**Table 3**  
The fate of slurry N following application to the Solepur site

	Summer application, this study (399 kg $NH_4^+-N$ /ha, 656 kg total N/ha)			Estimated by Martinez <sup>6</sup>
	kg N/ha	% of TAN applied	% of total N applied	% of total N applied
Ammonia volatilization	205	52	32	10-20
Nitrous oxide emission	5.5	1.4	0.8	
Dinitrogen emission	?	?	?	30-40
Plant uptake	100	26	16	15
Soil immobilization	199	51	31	25
Leaching	0	0	0	10

micro-plots were sampled, the cumulative  $\text{N}_2\text{O}$  emission for the first nine days was multiplied by five. There was no leaching of  $\text{NO}_3^-$  during this experiment and all the  $\text{NH}_3$  can be assumed to have been lost in the first 7 d. From Table 3, it can be seen that of the 656 kg total-N applied (399 kg  $\text{NH}_4^+-\text{N}$ ) in the slurry in June, almost 33% of it was lost through gaseous emissions whilst 47% of it was immobilized in the plant-soil system. Direct measurements of plant uptake, soil immobilization,  $\text{NH}_3$  and  $\text{N}_2\text{O}$  losses accounted for 78% of the slurry N added; the remaining unaccounted portion may be due to  $\text{N}_2$  emission.

Three further slurry applications were made to the same managed field between July and October and the soil  $\text{NO}_3^-$  concentration and  $\text{N}_2\text{O}$  emissions from the bare soil in the autumn prior to the slurry addition were high as a result of these previous slurry applications (Fig. 6). Therefore, it could not be assumed that the total  $\text{N}_2\text{O}$  and  $\text{N}_2$  losses and  $\text{NO}_3^-$  leached following the autumn application of slurry were solely attributable to the October application. For these reasons a nitrogen budget following the October application was not possible.

#### 4. Discussion

The application of slurry to the managed field resulted in significant emissions of  $\text{NH}_3$ ,  $\text{CH}_4$  and  $\text{N}_2\text{O}$  and in denitrification losses. The extent of these losses was affected by the soil conditions, slurry type, presence or absence of a crop and the cumulative effects of previous applications.

The application of slurry in the autumn to a bare soil resulted in significantly lower  $\text{NH}_3$  emission than after the June application to a ryegrass crop. There may be several explanations for the differences in  $\text{NH}_3$  emission rates following the two applications. The slurry total solids (TS) content was much greater in summer (10.4%) and therefore the slurry remained on the surface for longer than in the autumn when the more fluid slurry (TS = 4.5%) infiltrated the soil more rapidly. Also, the influence of the grass sward appeared to increase  $\text{NH}_3$  volatilization in this study, which contrasts with results of Faurie and Bardin<sup>22</sup> and Morvan *et al.*<sup>23</sup> Both of these studies demonstrated lower  $\text{NH}_3$  volatilization from slurry applied to a grass sward than to a bare soil. Faurie and Bardin<sup>22</sup> attributed this reduction to micro-climatic effects of the canopy whereas Morvan *et al.*<sup>23</sup> concluded that their result was due to absorption to  $\text{NH}_3$  by the canopy. The ryegrass sward in our study was over 15 cm in height and collapsed under the weight of the slurry application. The grass, therefore, acted as a barrier to the infiltration of the slurry into the soil and hence an avail-

able  $\text{NH}_3$  source existed at the surface for a longer period of time.

The difference in  $\text{NH}_3$  loss may also be due to the different rates of slurry applied. Thompson *et al.*<sup>24</sup> found that the proportion of TAN volatilized decreased as the application rate increased, up to approximately 60  $\text{m}^3/\text{ha}$ , thereafter the percentage loss did not change. Even though the rates of application were much greater than 60  $\text{m}^3/\text{ha}$  in this present study (95 and 227  $\text{m}^3/\text{ha}$  in summer and autumn, respectively) it is possible that the observed difference in emission was partly due to the large differences in rates applied. Also, soil temperatures were much lower in the autumn (10°C daytime average) compared with the summer (15°C) and  $\text{NH}_3$  volatilization has been shown to be temperature dependent.<sup>25</sup>

There were greater  $\text{N}_2\text{O}$  fluxes following the autumn application of slurry than in the summer after the June application. The soil was much wetter (35% soil moisture content) in the autumn than in the summer (20%) and therefore conditions were more favourable for denitrification.<sup>26</sup> Also, there was no crop to act as an alternative sink for available nitrate following the autumn application. The autumn slurry had a lower TS content and infiltration into the bare soil was quicker than in the summer. This resulted in less  $\text{NH}_3$  volatilization and more ammonium being present in the soil for nitrification.

The significant correlation between soil  $\text{NH}_4^+$  content and  $\text{N}_2\text{O}$  emission for the first 6 d of the October experiment indicates a strong involvement of nitrification and, although the mechanisms are not clear, it is a relationship that has been shown previously following applications of slurry<sup>27</sup> and dung and urine amendments<sup>28</sup> to soils.

The larger fluxes of  $\text{N}_2\text{O}$  following the October application may also be due to the antecedent soil conditions. It is possible that the nitrification and denitrification enzymes were active at the time the autumn application was made, as conditions had been favourable for denitrification for some time previously. However, because of the very dry conditions and low  $\text{NO}_3^-$  content of the soil in the summer, this may not have been the case after the application of slurry in June and, therefore, fluxes were lower. Several studies have pointed to the importance of antecedent soil conditions in controlling  $\text{N}_2\text{O}$  and  $\text{N}_2$  fluxes from soil.<sup>29</sup> Firestone and Tiedje<sup>30</sup> demonstrated a lag of 2–3 d in the depression of  $\text{N}_2\text{O}$  reductase compared with  $\text{NO}_3^-$  reductase after the onset of anaerobiosis, thus influencing the  $\text{N}_2:\text{N}_2\text{O}$  ratio.

These measurements of N losses through  $\text{NH}_3$  volatilization and denitrification and N transformations via soil immobilization and plant uptake are in general agreement with the estimated N balance for the "Solepur" experiment described by Martinez.<sup>6</sup> In Table 3, we

compare out measurements following the summer application with those for the annual estimated N flow in the Solepur experiment.<sup>6</sup> Our larger loss through NH<sub>3</sub> volatilization and much lower loss via denitrification reflect the influence of soil conditions on these loss pathways with peak losses by NH<sub>3</sub> volatilization and denitrification occurring at different times of the year.

The Solepur site was set up to remove NO<sub>3</sub><sup>-</sup> from pig slurries. It has been shown to be very successful at containing and denitrifying NO<sub>3</sub><sup>-</sup>-rich drainage water.<sup>8</sup> However, in constructing and managing the site to reduce a serious localized problem (i.e. NO<sub>3</sub><sup>-</sup> leaching) the system appears to be promoting the emission of gaseous pollutants with greater significance on regional (NH<sub>3</sub>) and global (N<sub>2</sub>O and CH<sub>4</sub>) scales.

Ammonia volatilization can be reduced by shallow injection of slurry into the ground<sup>31</sup> (also van der Weerden and Pain, personal communication of unpublished results), and this technique could be used in the Solepur system. However, injection of slurries has been shown to increase the risk of NO<sub>3</sub><sup>-</sup> leaching<sup>32</sup> and denitrification losses.<sup>33</sup> The major problem that the Solepur site has, is that instead of the soil acting as the "nitrification reactor" as intended, under wet soil conditions the managed field is also denitrifying considerable quantities of NO<sub>3</sub><sup>-</sup> and not all of it is leaving the soil as benign N<sub>2</sub>. It would be impossible to prevent all denitrification, but the future challenge is to manage such a system so that for any denitrification flux the N<sub>2</sub>O emission is minimized and the N<sub>2</sub> flux maximized. One option would be to add nitrification inhibitors to the injected slurry, which has been shown to reduce both NH<sub>3</sub> emissions and denitrification losses from slurry applications.<sup>34</sup> By including a nitrification inhibitor, NO<sub>3</sub><sup>-</sup> levels in the soil should be reduced, N<sub>2</sub>O reductase inhibition would therefore be reduced<sup>29</sup> which may in turn increase the N<sub>2</sub>/N<sub>2</sub>O ratio.

Other forms of slurry treatment based on nitrification and denitrification reactions, e.g. aerobic digestion, have the potential to emit gaseous N pollutants such as N<sub>2</sub>O. Burton *et al.*<sup>35</sup> demonstrated that up to 19% of the N lost from slurry during treatment was emitted as N<sub>2</sub>O. Therefore, a full assessment of N losses from different slurry treatment systems needs to be made so that the potential of these systems to pollute the atmosphere can be compared alongside their relative start-up and running costs.

## 5. Conclusions

After five years of repeated slurry applications, the Solepur soil treatment system has maintained its capacity to remove organic matter and N from pig slurry. However, the system would appear to promote emissions of gaseous pollutants.

- (1) Between 6 and 31% of the total N applied in the slurry was lost through NH<sub>3</sub> volatilization following the October and June applications, respectively. These losses are within the reported range following surface broadcasting of pig slurries at agronomic rates and represented between 0.3 and 1.5 kg N/m<sup>3</sup> slurry.
- (2) Soil conditions and rate of slurry application influenced CH<sub>4</sub> emissions. Slurry application to dry soil in June resulted in the total CH<sub>4</sub> loss representing 0.04% of the total C added, whilst the high application rate of slurry to the wetter soil in October resulted in a CH<sub>4</sub> loss representing 0.12% of the total C added.
- (3) Emissions of N<sub>2</sub>O were very high following the slurry application in October when a total of 272 kg N/ha was emitted as N<sub>2</sub>O in the 111 d following application. In contrast, N<sub>2</sub>O emissions totalled 1.1 kg N/ha 8 d after slurry application to the dry soil in June, representing 23 and 0.17% of the total N applied, respectively.
- (4) The October application of slurry resulted in large losses of N<sub>2</sub>, 139 kg N, as a result of denitrification. This loss represented 12% of the total N applied in the slurry.

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## References

- <sup>1</sup> van der Meer A Challenge for pigmeat production in the European Community. PIGS-Misset, September/October, Pp. 36–37 1990
- <sup>2</sup> Agreste A La Bretagne au premier rang (Brittany in the first rank). Statistique Agricole, 1995, **16**, 11–20
- <sup>3</sup> Abrassart J; Bertrand M; Herve A M Bilan global de l'azote, phosphore et potassium. Methode pour une évaluation à différentes échelles (Globale nutrients–N, P, K balance. An assessment at different scales). Informations Techniques du CEMAGREF 1993, Vol. 91, note 1



- <sup>4</sup> **Bertrand M** De la production à l'épandage: la gestion des lisiers de porc (From production to spreading: the management of pig slurry). Bulletin Technique d'Information, 1994, **14**, 53–71
- <sup>5</sup> **Willers H C; Derikx P J L; Ten Have P J W; Vijn T K** Emission of ammonia and nitrous oxide from aerobic treatment of veal calf slurry. Journal of Agricultural Engineering Research, 1996, **63**, 345–352
- <sup>6</sup> **Martinez J** Solepur: a soil treatment process for pig slurry with subsequent denitrification of drainage water. Journal of Agricultural Engineering Research, 1997, **66**(1), 51–62
- <sup>7</sup> **Martinez J; Guiziou F** Mise au point et évaluation de la faisabilité d'un procédé naturel de traitement du lisier de porcs par le sol (Development, evaluation and feasibility assessment of a soil treatment process for treating pig slurry). Journées de la Recherche porcine en France, 1995, **27**, 362–372
- <sup>8</sup> **Hao X; Martinez J; Svoboda I** Nitrogen removal from the leachate of SOLEPUR treated pig slurry. European Water Pollution Control, 1996, **6**, 31–36
- <sup>9</sup> **Estavillo J M; Rodriguez M; Domingo M; Muñoz-Rueda A; Gonzalez-Murua C** Denitrification losses from a natural grassland in the Basque Country under organic and inorganic fertilisation. Plant and Soil, 1994, **162**, 19–29
- <sup>10</sup> **Misselbrook T H; Laws J A; Pain B F** Surface application and shallow injection of cattle slurry on grassland: nitrogen losses, herbage yields and nitrogen recoveries. Grass and Forage Science, 1996, **51**, 270–277
- <sup>11</sup> **Eggington G M; Smith K A** Nitrous oxide emission from a grassland soil fertilised with slurry and calcium nitrate. Journal of Soil Science, 1986, **37**, 59–67
- <sup>12</sup> **Chadwick D R; Pain B F** Methane fluxes following slurry applications to grassland soils: laboratory experiments. Agriculture, Ecosystems and Environment, 1997, **63**, 51–60
- <sup>13</sup> **Denmead O T** Micrometeorological methods for measuring gaseous losses of nitrogen in the field. In: Gaseous Loss of Nitrogen from Plant–Soil Systems (Freney J R; Simpson J R eds) Pp. 133–157, Vol. 9, Developments in Plant and Soil Science. The Hague: Martinus Nijhoff, 1983
- <sup>14</sup> **Ryden J C; McNeill J E** Application of the micrometeorological mass balance method for the determination of ammonia loss from a grazed sward. Journal of Science, Food and Agriculture, 1984, **35**, 297–310
- <sup>15</sup> **Leuning R; Freney J R; Denmead O T; Simpson J R** A sampler for measuring atmospheric ammonia flux. Atmospheric Environment, 1985, **19**, 1117–1124
- <sup>16</sup> **Mosier A R** Chamber and isotope techniques. In: Exchange of Trace Gases between Terrestrial Ecosystems and the Atmosphere (Andrae M O; Schimel D S eds), Pp. 175–187. New York; Wiley (1989)
- <sup>17</sup> **Ryden J C; Lund L J; Focht D D** Direct in-field measurement of nitrous oxide flux from soils. Soil Science Society of America Journal, 1987, **42**, 731–737
- <sup>18</sup> **Bremner J M; Keeney D R** Steam distillation methods for determination of ammonium, nitrate and nitrite. Analytica Chimica Acta, 1965, **32**, 485–495
- <sup>19</sup> **Guiraud G; Fardeau J C** Dosage par la méthode Kjeldahl des nitrates contenus dans les sols et les végétaux (Kjeldahl determination of nitrate in soil and plant samples). Annales Agronomiques, 1977, **28**, 329–333
- <sup>20</sup> **Guiraud G** Contribution du marquage isotopique à l'évaluation des transferts d'azote entre les compartiments organiques et minéraux dans les systèmes Sol-plante (Contribution of isotopic labelling to the evaluation of nitrogen turnover between organic and mineral forms in the soil–plant system. Thèse de doctorat d'Etat, Université de Paris VI, France, 1984
- <sup>21</sup> **Misselbrook T M; Chadwick D R; Pain B F; Headon D M** Dietary manipulation as a means of decreasing N losses and methane emissions and improving herbage N uptake following application of pig slurry to grassland. Journal of Agricultural Science, in press
- <sup>22</sup> **Faurie G; Bardin R** La volatilisation de l'ammoniac II—Influence des facteurs climatiques et du couvert végétal. Annales Agronomiques, 1979, **30**, 401–414
- <sup>23</sup> **Morvan T; Leterme Ph; Arsene G G; Mary B** Nitrogen transformations after pig slurry spreading on bare soil and rye-grass using <sup>15</sup>N labelled (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. Fourth ESA-Congress, Book of abstracts, Session 3.3, 1996, Pp. 362–363
- <sup>24</sup> **Thompson R B; Pain B F; Rees Y J** Ammonia volatilization from cattle slurry following surface application to grassland II. Influence of application rate, wind speed and applying slurry in narrow bands. Plant and Soil, 1990, **125**, 119–128
- <sup>25</sup> **Moal J-F; Martinez J; Guiziou F; Coste C-M** Ammonia volatilization following surface-applied pig and cattle slurry in France. Journal of Agricultural Science, 1995, **125**, 245–252
- <sup>26</sup> **Maag M** N<sub>2</sub>O production rates and denitrification rates in soil amended with pig slurry. Mitteilung der Deutschen Bodenkundlichen Gesellschaft, 1990, **60**, 205–210
- <sup>27</sup> **Jarvis S C; Hatch D J; Pain B F; Klarenbeek J V** Denitrification and evolution of nitrous oxide after the application of cattle slurry to a peat soil. Plant and Soil, 1994, **166**, 231–241
- <sup>28</sup> **Allen A G; Jarvis S C; Headon D M** Nitrous oxide emissions from soils due to inputs of nitrogen from excreta return by livestock on grazed grassland in the UK. Soil Biology and Biochemistry, 1996, **28**, 597–607
- <sup>29</sup> **Dendooven L; Anderson J M** Maintenance of denitrification potential in pasture soil following anaerobic events. Soil Biology and Biochemistry, 1995, **27**, 1251–1260
- <sup>30</sup> **Firestone M K; Tiedje J M** Temporal changes in N<sub>2</sub>O and N<sub>2</sub> following onset of anaerobiosis. Applied and Environmental Microbiology, 1979, **38**, 673–679
- <sup>31</sup> **Rubæk G H; Henriksen K; Petersen J; Rasmussen B; Sommer S G** Effects of application technique and anaerobic digestion on gaseous nitrogen loss from animal slurry applied to ryegrass (*Lolium perenne*). Journal of Agricultural Science, 1996, **126**, 481–492
- <sup>32</sup> **Misselbrook T H; Shepherd M A; Pain B F** Sewage sludge applications to grassland: influence of sludge type, time and method of application on nitrate leaching and herbage yield. Journal of Agricultural Science, 1996, **126**, 343–352
- <sup>33</sup> **Thompson R B; Ryden J C; Lockyer D R** Fate of nitrogen in cattle slurry following the surface application or injection to grassland. Journal of Soil Science, 1987, **38**, 689–700
- <sup>34</sup> **Pain B F; Misselbrook T H; Rees Y J** Effects of nitrification inhibitor and acid addition to cattle slurry on nitrogen losses and herbage yields. Grass and Forage Science, 1994, **49**, 209–215
- <sup>35</sup> **Burton C H; Sneath R W; Farrent J W** Emissions of nitrogen oxide gases during aerobic treatment of animal slurries. Bioresource Technology, 1993, **45**, 233–235