DIVISION S-8—NUTRIENT MANAGEMENT & SOIL & PLANT ANALYSIS

Ammonia Volatilization and Selected Soil Characteristics Following Application of Anaerobically Digested Pig Slurry

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ABSTRACT

Ammonia volatilization occurs shortly following land application of pig slurry. Several slurry and soil characteristics modulate the intensity of this process, and their net effect on volatilization is still hard to predict. Our aim was to compare volatilization following application of anaerobically stored (ASPS) and anaerobically digested (ADPS) pig slurry to a bare loamy soil (loamy, mixed, frigid, Aeric Haplaquept). Ammonia volatilization was measured using wind tunnels. Soil pH and water, NH_4^+, NO_3^-, and volatile fatty acid (VFA) contents were monitored in the 0- to 0.5-, 0.5- to 2-, 2- to 5-, and 5- to 10-cm soil layers to explain volatilization rates. Following slurry application, pH increased by 1 to 3 units in the top 2 cm of soil, resulting in high volatilization rates in the first 6 h of experiment. Thereafter, pH decreased more slowly in ASPS than ADPS plots, possibly due to the degradation of VFAs present in ASPS. After 2 d, 35% of slurry-added NH_4^+–N was lost as NH_3–N for both slurries, corresponding well to the net decrease found in soil NH_4^+–N content. After 9 d, net soil NH_4^+–N disappearance accounted for about 60% of slurry-added NH_4^+–N for both slurries, whereas NH_3–N losses represented only 40%. Therefore, for the first 2 d of the experiment NH_3 volatilization explained most of the decline in soil NH_4^+. Afterwards, biological processes, such as immobilization and nitrification, were assumed to play a significant role in slurry NH_4^+ disappearance. Despite marked changes in slurry properties, anaerobic digestion did not significantly modify the proportion of slurry N that was lost as NH_3. Ammonia volatilization was related mostly to soil pH and NH_4^+ content in the top 2 cm of soil. Below 5-cm depth, slurry application had little effect on soil pH, water, VFA, or mineral N content. This finding stresses the importance of stratified soil sampling when studying the short-term effects of pig slurry on NH_3 volatilization and associated soil properties.

In Québec, Canada, about 9 000 000 m^3 of pig slurry (approximately 33 million Kg N) are applied annually on agricultural land. High NH_3 volatilization rates may occur in the few hours following land application of pig slurry (Pain et al., 1989; Gordon et al., 2001; Rochette et al., 2001), thereby altering the fertilizer value of the slurry (Jarvis and Pain, 1990; Morvan et al., 1997; Sørensen and Amato, 2002) and adversely affecting the environment (van Breemen et al., 1982). Initial slurry properties, such as pH (Génermont, 1996; Sommer and Hutchings, 2001), NH_4^+, carbonate, VFA (Sommer and Husted, 1995; Sommer and Sherlock, 1996), and total solid contents (Pain et al., 1989; Sommer and Olesen, 1991) have been identified as factors determining NH_3 volatilization. Soil characteristics, such as pH and nitrification activity (Génermont, 1996; Whitehead and Raistrick, 1993), also affect volatilization. Efforts to relate volatilization to relevant soil variables require adequate soil sampling strategy to identify the soil layer that interacts with the atmosphere (Sherlock and Goh, 1985; Génermont, 1996).

Anaerobic digestion of pig slurry is proposed as a treatment to convert slurry organic matter into biogas (Massé et al., 1996). In addition, anaerobic digestion decreases slurry viscosity and VFA content, while increasing slurry pH and inorganic C content (Pain et al., 1990; Kirchmann and Lundvall, 1993; Sommer and Husted, 1995). Reduced slurry viscosity could decrease the propensity of slurry NH_4^+ to volatilize (Pain et al., 1989; Sommer and Olesen, 1991), whereas increased pH and carbonate content could stimulate volatilization (Génermont, 1996; Sommer and Sherlock, 1996; Sommer and Hutchings, 2001). Pain et al. (1990) and Rubaek et al. (1996) measured similar NH_3 volatilization following application of undigested and anaerobically digested pig slurry on grasslands in the United Kingdom. The presence of plants may reduce NH_3 volatilization (Whitehead and Raistrick, 1992; Morvan et al., 1997). In Québec, pig slurry is often applied on bare soils, before planting or after harvesting annual crops. Therefore, the aim of our study was to compare NH_3 volatilization following spring application of ASPS or ADPS pig slurry to a bare loamy soil. Selected soil characteristics were also measured in surface soil layers to explain variations in volatilization rates.

MATERIALS AND METHODS

Pig Slurry, Site, and Experimental Set-Up

In March 2000, fresh pig slurry was collected from a commercial hog operation storage tank. Part of this slurry was kept for 12 wk in a closed 1-m^3 container under anaerobic conditions. The rest of the slurry was processed in a bioreactor for anaerobic digestion as described by Massé et al. (1996).

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Abbreviations: ADPS, anaerobically digested pig slurry; ASPS, anaerobically stored pig slurry; VFA, volatile fatty acid.

Table 1. Selected characteristics of the pig slurries at time of land application.

Slurry characteristics	Anaerobically stored	Anaerobically digested
pH	7.7 (0.1)†	8.1 (0.0)
	kg m^{-3}	
Dry matter	59.4 (2.1)	32.5 (0.6)
Total C	39.3 (0.5)	20.1 (0.7)
Total inorganic C	1.6 (0.0)	3.7 (0.1)
Total dissolved C	17.1 (1.9)	7.6 (1.8)
Total VFA-C	9.0 (0.7)	0.7 (0.1)
Total N	9.7 (0.1)	7.8 (0.1)
NH_4^+–N	6.7 (0.0)	5.4 (0.1)
NO_3^-–N	0.1 (0.0)	0.1 (0.0)
Total P	2.1 (0.0)	1.4 (0.0)

† Values are the means (standard deviations) of triplicate measurements in each slurry container.

Selected characteristics of the two slurries at time of spreading are reported in Table 1. The study was performed in June 2000 on a Le Bras loam (loamy, mixed, frigid, Aeric Haplaquept) at the St-Lambert Research Farm of the Institut de Recherche et de Développement en Agroenvironnement near Québec City, Canada (46° 05′ N, 71° 02′ W, altitude 110 m). Selected soil properties were: pH (water) = 5.9; 21.4 g C kg^{-1}; 1.4 g N kg^{-1}; 280 g kg^{-1} sand; 240 g kg^{-1} clay. The experimental site had been cultivated to timothy (*Phleum pratense* L.) for several years and the sod was plowed under in Autumn 1999. In Spring 2000, the soil was harrowed to a 10-cm depth 3 wk before initiation of the experiment. The soil was kept bare during the experiment by manual weeding. Two sets of experimental plots were established. The first set consisted of six plots of 3 by 3 m in size that was used for monitoring soil parameters. A second set of six plots of 0.5 by 2 m in size was used for measuring NH_3 volatilization. Both ASPS and ADPS were surface-applied between 900 and 1000 h at a rate of 90 m^3 ha^{-1}. This loading rate is common in the area of study. However, due to the exceptionally high N content of the slurries, this application rate resulted in the addition of approximately 700 kg N ha^{-1} for ADPS and approximately 800 kg N ha^{-1} for ASPS. Watering cans were used to apply the slurries on 1 m^2 subunit at a time.

Environmental Conditions and Ammonia Volatilization

Ammonia volatilization was measured for 19 d following slurry application using wind tunnels as described by Rochette et al. (2001). Briefly, six wind tunnels, each covering a 1-m^2 plot (0.5 × 2 m), were installed immediately after pig slurry addition, and the time elapsed between slurry addition and the start of measurement was <3 min. The tunnels consisted of an inverted acrylic plastic box (cross-section 0.5 by 0.1 m) connected to a steel duct housing a fan. Air temperature and velocity were measured inside the tunnels (5 cm above the soil) using a hot wire sensor (Model KM 4007, Comark Limited, Hertfordshire, UK) immediately down flow from a flange reducing the internal diameter of the steel duct. The NH_3 volatilization rate (F_{NH3}, mg N m^{-2} h^{-1}) was calculated as:

$$F_{NH3} = \frac{f}{A_s}(c_o - c_i)$$

where f is the air flow rate (270 m^3 h^{-1}) through the tunnel, A_s is the enclosed surface area (1 m^2) and c_o and c_i are the NH_3 concentration of the air leaving and entering the tunnel, respectively (mg NH_3–N m^{-3}). Values of c_o and c_i were obtained by trapping NH_3 in 0.005 *M* H_3PO_4 at an air-flow rate of 3 L min^{-1}. The tunnels were operated continuously except during two >10 mm rainfall periods (Day 3 and 7; Fig. 1), when the tunnels were removed and replaced at the same location after the rain. For the other rainfall periods (<5 mm), an equivalent amount of water was applied inside tunnels in <16 h after rain using watering cans.

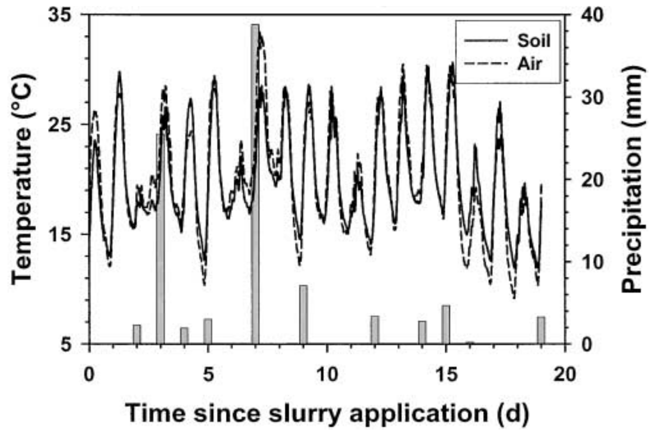

Fig. 1. Air and soil (2-cm depth) temperature in wind tunnels (lines), and daily precipitation (bars) for 19 d following application of anaerobically stored (ASPS) and anaerobically digested (ADPS) pig slurry to a bare loamy soil.

Soil temperature at 2 cm below the soil surface was monitored inside the tunnels using copper-constantan thermocouples. Rainfalls were recorded with a tipping bucket rain gauge (Model TE525M, Campbell Scientific, Edmonton, AB, Canada) located on the experimental site. Hot wire sensor, thermocouples, and rain gauge were read by means of a data logger (CR-10, Campbell Scientific Inc, Logan, UT). Air and soil temperatures were averaged hourly, while precipitation was reported on a daily basis.

Soil Sampling and Analyses

Soil samples were collected 3 h before and 1, 2, 4, 6, and 9 d after slurry application. At each sampling time, three soil cores (5.3 cm diam.) were collected to the 10-cm depth in each plot. The cores were subdivided in the 0- to 0.5-, 0.5- to 2-, 2- to 5-, and 5- to 10-cm layers and combined to make one composite sample per plot per soil layer. Soil bulk density was measured in experimental plots at the 0- to 5- and 5- to 10-cm depths using soil cores (Culley, 1993). Gravimetric water content of soil samples was determined after soil drying at 105°C for 24 h. Soil pH was measured in a 1:1 soil/water mixture. Soil mineral N was extracted by shaking 30 g of field-moist soil with 60 mL of 2 *M* KCl for 30 min in a 250-mL polypropylene bottle (Chantigny et al., 2001, 2002). The bottles were centrifuged (3000 × *g* for 10 min) and the extracts were filtered on filter papers (Whatman no. 42) prewashed with 2 *M* KCl to eliminate possible NH_4^+ contamination. Blank samples were used during extraction procedures to correct for possible NH_4^+ and NO_3^- background contamination. Ammonium-N content in the KCl extracts was quantified by colorimetry (N'konge and Ballance, 1982). The NO_3^-–N content was measured in the ultraviolet wavelength at 214 nm using a liquid chromatograph (Model 4000i, Dionex Corp., Sunnyvale, CA) equipped with Ion Pack CG5 and CS5 columns, and a variable wavelength VDM-2 UV detector (Ziadi et al., 1999). Volatile fatty acids were quantified in soil samples by shaking 5 g of field-moist soil with 15 mL of cold water (4°C) for 30 min in 50-mL centrifuge tubes. The extracts were centrifuged (16 000 × *g* for 10 min), filtered at 0.45 μm and stored frozen until analyzed by gas chromatography as described by Chantigny et al. (2002). Soil NH_4^+–N, NO_3^-–N, and VFA contents were expressed on a mass per area basis using measured bulk soil densities. Bulk density measured at 0- to 5-cm depth was used for the 0- to 0.5-, 0.5- to 2-, and 2- to 5-cm soil layers.

Statistical Analyses

In each set of experimental plots, slurry treatments were replicated three times and applied according to a completely randomized design. The analysis of variance (ANOVA) was done by soil depth using the GLM procedure of SAS (SAS Institute, 1989) with slurry treatments (ASPS vs. ADPS), sampling dates and their interaction as sources of variation. Significant slurry × date interactions occurred at most soil depths. Therefore, one-way ANOVAs were performed separately for each sampling date and soil depth to test the significance of the slurry treatment. Whenever statistical differences are indicated with $P < 0.05$ in the text, it is referencing the result of the one-way ANOVA test at the 5% significance level at the specified sampling date and soil depth. Soil VFA, NO_3^-–N, and NH_4^+–N contents did not always follow a normal distribution. Therefore, all VFA, NO_3^-–N, and NH_4^+–N data were log transformed for the ANOVAs.

RESULTS AND DISCUSSION

Pig Slurry Characteristics

Compared with ASPS, ADPS had higher pH but lower dry matter, C, VFA, N, and P contents (Table 1). Such modifications in pig slurry characteristics following anaerobic digestion have been reported elsewhere (Pain et al., 1990; Kirchmann and Lundvall, 1993; Sommer and Husted, 1995). As a result of decreased dry matter content, ADPS was more fluid than ASPS at time of spreading. Decreases in slurry total N and NH_4^+ contents during anaerobic digestion might be due to NH_3 loss from the digester (Pain et al., 1990), or to coprecipitation of NH_4^+ with PO_4^{3-} and Mg^{2+} to form struvite (Sommer and Husted, 1995). Such precipitate was not included in the ADPS used in the present study. Since the difference in N content was due to the digestion treatment, both slurry types were applied at the same rate (90 m^3 ha^{-1}) to avoid the confounding effect of water addition. Therefore, NH_3 losses reported below for ASPS and ADPS are compared as proportions of the total amounts of slurry N added.

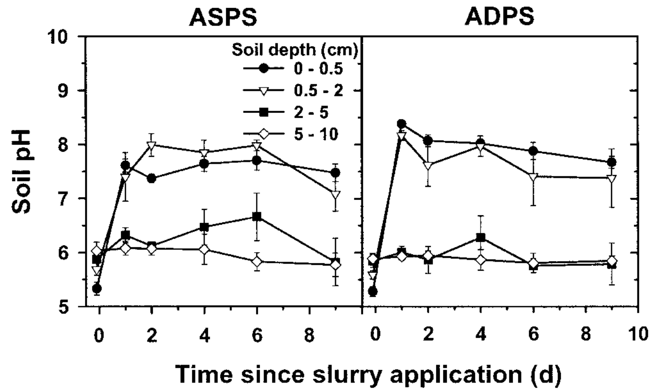

Fig. 3. Soil pH at the 0- to 0.5-, 0.5- to 2-, 2- to 5-, and 5- to 10-cm depth increments for 9 d following application of anaerobically stored (ASPS) and anaerobically digested (ADPS) pig slurry to a bare loamy soil. Bars represent standard deviation of the means.

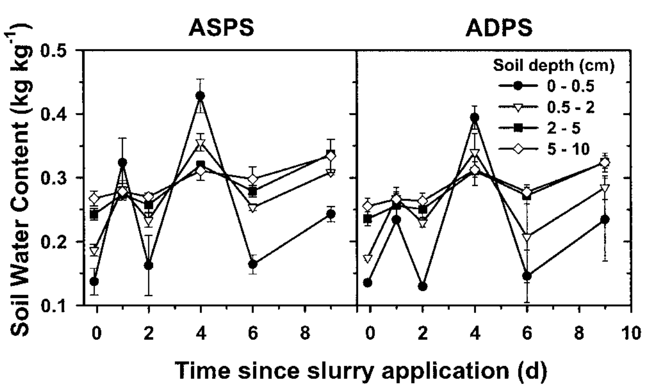

Fig. 2. Soil water content at the 0- to 0.5-, 0.5- to 2-, 2- to 5-, and 5- to 10-cm depth increments for 9 d following application of anaerobically stored (ASPS) and anaerobically digested (ADPS) pig slurry to a bare loamy soil. Bars represent standard deviation of the means.

Environmental Conditions and Soil Water Content

During the experiment, mean hourly air temperature varied between 9 and 33°C (Fig. 1). Those values compared reasonably well with the long-term averages (10 to 25°C) for the area of study at this time of the year. Soil temperature varied from 12 to 31°C and was not significantly ($P > 0.05$) different between slurry treatments. Rainfall occurred almost every 2 to 3 d during the experiment, but precipitation >10 mm were recorded only 3 (26 mm) and 7 d (39 mm) after slurry application (Fig. 1).

Throughout the experiment, differences in soil water content between ASPS and ADPS plots were not statistically significant. Following pig slurry addition, soil water content increased markedly in the first 2 cm of soil (Fig. 2). One day after slurry application, the proportions of slurry-added water present in the 0 to 2, 2 to 5, and 5 to 10 cm of soil were estimated to 60, 23 and 17%, respectively (data not shown). Those results suggest that most slurry-derived nutrients were concentrated in the top 5 cm of soil, but that a portion might have leached below the 5-cm depth. From 2 to 4 d and from 6 to 9 d, soil water content increased in all soil layers (Fig. 2), reflecting the large rainfalls that occurred on Day 3 and 7 of experiment (Fig. 1). The highest water contents were measured 1 and 4 d after slurry addition (Fig. 2), reflecting slurry addition and precipitation, respectively.

Soil pH and Volatile Fatty Acid Content

One day after ASPS addition, soil pH had increased by 2.3, 1.7, 0.4, and 0.05 units in the 0- to 0.5-, 0.5- to 2-, 2- to 5-, and 5- to 10-cm layers, respectively (Fig. 3). Increases in soil pH of 1 to 2 units have been previously reported in the first few centimeters of soils amended with animal slurry (Sommer et al., 1991; Sommer and Hutchings, 2001). The increase in pH in the 0- to 0.5-cm layer was significantly greater ($P < 0.05$) with ADPS

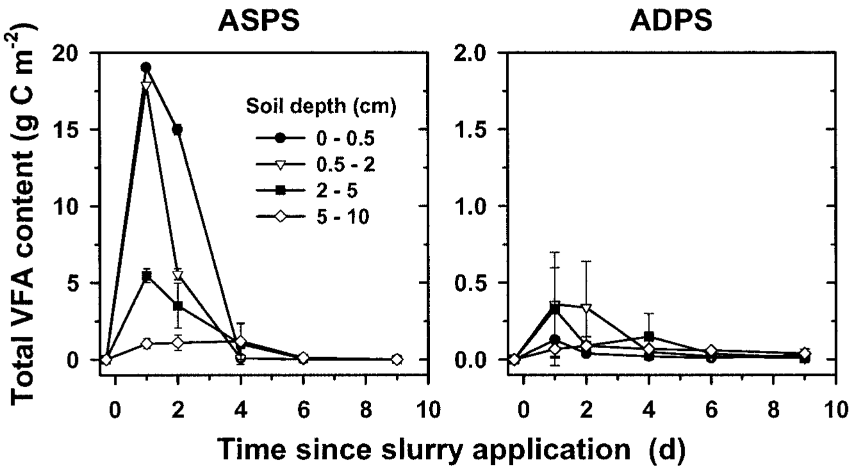

Fig. 4. Soil volatile fatty acid (VFA) content at the 0- to 0.5-, 0.5- to 2-, 2- to 5-, and 5- to 10-cm depth increments for 9 d following application of anaerobically stored (ASPS) and anaerobically digested (ADPS) pig slurry to a bare loamy soil. Note that *y*-axes of ASPS and ADPS have different scales. Bars represent standard deviation of the means.

(3.1 units) than ASPS (Fig. 3). Differences in pH between treatments were not significant in deeper soil layers. Increasing soil pH following pig slurry addition can be partly attributed to the alkaline slurry pH and to the dissociation of slurry carbonates (Génermont, 1996; Sommer and Sherlock, 1996), which occurs rapidly in acidic soils (Rochette et al., 2000; Chantigny et al., 2001). The greater effect of ADPS than ASPS on soil surface pH could thus be explained by its higher pH and carbonate content (Table 1).

From 1 to 6 d after slurry application, pH values remained stable in the 0- to 0.5-cm layer of ASPS plots, and tended to increase in the 0.5- to 2- and 2- to 5-cm layers (Fig. 3). These patterns contrasted with the gradual decrease in the 0- to 0.5- and 0.5- to 2-cm layers in the ADPS plots, and the stable values below the 2-cm depth. Gradual decline in soil pH could be attributable to the acidifying effects of NH_3 volatilization (Génermont, 1996; Sommer and Sherlock, 1996) and nitrification (Rochette et al., 2001), whereas increases in soil pH have been reported during the decomposition of VFAs (Sørensen, 1998). As VFAs were 13 times more abundant in ASPS than ADPS (Table 1), we hypothesized that changes in surface soil pH in the ADPS plots were mostly induced by NH_3 volatilization and nitrification, whereas in the ASPS plots, the rapid decomposition of VFAs partly offset (0- to 0.5-cm layer) or overwhelmed (0.5- to 2- and 2- to 5-cm layers) the effects of those acidifying processes. The small fluctuations found in soil pH in the 5- to 10-cm layer of both treatments (Fig. 3), indicated that slurry addition had little effect on the acidifying and alkalinizing processes below the 5-cm depth.

Following slurry addition, soil VFA content increased in the top 5 cm of soil, and only trace amounts were found below the 5-cm depth (Fig. 4). For the first 2 d of the experiment, the VFA content of the top 5 cm of soil was significantly ($P < 0.05$) higher in ASPS than ADPS plots, according to the higher VFA concentration of ASPS than ADPS (Table 1). Most slurry-derived VFAs were decomposed 4 d after slurry application (Fig. 4), confirming that those compounds are rapidly used by soil microbes (Paul and Beauchamp, 1989; Kirchmann and Lundvall, 1993; Sørensen, 1998). The low VFA contents measured below the 5-cm depth suggest that rapid consumption likely prevented migration of VFAs in the soil profile (Fig. 4). Those findings support our hypothesis that in ASPS plots, pH in the top 5 cm of soil was influenced by the decomposition of large amounts of VFAs.

Soil Mineral Nitrogen

The initial soil NH_4^+ content was close to zero, but increased sharply following slurry addition (Fig. 5a,b). For the first 2 d of experiment, soil NH_4^+ content was

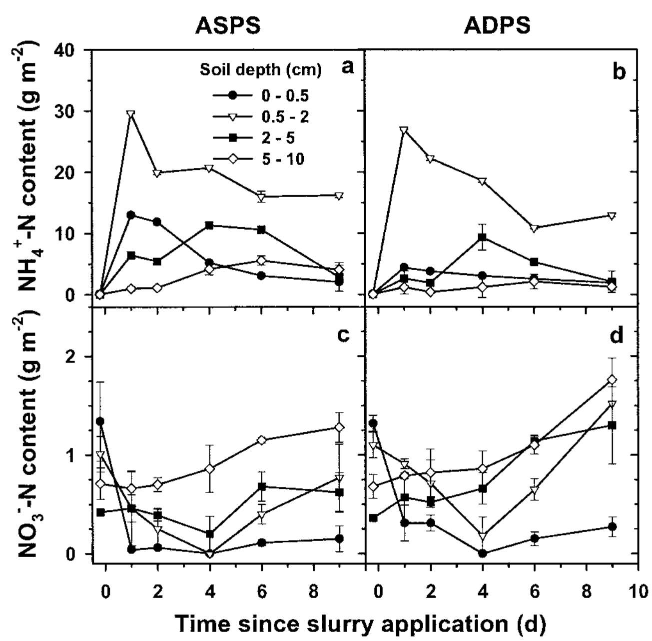

Fig. 5. (a, b) Soil ammonium (NH_4^+–N) and (c, d) nitrate (NO_3^-–N) contents at the 0- to 0.5-, 0.5- to 2-, 2- to 5-, and 5- to 10-cm depth increments for 9 d following application of anaerobically stored (ASPS) and anaerobically digested (ADPS) pig slurry to a bare loamy soil. Bars represent standard deviation of the means.

Table 2. Cumulative losses† in soil NH_4^+–N and NH_3–N 1, 2, and 9 d after application of anaerobically stored (ASPS) and anaerobically digested (ADPS) pig slurry to a bare loam.

	Anaerobically stored			Anaerobically digested		
Parameters	1 d	2 d	9 d	1 d	2 d	9 d
Soil NH_4^+	10.2 (17)	22.0 (36)	35.1 (58)	13.1 (27)	19.9 (41)	30.1 (62)
NH_3	11.7 (19)	20.6 (34)	23.7 (40)	13.6 (28)	17.1 (35)	20.0 (42)

† Losses are given in g N m^{-2} and figures in parentheses are the proportions of added slurry NH_4^+–N (60.3 and 48.2 g m^{-2} for ASPS and ADPS, respectively).

significantly ($P < 0.05$) higher in the surface soil layer of ASPS than ADPS plots due to the higher NH_4^+ content of ASPS (Table 1). From 1 to 9 d after slurry application, NH_4^+ concentration gradually decreased in the top 2 cm of soil (Fig. 5b). On the contrary, from 2 to 4 d after slurry application, NH_4^+ content increased in the 2- to 5- and 5- to 10-cm soil layers, indicating that some slurry-derived NH_4^+ migrated below 2 cm following the large rainfall on the third day of experiment. Beauchamp et al. (1982) reported that infiltration of cattle slurry NH_4^+ (loading rates of 90–130 m^{-3} ha^{-1}) was restricted to the first 2 cm of soil and only large rainfalls were able to leach slurry NH_4^+ deeper in the soil. This situation was also observed for pig slurry under the conditions of our experiment.

Since the initial soil NH_4^+ content was close to zero, the amounts of soil NH_4^+ recovered in the top 10 cm after slurry addition were assumed to represent slurry-derived NH_4^+. The net slurry NH_4^+ disappearance was then calculated 1, 2, and 9 d after slurry addition as the difference between the amounts of NH_4^+ recovered in the top 10 cm of soil and the initial amounts of slurry NH_4^+ added, that is, 60.3 and 48.2 g m^{-2} NH_4^+–N for ASPS and ADPS, respectively (Table 2). After 9 d, more NH_4^+ had disappeared from the ASPS than ADPS plots. However, the proportion of added slurry NH_4^+ that disappeared in 9 d of application was similar, representing 58 and 62% for ASPS and ADPS, respectively. Soil NO_3^- content was low and varied little during the experiment (Fig. 5c,d). In addition, values were not significantly different between treatments. Significant increases in soil NO_3^- content in the days following slurry application are often reported as a result of rapid nitrification of the applied slurry NH_4^+ (Morvan et al., 1997; Rochette et al., 2000, 2001; Chantigny et al., 2001). In the present experiment, small changes in soil NO_3^-–N content did not explain NH_4^+–N disappearance, indicating that nitrification was either low, or was masked by concurrent denitrification and leaching of NO_3^-. During the experiment, levels of soil water-filled pore space were generally high with levels up to 80% (data not shown), indicating that soil conditions were favorable to denitrification (Linn and Doran, 1984). Some NO_3^- leaching below the 10-cm depth also might have occurred following large rainfalls on Day 3 and 7 of experiment.

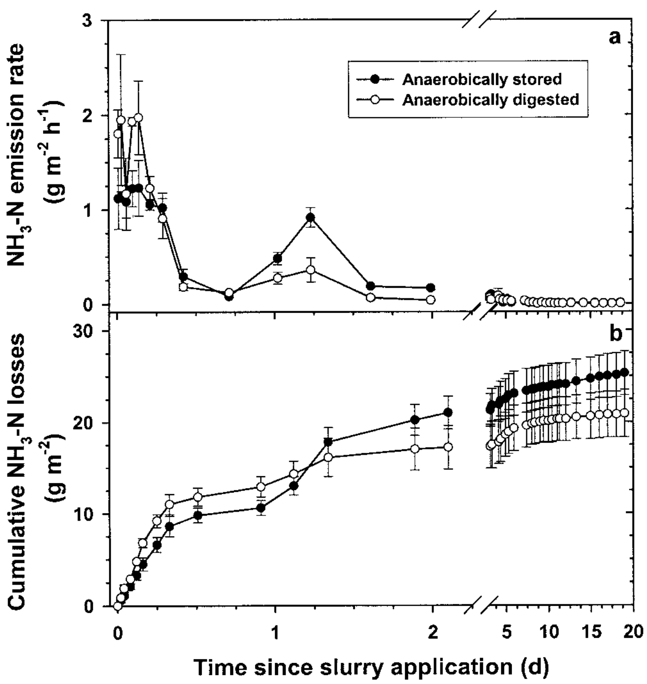

Fig. 6. (a) Ammonia (NH_3) volatilization rates and (b) cumulative NH_3–N losses in wind tunnels for 19 d following application of anaerobically stored (ASPS) and anaerobically digested (ADPS) pig slurry to a bare loamy soil. Bars represent standard deviation of the means.

Ammonia Volatilization

Ammonia emissions were highest during the first 6 h following slurry application (Fig. 6a), which is in accordance with the sharp increase measured in soil pH 1 d after slurry application (Fig. 3). However, volatilization decreased to near zero after 2 d, even though soil pH was still above 7.2 in the top 2 cm of soil. Ammonia volatilization is proportional to the NH_3 partial pressure at the soil surface, which decreases with decreasing NH_4^+ concentration and as NH_4^+ penetrates into the soil (Génermont, 1996; Sommer and Hutchings, 2001). Soil NH_4^+ content decreased by 35 to 40% in the first 2 d of experiment (Table 2), indicating that after 2 d the decrease in soil NH_4^+ content had a greater influence on volatilization than soil pH. Large rainfall on the third day of our experiment (Fig. 1) also likely decreased NH_3 emissions by leaching slurry NH_4^+ deeper into the soil (Whitehead and Raistrick, 1991; Rochette et al., 2001). The NH_3 emission rates showed a diurnal pattern for the first 2 d following slurry addition, with night values being 60 to 80% lower than daytime values (Fig. 6a). Such a diurnal pattern appears typical on soils amended with pig slurry (Brunke et al., 1988; Rochette et al., 2001; Sommer and Hutchings, 2001), and would be explained mainly by the absence of solar radiation and lower vapor pressure deficit at the soil surface at night than during the day (Gordon et al., 2001).

Visual inspection of the plot surface following treatments revealed that ASPS infiltrated more slowly in the soil than ADPS. Three hours after slurry application about 30% of the surface of ASPS plots was still covered with slurry water as compared with only 5% for ADPS plots. All other parameters being equal, lower infiltration rates would favor volatilization by decreasing resistance to and path length of diffusion from the volatilization sites to the atmosphere. In addition, the higher NH_4^+ content of ASPS than ADPS should have favored volatilization (Brunke et al., 1988; Sommer et al., 1991; Génermont, 1996). Nevertheless, NH_3 volatilization rates during the first 6 h of experiment tended to be higher ($P > 0.05$) with ADPS than ASPS (Fig. 6a), indicating that the expected depressing effects of a greater fluidity and lower NH_4^+ content were offset by other factors. The greater NH_3 fluxes measured in ADPS than ASPS plots during the first 6 h of experiment are in accordance with the higher soil pH measured in ADPS plots. As discussed earlier, greater increase in soil pH with ADPS than ASPS was likely caused by the higher pH and carbonate content of ADPS (Table 1). According to Sommer and Hutchings (2001), an increase in slurry pH from 7.7 to 8.0 could double NH_3 emissions. Sherlock and Goh (1985) reported that NH_3 volatilization was more closely related to soil pH in the surface 0.5 cm of soil than in deeper layers. In our case, even though the increase in pH was the highest in the top 0.5 cm of soil, values raised above 7 in the top 2 cm of soil (Fig. 3), indicating that conditions favorable to the NH_3 form also occurred in the 0.5- to 2-cm soil layer. This discrepancy could be due to the large amounts of slurry N applied in our experiment. As opposed to the first 6 h of experiment, NH_3 volatilization rates on the second day were most of the time significantly ($P < 0.05$) higher in soil treated with ASPS than ADPS (Fig. 6a), likely because of the slower infiltration rate of ASPS (Pain et al., 1989; Sommer and Hutchings, 2001).

Six hours after slurry application, the cumulative NH_3–N losses were significantly ($P < 0.05$) greater in ADPS than ASPS plots, representing 9.2 and 6.6 g m^{-2}, respectively (Fig. 6b). Differences between treatments in the cumulative NH_3–N losses were not statistically significant after 12 h. The cumulative NH_3–N volatilized increased to 20.6 and 17.1 g m^{-2} after 2 d in the ASPS and ADPS plots, respectively, but increased slowly thereafter because NH_3 volatilization rates were low. The proportion of slurry added NH_4^+ accounted for by the measured NH_3 losses were similar for both slurries, representing 35% after 2 d, 40% after 9 d (Table 2), and 42% after 19 d. Therefore, anaerobic digestion influenced the temporal pattern of volatilization, but not the overall proportion of slurry N lost as NH_3. Pain et al. (1990) and Rubaek et al. (1996) also observed similar NH_3 volatilization on grassland soils amended with either untreated or anaerobically digested pig slurry. Pain et al. (1990) suggested that increased pH of the digested slurry counteracted with its decreased viscosity, resulting in no net change in NH_3 losses compared with the untreated slurry. Our results indicate that this observation holds when slurry is applied to a bare soil.

For the first 2 d following ASPS and ADPS application, the cumulative amounts of NH_3–N lost corresponded well to the net decline in soil NH_4^+–N content (Table 2). After 9 d, the net decrease in soil NH_4^+–N content exceeded the measured NH_3–N losses by 11.4 and 10.1 g m^{-2} in the ASPS and ADPS plots, respectively. Those results indicate that the disappearance of slurry NH_4^+ was essentially explained by NH_3 volatilization for the first 2 d following slurry application. However, the differences found from 2 to 9 d suggest that biological processes, such as immobilization and nitrification, significantly contributed to slurry NH_4^+ transformations after NH_3 volatilization rates returned to low levels.

The present study demonstrates the importance of stratifying soil sampling in the first few centimeters of soil when determining the short-term effects of pig slurry on NH_3 volatilization and related soil parameters. At the end of the experiment the proportions of slurry N lost as NH_3–N or unaccounted for as soil NH_4^+–N were similar for both the digested and the undigested pig slurries. Therefore, even though anaerobic digestion modified many pig slurry characteristics, this treatment had no net influence on the proportion of applied N that could be lost through volatilization.

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