

Peat, zeolite and basalt as adsorbents of ammoniacal nitrogen during manure decomposition

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Abstract

The effectiveness of sphagnum peat, zeolite (clinoptilonite) and basalt in reducing ammonia losses during aerobic manure decomposition was determined in an incubation experiment. Peat placed in the spent air-stream adsorbed all of the ammonia volatilized during the first 8 days of decomposition, and reduced overall ammonia losses by 59%. Zeolite reduced total ammonia losses by 16%, and basalt by 6%.

All adsorbents were considerably less effective in reducing ammonia losses when mixed with the manure. Reductions in ammonia losses of 24% and 1.5% were obtained with the peat and zeolite, respectively. The addition of basalt increased losses.

Ammonia and ammonium adsorption isotherms were determined for the three materials. The adsorption capacities and affinity terms of the adsorbents calculated from the isotherms, reflected their ability to reduce ammonia losses in the incubation experiment. Zeolite had both the highest affinity for ammonium and the highest ammonium adsorption capacity. The peat had a very high affinity for ammonia and a high adsorption capacity ($23.4 \text{ mg NH}_3\text{-N g}^{-1}$), whereas zeolite and basalt had a much lower adsorption capacity (1.8 and $0.05 \text{ mg NH}_3\text{-N g}^{-1}$, respectively) compared with their capacity to adsorb ammonium (18.1 and $0.18 \text{ mg NH}_4\text{-N g}^{-1}$).

Introduction

Peat has a high cation exchange capacity and ability to adsorb a wide range of cations. When used as a bedding material in barns, peat adsorbs a significant amount of ammoniacal nitrogen in the manure and reduces nitrogen losses through ammonia volatilization (Peltola, 1986). Compared with other bedding materials such as straw and woodshavings, peat adsorbs four times more ammonia (Kemppainen, 1987). Indeed the high ammonia adsorption capacity of peat was exploited early this century to manufacture a slow release nitrogen fertilizer with a nitrogen content of 15%, produced under high temperature and pressure in the presence of gaseous ammonia (Ehrenberg and Heimann, 1930). Peat has also been used in so called biofilters to reduce ammonia emissions from animal housings (Scholtens *et al.*, 1987).

It is well known that the zeolite clinoptilolite has a high affinity for ammonium (*e.g.* Barbarick and Pirella, 1984; Breck, 1974). This has been successfully exploited to remove ammonium from wastewaters (Dyer, 1984; Liberti *et al.*, 1981; Umz and Davis, 1975), to retain ammonium in soils (Weber *et al.*, 1983), and to reduce ammonia emissions from animal housings (Koeliker *et al.*, 1978; Miner, 1984) and during sewage sludge composting (Witter and Lopez Real, 1988).

The use of ground 'rock powder' in animal litter has been advocated by farmers applying 'biological' or 'organic' farming methods to reduce nitrogen losses. No studies appear to have been carried out to test the effectiveness of such materials in retaining ammoniacal nitrogen.

This paper deals with the efficiency of peat, zeolite and basalt as adsorbents of ammoniacal nitrogen during aerobic decomposition of poultry

manure. Ammonia and ammonium adsorption isotherms for the materials were determined, as well as their effectiveness in reducing ammonia losses during manure decomposition.

Materials and methods

Manure and adsorbent materials

The manure used was commercially obtained, dried and pelletized poultry manure (Weibulls, Landskrona, Sweden), which was ground to < 2 mm. Analytical details of the manure is given in Table 1.

Three materials greatly differing in their cation exchange characteristics and base buffering capacity were used as ammonia adsorbents: basalt

Table 1. Analytical details of the poultry manure

Carbon (%)	36.3
Total nitrogen (%)	4.75
C/Norg	7.6
NH ₄ -N (%)	1.12
NO ₃ -N (ppm)	25
pH (H ₂ O)	6.76
Water holding capacity ($\mu\text{l g}^{-1}$)	4200

(Diabase, Askersund, Sweden) with a low cation exchange capacity, zeolite (clinoptilolite, USA) with a high CEC, but low base buffering capacity, and sphagnum peat (Hasselfors, Sweden) with both a high CEC and base buffering capacity. The zeolite and basalt were air dried and ground to < 0.2 mm, the peat was ground to < 2 mm. Analytical details of the adsorbents are given in Table 2.

Table 2. Analytical data of the adsorbent materials

Material	Particle size (mm)	pH (H ₂ O)	Ion exchange values ($\mu\text{eq g}^{-1}$) ^a					Surface area (m ² g ⁻¹)	Surface charge density ($\mu\text{eq m}^{-2}$)
			Ca	Mg	K	Na	CEC		
Basalt, diabase (Askersund, Sweden)	< 0.2	9.7	4	18	2	3	27	76	0.36
Zeolite, clinoptilolite (USA)	< 0.2	9.6	256	22	451	896	1625	340	4.78
Sphagnum peat (Hasselfors, Sweden)	< 2	3.9	53	64	2	9	1353	4250	0.31

^a CEC value for the zeolite is calculated as the sum of exchangeable cations. Exchangeable calcium on the basalt is estimated by difference (assuming 100% base saturation).

Incubation experiments

Carbon dioxide production and ammonia losses during manure decomposition over a 7-week period, were measured in an incubation trial using an aeration manifold as described by Kirchmann (1985) and Kirchmann and Witter (1989). Each tube contained approximately five grams of dried, ground manure mixed with 10 grams of acid washed sand (30-60 mesh) and brought to a moisture content of 1/3 of the moisture holding capacity. The moisture content of the mixture was regularly readjusted.

Two incubation trials were carried out, testing two different uses of the adsorbents. In the first experiment the adsorbents were loosely packed in 1-cm diameter tubes with glassfibre plugs on either side, and placed in the spent air-stream from the incubation tubes containing the manure/sand mixture, and before the CO₂ and NH₃ traps. In the second incubation trial the adsorbent materials were mixed with the manure. The moisture content of the adsorbents was adjusted to 65% of the waterholding capacity for the peat and 33% for the basalt and zeolite. Addition rates used were 250 mg adsorbent per gram of manure (dry weight/dry weight). There were three replicates per treatment in both experiments.

Analytical techniques

Total nitrogen was determined as Kjeldahl nitrogen (Bremner and Mulvaney, 1982). Organic carbon was measured as CO₂-C after dry combustion, using an infrared gas analyzer (Ströhlein Instruments). Ammonium and nitrate were exhaustively extracted with 2 N KCl from the manure and

adsorbents (repeated extractions were required to remove all the ammonium from the ammonium saturated peat and zeolite). Ammonium was determined colorimetrically using the indo-phenol blue reaction, using a method similar as described by Kempers and Zweers (1986). Nitrate was determined by the Gries-Ilosvay method after reduction to nitrate on a copperized cadmium column.

Cation exchange capacity (CEC) and exchangeable cations of the adsorbent materials was determined by extraction of cations and saturation with NH_4OAc (pH 7), followed by removal of soluble ammonium with iso-propyl alcohol and subsequent extraction of sorbed ammonium with 2 *N* KCl (Chapman, 1965).

Determinations of exchangeable cations were carried out by ICP spectroscopy (Plasma II Emission Spectrometer, Perkin Elmer, Norwalk, USA).

The specific surface area of the peat, zeolite and basalt was determined using a simplified ethylene glycol mono-ethyl ether procedure (Cihacek and Bremner, 1979).

Ammonia adsorption isotherms

Ammonia adsorption isotherms were obtained by exposing the peat, zeolite and basalt to air containing known concentrations of ammonia. About 5 grammes of each of the materials, wetted to 60% of their water holding capacity, was placed on a watch glass in a dessicator with a 10-L volume. Ammonia concentrations in the dessicator of 38–6200 mg $\text{NH}_3\text{-N m}^{-3}$ were obtained by adding known amounts of a 0.1 to 1.0% ammonium chloride solution to 100 ml of 5 *N* NaOH in the dessicator. The materials were incubated for 48 hours, during which time the ammonia atmosphere was renewed several times in order to maintain a constant concentration. Incubation at the lowest ammonia concentration was continued for 96 hours in order to ensure complete adsorption. After incubation the materials were air-dried at 25°C (to remove physically adsorbed ammonia) and analysed for pH, KCl extractable ammonium and total nitrogen.

Ammonium adsorption isotherms

Ammonium adsorption isotherms were obtained

by measuring ammonium adsorption in a static system using unbuffered NH_4Cl solutions over a range of 5–300 ppm for the basalt (at pH 7.5–8.5), and 10–1000 ppm $\text{NH}_4\text{-N}$ for the peat (at pH 5.0–6.5) and zeolite (at pH 7.5–8.5). Amounts of ammonium adsorbed was calculated from the reduction in ammonium concentration in the solution after shaking for at least two hours and centrifugation. When the ammonium concentration in the solution had been reduced to less than 90% of its original concentration, the old solution was discarded and fresh solution added. This procedure was repeated until the ammonium concentration in the solution was reduced by no more than 10% at equilibrium in presence of the adsorbent material.

Base buffering capacity of peat

The base buffering capacity of the peat was determined over a pH range of 3.5 to 7.2 through addition of 0.1 *N* KOH to a 1:15 peat-water suspension at intervals of approximately 0.1 pH units. The pH of the suspension after alkali addition was measured with a Beckmann pH-70 pH meter (Beckman Instruments Inc., Irvine, USA) which displays a reading when the pH has stabilized to a fluctuation of less than 0.01 pH units in 10 seconds.

Statistical analysis

Where appropriate, data were analyzed by analysis of variance. At *F*-values significant at $p < 0.05$, significance testing between means was done using the Newman Keul's Test. Where significant differences between means are indicated this is at $p < 0.01$.

Results

Base buffering capacity of peat

The relationship between the amount of base added and the hydrogen ion concentration in the peat showed a distinct break at around $\text{pH} = 4.4$, and the relationship between pH and base addition (meq $\text{OH}^-/100\text{ g peat}$) could be empirically described by the following equations:

$$\text{pH } 3.5\text{--}4.4: \text{pH} = 4.1 + 0.083 \times \log(\text{OH}^-);$$

$$R^2 = 0.86 \text{ (n = 5)}$$

$$\text{pH } 4.4\text{--}7.2: \text{pH} = 2.5 + 0.067 \times \log(\text{OH}^-);$$

$$R^2 = 0.99 \text{ (n = 15)}$$

Ammonia and ammonium adsorption isotherms

The ammonia and ammonium adsorption isotherms are given in Figures 1 and 2. The Langmuir model and 1st order kinetics model were fitted to the datapoints using non linear regression (SAS, 1985). The models were used to calculate an affinity factor and the adsorption capacities (Table 3). The adsorption capacities are expressed both as $\text{mg NH}_x\text{-N g}^{-1}$ adsorbent and as $\mu\text{eq NH}_4\text{-N g}^{-1}$. Expression in the latter units allows direct comparison of the adsorption capacity with the CEC value of the adsorbents. The adsorption capacities

calculated by both models corresponded closely, with—except for ammonia adsorption by the zeolite—the Langmuir model giving values for the adsorption capacities 4–18% greater than predicted by 1st order kinetics. The ammonium adsorption capacities of the materials were similar to their measured CEC. Zeolite and basalt had a very low affinity for ammonia compared with the peat, and had an absorption capacity which was only 8.6% and 14.4% of the measured CEC, respectively. The peat showed a very high affinity for ammonia, and had an adsorption capacity slightly exceeding the measured CEC value.

Reductions in ammonia loss during poultry manure decomposition

Adsorption of ammonia in the spent air on peat, zeolite and basalt. Ammonia losses during manure decomposition increased sharply from day three

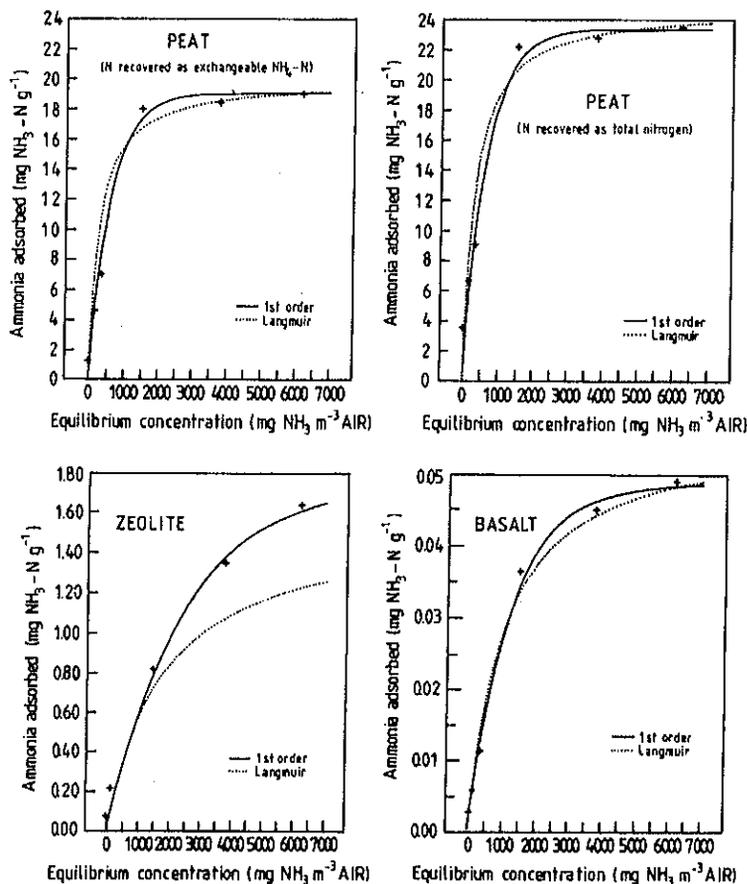


Fig. 1. Ammonia adsorption isotherms for peat, zeolite and basalt. Datapoints are fitted to first order and Langmuir models.

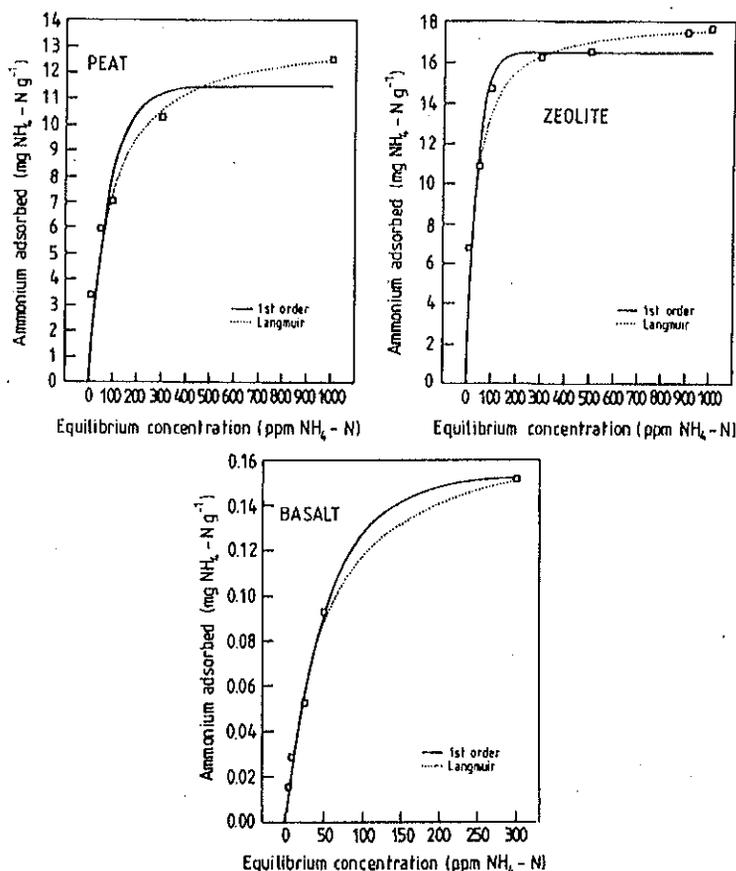


Fig. 2. Ammonium adsorption isotherms for peat, zeolite and basalt. Datapoints are fitted to first order and Langmuir models.

Table 3. Ammonia and ammonium adsorption isotherms for the peat, zeolite and basalt fitted to first order kinetics and Langmuir models

Model:	1st order kinetics $x/m = a \times (1 - (e^{-k \times C}))$				Langmuir $x/m = C / ((a \times b)^{-1} + a^{-1} \times C)$			
	Affinity k	Adsorption capacity R ²		Affinity b	Adsorption capacity R ²			
		$\mu\text{eq N g}^{-1}$	mg N g^{-1}		$\mu\text{eq N g}^{-1}$	mg N g^{-1}		
<i>Ammonia</i>								
Peat	0.0016	1364 ¹	23.4 ²	0.973	0.0036	1421 ¹	24.8 ²	0.998
Zeolite	0.00041	125	1.8	0.994	0.0006	111	1.6	0.967
Basalt	0.00081	3.47	0.05	0.994	0.0010	4.0	0.06	0.999
<i>Ammonium</i>								
Peat	0.012	820	11.5	0.853	0.012	966	13.5	0.999
Zeolite	0.027	1177	16.5	0.866	0.031	1292	18.1	0.999
Basalt	0.018	10.9	0.15	0.998	0.020	12.6	0.18	0.999

Legend:

C = equilibrium concentration ($\text{mg NH}_3 \text{ m}^{-3}$ for ammonia; $\text{ppm NH}_4\text{-N}$ for ammonium).

x/m = amount adsorbed ($\mu\text{eq g}^{-1}$).

a = adsorption capacity.

b = Langmuir affinity term.

k = First order model affinity term.

¹ = Ammonia adsorbed and recovered as KCl extractable $\text{NH}_4\text{-N}$.

² = Ammonia adsorbed and recovered as total nitrogen.

and reduced after 15 days of decomposition to become negligible after 35 days (Figure 3A). At the end of the incubation period between 20 and 25% of the nitrogen initially present had volatilized as ammonia (Table 4). These losses are only half those during decomposition of fresh poultry manure under similar conditions (Kirchmann and Witter, 1989), and may be explained by loss of easily mineralizable nitrogen during the pre-processing of the manure. All adsorbents placed in the spent air-stream adsorbed some of the volatilized ammonia, and reduced overall ammonia losses (Figure 3A). Peat was considerably more effective in adsorbing the volatilized ammonia than either the zeolite or basalt. The peat adsorbed all of ammonia in the air stream from the decomposing manure until day 8 (Figure 3A), and reached an adsorption maximum

of 24 mg NH₃-N g⁻¹ on day 18 (Figure 4A). Similar ammonia adsorption capacities for sphagnum peat have been reported by Virri (1941) and Kempainen (1987). After day 25 there was a small, but significant net release of ammonia from the peat (Figure 4A).

On day 8 ammonia retention by the zeolite and basalt were 75% and 42% of the total amount of ammonia volatilized from the manure, respectively. The amount of ammonia adsorbed by the zeolite and basalt at this point was 7 and 3 mg NH₃-N g⁻¹, respectively which did not change significantly over the period of manure decomposition (Figure 4A). An ammonia adsorption capacity of 6.7 mg NH₃-N g⁻¹ for clinoptilolite used as an ammonia scrubber in the vent air from a poultry house has been reported by Miner (1984).

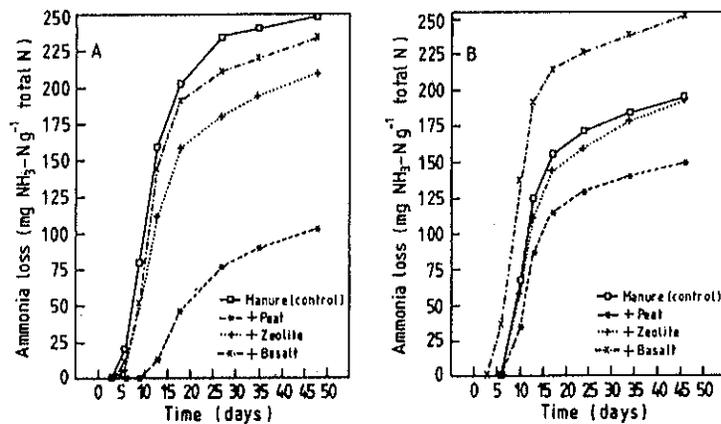


Fig. 3. Cumulative ammonia-nitrogen losses over a 7 week decomposition period and effect of adsorbents placed in spent air-stream (A) and mixed with manure (B). Losses are expressed per gram of total nitrogen initially present. Mean values of three replicates; the standard deviation of all mean values is less than 10.

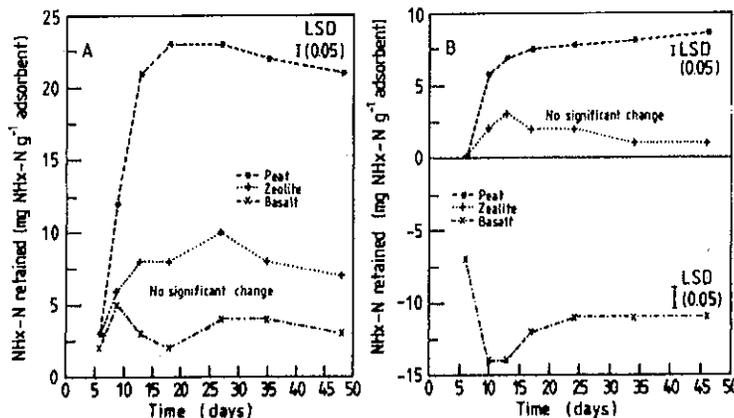


Fig. 4. Retention of ammoniacal nitrogen during manure decomposition by adsorbents when placed in spent air-stream (A) and when mixed with manure (B).

Table 4. Cumulative nitrogen losses (mg NH₃-N g⁻¹ total N initially present) over 7 week incubation period

	Time (days)							
	3	6	9	13	18	27	35	48
<i>Adsorbents placed in spent air-stream</i>								
Control	0	20	79	159	202	234	240	248
+ Peat	0	0	0	13	47	77	90	103
+ Zeolite	0	5	44	112	158	180	194	209
+ Basalt	0	11	52	143	190	210	219	233
	Time (days)							
	3	6	10	13	17	24	34	46
<i>Adsorbents mixed with manure</i>								
Control	0	0	66	124	155	171	184	195
+ Peat	0	0	35	87	115	129	140	149
+ Zeolite	0	0	57	111	143	159	178	192
+ Basalt	0	36	137	191	214	226	238	251

At the end of the incubation period of 48 days the peat, zeolite and basalt had reduced ammonia greater for all three materials compared with the

Table 5. Effect of adsorbent addition on manure pH. Effect of adsorbent addition on manure pH significant (F) at $p < 0.01$

	Initial	Final
Manure	6.76	7.28
M + Peat	5.94	7.13
M + Zeolite	6.77	7.37
M + Basalt	6.86	7.35
LSD (0.05)	0.07	0.06

Table 6. Adsorption capacity of peat, zeolite and basalt for ammoniacal nitrogen (mg NH₃-N g⁻¹ adsorbent) as determined by ammonia and ammonium adsorption isotherms. And actual retention of ammonia and ammoniacal nitrogen during decomposition of manure over a seven week incubation period. The adsorption capacity for ammonium is calculated with the Langmuir model, adsorption capacity for ammonia is calculated from the first order model

		Retention of NH ₃ in spent air			Retention of NH ₃ + NH ₄ ⁺ in manure		
		Peat	Zeolite	Basalt	Peat	Zeolite	Basalt
Adsorption capacity		23.4	1.8	0.05	23.4	18.1	0.18
Actual retention measured in incubation experiment (ng NH ₃ -N g ⁻¹ adsorbent)	a	16.1	1.7	0.05			
	b	21.6	6.6	2.56	8.6	0.6	c
Reduction in NH ₃ loss at application rate of 250 mg per g manure (%)	a	51	5	n.s.			
	b	59	16	6	24	1.5	-29 ^c

^a Calculated from amount of ammonia adsorbed and recovered in adsorbent at end of manure decomposition period.

^b Calculated from differences in ammonia volatilization rates between treatments and control.

^c Addition of basalt to manure increased ammonia losses.

n.s. Not significant.

losses by 59%, 16%, and 6%, respectively (Table 6).

The amount of ammonia adsorbed calculated from differences in ammonia loss during incubation was greater for all three materials compared with the amount of ammonia adsorbed calculated from the ammonia recovered in the adsorbent materials at the end of the incubation period (Table 6). The reason for this is that recovery of the adsorbed ammonia does not include physically adsorbed ammonia which was removed during drying of the material prior to analysis. The amount of ammonia physically adsorbed was only of significance for the zeolite and basalt which retained little of the ammonia as exchangeable ammonium (Table 6). The amount of physically adsorbed ammonia appeared to reflect the differences in the surface area of the materials (Table 2). Mortland (1955), amongst others, have used ammonia adsorption isotherms for the determination of specific surface area.

Adsorption of ammoniacal nitrogen on peat, zeolite and basalt in the manure. In the second incubation experiment the adsorbents were used at the same rate as in the first experiment, but were mixed with the manure so that both ammonia and ammonium adsorption could take place. All three materials proved to be considerably less effective in reducing ammonia losses when mixed with the manure, than when placed as scrubbers in the spent air-stream (Figures 3 and 4). The amounts of ammoniacal nitrogen retained by the peat and zeolite were only

40, and 10%, respectively of the amount of ammonia nitrogen adsorbed when the adsorbents were placed in the spent air-stream (Table 6). Adsorption of ammoniacal nitrogen by the peat virtually ceased after day 17 (Figure 4B) even though release of ammonia from the manure continued until the end of the incubation period. At the end of the experiment the peat and zeolite had adsorbed 8.6 and 0.6 mg $\text{NH}_x\text{-N g}^{-1}$, and reduced overall ammonia losses by 24 and 1.5%, respectively. The addition of basalt significantly increased the rate of initial ammonia losses resulting in a net increase in ammonia loss of 29% over the period of incubation (Figure 3B and Table 6). It is likely that the increased ammonia loss was due to the increase in manure pH upon addition of the basalt (Table 5). The rate of manure decomposition as measured by carbon dioxide evolution was not affected by the addition of the basalt (results not shown) so that increased ammonia losses could not be explained by increased rates of manure decomposition in the presence of basalt.

Discussion

Ammonia and ammonium adsorption isotherms

The Langmuir equation is often used to describe ammonium adsorption isotherms (*e.g.* Hunt and Adamsen, 1985; Weber *et al.*, 1983). However, use of the Langmuir equation to linearize the isotherms overestimates the degree of correlation as the variables used are not truly independent, and may seriously err in estimating the adsorption capacity if only low concentration data are used (Harter, 1984). Adsorption capacities and an 'affinity factor' describing the slope of the isotherms were also calculated by fitting first order equations to the isotherms. The Langmuir model appeared to fit the ammonium adsorption better (Figure 1), whereas the 1st order model fitted the ammonia adsorption data somewhat better, especially for the zeolite (Figure 2). Nevertheless, the adsorption capacities calculated by both models corresponded closely (Table 3).

The ammonium adsorption capacities (Table 3) reflected the measured CEC (Table 2) values of the materials. This can be expected as the CEC was measured as adsorbed ammonium in an am-

monium acetate solution. Zeolite had both the highest ammonium affinity and adsorption capacity. Only the peat had an ammonium adsorption capacity which was less than its capacity to adsorb ammonia. The ammonia adsorption capacity of the peat slightly exceeded the ammonium adsorption capacity of the zeolite.

Zeolite and basalt had a very low affinity for ammonia compared with the peat, and had an adsorption capacity which was only 8.6% and 14.4% of the measured CEC, respectively. Determination of total nitrogen at the higher concentrations showed that all the adsorbed ammonia could be recovered as KCl extractable ammonium. The low saturation of the CEC with ammonium indicates that formation of ammonium from ammonia was the limiting factor, rather than availability of suitable exchange sites. Proton donation to ammonia is likely to have been from water molecules strongly polarized in the vicinity of exchangeable bases, given the high pH (greater than 9.5) of the zeolite and basalt.

The peat showed a very high affinity for ammonia, and had an adsorption capacity slightly exceeding the measured CEC value (Tables 2 and 3). Three reaction mechanisms for ammonia retention by the peat were identified: 1. retention as 'fixed' ammonia; 2. as exchangeable ammonium after acquisition of a proton from solution; and 3. as exchangeable ammonium formed through direct reaction of ammonia with a proton on the exchange site, which did not contribute to the solution pH. Analysis of KCl extractable ammonium and total nitrogen showed that less than 40% of the ammonia adsorbed at the lower ammonia concentrations was recoverable as exchangeable ammonium. At the higher ammonia concentrations more than 90% of the adsorbed ammonia was recoverable as exchangeable ammonium. This indicates that adsorption of ammonia as 'fixed' ammonia takes place prior to adsorption onto sites of cation exchange. Nõmmik and Vahtras (1982) — relying largely on earlier literature reviewed by Mortland and Wolcott (1965) — suggested that this 'fixed ammonia' is formed from reactions with carbonyl, phenolic or enolic hydroxyls, or unsaturated carbon groupings leading to the formation of covalent compounds. From the titration curve of the peat the amount of ammonia required to increase the pH to a certain value could be calculated. It was

thus found that at all ammonia concentrations, around 30% of the adsorbed ammonia which was recoverable as exchangeable ammonium had reacted with protons which contributed to the solution pH. The remainder of the ammonia adsorbed as exchangeable ammonium must have reacted directly with protons held on exchange sites.

Use of adsorbents to reduce ammonia emissions from manures

The adsorbents can either be used as ammonia scrubbers by placing them in the spent air-stream, or can be used as adsorbents of both ammonia or ammonium nitrogen by mixing them with the manure. One might expect that the latter placement is more suitable for materials with a higher affinity for ammonium (such as zeolite and basalt), and that use of the adsorbent as air-scrubber is more suitable for materials with a higher affinity for ammonia than ammonium (such as the peat). Results from this experiment however showed that irrespective of the relative ammonia and ammonium affinities of the material, placement in the air-stream is considerably more effective in reducing ammonia emissions. A similar observation was made by Witter and Lopez-Real (1988) for adsorption of ammoniacal nitrogen onto zeolite during sewage sludge composting. Reduced effectiveness of the materials in adsorbing ammoniacal nitrogen when mixed with the manure may be explained by competition by other cations for available exchange sites. In addition, the zeolite and basalt increased the pH of the manure, thus increasing the ammonia volatilization potential. The base buffering capacity of the peat was largely neutralized by the alkalinity of the manure immediately upon addition of the peat, and resulted in only a small reduction in the pH of the manure (Table 5). This, together with competition for exchange sites by other cations will have reduced the ammonia retention efficiency of the peat when used mixed with the manure.

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