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Ammonia volatilization during aerobic and anaerobic manure decomposition

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Abstract
Ammonia volatilization, nitrogen immobilization, carbon decomposition and formation of volatile fatty acids was investigated in a laboratory incubation experiment with fresh poultry manure, to which increasing amounts of straw were added.

Less than 1% of the manure nitrogen was volatilized as ammonia during anaerobic decomposition due to low pH values. In aerobic manure alkaline conditions prevailed and between 9 to 44% of the nitrogen was volatilized as ammonia. The volatilization courses could be described by a parallel first-order model. Increasing straw additions reduced ammonia volatilization during aerobic decomposition. Straw caused no immobilization of nitrogen under anaerobic conditions. In aerobic manure, nitrogen was mainly bound in organic forms whereas in anaerobic manure about two-thirds of the nitrogen was in ammonium form. C/N ratios in the organic matter of anaerobic manure were higher (33.1–87.5) than in the aerobic manure (9.5–18.0).

Introduction

Livestock wastes have been identified as the major source of ammonia emissions in Europe, contributing 81% to total emissions. (Buijsman *et al.*, 1987). There is increasing concern about the role of atmospheric ammonia in enhancing acid deposition (ApSimon *et al.*, 1987; van Breemen *et al.*, 1982; Möller and Schieferdecker, 1985) and increasing the nitrogen load of natural ecosystems (Roelofs *et al.*, 1985).

The main pathway for nitrogen loss during handling, storage and spreading of manure is ammonia volatilization. The amount of ammonia volatilized is influenced by several factors shown in Figure 1. The principal mechanisms through which a reduction of ammonia losses during decomposition can be achieved are:

— Immobilization of ammonium through addition of easily decomposable, nitrogen-poor materials.
— Adsorption of ammonium and ammonia on suitable amendments.
— pH regulation of the manure solution.

The degradability of the organic nitrogen fraction in animal wastes determines the net amount of nitrogen mineralized. The pH value is the main factor regulating the equilibrium between NH_4^+-ions and NH_3 gas in the manure solution. The amount of litter and the availability of its energy content determines the amount of nitrogen that can be immobilized.

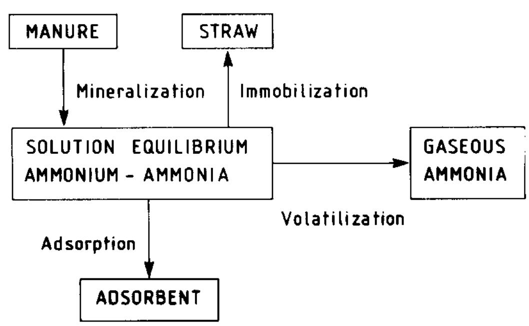

Fig. 1. Main processes affecting ammonia formation and volatilization during manure decomposition in absence of soil.

Russel and Richards (1917) and Glathe and Seidel (1937) found very small or no nitrogen losses from anaerobically decomposing manures whereas higher nitrogen losses were found during aerobic decompositions of organic materials (Jansson and Clark, 1952; Russel and Richards, 1917). During manure storage ammonia losses amounting to 20–40% of the nitrogen initially present were measured (Kirchmann, 1985). Significant reduction in nitrogen losses from manure have been obtained through addition of straw (Faassen and van Dijk, 1979; Hümbelein *et al.*, 1980; Meyer and Sticher, 1983), whereas no reduction (Köhnlein and Vetter, 1953) and even increased nitrogen losses have also been reported (Bucher, 1943).

Comparative studies on aerobic and anaerobic decomposition of organic materials by Acharya (1935b) and Tenney and Waksman (1929; 1930) showed that carbon dioxide production and decomposition rate of organic constituents were generally lower under anaerobic conditions. Anaerobic conditions induced acid formation, a decrease in pH and an accumulation of ammonium nitrogen (Acharya, 1935a).

Several factors influencing ammonia volatilization during manure decomposition were investigated. The present paper reports the effects of straw addition. The influence of various materials as adsorbents of ammoniacal nitrogen as well as the effect of Ca and Mg salts on ammonia volatilization will be reported in subsequent papers.

Materials and methods

Poultry manure

Fresh poultry manure from chicken (*Gallus domesticus*) and oat straw (*Avena sativa* L.) were used for the experiments. The materials were air dried, ground to pass a 2-mm mesh and analyzed for total N, inorganic N and total C. Analysis results of the fresh poultry manure and the straw used are shown in Table 1. The manure treatments used consisted of poultry manure mixed with 100, 213 and 429 dry weight % of straw, (*i.e.* 20.6 g, 41.4 g and 73.5 g of straw per gram of total nitrogen present), resulting in initial C/N ratios of 18, 24 and 36. The treatments were expressed by their initial C/N ratio throughout this paper. Pure straw was also used to determine ammonia release but no pure poultry manure.

Table 1. Characteristics of the organic compounds used. All values based on dry mass

Material	Org C (%)	Tot N (%)	NH_4-N (%)	C/N_{Tot}	WHC ($ml\,g^{-1}$)	pH (H_2O)
Fresh poultry manure	37.9	4.46	0.28	8.5	3.0	5.2
Oat straw	40.1	0.32	n.d.	125.3	6.3	6.3

n.d. = not determined.

Incubation experiment and chemical analyses

Fifty to 100 grams of each manure was wetted to 50% of WHC and incubated in 500 ml desiccators. The manures were placed on a perforated plate in the middle of the jar. Two replicates of each treatment were incubated. A moistened gas stream free of NH_3 and CO_2 was led through the jars. For aerobic conditions, air from the laboratory atmosphere ($30\,ml\,h^{-1}\,g^{-1}$), and for anaerobic conditions nitrogen (N_2) ($1\,ml\,h^{-1}\,g^{-1}$) was used. The incubation was performed at 25°C. Released ammonia and carbon dioxide were transported with the gas stream and trapped in gas wash bottles. Ammonia was absorbed in 50 ml 0.3 *M* H_3BO_4 (Kirchmann, 1985) and carbon dioxide in 200 ml 0.5 *M* NaOH (Stotzky, 1965). Ammonia samples were titrated with 0.02 *M* H_2SO_4, and carbon dioxide samples with 0.1 *M* HCl after addition of $BaCl_2$ in excess. Total nitrogen was analysed with the regular Kjeldahl method described by Bremner and Mulvaney (1982). Determinations were made on moist samples to avoid ammonia losses. Dry matter contents were measured in parallel set of samples. Ammonium and nitrate nitrogen were measured after extraction with 2 *M* KCl using the MgO-Devarda-alloy procedure (Bremner, 1965). Carbon was analysed after dry combustion as carbon dioxide using an infrared gas analyser (Ströhlein Instruments, C-mat 500). Volatile fatty acids (C_2–C_5 compounds) were determined in an aqueous manure extract on a gas chromatograph equipped with a flame ionization detector (Hewlett Packard, Model 5840) as described by Ackman (1972).

Statistical techniques

A first-order model (Jenny *et al.*, 1949) and a parallel first-order model (Andrén and Paustian, 1987; Jenkinson, 1977) were used to fit data on ammonia volatilization. The equations were inverted describing production rather than mass loss. The models were fitted to the data by least-squares technique using the SAS procedure NLIN (SAS Institute, 1985). Adjusted R^2 (R_a^2) values were used for comparison of the regression models (Kvålseth, 1985).

Results

Cumulative NH_3 volatilization during aerobic decomposition of the manures is shown in Fig. 2 and Table 3.

The highest amount of ammonia volatilized was 44% of the total initial amount of manure N present. Increased straw additions to manure progressively reduced ammonia volatilization during aerobic decomposition from 44% to 9%. Under anaerobic conditions the volatilization of ammonia nitrogen was less than 1% of the nitrogen initially present. Amounts volatilized were not significantly different ($P > 0.05$) between anaerobic manure with different straw contents. No ammonia was released from pure straw either under aerobic or anaerobic conditions. During incubation acid conditions had developed in the anaerobic manures (pH 5.0–6.2), and alkaline conditions in the aerobic manures (pH 8.4–8.9). The percentage distribution of ammonium and ammonia is affected by the pH value (Freney *et al.*, 1983) and relative concentrations of gaseous ammonia at 25°C are 0.005% at pH 5.0, 0.090% at pH 6.2, 13.7% at pH 8.4 and 31.1% at pH 8.9. The low concentrations of ammonia formed at the slightly acid pH values, measured in anaerobic manures, explained why very low ammonia losses occurred during anaerobic decomposition. The considerably higher ammonia concentrations at alkaline conditions induced a great potential for ammonia volatilization under aerobic conditions.

The course of ammonia volatilization from aerobic manure, shown in Fig. 2, was characterized by two phases. An initial phase of rapid NH_3 volatilization lasting several days followed by a second phase of slow NH_3 release. The results of the curve fitting with the regression models are given in Table 2.

The first-order model gave no good prediction of

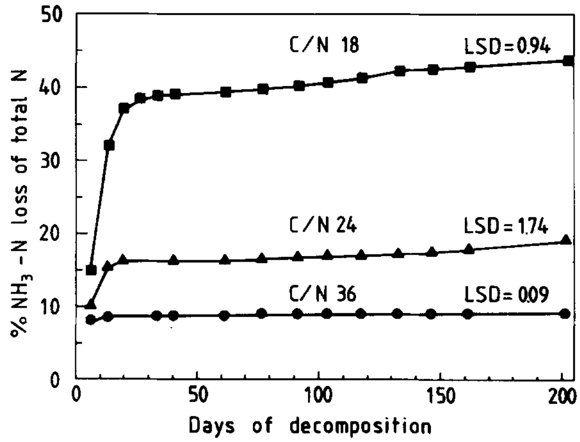

Fig. 2. Ammonia loss from manure with increasing straw content during aerobic decomposition.

the volatilization course. Calculated adjusted R^2 values were lower than for the parallel first-order model. The parallel first-order model, however, gave a satisfactory fit to the volatilization course. This means that ammonia volatilization was the result of the decomposition of two different (rapidly and slowly decomposable) nitrogenous fractions. Estimates of the rapidly decomposable nitrogen fractions causing ammonia release from the manures with C/N ratios of 18, 24 and 36 were 39%, 16% and 9.0% of the total initial nitrogen present with half-times of 6.3, 3.7 and 4.8 days, respectively.

In Table 3 the amounts of N immobilized by straw are shown. Nitrogen immobilization by straw was calculated over the C/N ratio intervals of 18—24 and 24–36, dividing the difference of N mineralized over the interval by the net amount of

Table 2. Kinetic parameters for ammonia volatilization during aerobic manure decomposition in absence of soil

Manure	Parallel first-order model: $N = N_0N_R(1 - e^{-k_Rt}) + N_0(1 - N_R)(1 - e^{-k_St})$				
	N_R	k_R day^{-1}	k_S day^{-1}	R^2	R_a^2
C/N 18	0.390	0.1105	0.00035	0.953	0.941
C/N 24	0.157	0.1867	0.00015	0.954	0.940
C/N 36	0.090	0.1446	0.00003	0.940	0.925

N = ammonia; N_0 = initial amount of nitrogen, N_R = rapidly volatilized nitrogenous fraction; $(1 - N_R)$ = slowly volatilized nitrogenous fraction; $k_{R,S}$ = corresponding rate constant; t = time.

Table 3. The effect of straw on N volatilization, mineralization and immobilization during aerobic and anaerobic manure decomposition (201 days)

Manure	Straw added $g\,g^{-1}$ init. N	Volatilization $mg\,NH_3$-N g^{-1} init. N	Ammonium conc. $mg\,NH_4$-N g^{-1} init N		Net mineralization mg N g^{-1} init. N	Immobilization mg N g^{-1} straw
			0	201 days		
Aerobic conditions						
C/N 18	20.6	437.4	5.8	11.6	443.2	
C/N 24	41.4	190.9	0.6	33.7	224.0	11.2 (C/N 18–24)
C/N 36	73.5	91.5	0.1	47.7	139.3	2.2 (C/N 24–36)
Anaerobic conditions						
C/N 18	20.6	9.4	5.8	742.0	745.6	0[a]
C/N 24	41.4	4.0	0.6	742.0	745.4	0
C/N 36	73.5	1.7	0.1	737.8	739.4	0

[a] As N mineralization in anaerobic manure with different straw contents was not statistically different, it was assumed that no immobilization occurred.

straw added. In aerobic manure there was an obvious trend for decreasing immobilization rate of N at high straw content. This could not simply be explained by a too low initial amount of nitrogen present per gram of straw because in the manure with the C/N ratio of 36, 13.6 mg of N per gram of straw were present at start. Immobilized amounts of N (2.2–11.2 mg N per gram of straw) were similar to those reported by Richards and Norman (1931). In anaerobic manures equal quantities of ammonium nitrogen per gram of manure N were measured independent of the amount of straw added. This indicated that straw caused no significant immobilization of nitrogen under anaerobic conditions.

Table 4. Total, organic, inorganic nitrogen concentrations and carbon to nitrogen ratios in manure after aerobic and anaerobic decomposition. Figures refer to % of dry matter

Tot-N	NH_4-N	Org-N	C/N_{Tot}	C/N_{Org}	$(C - C_{VFA})/N_{Org}$
Initial values					
2.43	0.14	2.29	18		
1.64	<0.01	1.64	24		
1.10	<0.01	1.10	36		
*After 201 days in **aerobic** manure*					
3.47	0.04	3.43	9.5	10.0	
2.97	0.10	2.87	13.0	13.3	
2.09	0.10	1.98	18.0	18.4	
*After 201 days in **anaerobic** manure*					
3.25	2.15	1.10	13.0	38.4	33.1
2.01	1.40	0.61	21.5	63.0	61.1
1.34	0.90	0.44	32.0	89.4	87.5

C_{VFA} = Carbon content of volatile fatty acids.

Concentrations of total, inorganic, organic N and carbon to nitrogen ratios in the manures after decomposition are given in Table 4. More than 95% of nitrogen in aerobic manure was bound as organic nitrogen and only low ammonium concentrations were found. Nitrate concentrations were less than 0.001% in dry matter and no nitrite was detected. However, in anaerobic manure about two-thirds of nitrogen was present as ammonium and about one-third as organic N (Table 4).

Evolution of carbon dioxide during decomposition was generally higher under aerobic than under anaerobic conditions. Total percentages of initially present manure C released as carbon dioxide amounted to 44.8 ± 1.9 (S.E.), 49.5 ± 2.4 and 56.3 ± 0.8% under 201 days of aerobic decomposition for manure with initial C/N ratios of 18, 24 and 36, respectively. Thus straw additions increased carbon dioxide production under aerobic conditions. However, the opposite trend was measured under anaerobic conditions. Manure C released as carbon dioxide decreased from 19.2 ± 1.3% for manure with an initial C/N ratio of 18 to 8.2 ± 1.7 and 5.7 ± 1.6 for manure with C/N ratios of 24 and 36 respectively.

Differences between carbon dioxide production and nitrogen volatilization rates during manure decomposition changed the C/N ratios in manure (Table 4). C/N ratios were calculated both based on total and organic nitrogen concentrations. This shows the differences of the energy to nitrogen ratios of aerobically and anaerobically decomposed manure. In aerobic manure a general decrease of the C/N ratio after decomposition was found, which means that more carbon than nitrogen was released. Only small differences were found between the two ratios, since nitrogen was mainly bound in organic form. In anaerobic manure there was a smaller decrease in the C/N ratio as less carbon was lost. When C/N ratios were calculated from organic N concentrations, the C/N ratios were considerably greater, varying between 38.4 and 89.4. This means that the organic matter of anaerobic manure was poor in nitrogen and rich in carbon. Even if the carbon content of soluble fatty acids, which do not contain any nitrogen, is subtracted from the total carbon content, the C/N ratios of the organic matter in anaerobic manure remain high (see last column in Table 4). The concentrations of volatile fatty acids measured in manure after 201 days of anaerobic decomposition are given in Table 5. Acetic, propionic and butyric acid were found. Acetic acid was the dominant form amounting to 7.3 per cent of dry matter. No iso-butyric, valeric or iso-valeric acid were detected in the poultry manure-straw mixtures, which is in agreement with determination of fatty acids in anaerobically stored poultry manure (Bell, 1970).

Discussion

This investigation showed that very low ammonia losses occurred during anaerobic manure decomposition due to the low pH value in these manures. Under aerobic conditions large ammonia losses were measured, partly dependent on the amount of straw added. The results throw some light on the question why large variations of manure N losses can occur during field conditions. Losses are both influenced by the redox conditions in decomposing manure and if aerobic conditions dominate, by the amount carbon-rich material present.

Table 5. Content of volatile fatty acids in anaerobically decomposed manures (201 days). Figures refer to % of dry matter

Manure	Acetic acid	Propionic acid	Butyric acid	Sum	C_{VFA}
C/N 18	7.4	0.6	4.2	12.2	5.5
C/N 24	7.1	0.7	2.7	10.5	4.6
C/N 36	7.3	0.8	0.9	9.0	3.8

C_{VFA} = Carbon content of the volatile fatty acids.

However, in the experiments of Bucher (1943) and Köhnlein and Vetter (1953) no reduction in ammonia losses and even increased losses were measured during manure storage with increasing amounts of straw. Their findings seem to be in contrast to the presented results. There are two possible explanations why ammonia losses from manure may increase if more straw is added:

a) Coexistence of both aerobic and anaerobic conditions seems to be the rule during practical manure storage conditions. If increased straw addition leads to an improved aeration of the manure, the redox conditions change from dominantly anaerobic to aerobic with consequently higher losses.
b) If more straw is added in the barn, the collected manure may absorb more urine and the initial C/N ratio will not be higher in straw-rich manure. Thus decomposition of manure with different C/N ratios cannot be compared.

Ammonia volatilization from fresh poultry manure was shown to be caused by two different nitrogenous fractions. High initial ammonia losses were presumably caused by uric acid and proteins that had resisted animal digestion. If, however, stored or predecomposed poultry manure would have been used, it is reasonable to assume that both lower losses and a different volatilization course would have been measured. Thus it is important to point out if fresh or manure collected from a storage place is used.

During anaerobic manure decomposition no nitrogen immobilization of manure N in straw was detected and the straw content had no influence on the amount of manure N mineralized. High ammonium concentrations were found in anaerobic manure whereas nitrogen in aerobic manure was mainly bound in organic form. This distinct compositional difference in the nitrogen content of aerobic and anaerobic manure is in accordance with findings of Novák (1970a, b), who predicted that inorganic nitrogen is not incorporated into organic compounds during anaerobic manure decomposition.

The high C/N ratio of the organic matter of anaerobic manure and the content of easily degradable fatty acids may cause immobilization of nitrogen upon application to soil. In studies on N mineralization from slurry and manure in soil by Flowers and Arnold (1983) and Herbst *et al.* (1987)

an immobilization of manure N was measured. Amberger *et al.* (1982) showed that the organic fraction of slurry with a C/N ratio of 13 caused N immobilization when applied to soil, followed by a slow rate of mineralization.

It is concluded that anaerobic manure decomposition is superior to aerobic decomposition concerning conservation of manure N during storage. Large quantities of straw are required under aerobic decomposition to achieve significant reduction in nitrogen loss. Assuming excretion of 250 gram nitrogen per cattle per day, 25 kg straw would be required to reduce ammonia losses by 50%. Straw amendments needed are too large to be practical under most farm conditions.

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