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## Gaseous NO, NO<sub>2</sub>, and NH<sub>3</sub> Loss During Cattle Feedlot Manure Composting

By

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Key words: NO, NO<sub>2</sub> and NH<sub>3</sub> atmospheric concentration, composting, cattle manure.

### S u m m a r y

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The emission of NH<sub>3</sub> and NO<sub>x</sub> gases during feedlot manure composting reduces the agronomic value of final compost as a soil amendment. In addition, NO<sub>x</sub> gases cause air smog and deplete stratospheric ozone. The effect of passive aeration treatment (no turning) and active aeration treatment (turned 6 times) on NH<sub>3</sub> and NO<sub>x</sub> emission during composting of feedlot manure was investigated in open windrows in summer 1997. The atmospheric concentrations of NH<sub>3</sub>, NO and NO<sub>2</sub> at the windrow surface and 50 cm above were monitored throughout the composting period (99 days). Composting increased the atmospheric concentration of NH<sub>3</sub> and NO, while NO<sub>2</sub> was not affected. The atmospheric NH<sub>3</sub> concentration was higher during early composting and decreased with the composting period for both aeration treatments. Active aeration resulted in a much higher early NH<sub>3</sub> concentration (5500 ppb) than passive aeration (1000 ppb) at the windrow surface, but there was little difference later in the composting. The lower NH<sub>3</sub> loss for the passive aeration treatment is consistent with the higher N retained in the compost at the end of the experiment. The atmospheric NO concentration increased up to 350 ppb at the surface of the passive aeration windrow during early composting, then decreased to much lower values (< 50 ppb) around day 50 and stayed low for the rest of composting period. Similar NO atmospheric concentration patterns were observed for the active aeration treatment, but the early NO concentration was much lower. Since the decomposition of manure/compost materials was incomplete for the passive aeration treatment, further studies are needed to investigate possible techniques to reduce NH<sub>3</sub> and NO losses (retaining more N in the finishing compost) while increasing the composting rate.

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## Introduction

Livestock production in southern Alberta has experienced major changes in recent years and cattle feedlots of 10,000 head and larger are now common (LETHBRIDGE COUNTY, personal communication). Associated with the increased intensity of livestock operations is the increased amount of feedlot manure produced each year. Proper utilization of manure is crucial to the long-term sustainability of feedlot operations. Traditionally, cattle manure is directly applied to nearby fields. However, this has created concern over environmental issues such as nitrate leaching to the groundwater (CHANG & JANZEN 1996).

The composting of feedlot manure has been proposed as an alternative to direct land application. Composting produces a stabilized product that can be stored or spread on land with little or no odor, pathogens, weed seeds, or fly breeding potential (RYNK 1992). Compost may also be trucked further distances since composting significantly reduces volume and mass (LARNEY & al. 2000).

Composting is a biological process in which organic matter is transformed into humus-like materials. But this process also releases various gaseous N compounds into the atmosphere, reducing the agronomic value of compost as a soil amendment and creating possible environmental concerns as well. Nitrous oxide emission from manure has been reported during composting (HELLMANN & al. 1997, HAO & al. 2001), storage (BROWN & al. 2000, PETERSEN & al. 1998) and after application to agricultural land (CHANG & al. 1998). Gaseous NH<sub>3</sub> loss has been reported during composting of sewage sludge (WITTER & LOPEZ-REAL 1988), liquid manure (MARTINES & DEWES 1992), and poultry manure (KIRCHMANN & WITTER 1989, KITHOME & al. 1999). Although most N emitted is in the form of NH<sub>3</sub>, we cannot ignore N losses in the form of NO and NO<sub>2</sub> since they may contribute to acid rain formation, photochemical smog generation and ozone depletion. The objective of this study is to investigate how aeration methods used during cattle feedlot manure composting affect atmospheric NH<sub>3</sub>, NO and NO<sub>2</sub> concentrations.

## Materials and Methods

On 20 May 1997, windrows were set up for summer composting of cattle feedlot manure at the Agricultural and Agri-Food Canada Research Centre in Lethbridge, Alberta. The manure contained wheat straw as the bedding material. Some physical and chemical characteristics of the manure used are shown in Table 1 (LARNEY & al. 1999).

Table 1. Characteristics of the feedlot manure used.

Moisture <sup>a</sup> g kg <sup>-1</sup>	pH	EC dS m <sup>-1</sup>	NH <sub>4</sub> <sup>+</sup> -N mg kg <sup>-1</sup>	NO <sub>3</sub> <sup>-</sup> -N mg kg <sup>-1</sup>	NO <sub>2</sub> <sup>-</sup> -N mg kg <sup>-1</sup>	Total C g kg <sup>-1</sup>	Total N g kg <sup>-1</sup>	Total P g kg <sup>-1</sup>	C/N
2389.8	7.6	7.5	2150	2.3	5.0	342	17.7	2.48	19.3

<sup>a</sup> based on manure dry matter weight, equivalent to 705 g kg<sup>-1</sup> wet weight.

Both active and passive aeration windrows were constructed, each with three replications. Each windrow covered an area of about 50 m<sup>2</sup> (3.6 by 14 m) and was 1.4 to 1.6 m high. The wet and

dry weights of each windrow were determined at the beginning and end of composting. For the active aeration treatment, the manure in the windrow was turned six times (day 14, 21, 29, 50, 70 and 84) during the 99-day thermophilic composting period.

For the passive aeration treatment, the windrows were never turned. Air was introduced into the windrows by a series of open-ended perforated steel pipes (10 cm diam.). Pipes were placed 45 cm apart on a 15 cm deep layer of cured compost. The manure was placed over the pipes, ensuring that the ends were not covered. The windrows were also covered with a 15 cm thick blanket of cured compost to reduce ammonia loss. On day 99, material from each treatment was moved into curing piles. Details on the physical changes that occurred during composting (LARNEY & al. 2000) and on greenhouse gas emissions (HAO & al. 2001) have been published elsewhere.

Air temperature, wind speed, pan evaporation and precipitation data were collected at the Lethbridge Research Centre weather station less than 200 m from the compost windrows. The concentration of  $\text{NH}_3$ , NO and  $\text{NO}_2$  at the compost windrow surface and 50 cm above each windrow were monitored throughout the composting period starting on day 16 using a chemiluminescent  $\text{NH}_3$  analyzer (Model 17, Thermo Environments Instruments). The lack of data for the first 15 days was due to equipment malfunction and, as a result, some major emissions may have been missed. Approximately 6 readings were obtained each day for each windrow. The atmospheric levels of  $\text{NH}_3$ , NO and  $\text{NO}_2$  were monitored periodically from May to October 1997 within a 50 km vicinity of the compost site. Values measured at points at least 1 km from the nearest livestock operation are treated as the background level for the area. The general linear model (GLM) procedure in SAS (SAS INSTITUTE 1996) was used to analyze the atmospheric concentration of  $\text{NH}_3$ , NO and  $\text{NO}_2$ . When treatment effects were significant at the 0.05 probability level, means were tested with the Tukey multiple range test.

## Results and Discussion

### Environmental conditions

Mean daily temperatures were close to normal for the composting period, between 10 and 25°C, except in the first week when mean air temperatures were 5 to 10°C (Fig. 1a). Daily mean wind speeds varied substantially and went as high as 40 km h<sup>-1</sup> (Fig. 1b). The mean daily pan evaporation varied from close to zero to as high as 15 mm, with the high evaporation values generally occurring when wind speed or air temperature were high (Fig. 1c). Most precipitation (75 %) occurred in the first 40 days of composting (Fig. 1d).

### Daily emission pattern of NO, NO<sub>2</sub> and NH<sub>3</sub>

The atmospheric concentration of  $\text{NH}_3$ , NO and  $\text{NO}_2$  at the composting windrow surface followed distinct daily patterns (Fig. 2). All data in Fig. 2 are an average of three replicated windrows. The atmospheric  $\text{NH}_3$  concentration (Fig. 2b) showed a similar pattern to the air temperature (Fig. 2a), with the maximum occurring in early afternoon and minimum after midnight each day. The small peak on the night of 16/17 was mainly due to depressed  $\text{NH}_3$  values in the evening of day 16 when 5.8 mm rainfall occurred. The daily patterns for NO and  $\text{NO}_2$  were more complicated, affected by wind speed in addition to temperatures (Fig. 2c & 2d). The measured atmospheric NO and  $\text{NO}_2$  concentrations were low whenever wind speeds were high. The large intra-day fluctuations demonstrate the need to take several readings each day, rather than relying on a single measurement to be representative. There were also variations among the three windrows with coefficient of

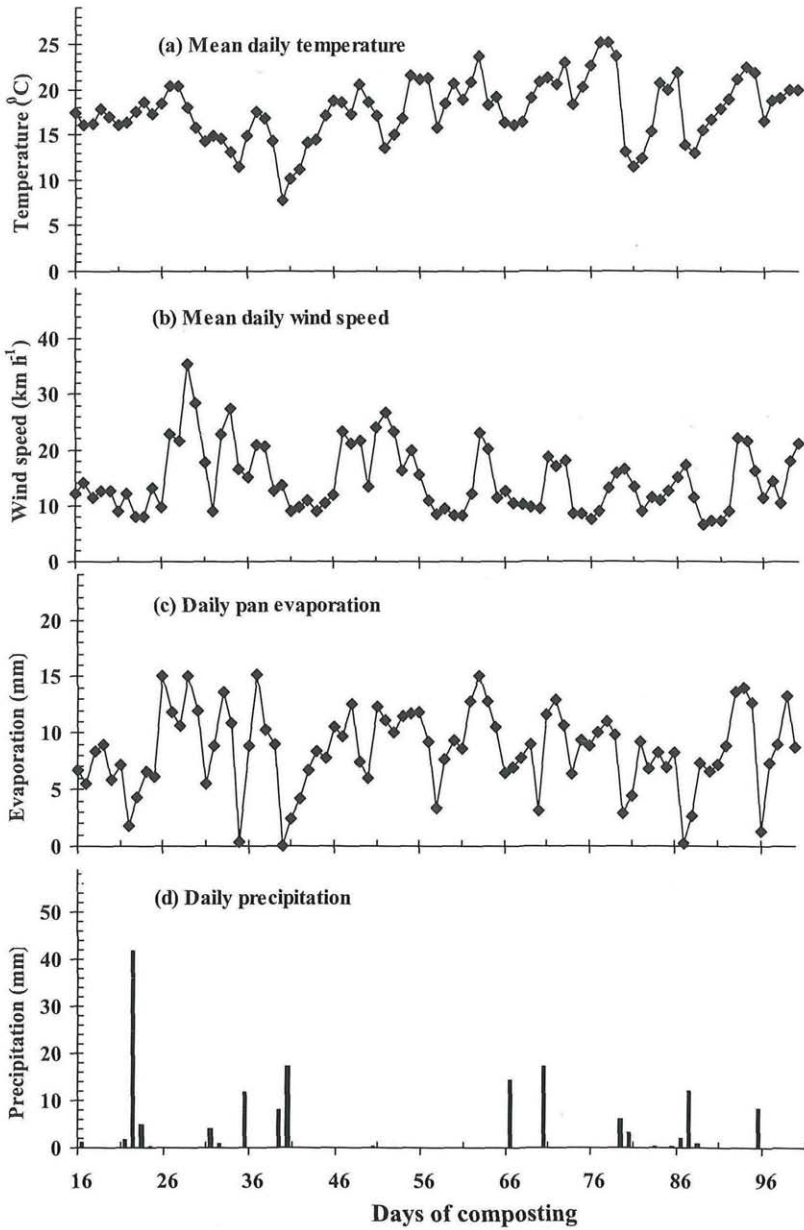


Fig. 1. Weather conditions during composting period.

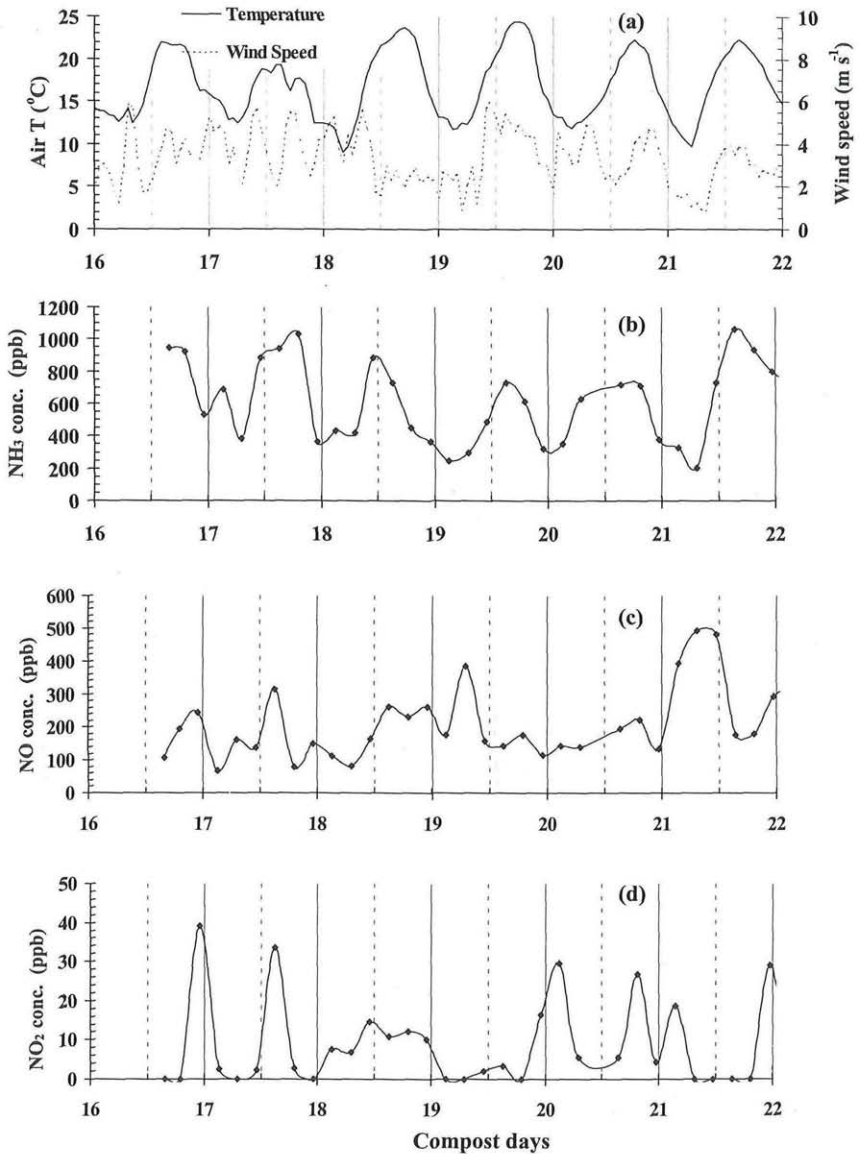
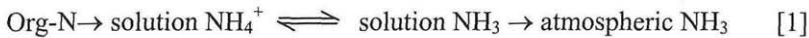


Fig. 2. Daily patterns of atmospheric NO, NO<sub>2</sub> and NH<sub>3</sub> concentration during early composting (at passive aeration windrow surface).

variance (C.V.) ranging from 2.9 to 22.8 % (average of 13.3 %) for NH<sub>3</sub>, 3.9 to 42.2 % (average 24.8 %) for NO and 7.6 to 76.8 % (average of 20 %) for NO<sub>2</sub> over the sampling period shown in Fig. 2.

The observed  $\text{NH}_3$ ,  $\text{NO}$  and  $\text{NO}_2$  patterns reflect the rate of their emission from the compost windrow surface and how fast they are being moved away from the emitting surfaces. As with any gas, the emission rate depends on its concentration at the emitting surface and how much of the gas is being produced and transported to the surface. The peaks of  $\text{NH}_3$ ,  $\text{NO}$  and  $\text{NO}_2$  reflect the higher rate of production and diffusion at higher temperatures. The rate of  $\text{NH}_3$  production is described in [1]:



The emission of  $\text{NH}_3$  is also affected by the rate of water evaporation since  $\text{NH}_3$  is highly soluble in water. An increase in temperature also leads to an increase in volatilization of  $\text{NH}_3$ , as there is less water in the compost to hold the  $\text{NH}_3$ .

The measured  $\text{NH}_3$ ,  $\text{NO}$  and  $\text{NO}_2$  atmospheric concentrations are also affected by how fast these gases move away from the emitting surface. A higher wind speed means more gases move away from the emitting surface, leaving lower concentrations of  $\text{NH}_3$ ,  $\text{NO}$  and  $\text{NO}_2$  to be detected.

#### Effect of passive aeration treatment on $\text{NH}_3$ , $\text{NO}$ and $\text{NO}_2$

The release of  $\text{NH}_3$ ,  $\text{NO}$  and  $\text{NO}_2$  from the passive aeration compost windrows increases their atmospheric concentration (Fig. 3). All data in Fig. 3 are an average of three replicated windrows, each with 6 measurements per day. The mean daily  $\text{NH}_3$  atmospheric concentrations were initially high (1000 ppb), but decreased with time and were less than 400 ppb around day 40 and stayed at 400 ppb for the rest of composting period (Fig. 3a). Compared to the background values of 50 to 150 ppb in this area, the  $\text{NH}_3$  concentration observed at the compost windrow surface and 50 cm above were much higher. Since no wind speed data was collected at the windrow surface, it is impossible to calculate the amount of  $\text{NH}_3$  lost from the compost. However, Fig. 3a clearly shows that  $\text{NH}_3$  volatilization was probably the major source of N loss, especially during early composting. The  $\text{NH}_3$  concentrations were generally higher at the surface than 50 cm above. A few exceptions were measurements taken just after turning the active aeration windrows, which released substantial amounts of  $\text{NH}_3$ . Since the windrows were all less than 30 m apart, it is likely that some of the  $\text{NH}_3$  released during active windrow turning had moved over the passive windrows. There were also variations among the three windrows with the C.V. ranging from 1.0 to 59.3 % (average of 14.2 %). The observed high  $\text{NH}_3$  atmospheric concentrations near compost windrows during early composting were due to higher  $\text{NH}_4^+$  (Table 2) and a higher temperature in the compost that favors  $\text{NH}_3$  volatilization. The higher rate of organic matter decomposition during early composting (LARNEY & al. 1999) should lead to more organic N being converted into  $\text{NH}_4^+$ . As composting progressed,  $\text{NH}_4^+$  concentration decreased as result of the volatile  $\text{NH}_3$  loss, slowing the rate of  $\text{NH}_4^+$  production. Most fresh organic-N had been converted into  $\text{NH}_4^+$  and humus near the surface. In addition, nitrification also reduced the amount of  $\text{NH}_4^+$  in the compost windrows.

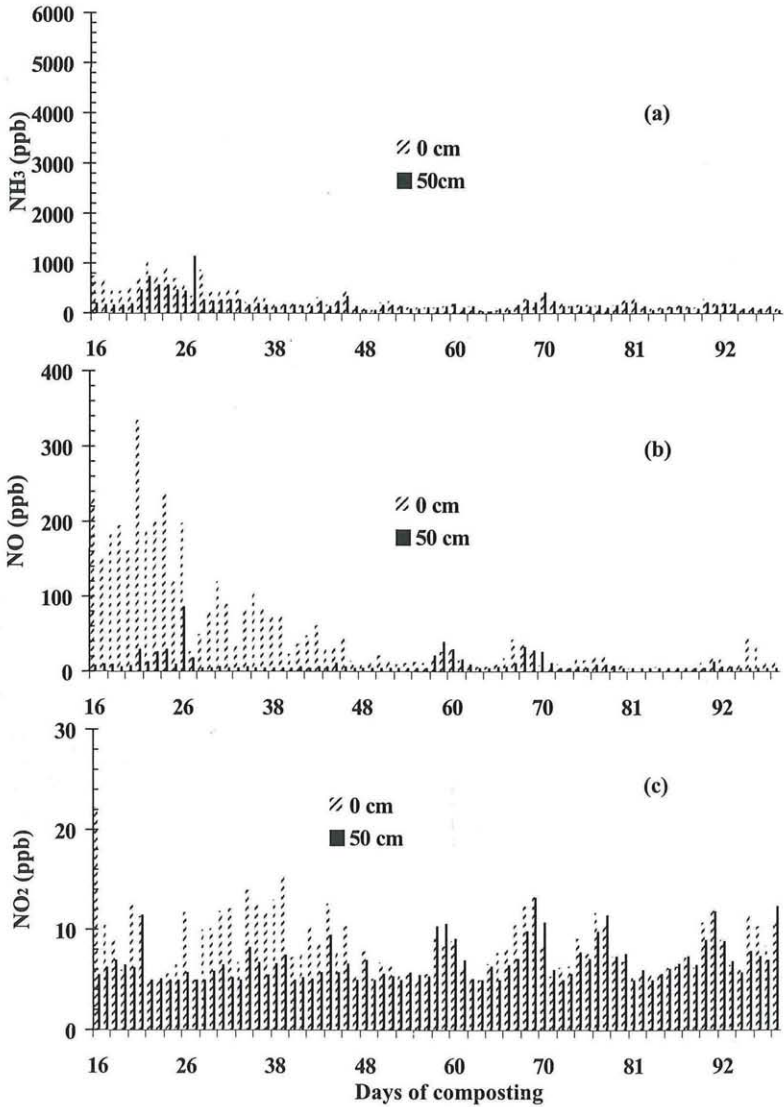


Fig. 3. Concentration of  $\text{NH}_3$ ,  $\text{NO}$  and  $\text{NO}_2$  at 0 and 50 cm above the windrow surface under passive aeration treatment.

The mean daily atmospheric  $\text{NO}$  concentration at the windrow surface showed similar patterns to  $\text{NH}_3$ , high during early composting (around 200 to 350 ppb) and decreasing with time to approximately 5 to 50 ppb towards the end of

composting (Fig. 3b). The concentration of NO was also higher at the windrow surface than 50 cm above. The daily atmospheric NO<sub>2</sub> concentrations at the compost windrow surface varied between 5 and 16 ppb for the most of the composting period except on day 16 (22 ppb). The NO concentrations observed at windrow surfaces during early composting were higher than the background level of 10 – 36 ppb while the NO<sub>2</sub> values were similar to the background levels of 1 to 20 ppb for this area. There were also variations among the three windrows, with the C.V. ranging from 0.1 to 68.3 % (average of 17.3 %) for NO and from 0.1 to 55.9 % (average of 14.3 %) for NO<sub>2</sub>.

Table 2. NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, and NO<sub>2</sub><sup>-</sup> changes during composting.

Treatment Sampling Time (day)	Passive <sup>a</sup>			Active		
	NH <sub>4</sub> <sup>+</sup> <sup>b</sup>	NO <sub>3</sub> <sup>-</sup>	NO <sub>2</sub> <sup>-</sup> mg	NH <sub>4</sub> <sup>+</sup> <sup>b</sup> kg <sup>-1</sup>	NO <sub>3</sub> <sup>-</sup>	NO <sub>2</sub> <sup>-</sup>
0	2030.7	2.1	4.0	2265.9	2.4	6.0
14	878.9	8.9	21.5	2700.0	1.2	3.1
21	701.5	4.6	17.0	1036.9	4.9	16.7
50	36.5	9.8	13.1	381.6	8.7	29.6
84	221.2	22.4	35.0	115.2	11.0	6.1
99	2540.5	20.6	21.4	28.2	18.8	7.1

<sup>a</sup> For passive treatment, samples taken on days 14, 21, 50 and 84 represent manure/compost materials in the top one-third of the windrow (as far as the sampling device goes) while day 0 and day 99 represent the average of the whole windrow profile.

<sup>b</sup> From LARNEY & al. 1999.

Nitric oxide and NO<sub>2</sub> can be formed from nitrification reactions, denitrification, chemo-denitrification or self-decomposition of nitrous acid (REMDE & CONRAD 1991, SMITH & CHALK 1980). The initial high atmospheric NO concentration was probably due to a high nitrification rate, since the NH<sub>4</sub><sup>+</sup> concentration in the windrow was high. As the composting process progressed, NH<sub>4</sub><sup>+</sup> concentration decreased due to NH<sub>3</sub> volatilization loss and nitrification converting NH<sub>4</sub><sup>+</sup> into nitrate. Thus, the amount of NO produced by nitrification rapidly decreased. Chemo-denitrification and/or self-decomposition of nitrous acid also played a role in NO emission, since there was a considerable amount of NO<sub>2</sub><sup>-</sup> (Table 2) and phenol and amine compounds in the manure/compost materials. Production of NO has been found to be correlated with NO<sub>2</sub><sup>-</sup> concentration (BAUMGARTNER & CONRAD 1992, KESTER & al. 1997). Denitrification played a limited role in NO production, especially during early composting, since most nitrates (NO<sub>3</sub><sup>-</sup>/NO<sub>2</sub><sup>-</sup>) were produced near the surface (through nitrification) and were stable under aerobic conditions. Nitrate had to be leached to the anaerobic sites (near bottom of the windrow) by precipitation in order for NO to be produced during the denitrification process. Because manure/compost is a mosaic of aerobic and anaerobic zones, it is likely that multiple processes were contributing simultaneously to NO production, but one might be more dominant than the others in composting windrows.



Slightly higher  $\text{NO}_2$  values during early composting were probably due to the greater  $\text{NO}$  production and the oxidation of  $\text{NO}$  into  $\text{NO}_2$ . Nitrogen dioxide values obtained at the surface were only slightly higher than those obtained 50 cm above the compost windrow, suggesting that composting was not the major contributor to  $\text{NO}_2$  levels in the air (Fig. 3c).

#### Effect of active aeration treatment on $\text{NH}_3$ , $\text{NO}$ and $\text{NO}_2$

Atmospheric concentration of  $\text{NH}_3$ ,  $\text{NO}$  and  $\text{NO}_2$  for the active aeration treatment (Fig. 4) followed similar patterns to the passive aeration treatment (Fig. 3). Similar to Fig. 3, all data in Fig. 4 are an average of three replicated windrows, each with 6 measurements per day. Ammonia volatilization from the composting manure was high during the first half of composting, reaching as high as 5800 ppb at the windrow surface (Fig. 4a), decreasing to 200 to 400 ppb and staying between those levels for the second half of composting. Compared to the passive aeration treatment, the atmospheric  $\text{NH}_3$  concentration was higher during early composting and increased when the windrow was turned. However, turning had very little effect after day 60. There were also variations among the three windrows with the C.V. ranging from 2.0 to 60.9 % (average of 18.7 %).

The higher  $\text{NH}_3$  atmospheric concentration above the active aeration treatment was due to the effect of windrow turning. Turning increases the rate of  $\text{NH}_3$  diffusion to the emitting surface, the rate of  $\text{NH}_4^+$  production and the re-distribution of mineral N ( $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ) in the windrow profile. First, turning directly releases the atmospheric  $\text{NH}_3$  trapped in the bottom of the windrow. Otherwise,  $\text{NH}_3$  would take a much longer time to diffuse through the windrow profile. Second, turning decreases the water content of the manure/compost materials, so less  $\text{NH}_3$  can be held in the manure/compost solution. Third, turning "fluffs" up the materials and increases both total and air-filled porosity. Higher air-filled porosity means a higher  $\text{NH}_3$  gas diffusion rate and faster supply of  $\text{NH}_3$  from the bottom to the emitting surface, resulting in a higher  $\text{NH}_3$  emission.

As discussed earlier, the emission of  $\text{NH}_3$  from the windrow surface is also affected by the concentration of  $\text{NH}_4^+$  in the manure/compost solution. Turning also affects the rate of  $\text{NH}_4^+$  production and its distribution in the windrow. First, periodic turning increases the aeration status of the windrow, leading to a greater rate of decomposition and  $\text{NH}_4^+$  production. Second, turning brings the less decomposed material from the bottom to the top at the same time as it moves well-decomposed materials to the bottom. This leads to a new round of decomposition and  $\text{NH}_4^+$  production near the surface, where  $\text{O}_2$  supply is more plentiful. Third, turning also redistributes  $\text{NH}_4^+$  from the bottom to the top of the windrow. The concentration of  $\text{NH}_4^+$  is much higher at the bottom because the  $\text{NH}_4^+$  produced during decomposition near the windrow surface is either volatilized to the atmosphere as  $\text{NH}_3$  gas or converted to  $\text{NO}_3^-$  through a nitrification process under aerobic conditions. However,  $\text{NH}_4^+$  is very stable at the bottom of the windrow where  $\text{O}_2$  supply is limited. Thus, turning would move material rich in  $\text{NH}_4^+$  from the bottom to the top and increase  $\text{NH}_3$  emission.

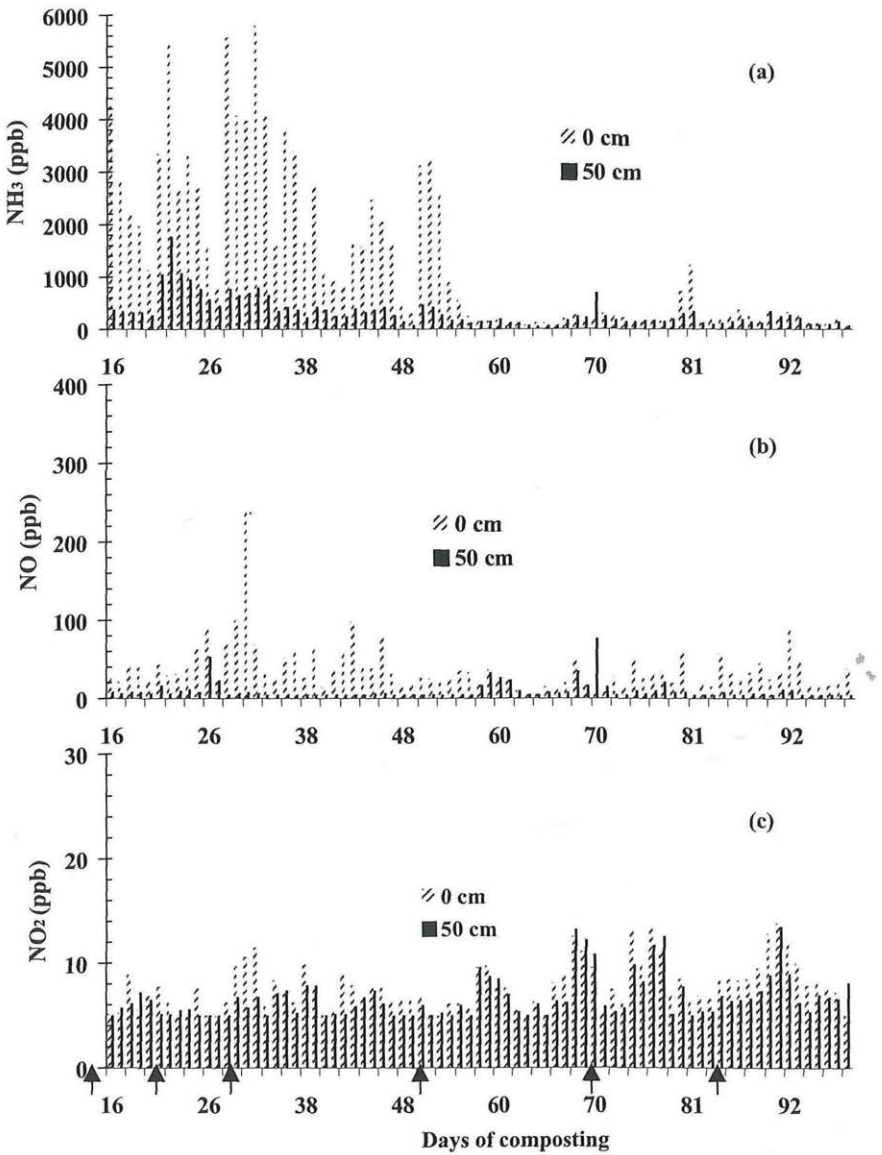


Fig. 4. Concentration of NH<sub>3</sub>, NO and NO<sub>2</sub> at 0 and 50 cm above the windrow surface under active aeration treatment (arrows pointing to data of windrow turning).

The small difference in  $\text{NH}_3$  atmospheric concentration between active and passive aeration treatments during late composting reflects similar  $\text{NH}_4^+/\text{NH}_3$  concentrations near the evaporating surfaces of the windrows. However, the  $\text{NH}_4^+/\text{NH}_3$  concentration would be much higher towards the bottom of the windrow, especially for the passive aeration treatment. Turning had little effect on atmospheric  $\text{NH}_3$  concentration during late composting, probably reflecting a more uniform distribution of  $\text{NH}_4^+/\text{NH}_3$  in the windrow profile for the active aeration treatment.

The cured compost cover for the passive aeration treatment also contributed to its low measured  $\text{NH}_3$  atmospheric concentrations. The cured compost cover at the windrow surface could adsorb some of the volatilized  $\text{NH}_3$  and the adsorbed  $\text{NH}_3$  could be leached back into the windrow below with rainfall events. This reduces  $\text{NH}_3$  volatilization, so the atmospheric concentration was below that of the active aeration treatment.

Similar to the passive aeration treatment,  $\text{NO}_2$  varied between 5 and 14 ppb throughout the entire composting period (Fig. 4c) while the daily atmospheric NO concentration near the compost surface varied from 240 ppb during early composting to 10 ppb during later composting. A higher atmospheric concentration at the windrow surface than 50 cm above was also observed (Fig. 4b). However, NO concentration for the active aeration treatment was lower at the beginning and higher towards the end of composting than for the passive aeration treatment. The lower atmospheric concentration during early composting was probably related to the lower rate of nitrification, since a greater rate of  $\text{NH}_3$  volatile loss (Fig. 4a) means less  $\text{NH}_4^+$  is available for nitrification and NO production in the active aeration treatment. On the other hand, the higher atmospheric NO concentration during late composting was probably related to greater denitrification during later composting. There were also variations among the three windrows with the C.V. ranging from 0.1 to 65.6 % (average of 20.2 %) for NO and from 0.1 to 39.9 % (average of 12.7 %) for  $\text{NO}_2$ .

As discussed earlier, turning not only mixes the material, but effectively moves nitrate-rich material from top to bottom while moving  $\text{NH}_4^+$ -rich materials from bottom to top. Besides starting a new round of  $\text{NH}_3$  emissions, turning also increases NO production through nitrification near the surface and denitrification near the bottom. Thus, a higher NO atmospheric concentration for the active aeration treatment was observed in the second half of the composting. Denitrification played an increasing role since  $\text{NO}_3^-$  concentration increases as composting progresses.

The average  $\text{NH}_3$  concentrations over the entire study period were 1316.0 ppb at the surface and 332 ppb 50 cm above the active compost windrow, which were significantly higher than 285.1 ppb at the surface and 210.0 ppb 50 cm above the passive composting windrow. In contrast, the average NO concentration at active windrow surface (39.1 ppb) was significantly lower than for the passive windrow (54.4 ppb) while similar values (10.0 – 10.8 ppb) were observed 50 cm above both windrow surfaces. There were no differences in the  $\text{NO}_2$  concentration between the passive and active compost treatment at both sampling heights. The

different atmospheric  $\text{NH}_3$  and  $\text{NO}$  patterns observed for the two aeration treatments in this study were caused by the different composting conditions created by the two aeration treatments. The aeration treatment not only affects the rate of composting, but, more importantly, the nitrogen transformation and transport in the windrow profile, the gaseous N emission through the windrow surface and, finally, the  $\text{NH}_3$ ,  $\text{NO}$  and  $\text{NO}_2$  atmospheric concentrations. The lower  $\text{NH}_3$  emission was further confirmed by the high concentration of  $\text{NH}_4^+$  retained in the passive aeration compost at the end. Since the manure had a narrower N to P ratio than most crops need, any N conserved during composting is a bonus. Supplementary N fertilizer is usually required if compost is applied to fields based on crop P need.

The relatively lower  $\text{NO}_2$  atmospheric concentration for both treatments suggests that  $\text{NO}_2$  production during composting of cattle feedlot manure is very limited. The high  $\text{NO}$  emission for passive aeration during early composting might be a concern and further study is needed to investigate possible methods to reduce  $\text{NO}$  and  $\text{NH}_3$  emission during composting of cattle feedlot manure.

#### A c k n o w l e d g e m e n t

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