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Nitrogen Transformation and Losses during Composting and Mitigation Strategies

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ABSTRACT

Composting organic material, such as livestock manure, reduces its odor and C:N ratio while sanitizing and improving its physical properties. However, the biggest challenge in composting is N loss, mainly as NH_3 and to a lesser extent as N_2O. Ammonia contributes to smog formation and reduces air quality. Near large feedlot operations, high atmospheric NH_3 depositions have been linked to plant diversity decline, soil acidification and surface water eutrophication. Emission of N_2O contributes to global warming and climate change. This paper reviews the mechanisms responsible for N transformation and NH_3 and N_2O emissions during composting, primarily of livestock manure, and strategies used to mitigate N losses.

Keywords: gaseous emission, leaching loss, NH_3, N_2O, N transformation

Abbreviations: bST, bovine somatotropin; **MP**, metabolizable protein; **NOB**, nitrite-oxidizing bacteria; **TAN**, total ammoniacal N

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INTRODUCTION

Composting has been proposed as an alternative to direct land application for livestock manure management. Composting has the advantage of stabilizing nutrients; killing pathogens (Vuorinen and Saharinen 1997; Larney *et al.* 2003) and weed seeds (Larney and Blackshaw 2003); reducing moisture content, odor, and C:N ratio (DeLuca and DeLuca 1997); and improving physical properties (Kuhlman 1990). Composting reduces the volume and weight of the original material, allowing the end product to be trucked further distances to cropland. Compost can also be more easily bagged and sold for use in gardens or nurseries (Larney *et al.* 2000b). When applied to soil, compost increases soil organic matter, increases soil water and nutrient holding capacity, reduces soil erosion and provides macro and micronutrients.

One of the main concerns associated with composting is N loss. This not only reduces the agronomic value of the final compost (Tiquia and Tan 2000), but also contributes to greenhouse gas (N_2O) and ammonia (NH_3) emissions (Peigné and Girardin 2004). Once in the atmosphere, NH_3 reacts with other particulates forming smog and reducing air quality (Aneja *et al.* 2001), while emission of N_2O contributes to climate change and global warming. The global warming potential of N_2O is 296 times that of CO_2 over 100 years (IPCC 2007). Atmospheric NH_3 deposition has also been linked to declining forests, reduced plant diversity in natural ecosystems, increased soil acidification, and accelerated eutrophication of surface water (Aneja *et al.* 2001; Krupa 2003). In some areas, runoff and leaching N loss from composting windrows may contribute to water pollution (Peigné and Girardin 2004).

The objective of this paper is to review the mechanisms responsible for N transformation and gaseous (e.g., NH_3 and N_2O) emissions during composting, and the strategies used to mitigate N losses. The primary focus is on livestock manure composting but some examples are based on other raw materials.

COMPOSTING PROCESS AND NITROGEN TRANSFORMATION

Composting processes and methods

Rynk (1992) defines composting as the aerobic decomposi-

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Invited Review

tion of organic materials by microorganisms under controlled conditions. During composting, microorganisms consume oxygen as they feed on the carbon and nitrogen contained in organic matter. This produces a considerable amount of heat along with carbon dioxide (CO_2) and water vapor as by-products. The composting process can be separated into mesophilic, thermophilic and maturing stages. During the mesophilic stage, the temperature rises to about 40 to 45°C and decomposition of easily degradable components (e.g., sugars and amino acids) begins. This stage lasts for a few hours to a few days, followed by the thermophilic stage with temperatures above 45°C to as high as 80°C. Heat-intolerant organisms become dormant or are destroyed. This stage can last a few days to several months. Most of the organic matter is decomposed and oxygen is consumed. After the thermophilic stage, the temperature drops below 45°C and maturing begins. Microbial activity decreases and is dominated by mesophilic microorganisms. This stage is important because humus-like substances are produced (Peigné and Girardin 2004). Although composting stages are characterized by the dominant temperature, in the thermophilic stage there will be a zone near the surface that remains mesophilic due to heat loss.

There are three general composting methods used: (1) passive, (2) active turning (windrows) and (3) in-vessel (or forced aeration). Passive composting, the most common, is simply piling solid livestock manure, with or without aeration ducts, and leaving it to compost over a long period of time. Very little, if any, activity is performed on the pile once it has been constructed. Initial composting parameters can be controlled but are not usually maintained during the entire process. This method relies on natural processes to draw cool air and oxygen into the pile as the warm air rises and is released, a process commonly referred to as the chimney effect. Passive aeration is energy efficient, and can be just as effective as active turning or in-vessel composting (Barrington *et al*. 2003). Lo *et al*. (1993) demonstrated that hog solid manure compost reaches thermophilic temperature (45 to 70°C) and meets regulatory requirements with or without aeration.

Active turning composting is similar to passive composting, but raw materials are piled in windrows (long rows that normally range from 1 to 4 m high and anywhere between 2 to 6 m wide). Windrows are turned or aerated mechanically to maintain temperature conditions for maximum microbial activity. Specially designed turners or a simple front-end loader could be used for this purpose. The size and shape of the windrow depends on the type of livestock operation and turning equipment available.

In-vessel composting takes place inside specially built structures or vessels. It relies upon mechanical aeration and turning to enhance the rate of composting and decreases the duration of the composting process. The disadvantage of in-vessel composting is that creating the controlled environment can be expensive.

Nitrogen transformation during composting

The major challenge in composting is conserving N, one of the major nutrients in raw compost material. Understanding N transformation and cycling during composting is crucial in developing management practices that increase the N content in the final compost product. Primary N transformation processes include mineralization of organic N to NH_4^+, nitrification of NH_4^+ to NO_3^-, and denitrification of NO_3^- to N_2O and N_2 (**Fig. 1**).

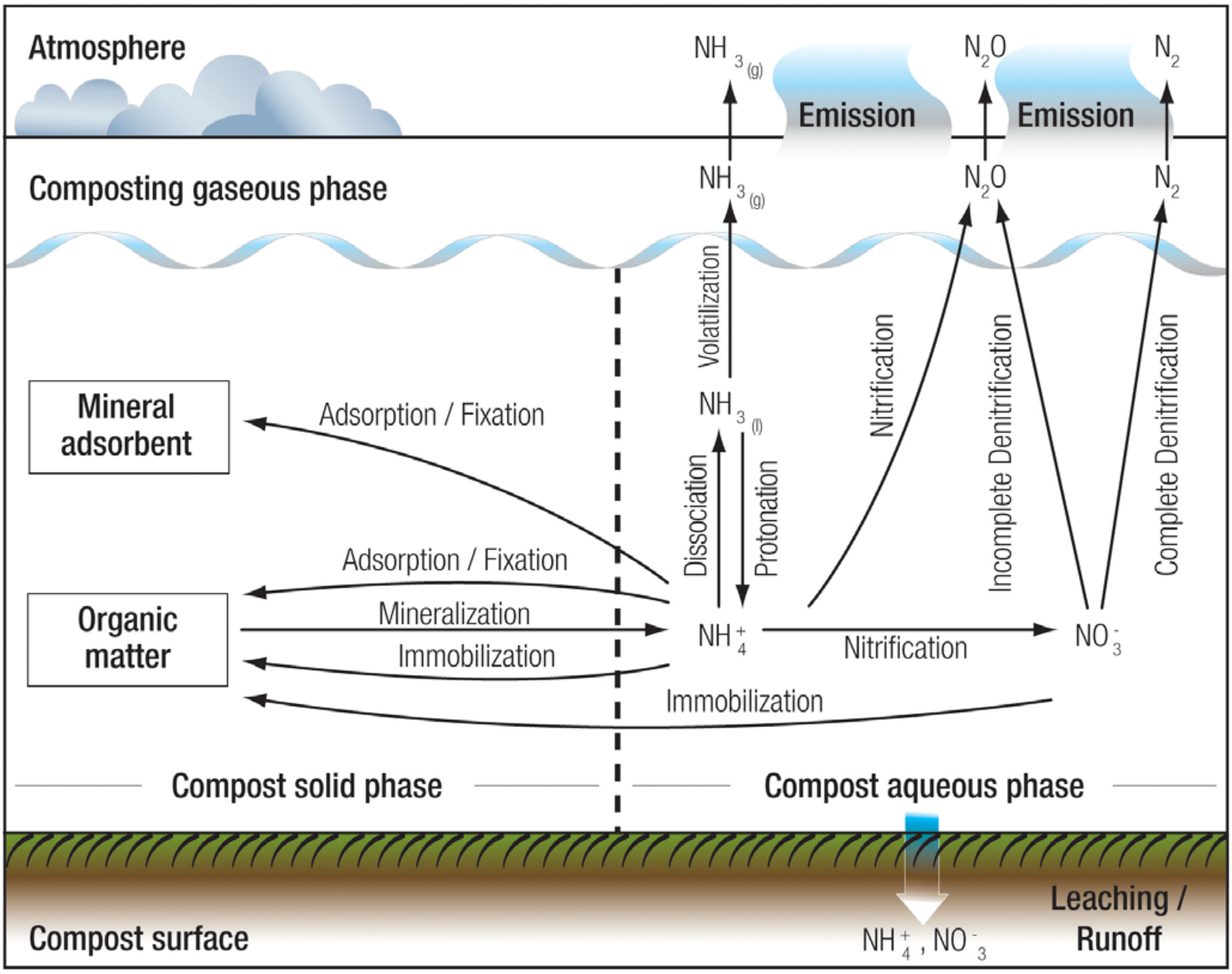

Fig. 1 Nitrogen transformation and losses during composting.

During composting, organic N is mineralized and released as soluble NH_4^+ ions. There are five competing pathways that remove NH_4^+ ions from the liquid phase in the compost: (1) volatilization loss as NH_3, (2) adsorption of NH_4^+ (becoming exchangeable ions) to organic and mineral surfaces, (3) immobilization by microorganisms, (4) nitrification to NO_3^- and (5) leaching and runoff (**Fig. 1**). By far the most important N loss is through volatilization (Kirchmann and Witter 1989).

Ammonium is not volatile until it is dissociated to NH_3. The rate of NH_4^+ conversion to NH_3 is controlled primarily by temperature, pH and NH_4^+ concentration (McCrory and Hobbs 2001). Most NH_3 loss occurs during the first few weeks of composting, when compost material pH and temperature are high (Bhoyar *et al.* 1979; Bishop and Godfrey 1983). During composting, the amount of NH_3 volatilization is second only to CO_2 emission (Beck-Friis *et al.* 2001).

As a cation, NH_4^+ is subject to adsorption by the negatively charged organic materials (specifically humus-like materials) and clay mineral surface. The clay particles come from soil that gets mixed with the manure by animals' treading in the feedlot pens. Adsorbed NH_4^+ is in a dynamic equilibrium with the liquid phase and can be easily desorbed. Ammonium ions could also undergo fixation by both humus and clay (Nommik and Vahtras 1982). These reactions can decrease the NH_4^+ concentration in the liquid phase, reducing the potential of NH_3 volatile loss as well as nitrification and immobilization.

The immobilization process converts soluble NH_4^+ from the liquid phase into organic N and is considered the main pathway competing with NH_3 volatilization during the first weeks of composting. This is particularly important when high amounts of low-N crop residues with high biodegradable C (e.g., straw, molasses) are added to the compost material (Kirchmann and Witter 1989; Paillat *et al.* 2005). The high content of carbohydrates in these residues stimulates the activity of microorganisms which in turn require N and other nutrients for their growth (Jansson and Persson 1982).

Under aerobic conditions, NH_4^+ is oxidized to NO_2^-, followed by NO_2^- oxidizing into NO_3^-, a two-step nitrification process. During nitrification, N_2O may be produced as a by-product (Czepiel *et al.* 1996). Under aerobic conditions NO_3^- is stable, but under anaerobic conditions NO_3^- is denitrified to N_2O and N_2 which are emitted in gaseous form to the atmosphere. The high temperature and elevated NH_3 concentration inhibit the activity and growth of nitrifying bacteria (Angelidaki and Ahring 1994; Bustamante *et al.* 2008), thus the observed low NO_3^- concentration in compost during early thermophilic composting (Hao *et al.* 2004). However, when temperature drops and the maturing stage begins, nitrification increases, enhancing NO_3^- and lowering NH_4^+ concentrations in the final compost product compared with the initial material (Tiquia *et al.* 2002; Hao *et al.* 2004).

Both nitrification and denitrification could potentially contribute to N_2O production and surface emission. Since the heterogeneous properties of manure/compost materials lead to a mosaic of aerobic and anaerobic sites, it is likely that multiple processes are contributing simultaneously to N_2O production. The initial stage of livestock manure composting, being characterized by high NH_4^+ and low NO_3^- concentration (Larney 1999), favors nitrification as the major contributor to the increased surface fluxes of N_2O (Hao *et al.* 2001). As composting progresses, NH_4^+ concentration decreases (mainly due to volatilization losses and nitrification) and NO_3^- increases, so denitrification plays an increasing role in N_2O emission. However, N loss in the form of N_2O is much lower than as NH_3 (Parkinson *et al.* 2004).

Both water soluble NH_4^+ and NO_3^- could also be lost from the composting system through leaching or runoff. The proportion of NH_4^+ and NO_3^- in compost leachates varies depending on composting stage and the content of N compounds in the raw material. Ammonium losses by leaching and runoff occur during the first days (or weeks) of composting while NO_3^- loss occurs following nitrification (Martins and Dewes 1992). Leaching loss accounts for a small fraction of total N loss during composting (Eghball *et al.* 1997).

AMMONIA EMISSION

Ammonia emission is the main form of N loss during composting, which occurs at a rate much higher than N_2O emission (Vuorinen and Saharinen 1997; Hellebrand and Kalk 2001; Parkinson *et al.* 2004). About 50 to 90% of all NH_3 losses occur during the first weeks of thermophilic composting, which coincide with high pH and high temperature (Bhoyar *et al.* 1979; Bishop and Godfrey 1983). Losses via NH_3 volatilization range from as low as 13% to as high as 70% of manure N (Hansen *et al.* 1989; Martins and Dewaes 1992; Eghball *et al.* 1997; Beck-Friis *et al.* 2001). The wide variations are due to differences in properties of the raw material used, environmental conditions and compost management practices.

Impact of manure properties on NH_3 emission

Manure physical properties such as pH, temperature and moisture content not only influence composting efficiency, but also play a vital role in N cycling and NH_3 loss during composting. Manure composition, particularly the level of easily degradable C and available N as well as the carbon to nitrogen (C:N) ratio, also influences compost efficiency, N cycling and NH_3 loss.

Owing to its effect of shifting the balance between free NH_3 and NH_4^+ ions in the compost liquid phase, pH plays an important role in N transformation and emission loss, particularly for N-rich material such as livestock manure. Dissociation of NH_4^+ to NH_3 rapidly increases as pH in compost rises above 6. Court *et al.* (1964) reported that the relative percentage of NH_3 in solution at pH 6, 7, 8, and 9 was 0.1, 1, 10 and 50%, respectively. Ekince *et al.* (2000) observed that NH_3-N losses decreased rapidly when pH was below 7 during composting of broiler litter mixed with paper mill waste. In their study, a 75% reduction in NH_3 loss was observed when initial pH decreased from 8.3 to 6.6. Several other researchers reported similar results during composting of livestock manure (Molloy and Tunney 1983; Derikx *et al.* 1994; Moore *et al.* 1997). An increase in pH during the thermophilic stage of composting is promoted by the degradation of organic acids, amino acids and urea into NH_4^+ and HCO_3^-, which act as buffers maintaining high pH (Varel *et al.* 1999; Bustamante *et al.* 2008).

Temperature is the other main factor influencing NH_4^+ dissolution to NH_3 and subsequent volatilization. Temperature affects the solubility of NH_3 in water and the diffusion rates in compost. As temperature rates increase, NH_3 diffusion rates increase while NH_3 solubility decreases (Smith *et al.* 1990). Urease activity, which converts urea in livestock urine discharge to NH_3, also increases with temperature and peaks at 70°C (Ladd and Jackson 1982). A positive exponential relationship between temperature and NH_3 emission has been reported during thermophilic stage composting (Pagans *et al.* 2006). High temperatures are fundamental to destruction of pathogens but temperatures above 72°C should be avoided (Finstein *et al.* 1986) to reduce NH_3 emissions.

Another manure physical property that affects composting is moisture content but to a much lesser degree than pH and temperature. Moisture content affects microbial activities and provides a means for transport of dissolved nutrients required for metabolic and physiological activities of microorganisms (Tiquia *et al.* 2002). Since NH_3 is highly soluble in water, emissions will increase when the moisture content is low.

Initial compost C:N ratio is another factor affecting organic N mineralization and subsequent NH_3 emissions. Too low a C:N ratio in the composting pile will lead to excessive N loss while too high a C:N ratio will prevent the composting pile from heating up properly or lengthen the time to reach the thermophilic temperatures. A negative correlation between C:N ratio and NH_3 loss has been observed by Ekince *et al.* (2000) during composting of broiler litter mixed with paper fiber. Hansen *et al.* (1989) reported that NH_3 emission from poultry manure compost piles with a C:N ratio of 15 was 4 times greater than from piles with a C:N ratio of 20. Hao *et al.* (2004) reported a smaller N loss from woodchip-bedded cattle manure compost than from straw-bedded. These authors attributed the reduced N loss in the woodchip-bedded manure to its higher C:N ratio and lower total N content (C:N ratio = 36, total N = 12.4 g kg^{-1}) compared with the straw-bedded manure (C:N ratio = 17 and total N = 19.9 g kg^{-1}).

A wide range of initial C:N ratios has been suggested as optimal for composting. For example, Poincelot (1972) suggests an optimum initial C:N ratio of 25 to 30, while Ekince *et al.* (2000) suggests 30 to 38. These differences may be related to variations in the concentration of easily decomposable N and C compounds in the raw material. Paré *et al.* (1998) found that N losses were better correlated with levels of easily degradable N and C than the total C:N ratio in raw material. Paillat *et al.* (2005) further demonstrated that for similar compost C:N ratios, a higher content of biodegradable C (e.g., pig manure amended with molasses) reduced NH_3 emission, while less biodegradable C content (e.g., pig manure amended with sawdust) increased NH_3 emission.

Environmental factors affecting NH_3 emission

Atmospheric temperature can also influence NH_3 volatilization from compost heaps, but seems to have a smaller impact than compost internal temperature. A large amount of heat is generated during the decomposition of organic matter. Fukumoto *et al.* (2003) observed higher NH_3 emission rates during the day than at night when composting swine manure mixed with sawdust. Parkinson *et al.* (2004) also reported that mean NH_3 emission rates from cattle manure compost under active (1 to 3 turnings) aeration were greater during the summer (June-September) than during the cool and wetter autumn period (September-December). These authors reported NH_3 losses of 11 to 18% of initial manure N during the summer compared to only 2% during the autumn period. However, Petersen *et al.* (1998) observed little difference in NH_3 emission between spring-summer (May-September) and autumn-winter (October-January) seasons during passive (no turning) aeration composting of cattle and pig straw-bedded manure. Because air temperatures were similar, the contrasting results in these experiments could be attributed to differences in compost pile size and turning rates.

Compost management practices and options to mitigate NH_3 emission

Compost management practice, such as compost windrow size, aeration rate and moisture content, along with the use of covers, bulking agents and additives, could potentially affect NH_3 gaseous loss, forming the basic options for mitigating NH_3 emission. Another important measure that could reduce NH_3 emission is decreasing animal N excretion by improving animal N utilization.

Fukumoto *et al.* (2003) studied the influence of pile size on NH_3 emission rate during swine manure composting and observed that emissions increase with an increase in the piling scale. A windrow pile of 1.5 m height was considered ideal by Hong *et al.* (1984) and Michel (1999). However, smaller piles require more land to compost the livestock manure (Fukumoto *et al.* 2003).

Another way to reduce NH_3 emission is by decreasing the number of pile turnings. Frequent turning stimulates aerobic decomposition processes and leads to elevated emissions of NH_3 (Parkinson *et al.* 2004). Turning effectively moves the higher NH_4^+ compost nearer the surface and higher NO_3^- materials towards the center, exposing fresh material for microbial colonization and bringing oxygen to microorganisms. This in turn increases the composting rate and causes a rise in temperature, which consequently enhances NH_3 emission (Gibbs *et al.* 2000; Tiquia *et al.* 2000). Turning also increases the gas diffusion rate by "fluffing up" the material, increasing the total porosity and air-filled porosity of the manure/compost materials.

The effect of passive (no turning) vs. active aeration (turned 6 times) on NH_3 emission in open windrows was investigated by Hao and Chang (2001). At the end of the experiment, passive aeration resulted in a much higher N content in the compost and therefore less NH_3 gaseous loss than active aeration. Li *et al.* (2008) and De Guardia *et al.* (2008) also found that emissions at higher aeration rates were higher than those at lower aeration rates.

Covering the compost pile has been shown to reduce air exchange and therefore NH_3 emission. Gottschall and Vogtmann (1988) found that gaseous N losses from an uncovered windrow were around 22% while the use of a 25-cm layer of straw reduced gaseous N losses to 13%; inserting a plastic sheet between the straw and the compost heap during the maturing stage further reduced losses to 7%. Sommer (2001) also reported reduced NH_3 volatilization after covering the compost with a porous tarpaulin.

Proper moisture content is necessary to support microbial activity. The range of 50-60% is generally recommended for composting (Tiquia *et al.* 1996; Liang *et al.* 2003). Higher moisture content could lead to early cooling of the pile, which could decrease the production of microbial activity and biomass (Tiquia *et al.* 1996). Even though higher moisture content could reduce NH_3 emission, it is not recommended because high moisture usually leads to lower temperatures and sanitization requires high temperatures (above 55°C) for at least 3 consecutive days (USEPA 1989).

Bulking agents (C-rich materials) are added to N-rich compost materials, such as livestock manure, in an attempt to decrease N losses (Kirchmann 1985; Mahimairaja *et al.* 1994). Carbon-rich material increases the compost C:N ratio and can promote NH_4^+ immobilization. Eklind and Kirchmann (2000) indicated that N losses were lower from peat- and straw-amended composting compared to the control. However, these authors indicated that N losses from the amended compost were still substantial.

The efficiency of numerous additives in reducing N losses from composting has been extensively investigated. Such additives vary in their mode of action and include: NH_4^+ immobilization stimulants, urease inhibitors, pH acidifiers, NH_4^+ adsorbents (McCrory and Hobbs 2001), and promoters of NH_4^+ precipitation into struvite ($MgNH_4PO_4 \cdot 6H_2O$) mineral (Jeong and Kim 2002). Since the performance of NH_4^+ immobilizers and urease inhibitor additives has generally been poor (McCrory and Hobbs 2001), only acidifying, adsorbent and struvite precipitating additives will be discussed here.

By decreasing compost pH, acidifying additives could reduce NH_3 volatilization. Both acids (e.g., sulfuric, hydrochloric, nitric and phosphoric) and base precipitating salts (e.g., $CaCl_2$, $MgCl_2$, $CaSO_4$, $MgSO_4$ and $Al_2(SO_4)_3$(alum)) have been proven to lower pH and reduce NH_3 emission from compost (Kithome *et al.* 1999a; McCrory and Hobbs 2001). Acids are more efficient in reducing compost pH than base precipitating salts; however, cost and hazards of use make acids impractical. Witter and Kirchmann (1989a) compared the addition of different Ca and Mg salts and observed that $MgCl_2$ was the most effective in reducing NH_3 volatilization during aerobic decomposition of poultry manure.

Other additives that have been tested as acidifying materials in compost are elemental sulfur (S^0) and phosphogypsum. Mahimairaja *et al.* (1994) reported that NH_3 loss was reduced by 60% in poultry manure amended with S^0. Under lab conditions a small decrease in NH_3 emission was observed when fresh poultry and dairy manures were amended with 1 to 3% gypsum (Termeer and Warman 1993). In a field scale experiment, addition of 20% phosphogypsum almost tripled the amounts of available NH_4-N in the straw-bedded compost compared to the control (Larney *et al.* 2000a). These materials are cheap and readily available.

Adsorbent additives have the capacity to adsorb NH_3 and/or NH_4^+, reducing the risk of volatilization. Clinoptilolite zeolite and *Sphagnum fuscum* peat are the most common adsorbent additives studied. However, clay (specifically 2:1 phyllosilicates) rich soil and coir (coconut fruit mesocarp) have also been used.

Turan and Ergun (2007) reported higher total N and lower water-extractable NO_3^- and NH_4^+ content when zeolite was added at 5 and 10% to municipal solid waste compost. Mahimairaja *et al.* (1994) investigated the use of zeolite, peat and soil mixed thoroughly with poultry manure in reducing NH_3 loss during composting. These authors reported that zeolite was the most efficient in reducing NH_3 loss, achieving a 60% NH_3 reduction. Witter and Kirchmann (1989b) studied the effectiveness of peat and zeolite either placed in the spent air-stream or mixed with poultry manure during manure aerobic decomposition in an incubator. Their results indicated that these additives were more efficient in reducing NH_3 emission when placed in the spent-air stream and, contrary to the results of Mahimairaja *et al.* (1994), peat was more effective than zeolite. Peat and zeolite efficiency in reducing NH_3 emission is related to their high cation exchange capacity and affinity for NH_4^+. The contrasting results observed in these two studies could be related to differences in the properties of the zeolite used.

A layer of coir was as effective as a layer of acidified zeolite (pH 5) in reducing NH_3 emission from poultry manure during composting under controlled conditions (Kithome *et al.* 1999a). Even though the amounts used in this trial were too high to be practical, the use of coir together with other management practices may have great potential in mitigating NH_3 emission from compost. Adsorption isotherm studies showed that coir has high pH buffering capacity and high affinity for NH_4^+ (Kithome *et al.* 1999b). Coir, which is easily available in some tropical countries, has the advantages of being a renewable resource and cheaper than zeolite.

Precipitation of NH_4^+ into struvite has been used to remove nutrients such as N and P in wastewater treatment facilities (Schulze-Rettmer *et al.* 1991). Recently this method was tested to reduce NH_3 emission and increase the fertility value of compost (Jeong and Kim 2002; Jeong and Hwang 2005). Addition of water soluble Mg and P salts equivalent (molar basis) to 20% of total N significantly increased total ammoniacal N (NH_3 + NH_4^+) in food waste mixed with woodchip compost (Jeong and Kim 2002). Furthermore, struvite is a valuable fertilizer (Wrigley *et al.* 1992). However, high levels of Mg and P salts are needed to efficiently reduce NH_3 emission when composting materials high in available N content, such as livestock manure. The use of elevated concentrations of Mg and P salts could increase compost salinity and inhibit microbial activity, causing incomplete degradation of organic materials (Jeong and Hwang 2005).

Kohn *et al.* (1997) evaluated N losses from dairy farms and concluded that there is great potential to reduce N excretion and therefore NH_3 emission by improving herd nutritional efficiency. Livestock N assimilation is inefficient, with about 70 to 80% of dietary N excreted (Jonker *et al.* 2002; Satter *et al.* 2002). Most of the excreted N is released as urea (Ginger-Reverdin *et al.* 1991; Jonker *et al.* 2002), except in poultry, where it is uric acid (O'Dell *et al.* 1960; Zhang and Day 1996). Under aerobic conditions, urea and uric acid are rapidly decomposed to NH_4^+ and CO_2 by the enzymes urease and uricase, present in both feces and soil (Ladd and Jackson 1982; Mobley *et al.* 1995). While urea excretion depends on animal species and type, it is also influenced by diet (Fernández *et al.* 1999).

The use of more accurate diet formulation for protein, such as metabolizable protein (MP) systems and phase-feeding, allows N inputs to be reduced by 10 to 20% in cattle diets without affecting animal performance (Klopfensteins and Erickson 2002). The resulting 12 to 21% decrease in N excretion led to a 15 to 33% reduction in N volatilization from manure. Jonker *et al.* (2002) indicated that the use of management practices to increase milk production, such as component testing, administration of bovine somatotropin (bST) and extending photoperiod with artificial light, increased efficiency of feed N utilization. These practices also have the potential to reduce N excretion from dairy farms.

Even though reducing N excretion through livestock management practices is an important step in controlling NH_3 emission, there is a limit to how much reduction can be achieved through diet manipulations (Klopfensteins and Erickson 2002). However, combining livestock management practices with the most proper compost management practices discussed above could result in substantial reductions in NH_3 volatilization loss.

NITROUS OXIDE EMISSION

The rate of N_2O emission varies considerably and results can be difficult to compare across studies as they are reported in different units, such as per unit surface area (Petersen *et al.* 1998; Brown *et al.* 2000), per unit dry weight (Hao *et al.* 2001), or per unit initial N in the composting materials (Hao *et al.* 2001). For example, N_2O emission rates of 0 and 0.33 g N m^{-2} d^{-1} (Petersen *et al.* 1998; Brown *et al.* 2000) or 0.11 kg to 0.19 kg N Mg^{-1} (Hao *et al.* 2001) or 0.62 and 1.07% of the total initial N (Hao *et al.* 2001) have been reported. The variations in N_2O emission rates are due to differences in properties of the raw material and compost management practices.

Impact of compost properties on N_2O emission

The N_2O emission patterns during composting depend on several factors, such as O_2 status, temperature, pH (Khdyer and Cho 1983; Scholefield *et al.* 1997), soluble C:N ratio (Yamulki 2006) and NH_4^+ and NO_3^- availability (Hao *et al.* 2001). These factors also influence the ratio of N_2O to N_2 during denitrification. For example, low NO_3^- concentration and higher pH favors N_2 as a denitrification end product (Khdyer and Cho 1983; Arah *et al.* 1991). On the other hand, increases in NO_3^- concentration and lower pH, water content and temperature as composting progresses, favor the production of N_2O over N_2 (Cho and Sakdinan 1978; Khdyer and Cho 1983; Scholefield *et al.* 1997; Stevens *et al.* 1998), leading to higher N_2O concentrations and surface emissions (Hao *et al.* 2001, 2004).

The concentration of O_2 is a crucial factor in the delicate balance between aerobic and anaerobic conditions inside the compost pile, influencing the processes of nitrification and denitrification and subsequent N_2O emission. Hellebrand (1998) indicated that emission of N_2O from compost started only after the peak CO_2 emission had passed and aerobic microorganisms had converted nearly all O_2 into CO_2, generating anaerobic conditions. However, Hochstein *et al.* (1984) pointed out that under extreme anaerobic conditions (i.e., below 3% O_2) N_2O may be unstable and is further reduced to N_2 (complete denitrification) (**Fig. 1**). Hao *et al.* (2001) reported that most N_2O production and emission occurs when O_2 concentration is 3 to 9% in the bulk pore space, while there is little N_2O production when the O_2 level drops below 3% as extreme anaerobic conditions favor N_2 over N_2O production. In the borderline between the aerobic and anaerobic state, specialized bacteria could utilize the denitrification chain as an O_2 source and generate N_2O. Denitrification under low (around 10%) O_2 conditions results in significant N_2O production (incomplete denitrification) (**Fig. 1**), possibly as an intermediate between NH_2OH and NO_2^- (Bandibas *et al.* 1994).

Nitrification becomes more dominant when O_2 concentration is higher and N_2O production could also be formed as a by-product. Hwang and Hanaki (2000) suggest that denitrification is the sole microbial process when the compost bulk O_2 content is under 5%, and nitrification and denitrification occur simultaneously when O_2 is above 5%. However, denitrification was still the main source of N_2O emitted when O_2 was at 10%. Amon *et al.* (2001) also measured much higher N_2O emission from anaerobically stacked farmyard manure compared to aerobic composting.

The microbes involved in the N_2O production are generally not thermophilic (Sommer 2001), and thus most N_2O emission has been reported with mesophilic temperature conditions (Hao *et al.* 2001; Chiumenti *et al.* 2007). The higher moisture and readily decomposable organic matter content during early thermophilic composting leads to anaerobic conditions with extremely low O_2 levels, which promote production of N_2 instead of N_2O. In addition, high temperature and pH in the early thermophilic stage favors the production of free NH_3 which is toxic to the nitrifying microbial community (Angelidaki and Ahring 1994; Bustamante *et al.* 2008). Under these conditions NO_3^- production and denitrification are reduced.

Hao *et al.* (2005) reported a significant negative relationship between N_2O emissions and compost pH. In their study, when pH decreased from 8.0 to 7.5, N_2O emissions almost tripled. This is consistent with findings that N_2O emission is generally highest under neutral or slightly acidic (pH = 6.5) conditions (Steven *et al.* 1998). Thomas *et al.* (1994) suggested that the optimum pH for denitrification by *Pseudomonas* species was 7.0 to 7.5.

Yamulki (2006) reported lower N_2O emissions from manure with high C content. This was attributed to the high C:N ratio and good aeration, suggesting that the use of high-C additives, such as straw, could be a promising strategy for reducing N_2O emissions.

The effects of NH_4^+ and NO_3^- availability on N_2O emission are illustrated by the increases in N_2O emissions after each windrow turning (Hao *et al.* 2001). During composting, organic N mineralizes to NH_4^+ which in turn could be nitrified to NO_3^- under good aeration, typically near the windrow surface. While NH_4^+ in the interior of the windrow is stable under anaerobic conditions, NO_3^- near the windrow surface is stable under aerobic conditions. This leads to concentration profiles of maximum NO_3^- and minimum NH_4^+ near the surface in contrast to minimum NO_3^- and maximum NH_4^+ in the windrow interior. Windrow turning homogenizes materials, transporting NH_4^+ to the surface and NO_3 to the interior of the windrow. As a result of the redistribution of NH_4^+ and NO_3^- in the windrow profile, more N_2O would be produced through aerobic nitrification of NH_4^+ near the windrow surface and anaerobic denitrification of NO_3^- in the interior where the O_2 supply is limited. Coupled with an improved gas diffusion rate, N_2O emissions increase after each windrow turning during the maturing stage (Hao *et al.* 2001).

Compost management practices and options to mitigate N_2O emission

Although the emission of N_2O during composting cannot be avoided, compost management practices, such as compost windrow size, aeration rate, windrow turning frequency, bulking agents, and additive use, could be modified and potentially reduce N_2O emissions. Measures to mitigate N_2O emission could interact with other important environmental issues, such as reduction in NO_3^- leaching and NH_3 emission (Monteny *et al.* 2006). Thus, these interactions should be considered when selecting management practices to reduce N loss from compost.

A higher rate of N_2O emission was observed from a large compost pile of swine manure (46.5 g N_2O-N kg^{-1} initial total N) compared with a smaller pile (37.2 g N_2O-N kg^{-1} initial total N) (Fukumoto *et al.* 2003). Similarly, a large compost pile of organic household waste had a higher N_2O emission rate than smaller ones (Beck-Friis *et al.* 2000). The higher emission rate from large compost piles was mainly due to a greater portion of compost manure being under anaerobic conditions leading to greater denitrification production of N_2O.

In a controlled laboratory setting, Hellebrand (1998) demonstrated that N_2O emissions were 13.3 mg h^{-1} kg^{-1} when the aeration rate was 0.02 L min^{-1} kg^{-1}, but were reduced to 2.2 mg h^{-1} kg^{-1} when the aeration rate increased to 0.1 L min^{-1} kg^{-1}. Similarly, Osada *et al.* (2000) observed that the N_2O emission rate decreases exponentially as aeration rate increases. Increasing compost aeration rates most likely resulted in more aerobic conditions and reduced denitrification production of N_2O.

Parkinson *et al.* (2004) reported that N_2O emissions during cattle feedlot manure composting were not influenced by turning frequency (not turned, turned once and turned three times). Others reported increases in N_2O emission after each windrow turning (Kuroda *et al.* 1996; Hao *et al.* 2001). As discussed previously, turning promotes a redistribution of NO_3^- formed near the windrow surface to the windrow interior (Chiumenti *et al.* 2007), where denitrification occurs (Hellebrand 1998; Fukumota *et al.* 2003), and NH_4^+ nearer the surface where nitrification occurs (Hao *et al.* 2001).

Bedding materials used in livestock production systems could also affect N_2O emission during composting of livestock manure. Deep litter collected from swine production with less straw bedding material generated around 58 g N T^{-1} N_2O emission while the litter with more straw bedding material generated no detectable N_2O emission (Sommer and Møller 2000). This difference in N_2O emission could be related to differences in compost bulk density. The bulk density of the litter with higher straw content was 0.23 kg L^{-1} and the one with less straw content was 0.44 kg L^{-1}. By decreasing compost bulk density, straw bedding increases compost aeration and reduces denitirification. In contrast, Hao *et al.* (2004) reported similar rates of N_2O emission from composting cattle feedlot manure bedded with either barley straw or woodchips. In this study there was little difference in the bulk density level for the two treatments, thus the aeration was similar and so were the N_2O emissions.

Fukumoto *et al.* (2006) demonstrated that N_2O emissions from swine manure composting were reduced by adding nitrite-oxidizing bacteria (NOB) after the thermophilic stage to inhibit NO_2^- accumulation. In this study, NOB was either mature swine manure compost or cultured material. Emission rates of N_2O were 17.5 (NOB from compost), 20.2 (NOB from cultured material) and 88.5 (no addition) g N-N_2O kg^{-1} initial TN, respectively. However, the use of phosphogypsum (P fertilizer manufacturing by-product) during cattle feedlot manure composting had no statistically significant effect on N_2O emissions (Hao *et al.* 2005).

As discussed in previous sections on NH_3, livestock assimilate N inefficiently with about 70 to 80% of dietary N excreted. Diet manipulation to reduce N excretion also has great potential to reduce N_2O emission, but we will not elaborate on this here. Combining livestock management with sound compost management practices such as proper aeration, fewer windrow turning events, and suitable amendments to change the pH, soluble C and N levels and microbial population (e.g., NOB), creates conditions that are less favorable for N_2O production from both nitrification and denitrification processes. This could achieve a substantial reduction in N_2O emissions during composting of livestock manure.

LEACHING AND RUNOFF N LOSS

Compared to gaseous N loss, leaching and runoff N losses from compost piles are very small or even negligible (Peigné and Girardin 2004; De Guardia *et al.* 2008). Eghball *et al.* (1997), Petersen *et al.* (1998) and Sommer (2001) reported that during composting of solid livestock manure N leaching loss accounted for about only 0.5 to 4% of total N. However, Martins and Dewes (1992) reported losses of 9.6 to 19.6% of the initial total N when composting cattle and poultry liquid manure mixed with chopped straw.

Most leaching and runoff occurs during the first weeks (thermophilic stage) of composting and the majority of the leachate N is in the form of NH_4^+ (Martins and Dewes 1992; Petersen *et al.* 1998). The NH_4^+ and dissolved NH_3 would be the dominant species in the leachate since nitrification of NH_4^+ to NO_3^- is inhibited by the high temperature and pH during the thermophilic stage (Bustamante *et al.* 2008). Sommer (2001) reported total ammoniacal N (TAN) concentrations of 20 to 430 mg L^{-1} in cattle deep litter compost leachate and NO_3^- - N concentrations of only 0.1 to 0.3 mg L^{-1}. Since NH_4^+ undergoes rapid nitrification to NO_3^- in soil, both forms of N in compost leachate pose similar risks of ground water pollution (Peigné and Girardin 2004). Nevertheless, significant soil NO_3^- - N accumulation with depth due to livestock manure composting has been observed only after several years of composting in the same location (Nienaber and Ferguson 1994).

The main factors influencing the amount of leachate produced during composting are moisture and the water holding capacity of the raw material (Peigné and Girardin 2004). The higher N loss in leachate reported by Martins and Dewes (1992) probably resulted from the higher moisture content (79 to 85%) used in their study. The sources of moisture are precipitation, water added to adjust compost moisture content, and water released by the composting process itself. The amount of water percolating through the compost when it rains could be reduced by covering the compost pile. Addition of bulking agents such as straw and wood chips could also enhance the compost water-holding capacity, and thereby reduce leachate loss (Ulén 1993). Turning windrows can also reduce moisture content by moving wetter material to the surface where it will dry.

Nitrogen loss from leaching and runoff is generally very small, particularly in semi-arid regions. Composting practices such as increasing water-holding capacity by adding bulking agents, covering the compost pile to reduce water entering the composting windrow, or controlling moisture content by turning frequencies, could all potentially play a role in reducing N losses in leaching and runoff.

SUMMARY

The main soluble N form generated during early composting is NH_4^+. Once formed, it undergoes several rapid transformations, such as dissociation, volatilization, adsorption, immobilization, nitrification, and leaching. These transformations are controlled by factors such as pH, temperature, microbial activities, initial C:N ratio, aeration and moisture. Since the composting process naturally increases pH and temperature, the dominant pathways to N loss during composting are NH_4^+ dissociation to NH_3 and consequent volatilization. Ammonia volatilization could account for over 70% of total N initially present in the raw material. Other pathways to N loss include N_2O production from nitrification of NH_4^+ and denitrification of NO_3^- and subsequent emission as N_2O, along with soluble NO_3^- and NH_4^+ in leaching and runoff water. However, these processes are responsible for much smaller losses compared to NH_3 volatilization. The main processes competing with NH_3 volatilization during composting are N adsorption and immobilization. Therefore, management and mitigation practices target ways to manipulate factors that reduce NH_3 volatilization and favor processes that compete with volatilization in order to reduce NH_3 emission from compost.

Several manure management practices have been shown to reduce NH_3, including reducing the pile size and number of turnings, pile covering, pH acidification (e.g., phosphoric acid, $MgCl_2$, $Al_2(SO_4)_3$(alum), S^0 and phosphogypsum), increasing initial C:N through the addition of C-rich materials (e.g., straw and woodchips), use of high adsorption capacity additives (e.g., zeolite, peat and coir) and precipitation of struvite crystals by the addition of soluble Mg and P salts. Even though volatilization cannot be eliminated by the implementation of any of these practices, a combination of several practices such as reduced pile size and no turning and addition of either elemental sulfur or phosphogypsum and C-rich material seem to be the most effective and economical. Where coir is cheaply available, its use in reducing NH_3 losses from compost seems promising and deserves more investigation. Adoption of practices to improve animal N utilization could further reduce N losses during livestock manure composting.

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