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Nitrogen Retention in Beef Feedlot Manure Composting

By

Jason David Price Ⓒ

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of *Master of Science*

in

Bioresource and Food Engineering

Department of *Agricultural, Food and Nutritional Sciences*

Edmonton, Alberta

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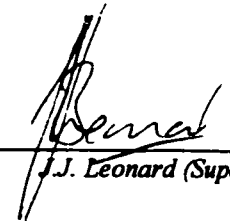
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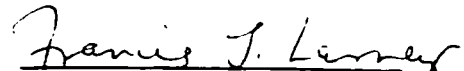
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ABSTRACT

Aspects of nitrogen retention during composting of straw-bedded (straw mix) or wood residuals-bedded (wood mix) feedlot manure were investigated in three parts. First, inexpensive acid sorbers were evaluated for their ability to give a relative measure among windrows of ammonia volatilized. Second, straw mix windrows were compared with wood mix windrows using various composting parameters. Third, a mathematical model simulating various aspects of composting was tested against experimental data gathered in the first two parts.

Sorbers detected significantly higher ammonia emission from the straw mix as compared to the wood mix. With composting, the wood mix lost a lesser proportion of its nitrogen and was more mature, but total nitrogen was greater in the straw mix. Model output was in agreement with experimental data for temperature, relative ammonia emission and rate of moisture loss. Refinements to the model to simulate full-course windrow composting more closely are suggested.

ACKNOWLEDGMENTS

A sincere and deep thank you to the following:

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CHAPTER 1

Introduction and literature review

1.1 Introduction

The recent growth of beef feedlot operations in Alberta has led to complications in

manure management. The so-called "bull's-eye effect" describes concentrations of land-

applied manure diminishing with distance from feedlot sources (Larney and Carcamo,

1999). High concentrations of land-applied manure may pose a threat to ground waters,

surface waters and the atmosphere (Sikora, 1999). Concurrent with feedlot growth has

been a growing interest in composting as a sustainable alternative to conventional manure

management strategies. Rather than view the great amounts of manure and bedding as a

waste to be disposed of, with risk of pollution, composting involves the manure and

bedding as a resource to be utilized. The benefits of nutrient content and soil

conditioning associated with composted manure and bedding are hampered somewhat,

however, by the high levels of lost nitrogen (N). Ammonia (NH_3) volatilization can

reduce the material's total N-content by as much as 50% (Mahimairaja et al., 1995;

Sikora, 1999). Improved nitrogen retention would add value to composted manure and,

therefore, is a topic for investigation.

This thesis describes research carried out in the summer of 2000, at the Lethbridge

Research Centre (LRC), Alberta, conducted in conjunction with Agriculture and Agri-

Food Canada (AAFC) studies. The AAFC research into the composting of two feedlot

bedding materials (wood residuals and barley straw) with manure, and into greenhouse

gas (GHG) emissions from the composting, was concurrent with this study. Objectives

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of the study described here were: 1) to evaluate an ammonia sorber methodology for its ability to measure relative amounts of ammonia nitrogen emitted from compost windrows, 2) to compare the composting of two mixtures of beef feedlot manure and bedding – one with straw and one with wood residuals, and 3) to test a mathematical simulation model for composting (Liang, 2000) in a windrow situation. This study ran from the time the windrows were established, on July 12, 2000, until the end of November of the same year. The AAFC studies maintained the windrows and continued until January, 2001.

This thesis is organized into five chapters. The literature review, below, is followed by chapters written in paper format. Chapter 2 presents the evaluation of the ammonia sorber methodology, Chapter 3 compares straw-bedded and wood residuals-bedded beef feedlot manure composting, and Chapter 4 tests results from Chapter 3 against results from the mathematical composting model. Finally, a synopsis of the complete project is presented in Chapter 5.

1.2 Literature review

1.2.1 What is composting?

Composting is an aerobic, self-heating, microbial process in which organic substances are biodegraded into a stable, humified material (Gray et al., 1971; Finstein and Morris, 1975; Crawford, 1983; de Bertoldi et al., 1983; McKinley and Vestal, 1985b). The process typically involves succession through various mixed populations of bacteria, actinomycetes and fungi as conditions of the microenvironment change (Herrmann and

Shann, 1997). Masses of organic material are microecosystems, serving as physical-support; gas-exchange matrix; source of organic and inorganic nutrients, water and diverse indigenous microbes; a sink for metabolic waste products; and thermal insulation (Finstein and Hogan, 1993). As various microbial populations thrive by breaking down the available material, their metabolic by-products, including heat, make conditions suitable for various other populations (Crawford, 1983). Available carbon (C) is used by microbes for energy and growth; available nitrogen is used for protein synthesis and reproduction (Rynk, 1992). Loss of material (mostly through gaseous emissions) and some compaction result in volume reductions of typically 50% after composting (Rynk, 1992). Among volatilized gases are carbon dioxide (CO_2), water vapour and ammonia (McKinley and Vestal, 1985b). The composting process comes to an end when the material is biologically and chemically stable (Pare et al., 1998), that is, it can no longer support any high degree of microbial metabolism. By this time, mineralization and humification reactions have occurred which have decreased the total organic content (de Bertoldi et al., 1983; McKinley and Vestal, 1985a) and, as Hardy and Sivasithamparam (1989) observed, increased nutrient availability. Oxidized end-products include nitrates (NO_3^-), sulphates (SO_4^{2-}) and other biologically stable compounds (Cardenas, 1979). Compost is humus-like, denser than starting material, neutral in pH, and virtually free of odour, pathogens and viable seeds (Rynk, 1992). Typical uses are as a soil-amendment or conditioner (Rynk, 1992).

Finstein (1980) describes the composting mass as exceptional in that the heat generated microbially (Browne, 1933; Nell and Wiechers, 1978) dissipates slowly enough for there

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to be an accumulation and consequent rise in temperature. Temperature is widely

accepted as the key environmental factor in microbial composting activity (Hardy and

Sivasithamparam, 1989). As adapted from Gray et al. (1971), Figure 1.2-1 shows the

temperature profile typical to the composting process, divided into four phases:

mesophilic (A), thermophilic (B), cooling (C) and maturation (D). Mesophilic organisms

thrive initially, metabolizing the most readily available nutrients until accumulated heat

inhibits them at around 40°C and instead stimulates thermophilic organisms. Likewise

under that regime, accumulating heat stimulates at first, but then inhibits – this time at

temperatures above 55 to 60°C (Finstein and Morris, 1975; Finstein and Hogan, 1993).

As available nutrients are degraded, overall metabolism and heat production slow, and

temperatures fall. Below around 40°C, mesophiles recolonize the material and

metabolize whatever available nutrients remain (Gray et al., 1971). Eventually
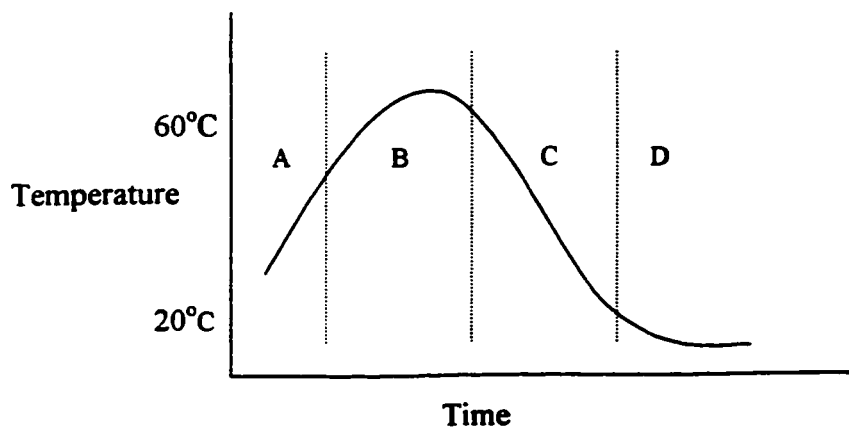
Figure 1.2-1 Typical composting temperature profile.
Letters indicate stages. A: mesophilic; B: thermophilic;
C: cooling; D: maturation   (Adapted from Gray et al., 1971)

temperatures fall to ambient. In terms of time, the first three stages of composting – the mesophilic, thermophilic and cooling stages – take days or weeks, whereas the maturation stage typically requires a period of months.

1.2.2 The relevance and importance of composting

Composting is practiced on a variety of organic materials as a means of recycling nutrients, of producing a soil conditioner and of waste treatment. With growing concerns about the global environment, composting presents itself as a potentially sustainable alternative to many traditional waste treatment processes. By employing it, nutrients are not lost from the system through landfilling or other waste disposal approaches, but instead have their value captured, thus imparting an economic importance to what is already agronomically effective. Composting holds possibility for meeting the goals of sustainable agriculture. It is applicable to the treatment of virtually any organic waste, and is practiced in a wide variety of industries. Municipal solid waste, sewage sludge, and wastes from the food processing, forest and agriculture industries are all commonly composted (Liang, 2000).

Beef feedlot manure serves as an example of a "waste" that can be treated through composting to further the goals of sustainability. Gray et al. (1973) observed that a period of development in intensive animal rearing between 1965 and 1975 led to a situation of there being more manure than there was land available for its disposal. Larney and Carcamo (1999) described the continuance of the trend and referred to the so-called 'bull's-eye effect' of feedlots being the centre of outwardly diminishing

concentrations of land-applied manure, with over-application of manure occurring in areas nearest the feedlots. DeLuca and DeLuca (1997) reported the situation as one of increasing pollution potential and difficulty in handling excess nutrients and organic matter. Among myriad problems contrary to agricultural sustainability, the application of organic matter that has not been partially humified can give rise to phytotoxic intermediate metabolites (Zucconi et al., 1981a, 1981b as cited in deBertoldi et al., 1983). The soil will become less fertile and a number of other complications result. For instance, a high proportion of N can be lost as NH_3 and there can be competition for nitrogen between plant roots and the microbes involved in biodegradation (Golueke, 1977 as cited in deBertoldi et al., 1983). With excessive application of raw manure, nutrient imbalances are common, there can be phosphorus (P) and N loading of surface waters (Swanson et al., 1971; Overcash et al., 1983; Keeney, 1989 all as cited in DeLuca and DeLuca, 1997), nitrate and salts can accumulate to potential pollution levels, and high levels of nitrification can lower soil pH (Chang et al., 1991). Treatment of the manure by composting before spreading it on the land mitigates some of these complications. With composting, an hygienic and aesthetically acceptable product (Witter and Lopez-Real, 1987) with one-half the bulk volume of the original substrate (Rynk, 1992) results, making what some view and manage as a waste, a source of economic and ecological benefit (Janzen et al., 1999).

The physical results of composting are in accord with the goals of sustainable agriculture. The literature contains a litany of advantages imparted to soil by compost. Compost is described as a beneficial soil conditioner (Finstein and Morris, 1975; Crawford, 1983;

McKinley and Vestal, 1985a) that lessens soil degradation (Pare et al., 1998) and improves soil structure by enhancing aggregation and improving texture. Compost also benefits aeration by improving permeability to air and water (Crawford, 1983; deBertoldi et al., 1983; Korner and Stegmann, 1999). Compost increases water infiltration into soil as well as soil's water and nutrient holding capacity (Mays et al., 1973; Crawford, 1983; Dick and McCoy, 1993 as cited in Oshins, 1995). Compost adds humus to soil, thereby increasing its humic acid content and consequently doubling its cation exchange capacity (Mustin, 1987 as cited in Barrington et al., 1994). From a materials management perspective, compost has improved handling characteristics over its untreated counterparts because of the mass and volume reductions effected by the losses of carbon dioxide and water throughout the process and also features more uniform and smaller particle size (Willson and Hummel, 1975 as cited in Eghball et al., 1997; DeLuca and DeLuca, 1997).

Opposite to the ideas of sustainability is pollution. In the case of manure management, in comparison with raw manure application, there have been assertions that compost lessens the risk of pollution by featuring decreased greenhouse gas emissions (Pare et al., 1998; Paul et al., 1998), less nitrate leaching and phosphorus accumulation (Chang et al., 1991), less risk of surface water eutrophication (Pare et al., 1998), an avoidance of run-off (Crawford, 1983) and less offensive odours (DeLuca and DeLuca, 1997). Several authors report that environmental risks like ammonia volatilization and the leaching of N and P may be less when composting is practiced or compost is applied than when raw or anaerobically stored manures are applied to soils (Levi-Minzi et al., 1986; Kirchmann

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and Witter, 1989; Dewes, 1995). In contrast, at least one group of authors (Eghball et al., 1997) report that feedlot manure ought to be applied to land without composting unless weed seeds, better handling of manure, or odour are of concern. They reason that runoff and leaching from composting sites are significant contributors of N, P, potassium (K) and sodium (Na) to surface and ground waters.

The recycling of nutrients is another important consideration in sustainable agriculture. Janzen's group (1999) points out the global trend of larger and larger production operations being concentrated in fewer geographic areas, meaning that manure – in one form or another – must be distributed over greater distances to recycle nutrients. Composting can contribute to meeting this need by lowering the mass and volume of the material typically by 50% (Rynk, 1992) and moreover by its effect on the material's nutrients. The immobilization of N and P during composting (Crawford, 1983) leads to a product with N and P that is slow to mineralize (Korner and Stegmann, 1998). Magdoff (1992) asserts that this slow release means plant nutrients will be available at the most active periods of plant nutrient uptake (as cited in DeLuca and DeLuca, 1997), not just during the period immediately following application. Readily available N and P, as is found in commercial fertilizer, are highly soluble and mobile, so over-application can contaminate water resources (Keeney, 1989). With composting, Crawford (1983) asserts there is less soluble N in agricultural wastes, both because manure is utilized rather than wasted and because the risk of overapplying fertilizer is reduced. DeLuca and DeLuca (1997) report a dramatic increase since 1950 in the use of commercial fertilizers. An increasingly expensive practice (Crawford, 1983), the use of fertilizer could be curtailed

through a shift towards the alternative of compost application. DeLuca and DeLuca (1997) report that such a shift would represent a significant energy savings, and reductions in greenhouse gas emission, in terms of production, transport and application. Additional advantages could be the improvement in soil quality with increased soil organic matter over time (Mays et al., 1973) and conservation of the organic material's naturally high energy value (Crawford, 1983).

The relevance and importance of composting, then, lies in its contributions to waste management aspects such as waste treatment, physical conditioning of soils, pollution avoidance and nutrient recycling. Composting warrants investigation because of the steps it could facilitate towards a goal of sustainable agriculture.

1.2.3 The importance of nitrogen retention

During composting, the loss of some nitrogen from the feedstock material is normal. The volatilization of nitrogenous compounds is part of the process, but minimization of these losses serves several interests. N retention in composting is important to compost fertility, as N is often the key limiting factor to crop production in agricultural ecosystems (Liang, 2000). With higher N content in compost, there is also the possibility of composts supplanting commercial fertilizers. Moreover, there is interest because compost N is made available to plants only gradually, thereby minimizing the risk of N-loss in run-off and leachate, which is wasteful of N and can be environmentally hazardous. N retention in composting, then, is important to a variety of agronomic, economic and environmental interests.

That large fractions of nitrogen can be lost during the composting process is hardly debated. While one may expect total N mass to decrease over the course of composting because of N losses, increases in total N concentration can be observed. These increases are explicable in that there is a concentration effect because of the decrease in overall pile mass and total N is commonly measured as a proportion of total dry mass (Bernal et al., 1996; Eghball et al., 1997; Tiquia and Tam, 2000). Nitrogen is the nutrient most susceptible to loss and is especially so in cases of N-rich feedstock, such as manure (Witter and Lopez-Real, 1987; Liang, 2000). Economically and agronomically it is frustrating to think of the N-content of fresh manure that could potentially be returned to the land, but is more often lost (Hutchinson and Mosier, 1981). Between 40 and 60% of the N in fresh livestock manure can be lost via ammonia volatilization within hours of excretion (Luebs et al., 1974 as cited in Sikora, 1999; Gracey, 1979 as cited in Sikora, 1999; Safley et al., 1983). Subsequently, during composting, some of the remaining N can be lost, mostly through more volatilization. Ranges for this value vary from 40 – 50% (Witter and Lopez-Real, 1987; Eghball et al., 1997) to 21 – 77% (Martins and Dewes, 1992). Losses in nutrients – specifically of N, but also of P and K through leaching and runoff – reduce the potential of compost as a plant nutrient source (Eghball et al., 1997). Some authors (Mustin, 1987 as cited in Barrington et al., 1994) assert that composting, because of the losses in nutrients, is not a treatment that can conserve the N content of fresh masses of organic matter.

Nitrogen is the most susceptible nutrient to being lost during composting and it is also often the key limiting factor to crop production (Bishop and Godfrey, 1983; Witter and

Lopez-Real, 1987; Liang, 2000). Because agricultural ecosystems bypass the detritus pool that is a part of natural ecosystems, there is far less nutrient recycling (Witter and Lopez-Real, 1987) and a need for periodic N addition. The retention of N in composting is important if the finished product is to be used as a source of nutrients (Hornick et al., 1984 as cited in Sikora, 1999).

Some authors report that the supply of nutrients from compost is comparable to that of commercial fertilizers, to the extent that it may be practical to supplant the latter with the former (Hyatt, 1995). Compost is typically low in total N (0.5-2%) and traditionally has not compared well economically with commercial fertilizers. Compost N, however, is organic and therefore slow to become available – it can release available N for several years after application (Hyatt, 1995).

The N dynamics of composting also needs to be considered with regard to pollution. A soil condition in which N is a limiting factor to crop production is also a situation in which the nitrogen-to-phosphorus (N/P) ratio is lower than optimum and there is potential for P build-up. That being the case, land-application rates of nutrients are restricted and the risk of environmental degradation increases (Wright, 1998 as cited in Liang, 2000). Similarly, when fertilizer N is applied in large amounts, there is concern about polluting ground and surface waterways (Schroder, 1985 as cited in Witter and Lopez-Real, 1987; Phillips-Howard, 1985; Anderson, 1985).

The composting process also has associated environmental hazards. The gaseous N emissions involved are associated with problems of odour and atmospheric degradation (Hutchinson and Mosier, 1981). Nitrous oxide has been hypothesized to contribute to the destruction of the ozone layer (Hutchinson and Mosier, 1981), to account for 4% of the greenhouse effect (Bouwman, 1990 as cited in Wagner-Riddle et al., 1996) and to have a global warming potential 310 times that of CO_2 (CO_2-C equivalent conversion factor) (Larney et al., 2000). Ammonia is tied to odour, corrosion and catalytic effects in stratospheric ozone depletion (Larsen and McCartney, 2000; Komilis and Ham, 2000). In Europe, agriculturally volatilized ammonia is implicated in modifying the direct influences of acid rain, in the degradation of stone buildings and monuments, in the death of forest trees and in lake acidification (Buijsman et al., 1987 as cited in Sherlock et al., 1995). And, specific to the composting process, Miller (1993) asserts that free ammonia affects substrate availability and is toxic to many microorganisms.

In summary, factors ranging from nitrogen's importance in compost fertility, to the slow release nature of compost N, to the possibility of compost N competing economically with fertilizer N, to the environmental hazards of lost N, all point to the importance of nitrogen retention in composting.

1.2.4 Pathways of nitrogen loss during composting

The dynamics of nitrogen transformation and prevailing conditions during composting can lead to the escape of nitrogen from the system in one of a number of forms. Nitrogen can be lost from a composting system through ammonia volatilization and, to a much

lesser extent, through leaching and denitrification (Safley et al., 1983; Eghball and Power, 1994).

Nearly all N losses in composting are attributable to ammonia volatilization (Willson and Hummel, 1975; Vogtmann and Besson, 1978; Witter, 1986 as cited in Witter and Lopez-Real, 1987; Tiquia and Tam, 2000). Eghball et al. (1997) included leached and run-off N as a pathway of N loss, and Tiquia and Tam (2000) made mention of denitrification, but NH_3 volatilization is by far the most significant.

Factors affecting volatilization include: total N content of the material, temperature, pH and aeration/turning frequency (Martins and Dewes, 1992; Liang, 2000). Total N content is important because if N is a limiting factor to microbial metabolism in the mass, it will most likely be taken up by cells before it can escape (Rynk, 1992). With N-rich materials volatilization will be higher. Temperature and pH are important factors in ammonia volatilization because they play important roles in regulating the NH_3/NH_4^+ equilibrium. Conditions of high pH and high temperature shift the balance towards ammonia, which is the volatilizable form (Korner and Stegmann, 1998). Under such conditions, ammonium in the matrix could transform to ammonia and volatilize as presented in Equation 1.1:

$$NH_4^+{}_{(aq)} \Leftrightarrow NH_{3(aq)} \Leftrightarrow NH_{3(g)} \rightarrow atmosphere \qquad (1.1)$$
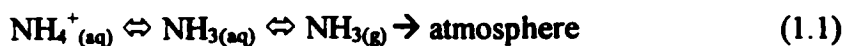
The amount of ammonium present in the matrix depends on several factors. Simpler nitrogenous compounds are immediately ammonifiable, whereas more complex

compounds need first to be broken down. So ammonium production will be higher in a matrix rich in proteins, for example, than in one heavy with nucleic acid. Jensen (1929) reported a negative correlation between the carbon-to-nitrogen ratio (C/N) and ammonification (i.e. mineralization of N). Typically, above a C/N of 30, which is reportedly optimum (Gray et al., 1971), there is excess immobilization and below this value, there is excess ammonification.

The contributions of pH and temperature to the above mechanisms of volatilization are clear. The equilibrium between $NH_4^+{}_{(aq)}$ and $NH_{3(aq)}$ is described by Equation 1.2:

$$NH_4^+ + OH^- \leftarrow K_b \rightarrow NH_3 + H_2O \qquad (1.2)$$
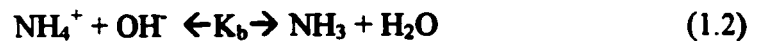
$$\text{where } K_b = [NH_4^+][OH^-]/[NH_3]$$

Conditions of high pH, and so of high concentrations of hydronium ion, will increase the concentration of NH_3, as illustrated by Figure 1.2-2. In general, at pH 7 and below, the ammonium ion is almost exclusively present and at pH 9 and above, free ammonia predominates (Koster, 1986).

Temperature affects K_b from Equation 1.2, with higher temperatures favouring the NH_3 half of the equation, but the main effect of temperature is on the equilibrium between $NH_{3\,(aq)}$ and $NH_{(g)}$, as described by Equation 1.3:

$$H = [NH_{3(g)}]/[NH_{3(aq)}] \qquad (1.3)$$
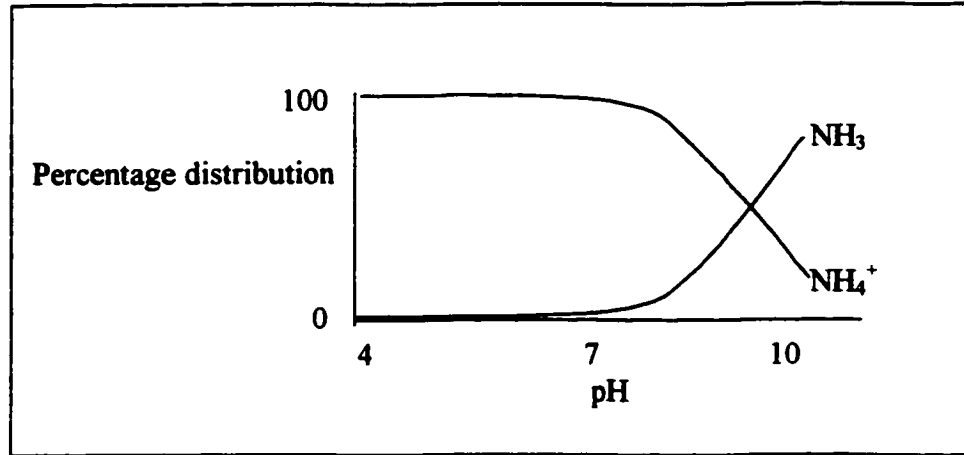
Figure 1.2-2 Relative concentrations of ammonia and ammonium between pH
4 and 10. (Adapted from Court et al., 1964 as cited in Liang, 2000)

where H is Henry's law constant which increases with temperature. In general, high

temperature composting is associated with substantial ammonia losses, the extent of

which are affected by both temperature and pH (Bhoyar et al., 1979). The ammonia gas-

liquid equilibrium is proportionally related to the concentration of ammonia in solution

and the partial pressure of ammonia gas in the atmosphere, but exponentially related to

temperature (Witter and Lopez-Real, 1987). Conditions conducive to aqueous ammonia

formation increase the probability of ammonia loss (Sikora and Sowers, 1985).

Once ammonia gas has formed, volatilization is a matter of diffusion or convection out of

the mass into the surrounding atmosphere. Obviously, the level of aeration and/or the

frequency of turning directly facilitates this. Observations such as those by Lauer's

group (1976), that faster-drying manure was prone to higher volatilization losses, gave

rise to the assertion that ammonia loss occurs primarily through moisture removal (Sikora

and Sowers, 1985). Flow rate of gas out of the pile also affects the rate of volatilization

by regulating the readsorption of volatile ammonia (Fenn and Kissel, 1973). As Witter and Lopez-Real (1987) point out, slow diffusion rates and correlated low air exchange will reduce the rate of N loss. The high partial pressure of $NH_{3(g)}$ will push the equilibrium away from the volatilizable form, increasing the opportunity for $NH_{3(aq)}$ and $NH_4^+_{(aq)}$ sorption in the mass. Additionally, a mass with slow diffusion will have higher levels of CO_2, meaning lower pH.

Nitrogen may also escape from the composting mass in the form of nitrate. Nitrate can form in the matrix through nitrification – the bacteria *Nitrosomonas* causes the transformation from ammonium to nitrite (NO_2^-), and the bacteria *Nitrobacter* carries out the transformation from nitrite to nitrate (Killham, 1996). In composting, formation of nitrate has been reported in the curing stage (Hoyle and Mattingly, 1954; Bishop and Godfrey, 1983; Witter, 1986 as cited in Witter and Lopez-Real, 1987) and nitrate leaching has been observed by researchers including Witter and Lopez-Real (1987), Eghball and Power (1994) and Safley et al. (1983). Morisaki et al. (1989) observed little nitrification which was ascribed to high temperatures and high levels of ammonia since these conditions have been shown to inhibit the actions of nitrifiers (Bernal et al., 1996).

Although typically responsible only for negligible amounts of nitrogen loss, denitrification can be another pathway. Denitrification is an anaerobic process involving the microbial reduction of nitrate or nitrite to nitrous oxide or molecular nitrogen. The rate of denitrification depends on the concentration of nitrate and can be slowed either by maintaining aerobic conditions or by immobilizing present nitrate (Mahimairaja et al.,

1995; Eghball et al., 1997). Tiquia and Tam (2000) reported a loss of NO_3^- and NO_2^- by way of denitrification, citing correspondingly high populations of denitrifying bacteria. And manure N has been reported as lost through denitrification under anaerobic conditions when spread on land by a number of studies (Sikora, 1999).

1.2.5 Nitrogen retention efforts

Given the long list of potential benefits from both composting and N-retention, and having knowledge on the various pathways of nitrogen's escape, the impetus for research has been strong. Various aspects of the process' N-dynamics have been targeted for adjustment, focusing mostly on available C-to-available N ratio, pH and temperature. Other approaches have included moisture content adjustment and incorporation of ammonia sorbers. Overall, the outlook for practical N-retention in composting is favourable, but some compromising seems unavoidable. The temperature and aeration conditions required for pathogen and seed destruction or for organic matter stabilization, for instance, are widely different to those for N-retention (Witter and Lopez-Real, 1987; Bishop and Godfrey, 1983).

Carbon-to-nitrogen ratio (a mass-to-mass ratio) is commonly used as a feedstock recipe guideline (Rynk, 1992; Haug, 1993; Epstein, 1997). Haug (1993) determined a theoretically ideal C/N ratio to be between 15 and 30. His stoichiometric calculations involved glucose as the organic source reacting with oxygen to yield free energy. The energy was subsequently used by the microbial cells to synthesize new microbial mass, the N for which came from ammonia. Larsen and McCartney (2000) investigated the

composting of pulp and paper biosolids of varying C/N and found a strong negative linear relationship between C/N and heat generation (highest at C/N 29), and between C/N and volatile solids (VS) destruction. They also noted a strong nonlinear relationship between N retention and C/N (% retention = 101 (1-0.92$^{C:N}$)). The higher the C/N, the more limiting a factor will be N, and the more it will be retained. The optimum C/N is associated with a net balance between ammonification and immobilization of N. At ratios below the optimum, excessive N loss can be expected. Above the optimum, composting is inhibited and there is a net immobilization of N (Gotaas, 1956; Finstein and Morris, 1975; Taiganides, 1977; Hammouda and Adams, 1987; Chaney et al., 1992; Al-Kanani et al., 1992).

Research supporting this generality is quite common. Jensen (1929) observed a negative correlation between ammonification and the carbon-to-nitrogen ratio of a range of organic materials. He found the optimum C/N to be approximately 26. Hansen et al. (1993) observed ammonia losses three times greater at C/N 15 than at C/N 20, suggesting it was lower than optimum. Michel et al. (1993) composted leaves and grass and found that with lower leaves-to-grass ratios (C/N), there was higher CO_2 evolution (indicative of metabolic activity) and N losses. And Larsen and McCartney (2000) found C/N ratios of 107, 55 and 29 composted with earthy odours whereas a ratio of 18 led to very strong ammonia odours.

Witter and Lopez-Real (1987) concluded that the most effective, and most practical way of reducing N losses in composting is to add carbonaceous materials to ones that are high

in nitrogen. The effectiveness of such a strategy depends on the microbial availability of the carbon compounds, so that with degradation of the C, there is demand for N. This would keep the system's nitrogen from being superfluous – if N is constantly in demand for microbial metabolism, its possibility of escape diminishes. Okerek and Meints (1985) reported that in soils with available carbon, immobilization of virtually all the mineral nitrogen they added was very rapid. Kirchmann and Witter (1989), reduced ammonia volatilization from 44 to 9% during manure and straw composting by adding straw (C/N = 125) to adjust the C/N from 18 to 36. They concluded, however, that an 'impractical' amount of straw would be required to cut ammonia losses by 50%. Nevertheless, the effectiveness of this approach is amply documented.

Increasing the carbonaceous fraction of the mixture seems to decrease N losses, and increasing the nitrogenous fraction seems to increase N losses. Hoyle and Mattingly (1954) made early observations on N loss during the composting of sewage sludge – straw mixtures. They found that N loss increased with increased proportions of sludge, even though there was no difference in total dry weight loss. Likewise, while composting pig slurry and straw, higher levels of slurry were reported to correlate with increased N loss (Faassen and van Dijk, 1979). Reports such as Ashbolt and Line's (1982), that adjusting the C/N of eucalypt bark and fish waste from 45 to 65 dropped N losses from 16 to 8% or that there is less ammonia loss with higher C/N (Kirchmann, 1985 as cited in Witter and Lopez-Real, 1987) are well-echoed and generally accepted. Improved aeration with straw addition also assists in preventing anaerobic conditions, which are detrimental to composting (Kirchmann and Witter, 1989).

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Exceptions include studies by Bucher (1943) and by Kohnlein and Vetter (1953) that

found no reduction, and even an increase, in ammonia loss with increasing proportions of

straw (as cited in Kirchmann and Witter, 1989). And an experiment by Willson and

Hummel (1975) led to the conclusion that, in composting manure and straw, there was no

effect of straw content on N losses. Seemingly contrary to the hypothesis of higher C/N,

lower N loss, these results were ascribed to the low availability of the carbon in the straw.

The C/N had indeed been increased, but if the ratio of available C to available N

remained unchanged, N would still become superfluous and escape. Nebiker (1976)

increased the availability of straw carbon by grinding up the straw, and thereby reduced

N losses from aerated pig slurry. Grinding the straw increases the surface area exposed

to microbial attack. Kuter et al. (1985) found wood chips to have little available C as

compared to sawdust for the same reasons of surface area. Further support for this comes

from the observation that, when composting cattle manure and straw, N losses can be cut

by increasing the proportion of ground straw to chopped, but maintaining a C/N of 31.6

(Meyer and Sticker, 1983 as cited in Witter and Lopez-Real, 1987). In the same vein,

Mote and Griffis (1982) reported that the type of carbon source affects the pattern and

rates of CO_2 production, reflecting an influence on the system's ability to immobilize

nitrogen. McKinley and Vestal (1985a) failed to find any correlation of total C, total N

or C/N with microbial biomass (measured as amount of phospholipid phosphate present)

or activity (measured as the rate of incorporation of radioactively labeled organic

substrate into cellular lipids). Galler and Davey (1971) experimented with composting

poultry manure and sawdust. They found that mixtures containing more manure and less

sawdust (lower C/N) had extended composting periods – results that were opposite to

what was generally accepted. Their data also show a reduction in VS parallel to manure content. Together, the observations suggest that the C in the sawdust was largely unavailable to microbes and batches with low total C/N had higher available C/N. Horwath et al. (1995) also reported evidence supporting the need for a measure of available C/N. They composted straw by itself and found that, far from the theoretical optimum C/N of 30, the microbial biomass required more C and less N to compost effectively. They concluded that the form of N is more indicative of substrate quality than a combined substrate C/N ratio.

Overall, the C/N ratio appears to be an important parameter for consideration, as an index of the balance between N mineralization and N immobilization. The variable microbial availability of C, however, appears to prevent there from being an undisputed optimum C/N ratio. Among the factors contributing to the microbial availability of a given material's carbon, would be the distribution within that material among substrate classes such as sugars, starches, hemicellulose, cellulose and lignin. Such classes can vary greatly in their microbial availability.

Adjustment of pH is another common approach for conserving nitrogen. That ammonia losses are substantially higher when fertilizer nitrogen is applied to calcareous soils than to acidic soils is well established (Terman, 1979; Nelson, 1982; Freney et al., 1983). Fenn and Kissel (1973) reported that in calcareous soils, the volatilization of ammonia is regulated by the solubility of potential-reaction products. The ammonium salts which they found led to high ammonia losses were those of F^-, SO_4^{2-} and HPO_4^{2-}, which react

with Ca^{2+} to form low solubility precipitates. Eghball and Power (1994) reported that acidifying materials are effective in reducing N loss from chicken litter. Similarly, Tunney (1980) found that lowering the pH of slurries led to reduced ammonia losses. In agreement with Figure 1.2-2, Willson and Hummel (1975) found that pH changes in between 7.0 and 8.3 had no effect on nitrogen losses from composting cattle manure. Muck and Steenhuis (1982) developed a model for predicting NH_3-N loss from anaerobic manure storage and it showed reduced losses with lower, acidic values of pH and temperature.

As described above, adjustments in temperature can influence the escape of N by changing the equilibrium between liquid-phase and gas-phase compounds. With higher temperatures, the equilibrium (illustrated in Equations 1.1 and 1.3) shifts towards the gas-phase and escape is facilitated. Beauchamp et al. (1978) found ammonia losses to be highest at midday when anaerobically digested sewage sludge was applied to soil. Similarly, Harmel et al. (1997) observed a diurnal fluctuating pattern of ammonia emission from applied biosolids. Keeping temperatures relatively low in composting, then, is another possible strategy for conserving nitrogen. Muck and Richards (1983) studied ammonia losses from non-bedded cattle buildings and found higher ammonia losses – up to 60% of the manure's initial N – with higher temperatures within the range of 5 to 25°C. And in a greenhouse experiment, Adriano et al. (1974) found increasing N loss with increasing moisture content and temperature when manure was applied to soil and N losses observed.

Adsorption of ammonia is another strategy. Since part of the volatilization mechanism is the diffusion of ammonia through the compost matrix, the presence of materials with an affinity for ammonia or ammonium could reduce the amount of ammonia that reaches the atmosphere and is lost. Phosphate, for example, can reduce N losses by the formation of ammonium phosphate complexes and by buffering pH (Witter and Lopez-Real, 1987):

$$NH_3 + H_3PO_4 \rightarrow NH_4H_2PO_4 \qquad (1.4)$$
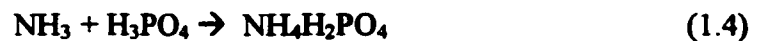
Ammonium can be held by any negative charge, like those on lattices of clay particles or the acidic phenol and carboxyl groups of humic acids (Witter and Lopez-Real, 1987). Ammonia, being polar and capable of hydrogen bonding, can compete with water in many reactions (Witter and Lopez-Real, 1987). In manure, ammonia is frequently found as ammonium carbonate, which can react with phosphoric acid or superphosphate to yield water, carbon dioxide and a stable ammonium salt (Safley et al., 1983). In the early 20th century, the addition of materials such as gypsum ($CaSO_4$-$2H_2O$), superphosphate ($CaH_4(PO_4)_2$-H_2O), phosphoric acid (H_3PO_4) or kainite ($KMg(SO_4)Cl_3$-H_2O) to freshly excreted manure was practiced to conserve manure nitrogen (Agee, 1913; Thorne, 1930, both as cited in Safley et al., 1983). Witter and Lopez-Real (1987) cite zeolite (in particular clinoptilolite) as another amendment effective in this regard and Prochnow et al. (1995) added phosphogypsum to the list. As for the relative effectiveness of the various amendments, Prochnow et al. (1995) found phosphogypsum to be better than superphosphate, and Safley et al. (1983) cautioned that superphosphate and phosphoric acid amendment were not economically cost effective. Safley et al. (1983) also criticized

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the use of gypsum as an ammonia adsorber because the ammonia – gypsum reaction is unlikely.

In an interesting synthesis of the N conservation body of knowledge, Korner et al. (1999) adjusted composting parameters like temperature, pH, CO_2 content and aeration to *maximize* ammonia volatilization. Escaped ammonia was captured in $H_2SO_{4(aq)}$ and later stripped and returned to the compost during the curing stage. This approach yielded finished compost with nearly double the N content of the unregulated variant.

1.2.6 Ammonia volatilization measurement

Witter (1986) asserted that, during the high-rate stage of composting, all losses of nitrogen can be attributed to the volatilization of ammonia (as cited in Witter and Lopez-Real, 1987). There is general agreement in the literature that ammonia volatilization is the most important route of nitrogen loss in the active phase of composting (Willson and Hummel, 1975 as in Witter and Lopez-Real, 1987; Vogtmann and Besson, 1978; Tiquia and Tam, 2000). Numerous and diverse methods for quantifying ammonia volatilization – both in the laboratory and in the field – have been described. The range of approaches stretches from a bowl full of acid at the simpler end, to complicated micrometeorological calculations at the more complex end. This section reviews the variety of methods in the literature for estimating ammonia volatilization.

Common to nearly all the methods is the inclusion of some kind of acid – usually sulfuric or phosphoric, but also boric and oxalic. Ammonia will react readily with these acids to

form stable end products (Safley et al., 1983). A simple approach to measuring volatilized ammonia, then, is to expose the ammonia to a volume of such acid. Prochnow et al. (1995) measured ammonia from manure by including in a manure-containing flask, a glass vial with 10mL of sulfuric acid and metil-orange indicator. The indicator solution served to indicate saturation of the acid with ammonia. A variation on this approach commonly used is to run an air line from an enclosed source of volatilizing ammonia, such as manure or compost in a digester, to a column of acid through which it is bubbled. Methods with such approaches have been described by Paul et al. (1998) and Komilis and Ham (2000) using sulfuric acid, and by Kirchmann and Witter (1987) using boric acid. Trapped ammonia is measured using titration or an autoanalyzer. Lauer et al. (1976) employed a similar setup, but used the concentration of trapped ammonia to determine the partial pressure of ammonia gas.

Marshall and Debell (1980) described four methods of measuring ammonia volatilization losses and compared their performances. One was a closed-dynamic laboratory method. It featured a chamber capable of accommodating a soil core and off-gas lines running through a series of traps. The core was fertilized and any ammonia present in the off-gas collected in a sulfuric acid trap. Nitrogen dioxide and nitric oxide (NO) were collected in a solution of 0.1N NaOH and 3% H_2O_2. The closed-static method, like the semi-open and ^{15}N methods, was for application in the field. Originally described by Volk (1970), it featured a cylindrical enclosure fitted over a small area of fertilized soil. Within the enclosure, volatilized ammonia would react with a solution of phosphoric acid and glycerine with which a disc-shaped sponge was charged. Glycerine was included in the

solution as a way of increasing its viscosity and slowing its evaporation. The semi-open sorber, originally described by Nommik (1973) was different from the closed-static sorber only in that, instead of the chamber being sealed, the top was replaced by another sponge, which served to strip atmospheric air entering the sorber of any ammonia, and to allow pressure equalization with the ambient air. The fourth method described by Marshall and Debell (1980) involved ^{15}N-labeled applied fertilizer. After a period of volatilization, ^{15}N remaining in the soil was measured. Since only remaining ^{15}N was measured, no distinction among various fates of nitrogen could be made.

Similar to the semi-open sorber was an enclosure employed by Peters and Reddell (1976). A very simple system for field measurement, it featured a cylindrical container inverted over a soil column. Air that had passed over the soil column bubbled through a solution of 0.3N H_2SO_4. The trapped ammonia was measured by titration. Adding a more realistic airflow to the design, Adamsen et al. (1995) adjusted the location of the inlet and outlet holes – moving the inlet close to the top of the chamber and outlet close to the bottom – and added a mixing fan.

Enclosed chamber methods like those described above have been criticized (McInnes et al., 1986) for failing to simulate the outside environment in all respects. Inside a chamber, influential factors like soil water content, water flux, soil temperature and wind are all altered (McInnes et al., 1986). To counter these shortcomings, wind tunnel, gradient and micrometeorological techniques were developed.

Sommer and Olesen (1991) provide an example of a wind tunnel approach. Other authors to have used wind tunnels in the measurement of volatilized ammonia include Morken (1992, as cited in Svensson, 1994) and Lockyer (1984). Sommer and Olesen (1991) inverted a U-shaped shell over the experimental plot and an electric fan pulled air through the shell, over the plot, and then through the fan and a flask of phosphoric acid. An anemometer in the tunnel measured wind speed and the ambient concentration of ammonia was measured at the intake for use in calculations of volatilization.

The integrated horizontal flux method of calculating ammonia emission is an example of a gradient technique. Sherlock et al. (1995) used this approach as their reference method while developing an indirect method of estimation (described below). The integrated horizontal flux technique involves a circular plot with masts on the circumference and one in the centre. Oxalic acid-coated test tubes are mounted at five heights between 0 and 2m above ground on each mast. Emitted ammonia entering the tubes reacts with the oxalic acid and is trapped. The concentration of trapped ammonia in two tubes of equal height, one at the centre of the plot and one at the upwind edge, are compared and a mean horizontal flux value is calculated. Mean vertical flux can then be calculated by deriving the differences between mean horizontal fluxes.

The indirect method of Sherlock et al. (1995) used calculations similar to those for determining ammonia flux using an exchange coefficient, wind speed, the concentration of ammonia at a reference height and the equilibrium concentration of ammonia at the soil surface, but avoided any direct measurement of ammonia. Instead, the concentration

of ammonium ions was measured in the upper layer of the soil (0-3mm deep), as well as pH, soil surface temperature and wind speed at a height of 1.2m. The combined effect of these influences form a linear relationship with vertical flux of ammonia.

Integrating the chamber-measurement approach with the detailed environmental calculations of the indirect method, Svennson (1994) used a vented, fan-mixed chamber to measure ammonia concentration values that were subsequently used in micrometeorological calculations. Ammonia was collected on passive diffusion samplers, charged with oxalic acid.

Freney et al. (1983) provides a detailed account of the various micrometeorological methods for measuring gaseous losses of nitrogen in the field. He asserts the superiority of micrometeorological approaches in principle, pointing out that they do not disturb the sampling environment or soil processes that affect gas exchange and they allow for continuous rapid measurement of average flux over a large area.

The central premise in a mass balance micrometeorological approach is that horizontal flux across a vertical plane of unit width that is downwind is equal to the surface flux from a unit width strip upwind (Freney et al., 1983). Horizontal flux at any height is equal to the horizontal wind speed multiplied by the gas concentration. Total flux, then, is obtained by integrating that product over the depth of the air layer modified by emissions from the ground. So point averages of ammonia concentration and wind speed can be used to calculate ammonia emissions, or vertical ammonia flux.

To summarize, micrometeorological methods have advantages of precision because they are less disruptive to the sampling environment, but can be labour and time intensive because of the many measurements and calculations required. Conversely, chamber methods have advantages of being straightforward and involve fewer calculations than micrometeorological techniques, but the changes in the microenvironment that a chamber can cause can result in a loss of precision and/or accuracy.

Spectroscopic techniques for measuring NH_3 emissions have also been reported. The ammonia analyzer used by Liang (2000) involved infrared gas analysis of vessel head space gas. Tunable diode lasers have been used in the measurement of N_2O and CO_2 (Wagner-Riddle et al., 1996) and could be applied to NH_3.

1.2.7 Comparison of wood chips and wheat straw as bulking agents in manure composting

The literature reflects very little research to date on the effect of bulking agent on manure composting. Since standard practice for feedlots is to line the pen with some sort of bedding, there seems to be good cause to conduct composting research into the comparison of different types. While comfort and cleanliness of the cattle and availability of candidate materials would no doubt be the most important considerations in the selection of a bedding material, those things being equal, compostability could be a deciding factor.

Given a choice between wood residuals and straw as bedding material/bulking agent, what composting parameters would be affected? Bulking agents are typically selected on the basis of the adjustments they would make to the available C/N ratio and porosity. Other important factors to consider may include water retention, pH and exposed surface area.

As discussed in section 1.2.5, in terms of the C/N ratio, it is important to consider the ratio of available carbon to available nitrogen rather than that of total C to total N. An important factor in the consideration of C availability is the lignin and lignocellulose content of the material. Lignin is decomposed slowly and its C is relatively unavailable. Its resistance is due to its structure of cross linking and ether bridges between phenylpropan polymers (Bernal et al., 1996). Lignin can also be found in association with cellulose as lignocellulose. Wood contains more lignin than does straw so the availability of its C could be expected to be lower (Rynk, 1992).

Swinker et al. (1997) compared three types of horse bedding in terms of compostability – telephone directory paper (C/N 772), sawdust (C/N 442) and straw (C/N 127) – and found that, despite its higher C/N, sawdust was a superior bulking agent to straw, having attained a higher mean temperature, higher microbial activity and displayed increased degradation. Moreover, Borazjani et al. (1997) reported that wood wastes from the furniture industry (mixtures of hard and soft wood, sawdust, wood flour, wood chips, wood flakes, fabric scraps and small amounts of finishing, polishing and gluing compounds) could be composted effectively. From an end-product perspective,

feedstock of high C/N has been reported (Sikora, 1999) to produce high C/N compost, which is of limited use as a fertilizer. As important as C/N may be, there are other characteristics of bulking agents that are important to their contribution to the process.

Free air space (FAS) is very important to effective aerobic composting. To avoid the development of anaerobic regions in a composting mass, air must be able to circulate. Conditions must allow atmospheric oxygen to penetrate the FAS and respiratory CO_2 to escape it. Swinker et al. (1997) concluded that sawdust was a superior bulking agent to straw (above) because it provided superior FAS. Straw, they reported, tends to become compacted, thus limiting air flow.

Moisture content of the material can be considered alongside FAS insofar as excessive levels of moisture will restrict gas transfer (Miller, 1993) and hamper composting. Larsen and McCartney (2000) found wood chips to be an excellent bulking agent because they are capable of maintaining a higher moisture content while retaining sufficient FAS.

The shape of the composting mass may also affect FAS. Finstein et al. (1980, as cited in Miller, 1993) asserted that masses in a windrow shape do not exhibit any substantial convection, as compared to cubical piles.

1.2.8 Approaches to modelling composting

In recent years, composting researchers have started to develop mathematical models in order to further their understanding of the process and their predictive power.

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Experimental data from the literature have been used to define equations and uncover generalities. With induction of any inherent rules or trends, there are improved possibilities for prediction and control. To model composting, it is assumed that the process is mechanistic or deterministic. That is, a network of causes and effects is examined and it is assumed that if absolutely all details could be taken into account, absolutely accurate predictions could be made. Along the spectrum, from knowing no details (and having no predictive power) to knowing all details (and having perfect predictive power), modellers will strive to include as small as possible a number of elements or aspects and have the maximum predictive power. A useful model is able to predict accurately using a small number of important factors.

Soil ecology research has given rise to a number of simulations that model phenomena important in composting. Liang (2000) refers to models that have been developed for carbon and nitrogen biodegradation (Reuss and Innis, 1977; Knapp et al., 1983), ammonia volatilization from soil organic matter and applied fertilizer (Parton et al., 1981; Freney et al., 1983; Jayaweera and Mikkelsen, 1990; Hengnirun et al., 1999), and N transformations associated with biodegradation (Parnas, 1975; Van Veen and Frissel, 1979; Juma and Paul, 1981; McGill et al., 1981).

Ammonia volatilization from land-applied biosolids has been modelled by Harmel et al. (1997) using equations. Volatilization losses were predicted as a function of site, season-specific potential evapotranspiration, biosolid NH_3-N content, application rate and time after application. Correlation between predicted and observed volatilization had a range

of r^2 values from 0.9 – 0.97. Correlation, assumedly, could be increased with inclusion of additional factors such as wind speed and direction. But given such strong predictive power, the contribution of additional factors would likely have been outweighed by the disadvantage of complication.

Weighing the importance of the various aspects of composting has led to a range of approaches to modelling. A model developed by Hamelers (1993) mathematically described the process from the particle level. Gradients of oxygen, biomass, soluble and polymeric substrates could all be calculated and predicted. Keener et al. (1993), in a less empirically objective approach, focused on the interdependence of physical and biological components using parameters like mass ratio (expressing how much of the original compostable material remains), depth, rate of composting, density and the enthalpy difference of air entering and leaving the mass.

The number of factors and the complexity of their interaction is another area where researchers' approaches have varied. Stombaugh and Nokes (1996), Kaiser (1996) and Liang et al. (1998) all modelled composting as a process of microbial populations metabolizing organic substrates under certain rules with certain effects, but the models varied in the level of detail.

While both Stombaugh and Nokes' (1996) and Kaiser's (1996) models featured equations describing the kinetics of microbial growth and substrate degradation, the former was simpler than the latter. Stombaugh and Nokes used a single term to represent total

microbial biomass – making no distinction among mesophiles, thermophiles, bacteria, actinomycetes, fungi, etc. – and a single term for substrate. In Kaiser's model, four biotic classes acted on four classes of substrate: bacteria (not including actinomycetes) metabolized sugars and starches, actinomycetes metabolized hemicellulose, brown-rot fungi metabolized cellulose and white-rot fungi metabolized lignin. Kaiser's model was less detailed in other respects however; with only the first trophic level being described and further levels being subsumed under *humification*.

By comparison, the model developed by Liang et al. (1998), for prediction of nitrogen losses as NH_3 volatilization, used the same approach for describing microbial kinetics as Stombaugh and Nokes (i.e. Monod kinetics), but was considerably more detailed in its description of substrate kinetics than either of the other two models. Liang et al.'s model (1998) was developed to predict N dynamics in general and NH_3 loss in particular. Carbon sources were divided into substrate C, microbial biomass C, microbial products C and respired CO_2-C. N sources included aqueous ammoniacal N, cumulative NH_3-N, microbial biomass N and microbial products N. Complex C was also divided into soluble C, non-fiber C and resistant/fiber C. All models were successful in reflecting well known composting phenomena, with more detailed models, such as that of Liang et al. (1998), able to predict for a wider variety of parameters.

Depending on the accuracy of prediction, simulation models could have several valuable applications in composting. With computers capable of performing seemingly countless operations in short periods of time, simulated experiments can be performed and the

results implemented quickly. Models could assist operators in the tailoring of the process

for aspects such as composting time, temperature profile and nitrogen retention, among

others.

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CHAPTER 2

The use of sorbers to measure ammonia losses in windrow composting

2.1 Introduction

Ammonia volatilization is the major pathway of nitrogen loss in composting

(Mahimairaja et al., 1994; Sikora, 1999). A relative measure of NH_3 emission among

windrows is essential to field comparisons of experimental treatments. McGinn and

Janzen (1998) provide a comprehensive review of ammonia sources in agriculture and

their measurement, but there is little in the literature specific to ammonia volatilization

from compost windrows. Accurate measurement of ammonia flux between the soil

surface and the atmosphere can be obtained using several techniques such as

micrometeorological methods, wind tunnels and integrated horizontal flux (McGinn and

Janzen, 1998), but many of these approaches require complex materials and calculations.

A less expensive and simpler method involves a passive sorber within a static chamber.

An accurate measurement of flux is forsaken for a relative measurement of emission, but

within the methodology's resolution, comparisons of treatment effects can be made.

Volk (1970) reported using a closed-static ammonia sorber for measuring gaseous loss of

NH_3 from prilled urea. The sorber comprised an inverted glass baking dish over a glass

wool pad carrying 18mL of $10\%H_2SO_4$ (by volume). In terms of sorber resolution, Volk

(1970) reported differences in ammonia loss between treatments of as little as 1%.

Marshall and Debell (1980) reviewed Volk's (1970) sorber along with two other

comparable methods of measuring volatilization losses of nitrogen – a semi-open sorber

and a closed-dynamic sorber. They found the closed-static sorber measured the lowest

percentage of applied N (13%), followed by the semi-open sorber (17%), followed by the closed-dynamic sorber (22-26%). Reasons given for the low estimations of ammonia loss by the closed-static sorber included restricted air flow and the low capacity for water vapour to diffuse to the atmosphere.

The objectives of the ammonia sorber component of the experiment were to evaluate the methodology for use on compost windrows.

2.2 Methods and materials

2.2.1 Compost windrow establishment

The study was conducted at the Agriculture and Agri-Food Canada (AAFC) Research Centre at Lethbridge, Alberta between July and October, 2000. On July 12, the research centre's beef feedlot was cleaned of its manure and bedding by a front-end loader and truck and the material was formed into windrows for composting. Bedding was of two types: a mixture of wood chips, bark peelings and sawdust (80% lodgepole pine (*Pinus contorta* var. *latifolia* Engelm.), 20% white spruce (*Picea glauca* (Moench) Voss)) (Sunpine Forest Products, Sundre, Alberta) and barley (*Hordeum vulgare* L.) straw. Of the four windrows made, two were a manure/wood mix (wood mix windrow) and two were a manure/straw mix (straw mix windrow). Windrows were arranged in a 2x2 grid on a concrete pad, beneath a roof, each running West-East lengthwise, with straw mix windrows in the Northeast and Southwest positions (Figure 2.2-1). Each truckload of material was weighed so as to know the initial mass of each windrow. Four 600 g samples were taken from each windrow to determine initial moisture content, before
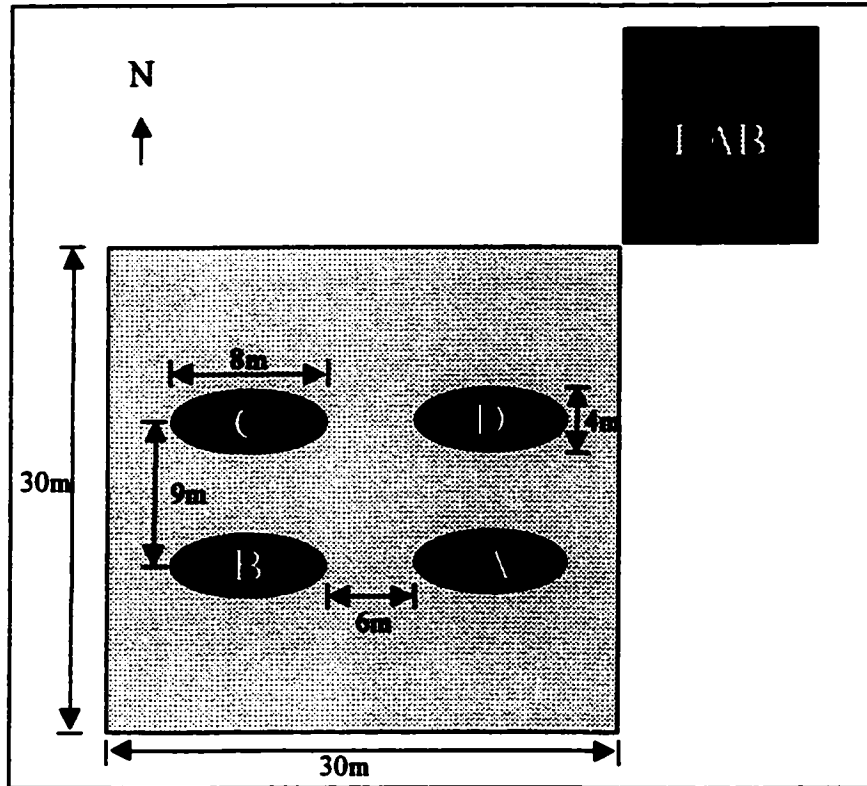
Figure 2.2-1 Diagram of composting site. Windrows A-D on concrete pad.

being analyzed for inorganic (NH_4^+-N, NO_3^--N) and total nitrogen (N), total carbon (C) and pH. Initial bulk density was determined and windrow dimensions measured included length, width at each end, and arch distance (up one side and down the other) at three locations along the length.

2.2.2 Turning and watering

A tractor-pulled windrow turner (*EarthSaver*™, Fuel Harvesters Corp., Midland, Texas) turned the windrows once a week for the first three weeks and then once every two weeks

after that (July 20, July 26, August 2, August 16). To counteract the hot dry climate typical to the area, windrows were watered on August 1. Volumes of water added varied from 619 litres to 1018 litres per windrow (Table 2.2-1), calculated to bring all windrows

Table 2.2-1 Litres of water added to windrows on August 1

Windrow	Litres added
A (Wood mix)	669
B (Straw mix)	1018
C (Wood mix)	863
D (Straw mix)	619

up to a moisture content of 55%. Water was added using a water truck equipped with a 100mm (I.D.) hose. No leachate was observed on the concrete pad at the time of watering, nor when the piles were turned the following day.

2.2.3 Temperature monitoring

A small front-end loader (Model 963, Bobcat Company, West Fargo, North Dakota) inserted temperature probe assemblies (Figure 2.2-2) into each windrow immediately following windrow establishment. Windrows C and D (Figure 2.2-1) had two probes each, dividing them into thirds lengthwise and windrows A and B each had one, dividing them in half. The probes (Figure 2.2-2) were aluminum, each with three prongs, each prong having three thermocouple sensors, giving a 3x3 grid of sensors for each probe. Wiring for the sensors ran through a PVC sheath to insulate it from the metal. Probes were inserted vertically and perpendicular to the lengths of the windrows. Data from the

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probes were displayed and recorded by a computer data logger in the laboratory adjacent to the compost pad. Temperature measurements were displayed in degrees Celsius on the monitor and intermittently logged to the computer's hard drive.
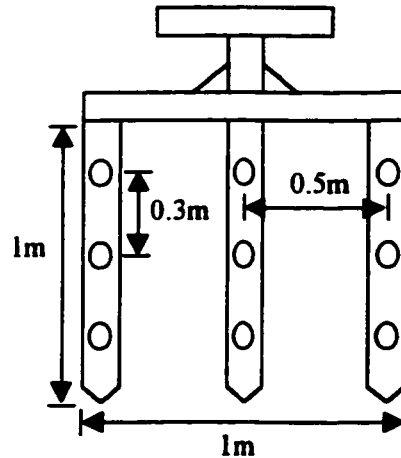
Figure 2.2-2 Temperature probe assembly. Evenly-spaced temperature sensors (circles) connected by wires in PVC pipe (not shown) within 3-pronged aluminum casing.

2.2.4 Compost windrow sampling

Samples of the material were collected at the time of windrow establishment and prior to each turning episode. The front-end loader cut open each of the windrows by pushing through the mid-section of its length, displacing that material (Figure 2.2-3), and leaving
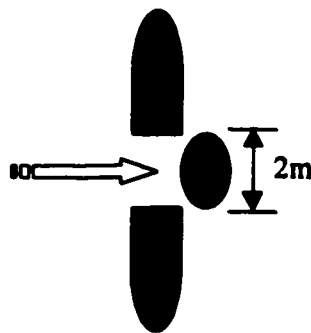
Figure 2.2-3 Diagram illustrating sampling procedure. Arrow indicates action of front-end loader.

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two exposed walls. Six samples of approximately 1.5 kg each were taken from each exposed wall for physical and chemical analysis. Working from top to bottom, samples were taken from depths 0, 76, 203, 457, 762 and 1067 mm, measured from the top surface of the windrow to match the depths of gas sampling done for the AAFC greenhouse gas study.

2.2.5 Ammonia trap construction and utilization

A modified version (Lambert, 2000) of the closed-static sorber presented by Marshall and Debell (1980) was used to measure the relative ammonia volatilization of the windrows. Seventy-five 4-litre ice cream pails (Pro-Western Plastics Ltd., St. Albert, Alberta) were fitted with screw hooks in the centres of the inverted pails' ceilings. Acid-soaked
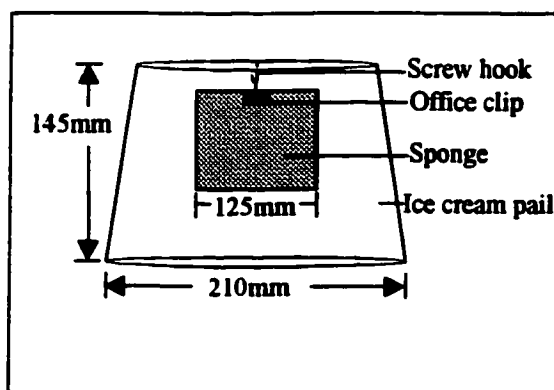
Figure 2.2-4 Diagram of ammonia sorber. Pail is open side down.

polyurethane plastic foam sponges were suspended from the hooks by use of medium-sized binder clips (#72050 ACCO Brands, Inc., Lincolnshire, Illinois) (Figure 2.2-4). Dimensions of the sponges were 125 x 125 x 26 mm. As described by Marshall and Debell (1980), the trap solution was ortho-phosphoric acid and glycerine in a ratio of 2:1,

respectively. Due to the stronger concentrations of ammonia encountered in this study, however, the strength of ortho-phosphoric acid was increased from 0.7M to 2.1M. Each sponge was charged with 25 mL of the acid-glycerine solution by soaking it in 75 mL and squeezing out 50 mL. Sponges were stored in plastic bags between time of soaking and time of trap placement and between trap removal and sponge rinsing.

The ammonia sorbers were placed open-side down along the top ridge and sides of the windrows, spaced as evenly as possible around the temperature probes (Figure 2.2-5). Traps were placed on the sides of the windrows to investigate the possibility of volatilization differences between top and side. Use of these traps has been described previously (Marshall and Debell, 1980) in the context of flat soil plots, but not windrows.
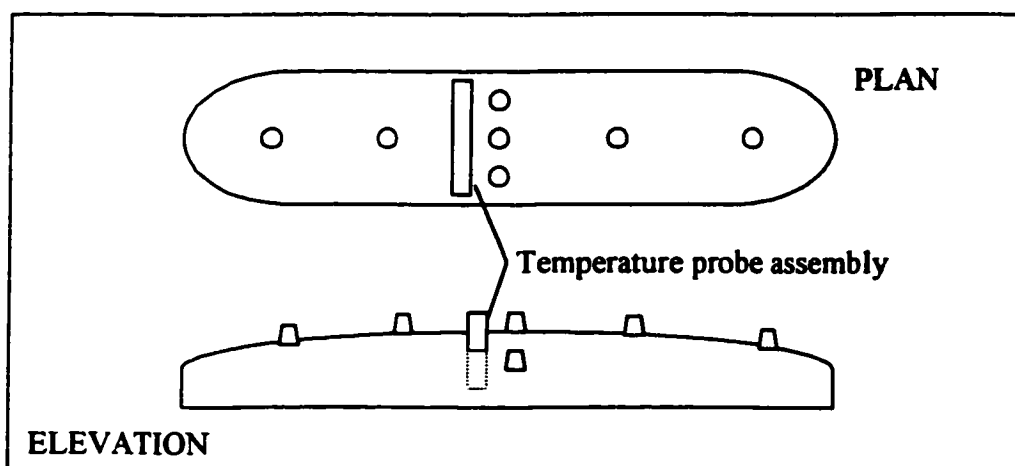
Figure 2.2-5 Diagram of ammonia sorber placement on windrows. In plan view, sorbers represented by circles. Rectangles represent temperature probe assembly.

Care was taken to avoid contact between the sponges and the surface of the windrow as well as to protect the traps from Lethbridge's strong winds by pushing windrow material

up against the outside of the traps. For the first two exposure sessions, a total of 68 traps were placed – 17 per windrow: nine along the top and four along either side. After finding that number of traps exceedingly difficult to process in the time between exposures, a decision to reduce the number was made. All other exposure sessions involved a total of 28 traps, each windrow having five along the top and one on either side. The first five exposure sessions were 12 hours, and all others were 24 hours except for two 48-hour exposures on 11th and 18th of August (Table 2.2-2). The exposure times varied according to the hypothesized ammonia emission of the windrow – as composting progressed, and the risk of surpassing the ammonia capacity of the sorbers decreased, sponges were exposed for longer and longer periods.

Table 2.2-2 Summary of sponge exposure sessions

DATE of removal	TIME of removal	SAMPLE ID	EXPOSURE TIME (h)	NO. OF SAMPLES
00/07/13	0700	0713A	12	68
00/07/13	1900	0713P	12	68
00/07/14	0700	0714A	12	28
00/07/14	1900	0714P	12	28
00/07/15	0700	0715	12	28
00/07/16	0700	0716	24	28
00/07/17	0700	0717	24	28
00/07/19	0700	0719	24	28
00/07/21	1100	0721	24	28
00/07/25	0930	0725	24	28
00/07/27	1200	0727	24	28
00/08/03	1400	0803	24	28
00/08/04	1400	0804	24	28
00/08/11	0930	0811	48	28
00/08/18	0800	0818	48	28
00/08/24	0800	0824	24	28
00/08/25	0800	0825	24	28

To compare the effect of exposure period on NH_3-N concentration in sponge rinse solution, three sorbers were placed as closely as possible on each of the windrows. One sorber was removed from each windrow after 12 h, another after 24 h, and the last after 48 h. Rinse analysis was done as described below.

2.2.6 Sponge extract analysis

Analysis for ammonia nitrogen (NH_3-N) trapped by the sponges involved rinsing them out with distilled, de-ionized (DD) water and running the rinse water through an autoanalyzer (AutoAnalyzer II, Technicon Corporation, Tarrytown, New York). Each sponge was rinsed with approximately 150 mL DD water and squeezed dry three times. The rinse water was made up to 500 mL and mixed before a 20 mL aliquot was taken. The aliquot was kept in a plastic scintillation vial at 4°C until analysis. Before re-loading the sponges with the acid-glycerine solution, they were thoroughly rinsed with tap-water and left in the laboratory to dry overnight.

The Technicon AutoAnalyzer II utilizes a Berthelot (1859, as cited in Searle, 1984) reaction of ammonia, a phenol and hypochlorite under alkaline conditions (~pH 13) to yield an emerald-green colour (Technicon, 1974). The ammonia-salicylate complex is read colourimetrically at 660 nm. For analysis of the sorber rinse solution, a modified method was followed, employing trisodium citrate in the buffer solution instead of sodium phosphate and sodium potassium tartrate. The AutoAnalyzer at the Lethbridge Research Centre is used primarily on soil extracts. Under the high pH conditions of the reaction (12.8-13.1) certain elements in the extracts (e.g. Ca, Fe, Mg) can precipitate out

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of solution and interfere. The trisodium citrate modification is associated with less of this interference (Gentry and Willis, 1988).

For a measurement to be taken, the AutoAnalyzer required a concentration in the range of 0 to 5 ppm. Rinse solutions of greater concentration were serially diluted with unexposed acid-glycerol solution until a reading was attained. Dilutions were as high as 500-fold.

2.2.7 Chemical analysis

Inorganic nitrogen: Immediately after collection, sub-samples were extracted using KCl. Ten grams of wet sample was agitated with 200 mL of KCl for one hour at low speed before being filtered through KCl-washed filter paper (Whatman No. 42). Filtrate was stored at $-15°C$ until analyzed for nitrate nitrogen (NO_3^--N) and ammonium nitrogen (NH_4^+-N) using an autoanalyzer (AutoAnalyzer II. Technicon Corp., Tarrytown, New York).

Total C; Total N; C/N: Oven-dried samples were finely ground in a Cyclone™ plant tissue grinder (UDY Corporation, Fort Collins, Colorado) and analyzed for total carbon and total nitrogen in an automated elemental analyzer (Carlo Erba™, Carlo Erba Corporation, Milan, Italy). C/N ratio was taken as total C over total N.

pH: Thirty grams of wet compost and 120 mL of deionized distilled water were agitated for one hour at low speed. The pH of the resulting solution was read on a

pH/conductivity meter (Accumet Model 50, Fisher Scientific, Denver, Colorado) calibrated with 0.1M KCl.

2.2.8 Physical analysis

Bulk density: On-site bulk density analysis was performed at each time of sampling. In triplicate, an aluminum garbage can of known mass and volume (0.7 m^3) was filled manually with material displaced from the windrow by the front-end loader and weighed. No shaking or tamping of the can was performed. Bulk density was taken to be the quotient of mass divided by volume.

Moisture content: Samples taken from each sampling height in the windrow were weighed, then oven-dried at 50°C for five days and then weighed again. The difference in mass after drying was taken to be water content and was recorded as a percentage of the sample's wet weight.

2.2.9 Statistical analysis

Statistical analyses were done using General Linear Models and Least Squares Means functions of SAS (SAS, 1999)

2.2 Results

The initial characteristics of the materials composted are presented in Table 2.3-1.

Table 2.3-1 Initial characteristics of materials composted

Material	Dry mass (kg)	%C	%N	C/N	%H₂O (w.b.)	D_b* (kg/m³)	pH
Wood mix	5560	44.7	1.24	36.7	59	183	7.0
Straw mix	6380	33.0	1.99	16.5	60	163	8.4

*bulk density

Figure 2.3-1 presents the changes in temperature of the windrows over the course of the ammonia sorber experiment. Thermophilic temperatures (>40°C) were reached quickly and windrow temperatures remained around 60°C – well above ambient – for the duration of the trial.
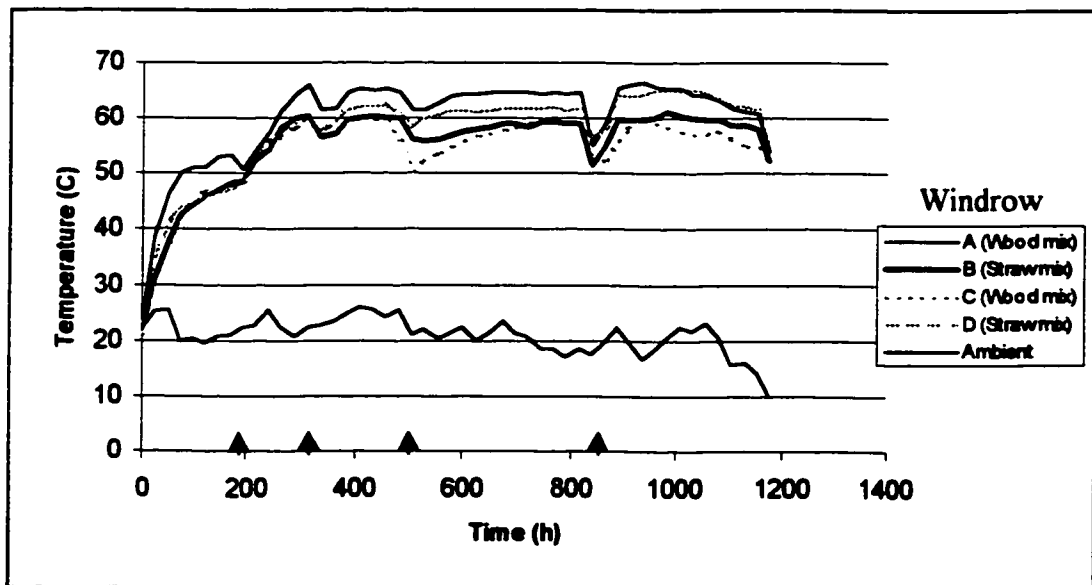
Figure 2.3-1 Windrow and ambient temperatures over time. Arrows indicate turning events.

Rinse solution from exposed sponges, when analyzed, consistently reflected concentrations of NH_3-N. Measured concentrations, when adjusted for dilution, ranged from 35 ppm (from the first 12 h exposure session; data not shown) to 1534 ppm (from the session ending after 108 h). Over the course of the trial, the mean for all measured concentrations was 340 ± 230 ppm.

Based on sorber measurements, a statistically significant (P=0.05, unless otherwise stated) difference between straw mix and wood mix windrows was discernible (Figure 2.3-2). The mean concentration for sorbers exposed to straw mix windrows was 510 ± 200 ppm. And for those exposed to wood mix windrows, the mean was 160 ± 100 ppm. In all but one case (session ending after 60 h), the means for the straw mix windrows were higher than the means for the wood mix windrows.
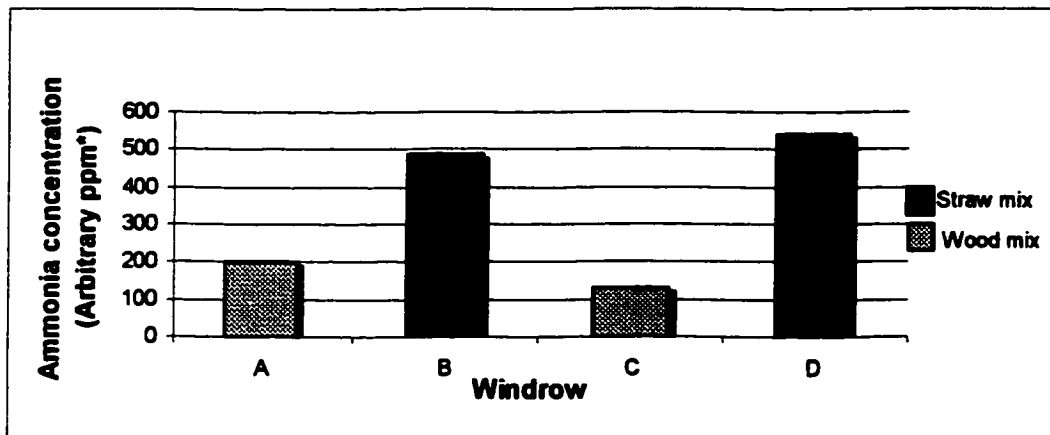
Figure 2.3-2 Mean ammonia concentrations of each windrow over the course of the experiment as measured by the sorbers. *value depends on rinse dilution factor.

Table 2.3-2 presents the experimentally observed N losses by windrow. Windrow A (wood mix) lost 11% of its initial N mass, while all other windrows lost 25 to 31%.

Table 2.3-2 Experimentally observed N loss (kg)

Windrow	Initial N mass (kg)	Final N mass (kg)	% loss
A (Wood mix)	71	63	11
B (Straw mix)	132	91	31
C (Wood mix)	67	46	31
D (Straw mix)	123	92	25

To investigate possible differences in ammonia volatilization between the top and sides of the windrows, one sorber was placed on either side, while the other five were placed along the centre ridge. After determining there was no significant difference in measured ammonia nitrogen concentration between one side and the other, side values were pooled for comparison to top values. No significant differences between top and side measurements were found, so all measured values were included for further analysis.

Sorbers were placed in seven positions on the windrows, as presented in Figure 2.3-3, and period of sponge exposure to windrow emissions varied among 12, 24 and 48 hours. For all windrows, position number five was found to yield significantly higher concentrations of NH_3-N than other positions. The least squares means for position are presented in Table 2.3-3.
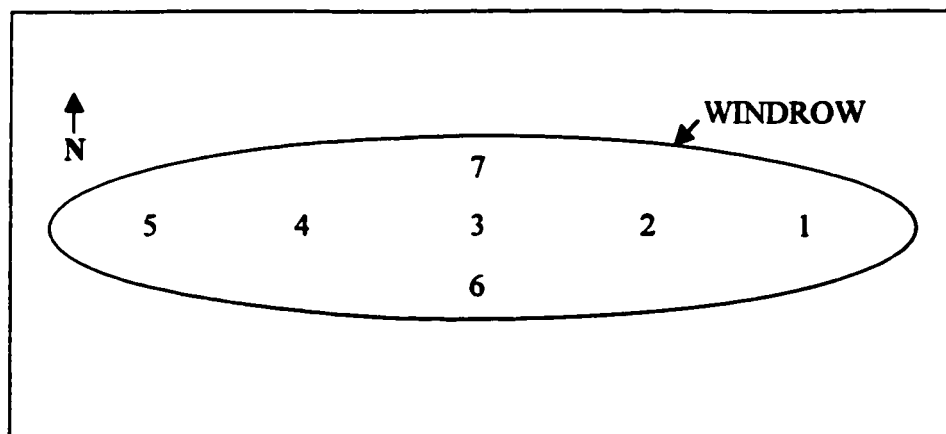
Figure 2.3-3 Diagram of numbering scheme for sorber placement.

Table 2.3-3 LS means for sorbers

POSITION	LSMEANS (ppm NH₃-N)
1	327
2	333
3	375
4	305
5	**422**
6	314
7	306

No significant difference among periods of exposure was found, and consequently no corresponding adjustment of measured concentrations was made. Measured values from all three periods were compared on par with each other.

Figure 2.3-4 presents the mean NH_3-N concentration measured for each windrow over time. Emissions from straw mix windrows followed each other closely, as did emissions from the two wood mix windrows. With the exception of one group of means, at 60 h,
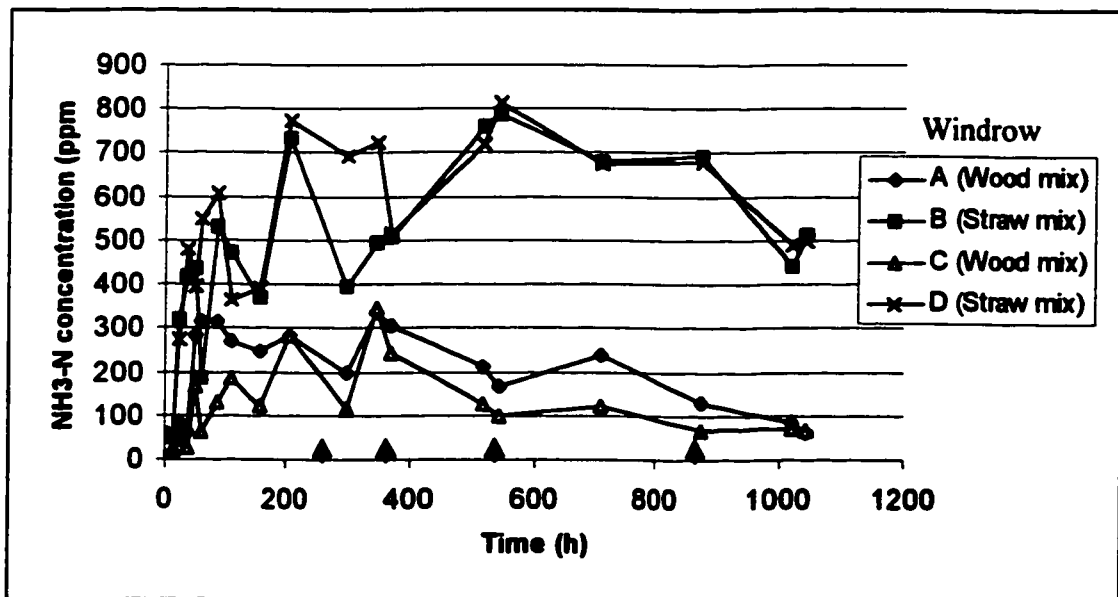
Figure 2.3-4 Profiles, by windrow, of mean sorber concentration of NH_3-N. Arrows Along the x-axis indicate turnings.

measurements from straw mix windrows (B and D) were higher than measurements from wood mix windrows (A and C). The maximum value for the emissions from straw mix windrows was approximately 800 ppm, whereas the maximum value for emissions from wood mix windrows was lower, at approximately 350 ppm. Turning incidents were, for the most part, associated with subsequent increases in NH_3-N concentration. All profiles show the same general trend of initial increase, followed by gradual decline.

The profile of each windrow's moisture content is presented in Figure 2.3-5. A decline over the course of composting is observable, with an interruption in the rate of decline between 400 h and 500 h – the timeframe within which the windrows were watered. All profiles are similar, with those for straw windrows very slightly lower after 1000 h. As can be seen in Figure 2.3-6, which presents the moisture content profiles over the course of the entire composting period, wood mix windrows were higher in moisture than straw mix windrows for most of the trial.
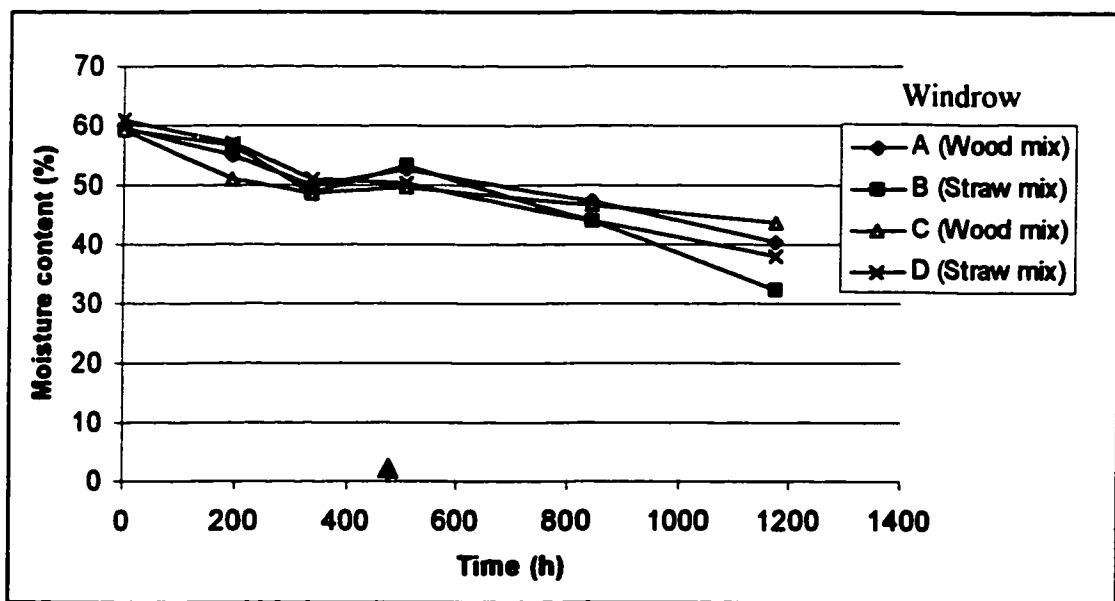
Figure 2.3-5 Moisture content profiles over first 1200 h. Arrow indicates time of water addition.
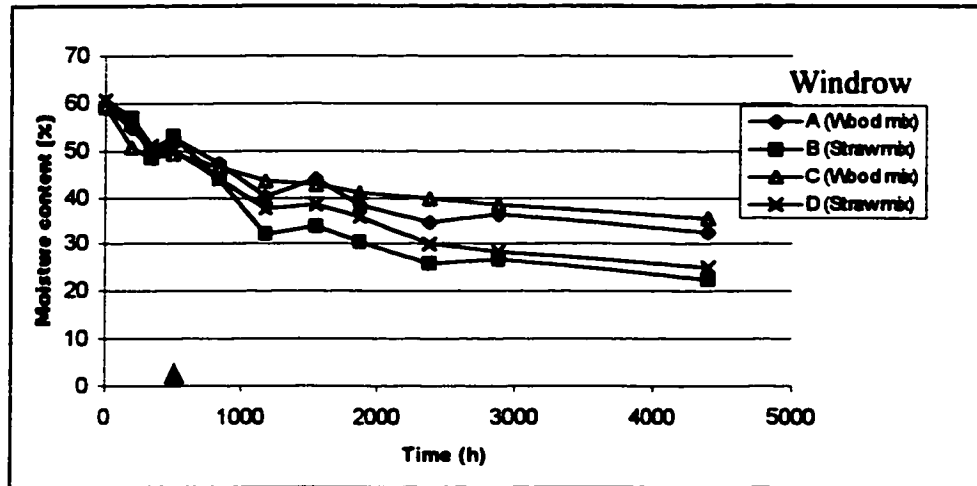
Figure 2.3-6 Moisture content profiles for entire composting trial. Arrow indicates time of water addition.

Figure 2.3-7 presents the changes in pH of the windrows over time. The profiles for the two wood mix windrows are virtually identical, as are those for the straw windrows. Initially, straw mix windrows were substantially higher in pH than wood mix windrows, but as composting progressed, the difference narrowed and after approximately 1000 h there was little difference among windrows. The pH profile for the wood mix hovered around 7, while the pH for the straw mix started above pH 8 and gradually declined to slightly above 7.
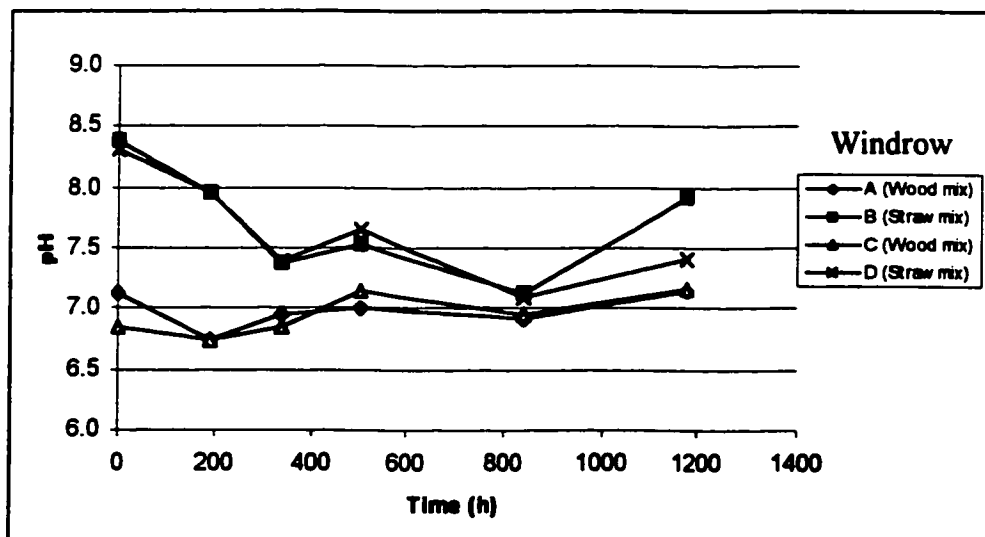
Figure 2.3-7 pH values of the windrows over time.

2.4 Discussion

The objective for the sorber experiment was to evaluate the methodology as applied to windrow composting, during the collection of relative measures of ammonia volatilization. The experiment investigated the extent to which volatile ammonia sorbers designed for use on soil plots could be used on windrows of compost. Concerns involved with this novel application included differences between fertilized soil plots and windrows of composting feedlot manure in terms of the concentrations of volatilized ammonia, the topography and the material itself. Ammonia concentration data that were gathered using the sorbers over the course of the experiment were utilized not in terms of flux, nor as accurate concentration values, but as relative measures of emission.

Sorbers placed on straw mix windrows were predicted to measure higher concentrations of volatilized ammonia than those placed on wood mix windrows. A manure and straw mixture, it was reasoned, has a higher pH and lower carbon-to-nitrogen ratio and could be expected to lose more nitrogen in the form of ammonia than a mixture of wood residuals and manure. It was predicted that airflow through the windrow would follow convection currents to some degree and these currents would carry most of the ammonia that would volatilize out of the pile. Most sorbers were therefore placed along the summit ridge of the windrows in order to be in the predicted path of ammonia escape. Sorbers placed on the sides of the windrow were predicted to yield lower ammonia concentrations because it was reasoned that ambient air would enter through the side to replace hot, ammonia-laden air escaping from the top. Because of the site's strong winds, some difficulty in keeping the sorbers in place was also predicted.

The materials used in the construction of the sorbers were inexpensive and available. Sorber assembly was straightforward and fast. Measurements made using the sorbers were accurate enough to suggest statistically significant differences between treatments. These advantages supported the methodology as being a simple and economical approach to measuring windrow ammonia volatilization, but there were also disadvantages encountered. The process was found to be very time consuming, it was difficult to ensure proper sponge placement relative to the windrow surface and, when not in use, the materials occupied a lot of space.

The time required for a measurement session was substantial when one considers that it included time spent: charging the sponges with the acid-glycerol solution, loading the sponges into the chamber, placing the sorbers on the windrows, collecting the sorbers from the windrows, collecting the sponges from the chambers, rinsing the sponges and analyzing the rinse solution. Because of the large time commitment, the number of sorbers employed in the experiment was cut down from 68 to 28, after the early sessions proved overwhelming.

The opaque plastic of the chamber presented problems in ensuring proper sponge placement above the windrow. Contact between the sponges and the windrow was to be avoided so that measurements reflected only volatilized ammonia. Direct diffusion of ammonia from the windrow to the sponge, without volatilization, would result in overestimates of ammonia emission. Windrow surfaces were lumpy, especially in the early stages of the trial, and they affected sponge placement in two ways. Firstly, in

order to have all of the chamber's lip in contact with the windrow material, the chamber would occasionally need to be depressed into the windrow. Secondly, the greater the depression, the greater was the chance that lumps or high points covered by the sorber would come in direct contact with the sponge. The opaque chambers also prevented monitoring of conditions inside the sorber. Without disturbing the sorber, one could not determine if the sponge was in contact with the windrow, or if the sponge had fallen off the hook. During harvesting of exposed sponges, when a sponge was found in contact with the windrow, it could not be determined if the sponge had been off the hook for the entire exposure session or if it had fallen off when the chamber had been lifted. Lifting the sorber often entailed shaking it, to free it of windrow material that had been pushed up against its sides for wind protection. Replacing the hook with a ring that could be opened and closed, or even with a hook that had a smaller opening, could easily mitigate this complication (Figure 2.2-4).

The acid-glycerol solution was simple to prepare, but there were difficulties in determining what an appropriate molar strength of the acid component would be. Unspecified ammonia volatilization rates coupled with unspecified reaction dynamics of volatilized ammonia with sponge acid made it difficult to determine factors such as sponge capacity for ammonia and how long a sponge would take to reach capacity. There were uncertainties as to the dynamics of diffusion within the sponge and whether all of the acid-glycerol solution, with which a sponge was charged, would be available for reaction with ammonia.

Results showing significant differences between windrows of straw/manure mixtures and those of wood residuals/manure (Figure 2.3-2) suggest that sponge capacities were adequate for the goals of the experiment. However, the lack of a significant difference in ammonia concentration among sponges exposed for 12, 24 and 48 h suggests that some sort of absorption capacity was reached. Since sponge data for wood mix windrows were significantly lower than data for straw mix windrows, even after 48 h, the capacity appears not to be a matter of ammonia capacity but a matter of time. That is, if the reason for there being no significant difference among 12, 24 and 48 h exposures was one of ammonia capacity, it could be expected that after 48 h all sponges would have similar ammonia concentrations. They would be at capacity concentration. However, if the sponge capacity was time determined, and it was a matter of absorption slowing or stopping after a certain period of exposure, then results showing differences between treatments could be expected. That there were no significant differences between sponges exposed for 12 and 48 h suggests that the temporal capacity is reached in under 12 h. Speculation into the nature of the temporal capacity leads to the hypothesis that as the sponge loses moisture at its surface, its ability to react with ammonia is compromised. Early stages of an exposure session would hypothetically feature good reaction of ammonia with acid and good diffusion into the sponge core, but as drying of the sponge progressed, the rate of ammonia collection in the sponge would slow or stop. The observation of condensation on the roof of the sorber, and dampness directly beneath it provides a possible pathway of moisture out of the sponge. Taking this to be the case, all sponge results were analyzed on par with each other, as if having been exposed, in effect, for 12 h.

The ammonia concentration values measured by the sorbers require qualification in terms of accuracy. It was not expected that they would closely reflect the value of total emitted ammonia over the exposure period. Neither were they expected to allow calculations of ammonia flux to be made. It was expected that the values would be, for various reasons, inaccurate reflections of ammonia emission, but useful nonetheless as relative measures for comparison of treatments.

Marshall and Debell (1980) compared four designs of ammonia sorber and found air flow-restricting designs – such as the closed-static, which is similar to the sorbers described here, and the semi-open sorber – underestimated the amount of ammonia emitted. The semi-open sorber differs from the closed-static sorber in that its chamber is air permeable. Marshall and Debell (1980) reported that semi-open sorber measurements were 25% higher than closed-static sorber measurements. They speculated the reason to be the capacity for water vapour to diffuse from the semi-open sorber to the atmosphere, thereby increasing the rates of drying and volatilization.

The microclimate inside a chamber is reported to be modified relative to the exterior environment in terms of air temperature, soil temperature and airflow (McGinn and Janzen, 1998). Microclimate modifications complicate calculations of flux. The sorbers used in this experiment featured little or no airflow and ammonia volatilization would occur only through diffusion, so an underestimate of volatilization could be expected in this regard. Condensation observed within the chamber (discussed above) could also be a reason for sorber values being an underestimation of ammonia emission because

ammonia is highly soluble in water (NRC, 1979 as cited in McGinn and Janzen, 1998). The sorber could not detect ammonia that absorbed into condensation droplets.

A major difference in the application of the sorbers in this experiment as compared to previous applications (Marshall and Debell, 1980; Volk, 1970) was in the topography of the experimental plot. The sorbers have been used to measure ammonia emissions from flat, uniform soil plots, but not from compost windrows. Emissions from a pile instead of from a flat plot were expected to behave differently. Furthermore, emissions from the pile were expected to vary with position. Sorbers were placed primarily along the top ridge of the windrows because airflow was expected to follow convection currents. Sorbers were also placed on the sides of the windrow for comparison with sorbers on the top. The expected convection current would feature ambient air entering the windrow on the sides near the bottom, and heated air exiting out the top. Side sorbers were therefore expected to record lower values than top sorbers.

Statistical analysis of values recorded by all sorbers revealed no significant difference between side and top. This suggests that either the convection airflow pattern described above does not occur (at least not to the extent described) or else placing the sorbers on the sides facilitated ammonia volatilization.

The high temperatures of the windrows (Figure 2.3-1) suggest that there should be a convection pattern, at least insofar as heated air would rise and be replaced, but the airflow may not be so strong as to penetrate to the core of the windrow. Rather, it may be

a situation of little lateral movement of air, but with air rising throughout the windrow. High concentrations of methane (indicative of anaerobic conditions) at the bottom of composting windrows of feedlot manure have been reported (Hao et al., 2000) supporting the hypothesis that air penetration does not reach the core.

With airflow being mostly upwards and only slightly laterally, we should still expect there to be higher ammonia volatilization at the top rather than the side because there is more material beneath the peak, and therefore more potential for ammonia formation. However, with farther distances through the compost matrix to travel, there is increased probability of ammonia meeting a fate other than volatilization. Other possible fates include adsorption, nitrification and immobilization. Volatilized ammonia may not be the product of the entire volume of material beneath a sorber, but rather of some portion of that material. If that lesser depth was less than the height of a side sorber above ground, side and top sorbers could be expected to capture similar amounts of ammonia.

The disruption of surface material when placing side sorbers provides another possible explanation for the difference in volatilization rates between top and side. The slope of the windrow sides meant that an area needed to be leveled if the sorber was to stay put and not roll off the windrow. Clearing an area for the sorber uncovered moist inner material in contrast to the generally dry outer layer of the windrow. The drying of material directly beneath the sorbers would provide a vehicle for ammonia volatilization and higher concentrations in those sorbers could be expected. Placement of sorbers along

the top of the windrow involved less disruption to the surface and uncovering of moist inner material.

No significant difference was observed in the values recorded by sorbers on the north side of the windrows and those on the south (Figure 2.2-1). This was to be expected because conditions are similar in terms of wind and sun exposure. Wind came primarily from the west and, except for early morning and evening, the windrows were all shaded from direct sunlight.

Sorbers in position #5 on the windrows (Figure 2.3-3) featured significantly higher (Table 2.3-3) concentrations of ammonia than the other positions on 9 out of 18 occasions. Position #5 is the farthest west of a given windrow and therefore is subject to the most wind. Being in the wind may lead to higher volatilization levels by way of increased airflow within the windrow. An increase in airflow through even a very small volume of material near the sorber could significantly raise the amount of emitted ammonia measured by the sorber. Evaporation rate would increase with increased airflow and drier material may facilitate diffusion of ammonia from deeper in the windrow to the atmosphere. Another possibility is that increased airflow through the material near sorber #5 leads to better oxygenation and microbial activity, thereby increasing the amount of ammonia produced. That position #5 is correlated with higher ammonia concentrations than any other position, including position #4 which was often less than 0.5 m distant, suggests that any effect of the wind on volatilization rates is spatially limited.

Overall, the evidence concerning a relationship between position and ammonia emission rates suggests that airflow within the windrow is limited. There being no significant difference between left side, right side and top of the windrow suggests that any convection current that is present is slow and of shallow penetration. It suggests also that differences in volatilization from windrow topography versus flat plot topography is not obvious at the level of resolution offered by the sorbers. That the most windward position was correlated with the highest mean ammonia concentrations suggests an effect of wind and airflow on volatilization, but that no gradient of decreasing concentration from West to East was observed suggests that any such effect is not far-reaching.

The windrows were shaded from direct sunlight by a roof above the compost pad, and wind was partially blocked by screens. Statistical analysis was performed to evaluate the correlation of sorber ammonia concentrations with hourly weather data (not shown). No direct correlation was found between ammonia concentration and ambient temperature, nor with wind speed and direction. There was no obvious relationship between values for relative humidity and ammonia concentration in the sorbers, but higher values for vapour pressure were associated with higher values in the sorbers. Since vapour pressure would certainly be expected to influence ammonia volatilization rates, this correlation reflects some measure of accuracy for the sorbers.

Comparing weather conditions between the experimental compost pad and windrows in the field, the parameters that would most markedly affect composting would be sunlight and wind. Without shade from the roof or wind shields, the rate of drying for composting

material could be expected to increase dramatically. Even under experimental compost pad conditions, researchers felt it necessary to add water once over the course of the trial. Battling water loss in the field would be a practical concern.

According to the concentrations of ammonia measured by the sorbers, the prediction that straw mix windrows would lose more nitrogen as ammonia than wood mix windrows was correct (Figure 2.3-4). The prediction that the sorbers would provide a only a relative measure of NH_3 volatilization could not be validated since no secondary method of measuring ammonia emissions was available, but the distinct differences in ammonia emission profiles between treatments lends credence to this hypothesis. The observed losses in total N are in agreement with the sorber measurements, with the straw mix losing a greater amount than the wood mix (Table 2.3-2) (described in detail in Chapter 3). The similarity in sorber concentrations between top and side positions was unexpected and suggests that convection airflow within the windrows either did not occur or occurred to less of an extent than predicted.

The objective of evaluating the sorbers as a method of measuring relative ammonia volatilization in windrow composting was met. The sorbers can measure ammonia emissions with enough resolution as to distinguish between wood mix-based and straw-based feedlot manure composting. The similarity in ammonia concentrations of sorbers placed on the sides of the windrow and on the top satisfies the objective of investigating whether a methodology designed for use on flat soil plots could be applied to windrow topography. The differences in volatilization among different positions on the windrow

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appear to be below the resolution of the sorbers. The similarity in sorber data for each type of material indicates that the method is repeatable and has good precision.

The sorber methodology described here could be applied to investigations comparing ammonia emissions involving suitably different treatments. The resolution of the methodology appears to be insufficient for detecting differences between the top and side of a windrow or pile topography, but sufficient for detecting differences between varying feedstocks. Modifications to be suggested for the sorbers include replacing the screw hook inside the chamber (Figure 2.2-4) with a gated ring to prevent sponges from falling onto the material and a transparent material for the chamber to allow inspection of the sponges in position above the material. Evaluation of measured sorber concentrations as compared to measured ammonia flux is an area for further research, as is the investigation of the methodology's resolution.

2.5 Conclusions

The ammonia sorber methodology was found to be effective in estimating relative emissions of ammonia between feedlot manure windrows with bedding material of either wood residuals or straw. The sorber measurements consistently suggested a significant difference in ammonia volatilization between windrows, with straw-manure mixtures being higher than wood-manure mixtures. Any differences in windrow emissions of ammonia that may exist between top and side, however, were not obvious given the resolution of the sorbers. Differences in sorber-measured concentrations among positions on a windrow were broad enough to suggest that airflow within a windrow follows

convection currents only weakly, without deep penetration of ambient air, or not at all.

The lack of a statistically significant difference in NH₃ concentrations among sorbers

exposed for 12, 24 or 48 h suggested a maximum length of exposure, of less than 12 h,

beyond which ammonia absorption slowed down greatly or stopped. This temporal

capacity is hypothesized to be due to drying of the sponge surface. Sorber materials were

inexpensive and available, assembly was straightforward and fast, and sorber placement

was unaffected even by the strong winds of Lethbridge.

2.6 References

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CHAPTER 3

Comparison of ammonia emissions from composting of beef feedlot manure with either wood residuals and straw bedding

3.1 Introduction

The traditional practice for beef feedlot operations in southern Alberta is to bed cattle on cereal straw. An alternative bedding material, gaining interest in recent years, is the residual from wood processing, which is readily available from nearby forest product companies. A mixture of bark, post peelings and sawdust, the residual has been reported to contribute to cattle cleanliness by reducing tag (McAllister et al., 1998). Larney et al. (2000) also proposes that wood chip bedding may be better for feedlot cattle in that cattle will not eat wood residuals as they may straw.

Nitrogen (N) can be lost from feedlot composting operations via ammonia volatilization, nitrate leaching and denitrification. Nitrogen retention strategies (Janzen et al., 1997) generally aim to keep the $NH_3 \leftrightarrow NH_4^+$ equilibrium to the right and facilitate N immobilization. Although difficult because compost mixtures tend to be highly buffered, pH can be regulated to prevent deprotonation of NH_4^+ and nitrogen immobilization can be facilitated by a favourable balance in availability of C, N, O_2, and H_2O. To promote nitrification and prevent denitrification, adequate aeration is recommended (Brady and Weil, 1996).

Agriculture and Agri-Food Canada (AAFC) researchers investigated the composting of straw-bedded and wood residuals-bedded beef feedlot manure during the summer of 1998

(Larney et al., 2000). They found that wood residuals based compost had greater amounts of inorganic N (NH_4^+-N, NO_3^--N) after the thermophilic composting stage and that, based on maturity indices of the ratio of ammonium to ammonia, the wood mix compost stabilized sooner. They concluded that the wood mix had a better ammonia trapping ability than the straw mix since the wood mix retained N as ammonium rather than ammonia.

The objective of the work described in this chapter was to evaluate the two bedding materials (wood residuals and straw) in terms of nitrogen retention during composting of beef feedlot manure.

3.2 Methods and materials

3.2.1 Compost windrow establishment

The study was conducted at the AAFC Research Centre at Lethbridge, Alberta between July and October, 2000. On July 12, the research centre's feedlot was cleaned of its manure and bedding by a front-end loader and truck and the material was formed into windrows. Bedding was of two types: a mixture of wood chips, bark peelings and sawdust (80% lodgepole pine (*Pinus contorta* var. *latifolia* Engelm.), 20% white spruce (*Picea glauca* (Moench) Voss)) (Sunpine Forest Products, Sundre, Alberta) and barley (*Hordeum vulgare* L.) straw. Of the four windrows made, two were a manure/wood residuals mix (wood mix windrow) and two were a manure/straw mix (straw mix windrow). Windrows were arranged in a 2x2 grid on a concrete pad, beneath a roof, each running West-East lengthwise, with straw windrows in the Northeast and Southwest

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positions (Fig. 3.2-1). Each truckload of material was weighed so as to know the initial

mass of each windrow. Four 600 g samples were taken from each windrow to determine
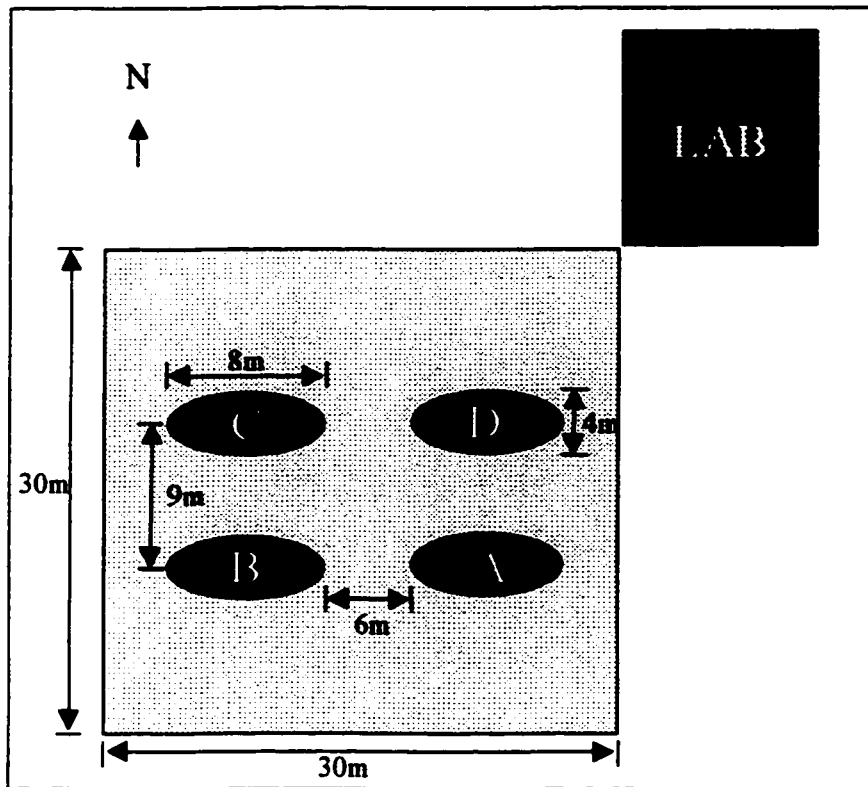

Figure 3.2-1 Diagram of composting site. Windrows A-D on
concrete pad.

initial moisture content, before being analyzed for inorganic (NH_4^+-N, NO_3^--N) and total

nitrogen (N), total carbon (C) and pH. Initial bulk density was determined and windrow

dimensions measured included length, width at each end, and arch distance (up one side

and down the other) at three locations along the length.

3.2.2 Turning and watering

A tractor-pulled windrow turner (*EarthSaver*™ Fuel Harvesters Corp., Midland, Texas)

turned the windrows once a week for the first three weeks and then once every two weeks

after that (July 20, July 26, August 2, August 16). To counteract the hot dry climate

typical to the area, windrows were watered on August 1. Volumes of water added varied

from 619 litres to 1018 litres per windrow (Table 3.2-1), calculated to bring all windrows

up to a moisture content of 55% (wet basis). Water was added using a water truck

equipped with a 100mm diameter hose. No leachate was observed on the concrete pad at

the time of watering, nor when the piles were turned the following day.

Table 3.2-1 Litres of water added to windrows on August 1

Windrow	Litres added
A (Wood mix)	669
B (Straw mix)	1018
C (Wood mix)	863
D (Straw mix)	619

3.2.3 Temperature monitoring

A small front-end loader (Model 963, Bobcat Company, West Fargo, North Dakota) was

used to insert temperature probes into each windrow immediately following windrow

establishment. Windrows C and D (Figure 3.2-1) had two probes each, dividing them

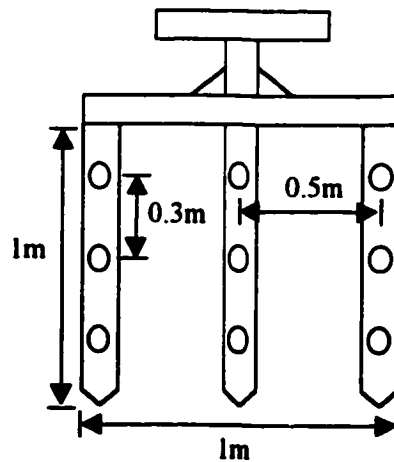into thirds lengthwise and windrows A and B each had one, dividing them in half. The

Figure 3.2-2 Temperature probe assembly. Evenly-spaced temperature sensors (circles) connected by wires in PVC pipe (not shown) within 3-pronged aluminum casing.

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probes (Fig. 3.2-2) were aluminum, each with three prongs, each prong having three

thermocouple sensors, giving a 3x3 grid of sensors for each probe. Wiring for the

sensors ran through a PVC sheath to provide electrical insulation from the metal. Probes

were inserted vertically, and perpendicular to the lengths of the windrows. Data from the

probes were displayed and recorded by a computer data logger in the laboratory adjacent

to the compost pad. Centigrade measurements were displayed on the monitor and

intermittently logged to the computer's hard drive.

3.2.4 Compost windrow sampling

Samples of the material were collected at the time of windrow establishment and prior to

each turning episode. The front-end loader cut open each of the windrows by pushing

through the mid-section of its length, displacing that material (Figure 3.2-3), and leaving

two exposed walls. Six samples of approximately 1.5kg each were taken from each

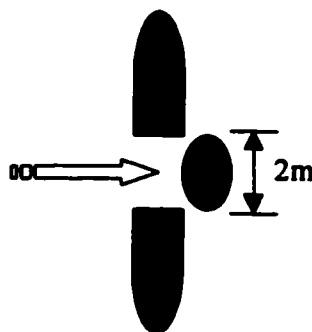exposed wall for physical and chemical analysis. Working from top to bottom, samples

2m

Figure 3.2-3 Diagram illustrating sampling procedure.
Arrow indicates action of front-end loader.

were taken from depths 0, 76, 203, 457, 762 and 1067 mm, measured from the top surface of the windrow to match the depths of gas sampling done for the AAFC greenhouse gas study.

3.2.5 Chemical analysis

Inorganic nitrogen: Immediately after collection, sub-samples underwent potassium chloride (KCl) extraction. Ten grams of wet sample were agitated with 200 mL of KCl for one hour at low speed before being filtered through KCl-washed filter paper (Whatman No. 42). Filtrate was stored at $-15^{\circ}C$ until analyzed for nitrate nitrogen (NO_3^--N) and ammonium nitrogen (NH_4^+-N) using an AutoAnalyzer (Technicon Corp., Tarrytown, New York).

Total C; Total N; C/N: Oven-dried sub-samples were finely ground in a Cyclone™ plant tissue grinder (UDY Corporation, Fort Collins, Colorado) and analyzed for total carbon and total nitrogen in an automated elemental analyzer (Carlo Erba™, Carlo Erba Corporation, Milan, Italy). C/N ratio was taken as total C divided by total N.

pH: Thirty grams of wet compost and 120 mL of deionized distilled water were agitated for one hour at low speed. The pH of the resulting solution was read on a pH/conductivity meter (Accumet Model 50, Fisher Scientific, Denver, Colorado) calibrated with 0.1M KCl.

3.2.6 Volatilized ammonia sorbers

Ammonia that volatilized from the windrows was evaluated using sorbers and

AutoAnalyzer analysis (Technicon Corporation, Tarrytown, New York), as described in

Chapter 2.

3.2.7 Physical analysis

Bulk density: On-site bulk density analysis was performed in triplicate at each time of

sampling. An aluminum garbage can of known weight and volume (0.7 m^3) was filled

manually with material displaced from the windrow by the front-end loader and weighed.

No shaking or tamping of the can was performed. Bulk density was taken to be the

quotient of mass divided by volume.

Moisture content: Samples taken from each sampling height in the windrow were

weighed, then oven-dried at $50°C$ for five days and then weighed again. The difference

in mass after drying was taken to be water content and was recorded as a percentage of

the sample's wet weight.

Volume: Volume was determined using measurements of windrow dimensions taken at

each sampling occasion. Length and width at the base were measured as well as the

distance over the width of the windrow, going up one side and down the other.

Windrows were assumed to be hemi-cylindrical and this arch distance equal to the hemi-

circumference. Hemi-circumference was measured at three locations along the length of

each windrow. Radius (r) was calculated as:

$$r = C/\pi$$

where C is the hemi-circumference. The volume (V) of the windrow can be estimated as:

$$V = \pi r^2 L/2$$

where L is windrow length.

3.2.8 Statistical analysis

Statistical analyses were done using General Linear Models and Least Squares Means functions of SAS (SAS, 1999).

3.3 Results

Table 3.3-1 Mean parameter values of wood and straw mixes before and after composting

Parameter	Units	Wood mix			Straw mix		
		Before	After	% Change	Before	After	% Change
Total mass	kg	13720	5210	62	15990	6560	59
Dry mass	kg	5560	3430	38	6380	4980	22
Water mass	kg	8160	1780	78	9610	1580	84
Water	%	59	34		60	24	
pH		7.0	7.0		8.4	8.2	
Bulk density	kg/m^3	184	196		163	246	
Volume	m^3	40	25	38	42	27	36
C	%	44.7	40.3		33.1	25.9	
C	kg	2490	1380	45	2110	1290	39
C/N		37	25		17	14	
N	%	1.24	1.59		1.99	1.85	
N	kg	70	55	21	127	92	28
NO$_3$	ppm	242	935		182	207	
NO$_3$	kg	3	5	(67)	3	1	67
NH$_4$	ppm	2666	142		2090	753	
NH$_4$	kg	37	1	97	33	5	85

Mean values of various parameters for the wood mix and the straw mix are presented in Table 3.3-1. Composting reduced the mass of the wood mix and straw mix piles by 62% and 59% respectively and volume was reduced by 38% and 36% respectively. The increase in bulk density after composting was substantially higher for the straw-based material than for the wood-based.

Within 24 h, straw mix windrows developed a surface crust, about 50 mm thick, of dried manure/straw conglomerate. By comparison, the surfaces of wood mix windrows were looser.

Figures 3.3-1 and 3.3-2 present the temperature profiles of the four windrows over the course of composting. All windrows had thermophilic temperatures (>40°C) over the period of time from 50 to 2000 h. In general, the profiles are typical of the composting process, displaying stages representative of the typical mesophilic, thermophilic and cooling stages of the process (cf. Figure 1.2-1).
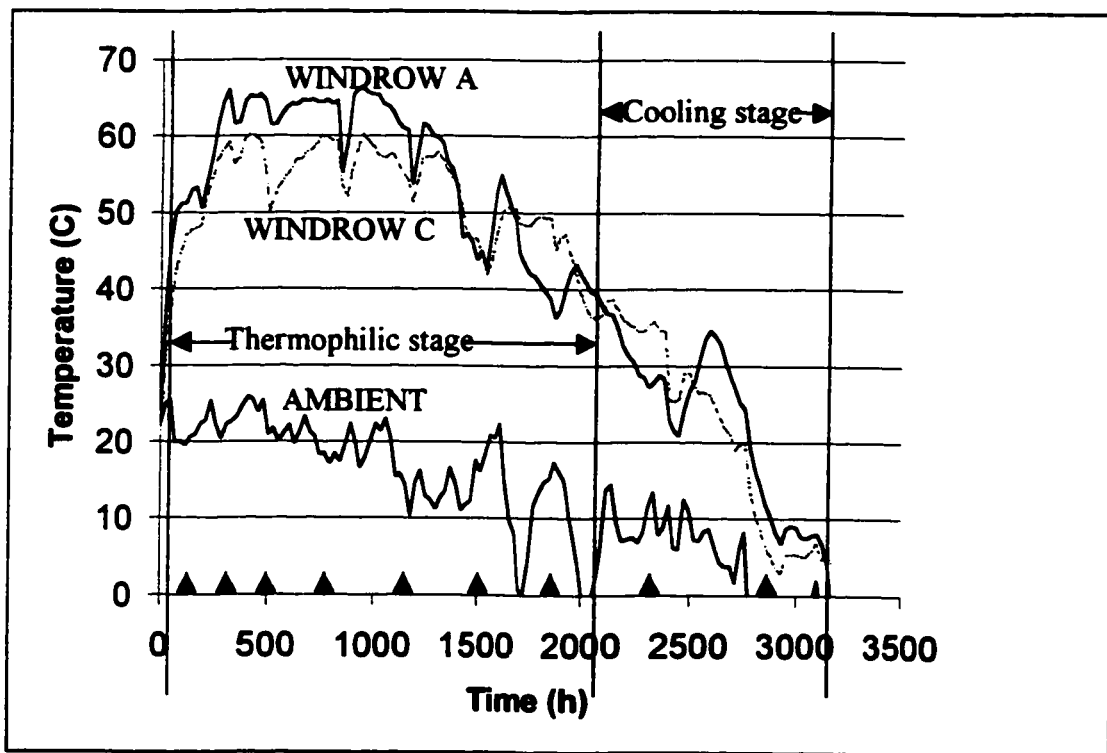

Figure 3.3-1 Temperature profiles for wood-based windrows. Arrows indicate turning events.
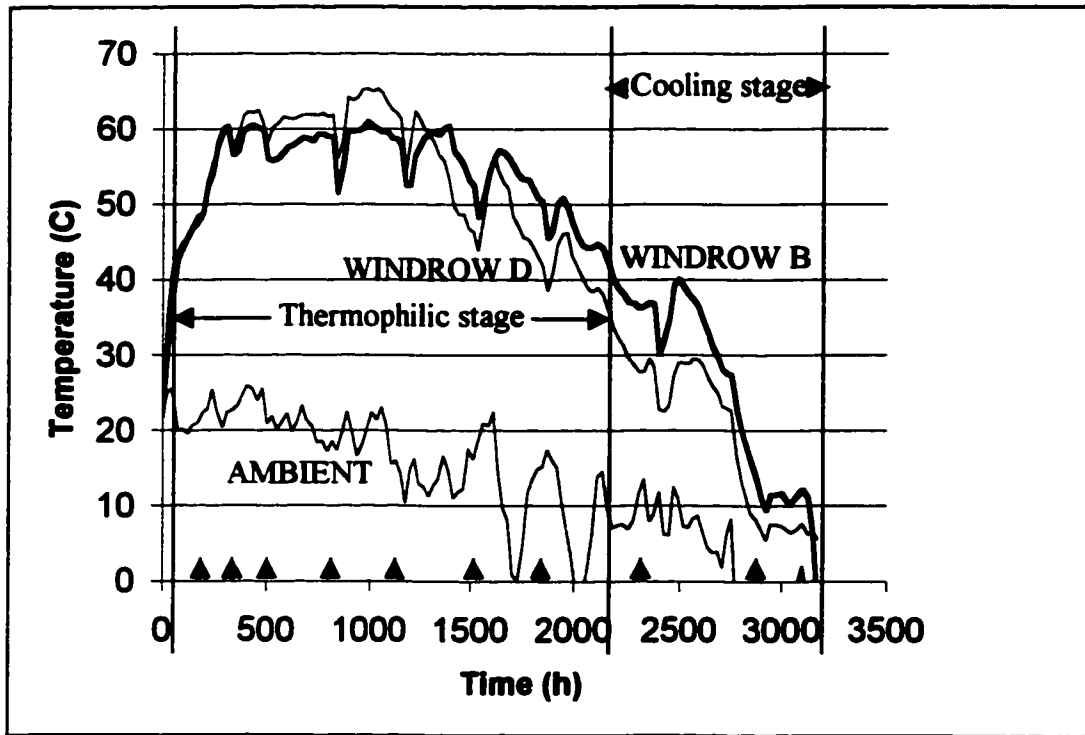
Figure 3.3-2 Temperature profiles for straw-based windrows. Arrows indicate turning events.

All windrows began the trial with ~60% (wet basis) moisture (Figure 3.3-3). By the end of the trial, the moisture contents of the wood mix windrows were distinctly higher than those of the straw mix windrows, but the general trend for all windrows, in terms of moisture content, was one of gradual decline.

The pH profiles of the windrows (Figure 3.3-4) show a distinct difference between wood-based material and straw-based. The pH value of the straw mix dropped during the early stages of the trial to approximately the same level as the wood mix. Final pH values were close to initial values: approximately 8 for the straw mix and approximately 7 for the wood mix.
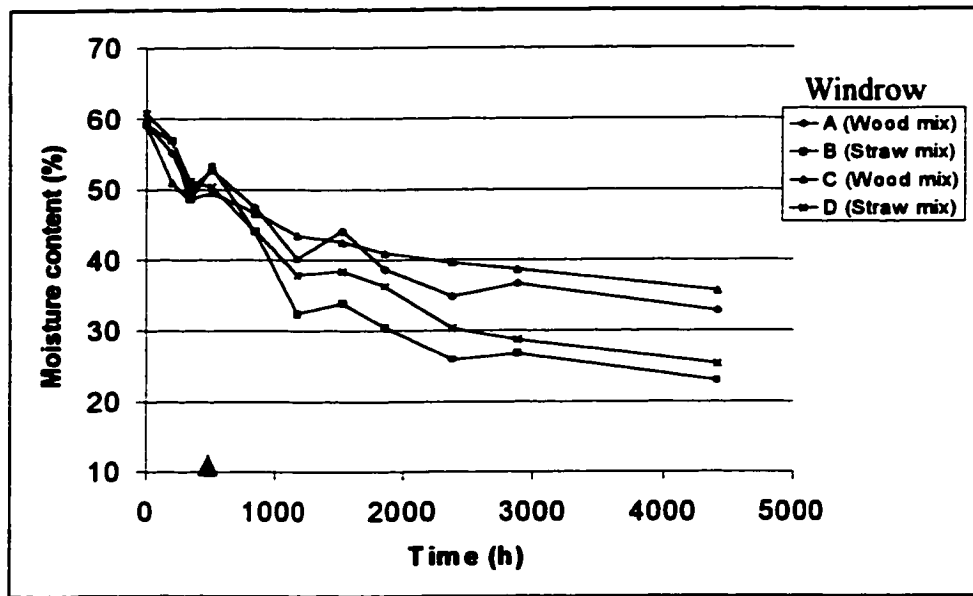
Figure 3.3-3 Percent moisture content (wet basis) profiles by windrow. Arrow (x-axis) indicates time of water addition.
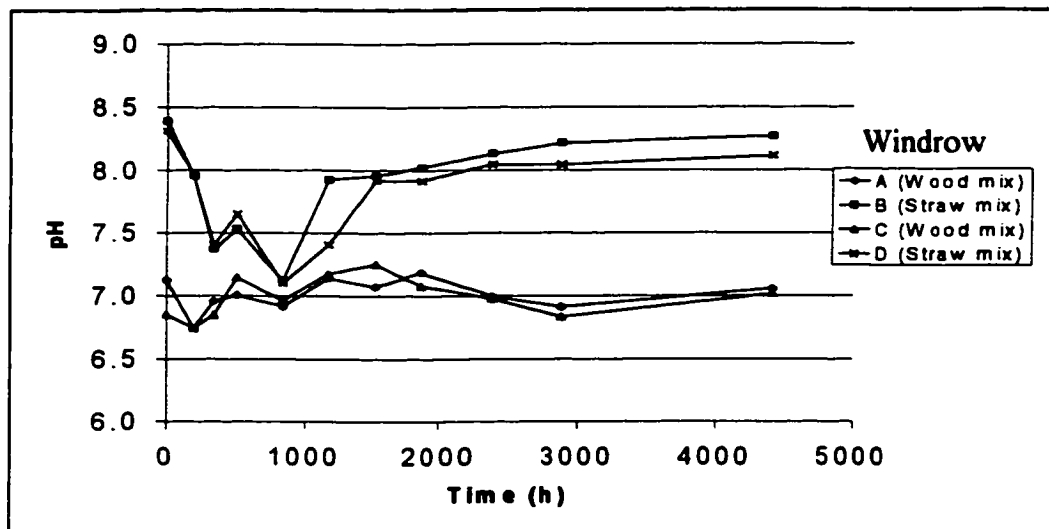

Figure 3.3-4 pH profiles by windrow.

Initially, the wood mix had a higher percentage of C, but during composting, the percent C in the straw mix decreased more than did percent C in the wood mix. In terms of raw mass, however, the wood mix lost more carbon (~1100 kg) than the straw mix (~820 kg). After composting, the straw-based material still had a greater proportion of nitrogen than the wood-based material despite the straw mix windrows having decreased in %N while

the wood mix windrows increased. By mass, straw mix windrows lost more than twice as much nitrogen as wood mix windrows (~35 kg and ~14 kg, respectively), but still had substantially greater N content (92 kg N for straw mix, 55 kg N for wood mix). The C/N ratio of the wood residuals-based compost decreased to a much greater extent than did that of the straw-based compost.

Statistical analysis revealed significant differences between surface (0, 76 and 203 mm deep) and core regions (457, 762 and 1067 mm deep) of the windrows in terms of ammonium and nitrate content, so data have been presented in three ways: pooled (Figures 3.3-5 and 3.3-8), surface only (Figures 3.3-6 and 3.3-9) and core only (Figures 3.3-7 and 3.3-10).

In the nitrate content data, wood mix windrows were distinct from straw mix windrows and by the end of the trial, wood-based windrows had accumulated nitrate to a greater extent than had straw-based windrows (Table 3.3-1). All windrows had an initial period
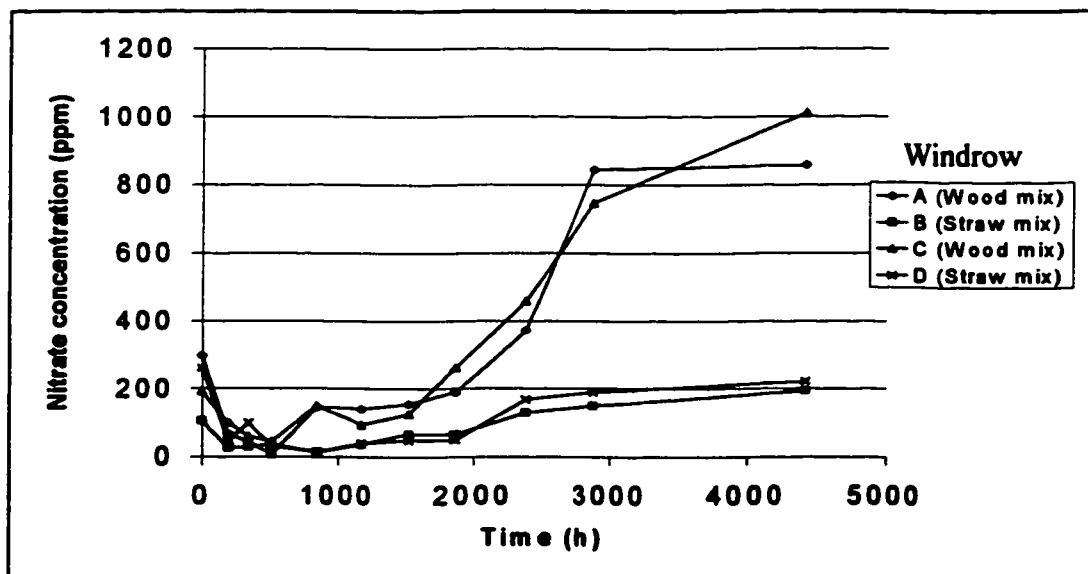
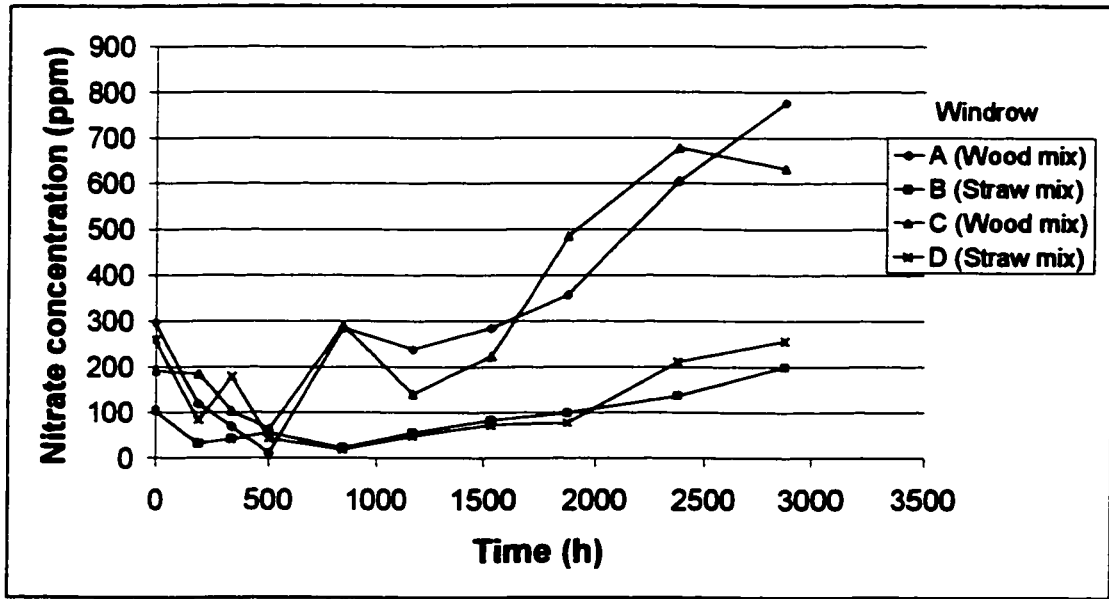Figure 3.3-5 Pooled nitrate concentration (ppm) profiles by windrow.

Figure 3.3-6 Surface nitrate concentration (ppm) profiles by windrow.
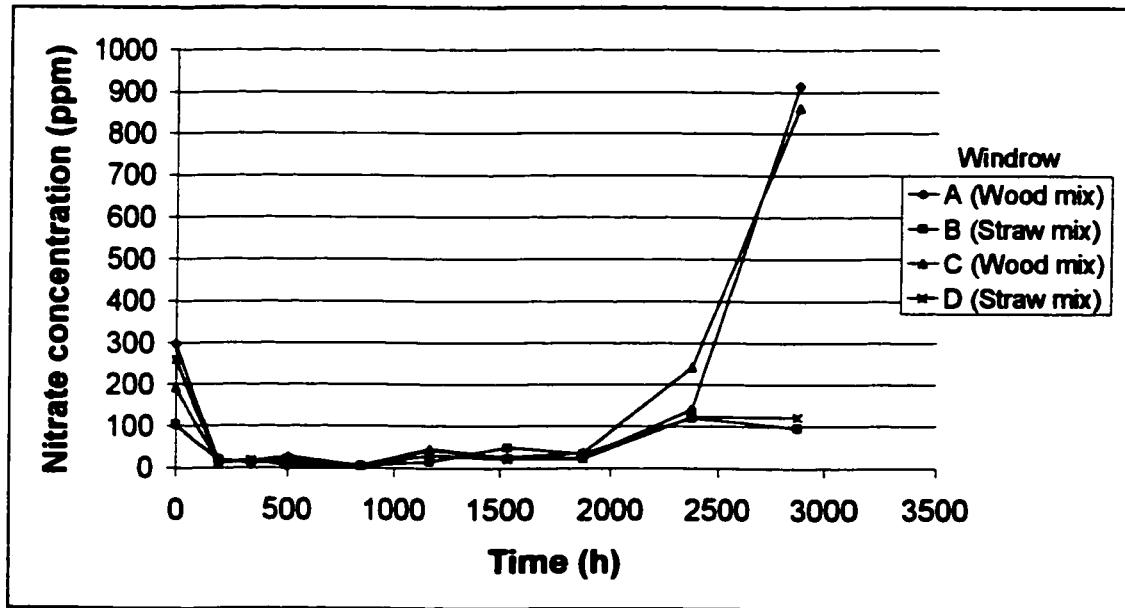

Figure 3.3-7 Core nitrate concentration (ppm) profiles by windrow.

of nitrate depletion, followed by accumulation. The nitrate content of the core region (Figure 3.3-7) dropped to near zero relatively quickly and remained low until approximately 2000 h. After 2000 h, the nitrate content of the wood mix windrows increased very rapidly to levels even higher than the surface region, while in the straw mix windrows the increase after 2000 h was less. By comparison, the surface region also had an initial drop in nitrate content, but began accumulating nitrate sooner than the core (Figure 3.3-6). The rate of nitrate accumulation in the surface was greater in the wood mix windrows than in the straw mix windrows.

There was no obvious distinction between the ammonium contents of the wood-based material and those of the straw-based material (Figures 3.3-8 to 3.3-10). The pooled data display an initial period of rapid increase in ammonium concentration for all windrows, followed by gradual decline. The surface data (Figure 3.3-9) are more variable than the core data. All surface profiles displayed a general trend of gradual decline. The values for the wood mix and for the straw mix in the core data were not as similar (Figure 3.3-10). The core region in the wood mix had an initial sharp increase in concentration, peaked at approximately 330 h, and immediately began a slow decline, approaching zero at approximately 3000 h. The core region in the straw mix rose sharply in concentration and there was a plateau at a peak value similar to that of the wood mix. The plateau spanned approximately 400-900 h and then dropped sharply to between 1000 and 2000 ppm of NH_4^+-N, where concentrations appeared to level off.
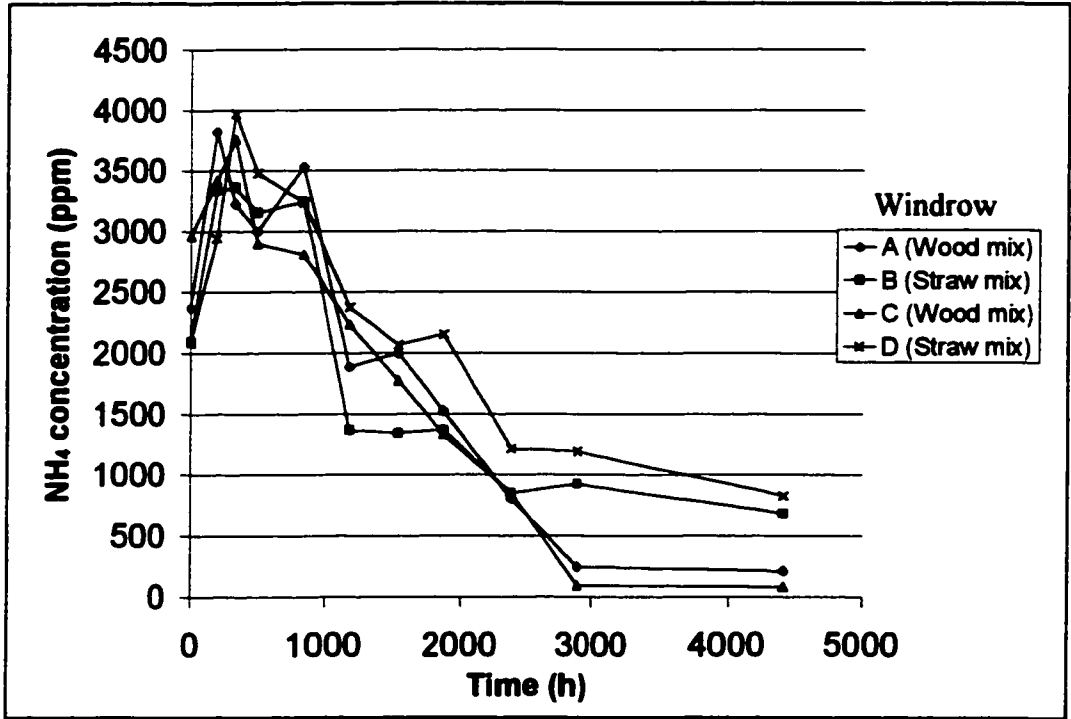
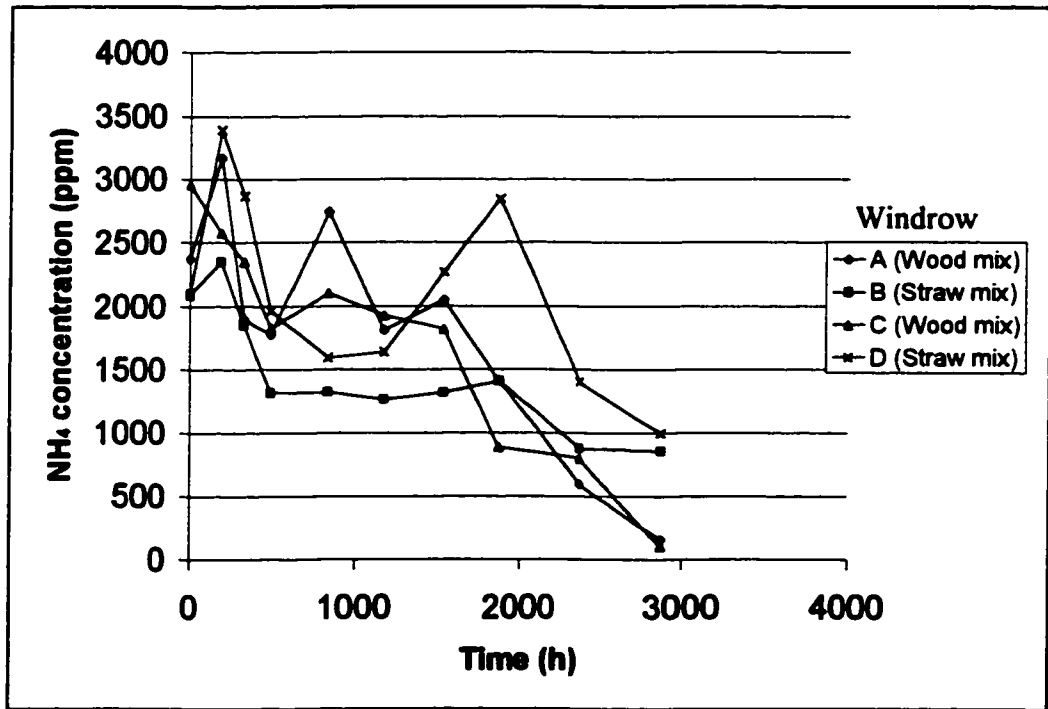**Figure 3.3-8** Pooled ammonium concentration (ppm) profiles by windrow.

Figure 3.3-9 Surface ammonium concentration (ppm) profiles by windrow.
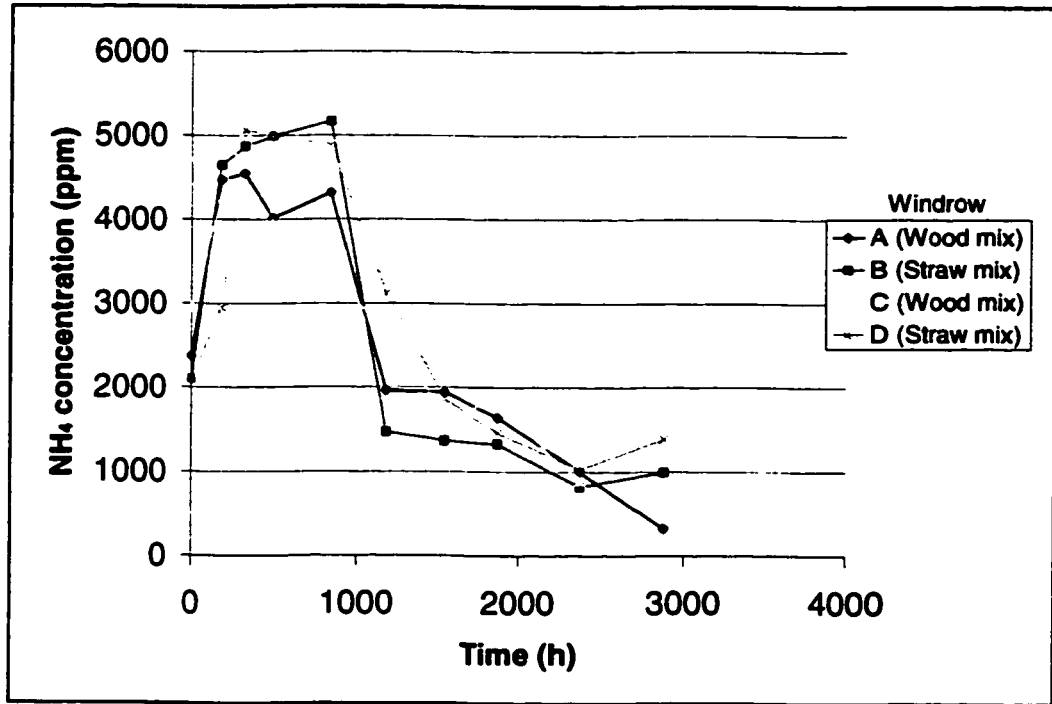
Figure 3.3-10 Core ammonium concentration (ppm) profiles by windrow.

As described in Chapter 2, ammonia emissions of the windrows were measured using closed-static sorbers from the beginning of the trial (July 12; 0 h) until the end of August (~2000 h). Straw mix-based values follow each other closely, as do the wood mix-based values (Figure 3.3-11). With the exception of one group of means, at 60 h, measurements from straw mix windrows (B and D) were higher than measurements from wood mix windrows (A and C). The maximum value in the straw mix data was approximately 800 ppm, whereas the maximum value in the wood mix data was lower, at approximately 350 ppm. Turning incidents were, for the most part, associated with subsequent increases in NH_3-N concentration. All profiles show the same general trend of initial increase, followed by gradual decline.
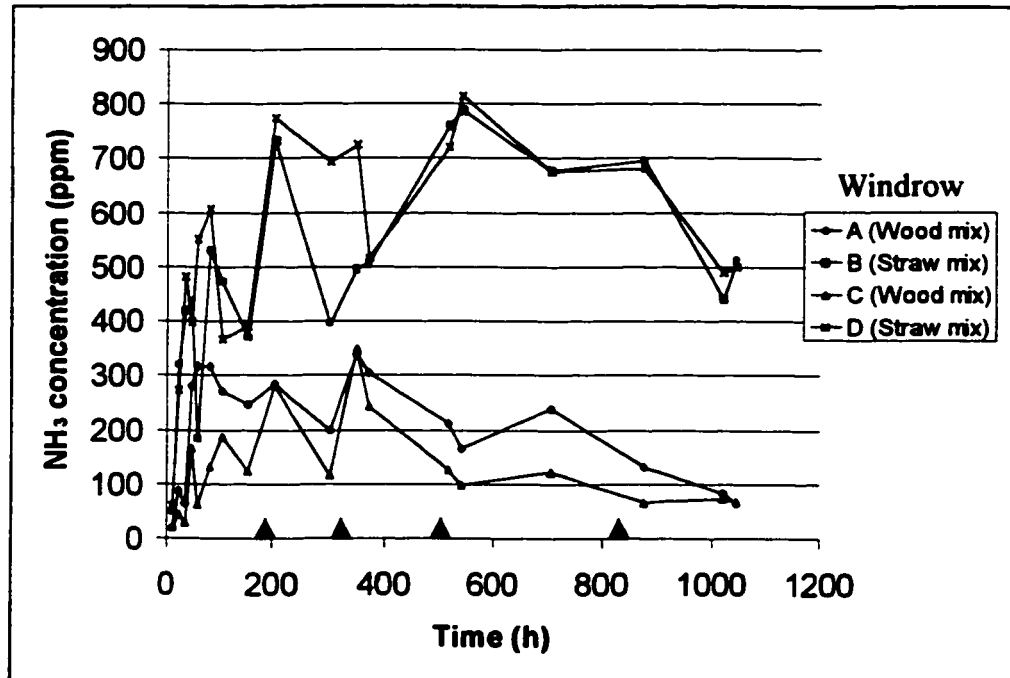
Figure 3.3-11 Sorber ammonia concentrations (ppm) over time. Arrows indicate turning events.

3.4 Discussion

The objectives of the study were to compare nitrogen losses from composting windrows of feedlot manure with either of two types of bedding material. The experiment investigated the influences of various parameters on nitrogen dynamics in composting. It was assumed that most of the nitrogen lost would be through ammonia volatilization, for which relative measures were obtained for each windrow, using the sorbers described in Chapter 2. Nitrogen losses through pathways such as leaching and denitrification were assumed to be negligible in comparison to the volatilization losses. Indeed, no leaching onto the concrete pad was observed over the course of the experiment. Nitrogen species measured throughout the trial included NH_3-N (relative measure, see chapter 2), NH_4^+-N, NO_3^--N and total-N.

Based on the initial measurements of various parameters (Table 3.3-1), wood mix windrows were predicted to compost more effectively than straw mix windrows. Moisture content and bulk density were comparable between the two materials and the wood mix had greater concentrations of inorganic nitrogen that could be used early in the process in the synthesis of decomposer microorganisms. The ratio of total C to total N in the wood mix was closer to the optimum value of 30 (Rynk, 1992) than it was in the straw mix; whether that ratio approximated the ratio of microbially available carbon to microbially available nitrogen was an important consideration in the comparison of the two materials. Wood carbon tends to be tied up in lignins which are less available than the cellulose carbon found in straw (Table 3.4-1). Low availability of the wood carbon would mean the effective C/N ratio was lower than the total C/N ratio and perhaps, depending on how low the availability, well below the optimum. Regardless of the microbial availability of the carbon in the straw, the C/N ratio was well below the optimum and, with close to twice the amount of nitrogen than the wood mix, higher losses of N from the straw mix were predicted.

Table 3.4-1 Dry matter composition of barley straw and wood shavings. (as percentage of dry matter) (Narasimhalu et al., 1998; Ward et al., 2000)

	Barley straw	Wood shavings
Hemicellulose	36.1	10.7
Cellulose	44.0	49.5
Lignin	0.7	29.0

Porosity and pH were other limiting factors predicted for the composting of the two

materials. Greater porosity would facilitate greater air flow, allowing for maintenance of

aerobic conditions, but would also facilitate vapour escape. The lower pH of the wood

residuals was predicted to be beneficial to the goal of nitrogen retention in its effect on

the ammonia-ammonium equilibrium.

In terms of the composting process, the methodology was straightforward. There were

no amendments to material leaving the feedlots and after windrow establishment, the

only maintenance of the piles was turning and a single incident of water addition. The

research was conducted without the economic constraints that may face operators,

however. The windrow turner is expensive machinery to operate and the turning

frequency was greater than would likely be used by feedlot operators. Nevertheless, the

methodology is valid because it investigates the possibilities for composting different

bedding materials. Given enough of a difference in quality between processes, as

revealed by research, the economic constraints may be mitigated.

Both materials displayed the high levels of microbial activity and associated

biodegradation related to effective composting (Table 3.3-1, Figures 3.3-1 and 3.3-2).

Temperatures well into the thermophilic range were recorded for all piles for extended

periods of time (adequate for destruction of seeds and pathogens (Rynk, 1992)) and there

were substantial reductions in mass and volume. Despite volume losses that were less

than the typical 50% (Rynk, 1992), the reductions observed from composting would

facilitate haulage of feedlot material substantially. With 85% of the mass reduction in

straw mix windrows accountable as losses of water, compared to 75% in the wood mix windrows, it appears that the wood mix windrows lost mass elsewhere, such as in the production and volatilization of CO_2. Despite losing less carbon than straw percent-wise, the wood mix lost more carbon mass-wise: ~1100kg for the wood mix and ~820kg for the straw mix.

End products of both materials were stable insofar as they would no longer self-heat and they had cured for longer than 21 days (CCME, 1996). Maturity tests for oxygen uptake and germination were not performed.

The straw mix lost a higher percentage of its initial N mass than the wood mix, suggesting that the availability of the straw's carbon was insufficient – given the straw's N content – to prevent N loss. Immobilization of available N in the straw was likely hampered by low availability (and/or low amounts) of C in the straw. The straw mix, however, was still higher than the wood mix in % N after composting. That wood mix compost was high in nitrate and low in ammonium and straw mix compost was low in nitrate and high in ammonium is important for a number of reasons. The high mobility of nitrate through most soils means that nitrate can reach plant roots more easily than cations such as ammonium, but also means that nitrate can be more easily lost through leaching than ammonium (Brady and Weil, 1996). Most plants grow best with approximately equal amounts of each ion (Brady and Weil, 1996). The wood mix compost would be high in available nitrogen easily taken up by plants, but nitrogen losses by leaching might pose a threat. The nitrogen in the straw mix compost would be less

likely to leach away, since ammonium is cationic and most soils are anionic, but less

mobility also means more difficult plant-uptake and excessive concentrations of NH_4^+

can lower pH and increase salinity enough to be phytotoxic (Malhi and McGill, 1982).

Ammonium will transform into ammonia under conditions of high pH and/or high

temperature. With temperatures comparable among all windrows (Figures 3.3-1 and 3.3-

2), pH was likely more important to this equilibrium. As could be expected due to its

higher pH (Figure 3.3-4), straw mix windrows volatilized more ammonia (Figure 3.3-11).

The dip in pH value of straw mix windrows that occurred early in the trial was not

observed for the wood mix windrows. Such a drop in pH early in the composting process

is typical, concurrent with the production of carbon dioxide and organic acids by early-

stage decomposers metabolizing readily available substrates (Rynk, 1992). That such a

drop was absent from the pH profiles of the wood mix windrows may reflect a situation

of less nutrient availability and less early-stage decomposition.

Early-stage accumulation of ammonium content reflects mineralization of nitrogenous

organic compounds (Figure 3.3-8). All windrows were similar in this regard because of

the similarity in manure content and the manure's readily available substrates. The

subsequent gradual decline of ammonium concentration occurs as NH_4^+-N is

immobilized, nitrifies or volatilizes as NH_3. The slightly higher concentration of

ammonium in the straw mix windrows by the end of the trial may be due to a retarded

maturation in the straw. Supporting this hypothesis are the nitrate accumulation data

showing a clear difference between wood mix and straw mix windrows. The relative

depletion of ammonium and accumulation of nitrate can be an index of compost maturity (Larney et al., 1998).

The differences between the surface region and the core region in concentrations of both ammonium and nitrate were as expected given the different conditions of the regions (Figures 3.3-6, 3.3-7, 3.3-9 and 3.3-10). The sharp drop in ammonium in the core of straw windrows after approximately 1000 h may have been due to increased ammonia volatilization at that time. The drop occurred just as pH levels increased and the equilibrium between ammonium and ammonia would have shifted towards the latter. No measurements of ammonia concentration were made after 1000 h, and by 1000 h ammonia emissions appear to be waning (Figure 3.3-11), but the volatilization decrease corresponds with the lowest values of pH for those piles (just prior to 1000 h). The decrease, then, may not have signified the end of a period of ammonia volatilization but a dip, to be followed by a period of higher rates.

That no similar drop in ammonium concentration was observed in the surface region of the same windrows could be explicable by the fact that the surface region is very shallow (0-203 mm). Surface material was dry, especially for the straw mix windrows on which a hard crust formed, and there would be little aqueous activity as would be required for the transformation of NH_4^+ to NH_3 (Eq. 1.2). Surface ammonium content, therefore, would be less affected by changes in pH and, as seen in Figure 3.3-9, ammonium concentrations in the surface layer would generally be lower than in the core.

The difference between surface and core regions of the wood mixes was pronounced for the nitrate content profiles (Figures 3.3-6 and 3.3-7). The gradual accumulation of nitrate in the surface layer of the wood mix windrows, from relatively early in the process, contrasts with the relatively late, but rapid accumulation in the core region. The apparent suppression of nitrification in the core, but not in the surface is likely due to temperature. The optimum temperature for nitrification is usually cited as being 30°C, with a cessation in nitrifying bacteria activity around 40°C (Malhi and McGill, 1982; Walden and Wright, 1995; Niemiera and Wright, 1987). Nitrate accumulation in the core of wood mix windrows began after approximately 2000 h of composting – the same time that temperatures fell below 40°C (Figures 3.3-1 and 3.3-2). The gradual accumulation of nitrate in the surface of the same windrows over the first 2000 h of composting suggests that temperatures were cooler than 40°C and nitrification was possible.

The difference between surface and core nitrate accumulation in the straw mixtures was not as pronounced as in the wood mixtures, despite similar changes in temperature over time for the two mixtures (Figures 3.3-6 and 3.3-7). This apparent lack of nitrification in the straw mix may have been due to a lack of oxygen in the core. In comparison to the surface region, the core region had slightly retarded nitrate accumulation, perhaps due to more compaction in the straw mix and the consequent loss of free air space.

Also of note in the straw mix core region, is a period of ammonium concentration increase between approximately 2500 h and approximately 3000 h (Figure 3.3-10). While ammonium concentrations in the wood mix were declining, likely due to

nitrification, ammonium concentrations in the straw mix were increasing. This situation of net mineralization of N species instead of net nitrification suggests that each mixture contained different microbial species between 2500 and 3000 h. Whether the reason for such a discrepancy in microbial populations between the mixtures was a lack of oxygen or another factor is unclear.

The significantly higher quantities of volatilized ammonia measured by the sorbers on the straw mix windrows were as expected based on the low C/N ratio and high pH of that material in comparison to the wood-based material. How the microbial availability of the substrates' carbon affected NH_3 volatilization is unclear. The C/N ratio of the wood-based material was higher than the C/N ratio of the straw-based material and closer to the ideal (Rynk, 1992) ratio of 30. On that basis, one could expect there to be little NH_3 volatilization from the wood mix as compared to the straw mix. But wood is associated with less available carbon because it is high in lignins, which are slower to decompose than the cellulose in straw. On that basis, the available C/N ratio is lower than measurements would suggest and one could expect there to be NH_3 volatilization. However, the fact that the wood mix volatilized significantly less ammonia than did the straw mix suggests that the carbon in the wood mix was not unavailable to the extent that it would prevent substantial microbial activity. The balance between N immobilization and mineralization in the wood mix inhibited NH_3 volatilization to a greater extent than in the straw mix. The small particle size and large surface area of the wood residual (a mixture of bark, post peelings and sawdust) may have contributed to increased carbon availability.

Overall, the objective of following the nitrogen dynamics during composting of the two materials was adequately met. Profiles of sorber ammonia concentration, ammonium and nitrate contents complemented each other and were in agreement with published theory. As predicted, the straw mix volatilized more ammonia than the wood mix and based on nitrate and ammonium profiles, the wood mix windrows composted more effectively.

The early cessation of ammonia measurements relative to the rest of the trial created difficulties in analysis of volatilization over time. Extension of that sampling period would have been beneficial to this study. Germination and growth trials using each compost is recommended as an area for further research, as is investigation into the time that various manure/bedding recipes take to reach maturity.

3.5 Conclusions

Temperature profiles resembled the typical temperature profile (Figure 1.2-1) and proceeded through the typical stages of mesophilic, thermophilic and cooling (Figures 3.3-1 and 3.3-2). This and substantial reductions in mass and volume indicated effective composting for both treatments. The lower C/N ratio and higher pH of the straw and manure mixtures led to greater N-losses through ammonia volatilization. Less depletion of ammonium, less accumulation of nitrate and less carbon mass loss in the straw suggests that straw compost matured to a lesser degree than wood compost.

Despite losing more than double the mass of nitrogen that wood windrows lost, straw windrows after composting still had a greater final mass and mass percentage of nitrogen.

Inorganic nitrogen present in the final straw mix compost, however, was more ammonium than nitrate, while in the final wood mix compost the situation was the opposite.

From a perspective of maximizing compost N content, straw bedding in feedlots appears to be a better choice. The compost product is richer in nitrogen and hauling costs and application rates would be lesser than with wood residuals-based compost. From a perspective of minimizing N losses and composting quickly and effectively, with less risk to environmental well-being, wood chips appear to be the superior bedding.

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CHAPTER 4

Performance of a simulation model describing ammonia

volatilization during windrow composting

4.1 Introduction

Composting is an effective treatment method for converting organic by-product, such as

manure, into a valuable resource such as a soil amendment with fertilizing qualities.

How valuable the compost may be in terms of its nutritive value, however, depends on

the extent of nutrient retention during composting. Nitrogen (N) in particular is an

important compost nutrient that can be lost during the composting process in large

measures. While N may escape as an oxide of nitrogen (NO_x) or in leachate (NO_3^-), by

far the greatest amount of N escapes the composting system by way of ammonia (NH_3)

volatilization (Safley et al., 1983; Eghball and Power, 1994). Liang (2000) developed a

mathematical model to simulate aerated in-vessel composting processes with the

objective of identifying strategies for nitrogen retention.

Model input included values in kilograms per kilogram of dry matter for volatile

substances, non-volatile substances, water content, etc. Flows between variables in each

time step were in kg (kg d.m. h)$^{-1}$. A flowchart for the simulation model is presented in

Figure 4.1-1. Temperature was defined as a state variable to simulate temperature

changes due to the changes in the mixture's heat content. Water content was also defined

as a state variable to simulate water generation by bioreaction and water removal by
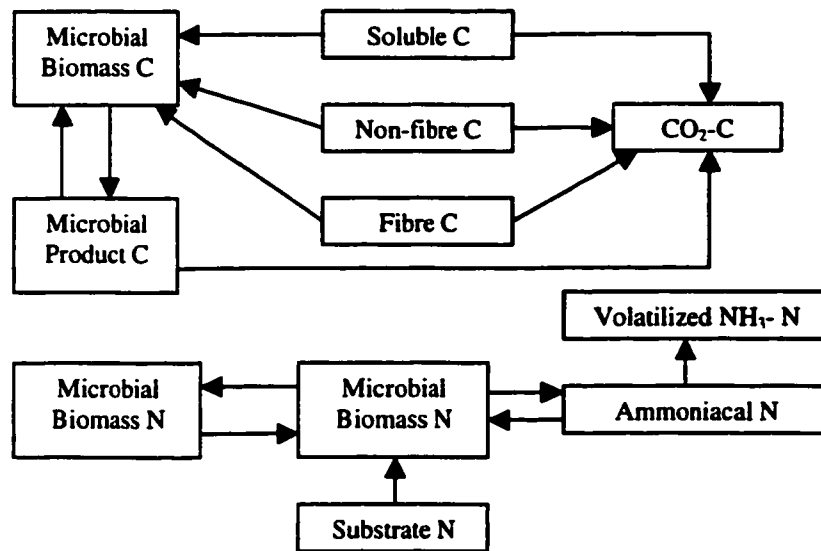
evaporation (Liang, 2000).

Microbial Biomass C

Soluble C

Non-fibre C

CO_2-C

Microbial Product C

Fibre C

Volatilized NH_3- N

Microbial Biomass N

Microbial Biomass N

Ammoniacal N

Substrate N

Figure 4.1-1 Flow chart of C and N transfers in the simulation model. (Adapted from Liang, 2000)

Carbon sources were divided into substrate C, microbial biomass C, microbial products C and respired CO_2-C. N sources included aqueous ammoniacal N, cumulative NH_3-N, microbial biomass N and microbial products N. Complex C was also divided into soluble C, non-fiber C and resistant/fiber C.

This study tested Liang's (2000) model against results from a windrow composting experiment (Chapter 3). Characterizations of the initial materials used in the experimental trials were used as the model's initial conditions. Observed results from the field were compared with model outputs and the model's simulative powers were assessed.

The objectives of the study were to assess the extent to which the model's predictions were in agreement with observed windrow composting data and to shed light on where improvements to the model could be made for simulating windrow composting.

4.2 Model application

A number of simple modifications of the model's program were made to account for general differences between vessel and windrow composting as well as some conditions specific to the experimental trials. Windrows lack the constant forced aeration and temperature feedback aeration featured in the vessels for which the program was developed. To account for this lack, program commands concerning the temperature feedback aeration system were deleted. Constant aeration in the vessels was reflected in the model's program as an airflow rate of 0.02 kg air/kg DM (dry matter). The value of the airflow rate variable was lowered to 0.0025 kg air/kg DM for this study to describe the convection aeration of the windrows. Convection airflow through the windrows was thought to be very low based on the emergence of gases typical to anaerobic conditions within half an hour of turning (Hao et al., 2000). Several airflow rate values were considered and 0.0025 kg air/kg DM was chosen on the basis of close agreement between the resulting temperature profiles and temperature profiles from the windrow experiment. Windrow turnings were treated as hour-long periods of heavy aeration in the program with the airflow rate set at 0.2 kg air/kg DM – the same as the temperature feedback aeration system in the vessels, which was 0.2 kg air/kg DM (Liang, 2000).

Linear equations were inserted into the model's program to describe mean daily ambient temperature and pile volume – both of which were considered to be constant in the model. Volume equations were calculated using initial and final values. The ambient temperature equation was the line of best fit from the field data.

The number of simulated hours was increased from 200 to 4420 and time-dependent conditional operations were accordingly adjusted. The program was further altered to reflect the windrow experiment's water addition at 480 h (calculated to adjust all windrows to 55% moisture content), by having all moisture contents change to 55% (wet basis) at that time.

The calculations of initial parameter values for the four windrows described in Chapter 3 were done as described by Liang (2000), and are summarized in Table 4.2-1. Table 4.2-2 presents the parameter values entered into the model for each of four simulations run. Soluble C content was not measured and Liang's (2000) assumed value of 0.02 kg/kg DM generated temperature data that appeared to overestimate early substrate availability. A value of 0.01 kg/kg DM generated temperature data more consistent with observed data and 0.005 kg/kg DM was selected for use in wood mixture simulations to account for the lower availability of carbon in wood compared to straw.

Table 4.2-1 Calculations of initial parameter values

Parameter	Calculation
Ammoniacal N	30% of total N
Non Fiber N	70% of total N
Non Fiber C	4*(Non Fiber N)
Fiber C	Total C – Non Fiber C – Soluble C
Ash, Volume, Mass, Moisture, pH	Measured

Table 4.2-2 Characterization values for model input

Parameter	Windrow A	Windrow B	Windrow C	Windrow D
Total mass (kg)	13746	15964	13689	16014
Dry mass (kg)	5558	6501	5562	6269
Ash *	0.1759	0.4024	0.1475	0.4902
Volume (m^3)	40	41	43	40
Water*	1.473	1.456	1.461	1.554
pH	7.13	8.39	6.85	8.31
Soluble C*	0.005	0.01	0.005	0.01
Fiber C*	0.413	0.270	0.402	0.259
Non-fiber C*	0.0358	0.0568	0.0336	0.0549
Ammoniacal N*	0.00384	0.00609	0.00360	0.00588

*units: kg/kg dry mass

4.3 Results

Figures 4.3-1 to 4.3-4 present comparisons of experimental and simulated temperature profiles. Overall, the simulated profiles provide a close approximation of the experimental ones. The changes in windrow temperature due to the turnings were reflected clearly in all profiles. In all comparisons, the model predicted peak temperatures that were higher and occurred earlier than were observed in the field. Peak simulated temperatures were slightly over 70°C, occurring within the first week, while peak experimental temperatures were up to 1000 h later and between 60 and 65°C. Simulated temperatures declined steadily from their early peak, whereas the higher experimental temperatures persisted for longer periods of time. Following the reheating associated with turning events, temperatures, for the most part, appear to have cooled more rapidly in the experiment than in the simulation. For wood mixtures, simulated and experimental temperatures drop out of the thermophilic zone (>40°C) at approximately the same time; but for straw mixtures, the simulated profiles re-enter the mesophilic zone (<40°C) before the experimental profiles.

The loss of moisture content with time was smoother in the simulation than in the experiment (Figures 4.3-5 to 4.3-8), but there was close agreement between the simulated and experimental data in terms of overall trends. Simulation trials featured less overall moisture content loss, with final moisture content values being in the range of approximately 10% to 20% higher in the simulations. The water addition at 480 h – intended to bring all windrows up to 55% moisture – fell short of the target moisture content in all windrows.
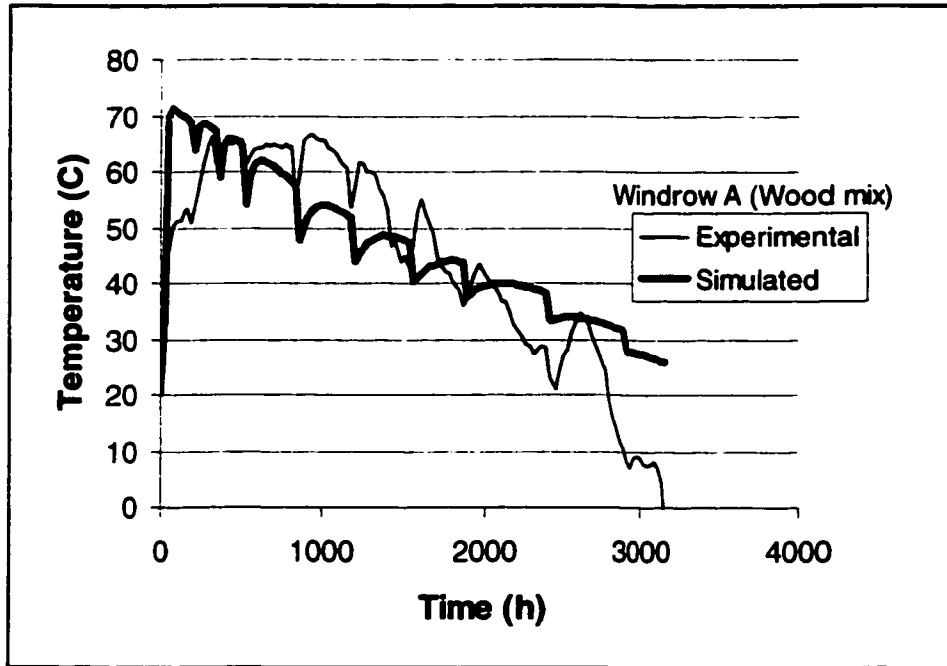
Figure 4.3-1 Comparison of experimental and simulated temperature profiles for windrow A (wood mix).
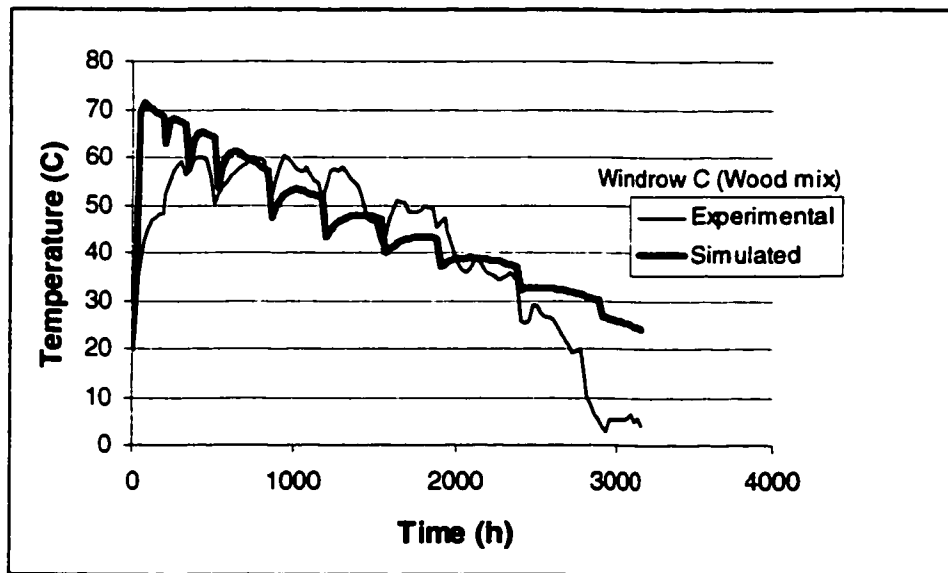

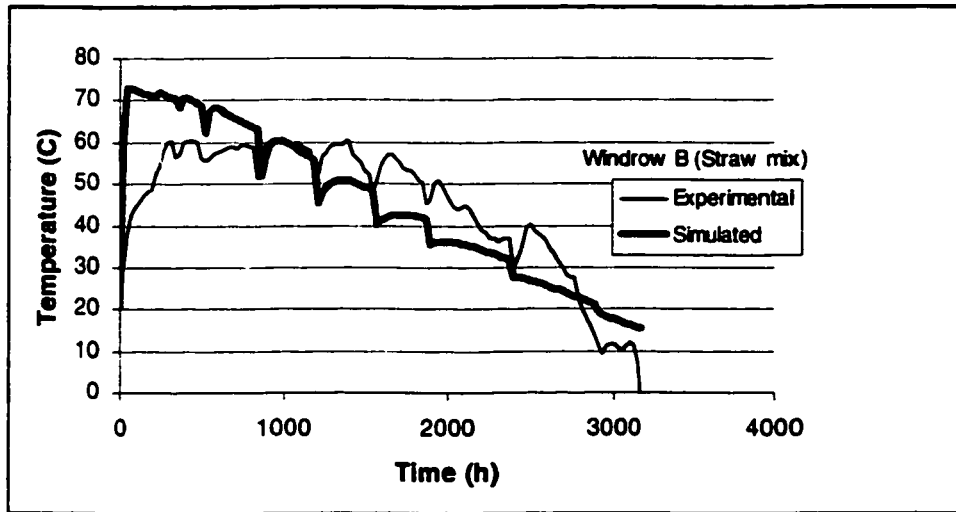**Figure 4.3-2** Comparison of experimental and simulated temperature profiles for windrow C (wood mix).

Figure 4.3-3 Comparison of experimental and simulated temperature profiles for windrow B (straw mix).
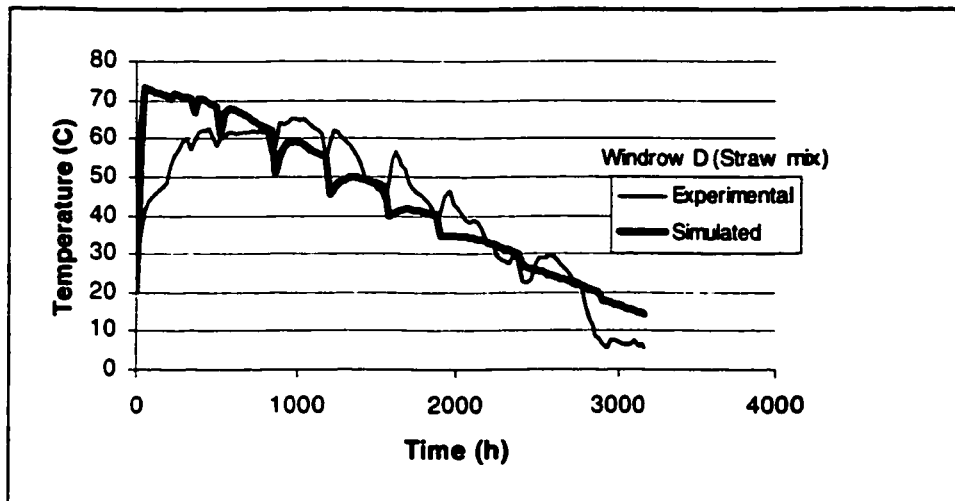

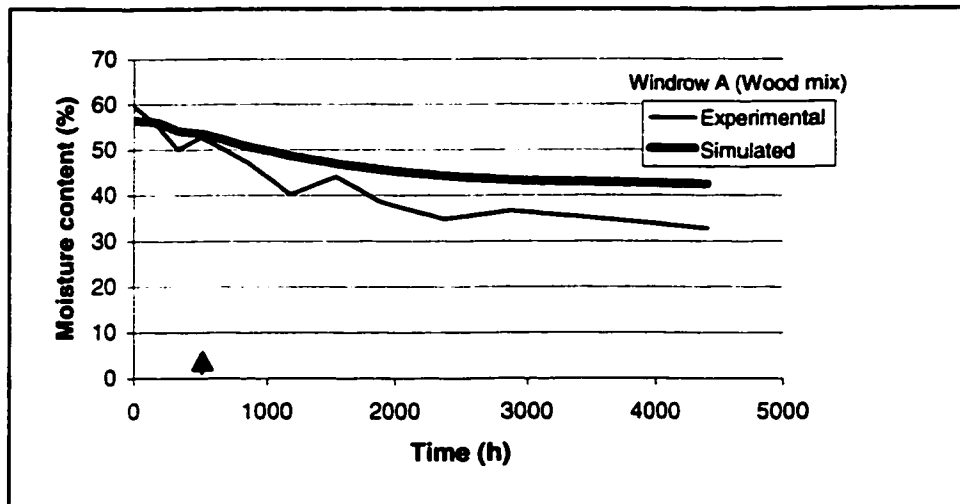**Figure 4.3-4** Comparison of experimental and simulated temperature profiles for windrow D (straw mix).

Figure 4.3-5 Comparison of experimental and simulated moisture content profiles for windrow A (wood mix). Arrow indicates time of water addition.
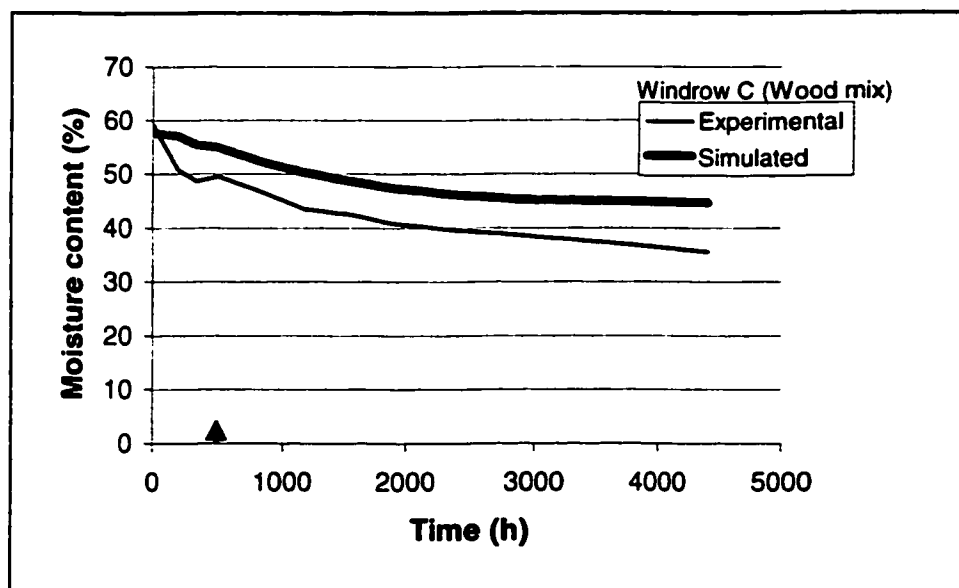

Figure 4.3-6 Comparison of experimental and simulated moisture content profiles for windrow C (wood mix). Arrow indicates time of water addition.
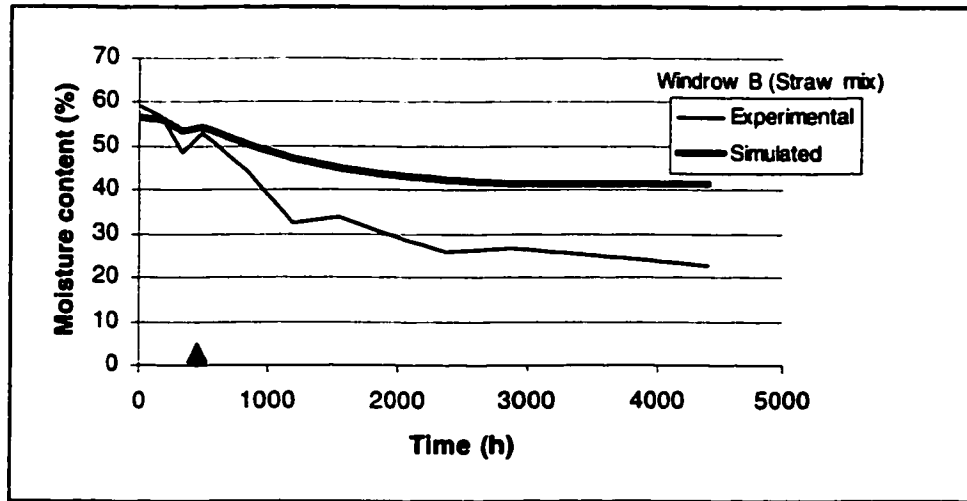
Figure 4.3-7 Comparison of experimental and simulated moisture content profiles for windrow B (straw mix). Arrow indicates time of water addition.
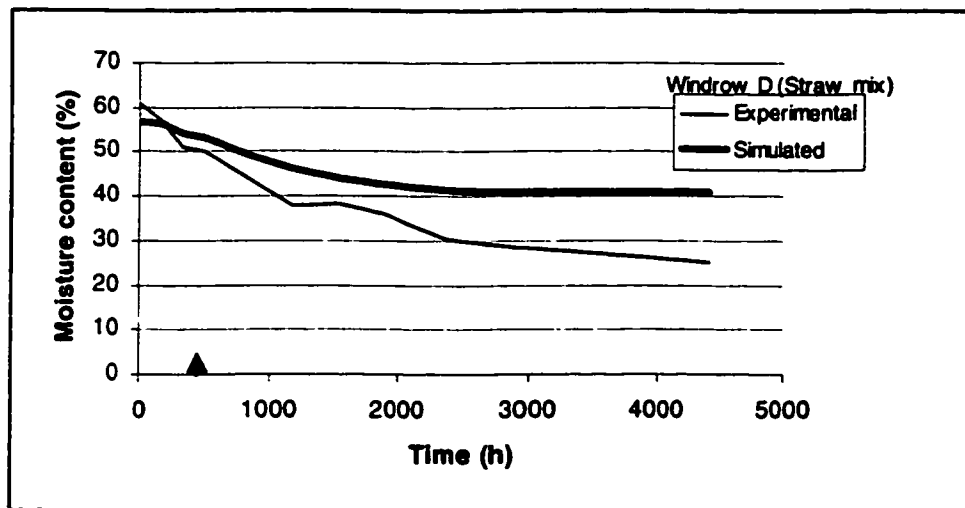

Figure 4.3-8 Comparison of experimental and simulated moisture content profiles for windrow D (straw mix). Arrow indicates time of water

As discussed in Chapter 2, the ammonia concentration measurements taken by the acid sorbers were not intended to give an accurate measure of ammonia flux, but rather a relative measure. Simulated ammonia concentration values were far greater than experimental values (Figures 4.3-9 to 4.3-12) because the simulation presents ammonia concentration in the air leaving the windrow, rather than concentration in the sorber liquid.

The concentration profiles predicted by the model followed similar relative trends to the observed ammonia concentration profiles. Straw mix windrows in both experimental and simulated trials had higher ammonia concentrations than wood mix windrows. A convergence between straw mix and wood mix NH_3 emissions occurred between 200 and 400 h in both simulated and experimental trials. The ammonia flux over the first 200h in the simulated data was elevated relative to the experimental profiles.

Table 4.3-1 Comparison of simulated and experimental N loss

Windrow	Simulated NH_3-N lost (kg)	Observed total N lost (kg)
A	55.9	7.8
B	90.0	40.5
C	59.0	20.3
D	95.9	30.9

Table 4.3-1 presents ammonia nitrogen losses predicted by the model and total nitrogen losses observed experimentally. Simulated NH_3-N losses range from being 1.6 to 5.9 times greater than experimental total N losses.
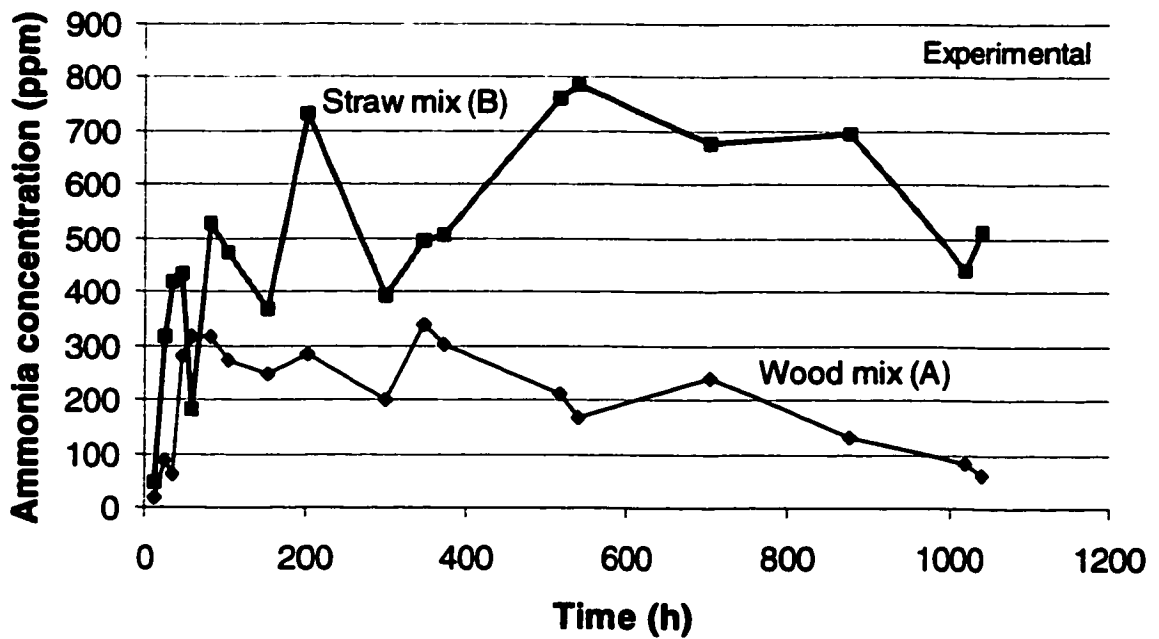
Figure 4.3-9 Experimental sorber ammonia concentration profiles for windrows A and B.
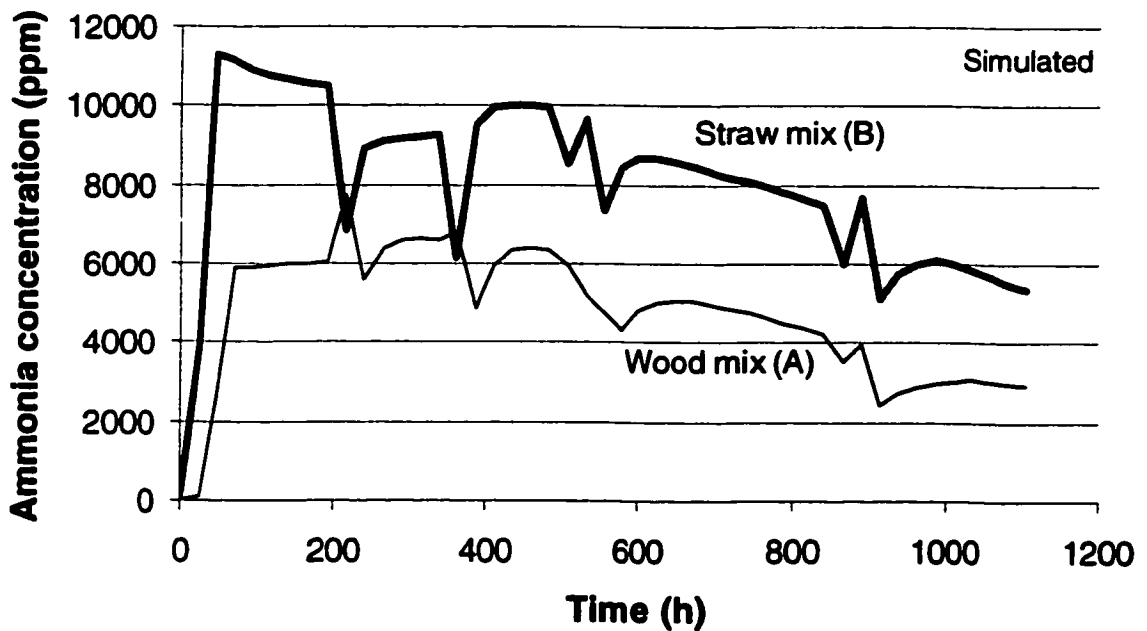

Figure 4.3-10 Simulated exhaust air ammonia concentration profiles for windrows A and B.
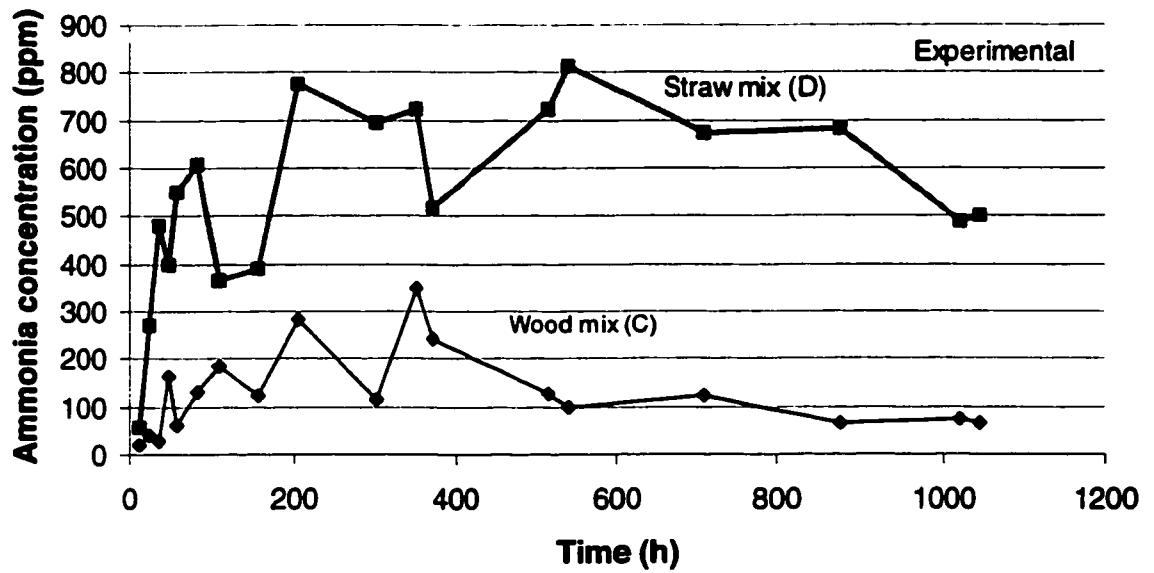
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Figure 4.3-11 Experimental sorber ammonia concentration profiles for windrows C and D.
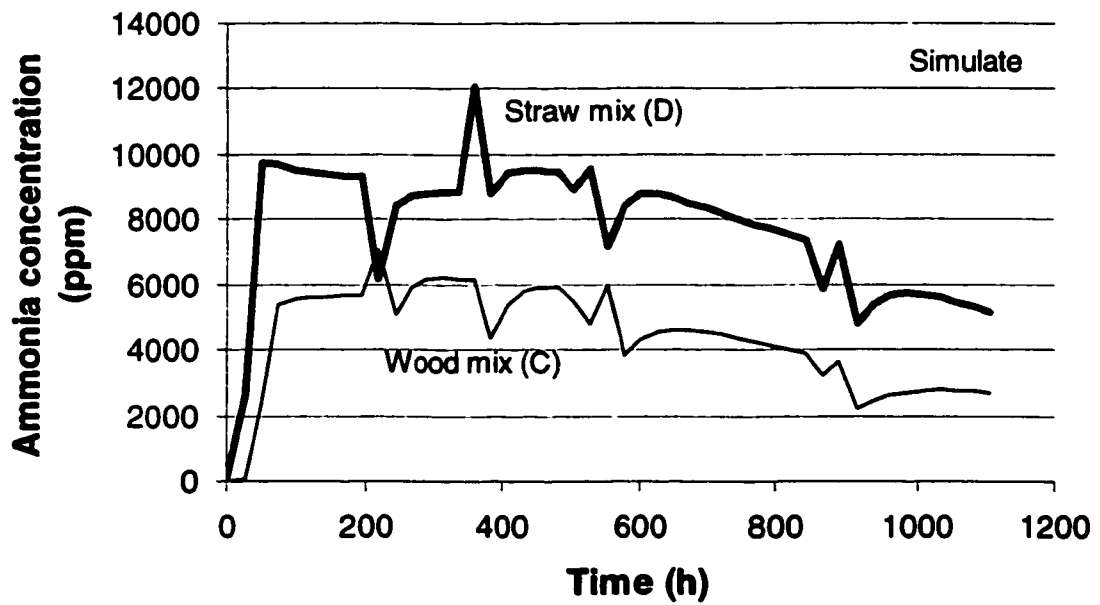

Figure 4.3-12 Simulated exhaust air ammonia concentration profiles for windrows C and D.

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Simulated pH profiles were different than experimental pH profiles in that the model predicted an initial increase in pH value while the experimental data feature an initial decrease (Figures 4.3-13 to 4.3-16). Both simulated and experimental data feature pH values leveling off, but the leveling occurs sooner in the simulated data than in the experimental data and the final pH values in the simulation were higher than in the experiment by up to one pH unit.

Table 4.3-2 presents the total mass loss from experimental and simulated trials. Simulated mass loss was 22% less than experimental mass loss for both wood mixtures and 23% less than experimental mass loss for both straw mixtures.

Table 4.3-2 Comparison of observed and simulated mass loss as percent

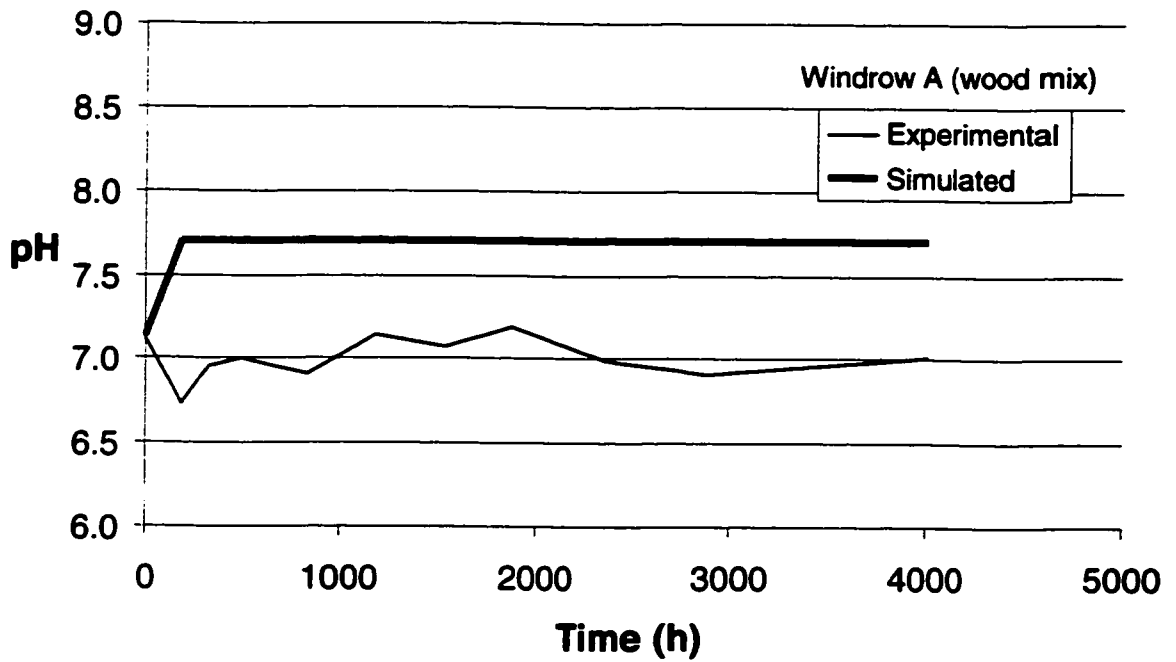|	Windrow A Wood mix	Windrow B Straw mix	Windrow C Wood mix	Windrow D Straw mix
Observed total mass loss (%)	57	61	67	57
Simulated total mass loss (%)	35	38	34	38

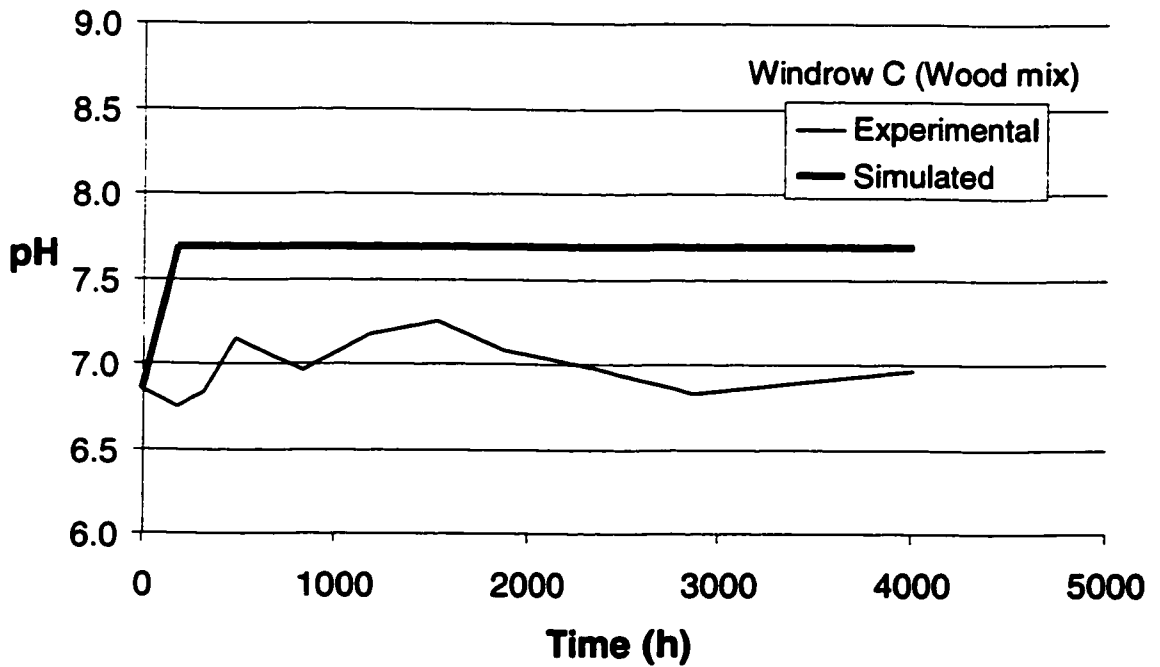**Figure 4.3-13** Experimental and simulated pH profiles for windrow A (wood mix).

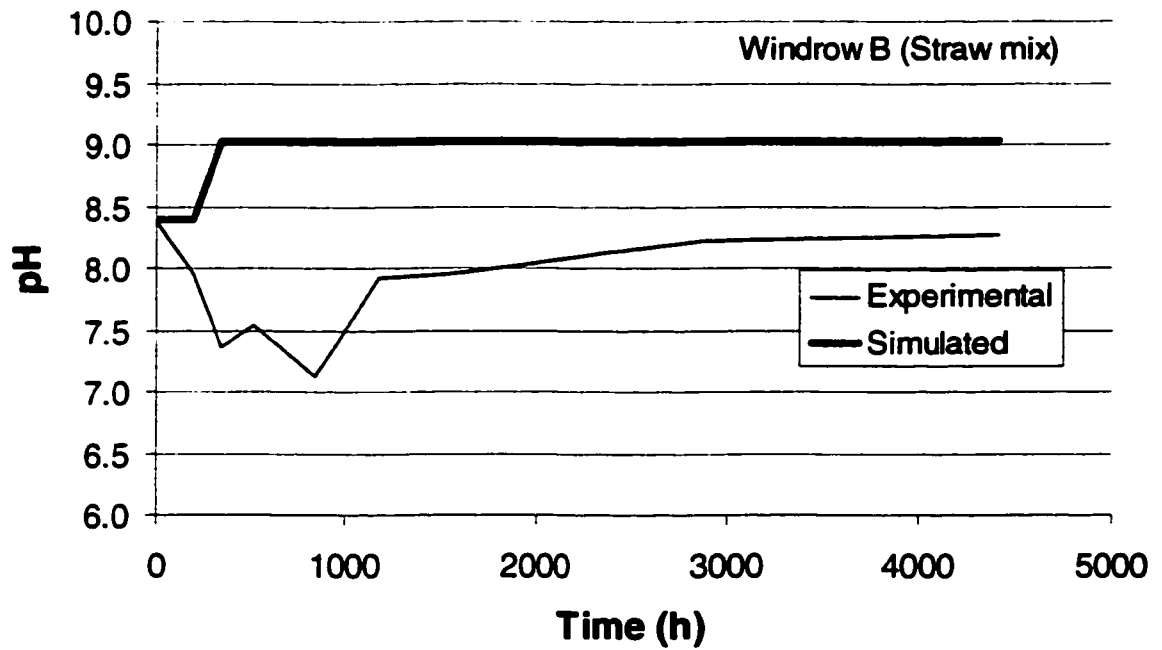**Figure 4.3-14** Experimental and simulated pH profiles for windrow C (wood mix).

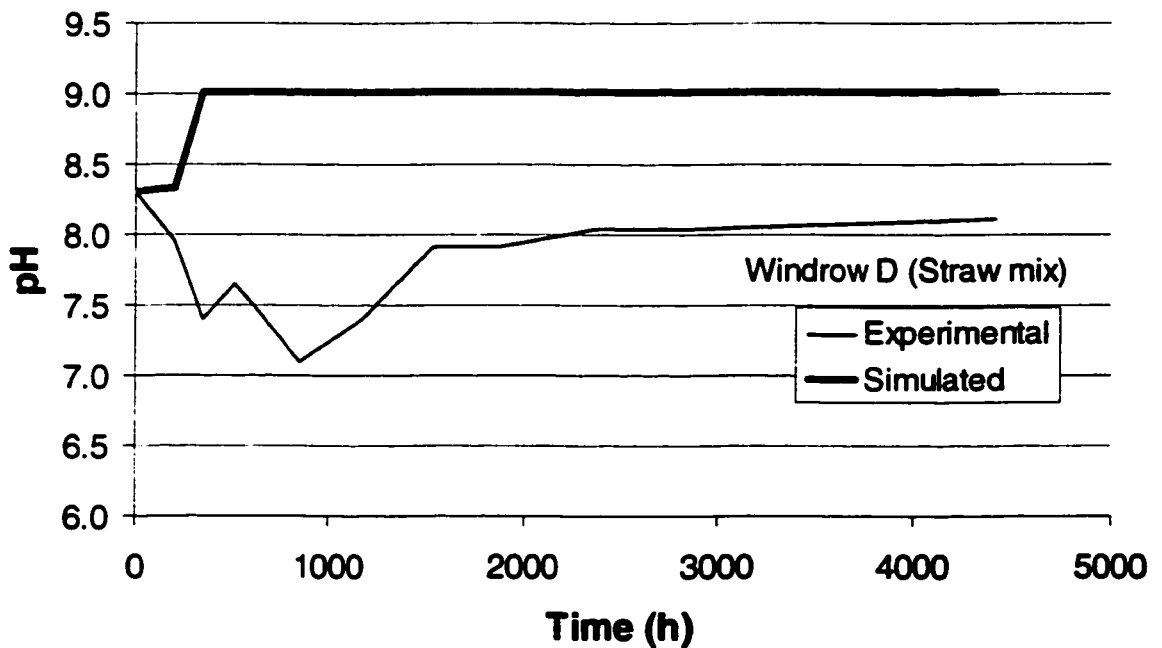**Figure 4.3-15** Experimental and simulated pH profiles for windrow B (straw mix).

Figure 4.3-16 Experimental and simulated pH profiles for windrow D (straw mix).

4.4 Discussion

4.4.1 Temperature

Although temperature data were used to "calibrate" the model, the degree to which simulated temperature curves approximated the temperature curves generated from the experimental data (Figures 4.3-1 to 4.3-4) indicates that the model provided a good representation of overall microbial activity. Drops in temperature associated with turning events are clear in both sets of profiles and are of approximately the same magnitude.

The higher initial temperatures seen in the simulations reflect a discrepancy between simulated and actual composting in terms of microbial metabolism. The early regions of the simulated curves reflect a level of microbial activity that was not reflected in the curves generated from the experimental data. That the simulated curves are much steeper than the experimental curves initially, suggests that the rate of microbial growth in the model is greater than in the actual windrows. That the peaks of the simulated curve are five to ten degrees greater than the experimental curves' peaks suggests that the model features faster microbial metabolism, greater microbial populations and/or a more available substrate. Simulated temperature is a reflection of the interactions among settings for these factors within the model. Liang (2000) discussed the need for further research into parameter values such as microbial death rate, heat transfer coefficient and maximum growth rate on non-fiber C substrates, all of which could influence the simulations' temperature peaks and rates of initial heating.

The experimental data for all four windrows suggest a temperature maximum in the range of 60 to 65°C approximately. Experimental temperatures fluctuated within this range for prolonged periods of time (~1000 h), creating a plateau in the temperature curves. Simulated data feature no such plateau in temperature. Simulated temperature curves decline steadily from their early respective peaks, suggesting that the model accounts for no temperature maximum in the 60 to 65°C range. In the model, the assumed temperature effect on decomposition rate features maximal activity from 30 to 55°C and a linear decline to zero activity at 75°C (Liang, 2000). At 65°C, where the experimental data suggest a metabolic maximum, microbial metabolic activity in the model has only dropped to 50%.

The steadier, more linear decline of the simulated temperature data suggests static conditions and steady degradation of the substrate over time. The simulated curves fit with conditions of metabolic activity, as represented by temperature, decreasing linearly as substrate is degraded. The bowed curves of the experimental data, with their more abrupt drop in activity/temperature suggest that conditions become less optimal for metabolic activity at a certain stage, perhaps with the exhaustion of a particular class of substrate, or the re-colonization of the substrate by mesophilic organisms. While the slopes of the simulated temperature curves remain approximately the same in thermophilic and mesophilic temperature zones, the slopes of experimental temperature curves become steeper as temperatures fall below 40°C (leaving the thermophilic zone for the mesophilic zone) (Figures 4.3-1 to 4.3-4). The comparisons of simulated temperature

curves with experimental curves suggest that the model overestimates maximum rates of microbial metabolism and mesophilic activity levels.

4.4.2 Moisture content

Despite temperatures of simulated and experimental trials being similar (Figures 4.3-1 to 4.3-4), simulated moisture content values were consistently higher than observed values. Most likely, the discrepancy was due to differences in relative humidity of aeration air between the model and the experiment. The experimental site is relatively hot and dry compared to the laboratory conditions under which the model was developed. The losses in moisture content at the site could be expected to exceed the predictions of the model. Also, because of the difference in method of aeration between the laboratory (forced ventilation) and the field (windrow turning) the airflow rate settings in the model may not have been accurate reflections of the air exchange that occurred in the field and simulated moisture loss was underestimated.

Nevertheless, the rate of moisture loss, as suggested by the general shape of the curves, was in good agreement between the experimental and simulated data.

4.4.3 Mass

The differences between simulated and experimental moisture content data (Figures 4.3-5 to 4.3-8) explain much of the differences between simulated and experimental mass data (Table 4.3-2). Another contributing factor to the greater mass losses observed in the field might be the prolonged period of peak heating displayed in the experimental but not

simulated data (Figures 4.3-1 to 4.3-4). Longer exposure to high temperatures (>55°C) would correspond with greater extents of degradation and greater moisture and mass loss.

4.4.4 pH

Calculation of pH in the model is based on the multi-solute NH_3-CO_2-H_2O aqueous system (Liang, 2000). The model's program requires input of the initial pH of the material, but this value and the model's calculated pH value are independent of each other. These values are reconciled gradually and arbitrarily over the course of the trial. This method of calculation may contribute to the discrepancies observed between simulated and experimental pH data. That all simulated pH profiles hold constant after an initial increase (the reconciliation between initial measured pH and model-calculated pH) suggests that the model would calculate a higher pH for the starting material based on its representation of the substrate. This explains the conspicuous absence of an initial pH drop in the simulated pH profiles. Such a drop did occur in all the experimental trials and is due to the release of CO_2 and organic acids into the system.

4.4.5 Ammonia (NH_3)

The relative patterns of ammonia emission as measured by acid sorbers (Chapter 2) and simulated by the model were in good general agreement. The model successfully predicted that the higher rates of ammonia emission would be from the straw mixture and not the wood mixture. Early NH_3 emissions for straw and wood mixtures were exaggerated in the simulations, in agreement with the exaggerated temperatures in the simulations for that period. Differences between the mixtures in late NH_3 emission were

underestimated. These discrepancies can be partially explained by the apparent overestimation of microbial growth in the model, as mentioned in the discussion of temperature, above. Another contributing factor to the simulations' overestimation of ammonia loss from the composting system was that ammonia emission in the model is closely related to aeration (Liang, 2000). Difficulties in representing the air exchange involved with turning a windrow in terms of the forced aeration framework of the model would no doubt lead to inaccuracies in ammonia loss prediction.

The discrepancies between simulated and observed losses in N mass (Table 4.3-1) reflect an overestimation of NH_3 flux in the model. Temperature (Figures 4.3-1 to 4.3-4) and pH (Figures 4.3-13 to 4.3-16) were both higher in the simulated data than the observed data. Furthermore, laboratory trials around which the model was developed were considerably shorter than field trials, lasting only 200 h as compared to 4000+ h for simulated field trials. Conditions of increased pH and high temperature in composting are conducive to increased ammonia volatilization (Korner and Stegmann, 1998). The model's predicted high values for temperature and pH, and the extended simulation time, would contribute in explaining the model's overestimate of ammonia losses.

4.5 Recommendations

Refinements to the model to simulate large-scale, outdoor, windrow composting more closely would make the model a practical tool for composting operations such as feedlots. The dissimilarities in temperature curves between the model and the field suggest that a more accurate representation of microbial metabolic activity could be implemented,

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although the effect on the overall shape of the temperature curve, if any, of discarding the temperature feedback aeration features of the model is uncertain. Observed differences in the rate of temperature change between thermophilic and mesophilic temperature zones not reflected in the simulations stress the need for further development in terms of later-stage composting and curing.

Much of the error associated with estimation of ammonia emission in the model was likely due to an inexact representation of processes that affect pH. Liang (2000) discussed the possibility of factors that were not accounted for in the model such as organic acids generated in early composting stages or unknown buffering chemicals in original mixtures influencing pH. A more comprehensive understanding of pH dynamics would contribute to the accuracy of predicted NH_3 volatilization.

Accounting for variable relative humidity in the model would contribute to a more precise simulation of moisture losses. The comparatively hot, dry air of the study site was not represented in the model and simulated moisture losses were inevitably underestimated.

Finally, "user friendliness" would be an important consideration if the model were to be developed into a practical tool. Input fields for the various variables used in characterizing material to be composted and charted outputs would facilitate model operation greatly.

4.6 Conclusions

Close agreement was observed between simulated and experimental results in the areas of temperature, relative ammonia emission and rate of moisture loss. This suggests that the model could provide valuable assistance in predicting composting processes, especially nitrogen retention. Given the many differences between laboratory in-vessel composting and outdoor windrow composting, and the extension in simulated composting time by more than 20-fold, the accuracy of the simulated results warrant further development of the model.

4.7 References

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CHAPTER 5

Synthesis

5.1 Summary

Various aspects of nitrogen (N) retention during the composting of feedlot manure with either wood processing residuals or straw bedding were investigated. First, inexpensive, passive, ammonia (NH_3) sorbers were evaluated for their ability to give relative measures among windrows of ammonia escape. Sponges charged with phosphoric acid and glycerol were housed within inverted 4 L pails and exposed to windrow exhaust air for set periods of time. The concentration of accumulated volatilized NH_3-N was taken as a relative measure of NH_3 flux. Second, the composting of straw-based and wood-based windrows of feedlot manure were compared, with specific attention paid to N-retention. Samples were taken just prior to periodic windrow turning and analyzed to give characterizations of the various materials. And third, experimental data from the first and second components were compared to simulated data generated by a mathematical model developed by Liang (2000). Input into the simulation model consisted of material-characterizing variables based on a number of parameters. The model partitioned substrate into several groups based on chemical components and decomposition rates. Utilized model output consisted of simulated data for a composting trial including profiles for temperature, ammonia flux, moisture content, pH and mass. Model accuracy was evaluated and recommendations for refinement were made.

5.2 Conclusions

The sorbers were deemed to be inexpensive, practical and available, and capable of effectively estimating relative NH_3 emission between different composting materials. Sorbers consistently discerned a significant difference in NH_3-N concentration between wood residuals-based and straw-based windrows. No significant difference in ammonia nitrogen concentration between tops and sides of windrows was detected, likely because the sorbers' resolution was inadequate. The lack of a significant difference in NH_3-N concentration among sponges exposed for 12, 24 or 48 h suggested a time limitation to effective ammonia sorbing of under 12 h. A notable limitation of the methodology was the extensive time requirement.

In the comparison of wood residuals and straw as bedding material for composting with beef feedlot manure, lower carbon-to-nitrogen (C/N) ratios and higher pH in the straw mixtures was associated with greater ammonia nitrogen losses. After composting for equivalent lengths of time, straw-based compost was less mature than wood residuals-based compost, having less depletion of ammonium, less accumulation of nitrate and less carbon-mass reduction. Despite straw-based mixtures having lost more nitrogen – both in total and as a percent of dry mass – straw-based mixtures were still higher in total N after composting. Wood residuals-based mixtures reached compost maturity sooner than straw-based mixtures, and retained nitrogen to a greater extent proportionally, but had less nitrogen to retain. Inorganic nitrogen in wood residuals-based composts was predominantly nitrate nitrogen whereas in straw-based composts the inorganic N was predominantly ammonium nitrogen. The wood mix compost would be high in available

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nitrogen, easily taken up by plants, but nitrogen losses by leaching pose a threat. The nitrogen in the straw mix compost would be less likely to leach away, since ammonium is cationic and most soils are anionic, but less mobility also means more difficult plant-uptake and excessive concentrations of NH_4^+ can lower pH and increase salinity enough to be phytotoxic (Malhi and McGill, 1982). Given the apparent immaturity of the straw mix compost, however, the distribution of ammonium and nitrate nitrogen may have changed with additional curing time.

The evaluation of the composting simulation model revealed close agreement between simulated and observed data for temperature, relative ammonia emission and rate of moisture loss. Differences between laboratory in-vessel composting, around which the model was developed, and windrow composting done in the field led to expected disagreement between simulated and observed data. The model, however, was deemed to have potential for being a valuable tool in predicting characteristics of composting processes for various materials. For further development of the model, refinements to several areas are recommended. Some discrepancy between overall temperature curve shapes for simulated and observed data suggested that microbial metabolic activity in composting could be represented in the model more precisely. The overestimation of ammonia losses predicted by the model was likely contributed to by the overestimation of pH. The inclusion in pH calculations of factors such as organic acids generated in early stages of decomposition is recommended. Overestimation by the model of moisture losses was thought to be due to differences in relative humidity between laboratory and field air conditions. Accounting for the relative humidity of aeration air in the model

could help mitigate these disagreements. Increased user friendliness is also

recommended as a refinement to the model.

5.3 References

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