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A PROCESS-BASED NUTRIENT MODEL FOR THE BEDDED MANURE PACK OF CONFINED BEEF SYSTEMS

BY

FEROUZ Y. AYADI

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South Dakota State University

2015

A PROCESS-BASED NUTRIENT MODEL FOR CONFINED BEEF SYSTEMS

This dissertation is approved as a creditable and independent investigation by a candidate for the Doctor of Philosophy in Agricultural, Biosystems, and Mechanical Engineering degree and is acceptable for meeting the dissertation requirements for this degree. Acceptance of this does not imply that the conclusions reached by the candidate are necessarily the conclusions of the major department.

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ABBREVIATIONS

Δ	Time step, h
A	surface area, m^2
a	line of regression intercept
b	line of regression slope
BP	bedded manure pack
c	concentration, g kg^{-1}
CO_2	carbon dioxide
CH	methane
d	depth, cm
DM	dry matter (%)
E	emission, kg m^{-2} h^{-1}
Ev	evaporation, kg m^{-2} d^{-1}
F	ammonia fraction of TAN
FB	feces/bedding mixture
GHG	greenhouse gases
H	Henry constant
H	height, m
IFSM	Integrated Farm System Model
J	flow, cm d^{-1}
K	overall mass transfer coefficient
K_M	Michaelis-Menten constant, kg N m^{-3}

L	layer
MC	moisture content, %
N	nitrogen
N_2	nitrogen gas
NAP	short-term nitrification activity potential
NH_3	ammonia
NO	nitric oxide
NO_2	nitrogen dioxide
NO_2^-	nitrite
NO_3^-	nitrate
N_2O	nitrous oxide
NH_3-N	Total mass of nitrogen in ammonia form
NH_4-N	Total mass of nitrogen in ammonia and ammonium forms
NMSE	Normalized mean square error
pH	negative log of hydrogen ion concentration
r	correlation coefficient
T	temperature, K (unless otherwise stated)
TAN	total ammoniacal nitrogen, kg m^{-3}
TN	total nitrogen
TP	total phosphorus
TK	total potassium
v	velocity, kg h^{-1}

V	Volume, m^{-3}
W	water mass, kg
wk	week
ww	wet weight, kg

Subsripts

0	Initial
ρ	density (g mL^{-1})
AT	acid traps
act	actual
BP	bedded manure pack
Ex	excess
FB	feces/bedding mixture
L	Layer
NA	natural abundance
Sl	slurry
t	Time
TAN	total ammoniacal nitrogen
TK	total potassium
TN	total nitrogen
Tot	total
TP	total phosphorus

U	urine
unsat	unsaturated
WEP	water-extractable phosphorus
wk	week

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ABSTRACT

A PROCESS-BASED NUTRIENT MODEL FOR THE BEDDED MANURE PACK OF CONFINED BEEF SYSTEMS

FEROUZ Y. AYADI

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Manure management is of growing concern for beef cattle producers and the general public. The overall objective of this research was to develop a process-based model that predicts concentration and gaseous emission from the bedded manure pack of a confined beef cattle system, with respect to different bedding material, manure storage time, and ambient temperature. The model incorporated the data collected in three experiments designed to understand transformations and processes occurring in the bedded pack.

The first study evaluated the source of volatilized ammonia nitrogen from beef cattle manure. Isotope ratio mass spectrometry was used to determine the origin of aerial ammonia nitrogen losses (urine or fecal material) from the relative isotopic abundance of nitrogen in the ^{15}N -labeled slurry mixture. On average 84% of total ammonia nitrogen losses originated from the urine portion and were highest during the first two to four days, when fresh material was added.

The second and third experiments were conducted to determine differences in ammonia, carbon dioxide, nitrous oxide, and methane concentrations and moisture content, nutrient concentrations (ammonium nitrogen, total nitrogen, total phosphorus, total potassium), short-term nitrification activity potential, and denitrification enzyme activity from simulated beef cattle bedded manure packs related to storage length (0 to 3, 3 to 6, and 6 to 9 weeks), bedding material (corn stover or soybean stubble), and temperature (10°C or 40°C). Temperature impacted all nutrient concentrations, while most variables differed with age and sample depth. A strong relationship between water and nutrient movement existed. Nitrous oxide concentrations occurred as high pulses right after material addition which was most likely caused by incomplete denitrification from pulse nitrate concentrations available in the dried bedding material. Ammonia concentrations were three times higher above bedded packs at 40°C assumedly because major ammonia losses occur through urea hydrolysis which is temperature-dependent and completed faster at higher temperatures.

A model was developed based on the Integrated Farm Systems Model (IFSM). The main process for water movement was considered evaporation. Ammonia emissions were simulated based on the urea degradation process in the urine, while nitrous oxide emissions were predicted as denitrification losses. Compared to data from the bedded pack experiments, the model did not adequately capture observed hourly conditions for ammonia and nitrous oxide conditions which did not affect total nitrogen concentration. Ammonia emission at times of material addition were realistically predicted which is important for real-life barns. Depending on bedded manure pack age, the bias in model prediction for moisture content, nitrogen, phosphorus and potassium concentrations were on average 3%, 20%, 0% and -25% , respectively. Overall, the simulations showed that the model can be used to predict N-P-K fertilizer concentration for bedded manure packs.

CHAPTER 1
INTRODUCTION AND BACKGROUND

1.1 Introduction

Animal feeding operations accumulate large quantities of manure and generate gaseous emission such as carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O). These gases are well known as greenhouse gases (GHG) that contribute to global warming, and are generally expressed in CO_2 equivalents to show their global warming potentials on a mass basis. Methane has a 23-fold greater warming potential than CO_2 while N_2O contributes 296 times more to global warming than CO_2 on a 100-year time scale (IPCC, 2001) and is considered the major stratospheric ozone-depleting substance (Ravishankara et al., 2009). In 2011, activities related to agriculture contributed approximately 8% of total GHG emission in the United States (U.S.), with an increase of approximately 16% since 1990 (U.S. Climate Action Report, 2014). In the same year, agricultural soil management was the largest contributor to total N_2O emission (69%) in the U.S., while manure management constituted approximately 7% (U.S. Climate Action Report, 2014).

Besides GHG, ammonia (NH_3) is a major air pollutant from agriculture that is associated with eutrophication, acidification (Amon et al., 2006; Koerkamp et al., 1998), visibility degradation, and respiratory health concerns (Arogo et al., 2003). Livestock production is the largest contributor to global (70%; Oenema et al. (2008)) and U.S. (85%; EPA (2004)) anthropogenic NH_3 emission. Animal manure, particularly from cattle, contributes the majority to NH_3 emissions (OECD, 2008). Ammonia is also a precursor for fine suspended particulate matter with aerodynamic diameters less than or equal to 10 µm (PM_{10}) and 2.5 µm ($PM_{2.5}$). Volatilized NH_3 reacts in the atmosphere with sulfuric, hydrochloric, and nitric acids to form ammonium sulfate, ammonium chloride, and ammonium nitrate (LUBW, 2008; Reche et al., 2012). These salts contribute to secondary inorganic aerosol, the major constituents of PM_{10} and $PM_{2.5}$ (Weijers et al., 2010), and can move long distances (3000-4000 km; WHO (2006)). Irritations to the human upper respiratory tract and eyes occur immediately at NH_3 levels over 50 ppm and 100 ppm, respectively, while concentration between 5000 – 10,000 ppm cause rapid death (ATSDR, 2004). Atmospheric NH_3 varies largely within season, time of the day, and measuring location and varies between concentrations of ppt to ppb (Gong et al., 2011).

Besides releases of gases, manure can have detrimental impact on water quality when over-applied to land. After land deposition, nitrogen (N) can be lost via nitrate leaching and phosphorus (P) leaching and runoff, and potentially harm ground water resources (Hart et al., 2004; Rotz, 2004). Because of negative impacts on the environment and high accumulation, manure has developed a bad image. However, manure offers many positive attributes. Applied as fertilizer, manure has advantages over chemical fertilizers. Manure promotes microbiological activities in soils (Parham et al., 2002) and improves soil organic matter which is a measure of soil quality (Yan et al., 2007). For some crop production, such as wheat, manure provides adequate nutrients (Parham et al., 2002). Agriculture uses large amounts of commercial fertilizer to meet the nutrient requirements for field crop production. The U.S. fertilizer consumption for N, P, and K in 2011 were 13 Tg, 4 Tg, and 5 Tg, respectively (ERS, 2013). Generally, in livestock production, manure is readily available and could be used as a valuable fertilizer for crop producers.

In the Northern Great Plains, several beef cattle producers raise beef cattle in deep-bedded confined facilities. As a form of manure management, most producers apply bedding material in these type of barns. If producers could have a tool to control the bedded manure mixture by predicting its quality, quantity, and fertilizer content, nutrients could be retained and manure over- or under-application reduced while minimizing air and water pollution. Through field experiments, it can be determined which manure management practices impact air emission and manure quantity and quality. These studies can be very time-consuming, costly and sometimes not possible to conduct (Li, 2011). A process-based model that predicts NH_3 and N_2O emission and N-P-K value of the bedded manure can help improve manure management practices to optimize manure quality and avoid nutrient losses to the environment and obtain sustainable beef cattle manure management.

The objective of this chapter is to provide background information on confined beef cattle systems, different cattle manure management options, and processes affecting N, P and K transformations and movements in the manure. The literature review addresses the state of research in existing N, P, and K transformation and movement models, as well as the effect of temperature, bedding material and storage time on nutrients in and from the beef bedded manure. Based on the missing information found in the literature, the hypotheses and objectives of this research were generated.

1.2 Literature Review

1.2.1 United States Beef Cattle Production

There were 89.8 million cattle and calves in the U.S. in January 2015 of which 29.7 million were beef cattle (NASS, 2015). Tremendous amounts of manure are produced that impact the surrounding and distant environment. In 2010, around 83% of beef cattle were raised in facilities with less than 500 head capacity (NASS, 2010). This means there are approximately 625,000 operations with less than 500 head capacity, and demonstrate that a prevalent number of smaller-sized facilities have to responsibly manage manure.

Runoff is a concern when beef cattle are kept outside on pasture, or in open or partially covered feedlots. Beef operations that are discharging wastewater from a point source into a water of the U.S. require a National Pollution Discharge Elimination System permit (EPA, 2012) to control water pollution and protect surface and groundwater. Confined facilities reduce the risk for runoff and can protect the animals from extreme weather conditions. In the Midwestern U.S., monoslope and hoop barns are becoming increasingly popular in beef cattle production. Based on the design of these barns, natural ventilation is facilitated and additional mechanical ventilation is not required.

Figure 1.1. Hoop barn (USDA NRCS, 2012)

Figure 1.2. East side view of a monoslope barn

Hoop barns (Figure 1.1) have steel arches that are connected to posts or concrete sidewalls. The steel arches are covered with polyvinyl fabric (Honeyman et al., 2010) and provide shade and shelter from the weather. Monoslope barns (Figure 1.2) have a sloped roof which provides shade for the animal in the summer when the sun is close to the zenith. In contrast, in the winter when the sun does not rise as high, these confined barns let sun flow through the barn due to the large south wall opening.

An advantage for both barn types is that the natural ventilation does not require additional mechanical ventilation. Thus, no energy is required to operate fans, and cattle are not affected if ventilation fails. Natural ventilation uses natural forces such as wind pressures or pressure generated by the difference in indoor and outdoor air density. Hence, one of the downsides is the inability to control air flow. For these barns, energy is also saved by accessing daylight without the need for electric light.

In monoslope and hoop barns, most producers apply bedding material to provide comfort for the animal and manage moisture in the barn. Producers in the Midwestern U.S. apply bedding material such as wheat straw, corn stover, soybean stubble, and wood chips (Doran et al., 2010). Some producers let the manure and bedding mixture build up to a bedded manure pack (BP) that is compacted over time by cattle activity. In this management style, manure is only removed from the bunk apron once or twice weekly to establish a BP in the center of the pen. The BP might be removed between groups of cattle (only once or twice a year) or may be maintained for several years depending on producer’s preference (Doran et al., 2010). Other producers remove all bedding and manure mixture as frequently as once per week to avoid a BP with the intention to keep cattle cleaner and healthier. Producers choose cleaning procedures based on their experiences. It has not yet been determined which method optimizes production and cattle well-being. A recommendation is to provide deep bedding in the winter to increase the bedpack temperature while maintaining a shallow BP in the summer to reduce the BP temperature (Doran et al., 2010). Either way, hauled manure has to be disposed. Manure can be used directly as fertilizer, stored, or treated prior to field application.

Whether producers choose to maintain a BP or a scrape-and-haul system, bedding material and pen cleaning frequencies affect manure quality, quantity and gaseous emission. Information on these impacts is limited. There are only a few monoslope beef barns studies available and these have focused on NH_3 concentrations (Spiehs et al., 2011), GHG and NH_3 concentrations from different bedding material (Spiehs et al., 2012), and airflow monitoring methods (Al Mamun, 2012). Additionally, it still has to be determined if N gases (NH_3 and N_2O) increase when barns are scraped frequently or a BP develops. The impact of bedding material, temperature and storage time on these factors has to be analyzed to optimize manure management.

The processes affecting nutrient flow and transformation within BP have to be understood to estimate the fate of N, P, and K compounds. Ni et al. (2009) stated it is necessary to understand the release mechanism of gases to accurately model gas emission and suggest gas mitigation strategies. The base information on N, P, and K processes for the bedded manure and the floor surface transformations will be drawn from the Integrated Farm Systems Model (IFSM; Rotz et al. (2015)) and on other existing process-based models from the literature. The transformations of the individual elements N, P and K and the release mechanism of gases will be discussed briefly in the following.

1.2.2 Nitrogen, Phosphorus and Potassium Transformations and Movements

1.2.2.1 Nitrogen Transformations

Nitrogen is exposed to the BP through feces, urine, air and the bedding material and leaves the system in form of N emission and air. The change of N in the BP can be expressed as the total balance of N:

$$\frac{dN_{BP}}{dt} = N_{in} - N_{out} = \left(N_{Feces} + N_{Urine} + N_{Bedding} + N_{Air}\right) - \left(N_{emission} + N_{Air} + N_{BP}\right) \quad (1.1)$$

and is based on the law of mass conservation of N. The N concentration in the system equals the N that entered the systems (N_{in} in kg d^{-1}) minus the loss of N that left the system as gaseous N (N_{out} in kg d^{-1}) and the loss of N in the BP (N_{BP}) that is removed from the BP.

Depending on the form of manure management, the majority of N in manure can be lost through NH_3 volatilization. This depends on substrate concentrations, temperature, surface pH, air stream, disturbances, and differences in physicochemical properties (Blanes-Vidal et al., 2010; Ni et al., 2009). Once urine is exposed to both heat and the enzyme urease, which is present in fecal material and soil, it is first hydrolyzed to ammonium (NH_4^+) (1.2) (Cartes et al., 2009). Equation (1.2) also shows that with urea hydrolysis the pH increases due to the OH^- release:

$$\mathrm{CO(NH_2)_2 + 3H_2O \xrightarrow{Urease} 2NH_{4\,(aq)}^{+} + HCO_{3\,(aq)}^{-} + OH_{(aq)}^{-}} \quad (1.2)$$

Ammonia dissolved in water forms the positively charged NH_4^+ cation which cannot be released to the atmosphere. Gas release from manure occurs by transport across the liquid-air system through a partial pressure gradient between dissolved and gaseous compounds (Blanes-Vidal et al., 2010). In equilibrium, ammonia is dissociated in the aqueous form as:

$$NH_3(aq) + H^+ \rightleftarrows NH_4^+ \tag{1.3}$$

The sum of NH_4^+ and NH_3 is referred to as the total ammoniacal nitrogen (TAN). Equation (1.3) shows the dependence of NH_3 release on pH ($pH = \log[H^+]$). Most gases released from manure depend on pH because they are weak acids or bases (Blanes-Vidal et al., 2010). As an example, NH_3 release increases with higher pH (Hansen et al., 1998) since NH_3 is a weak base and the dissociation equilibrium shifts to free NH_3. Carbon dioxide, in contrast, is an acidic gas that is more volatile than NH_3 and increases surface pH when it is released which in turn, enhances NH_3 release (Blanes-Vidal et al., 2010).

Ammonia volatilization is considered a function of convective mass transfer and the difference between the gas concentration in the manure surface and the gas concentration of the free air surrounding it (Ni, 1999):

$$\mathrm{E_{NH_3}} = \mathrm{k_t} \cdot \mathrm{A} \cdot (\mathrm{C_{Manure}} - \mathrm{C_{Air}}) \tag{1.4}$$

where E_{NH_3}= NH_3 rate release (g s^{-1}); k_t = convection mass transfer coefficient (m s^{-1}); A = the area of NH_3 release (m^2); and C_{Manure} = NH_3 concentration at the manure gas phase; and C_{air} = NH_3 concentration in the free air stream, respectively (g m^{-3}).

Ambient NH_3 air concentration is much lower than manure NH_3 concentration and can be neglected (Montes et al., 2009; Ni, 1999; Sommer et al., 2006). As stated earlier, NH_3 volatilization depends on air flow and the concentration gradient between manure gas near the surface and manure surface gas. Thus, under steady-state conditions, NH_3 emissions equal NH_3 volatilization whereas under transient state, air flow and concentration gradient govern emissions. Ammonia movement within the manure is caused by diffusion and governed by concentration and temperature differences (Ni et al., 2009). The equilibrium between NH_3 and NH_4^+ in the manure is controlled by the equilibrium constant while the equilibrium between the liquid NH_3 in the manure surface and the gaseous NH_3 in the atmosphere near the manure surface is controlled by Henry's law constant. Both equilibrium constants are exponential functions of the temperature which results in increased NH_3 release with higher temperatures (Sommer et al., 2006).

Besides gaseous N losses through ammonia, manure N can be released to the atmosphere as nitrous oxide, nitric oxide (NO), and nitrogen gas (N_2) through microbiological activities, which are nitrification and denitrification. Nitrogen gas is an inert gas and is the major component of the earth atmosphere (78% by volume; Spott et al. (2006)). Nitric oxide is a free radical that when exposed to air is oxidized to nitrogen dioxide (NO_2) (O'Donnell et al., 1999); both gases are major air pollutants. During the aerobic nitrification process NH_4^+ is oxidized through nitrite to nitrate (eq. 1.5; Hellinga (1999)). Denitrification is an anaerobic process that requires a carbon source where NO and N_2O are products of the stepwise reduction of nitrate to N_2 (eq. 1.6) when optimum conditions are met (Groenestein & VanFaassen, 1996; Li et al., 2012). Nitrous oxide can also be produced during nitrification when optimum conditions are not met while, during denitrification, N_2O is a regular intermediate (Wrage, 2001).

$$\mathrm{NH_4^+ + 2\,O_2 \rightarrow NO_3^- + 2H^+ + H_2O} \quad (1.5)$$

$$\mathrm{NO_3^- + 2e^- \rightarrow NO_2^- + e^- \rightarrow NO + e^- \rightarrow N_2O + 2e^- \rightarrow N_2} \quad (1.6)$$

Nitrification processes occur likely near the BP and manure surface layer which is aerated through animal movement and contains abundant N through fresh additions of urine and feces. Thus, increased amount of nitrite and nitrate would be expected in the

BP top layer near the surface. With increasing depth, denser and more compacted material with reduced oxygen is expected where leached nitrite and nitrate from upper zones fuel denitrification (Woodbury et al., 2001). In cattle farmyard manure, the highest N_2O production was observed in the middle and surface zone while higher N_2 proportions were found in the wetter bottom zone (Moral et al., 2012). The cattle farmyard manure heap was 110 cm deep, the surface zone was 0 – 25 cm deep and the middle zone was 25 – 60 cm below the surface (Moral et al., 2012). Thus, more anoxic and richer C conditions are expected in the BP bottom zone generating higher N_2 via microbial denitrification. At the same time, increased N_2O production would be expected in the zones closer to the BP surface where more oxygen is available

1.2.2.2 Nitrogen Transformations and Movement Models

Nitrogen losses through ammonia volatilization particularly relating to liquid livestock manure have been extensively studied and different models exist that describe the transformations (Li et al., 2012; Montes et al., 2009; Rigolot et al., 2010; Velthof et al., 2012; Waldrip et al., 2012). Models of nitrification and denitrification processes are predominantly available for waste water treatment systems (Gao et al., 2010; Moya et al., 2012), soil (Davidson et al., 2000; Del Grosso et al., 2010), and manure application on soil (Sogbedji et al., 2006; Stange & Neue, 2009). Fewer models are available for pig slurry treatment (Fernandes, 1994; Magri et al., 2009; Rigolot et al., 2010).

A model applicable to N transformation is the Manure-DNDC which is a process-based model of manure life cycle on livestock farms based on C and N biogeochemistry (Li et al., 2012). The model focuses on biochemical and geochemical processes that govern transformation and movements of C, N, P and water in the manure cycle. The core processes of the model are based on decomposition, hydrolysis, nitrification, denitrification, ammonia volatilization, and fermentation driven by microbial activities. Manure-DNDC describes manure organic matter turnover and predicts gas emissions (NH_3, CO_2, N_2O, NO, N_2, VOC, and CH_4), N leaching, crop growth and yield on a farm-scale by integrating feedlot, compost, lagoon, anaerobic digester, and cropping field components together in a farm system. Manure-DNDC correlates the environmental factors to the biogeochemical reactions and the gas emissions, which means that any change in one of these factors will impact the other factors. Thus, N and C processes are directly linked to another. Manure-DNDC is based on biogeochemical processes of soil organic matter of the Denitrification-Decomposition model (Li, 2011).

Another available model is the Integrated Farm System Model (IFSM) that simulates all major farm components from animal performance, feed use, and crop production to harvest and manure handling on a process level (Rotz et al., 2015). Interactions between biological and physical processes on the farm are linked and account for environmental impacts to model nutrient flows. Nutrient losses to the environment can be determined. No model exists yet to predict manure quantity and quality based on bedding materials and cleaning frequencies in deep-bedded beef barns.

1.2.2.3 Phosphorus Movements

Phosphorus is added to the BP through feces, urine, and the bedding material and leaves the system in the form of manure. The change of P in the system can be expressed as:

$$\frac{dP}{dt} = P_{in} - P_{out} = (P_{Feces} + P_{Urine} + P_{Bedding}) - (P_{Manure}) \tag{1.7}$$

and is based on the law of mass conservation of P. Phosphorus that enters the systems (P_{in} in kg d^{-1}) equals P that leaves the system (P_{out} in kg d^{-1}).

In livestock manure, around 60 to 90% of the P typically exists mostly in the inorganic form (Sharpley & Moyer, 2000) which is highly plant-available (Eghball et al., 2002). In dairy and beef manure, inorganic P occurs predominantly as orthophosphate and accounts between 62 to 70% of the total P (He et al., 2007). Poultry manure typically has a lower inorganic P content (49-63%) (He et al., 2007; Turner & Leytem, 2004) while swine manure has the highest inorganic P content (90%; Turner, 2004). A different study concluded that inorganic and organic P from non-ruminant manure can be three to five times greater than from ruminant manure (Pagliari & Laboski, 2012). This shows that the fractionation of P between organic and inorganic is highly variable and thus difficult to estimate (Pagliari & Laboski, 2012; Sharpley & Moyer, 2000).

The inorganic P forms detected in beef cattle manure include orthophosphates, pyrophosphates, and polyphosphates with orthophosphates as the major inorganic P form (Turner, 2004). Turner and Leytem (2004) determined that feedlot cattle manure consists of 42% orthophosphates and 57% organic P. Organic P forms quantified in beef cattle manure are phytate, DNA, phospholipids, and other orthophosphate monoesters and diesters (Turner, 2004; Turner & Leytem, 2004). Using Hedley fractionation procedure, total P discovery for P from beef cattle manure was 79%; only 11% of P was recovered in the water extract (Turner & Leytem, 2004).

Thus, P can be leached from manure if land applied (Sharpley & Moyer, 2000). However, most P movements are caused by runoff rather than leaching (Confesor et al., 2007) particularly when rainfall occurs (Hart et al., 2004). Most of the studies published focus on P movement within soil or from manure applied on soil. From these studies it can be concluded that P moves when attached to particles or dissolved in water.

1.2.2.4 Phosphorus Movement Models

One of the few P models available is on P dynamics in a dairy soil-crop-animal-manure system. The model predicted that P inflows (feed, heifers, water, and bedding) and outflows (milk, carcass, and manure) to the barn were more than 90% in balance (Öborn et al., 2005). The study showed the stable characteristics of P in a barn system including the manure. Another available process-based model simulates P transformations and P losses in runoff from grazing cattle (Vadas et al., 2011). The model was based on conditions that dung decomposition depends on air temperature and rainfall and that only water-extractable P can be leached from manure through precipitation. The model predicted P transformations and P loss in runoff from grazing cattle dung. Most other existing models on P transformations can be found on manure application on agricultural soils under the assumption that most P losses occur during rainfall through runoff and leaching (Gerared-Marchant et al., 2005; Grant et al., 2004; Walter et al., 2001).

1.2.2.5 Potassium Transformations

Potassium enters the operating barn system via feed and leaves the system in form of carcass and the manure/bedpack. Potassium entering the system through water is assumed to be negligible. The change of K in the system can be expressed as:

$$\frac{dK}{dt} = K_{in} - K_{out} = (K_{Diet}) - (K_{Carcass} + K_{Manure} + K_{Bedpack}) \qquad (1.8)$$

and is based on the law of mass conservation of K. Potassium that enters the systems (K_{in} in kg d^{-1}) equals K that leaves the system (K_{out} in kg d^{-1}).

Potassium losses occur faster than P losses, since K occurs predominantly in the dissolved form and is leached out rapidly from manure compared to P or other cations (Öborn et al., 2005). More than 70% of the K in dairy manure is from urine and exists in the dissolved form (COESA-Report, 1998). One existing model on K movement showed that unaccounted K losses occurred in a dairy farming system (Öborn et al., 2005). The losses were related to urine residues that remained in the pit after cleaning. Beside this paper no models on K movements were found. This can be explained by the fact that K does not directly cause eutrophication (Alfaro et al., 2004) and is thus less studied in the literature.

1.2.3 Temperature, Storage Time and Bedding Material Effects on Nutrient Concentrations in and from the Bedded Manure

1.2.3.1 Temperature Effects on Ammonia Emission

Ammonia emission monitoring from beef cattle feedyards for two years showed that emissions were correlated with air temperature. Ammonia emission were approximately twofold higher during summer than those in the winter season (Todd et al., 2011). Other studies with dairy cattle also demonstrate the significance of temperature on NH_3 emission increase (Pereira et al., 2012; Zhang et al., 2005a). The majority of the ammonia emission comes from the urine and results from urea hydrolysis which is catalyzed by the enzyme urease (Pereira et al., 2012; Todd et al., 2013). This reaction has been described by the Arrhenius equation that shows the temperature dependence of urea degradation and could be used to estimate NH_3 emission for cattle feedyards. In studies with beef cattle farmyard manure, Moral et al. (2012) observed that ammonia emission were highest when manure temperature peaked. Similar findings were made by Spiehs et al. (2011). The scientists determined that ammonia concentrations from the pen surface of a beef deep-bedded monoslope barn were highest during the summer months and lowest during the cold winters. During moderate temperature seasons, ammonia concentrations were intermediate (Spiehs et al., 2011). This again can be explained by the temperature effect on urea hydrolysis.

1.2.3.2 Temperature Effects on Nitrous Oxide Emission

Limited information exists on N_2O emission from beef manure relating to temperature. Pereira et al. (2012) investigated the effects of four different temperatures (5, 15, 25, and 35°C) on N_2O emission from dairy feces and urine on concrete floors in laboratory chambers over 120 h. Cumulative N_2O emission showed no significant differences between the various temperatures. However, in a previously experimental set-up where N_2O emission were measured for 72 h after dairy manure application on solid floors, N_2O emission were significantly higher at 25°C than at 5 or 15°C (Pereira et al., 2011). In studies with beef cattle farmyard manure, Moral et al. (2012) reported that N_2O emission decreased with higher temperature. The authors explained this observation with the fact that the majority of nitrifying and denitrifying bacterial are not thermophilic. In contrast, in studies with two to four month old dairy cattle slurry N_2O emission there was no relation between N_2O emission and temperature observed (Sommer et al., 2000).

Nitrous oxide is produced during the incomplete denitrification or nitrification process. Nitrification requires ammonium which is oxidized and yields nitrate as the end product which is at the same time the source for denitrification (Chadwick et al., 2011;

Oenema et al., 2005). For nitrification to occur, nitrate and nitrifying bacteria have to be present. There is likely not sufficient nitrate available for the denitrifying bacteria because of the slow growth of nitrifying bacteria in manure (Pereira et al., 2012; Woodbury et al., 2001). In addition, with increasing NH_3 emission, there will be less NH_3 available for nitrifying organisms (Pereira et al., 2012) resulting in lower N_2O emissions (Oenema et al., 2005).

1.2.3.3 Temperature Effects on Nitrogen, Phosphorus and Potassium Concentrations

When comparing manure N concentration from an open beef cattle feedlot between all seasons, winter had the highest N concentration and lowest N volatilization losses, whereas fall had the lowest N concentration and highest N volatilization losses (Cole et al., 2009). Nitrogen volatilization losses were estimated by calculating the N:P ratio between the diet and the air-dried manure. Nitrogen intake and urinary N excretion were found to be lower in winter when compared to other seasons which likely resulted in reduced N volatilization losses. Nitrogen is readily transformed through processes such as ammonia volatilization, nitrification and denitrification, mineralization and immobilization which can result in major nitrogen loss from the manure (Petersen et al., 1998b). Pereira et al. (2012) found in experiments with dairy manure applied on a concrete floor at temperatures above 15°C that gaseous N emission were above urea N availability which can explain the higher N loss from different N sources at higher temperatures. Phosphorus concentration from open feedlot beef cattle manure appeared not to be affected by seasonal changes (Cole et al., 2009). No further studies were found that discuss temperature effects on P and K concentration in cattle manure.

1.2.3.4 Storage Time Effects on Ammonia Emission

Spiehs et al. (2011) observed no further NH_3 concentration decreases after 10 h from a location where cattle urine in deep-bedded manure packs had been added prior to monitoring. Similar observation was made for the NH_3 air concentration of the complete pen: after cattle were removed NH_3 concentrations declined significantly up until seven hours of monitoring. They also observed that concentrations measured at 10 h were not lower compared to 7 h. However, no continuous NH_3 measurements were performed after 10 h. The authors concluded that NH_3 was highest in areas where cattle had freshly urinated and that the majority of NH_3 was volatilized after 4 h from fresh deposition.

Studies with dairy deep-liter manure with straw stored for 7 weeks showed that NH_3 emission were highest on day 0 and then decreased steadily until the end of study (Külling et al., 2001). It was found that NH_3 emissions were positively related to the crude protein content of the diet. The authors suggested that the increasing C:N ratio though the straw addition might have reduced ammonia emission.

The majority of ammonia volatilization depends on urease and occurs from urea hydrolysis when urine is exposed to a fouled surface (Pereira et al., 2012). Thus, if a location is measured where fresh dairy urine has been deposited on manure, a peak of NH_3 emission rate typically follows after 1 to 6 h depending on the ambient temperature. After the peak, NH_3 emission decreases when observed during a short-time period, between 0 and 120 h (Pereira et al., 2012). During 136 d long-term storage of dairy manure in 200-L barrels, NH_3-N emission was highest on day 0, then decreased until day 6 after which it increased rapidly until day 12 and then remained numerically higher until day 136 of monitoring (Aguerre et al., 2012). The continued NH_3 emission can be related to evaporation of water (increase in TAN concentration) and mineralization of more stable N compounds in the fecal material (Aguerre et al., 2012).

1.2.3.5 Storage Time Effects on Nitrous Oxide Emission from Beef Manure

Information on N_2O emission focuses mostly on studies with liquid dairy manure. In 2 to 4 month old dairy cattle slurry, N_2O emissions were only observed from slurries that developed a natural crust (Sommer et al., 2000). Nitrous oxide emission increased when the surface layer was drying and developed a crust which was likely enriched with oxygen and allowed nitrification to occur (Sommer et al., 2000). Low N_2O emissions (0 to 1.6 mg N_2O-N m^{-2} h^{-1}) were reported from dairy deep litter and emission peaked within 1 hour after material addition. No difference in N_2O was observed for litter stored at 15, 25 and 35°C which was explained by the absence or slow-growth of nitrifying organisms because of the absence of nitrate, thus providing no substrate to fuel denitrification (Pereira et al., 2012).

1.2.3.6 Storage Time Effects on Nitrogen, Phosphorus and Potassium Concentration

During 136 d storage of dairy cattle manure, total N (on a DM basis) and total NH_3-N increased by 10% and 55%, respectively, whereas organic N was reduced by 13% (Aguerre et al., 2012). During 9 weeks of outside storage where dairy manure with straw as the bedding material was exposed to the weather including precipitation, there was no difference in P concentration detected between the manure heaps stored during summer-spring condition and autumn condition (Petersen et al., 1998b). No studies were found on storage time effects on manure K concentration.

1.2.3.7 Bedding Material Effects on Ammonia and Nitrous Oxide Emission from Beef Manure

Misselbrook and Powell (2005) conducted laboratory experiments to test for differences in NH_3 emission after 48 h of urine and feces application from dairy cattle on various bedding materials. The lowest NH_3 emissions were from sand and pine shavings and were significantly lower from chopped newspaper, chopped corn stalks, and recycled manure. This might be ascribed to the high urease activity that can be found in plant materials and recycled manure compared to sand. However, in this study the bedding materials were saturated with urine resulting in increased emission which made it difficult to detect significant differences in NH_3 emission related to bedding materials. In long-term studies where chopped wheat straw was added to dairy manure (22 g straw/kg of manure), ammonia emission were also not significantly different than the treatment without bedding. However, after 12 to 28 days of monitoring a crust formed on the manure surface and NH_3 from treatments with straw were then significantly lower and declined to almost no NH_3 emission after 136 days (Aguerre et al., 2012). Declining NH_3 emission could be related to a decreased pH level and the addition of a C source provided by the wheat straw. Bacterial breakdown of the organic material either through aerobic or anaerobic conditions produces CO_2, an acidic gas, that decreases the pH on the manure surface (Moral et al., 2012; Ni et al., 2009).

Külling et al. (2001) reported that straw addition to dairy slurry increased N_2O emission, whereas NH_3 emission was reduced. No studies were found that discuss how bedding material affects manure N, P and K concentration.

1.3 Research Hypotheses

Ammonia has been extensively studied in dairy cattle facilities as well as in open feedlots. Tools exist to calculate gaseous emission and manure fertilizer content from livestock operations. However, these tools are not applicable for the bedded manure of confined beef systems. Applying bedding material to the manure impacts the manure nutrient concentration, but no research has yet been conducted on how bedding material and storage time impact manure nutrient content and gaseous N emission. The processes affecting nutrient flow and transformation within the bedpack have to be understood to estimate the fate of nitrogen (N), phosphorus (P), and potassium (K) compounds. A process-based model is based on transformations and processes that convert fundamental N, P, K elements between forms and mass transfer of nutrients between areas in the system. Microbiological activities such as nitrification and denitrification and enzyme activity cause transformations. Processes and transformations in turn, are affected by bedding material, bedpack depth and factors like temperature and storage time.

The hypothesis of this study is that N_2O and NH_3 emissions and manure N-P-K concentration and monetary fertilizer value of beef cattle bedded manure can be modeled by considering the transformations within and the movement from the bedded manure and the floor surface, respectively. The process-based model will describe the physical, chemical and biological activities occurring in the bedded manure to allow quality and quantity estimates of emission and manure. The processes in the BP and the fouled surface will be discussed separately.

1.4 Research Objectives

The overall objective was to develop a process-based model that predicts the quantity and quality of manure, N, P and K concentration, and NH_3 and N_2O emissions from the BP and floor surface of a confined beef cattle system with respect to different bedding material, manure storage time, and ambient temperature. The overall objective is subdivided into the following specific objectives:

1. Develop a model to simulate the physical, chemical and biological transformations and movements of N, P and K in the BP and NH_3 and N_2O volatilization from the bedded manure pack surface with respect to different manure storage time, bedding material, and ambient air temperature.
2. Develop a model to simulate the physical, chemical and biological transformations and movements of N, P and K at the floor surface and NH_3 and N_2O volatilization from the floor surface with respect to different manure storage time, bedding material, and ambient air temperature.
3. Develop a process-based model that predicts quantity and quality of manure, N, P and K concentration and NH_3 and N_2O emission from the bedded manure pack in a confined beef cattle barn by linking the individual transformations in the bedded manure and the floor surface.

1.5 Dissertation Outline

Chapter 2 describes a bench-scale manure storage experiment to determine NH_3 emission from beef cattle feces and synthetic urine mixtures. Data was collected to evaluate the source of volatilized ammonium N from the slurry mixture. Chapters 3 and 4 analyze NH_3 and N_2O concentration and N, P and K concentration from simulated lab-scale beef cattle bedded manure packs for different ambient temperature, bedding material and BP age. Chapter 5 describes the model development for the process- model using the results gained from Chapters 2 to 4. In the final chapter, important results of this research are discussed. The dissertation ends with recommendations for model improvement and future work.

CHAPTER 2

ISOTOPE RATIO MASS SPECTROMETRY MONITORING OF NITROGEN VOLATILIZATION FROM CATTLE FECES AND ^{15}N LABELED SYNTHETIC URINE

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Synopsis

Identifying the source of ammonium losses from beef cattle manure and the time when emission are highest is a critical step to understand and model NH_3 emission. A 15-day bench-scale manure storage experiment investigated NH_3 emission from beef cattle feces and synthetic ^{15}N-labeled urine. This chapter has been published in *Atmosphere* as a communication. The notation was changed and headings were added. In addition, the first paragraph has been removed to reduce repetition in the content of the dissertation.

2.1 Introduction

The ^{15}-N labeling method has been used to track N in dairy cows from feed intake to manure excretion (Powell et al., 2004) and cycling of manure N in crop systems (Munoz et al., 2004; Paul & Beauchamp, 1995). Isotope ratio mass spectrometry is typically used to determine the ratio of ^{15}N and ^{14}N of plant and soil samples with high accuracy to detect even small differences between isotopic abundances of sample and standard conditions (Muccio & Jackson, 2009; Robinson & Smith, 1991). Few studies have been conducted that discuss labeled N movements through manure management systems (Lee et al., 2011; Thomsen, 2000) and have focused on compost (Lynch et al., 2006; Maeda et al., 2010; Tran et al., 2013) and anaerobic systems (Béline et al., 1998; Mariappan et al., 2009).

It is commonly assumed that NH_3 from manure predominantly originates from urea when urine comes in contact with fecal urease (Sommer et al., 2006; Varel et al., 1999; Wilkerson et al., 1997; Zhang et al., 2005b). However, only limited research examines the quantity of NH_3 originating from urine versus feces in the manure. Thomsen (2000) and Lee et al. (2011) investigated urinary vs. fecal-N contribution to gaseous N emission from composted and anaerobically stored ^{15}N-labeled sheep manure with bedding and stored dairy cattle manure, respectively. Both studies showed that urinary N accounted for the highest N loss from the manure.

Gaseous NH_3 emissions from cattle manure are affected by a variety of factors, such as manure characteristics (Huijsmans et al., 2003; Sommer et al., 2003) and type and duration of manure storage (Amon et al., 2006; Külling et al., 2001). In the long-term, recognizing the source of aerial N losses from beef cattle manure and the time when N emission are highest will help with beef cattle manure management decisions. Our research complements research conducted by Thomsen (2000) and Lee et al. (2011) and specifically considers NH_3 emission from beef cattle manure with respect to time after fresh manure addition. Compared to ^{15}N-labeled urine obtained from the animal, the applicability of synthetic ^{15}N-labeled urine would allow advanced control over the ^{15}N concentration in the manure mixture and provides a less costly and time-consuming alternative. Thus, the objectives of this study were 1) to verify the use of synthetic urine amended with ^{15}N-labeled urea as a valid means to determine the fate and origin of N in manure; and 2) to monitor labeled-N movement in a bench-scale manure storage system for beef cattle manure.

2.2 Materials and Methods

2.2.1 Simulated Slurry Systems

The bench-scale manure storage test system consisted of four 2-L wide-mouth glass jars (Figure 2.1). The lid of each jar was equipped with three inlet holes and one exhaust hole. A Teflon tube was connected to the exhaust hole to draw air out of the system through an acid trap solution. Combination airflow meters and valves (RMA-26-SSV, Dwyer Instruments, Inc., IN) for each sampling line were situated after the acid trap and prior to the common vacuum pump (DOA-P707-AA, Gast Manufacturing Inc., Benton Harbor, MI) to ensure equal air flow of 1 L min^{-1} through each jar. A baffle placed in the middle of the jar lid was adjusted approximately 1 cm above the slurry surface to disperse air flow through the headspace of the jar. Thermocouples were placed in the slurry mixture and in the ambient air to monitor temperature changes with measurements recorded on 5-min intervals.

Fresh fecal material was hand-grabbed from an open beef feedlot, combined, stored in a freezer (-18°C), and thawed over 24 h prior to addition. The synthetic urine was prepared immediately before addition following procedures by Parker et al. (2005). Synthetic labeled urine contained 22.6 g L^{-1}. ^{15}N-labeled urea (10 atom %, Sigma-Aldrich, St. Louis, MO) in combination with 23.1 g L^{-1} potassium bicarbonate, 1.9 g L^{-1} potassium sulfate, and 3.8 g L^{-1} potassium chlorate using nanopure water (E-Pure, Barnstead, Thermo Scientific, Dubuque, IA, USA) . Daily subsamples of feces and urine were taken after material addition and stored at -18°C for further analysis. For the first four days, 200 mL of synthetic urine and 90.9 g of beef cattle feces were added to each jar daily. After each material addition, the mixtures were stirred briefly and the lids were closed. The 100-mL acid traps were prepared with 0.3 M sulfuric acid in nanopure water. The acid traps were replaced daily from the beginning until the end of the 15-day monitoring period and a subsample from each acid trap was stored at -18°C until subsequent analysis. After the first four days of the material addition, the lids were not opened for the remainder of the 15-day monitoring period. At the end of the monitoring period, 50 mL of 0.3 M sulfuric acid was added to the slurries and approximately 100 g of raw feces was acidified with 20 mL 0.3 M sulfuric acid to prevent loss of N through volatilization.

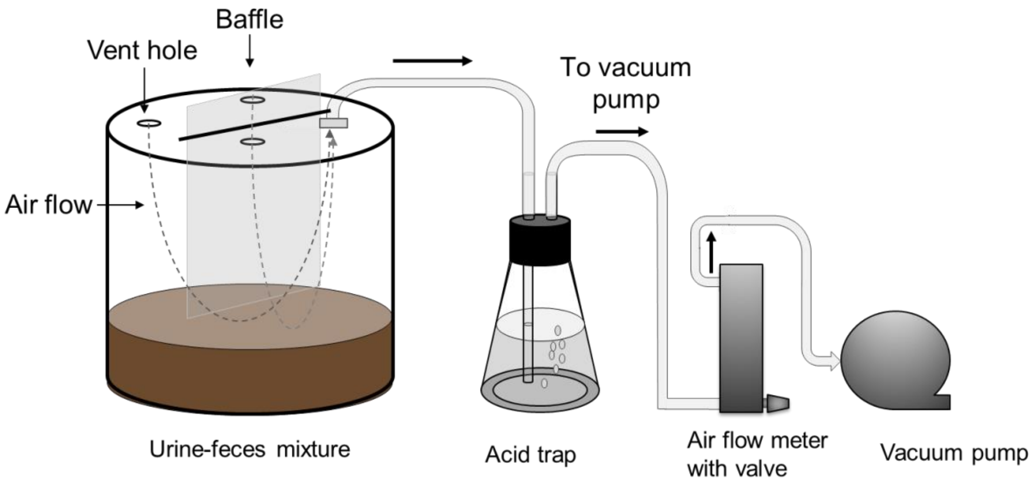

Figure 2.1. Schematic of one acid trap unit within the bench-scale manure storage system (not to scale).

2.2.2 Physical and Chemical Analysis

Moisture content (MC) of 350-g subsamples of the acidified slurry mixtures and fecal samples were determined by weighing the subsamples before and after drying in a forced-air oven at 80°C for 24 h and 38 h, respectively. One-gram subsamples of the dried slurry mixtures were dried further at 135°C for 2 hours to determine absolute MC, because crust formation prevented complete drying of the larger sample. Dried slurry mixtures and dried fecal material were ground through a 2-mm screen with a centrifugal grinding mill (Retsch ZM-1, Brinkmann Instruments Co., Westbury, NY). Three-mg samples of both the ground fecal material and ground slurry samples were analyzed for total N and atom % ^{15}N (^{15}N relative to total ^{14}N + ^{15}N) on a 20-20 Europa isotope ratio mass spectrometer (Europa Scientific Ltd., Crewe, Cheshire, UK). Ten-µL subsamples of both the urine and the acid trap solutions were mixed with 3 mg Chromosorb W, acid washed (Europa Scientific Ltd., UK) and also analyzed for total N and atom % ^{15}N. A standard sample was run after every eight samples with the mass spectrometer. The standard used for the ground fecal samples was bleached all-purpose wheat flower purchased from a local market source with standard values previously verified through multiple testing labs for use as standard values. For samples from labeled final slurry mixtures, a1:1.2 unlabeled urea (Sigma-Aldrich, St. Louis, MO) dilutions was used as the standard for the mass spectrometer. A 1:10 dilution of the ^{15}N-labeled urea was used as the standard for treatment acid trap subsamples.

The daily total volatilized NH_3 was calculated based on the detected total N (%) measured in each acid traps and converted to g day^{-1} as follows:

$$\mathrm{E_{NH_3}} = \mathrm{c_{NH_{3\_AT}}} \times \mathrm{V_{AT}} \times \rho_{\mathrm{AT}} \tag{2.1}$$

where E_{NH3} = slurry N recovered as NH_3 in the acid trap solution (g day^{-1}); $c_{NH3_{AT}}$ = NH_3-N concentration in acid trap (g g^{-1} acid trap solution day^{-1}); V_{AT} = volume acid trap solution (mL); and ρ_{AT} = density of the acid trap solution (assume 1 g mL^{-1}).

The proportion of NH_3-N volatilized from the urine in the labeled slurry mixtures was calculated under the assumption that all ^{15}N recovered as NH_3-N in the acid trap solution originated solely from the urine portion (Eq. (2.2)):

$$\mathrm{E_{NH_{3\_U}}} = \mathrm{E_{NH_3}} \times \left(\frac{{}^{15}\mathrm{N_{AT}} - {}^{15}\mathrm{N_{NA}}}{{}^{15}\mathrm{N_{U}} - {}^{15}\mathrm{N_{NA}}} \right) \tag{2.2}$$

where E_{NH3_U} = recovered NH_3-N from treatment urinary N (g day^{-1}); $^{15}N_U$ = ^{15}N content in the urine before addition to treatment (g g^{-1} urine) ; $^{15}N_{AT}$ = ^{15}N content captured in acid trap (g g^{-1} acid trap solution); and $^{15}N_{NA}$ = natural abundance of ^{15}N in air (g g^{-1} air) = 0.0037 (Bax et al., 1983).

A similar approach was used to determine total N from the urine portion in the final dried slurry:

$$\mathrm{TN_{Sl\_U}} = \mathrm{TN_{Sl}} \times \left(\frac{^{15}\mathrm{N_{Sl}} - {}^{15}\mathrm{N_{NA}}}{^{15}\mathrm{N_{U}} - {}^{15}\mathrm{N_{NA}}}\right) \tag{2.3}$$

where TN_{Sl_U} = total N from the urine portion in the final dried slurry; TN_{Sl} = total N in the final dried slurry; and $^{15}N_{Sl}$ = ^{15}N content in the final dried slurry.

The proportion of NH_3-N volatilized from the feces in the labeled slurry mixtures was calculated as the difference between E_{NH3} and E_{NH3_U}. Uncaptured N was calculated as the difference between the input slurry N (sum of N added from the urine and the fecal material) and the measured output slurry N (sum of final slurry N and recovered acid-captured NH_3-N).

2.2.3 Statistical Analysis

The experiment was designed to verify the use of synthetic urine with ^{15}N-labeled urea, to quantify NH_3-N losses from the slurry mixture and to determine the ratio of feces versus urine contribution to ^{15}N loss and total N. The glass jar was the experimental unit with four replicates of labeled slurry. The PROC GLM (SAS Institute Inc., Cary, NC, USA) procedure was used to test for differences in daily captured NH_3-N from labeled slurries. If significant differences existed ($p < 0.05$) post-hoc Tukey HSD was used to determine where and when differences occurred.

2.3 Results and Discussion

At times of material addition, the slurry temperature decreased about 2°C because added urine and fecal material were colder (20°C) than the average slurry temperature (27°C, CV = 0.04). Ammonium-N losses were highest between day 2 and 4 (Figure 2.2). After day 4, which coincided with the end of material addition, NH_3-N emission gradually decreased until the end of the 15-day monitoring period. Previous studies with incubated dairy manure at 25°C and beef manure at 40°C reported NH_3 peak emission between 2 and 5 day (Lee et al., 2011) and within 2 day after manure addition (Ayadi et al., 2015c), respectively, followed by a gradual decrease in NH_3 emission. Lee et al. (2011) added manure only once in the beginning of the trial but took daily manure samples; sampling may have enhanced mixing and facilitated NH_3 volatilization which may explain the extended period of higher emission in their study. In our study, NH_3-N emission decreased one day after the last material addition with no subsequent mixing. Other field-scale studies with cattle manure also observed highest NH_3 volatilization within 24 hours of manure application (Thompson et al., 1990; Whitehead & Raistrick, 1993).

The majority (84%) of captured NH_3-N losses originated from urinary urea with the highest proportion of emission from the urine portion occurring between day 2 (0.46 g day^{-1}, CV = 0.08) and 4 (0.53 g day^{-1}, CV = 0.08). Our findings conform to findings of Lee et al. (2011) who reported that during the first ten days of incubated dairy manure 90% of NH_3-N losses originated from urinary N. Lee et al. (2011) found initial NH_3 volatilization from the fecal portion to be negligible during the first 48 h of incubation, whereas after 10 incubation days, 10% of the NH_3-N losses originated from fecal N. Interestingly, in our study the relative fecal contribution to NH_3-N loss in the first 48 hours ranged between 23% and 25%, remained constant between days 3 and 5 (9%) and then gradually increased after day 5 from 10% to 31% on day 15. However, except for day 2 (0.14 g day^{-1}, CV = 0.06), NH_3-N emissions from fecal N were constant throughout the monitoring period ranging between 0.04 and 0.06 g day^{-1} and averaged 0.05 g day^{-1} (CV = 0.47). The urinary portion of the labeled slurry was the significant source of NH_3-

N emissions. However, further research needs to be conducted to evaluate N transformation processes in fecal material that contribute to NH_3 production, or if the ratio is affected by temperature or other environmental factors.

On average, 34% of the N losses were uncaptured (Table 2.1). Lee et al. (2011) reported up to 25% uncaptured N losses from simulated dairy manure stored for 20 days, and proposed that those N losses originated most likely from dinitrogen gas. However, under these experimental conditions, nitrous oxide production may have as likely occurred as dinitrogen gas. Amon et al. reported total net nitrous oxide emission (20.2 g N_2O per m^3 slurry) were half as high as NH_3 emission (41.0 g NH_3 per m^3 slurry) during storage of untreated dairy cattle slurry.

Future studies should incorporate additional techniques to quantify other N gases that are not captured by the acid trap. Nitrogen mass balance calculations showed that more than 80% of the total final slurry N content was from fecal N while less than 20% was from the urine portion (Table 2.1). The calculations also showed an imbalance in fecal N masses; the negative values for uncaptured N from feces would translate to a 15% increase in fecal N content after incubation. The error in the fecal N mass balance may be caused by the inconsistency in fecal N concentration which was reflected in the coefficient of variation for N concentration for the added fecal material (CV = 0.15).

Total N losses (captured and uncaptured) originated with 95% from urinary N. Thomsen (2000) came to similar findings with anaerobically stored sheep compost and reported that urine N accounted for 94% of total N losses after 28 days of storage. Overall, the N balance (Table 2.1) and similar findings to Lee et al. (2011) suggest that using synthetic urine with ^{15}N-labeled urea is applicable to measure NH_3-N losses and determine the source of volatilized NH_3-N from beef cattle manure. However, additional studies are necessary to not only determine the uncaptured N gases but also to confirm the source of uncaptured losses.

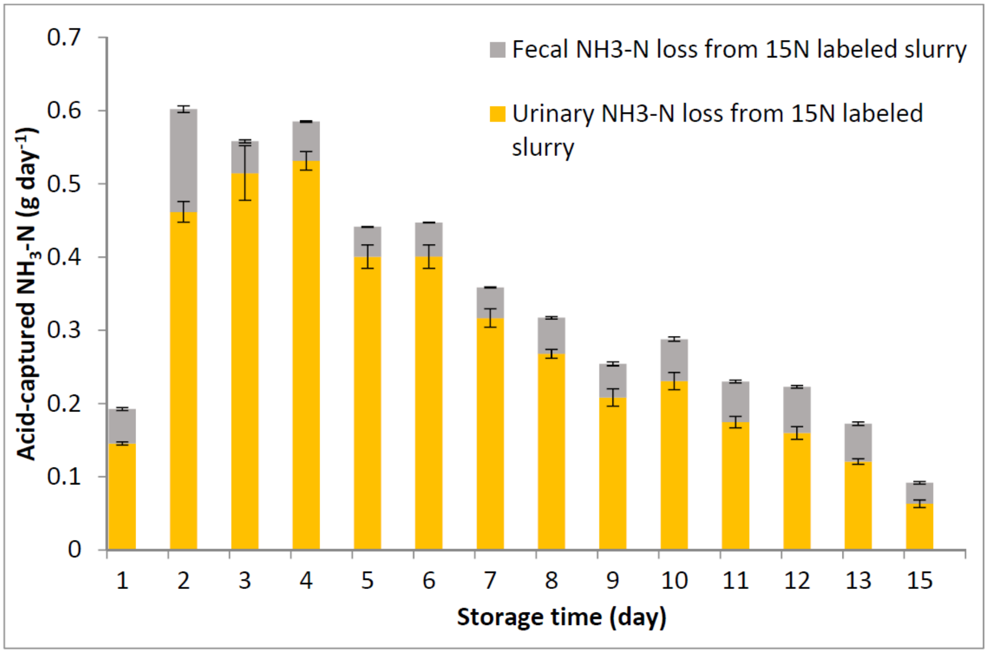

Figure 2.2. Average daily NH_3-N losses captured in sulfuric acid traps for ^{15}N-labeled slurry mixtures. The proportion of fecal versus urinary contribution to NH_3-N losses was calculated based on the ^{15}N atom % in the acid trap solution. Error bars indicate the standard error of the mean.

Table 2.1. Nitrogen (N) balance for the control and treatment.

	Input N (g)[2]			Output N (g)								
				Acid-captured NH_3-N			Final Slurry N[3]			Uncaptured N Losses		
Source	Urine	Feces	Total	Urine	Feces	Total	Urine	Feces	Total	Urine	Feces	Total
Slurry	8.89	2.69	11.58	4.06	*0.79*	4.85	0.47	*2.29*	2.76	*4.36*	*-0.39**	*3.97*
CV (-)	(-)	(0.15)		(0.02)	*(0.02)*	(0.02)	(0.06)	*(0.03)*	(0.03)			
Slurry ^{15}N	0.880	0.010	0.890	0.398	*0.003*	0.401	0.046	*0.008*	0.054	*0.436*	*-0.001**	*0.435*
CV (-)	(-)	(0.00)		(0.02)	*(0.02)*	(0.02)	(0.06)	*(0.03)*	(0.06)			

[1] Averages are shown with coefficient of variation in parentheses (CV) for four replicates with underlined values calculated based on ^{15}N signature and values in italic font based on mass balances; [2] Total nitrogen input after 4 days of material addition; [3] Nitrogen content after 15 days of storage; * Imbalance in fecal N masses calculation of the difference between the fecal N input and the measured fecal N output (acid-captured NH_3-N and slurry N).

2.4 Conclusions

Compared to studies with cannulated beef cattle as donors, the ^{15}N-labeled urea tracer method presents a simple and inexpensive alternative with more control over the ^{15}N concentration in the labeled synthetic urine solution. Urinary N accounted for the majority (84%) of NH_3-N volatilization, with highest losses occurring for the days with urine and feces addition. Ammonium-N losses from the feces were similar throughout the trial, but as a percentage of total emission, gradually increased during storage time. Over 35% of the N losses were uncaptured and most likely originated all from urinary urea. Further research has to be carried out to confirm N release from fecal material and different measurements techniques should be added to determine other N gases that were not captured by the acid trap.

Acknowledgements

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CHAPTER 3

AMMONIA AND GREENHOUSE GAS CONCENTRATIONS AT SURFACES OF SIMULATED BEEF CATTLE BEDDED MANURE PACKS

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Synopsis

For modeling gaseous emission, it is necessary to understand how environmental conditions and bedpack characteristics impact gas concentrations from BP. We conducted a lab-scale experiment to understand nutrient transformations and movements as reflected in changes in gas concentrations over simulated BP with respect to different air temperature, storage length, and bedding material. The NH_3 and N_2O data gained from this study is used to calibrate and validate the final model. This chapter has been accepted as a Full-length article in the *Transactions of the ASABE* 58(3). The notation was changed and headings were added. In addition, part of the introduction was removed to avoid duplication in the content of the dissertation.

3.1 Introduction

Traditionally, beef cattle have been kept outside on pasture or in open or partially covered feedlots. In the Northern Great Plains, there is an increasing interest in raising beef cattle in confined housing, such as hoop and monoslope barns, because of extreme weather conditions, reduced risk of runoff, and/or high land prices that make additional open feedlots cost-prohibitive to build. Removed manure and bedding needs to be managed properly and is either stored, applied directly to cropland as fertilizer, or treated (e.g., by composting) prior to field application.

When managing manure, nutrients can be lost to the atmosphere as gaseous emission including CO_2, CH_4, NH_3, and N_2O. Most cattle manure and cattle emission studies focus on managing liquid dairy manure (Amon et al., 2006; Leytem et al., 2011; Rotz & Oenema, 2006; Sommer et al., 2007) or manure in open feedlots (Borhan et al., 2011; Hristov et al., 2011; Todd et al., 2011). There is limited information on how manure management practices impact NH_3 and GHG emissions from beef cattle BP. Measuring gas concentrations above simulated BP can show trends for emission rates, if conditions are consistent among simulations. Spiehs et al. (2011) reported increases in NH_3 concentrations of beef cattle BP with warmer season and increased pack temperature. In simulated beef cattle BP with different bedding materials, NH_3 and CO_2 headspace concentrations were higher for treatments containing pine chips and corn stover than for green and dry cedar chips, whereas CH_4 headspace concentration was highest for treatments with green cedar chips, and N_2O was similar among all bedding treatments (Spiehs et al., 2014). Information is needed on impacts of different environmental conditions and BP characteristics on NH_3 and GHG emissions from BP of confined beef systems. Thus, the objective of this study was to detect differences in NH_3, CO_2, CH_4, and N_2O headspace concentrations of simulated beef cattle BP for different storage temperatures, bedding materials, and over time.

3.2 Materials and Methods

3.2.1 Simulated Bedded Manure Packs

Beef cattle BP conditions were tested in laboratory-scaled simulated BP using a 2 × 2 × 3 factorial design of temperature (Cold = 10°C, and Hot = 40°C), bedding material (corn stover (CS) and soybean stubble (SB)), and age (0-3, 3-6, and 6-9 week old BP) with doubly repeated measurements (by hour and week) over a three-week period. Each BP surface was measured repeatedly 0, 5, 8, 22, 32, 46, and 142 h after material addition for NH_3 and after 0, 22, 46, and 142 h for CO_2, CH_4, and N_2O concentrations for three consecutive weeks. The bedding materials were obtained locally, ground in an Earthquake chipper/shredder (Ardisam, Inc., Cumberland, Wisc.) and then sifted through a 6.4 mm screen to remove fine particles. Fresh feces were collected from an open beef feedlot, and moisture content was adjusted with distilled water to achieve a consistent moisture content of 70% throughout the trial. Subsamples from feces and bedding were dried and stored at room temperature (21°C) until further analysis. Fecal material was collected from cattle that were fed growing diets containing dry rolled corn and up to 20% wet distillers grains with solubles. Urine was collected individually from eight growing-finishing cattle used in a balance study. These cattle were fed diets containing dry rolled corn and high-moisture corn, and up to 45% of the diet was wet distillers grains with solubles. Urine was aspirated from a urine collection harness on each steer into a corresponding 18.9 L polypropylene jug containing 100 mL of 3.6 M HCl as described by Spiehs et al. (2013) and Spiehs & Varel (2009). After individual urine samples were collected for the balance study, the remaining urine from the jugs was mixed into a common container. This mixture was further acidified to a pH of 4 using 4 mL of 3.6 M HCL per L of urine to prevent both microbial growth and volatilization of N and then immediately stored in a freezer (-18°C). Frozen urine was thawed 24 h prior to material addition and when thawed, the pH was adjusted to 7.0 with 4 mL of 3.6 M NaOH per L of urine to simulate the physiological pH of urine from beef cattle in confined systems.

The simulated BP were prepared and maintained in 38 L plastic containers with a diameter of 0.38 m using the same ratio of bedding material and beef cattle manure used in previous simulated BP studies conducted by Spiehs et al. (2013). The simulated BP were prepared by adding 400 g bedding material, 900 g fresh feces, and 900 g thawed urine to each container on a weekly basis. After material addition, an iron rod was used to slightly agitate the surface of the packs until the material was mixed. This was done to imitate cattle hoof action observed in confined beef systems with BP. At each interval of six weeks prior, three weeks prior, and at the start of the monitoring period, twelve BP were constructed. The 0-3, 3-6, and 6-9 week old BP were 0, 3, and 6 weeks old, respectively, at the start of the monitoring period. The 0-3 week old BP were also referred to as fresh BP, and the 3-6 and 6-9 week old BP were also referred to as mature BP. In previous studies, nutrient composition (Spiehs et al., 2013; Spiehs et al., 2014), physical characteristics (Spiehs et al., 2013), and NH_3 concentrations (Spiehs et al., 2014) of simulated BP were similar to BP of commercial deep-bedded beef cattle barns that maintained their bedded packs for six months or longer. Those studies showed that the use of simulated BP during a short-time monitoring period is representative as a model to study farm-scale BP.

Simulated BP were housed in four humidity- and temperature-controlled environmental chambers (Brown-Brandl et al., 2011). Negative pressure was maintained in the chambers to ensure that outside air could flow into the chambers but that no air could escape the chambers. The chambers were equipped with air handling units and had a set air exchange rate of 0.14 m^3 min^{-1} to ensure proper air mixing and avoid excessive buildup of gases that would suppress NH_3 emissions within the chamber. Each environmental chamber was tested to verify that no air leaked out of the chamber (no exfiltration occurred). The chamber height was 2.4 m, and the floor area was 1.5 m × 1.6 m and held nine BP. The two Cold chambers were set at a constant ambient temperature of 10°C with a dew point of 5°C, and the two Hot chambers were set at a constant ambient temperature of 40°C with a dew point of 15°C. For brevity, Hot and Cold treatment descriptors are used. Three BP (replicates) for each age and bedding treatment combination (nine BP total) were assigned to each chamber. Gas measurements were only collected from two of the three replicates (n = 2) per treatment due to a limited number of static flux chambers available for the 20 min collections.

3.2.2 Gas Concentrations in Headspace Samples

Air samples were collected from the headspace above the BP with stainless steel hemispherical static flux chambers (Miller & Woodbury, 2006; Woodbury et al., 2006). Although flux chamber gas measurement methods modify climatic conditions inside the chamber compared to the adjacent chamber and may not provide actual emission rates of released gases (Arogo et al., 2003), in this study static flux chambers were used only for comparison of differences in gas concentrations from different samples under the same conditions. During storage of the BP, gas emissions were likely to occur. Thus, intermittent measurements of gas concentrations for a short time interval would show trends for emission.

Each static flux chamber had a surface area of 0.064 m^2 and an internal volume of 7 L. A 40 mm, 12 V axial-flow fan was attached to the inside of the static flux chamber to mix air above the pack surface and within the static flux chamber. Rubber skirts were attached around the flux chamber to prevent air from leaving or entering the headspace during measurements. The static flux chambers remained on the BP with the fan running throughout GHG and NH_3 gas measurements (including equilibration). For NH_3 gas measurements, headspace gas was circulated through acid traps and back to the bottom of flux chambers through inlet ports. Because the air was recirculated, there was only a minimal pressure gradient from outside the chamber to inside (Woodbury et al., 2006). Air withdrawn for GHG measurements was small (0.4%) compared to the total volume of the flux chamber, also creating only a minimal pressure gradient. Greenhouse gas concentrations were measured 0, 22, 46, and 142 h after material was added to the BP each week during the monitoring period. The static flux chambers were placed on the BP for 10 min to allow the gases to equilibrate. Following procedures of Spiehs et al. (2014), after 10 min, a single 25 mL air sample was taken with a glass syringe from the septa port at the top of the static flux chamber of each BP, transferred to an evacuated glass bottle, and later analyzed for CH_4, CO_2, and N_2O with a gas chromatograph (8610C, SRI Instruments, Torrance, Cal.). The gas chromatograph was equipped with helium ionization and thermal conductivity detectors and configured for multiple gas analysis according to the manufacturer specification using a 10-port gas sampling valve with 1 mL injection loop, a 91 cm long column (3 mm i.d.) packed with silica gel, and a 91 cm long column (3 mm i.d.) packed with molecular sieve 5A. Gases were separated using He gas (241 kPa or 35 psi) during a 6 min run with the silica gel column and the molecular sieve column submerged in an ice water bath. To produce a range of standard gas concentrations, three gas standard mixes (Scotty Specialty Gases, Plumsteadville, Pa.) were non-diluted and diluted in air.

Ammonia gas measurements were taken immediately after GHG measurements. Ammonia concentrations were sampled using acid traps that contained a 2 M sulfuric acid solution following the procedure described by Woodbury et al. (2006). The acid trap was connected to the static flux chamber, and air from the BP was recycled through the solution at a flow rate of 1 L min^{-1} for 20 min. This procedure was repeated 0, 5, 8, 22, 32, 46, and 142 h after material addition, since the majority of NH_3 losses occur within the first 24 h (Whitehead & Raistrick, 1993). The acid trap samples were stored at room temperature until further analysis. The NH_3 concentration was determined following the procedures used by Spiehs et al. (2011). Two duplicate 5 μL samples of the acid trap solution were pipetted into a 96-well microtiter plate and mixed with 50 μL phenol nitroprusside, 50 μL alkaline hypochlorite, and 250 μL distilled water. After a 20 min reaction time, absorbance at 620 nm was measured with a microplate reader (Ceres UV900C, BioTek Instruments, Inc., Winooski, Vt.). Ammonia concentrations of each plate were calculated in mM from a standard curve run with the plate. The coefficient of variation of each duplicate sample in the plate was less than 3%. Calculated NH_3 concentrations in mM were transformed to ppm on a mass basis (mg kg^{-1}) under the assumption that air is an ideal gas and that the air density in both Hot and Cold chambers was similar as under standard reference conditions at 1013 mbar and 15°C (ISO, 1996; eq. (3.1)):

$$\mathrm{NH_3} = \frac{[\mathrm{NH_3}] \times \mathrm{M_{NH_3}} \times \mathrm{V_{AT}}}{\mathrm{V_{Air_{AT}}} \times \frac{1\ \mathrm{m^3}}{1000\ \mathrm{L}} \times \rho_{\mathrm{Air}}} \tag{3.1}$$

where NH_3 = concentration of NH_3 on a mass basis (ppm); $[NH_3]$ = concentration of NH_3 in the acid traps (mM); M_{NH3} = molecular mass of NH_3 (mg $mmol^{-1}$); V_{AT} = volume of the acid trap solution (L); V_{AirAT} = air volume sampled for 20 min at 1 L min^{-1} airflow rate (L); and ρ_{Air} = air density at standard reference conditions (kg m^{-3}).

3.2.3 Gas Pore Space

Gas pore space was measured at the end of the monitoring period by recording the mass of water that could be added to the known volume of each BP until the water reached the surface of the BP stored in the plastic container (Spiehs et al. (2014); eq. (3.2)):

$$\mathrm{GS} = \frac{\mathrm{m_W}}{\mathrm{V_{BP}} \times \rho_{\mathrm{W}}} \times 100 \tag{3.2}$$

where GS = gas pore space (%); m_W = mass of water added (kg); V_{BP} = BP volume (m^3); and ρ_W = water density at standard reference conditions (1 kg m^{-3}).

3.2.4 Temperature and PH

At 5, 8, 22, 32, and 142 h after material addition and immediately before NH_3 concentration measurements, a 5-g subsample of fresh BP material was taken approximately 5 cm below the surface and diluted with 10 g of distilled water. The sample pH was then measured with a handheld pH meter (IQ150, Spectrum Technologies, Inc., Plainsfield, Ill.). The meter was calibrated with pH 4 and 7 buffers before measurements. The surface temperature was measured with a handheld infrared temperature device (Raynger ST80, Raytek Corp., Santa Cruz, Cal.) 22, 46, and 142 h after material addition immediately before static flux chambers were attached for gas measurements.

3.2.5 Statistical Analyses

The gas concentration data were analyzed as a 2 × 2 × 3 factorial design for 12 treatment combinations applied to two random experimental units (simulated BP; $n = 2$) with doubly repeated measurements using the SAS PROC MIXED procedure (SAS Institute, Inc., Cary, N.C.). The response variables were measured repeatedly by week and hour on each experimental unit. Age as a main effect referred to differences in BP age that existed at the start of the experiment. Week related to the timing of bedding, feces, and urine addition relative to the start of the experiment, and hour was relative to the weekly addition of bedding, urine, and feces. For the covariance model structures tested (AR (1) autoregressive structure, compound symmetry or unstructured covariance model), the selected structure was based on the lowest Akaike information criterion (AIC) value, as described by Littell et al. (2006). For certain associated p-values of the Type III tests for fixed effects, results were sensitive to the covariance structure. For the response variables CO_2 and CH_4, the unstructured covariance model for week and the compound symmetry for hours were chosen, for NH_3 the unstructured covariance model for week and the AR (1) autoregressive structure for hours were chosen, and for N_2O the unstructured covariance model for week and the unstructured covariance model for hour were chosen. Because of the non-normality of the residuals, the NH_3, CO_2, and CH_4 concentration data were transformed using the base 10 logarithm (log). Extreme observations were determined with the SAS PROC UNIVARIATE procedure; therefore, two data points for CH_4 concentration were removed to allow convergence of the model in the SAS PROC MIXED procedure. Inspection of the residual and Q-Q plots clearly showed two extreme observations (values of 435 and 455 ppm). Tukey's honestly significant difference (HSD) was used as a mean separation test when significant differences were detected to determine differences related to temperature, bedding material, age, and week using the SAS macro "pdmix800" (Saxton, 1998). Differences were considered significant when $p < 0.05$.

3.3 Results

Main effects, two-way interactions, and three-way interactions of all treatment variables were analyzed to understand where and when changes in the response variable, measured from the headspace from the BP, occurred. The results are presented in the fixed effect table showing the p-values (Table 3.1) and are discussed in the following sections. Table 3.2 and Table 3.3 are summary statistics for data collected during the three-week monitoring period. Table 3.2 shows the LS means (marginal means) of the gas concentrations with standard errors (SE) for temperature × bedding × age treatments; the differences across these treatments help in understanding why certain significant three-way interactions were detected. The average surface temperatures, pH, pack heights, and gas pore space data of all temperature and age treatments with SE and the average moisture contents, ammonium N and total N concentrations of the added material with SE are presented in Table 3.3 and Table 3.4, respectively, to help to interpret why changes in gas concentrations occurred. Some of the significant three-way interactions of the analyzed gas concentrations are graphically plotted as box plots in Figures 3.1 to 3.5.

Table 3.1. Probabilities (expressed as p-values) that the gas concentrations above the simulated BP were affected by the main effects and interactions (up to third order) of the treatments.[a]

Treatment Factors	log NH_3	log CO_2	log CH_4	N_2O
Temperature	**<0.0001**	**<0.0001**	**<0.0001**	**0.001**
Bedding	**0.0003**	0.07	**0.01**	0.74
Age	0.85	**<0.0001**	**<0.0001**	0.10
Week	**<0.0001**	**0.001**	**<0.0001**	0.21
Hour	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**
Temperature × bedding	**0.01**	0.84	0.97	0.07
Temperature × age	0.19	**<0.0001**	**0.03**	0.62
Temperature × week	**0.001**	0.26	**0.03**	0.30
Temperature × hour	**<0.0001**	**<0.0001**	**<0.0001**	**0.0002**
Bedding × age	0.66	0.88	0.27	0.52
Bedding × week	0.99	0.81	0.22	0.53
Bedding × hour	0.78	**0.01**	0.18	0.22
Age × week	0.85	0.07	0.32	0.98
Age × hour	**0.01**	0.11	**<0.0001**	0.48
Week × hour	**0.02**	**<0.0001**	**<0.0001**	**<0.0001**
Temp. × bedding × age	0.75	0.16	**0.04**	0.85
Temp. × bedding × week	0.71	**0.001**	0.15	0.46
Temp. × age × week	**0.03**	0.16	0.004	0.18
Bedding × age × week	0.31	0.19	0.08	0.57
Temp. × bedding × hour	0.48	**<0.0001**	**0.02**	0.06
Temp. × age × hour	0.57	**0.001**	**0.003**	0.15
Bedding × age × hour	0.10	0.43	0.86	0.24
Temp. × week × hour	**<0.0001**	0.20	**0.03**	**0.01**
Bedding × week × hour	**0.04**	0.13	0.43	0.93
Age × week × hour	0.07	0.84	0.12	0.95

[a] The treatment factors consisted of temperature (10°C and 40°C), bedding (corn stover and soybean stubble), age (0-3, 3-6, and 6-9 week old BP), week (1, 2, and 3), and hour (NH_3 at 0, 5, 8, 22, 32, 46, and 142 h; CO_2, CH_4, and N_2O at 0, 22, 46, and 142 h after material addition). Significant effects ($p < 0.05$) are shown in bold; log NH_3 = base 10 log-transformed ammonia concentration, log CO_2 = base 10 log-transformed carbon dioxide concentration, log CH_4 = base 10 log-transformed methane concentration, and N_2O = nitrous oxide concentration.

Table 3.2. Average gas concentrations for temperature × age × bedding treatment combinations.[1]

		10°C Treatments			40°C Treatments		
		0-3 Week Storage	3-6 Week Storage	6-9 Week Storage	0-3 Week Storage	3-6 Week Storage	6-9 Week Storage
NH_3 (ppm)[2,3]	Corn stover	409 (25)	388 (14)	403 (20)	1584 (180)	1375 (98)	1206 (88)
	Soybean stubble	425 (32)	381 (17)	396 (18)	1104 (119)	944 (68)	928 (65)
CO_2 (ppm)[2,4]	Corn stover	2322 (233)	4248 (277)	5564 (466)	5510 (483)	6414 (480)	6149 (512)
	Soybean stubble	2450 (259)	3926 (287)	4913 (332)	5309 (587)	6917 (589)	5904 (425)
CH_4 (ppm)[2,5]	Corn stover	8.3 ef (1.1)	15 d (1.7)	43 b (6.9)	17 de (4.8)	39 bc (5.4)	67 a (7.5)
	Soybean stubble	7.2 f (1.1)	17 d (3.5)	34 bc (4.5)	15 def (4.0)	26 c (3.4)	87 a (12)
N_2O (ppm)	Corn stover	0.31 (0.04)	0.42 (0.07)	0.57 (0.13)	0.44 (0.09)	0.62 (0.09)	0.60 (0.11)
	Soybean stubble	0.35 (0.06)	0.36 (0.05)	0.34 (0.05)	0.58 (0.10)	0.77 (0.17)	0.68 (0.12)

[1] Averages are shown with standard errors in parentheses for two replicates of each treatment combination. A significant temperature × bedding × age interaction existed only for the natural log-transformed CH_4 data.

[2] The original data are shown, but for statistical analyses the data were transformed using the base 10 logarithm.

[3] A significant ($p < 0.05$) temperature × bedding interaction existed for the natural log-transformed NH_3 data.

[4] A significant ($p < 0.05$) temperature × age interaction existed for the natural log-transformed CO_2 data.

[5] Letters a to f indicate significant differences ($p < 0.05$) within all rows and columns of each response variable.

Table 3.3. Physical and chemical properties of simulated bedded manure packs at the two different storage temperatures and at the three different ages.[1]

	Temperature Effects			Storage Length Effects			
	10°C	40°C	p-Value	0-3 Week	3-6 Week	6-9 Week	p-Value
Surface temperature (°C)	12.7 b (0.1)	33.6 a (0.3)	<0.01	22.5 b (2.0)	23.2 a (2.3)	23.7 a (2.4)	<0.01
pH	8.4 b (0.1)	8.7 a (0.1)	<0.01	8.7 a (0.1)	8.5 b (0.1)	8.5 b (0.1)	<0.01
Pack height (cm)	16 a (1)	16 a (1)	0.40	8 c (1)	17 b (1)	23 a (1)	<0.01
Gas pore space (%)	30 b (2)	41 a (1)	<0.01	40 a (2)	35 ab (3)	31 b (3)	0.02
Moisture content (%)	69 (1)	56 (2)	<0.01	72 (1)	63 (2)	58 (2)	<0.01
Ammonium-nitrogen (g kg^{-1}, dry basis)	1.01 (0.04)	0.96 (0.04)	<0.01	0.99 (0.06)	1.06 (0.05)	0.93 (0.04)	<0.01
Total nitrogen (g kg^{-1}, dry basis)	18.7 (0.3)	17.8 (0.2)	<0.01	16.4 (0.4)	18.7 (0.3)	18.5 (0.3)	<0.01

[1] Averages are shown with standard errors in parentheses for two replicates of each treatment during the 3-week monitoring period. Letters a to c indicate significant differences ($p < 0.05$) within a row of each response variable. There was no significant ($p < 0.05$) temperature × bedding × age interaction, and the main effect of bedding was not significant ($p > 0.05$). Ammonium-nitrogen and total nitrogen concentrations are given on a dry matter basis for three replicates.

Table 3.4. Nutrient composition of feces, urine, and bedding material that were added weekly to the simulated bedded manure packs.[a]

	Feces Added to Cold Treatments	Feces Added to Hot Treatments	Urine	Corn Stover	Soybean Stubble
Moisture content (%)	70 (2)	78 (4)	93 (2)	23 (-)	13 (-)
Ammonium-nitrogen (g kg^{-1}, dry basis)	0.27 (0.04)	0.21 (0.02)	NA	0.15 (-)	0.15 (-)
Total nitrogen (g kg^{-1}, dry basis)	22.6 (0.7)	22.5 (2.8)	200 (3)	8.3 (-)	7.5 (-)

[a] Averages are shown with standard errors in parentheses for three replicates. Fecal material was freshly collected at days of material addition and thus varied when added to treatments in Cold (10°C) and Hot (40°C) chambers.

3.3.1 Ammonia Concentrations

Increased NH_3 concentrations in the headspaces over the simulated BP were observed at the higher storage temperature, between weekly additions, between 8 and 46 h after fresh material addition, and when CS bedding was used. Comparing the Hot and Cold treatments (Figure 3.1), headspace concentrations of NH_3 in the Hot treatments were nearly three times higher than headspace concentrations in the Cold treatments (1190 ppm, SE = 47 vs. 400 ppm, SE = 9, respectively). Over the three-week monitoring period, differences were observed in the pattern of NH_3 concentrations after the addition of bedding, feces, and urine. Ammonia concentrations over the fresh Hot treatments decreased in week 3, whereas concentrations over Cold treatments and mature Hot treatments were similar across weeks. Within each week, NH_3 concentrations at the time of material addition (hour 0) were lowest. This is particularly evident in the weekly repeated pattern of NH_3 concentrations observed above Hot treatments. Above Hot treatments, NH_3 concentrations were similar at hour 0 from one week to the next but increased quickly, reaching peak concentrations between 22 and 46 h after material addition, before declining. Cold treatments, however, did not display this pattern from week to week; during the first week, concentrations rapidly increased and peaked at least 142 h after material addition. In the second week, a gradual increase to 46 h after material addition was observed. In the third week, NH_3 concentrations were similar at all points, giving an overall plateau appearance of NH_3 concentrations from week 1 to week 3.

Bedding material was a significant factor affecting the NH_3 concentrations but was also temperature dependent. In the Hot treatments, NH_3 concentrations were higher above CS (1389 ppm, SE = 75) than above SB packs (992 ppm, SE = 51). In the Cold treatments, NH_3 concentrations were similar between CS and SB treatments (400 ppm, SE = 13). Peak concentrations for CS and SB treatments occurred at least 142 and 46 h after material addition in week 1, respectively, while peak concentrations in week 2 and 3 were similar at 46 h after material addition for CS and SB treatments.

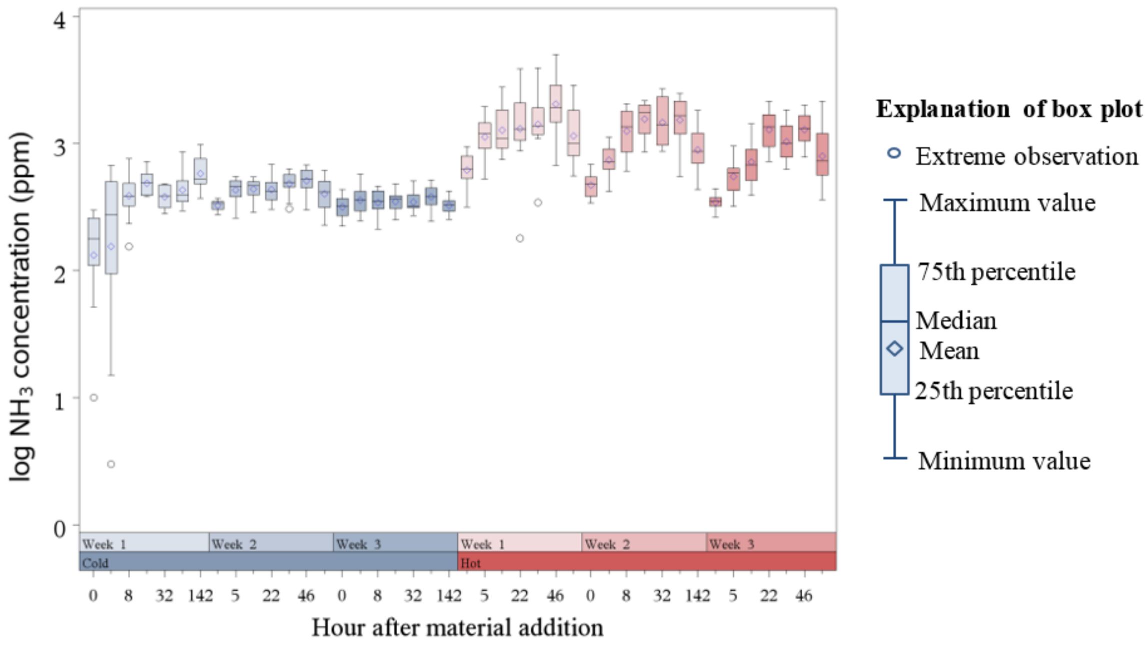

Figure 3.1. Temperature × Week × Hour distribution of base 10 log-transformed NH3 concentration data from simulated bedded manure packs.

3.3.2 Carbon Dioxide Concentrations

Differences were observed in the CO_2 headspace concentrations when bedding material, temperature, age, weeks of monitoring, and hours after fresh material addition varied. Similar to NH_3 concentrations, the concentrations of CO_2 above Hot treatments were nearly twice as high compared to the Cold treatments (6033 ppm, SE = 211 vs. 3902 ppm, SE = 161, respectively). In the Cold chambers, CO_2 concentrations increased with BP age (0-3 week old BP = 2384 ppm, SE = 172; 3-6 week old BP = 4087 ppm, SE = 199; 6-9 week old BP = 5231 ppm, SE = 285), whereas in the Hot chambers, concentrations were similar across mature packs (3-6 week old BP = 6660 ppm, SE = 376; 6-9 week old BP = 6027 ppm, SE = 330) but higher than above fresh packs (5412 ppm, SE = 375; Figure 3.2).

In the Cold chambers, peak CO_2 concentrations occurred at 0 h, and the lowest concentration was measured at 46 h after material addition for all pack ages and both bedding treatments. Peak CO_2 concentrations over Hot treatments were observed around 22 h after material addition for both bedding materials and all ages. In the Hot chambers, the lowest CO_2 concentrations above CS treatments occurred when material was added (0 h) and at 142 h after material addition above SB treatments. Carbon dioxide concentrations were higher over CS treatments compared to SB treatments in week 3 in the Cold chambers (4938 ppm, SE = 471 vs. 4419 ppm, SE = 412) and in week 1 in the Hot chambers (6161 ppm, SE = 466 vs. 5244 ppm, SE = 542).

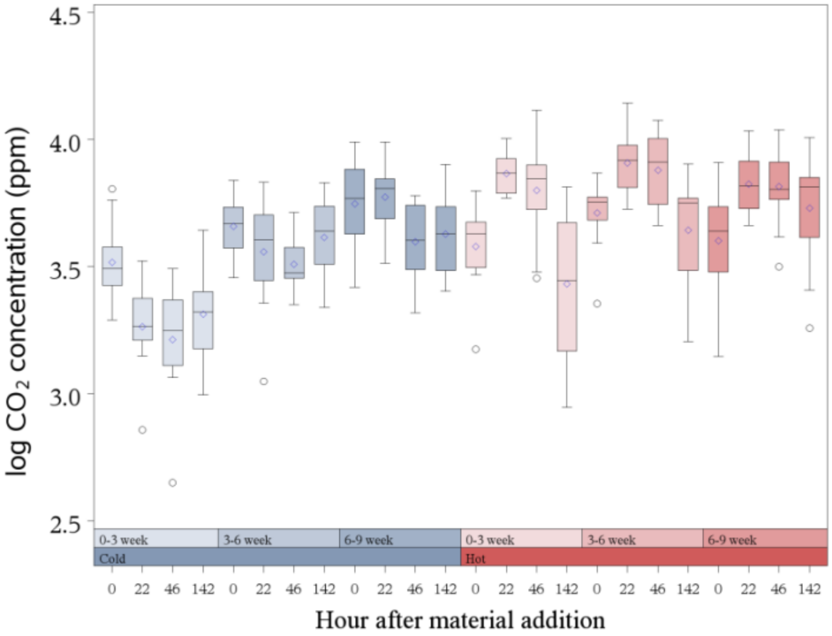

Figure 3.2. Temperature × Age × Hour distribution of base 10 log-transformed CO$_2$ concentration data from simulated bedded manure packs

3.3.3 Methane Concentrations

Methane concentrations from air samples above BP increased with the higher storage temperature, CS bedding, storage length, and fresh material addition. Methane concentrations were twice as high above Hot treatments (42 ppm, SE = 4) compared to Cold treatments (21 ppm, SE = 2). With increased age and elapsed weeks, CH$_4$ concentrations doubled (Figure 3.3) and were on average 12 ppm (SE = 2), 24 ppm (SE = 2), and 57 ppm (SE = 5) over 0-3, 3-6, and 6-9 week old packs, respectively. During the first two weeks, CH$_4$ concentrations over fresh BP showed no difference with respect to storage temperature. However, in the third week, CH$_4$ concentrations above fresh BP increased with higher temperature. In the Hot chambers, peak CH$_4$ concentrations occurred at different hours across ages and for both bedding materials. The 0-3, 3-6, and

6-9 week old BP showed peak CH_4 concentrations at 22, 46, and 0 h, respectively, with the highest CH_4 concentrations resulting from 6-9 week old packs (Figure 3.4). The CH_4 concentration at time of application (0 h) was similar across weeks but increased with age. The lowest CH_4 concentration was observed at 22 h after material addition above mature packs in the Cold chambers.

In Hot chambers, peak CH_4 concentration occurred at 22 h after material addition over CS treatments (50 ppm, SE = 6) and at 0 h for SB treatments (51 ppm, SE = 12), whereas in Cold chambers, peak CH_4 concentration occurred at 0 h over both CS (40 ppm, SE = 9) and SB treatments (27 ppm, SE = 4). For CS treatments in the Hot chambers, differences in CH_4 concentrations were greater between fresh and 3-6 week old BP compared to SB treatments, whereas differences in CH_4 concentrations were greater between 3-6 and 6-9 week old BP with SB compared to CS in the Cold chambers (Table 3.2).

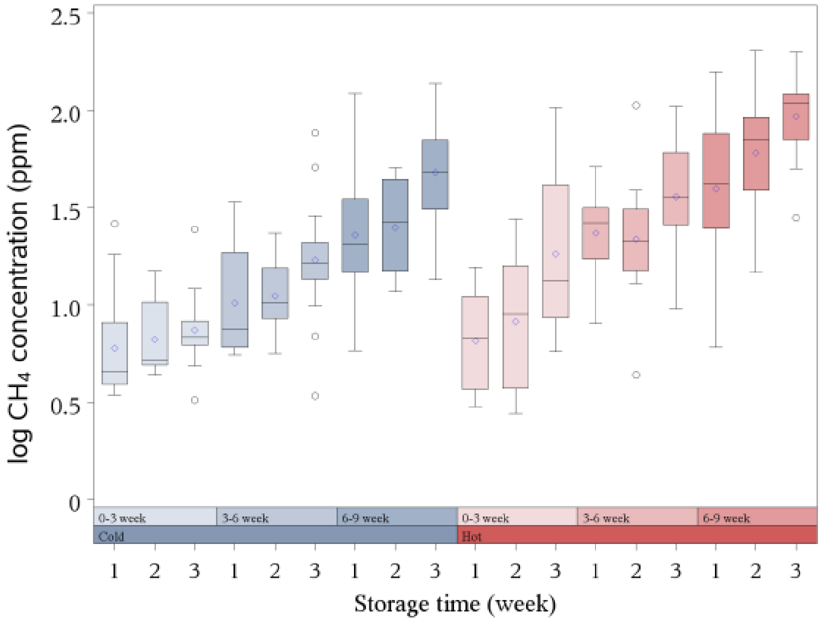

Figure 3.3. Temperature × Age × Week distribution of base 10 log-transformed CH_4 concentration data from simulated bedded manure packs.

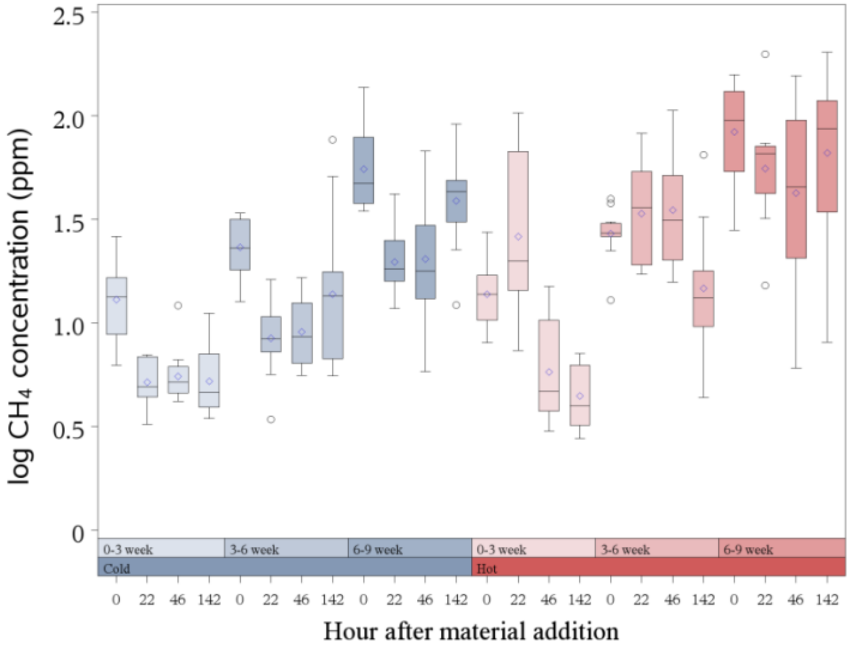

Figure 3.4. Temperature × Age × Hour distribution of base 10 log-transformed CH4 concentration data from simulated bedded manure packs.

3.3.4 Nitrous Oxide Concentrations

Nitrous oxide concentrations were impacted by temperature and elapsed time after addition of material. Concentrations of N_2O were higher above Hot treatments (0.61 ppm, SE = 0.05) than Cold treatments (0.39 ppm, SE = 0.03). Concentrations above Cold treatments were higher than average background laboratory N_2O concentrations (0.24 ppm, SE = 0.01), confirming that N_2O production in simulated BP occurred. Peak N_2O concentrations occurred as high pulses at the time of material addition (0 h) and were up to three times higher than concentrations measured in subsequent hours (Figure 3.5). Ignoring the initial pulses, N_2O concentrations were generally not different across weeks.

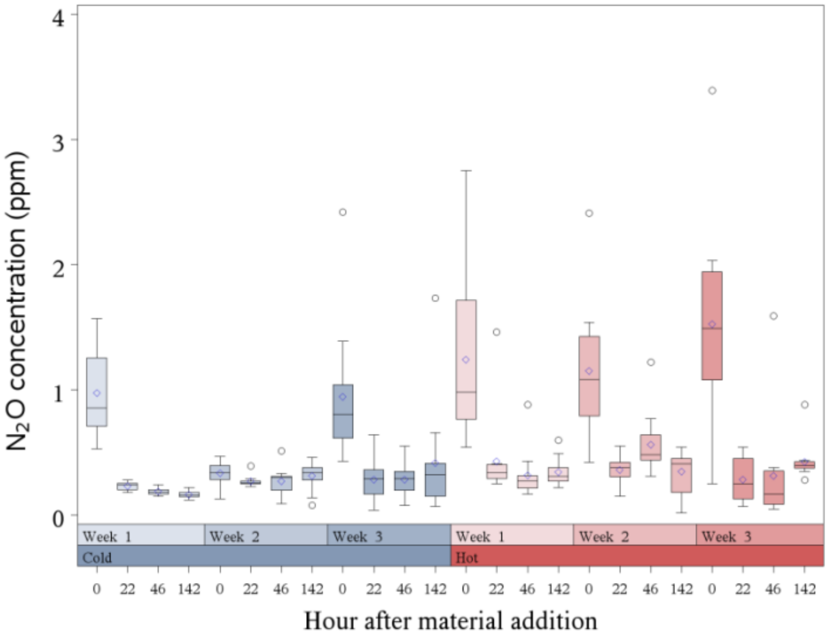

Figure 3.5. Temperature × Week × Hour distribution of N_2O concentration data from simulated bedded manure packs

3.4 Discussion

During the monitoring period, the environmental conditions in the temperature- and humidity-controlled chambers were consistent. In addition, the environmental chambers were provided with adequate air circulation to ensure that gas concentrations were not suppressed. Since emission or volatilization likely occurred from the BP surface during the incubation of the BP, the intermittent concentrations measured in this study would show trends in emission.

3.4.1 Temperature Effects

All gas concentrations increased with higher temperature. Ammonia and CH_4 concentrations, which were three and two times higher, respectively, compared to low temperature conditions, had the greatest increase with temperature, while CO_2 and N_2O concentrations showed a 1.5-fold increase with temperature. Generally, the rates of chemical and biological processes (urea hydrolysis and microbial activity) increase with higher temperatures (Ni, 1999; Sánchez et al., 2000), resulting in higher NH_3, CO_2, CH_4, and N_2O formation and concentrations. For example, in previous studies with stored beef urine, urea hydrolysis was completed within 21 days when stored at 10°C but within 48 h at 35°C (Whitehead and Raistrick, 1993).

The major source of NH_3 is urea hydrolysis, whereas CO_2 is a product of both urea degradation and microbial aerobic and anaerobic decomposition of organic material (Møller et al., 2004; Moral et al., 2012). Ammonia concentrations were low at the time of material addition for Hot and Cold treatments because the urine, feces, and bedding were added separately and mixed in the pack. Once mixed, the urease enzyme, which is produced by microorganisms in the feces (Elzing and Monteny, 1997; Varel, 1997) and the BP, hydrolyzed urea in the urine to ammonium and CO_2 (Mobley and Hausinger, 1989). The degradation of urea is temperature dependent and is described by the Arrhenius equation (Yadav et al., 1987), which helps to account for the higher NH_3 concentrations above the Hot treatments relative to Cold treatments. The increase in CO_2 concentration with a higher temperature has been documented in studies with swine slurry (Møller et al., 2004; Ni, 1999) and dairy manure (Hafner et al., 2013) and is attributed to both urea hydrolysis and microbial organic matter decomposition.

Ammonia volatilization depends on a number of factors, including the NH_3 concentration gradient, pH, surface area, temperature, air movement over the surface (Blanes-Vidal et al., 2010; Ni et al., 2009), and the transport and surface resistance (Olesen and Sommer, 1993). In aqueous solutions, ammonium ions (NH_4^+) and free ammonia (NH_3 (aq)) exist in equilibrium (Zhang et al., 2005a), while at higher temperatures the dissociation equilibrium shifts to free NH_3 (aq) (Sommer et al., 1991). Only free NH_3 (aq) can be released into the free air stream as gaseous NH_3 (Zhang et al., 2005a). The increase in free NH_3 (aq) concentration at higher temperatures accelerates convective mass transfer through the gas phase on the surface of the BP because the equilibrium NH_3 concentration at the emitting surface is higher. In addition, the depletion of NH_4^+ and NH_3 (aq) at the surface of the BP increases diffusion through the liquid solution. Thus, the headspace concentrations in the packs increased, and NH_3 concentrations above Hot treatments peaked earlier than above Cold treatments. Spiehs et al. (2011) used the same methods to measure gas phase NH_3 concentrations as described in our study and reported NH_3 concentrations of 57.6 and 99.5 mM in flux chamber acid-trap solutions above commercial-scale deep-bedded beef cattle manure packs for ambient temperatures from 0°C to 21°C and above 21°C, respectively. The acid-trap solution NH_3 concentrations from our simulated BP (73.8 and 218 mM at 10°C and 40°C, respectively) were in a similar range to that reported for full-scale conditions (Spiehs et al., 2011). Ammonia emission monitoring from beef cattle feedyards conducted for two years showed that emissions were correlated with air temperature and approximately two-fold higher during summer than emissions recorded in the winter months (Todd et al., 2011). Other studies with dairy cattle also demonstrated the impact of temperature on NH_3 emissions (Powell et al., 2008; Pereira et al., 2012; Zhang et al., 2005b).

Methane is a major end product of anaerobic decomposition of organic matter by methanogenic archaea (Thauer et al., 2008). Methane concentrations were higher above Hot treatments, which may have been due to a combination of factors, including a more active microbial biomass scavenging O_2 deep within the BP and because the BP incubation temperature was close to optimum for CH_4 production in many environments (Reay et al., 2010). Our results are consistent with several studies of stored dairy manure in which CH_4 emissions increased with higher temperatures (Massé et al., 2008; Sommer et al., 2007). Methane-producing microorganisms (methanogens) only develop when specific environmental conditions are met and can only utilize a limited array of substrates (H_2, CO_2, acetate, methanol, methylamines, and formate), which are provided by an active anaerobic microbial community (Blaut, 1994; Mackie et al., 1998; Maier et al., 2000). Møller et al. (2004) reported the increase of acetic acid from stored cattle manure at 20°C compared to 15°C, which may show that potential substrates available for methanogens also increase with a higher temperature.

Higher CO_2 concentrations above the BP suggest that microbial activity was increased in Hot treatments compared to Cold treatments, thus providing more substrate for methanogens. Much higher CO_2 (4967 ppm, SE = 147) than CH_4 concentrations (31 ppm, SE = 2) were an indication that aerobic microbial degradation, versus anaerobic processes, dominated the BP system and that significant CO_2 was produced at the interface of the BP and the free atmosphere via aerobic decomposition (Møller et al., 2004). Carbon dioxide was also much higher than NH_3 concentrations (795 ppm, SE = 30), which supported the fact that predominantly aerobic conditions existed in the BP system and that the majority of CO_2 was likely produced during aerobic respiration versus urea hydrolysis.

Nitrous oxide is produced through incomplete microbial nitrification and denitrification processes (Barton and Schipper, 2001). The higher N_2O concentration observed above Hot treatments may be partially attributable to the increase in biological reaction rate and an increase in reaction rates (Abdalla et al., 2009; Dobbie and Smith, 2001). Soil studies using ammonium nitrate as the N source showed that temperature impacts N_2O fluxes or emission (Abdalla et al., 2009; Dobbie and Smith, 2001), and a similar process is likely in these BP systems.

3.4.2 Bedding Effects

Ammonia concentrations were higher above CS treatments than SB treatments in the Hot chambers. For NH_3, CO_2, and CH_4, peak concentrations, weekly differences in concentrations at the different temperatures, and differences in concentrations across ages, respectively, varied between CS and SB treatments, whereas N_2O concentrations were not affected by bedding material. Differences between bedding material may be attributed to differences in substrate quality (proteins more accessible and easily degraded to NH_3 in CS) and by differences in moisture content (CS was 10% higher than SB bedding; Table 3.4). The higher NH_3 concentrations above CS treatments within the first 22 h after manure application compared to SB treatments indicated urea hydrolysis, with some contributions attributed to rapid protein hydrolysis in the CS treatments. Carbon dioxide concentrations above CS packs in the Hot chambers were still elevated 146 h after addition and were higher than above SB packs. Since those CS packs had a higher moisture content, anaerobic microbial communities continued to thrive and stayed active longer than in SB treatments.

Methanogenic communities are only found in certain specific anaerobic environments (Zhang et al., 2008) and are usually affected by the availability of certain substrates. In simulated BP, treatments with CS had similar odorous volatile organic compounds as treatments with SB, while both treatments showed higher volatile organic compounds than from wood shavings (Spiehs et al., 2013). The odorous volatile organic compounds measured included predominantly short-chain fatty acids, which are produced during the incomplete microbial fermentation of starch and other easily degradable carbohydrates (Miller and Varel, 2001, 2002). In a similar study, highly available short-chain fatty acids were observed in simulated wet cattle feedlot surface material (Miller and Berry, 2005). Thus, differences in CH_4 concentrations between CS and SB treatments may have been related to the availability of particular substrates (carbohydrates, proteins, and cellulose), leading to differences in H_2 and the availability of simple organic compounds that fuel methanogenesis. In addition, BP structure was likely different between CS and SB treatments, perhaps affecting the release and influx of gases. Because of differences in structure and substrate availability, different methanogenic populations may have become established with potentially different growth rates, as discussed by Bryant (1979). These differences may have led to differences in CH_4 concentration between CS and SB treatments with increased maturity.

In the Cold chambers, SB treatments (15 cm, SE = 2) were numerically lower in height than CS treatments (17 cm, SE = 2 cm). Similar observations were made for differences in gas pore space (Cold SB treatments = 27%, SE = 3; Cold CS treatments = 33%, SE = 3). Even though gas pore space was only measured at the end of the monitoring period, a lower gas pore space and/or lower height may indicate increased compaction and more anaerobic areas that are favored by methanogens. However, since there were no differences in both gas pore space and height between CS and SB treatments in the Hot chambers, the difference in CH_4 concentration may be ascribed to differences in substrate availability and microbial population/growth rather than to differences in anaerobic conditions. For future studies, an air pycnometer, as used in composting studies (Agnew et al., 2003; Su et al., 2006), might be more useful to measure air space in the BP pores.

3.4.3 Storage Length Effects

For the nine-week storage period tested, average NH_3 and N_2O concentrations were not different across all age treatments. However, within each age treatment, NH_3 concentrations increased within 46 h after bedding, feces, and urine addition. Carbon dioxide concentrations were not different across ages above the Hot treatments but increased with maturity above the Cold treatments. Methane concentrations increased with maturity above Hot and Cold treatments.

From visual observations, a crust formed on the surface of the Hot treatments approximately three to five days after material addition. The crust formation is not expected to occur on BP in actual barns, and future studies should apply more continuous simulated hoof action to prevent a crust from forming. Crust formation can prohibit convective NH_3 transport from the pack to the surface and increase surface resistance (Sommer et al., 1993), which in turn limits NH_3 release and results in decreased NH_3 concentration. Crust buildup may explain the decline in NH_3 concentration between 46 and 142 h after material addition, specifically above Hot treatments after the bedding, feces, and urine were added. Fresh packs were constructed at the beginning of the monitoring period. Compared to mature BP with greater depth, fresh BP had a larger proportion of surface area to depth. The shallow depth likely prevented N migration downward, and in combination with increased NH_3 production at higher temperature,

NH_3 concentrations in the first two weeks above fresh packs in the Hot chambers were higher than in the third week.

Carbon dioxide can be released more rapidly than NH_3 from liquid manure (Ni et al., 2009) because it is 1000-fold less soluble than NH_3 (Hafner et al., 2013). Assuming similar gas behavior in solid as in liquid manure, CO_2 emissions are typically higher and occur earlier than NH_3 emission when adding or mixing manure. Our data conform to the pattern of faster release of CO_2 compared to NH_3. Peak CO_2 concentrations occurred prior to peak NH_3 concentrations. However, as indicated earlier, increased CO_2 concentrations at the time of material addition were likely a product of aerobic degradation of freshly added organic material instead of exposure to partially degraded organic matter to the air and anaerobic processes.

Interactions between CO_2 and NH_3 emissions and surface pH in liquid swine manure have been discussed in the literature; researchers reported that CO_2 losses increased pH, while NH_3 release decreased pH (Olesen and Sommer, 1993; Ni et al., 2009; Hafner et al., 2013). A similar dynamic was observed in our simulated BP treatments. Carbon dioxide release from the BP likely increased pH, and the pH remained high because of continued CO_2 emissions and because CO_2 concentrations were much higher than NH_3 concentrations over the BP. In Hot treatments and fresh Cold treatments, the surface pH was higher at hour 142 (pH = 8.89, SE = 0.03) than at hour 8 (pH = 8.30, SE = 0.08) after material addition, whereas the pH in mature Cold treatments did not change after material addition. Lower CO_2 concentrations at 142 h after material addition above Hot treatments may be related to lower aerobic microbial activity caused by depletion of available substrate and water for breakdown. This is supported by the distribution of the surface temperature in the Hot treatments that likewise showed decreasing temperature between 22 and 142 h after material addition. In soil studies, elevated CO_2 concentrations were reported with increasing temperatures from 5°C to 25°C, which occurred during a 20-week monitoring period (Zogg et al., 1997). In the Hot chambers, CO_2 concentrations were similar across ages. Compared to fresh and 3-6 week old Cold treatments, CO_2 concentrations were higher above Hot treatments of fresh and mature BP because microbial populations generally establish faster in hot environments than in cold environments (Ratkowsky et al., 1982), which enhances aerobic and anaerobic degradation and increases CO_2 production (Maier et al., 2000).

Methane production in manure depends predominantly on storage time and temperature (Monteny et al., 2001) and can only occur under strict anaerobic conditions (Maier et al., 2000). Sommer et al. (2007) observed that CH_4 production of stored cattle slurry at 20°C rose immediately when an inoculum (1.5 month long incubated slurry) was added, whereas without the inoculum, significant CH_4 emissions occurred only after 12 days of incubation. A reduction in gas pore space with increased age (Table 3.3) indicates enhanced anaerobic conditions (Spiehs et al., 2014a). With increased maturity, deeper BP become more compacted, support greater anaerobic fermentation of the BP material, and methanogens become established and grow in abundance. A steady increase in CH_4 concentrations was observed with increased maturity (Figure 3.3) and is attributed to a larger population of methanogens increasing in abundance with elapsed time. This trend was observed through all BP ages (fresh and mature) and was also observed in a previous study of simulated BP with CS and wood-based materials as the bedding in which CH_4 concentrations increased with maturity of BP for all bedding materials after week 3 of the monitoring period (Spiehs et al., 2014a).

The sudden increase of N_2O concentrations at times of material addition may be related to either sudden production of nitrate from ammonium within BP or, more likely, the addition of nitrate in the bedding and manure added weekly to the BP. During the nitrification process, NH_3 is first oxidized to nitrite with hydroxylamine as an intermediate product (Ni et al., 2011). Under aerobic conditions, ammonia-oxidizing bacteria produce N_2O as a by-product (Schneider et al., 2013) from incomplete oxidation of hydroxylamine (Ni et al., 2011; Wrage, 2001). However, nitrifiers are slow-growing bacteria (Schmidt and Belser, 1994) and are most likely at low abundance or relatively inactive at times of material addition. Nitrous oxide is also a commonly observed intermediate during the denitrification process (Wrage, 2001). Denitrifying bacteria are ubiquitous facultative anaerobes that can reduce nitrate to N_2O under anaerobic and aerobic conditions (Michotey et al., 2000; Patureau et al., 2000). Denitrification in soils occurs typically under anaerobic conditions (Meyer et al., 2002), which may also be true for BP. Meyer et al. (2002) reported that nitrifying bacteria produced nitrate after five days, whereas denitrifying bacteria quickly metabolized available nitrate after soil was added to homogenized beef manure. Large quantities of soluble organic matter in the fresh manure inhibit the development of nitrifying bacteria, whereas denitrifying bacteria are abundant in the bedded manure mixture (Lipman, 1908). This is supported by the analysis of the denitrification enzyme activity (DEA) and nitrification activity potential

(NAP) measured from BP samples, showing 1000-fold higher DEA compared to NAP (Ayadi et al., 2015d). Thus, increasing water content, available carbon substrates, and potential nitrate availability at the time of material addition likely stimulated denitrification and resulted in increased N_2O production by denitrifiers (Barton and Schipper, 2001) and led to a pulse of increased N_2O concentration. In soil studies, an immediate increase in N_2O emissions occurred following dairy effluent application to a soil surface and returned to control concentrations within 24 h (Barton and Schipper, 2001). Amon et al. (2006) reported an intense increase in N_2O from aerated dairy slurry compared to separated, digested, or untreated slurry. Analysis of the bedding material showed that oxidized N in the form of nitrite (3.45 and 2.25 mg kg^{-1} dry bedding material) was present in the bedding before addition to the BP. Rapid denitrification of available nitrite produced peak N_2O concentrations measured above fresh BP during week 1, when the BP were first constructed of added material, and subsequently when fresh bedding material was added each week. Thus, both bedding material addition and a low rate of nitrification in mature BP supplied the oxidized N that when denitrified produced N_2O.

3.4.4 Manure Management Impacts

Higher NH_3, CO_2, CH_4, and N_2O concentrations were expected, and measured, with a higher storage temperature. The bedding material (CS) affected only NH_3 at the higher temperature and yielded a higher NH_3 concentration in BP constructed from CS material. The results of this bench-scale experiment are consistent with field-scale measurements done by Spiehs et al. (2011) and by Powell et al. (2008) for NH_3. Producers make decisions regarding the choice of bedding material and how frequently to remove the manure including the bedding, all in conjunction with the current and predicted weather patterns, bedding availability, and labor. Based on the observations made in this study, the following predictions are provided:

- Higher releases of gaseous NH_3, CO_2, CH_4, and N_2O can be expected from BP during the hot summer season (approaching 40°C) compared to the moderate season (at temperatures around 10°C).
- Ammonia concentration will likely be higher when using CS compared to SB during warmer weather. In contrast, CO_2, CH_4, and N_2O concentrations should not vary with the choice of bedding material.
- While maintaining a BP during moderate seasons, CO_2 and CH_4 concentrations are expected to increase with storage time, whereas NH_3 and N_2O concentrations should not change as the bedded manure accumulates.

Thus, management decisions of when to remove the BP and bedding material become more critical during the summer months. In general, more frequent removal of the bedded manure during the warmer weather will reduce gaseous emissions within the barn. However, the producer’s ability to store and/or apply the bedded manure also needs to be considered in these decisions.

3.5 Conclusions

- Ammonia, CO_2, CH_4, and N_2O concentrations in the fixed headspace above simulated BP increased with a higher storage temperature of 40°C compared to 10°C. The concentrations of NH_3 and CH_4 were up to three and two times higher, respectively, in the headspaces above simulated BP in the Hot chambers compared to the Cold chambers.
- Ammonia concentrations were higher above Hot treatments when CS was used as the bedding, whereas CO_2 and CH_4 concentrations were only different between CS and SB treatments at certain hours after material addition and weeks after start of the experiment. Differences in CH_4 concentrations between ages varied with temperature for CS treatments.
- Nitrous oxide and NH_3 concentrations were similar across BP ages. Methane concentration doubled with increased bedpack age and elapsed weeks. Carbon dioxide concentration increased with age only above Cold treatments, while above Hot treatments, CO_2 concentration was similar above mature BP but higher than above 0-3 week old BP.
- This study improves the understanding of how storage temperature and storage length affect gas concentration over time for the bedded manure. In the long term, this research will help improve prediction of nutrient loss in gaseous emissions and improve management practices of BP.
- Seasonal management is expected to impact gas production in BP. Carbon dioxide

and CH_4 concentration are expected to be higher with increased storage length during moderate seasons (at temperatures around 10°C), while NH_3 concentrations may be higher when using CS in hot seasons.

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CHAPTER 4

PHYSICAL, CHEMICAL AND BIOLOGICAL PROPERTIES OF SIMULATED BEEF CATTLE BEDDED MANURE PACKS

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Synopsis

The results from this study will assist in modeling the moisture content and the nutrient concentrations in the different zones of the BP. The lab-scale experiment consisted of simulated BP and showed how moisture content, N, P, and K concentrations were affected by different ambient temperature, storage time, and bedding material. The nutrient concentration and moisture content data is used to calibrate and validate the final model. This chapter has been published in *Transactions of the ASABE.* The notation was changed and headings were added. Sections from the introduction and materials methods were removed to avoid duplication in the content of the dissertation.

4.1 Introduction

Manure contains macronutrients (nitrogen (N), phosphorus (P), and potassium (K)), micronutrients (zinc, manganese, sodium, copper, sulfur, and boron), and organic matter which are all essential for crop production and soil sustainability (Eghball et al., 2002). Manure and manure/bedding mixtures have many benefits (slow-release nutrients, organic matter, and micronutrients) and in some situations result in better nutrient uptake for the plant and increase crop yield compared to commercial N fertilizer (Ferguson et al., 2005). However, uncertainties in manure nutrient composition and nutrient availability to plants make it difficult to apply manure at accurately-balanced rates. Over-application of manure increases the risk of N and P loss through runoff and/or leaching, and can contaminate surface and ground water (Carpenter et al., 1998). Under-application of nutrients results in decreased crop yield (Van Kessel and Reeves, 2002). Additional challenges to efficient manure utilization are the dynamic transformations and movements of nutrients in and from the manure over time, both in storage and after land application.

Mineral forms of N, such as ammonium (NH_4-N) and nitrate, are immediately available for plant uptake; whereas, the organic portion of total nitrogen (TN) content is more slowly available for plant uptake (Chadwick et al., 2000; Eghball et al., 2002). Ammonium production in the manure leads to ammonia emission which can contribute to eutrophication of ecosystems, soil acidification and irritate upper respiratory tracts of humans and animals (Koerkamp et al., 1998; Phillips et al., 2010) at concentrations of 50 ppm and higher (ATSDR, 2004). Nitrification of NH_4-N results in highly mobile nitrate that can leach and runoff, affecting ground and surface water (Dinnes et al., 2002). Most

P in beef cattle feedlot manure (> 75%) is in the inorganic form, which represents the most available form for plant uptake; organic P may not be immediately accessible for crops unless mineralized (Eghball et al., 2002). Potassium in manure is highly available for plant uptake (Eghball et al., 2002) because it originates predominantly from the urine, where it is present in the water-soluble form. Because of the high solubility, P and K can also be lost through runoff and leaching (Alfaro et al., 2004; Ferguson et al., 2005). However, in contrast to P, K does not result in direct eutrophication (Ferguson et al., 2005) and thus is less of an environmental concern.

Improved understanding of the nutrient composition of manure from bedded beef facilities provides beef producers with information to guide manure management decisions to reduce nutrient losses to the environment. Spiehs et al. (2011) provided baseline information on nutrient composition (N, P, K, and dry matter) of beef cattle BP. Yet, it is unknown how storage temperature and BP characteristics affect manure nutrient value and moisture content over time. A better understanding of nutrient transformations and movements will help optimize nutrient and moisture management practices of BP and increase efficiencies and yields. Thus, the objective of this study was to determine if the moisture content (MC), the nutrient value (NH_4-N, TN, total P (TP), and total K (TK)), the denitrification enzyme activity (DEA) and the short-term nitrification activity potential (NAP) of simulated beef BP were affected by temperature, age, bedding material, or pack depth.

4.2 Materials and Methods

4.2.1 Simulated Bedded Manure Packs

Over a three-week monitoring period, laboratory-scaled simulated BP were evaluated for two bedding materials (soybean stubble (SB) and corn stover (CS)), three ages (0-3, 3-6 and 6-9 week old BP), and three zones (top, middle, and bottom) at 10°C (Cold) and 40°C (Hot). Each BP was then repeatedly sampled at weekly intervals over a three-week monitoring period. Because BP depth increased with age, samples were taken from one, two and three zones of 0-3, 3-6 and 6-9 week old BP, respectively. Each age group was treated with two different bedding materials at two different temperatures, resulting in twelve treatments each with three replicates (36 BP total).

The simulated BP were housed in four humidity and temperature-controlled environmental chambers (Brown-Brandl et al., 2011). Since each chamber could only hold nine BP, three BP (replicates) for each temp × bedding × age treatment combination (nine BP total) were assigned to each chamber (Figure 4.1). A water leak contaminated one of the 3-6 week old BP in the Cold chamber containing CS and was eliminated from the study. Therefore, the treatment combination of Cold × 3-6 week old BP × CS consisted of only two replicates.

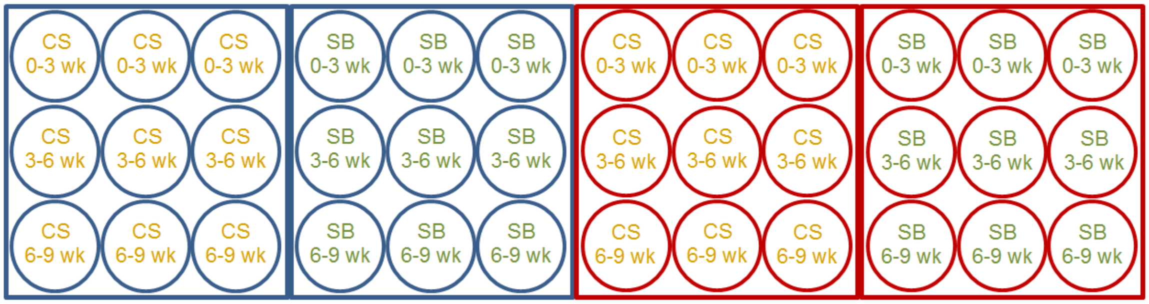

Figure 4.1. Layout of the four environmental chambers with simulated bedded manure packs (not to scale). Blue and red-framed circles refer to treatments stored at 10°C and 40°C, respectively; 0-3, 3-6 and 6-9 week refers to age of the simulated bedded manure pack in weeks, and CS and SB refers to treatments with corn stover or soybean stubble bedding, respectively.

4.2.2 Physical, Biological and Chemical Analysis

4.2.2.1 Sample Collection

Samples for physical, biological and chemical analyses were collected weekly immediately before bedding material, feces, and urine were added to the simulated BP. Before any samples were collected, the surface temperature was measured with a hand-held infrared temperature gun (Raynger ST80, Raytek Corporation, Santa Cruz, Cal.) and temperature in middle (approximately 15 cm below the surface of the dried material) and bottom zones (approximately 1 cm above the bottom of the BP) was recorded with a hand-held meter (Iq150, Spectrum Technologies, Inc., Plainsfield, Ill.). As material was added to the simulated BP, the depth increased and distinct zones developed (Figure 4.2). Grab samples from 0-3, 3-6 and 6-9 week old BP were collected from one, two and three depths, respectively. Top zone samples were taken approximately 2 cm below the surface of the dried material, middle zones from the approximate middle, and bottom zones samples from the area approximately 2 cm above the bottom of BP. Since 0-3 week old BP were shallow and had not developed distinct zones, all samples collected from these fresh BP were designated as sampled from the top zones. Similarly, 3-6 week old BP samples were designated as collected from top or bottom zones, and samples from 6-9 week old BP were designated as coming from top, middle or bottom zones. Each sample was placed in a 3.8 L plastic bag, and subsamples were immediately prepared for the DEA, short-term NAP, and pH analyses. The remaining sample material in the bag was then stored at -18°C until further analyzed for MC, ash and nutrients. Sample collection from the BP began one week after the trial was initiated.

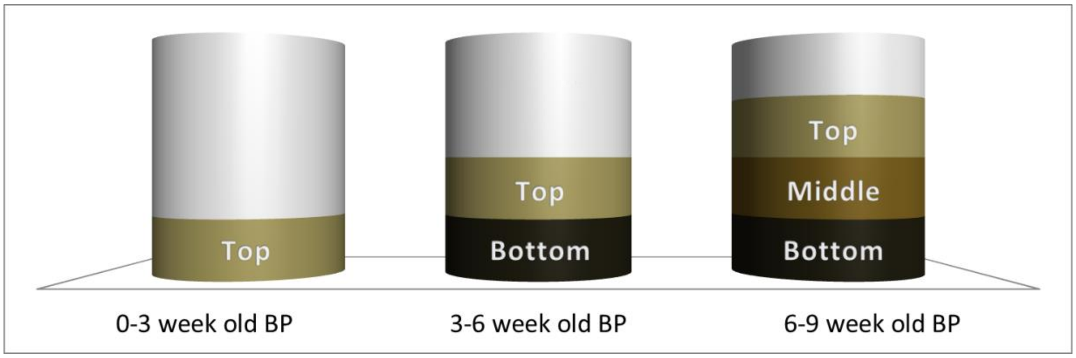

Figure 4.2. Assigned zones to the simulated beef bedded manure packs from which samples for nutrient measurements were taken.

4.2.2.2 Denitrification Enzyme Activity

Denitrification enzyme activity analysis was adapted from the methods described by Woodbury et al. (2001) used to measure DEA in cattle feedlot surface material. A 10-g subsample of the fresh BP material was funneled into a 160 mL serum bottle. A 90-mL solution of 0.1 g chloramphenicol, 5 m*M* glucose, and 10 m*M* KNO_3 was added to the serum bottle. At the same time, a control sample was prepared that contained only the reagents. All bottles were capped with stoppers and briefly mixed. The headspace of the bottles was then flushed with N gas. A 1-mL liquid subsample was transferred to a 2 mL vial, immediately shock-frozen in liquid N and stored at -18°C until subsequent chemical analysis. Serum bottles were incubated at room temperature (21°C) and sampled again after 6, 24, 30, 48 and 56 h. Samples from each 2-mL vial were run in duplicate and analyzed for nitrite N and combined nitrite-nitrate N by the ASTM standard D3867 method (2009) using a Lachat flow-injection ion analyzer (Zellweger Analytics, Lachat Instruments Div., Milwaukee, Wisc.) equipped with an automated cadmium reduction column. Standards were run at the beginning and at the end of each run. Additionally, check samples of the lowest and highest concentration standards were run every 10 to 15 samples during the run. Samples that had higher concentrations than the standard range were diluted with distilled water and subsequently rerun.

The denitrification enzyme activity (DEA) was calculated as follows:

$$\mathrm{DEA} = \frac{\Delta \mathrm{c}_{\mathrm{NO_3^-+NO_2^-}} \times \mathrm{V_L}}{\mathrm{m_S}} \tag{4.1}$$

where DEA=denitrification enzyme activity (mmol g_{bedpack}^{-1} h^{-1}); $\Delta c_{NO_3^-+NO_2^-}$= hourly change of nitrate and nitrite concentration per 90-mL solution ($\text{mmol}_{\text{nitrate+nitrite}}$ L^{-1} h^{-1}) ; V_L = 90-mL solution prepared from the BP sample; and m_S= wet weight (as is basis) of the subsample taken from the fresh BP.

4.2.2.3 Short-term Nitrification Activity Potential

Short-term nitrification activity potential analysis (NAP) was adapted from methods of Schmidt and Belser (1994) and Woodbury et al. (2001). A 5-g subsample of the fresh BP material sample was put in a 160-mL narrow mouth dilution bottle and mixed with 50 mL of a reagent solution containing 20 mM potassium chlorate, 0.5 mL of 0.5 M phosphate buffer, and 0.1 mL of 0.25 M ammonium sulfate. The dilution bottle was briefly shaken and a 1-mL subsample from the liquid was taken, immediately shock-frozen and stored at -18°C until subsequent analysis. Immediately after sampling, the dilution bottles were placed on an incubating shaker at room temperature. Subsamples were withdrawn again after 24, 48, 72, 96, 120 and 144 h. For analysis, samples were thawed at room temperature and centrifuged at 16,000 x g for 2 min to clarify the supernatant. Forty microliters of the sample or standard were pipetted into a 96-well microtiter plate followed by the addition of 100 µL diazotizing and 100 µL coupling working agent. The reagents were allowed to incubate for 20 min at room temperature to develop color. A microplate reader (ELX 808 IU, Bio-Tek Instruments, Inc., Winooski, Vt.) measured absorbance at 540 nm, and a standard curve was used to determine nitrite concentration from BP samples. Standards were run in duplicate at the beginning of the first microtiter plate.

The short-term nitrification activity potential (NAP) was calculated as follows:

$$\mathrm{NAP} = \frac{\Delta \mathrm{c}_{\mathrm{NO}_2^-} \times \mathrm{V}_\mathrm{L}}{\mathrm{m}_\mathrm{S}} \tag{4.2}$$

where NAP = short-term nitrification activity potential (nmol $\mathrm{g}_{\mathrm{bedpack}}^{-1}$ h^{-1}); $\Delta c_{NO_2^-}$= hourly change of nitrite concentration per 90-mL solution ($\mathrm{nmol}_{\mathrm{nitrite}}$ L^{-1} h^{-1}); V_L = 50-mL solution prepared from the BP sample; and m_S = wet weight (as is basis) of the subsample taken from the fresh BP (g).

4.2.2.4 pH

A 5-g subsample of fresh BP material was diluted with 10 g of distilled water. The sample pH was then measured with a hand-held pH meter (IQ150, Spectrum Technologies, Inc., Plainsfield, Ill.). The meter was calibrated with pH 4 and 7 buffers before measurements.

4.2.2.5 Moisture Content, Total C and N-P-K Composition

The bulk samples were thawed, weighed and placed in a forced-air oven at 100°C. After 24 h of drying, samples were weighed again to calculate MC. The dried BP, feces and bedding samples were ground with a hammer mill through a 1-mm screen. A 5-g sample of the ground dried samples was combusted at 550°C over night to determine the ash content. A dried and ground subsample was also sent to a commercial laboratory (Ward Laboratory, Inc., Kearney, Neb.) for TN analysis (Watson et al., 2003), NH_4-N (AOAC, 1990) and TP and TK analysis (Wolf et al., 2003). The nutrient concentrations are given on a dry matter basis. Ash content of the BP was used as an approximation of total carbon (TC). Equation 3 is prescribed by Combs and Nathan (1998) for TC and is based on the assumption that soil organic matter contains 58% C:

$$Total\ C = (100 - c_{Ash}) \times 5.8 \qquad (4.3)$$

where $Total\ C$ = total carbon concentration based on ash content of BP sample on a dry matter basis (g kg^{-1}); and c_{Ash} = ash content of BP sample on a dry matter basis (%).

4.2.3 Statistical Analyses

The zone data was analyzed using the SAS PROC MIXED (SAS Institute Inc., Cary, NC, USA) procedure. The experimental design included an incomplete 2 (chamber conditions) × 2 (bedding types) × 3 (ages) × 3 (zones) factorial design and each of the 24 treatment combinations were applied to three randomly selected BP (n=3). Zone levels were incomplete because zone was nested in age and each age group had specific zones (one, two and three zones were assigned to 0-3, 3-6 and 6-9 week old BP, respectively). Age, also referred to as storage time, was a main effect and related to differences in BP age that existed at the start of the experiment. Week related to the timing of bedding, feces and urine addition relative to the start of the experiment. Samples collected each week were repeated measures of the experimental units over three time points. Because of the non-normality of the residuals, the NH_4-N concentration data was transformed using the natural log function (ln). The covariance model structure for the repeated measures was chosen based on the lowest Akaike information criterion (AIC) as described by Littell et al. (2006) and selected based on the model that included all main effects and interactions up to order three except for interaction terms including both age and zone as treatment factors. The AR (1) autoregressive structure resulted in the lowest AIC for TP, TK, NAP and DEA and thus chosen as the covariance model structure for these response variables. The ARH (1) heterogeneous autoregressive structure resulted in the lowest AIC for MC, zone temperature, ln (NH_4-N), TN, and TC and chosen as the covariance model structure. The CSH heterogeneous compound symmetry structure was selected for pH. The model was rerun with the selected covariance structure for each response variable and interaction terms with $P > 0.20$ were removed from the original model. The reduced model was rerun to generate the final results as reported in Table 4.1. Denitrification enzyme activity and NAP were only determined for week 2 and 3 of the monitoring period. The Kenward and Roger degrees of freedom method was used. Differences for zone data were considered statistically significant if $P < 0.05$. If significant differences were detected, mean separation was performed by the SAS macro “pdmix800” (Saxton, 1998) with Tukey’s honestly significant difference (HSD) to determine differences related to temperature, bedding material, age, and week.

4.3 Results

The depth of BP increased throughout the three-week monitoring period. At the start of the monitoring period 0-3, 3-6 and 6-9 week old BP were 0 (not established yet), 15.9 (SE = 0.3) and 23.9 cm (SE = 0.6) deep, respectively. At the end of the trial after three weeks of bedding, feces and urine addition, 0-3, 3-6 and 6-9 week old BP were 11.4 (SE = 0.5), 19.4 (SE = 0.6) and 25.3 cm (SE = 0.6) deep, respectively.

Main effects, two-way and three-way interactions of all treatment variables were analyzed to understand how these factors alone and in combination related to the response variables measured in BP constituents (Table 4.1). Table 4.2 shows the average dry matter, N, P, K, and C concentrations for the added material. Table 4.3 reports the LS means with standard errors (SE), and results of the mean separation tests for each temperature × age × zone treatment combinations collected during the three-week monitoring period. The results and implications of the data and statistical analyses presented in these two tables are explored in the following Results and Discussion sections. Some of the significant three-way interactions of the analyzed response variables are graphically plotted as box plots displayed in Figure 4.3 to Figure 4.12.

Table 4.1. Probabilities (expressed as P-values) that the physical, chemical and biological properties[a] of the simulated bedded manure packs were not affected by the main effects and interactions (up to third order) of the treatments. Significant effects ($P < 0.05$) are shown in bold.[b]

Treatment Factors	MC	Zone Temp	pH	Ln NH_4-N	TN	TP	TK	TC	NAP	DEA
Temperature	**<0.01**	**<0.01**	**<0.01**	**0.02**	**<0.01**	**<0.01**	**<0.01**	**<0.01**	**<0.01**	**<0.01**
Bedding	**<0.01**	0.28	0.11	**<0.01**	0.46	0.80	**<0.01**	**<0.01**	**<0.01**	0.30
Age	**<0.01**	**<0.01**	**<0.01**	**<0.01**	**<0.01**	**0.04**	**<0.01**	0.07	**<0.01**	**<0.01**
Week	**0.03**	**<0.01**	**<0.01**	**<0.01**	**0.01**	**<0.01**	0.56	**0.01**	0.23	**<0.01**
Zone (Age)	**<0.01**	**<0.01**	**<0.01**	**<0.01**	**0.04**	**<0.01**	**<0.01**	0.83	**<0.01**	0.14
Temp × Bedding	0.17	**<0.01**	-	-	0.20	**0.04**	-	**0.03**	**<0.01**	**<0.01**
Temp × Age	**<0.01**	**<0.01**	**0.03**	-	-	**0.03**	-	-	**<0.01**	**<0.01**
Temp × Week	**<0.01**	**<0.01**	**<0.01**	**<0.01**	0.08	0.12	**0.02**	0.12	**<0.01**	**<0.01**
Temp × Zone (Age)	**<0.01**	**<0.01**	**<0.01**	0.12	-	**<0.01**	**<0.01**	**<0.01**	**<0.01**	0.11
Bedding × Age	-	0.17	-	-	-	-	-	-	0.10	0.16
Bedding × Week	-	0.09	0.10	**<0.01**	0.07	0.07	0.15	**<0.01**	**<0.01**	-
Bedding × Zone (Age)	-	0.16	-	-	-	-	-	-	**<0.01**	-
Week × Zone (Age)	**0.03**	**<0.01**	-	0.17	-	0.16	-	-	-	0.18
Age × Week	**0.03**	**<0.01**	0.16	-	0.24	0.11	**<0.01**	-	-	-
Temp × Bedding × Age	-	-	0.10	**0.04**	-	-	-	-	0.12	-
Temp × Age × Week	**0.02**	**<0.01**	-	-	-	0.18	-	0.13	-	**0.01**
Bedding × Week × Age	-	0.08	-	-	-	-	-	0.19	-	**0.04**
Temp × Bedding × Week	0.11	-	0.09	**<0.01**	-	**<0.01**	**0.01**	**<0.01**	-	-
Temp × Bedding × Zone (Age)	-	-	0.16	0.06	-	-	-	0.16	**<0.01**	-
Temp × Week × Zone	**0.04**	-	-	**0.04**	0.12	**0.04**	-	**0.01**	-	-
Bedding × Week × Zone (Age)	-	-	-	0.15	0.14	0.19	-	0.08	-	-

[a] MC = moisture content; Zone temp = zone temperature; ln NH_4-N = ammonium nitrogen transformed using the natural log; TN = total nitrogen; TP = total phosphorus; TK = total potassium; TC = total carbon (based on measurements of the ash content of the simulated bedded packs); NAP = short-term nitrification activity potential; DEA = denitrification enzyme activity.

[b] Cells with a hyphen indicate that those interaction terms had p-values > 0.20 and were removed from the original model.

Table 4.2. Nutrient composition of feces, urine, and bedding material added to the simulated bedded manure packs on a dry matter basis.[a]

	Feces added to Cold treatments	Feces added to Hot treatments	Urine	Corn Stover	Soybean Stubble
Dry Matter (%)	31.3 (1.0)	27.2 (3.0)	6.89 (0.4)	77.1 (3.3)	87.5 (0.3)
Total Nitrogen (g kg^{-1})	22.6 (0.7)	22.5 (2.8)	200 (3)	8.3 (-)	7.5 (-)
Total Phosphorus (g kg^{-1})	10.3 (0.3)	10.2 (0.1)	23.1 (1.6)	1.4 (-)	1.3 (-)
Total Potassium (g kg^{-1})	6.4 (0.1)	6.5 (1.0)	72.9 (3.4)	13.0 (-)	10.8 (-)
Total Carbon (g kg^{-1})	NA	NA	NA	437 (14)	488 (16)

[a] Averages are shown with standard errors in parentheses for three replicates. Fecal material was freshly collected at days of material addition, and thus varied when added to treatments in Cold (10°C) and Hot (40°C) chambers. Total Carbon was estimated based on the ash content of the samples.

Table 4.3. Averages of all response variables tested in simulated bedded manure packs with standard errors in parentheses for temperature × age × zone treatment combinations.[a]

Temperature	10°C			40°C		
Storage Age	0-3 week	3-6 week	6-9 week	0-3 week	3-6 week	6-9 week
MC (%)[b]						
Top	73a (1)	63bc (1)	58cd (1)	71ab (1)	42e (4)	23f (2)
Middle	-	-	70ab (1)	-	-	51d (3)
Bottom	-	76a (1)	74a (1)	-	73a (1)	74a (0)
Zone temperature (°C)[c]						
Top	13 (0)	12 (0)	12 (0)	32 (0)	34 (0)	35 (0)
Middle	-	-	15 (0)	-	-	35 (0)
Bottom	-	14 (0)	14 (0)	-	35 (0)	35 (0)
pH						
Top	8.8 (0.1)	8.5 (0.1)	8.5 (0.1)	9.0 (0.0)	8.9 (0.0)	8.8 (0.0)
Middle	-	-	8.7 (0.1)	-	-	9.0 (0.1)
Bottom	-	8.6 (0.1)	8.4 (0.1)	-	9.0 (0.0)	9.0 (0.1)
NH_4-N (g kg^{-1})[d]						
Top	1.0 (0.1)	0.9 (0.1)	0.7 (0.1)	1.0 (0.1)	0.9 (0.1)	0.7 (0.1)
Middle	-	-	1.2 (0.2)	-	-	1.0 (0.1)
Bottom	-	1.3 (0.1)	1.1 (0.1)	-	1.3 (0.1)	0.9 (0.1)
TN (g kg^{-1})[e]						
Top	17.2 (0.6)	18.6 (0.8)	18.0 (0.9)	15.6 (0.5)	18.6 (0.5)	17.4 (0.5)
Middle	-	-	19.8 (0.9)	-	-	18.9 (0.4)
Bottom	-	19.4 (0.5)	19.2 (0.7)	-	18.2 (0.4)	17.9 (0.4)
TP (g kg^{-1})[f]						
Top	7.1 (0.4)	6.7 (0.4)	7.2 (0.4)	8.5 (0.5)	7.9 (0.4)	6.8 (0.3)
Middle	-	-	7.1 (0.4)	-	-	8.7 (0.5)
Bottom	-	7.3 (0.2)	7.0 (0.4)	-	11.2 (0.5)	9.8 (0.4)
TK (g kg^{-1})[f]						
Top	20.8 (0.9)	18.8 (0.8)	16.1 (0.6)	25.6 (0.7)	18.9 (0.8)	17.6 (0.5)
Middle	-	-	22.3 (0.9)	-	-	22.8 (1.0)
Bottom	-	24.3 (0.8)	22.0 (0.6)	-	29.6 (0.6)	29.4 (0.7)
TC (g kg^{-1})[g]						
Top	409 (8)	409 (5)	399 (7)	384 (6)	404 (8)	409 (6)
Middle	-	-	419 (5)	-	-	387 (8)
Bottom	-	428 (5)	419 (5)	-	385 (8)	381c (6)
NAP (nmol $g_{\mathbf{bedpack}}^{-1}$ hr^{-1})[b,h]						
Top	0.3e (0.1)	0.9de (0.1)	0.4e (0.1)	0.7de (0.2)	2.0bc (0.5)	2.3ab (0.4)
Middle	-	-	1.3cd (0.2)	-	-	3.0a (0.5)
Bottom	-	0.8de (0.1)	0.8de (0.3)	-	1.0de (0.2)	1.0de (0.1)
DEA (mmol $g_{\mathbf{bedpack}}^{-1}$ hr^{-1})[h]						
Top	1.4 (0.4)	3.3 (0.4)	3.4 (0.4)	0.8 (0.3)	1.2 (0.3)	1.5 (0.4)
Middle	-	-	3.6 (0.3)	-	-	0.5 (0.4)
Bottom	-	3.4 (0.2)	3.0 (0.4)	-	0.7 (0.4)	0.7 (0.4)

[a] Averages are shown with standard errors in parentheses for three replicates of each treatment

combination. A significant temperature × bedding × age interaction existed only for MC and NAP. MC = moisture content; NH_4-N = ammonium nitrogen on a dry matter basis; TN = total nitrogen on a dry matter basis; TP = total phosphorus on a dry matter basis; TK = total potassium on a dry matter basis; TC = total carbon (based on measurements of the ash content of the simulated bedded packs); NAP = short-term nitrification activity potential; DEA = denitrification enzyme activity.

[b] Letters a to f indicate significant differences ($P < 0.05$) within all rows and columns of each response variable.

[c] A significant ($P < 0.05$) temperature × age and temperature × zone interaction existed for the zone temperature data.

[d] The original data for NH_4-N is shown, but for statistical analysis the data was transformed using the natural log. A significant ($P < 0.05$) temperature × zone and bedding × age interaction existed for the ln NH_4-N data.

[e] A significant ($P < 0.05$) temperature × bedding interaction existed for the TN data.

[f] A significant ($P < 0.05$) temperature × age and temperature × zone interaction existed for the TP and TK data.

[g] Total C was calculated from ash. A significant ($P < 0.05$) temperature × zone interaction existed for the TC data.

[h] A significant ($P < 0.05$) temperature × bedding, temperature × age and temperature × zone interaction existed for the NAP and DEA data.

4.3.1 Moisture Content

Moisture content is important for understanding nutrient composition and evaluating manure transportation and handling decisions. The MC of all BP decreased with a higher storage temperature, length of storage, SB as the bedding material, and towards the top of the packs. The significant three-way interactions of the treatment factors indicate differences in the rate of change based on these factors in combination. In addition to the temperature difference, the change in MC was also caused by the different drying conditions in the Hot and Cold chambers, which had dew points of 15°C and 5°C, respectively.

With longer storage time and weekly material addition, the depth of BP increased and distinct zones developed. We assumed that a bottom and top layer established after the first three weeks of storage and a top, middle and bottom zone after six weeks of storage. For the bottom layer, the MC (74%, SE = 0.3) did not change over time and was not different between Hot and Cold treatments (Figure 4.3 and Table 4.3). Top (55%, SE = 2) and middle zones (60%, SE = 2) had lower MC than the bottom zones, and in top and middle zones MC was lower in Hot treatments (48%, SE = 3) than in Cold treatments (67%, SE = 1). There was no difference in MC across ages in Cold treatments, whereas MC in Hot treatments decreased with age (Figure 4.4). No difference in MC was observed between fresh Hot (73%, SE = 1) and Cold treatments (71%, SE = 1), whereas 6-9 week old treatments had higher MC in Cold treatments (67%, SE = 1) than in Hot treatments (49%, SE = 3). For 3-6 week old BP, only in week 3 the MC of Hot BP was lower than in Cold BP (Figure 4.4). Regarding differences between bedding material, the MC of SB treatments (60%, SE = 2) was lower than the MC of CS treatments (64%, SE = 2).

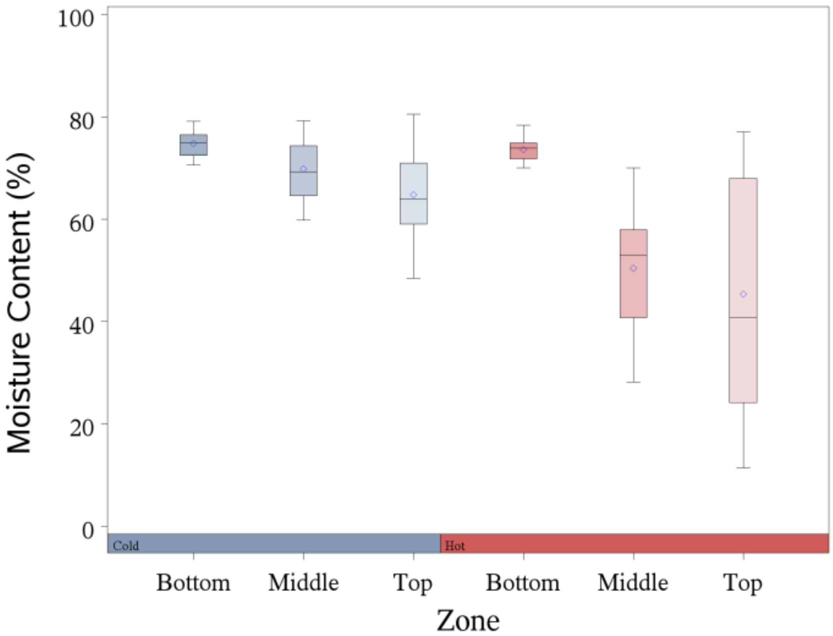

Figure 4.3. Temperature × Zone distribution of the moisture content in the simulated bedded manure packs. Cold and Hot refer to treatments stored at 10°C and 40°C.

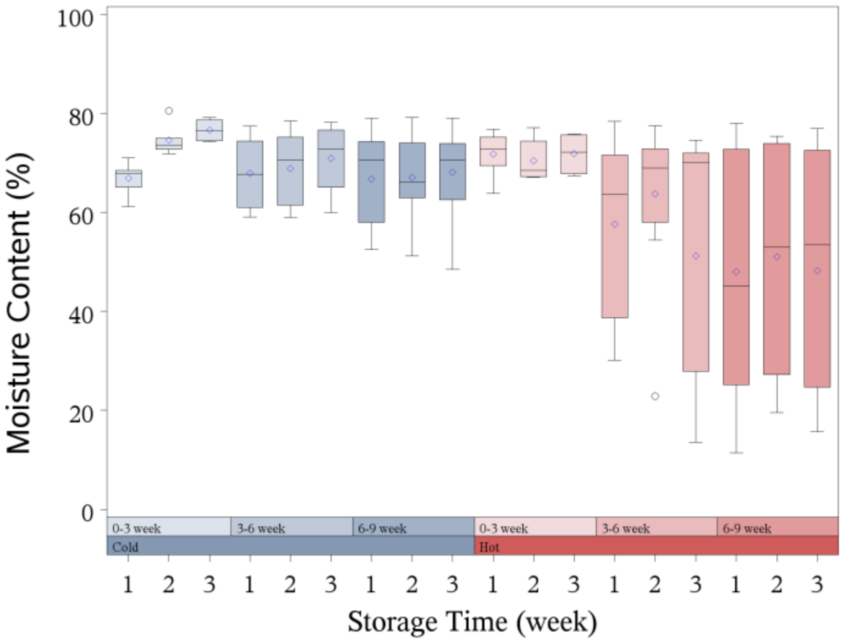

Figure 4.4. Temperature × Age × Week distribution of the moisture content in the simulated bedded manure packs. Cold and Hot refer to treatments stored at 10°C and 40°C; 0-3, 3-6 and 6-9 refer to age of the simulated bedded manure pack in weeks.

4.3.2 Total Nitrogen

The TN concentration (dry matter basis) of BP was impacted by elapsed storage time in weeks, increased with BP age and at lower storage temperature and decreased towards the top of BP. Total N was higher in Cold treatments (18.7 g kg^{-1}, SE = 0.3) than in Hot treatments (17.8 g kg^{-1}, SE = 0.2). Lower TN concentrations were observed in fresh BP (16.4 g kg^{-1}, SE = 0.4) than in mature BP (18.6 g kg^{-1}, SE = 0.3). Middle (19.4 kg^{-1}, SE = 0.5) and bottom zones (18.7 kg^{-1}, SE = 0.3) had higher TN concentration than top zones (17.5 kg^{-1}, SE = 0.3). No differences in TN concentration between CS treatments and SB treatments in Hot and Cold chambers were detected. Overall, the TN concentration (18.2 g kg^{-1}, SE = 0.2) was higher than the NH_4-N concentration (0.98 g kg^{-1}, SE = 0.03) which indicates that most of the N was present in the organic form.

4.3.3 Ammonium Nitrogen

Ammonium N concentrations (dry matter basis) decreased with a higher storage temperature, SB bedding, towards the top of the packs, and varied with maturity of BP and elapsed storage time in weeks. Yet, the analysis of two and three-way interactions of all treatment factors suggests certain combinations of factors promote a faster release. Generally, CS treatments (1.07 g kg^{-1}, SE = 0.05) had higher NH_4-N concentrations than SB treatments (0.90 g kg^{-1}, SE = 0.03). In Hot environments, NH_4-N concentrations were lower in week 1 compared to week 2 and 3 for both CS and SB treatments (Figure 4.5). The same was observed for Cold CS treatments, whereas no clear pattern was detected for Cold SB treatments.

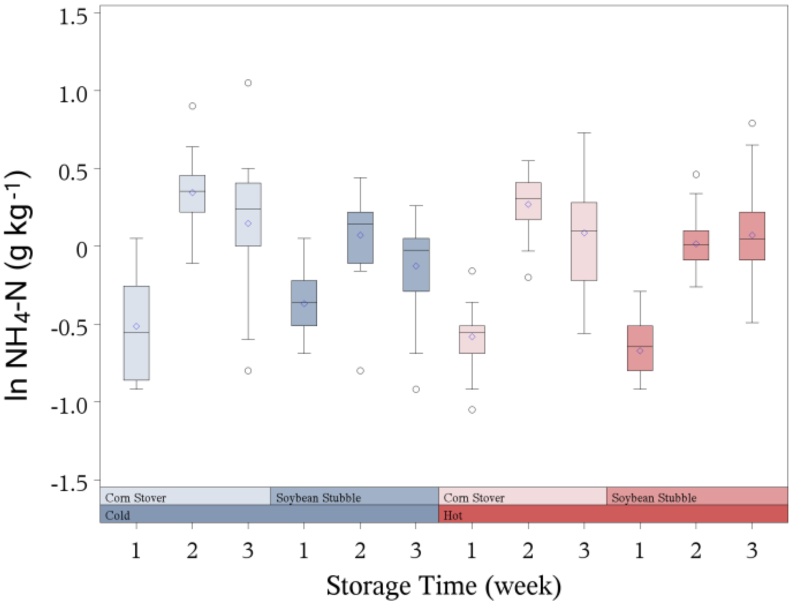

Figure 4.5: Temperature × Bedding × Week distribution of natural log-transformed ammonium N concentrations in simulated bedded manure packs. Cold and Hot refer to treatments stored at 10°C and 40°C; Corn Stover and Soybean Stubble refers to treatments with corn stover or soybean stubble bedding.

4.3.4 Total Phosphorus

Total P concentrations (dry matter basis) in the BP increased with a higher chamber temperature, towards the bottom of the packs, and varied with elapsed time in weeks and storage length. Total P concentration increased with a higher storage temperature for bottom and middle zones (Figure 4.6). In contrast, TP concentration did not vary across zones in Cold treatments.

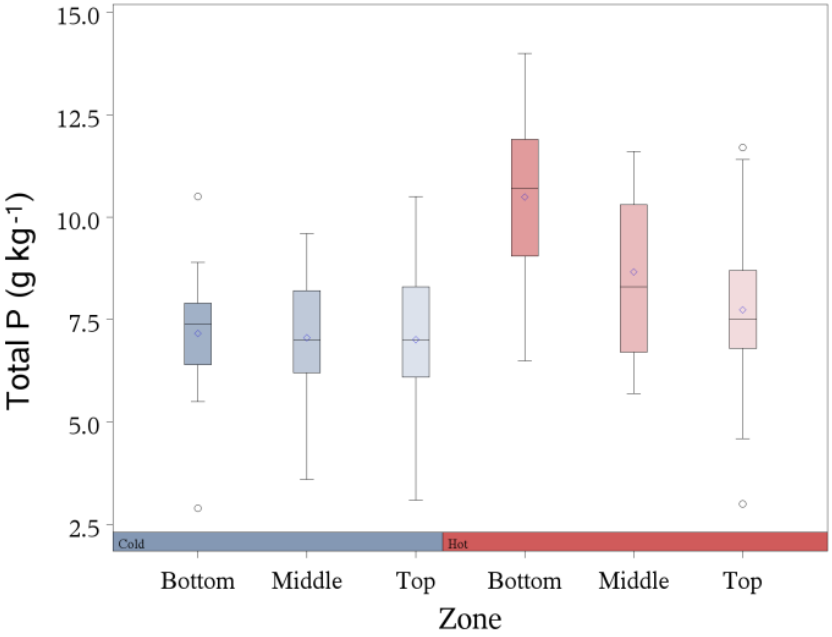

Figure 4.6. Temperature × Zone distribution of total P concentrations in the simulated bedded manure packs. Cold and Hot refer to treatments stored at 10°C and 40°C; B, M, and T refer to bottom, middle and top zone, respectively, in the simulated bedded manure pack in weeks.

4.3.5 Total Potassium

Total K concentrations (dry matter basis) increased with a higher chamber temperature, CS bedding, and towards the bottom of the BP but decreased with longer storage length. Total TK concentrations in bottom zones were higher in Hot treatments than in Cold treatments (Figure 4.7). Potassium concentrations were not different across weeks in both fresh BP and 6-9 week old BP, whereas 3-6 week old BP had lower K concentration in week 3 (21.3 g kg^{-1}, SE = 1.2) than in week 1 (24.2 g kg^{-1}, SE = 1.2).

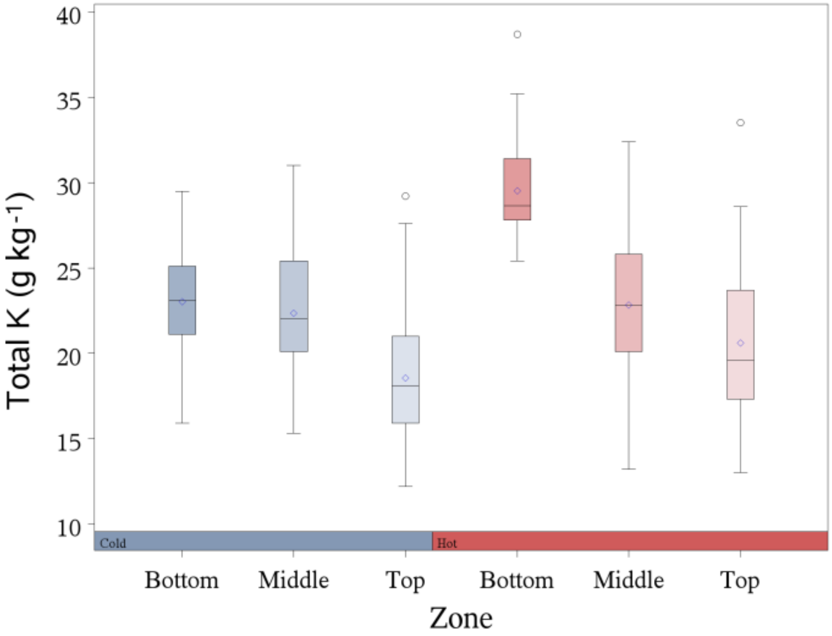

Figure 4.7. Temperature × Zone distribution of total K concentrations in the simulated bedded manure packs. Cold and Hot refer to treatments stored at 10°C and 40°C; B, M, and T refer to bottom, middle and top zone, respectively.

4.3.6 Short-term Nitrification Activity Potential

The NAP increased with the higher storage temperature, storage length and CS bedding, and was higher in middle zones than in bottom zones of the simulated BP. Comparing just Hot and Cold treatments, NAP in Hot treatments was more than twice as high as in the cold treatments (1.67 nmol $g_{bedpack}^{-1}$ h^{-1}, SE = 0.17 and 0.75 nmol $g_{bedpack}^{-1}$ h^{-1}, SE = 0.08, respectively). Significant interactions demonstrate the influence of BP age, zone, and bedding material on NAP in the simulated packs. Fresh packs had limited NAP in both Hot and Cold treatments (0.52 nmol $g_{bedpack}^{-1}$ h^{-1}, SE = 0.10) but NAP increased quickly as BP matured (1.20 nmol $g_{bedpack}^{-1}$ h^{-1}, SE = 0.17 (3-6 week old); 1.48 nmol $g_{bedpack}^{-1}$ h^{-1}, SE = 16 (6-9 week old)). Middle zones monitored only in 6-9 week old

BP had higher NAP (2.15 nmol $g_{bedpack}^{-1}$ h^{-1}, SE = 0.32) than top (0.90 nmol $g_{bedpack}^{-1}$ h^{-1}, SE = 0.09) and bottom zones (1.12 nmol $g_{bedpack}^{-1}$ h^{-1}, SE = 0.15). When top and middle zones were compared, NAP in Hot treatments with CS bedding were twice as high as top and middle zones of Hot treatments with SB bedding (Figure 4.8). Overall in Hot chambers, CS treatments (2.13 nmol $g_{bedpack}^{-1}$ h^{-1}, SE = 0.43) had higher NAP than SB treatments (1.21 nmol $g_{bedpack}^{-1}$ h^{-1}, SE = 0.13), whereas in Cold treatments, NAP did not differ between CS (0.70 nmol $g_{bedpack}^{-1}$ h^{-1}, SE = 0.08) and SB treatments (0.79 nmol $g_{bedpack}^{-1}$ h^{-1}, SE = 0.13).

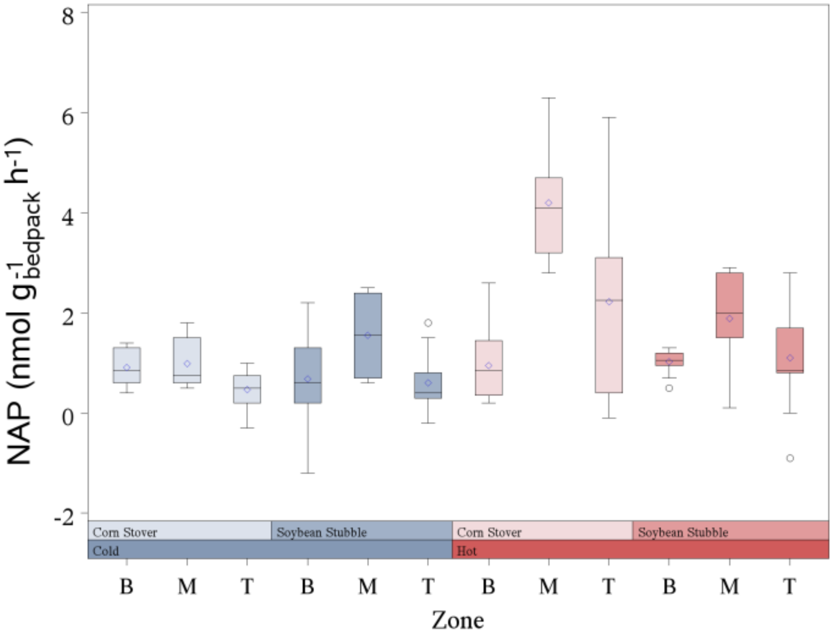

Figure 4.8. Temperature × Bedding × Zone distribution of short-term nitrification activity potential in simulated bedded manure packs. Cold and Hot refer to treatments stored at 10°C and 40°C; B, M, and T refer to bottom, middle and top zone, respectively.

4.3.7 Denitrification Enzyme Activity

Denitrification enzyme activity increased with the lower storage temperature, maturity, and elapsed time in weeks. Significant three-way interactions indicate which treatment and incubation combinations stimulated DEA. In Cold chambers, DEA decreased from week 1 to 2 only for 6-9 week old BP (Figure 4.9). In contrast, DEA increased sharply for all ages from week 1 to week 2 in Hot treatments. On average, DEA in Cold treatments (3.01 mmol $g_{bedpack}^{-1}$ h^{-1}, SE = 0.16) was more than three times higher than in the Hot treatments (0.93 mmol $g_{bedpack}^{-1}$ h^{-1}, SE = 0.14). In the Cold environment, DEA of SB treatments (3.39 mmol $g_{bedpack}^{-1}$ h^{-1}, SE = 0.23) was higher than CS treatments (2.57 mmol $g_{bedpack}^{-1}$ h^{-1}, SE = 0.21).

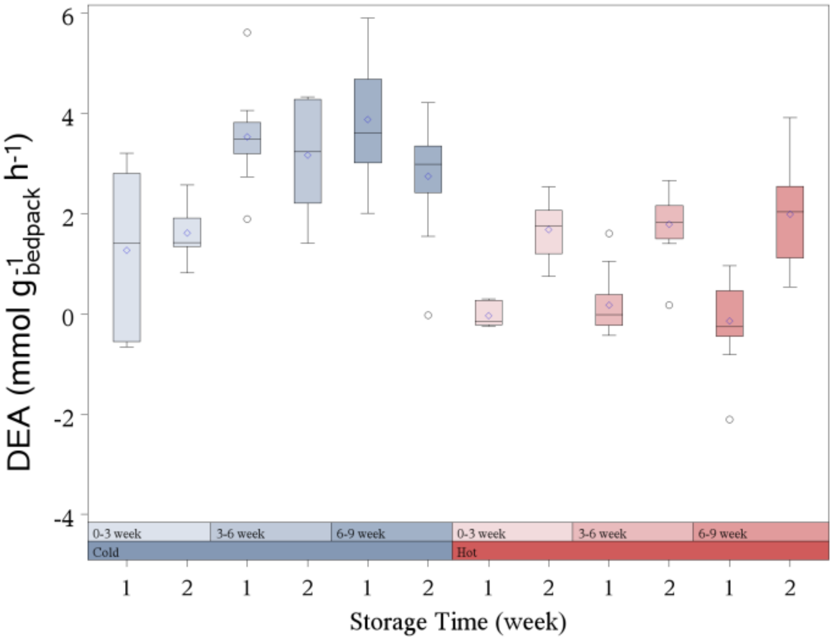

Figure 4.9. Temperature × Age × Week distribution of denitrification enzyme activity in the simulated bedded manure packs. Cold and Hot refer to treatments stored at 10°C and 40°C; 0-3, 3-6 and 6-9 refer to age of the simulated bedded manure pack in weeks.

4.3.8 Zone Temperatures, pH, and Total Carbon

The air temperature in the chambers was controlled. However, the temperatures in the different zones (as measured by the hand-held probe) varied and were not uniform for the different treatment combinations. Generally, the temperature in the different zones increased with the higher chamber temperature, elapsed storage time in weeks, and BP maturity, and was higher in middle and bottom zones and lower in top zones. In Cold chambers, pack temperature within each age treatment was higher in week 2 and 3, while fresh BP had the greater weekly increase in temperature (Figure 4.10). In cold chambers, generally zone temperature did not differ across ages, whereas in Hot chambers, zone temperature increased from 32°C (SE = 0.4) in fresh BP to an average of 35°C (SE = 0.2) in mature BP. In Hot chambers, fresh BP showed a sharp weekly increase in pack temperature, whereas temperature in 3-6 week old BP was not different across weeks, and was lower in week 3 than in week 1 in 6-9 week old BP (Figure 4.11). Temperature was higher in the middle zone of 6-9 week old BP (25°C, SE = 2) and towards the bottom of 3-6 week old BP (25°C, SE = 1). The pH decreased with the lower storage temperature. In Cold chambers, pH was lower in mature packs than in fresh packs.

Total C was based on measurements of the ash content of BP samples and thus only an indicator and not a direct estimate of TC in the BP. Total C decreased with a higher storage temperature, CS bedding and over the three week period. Significant three-way interactions indicate that TC was impacted by the combination of the treatment variables. In Cold environments, total C in SB treatments (425 g kg^{-1}, SE = 3) was higher than in CS treatments (400 g kg^{-1}, SE = 3). The weekly decrease in TC varied for CS and SB treatments in Hot and Cold chambers. In Cold chambers, total C was similar across weeks in both CS and SB treatments (Figure 4.12). In the Hot chambers, TC was lower for SB treatments during week 3 but similar in week 1 and 2, while TC in CS treatments was higher in week 3.

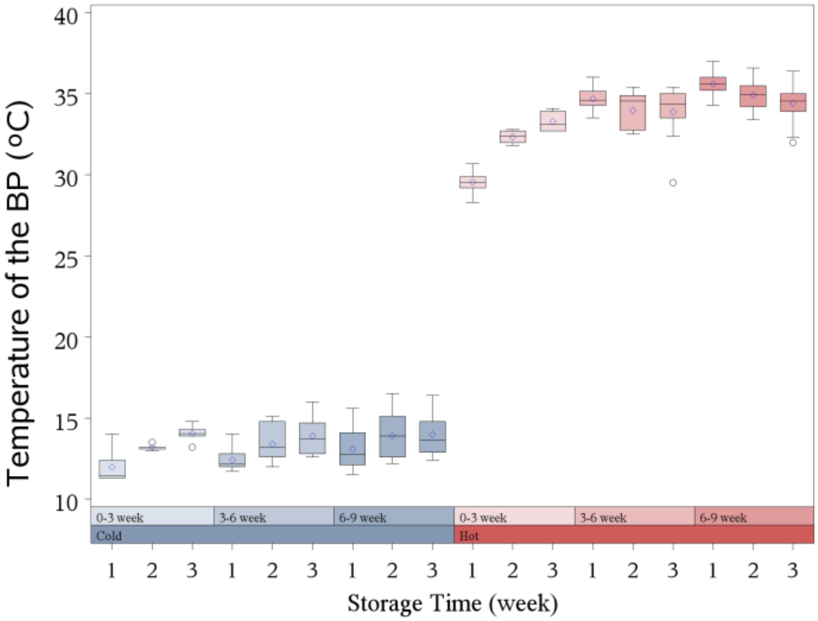

Figure 4.10. Temperature × Age × Week distribution of average temperatures in the simulated bedded manure packs.

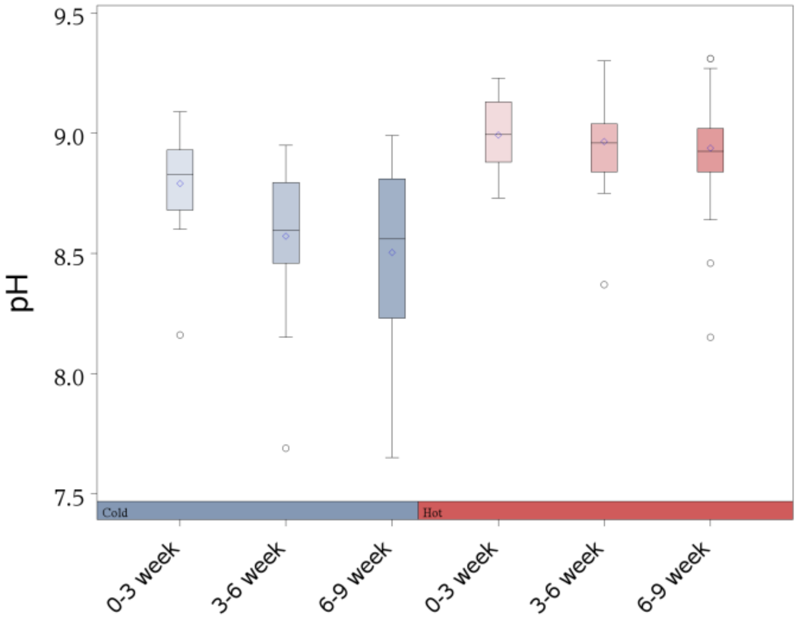

Figure 4.11. Temperature × Age distribution of pH in the simulated bedded manure packs.

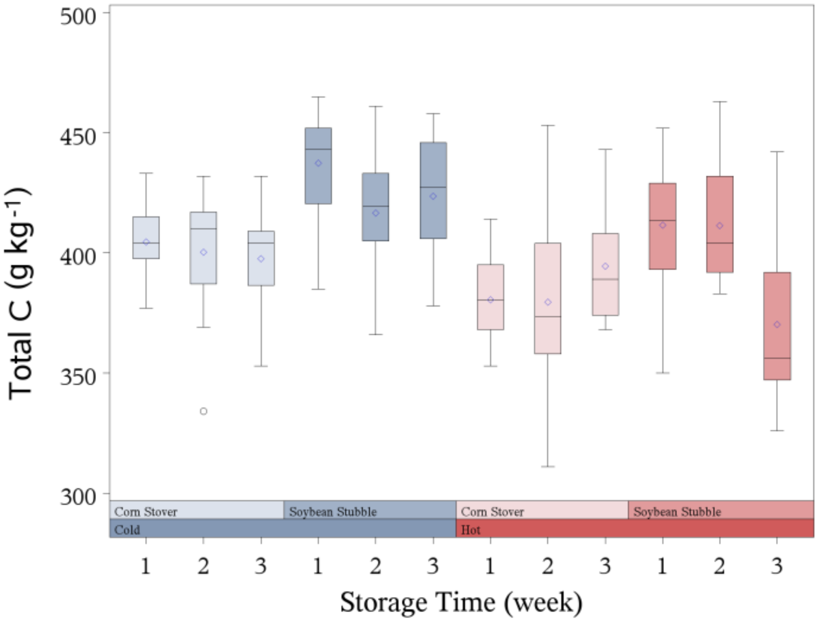

Figure 4.12. Temperature × Bedding × Week distribution for total C in the simulated bedded manure packs.

4.4 Discussion

Euken (2009) measured MC from beef cattle bedded confinement facilities between January and July 2008 and reported average MC of 70% for the bedded manure which is in agreement with MC measured in our Cold treatments (69%, SE = 1). Furthermore, MC and temperature measured for middle zones were similar to data reported by Spiehs et al. (2011) for commercial BP. Samples were hand-grabbed and temperature was measured 8-10 cm under the surface layer (Spiehs et al., 2011) which would be comparable with the top or middle zones of our simulated BP. Moisture content and temperature of BP at moderate temperatures (0°C and 21°C) were reported at 68% and 19°C, respectively (Spiehs et al., 2011), which was similar to 70% and 15°C measured for middle zones of our simulated BP. At hot temperatures above 21°C, pack temperature and MC of BP were reported at 29°C and 63%, respectively (Spiehs et al., 2011), while we measured 35°C and 51% MC for the middle zones of Hot treatments.

4.4.1 Impacts of Temperature

Storage temperature (Hot vs. Cold treatments) impacted all response variables. Moisture content, DEA, TAN, TN, and TC decreased at 40°C, whereas NAP, zone temperature, pH, and TP and TK concentration increased in the Hot treatments. Generally, temperature accelerates microbial activity and nutrient decomposition (Sánchez et al., 2000) and microbial activity results in additional metabolic heat production (MacGregor et al., 1981) during aerobic and anaerobic decomposition. Mature BP had similar zone temperatures but higher than fresh BP, assumedly because microbial communities were more active and abundant in older packs. The increase in temperature as fresh BP aged may be related to more vigorous microbial growth and/or the increasing pack depth. The proportion of surface area to BP volume decreased as fresh packs aged preventing heat loss via vaporization and contributed to increasing temperature as the fresh packs aged/matured. Similar temperature in mature BP across weeks may have been caused by reaching inhibitive temperature levels limiting additional microbial activity (MacGregor et al., 1981). The decrease in temperature during week 3 in 6-9 week old Hot treatments may indicate that inhibitive levels were reached.

The dew point temperatures for Hot and Cold chambers were set at 5°C and 15°C, respectively, which created a larger drying gradient in the Hot chambers due to the difference in relative humidity. This may explain why Cold treatments had similar MC across ages. Drying involves two main processes: (1) evaporation of the moisture of the surface of a material and (2) the diffusion of the moisture through the material to the surface (Mainguy et al., 2001). Hot treatments had lower MC in upper zones than in Cold treatments because of higher evaporation of moisture on the surface of BP caused by increased temperature and the larger drying gradient. The effect of the higher drying gradient was also reflected in BP temperatures (Figure 4.10). Cold treatments reached their treatment design temperature of 10°C because of the lower drying gradient. In contrast, Hot treatments were cooler than the chamber temperature because latent heat loss cooled the BP. Furthermore, moisture diffusion is inversely proportional to the distance to be traveled (Kramer, 1983), resulting in increased moisture in lower depths which lead to a consistent MC in the bottom of Hot and Cold treatments. In addition, the increased MC with lower depth in mature BP could be ascribed to more water moving downwards via gravity rather than upwards by diffusion, as was observed in the BP appearance. Cold and Hot treatments had a soupy consistency in the bottom zones and drier material in upper zones. The average MC observed for the simulated lab-scale BP (62%, SE = 1) was within a similar range of field-scale measurements reported at 70% (Euken, 2009) and 68% (Spiehs et al, 2011).

The lower TN content in BP housed in the Hot chambers was likely attributed to increased N volatilization loss. As reported in our companion paper, ammonia (NH_3) and nitrous oxide (N_2O) concentrations observed in the headspace of BP were three and two times higher in Hot treatments than in Cold treatments, respectively (Ayadi et al., 2015c). Studies with digested cattle manure (Muck and Richards, 1983; Sánchez et al., 2000) and pig manure (Park et al., 2005) also reported decreases in N with higher temperatures, with NH_3 representing the major source for N losses. The rapid increase in NH_4-N concentration in BP at 40°C may be related to enhanced microbial activity, organic N degradation, and faster chemical reactions at the higher temperature (Sánchez et al., 2000).

Similar TK and TP concentrations across Hot and Cold treatments were expected, because in contrast to nitrogen compounds, which may leach, runoff, or volatilize, K and P losses can occur only through leaching and runoff (Eghball et al., 1997), while runoff is the main mechanism for P losses (Confesor et al., 2007; Eghball et al., 1997; Hart et al., 2004). The experimental set-up ensured that runoff did not occur during our studies (BP were confined in buckets where no material was removed except during weekly sampling). Total K and TP most likely accumulated where the water moved within the BP column. This was particularly evident in wetter bottom zones of the Hot treatments where TP and TK concentration were higher than in drier top zones (Table 4.3). Phosphorus concentrations did not differ across depths in Cold treatments, whereas TK concentration increased with depth in Cold treatments. It is likely that the differences observed between TK and TP in the Cold treatments is because K leaches faster than P (Öborn et al., 2005).

The nitrification rate is strongly affected by substrate concentration (Kemp and Dodds, 2002), oxygen availability (Kemp and Dodds, 2002; Prinčič et al., 1998), temperature (Willers et al., 1998), and pH (Prinčič et al., 1998; Shammas, 1986; Willers et al., 1998). Looking just at temperature effects, the optimum temperature for nitrification has been reported at 30°C for activated sludge (Shammas, 1986), 35°C for pig slurry, and 40°C for aerated veal-calf slurry (Willers et al., 1998). Willers et al. (1998) observed a linear increase in nitrification activity between 20°C and 45°C. At 40°C, temperature was near the optimum temperature for nitrification which explains the faster increase in NAP with maturity of the BP compared to treatments at 10°C. As expected, the highest rates of NAP occurred in top and middle depths of the Hot treatments where oxygen would be more available. Nitrification at or near the surface has an important role in these BP since it would be the only source of oxidized N fueling denitrification.

Denitrification is described as the dissimilatory reduction of nitrate or nitrite to gaseous N_2O or N_2, typically performed by facultative anaerobic microorganisms (Maier, 2000; Shieh et al., 2004; Wallenstein et al., 2006) during a respiratory process (Saleh-Lakha et al., 2009; Wallenstein et al., 2006). Like nitrification, denitrification is also affected by a variety of environmental factors. Oxygen availability, nitrate concentration, and substrate availability (C and nitrate) are described as critical factors controlling denitrification rates (Clough et al., 2003). Microorganisms that are able to denitrify may simultaneously utilize nitrate and oxygen (Robertson and Kuenen, 1984) and thus are able to grow in aerobic and anaerobic environments. In addition, temperature and pH are also reported to affect the growth and metabolism of denitrifying communities (Saleh-Lakha et al., 2009). Examining just temperature as an effect, most soil studies reported increases in DEA with higher temperature as observed in this study with sharply increasing DEA from week 1 to 2 in Hot treatments. For example, Fischer and Whalen (2005) investigated temperature effects on DEA in incubated homogenized soil samples and reported increases in DEA between 10°C and 50°C, with 50°C resulting in the optimal temperature. Woodbury et al. (2001) monitored DEA every two to four weeks from October 1999 to May 2000 at three different locations and three different depths in soil of a feedlot pen in Nebraska and reported DEA between 0.0 and 215 mmol g_{soil}^{-1} h^{-1}. A positive correlation between DEA and soil temperature was found for different depths including the unconsolidated surface material, 0-0.10 m, and 0.10-0.20 m at different locations in the feedlot soil (Woodbury et al., 2001).

Beyond the direct effects of temperature on metabolic processes, temperature also may indirectly affect DEA through multiple mechanisms that affect NAP, pH, total C, MC, and free air space of BP. These indirect effects may explain why DEA in Cold treatments were generally higher than in Hot treatments. Free air space measurements were taken at the end of the monitoring period and are reported in a companion paper (Ayadi et al., in review). Free air space was significantly higher for Hot treatments (41%, SE = 1) than in Cold treatments (30%, SE = 2). In addition, free air space decreased as Cold treatments aged, likely due to compaction. In Hot treatments, the MC was almost twice as low in zones towards the top compared to Cold environments (Table 4.3). An increase in compaction and a higher MC may have limited oxygen availability and promoted areas of fermentation which are favored by denitrifying organisms and explain why DEA increased with maturity in Hot treatments. Total C in Cold treatments was higher than in Hot treatments (Table 4.3). The lower C and MC and higher free air space in Hot treatments may have suppressed denitrifier activity and/or growth because of less available substrates and less anoxic areas, thus resulting in lower DEA in Hot treatments than in Cold treatments. Wallenstein et al. (2006) reported that nitrate availability impacts instantaneous denitrification rates, while temperature, moisture conditions, and C availability impact soil denitrifier communities in the long-term. Nitrate availability would be determined by NAP, which was 1000-fold lower than DEA rates, and likely limited DEA. Miller and Berry (2005) also found MC and manure content affected presumptive denitrification rates in simulated cattle feedlot surface material with obvious N_2O emission observed only under high moisture, anaerobic, conditions.

4.4.2 Impacts of Bedding

Treatments with CS bedding had a higher MC, NH_4-N and TK concentration and NAP than monitored in SB treatments, whereas the TC content was lower in CS treatments and differences in DEA varied with weeks. Because nitrifiers require NH_4 as a substrate (Schmidt and Belser, 1994), the higher NH_4-N concentration measured in CS treatments stored in Hot chambers may explain why NAP was higher compared to SB treatments. The variation in DEA observed in Cold chambers between CS and SB treatments can be traced back to different microbial communities that established in CS and SB treatments and denitrify at different rates (Wallenstein et al., 2006). The higher TK concentration in CS treatments can be attributed to a higher TK content in CS material (13.0 g kg^{-1}) than SB material (10.8 g kg^{-1}). The TC content of CS bedding (437 g kg^{-1}) was lower than the TC content of SB material (488 g kg^{-1}) which explains the higher TC content in SB treatments. Treatments with CS as the bedding material had higher MC than SB treatments because CS material can hold about 14% more water than SB material (Spiehs et al., 2013b). The weekly increase in NH_4-N and TC (only in Hot chambers) in CS treatments was likely higher than SB treatments because of the stronger water holding capacity of CS material which promotes nutrient transport and leads to increased microbial activity and thus advanced degradation of organic N compounds.

4.4.3 Impacts of Storage Length and Depths of the Bedded Manure Packs

Except for TC, all physical, biological and chemical measurements changed with maturity and depth of BP, respectively. Water within the various layers in the BP affects oxygen diffusion and other processes such as bacterial activity and mineralization. As BP grew in depth, water from the added material moved downward and water with water-soluble P and K accumulated in the bottom zones (Table 4.3). The high solubility of P (Turner and Leytem, 2004) and K (Öborn et al., 2005) in water explains why TP and TK concentrations accumulated towards the bottom of the BP. The increase in TP and TK concentration towards the bottom of BP was more pronounced in Hot treatments than in Cold treatments which can be attributed to the higher moisture loss from upper zones of BP housed in the Hot chambers.

Over the monitoring period, the urine and bedding material were each taken from the same source and thus should not have varied in nutrient concentration. In contrast, the nutrient composition of fecal material collected right before material addition was more variable. During week 2, the average fecal TN (25.1 g kg^{-1}) and fecal TP concentration (11.1 g kg^{-1}) for Hot and Cold BP were higher than during week 1 (20.2 g kg^{-1} (fecal TN); 9.3 g kg^{-1} (fecal TP)) and week 3 (22.4 g kg^{-1} (fecal TN); 10.3 g kg^{-1} (fecal TP)) which corresponds to the significant increase in total N for week 2.

The increase in NH_4-N concentration with depth may result from a combination of leaching from upper zones and enhanced mineralization in the aged material, where advanced protein fermentation yielded higher NH_4-N concentration compared to upper zones with less mature material. Sørensen (1998) reported increased NH_4-N concentration after a 20-week incubation time of dairy slurry with barley straw at 5°C and 15°C. Patni and Jui (1991) reported significant increases in NH_4-N with decreasing depths between 0.3 and 2.5 m below the surface of 60 days stored dairy slurry. Ammonia volatilization loss from the surface of liquid manure is governed by the difference in NH_3

partial pressure in the liquid phase and in the adjacent gas phase in the manure surface (Ni, 1999). The loss of NH_3 from the surface layer would promote diffusion from the lower layer to reestablish equilibrium within the BP. However, the NH_4-N concentration was likely higher in lower depth because of decreasing diffusion with decreasing depth. In addition, water-soluble NH_4 from upper zones may have moved with water downward, contributing to increased NH_4-N concentration in lower depths.

The TN was lower for fresh BP than mature BP. The opposite was expected based on literature. For example, studies with stored dairy manure reported a decrease in TN by 21% after 9 weeks of monitoring, with major losses resulting from gaseous N volatilization (Petersen et al., 1998). Eghball et al. (1997) reported N losses between 19% and 42% during composting of beef cattle feedlot manure, with NH_3 volatilization accounting for more than 92% of those losses. In the cited studies, however, manure was stored without additional material addition, whereas in our study, the bedding, feces, and urine were added consecutively for three weeks and likely contributed to the increase in TN with storage length. Miller and Berry (2005) conducted a study of simulated beef cattle feedlot surface material and found an increase in N content over time in high manure, moderate moisture conditions similar to the BP incubations in this study.

Total N by Dumas combustion measures organic N, TAN, and in contrast to the Kjeldahl method accounts also for nitrate and nitrite (Watson et al., 2003). Compared to average TN (18 g kg^{-1}, SE = 0.2), average NH_4-N concentration (1.0 g kg^{-1}, SE = 0.03) was considerably lower and only trace amounts of nitrate and nitrite were likely present since DEA and NAP were low. Thus, TN was largely organic N. In fresh urine, organic N is predominantly (up to 97%) in the form of urea (Mackie et al., 1998). In feces, half of the N is ammonia, while the other half is organic N (Mackie et al., 1998) and originates from undigested feed, endogenous sources, and microbial biomass (Jost et al., 2013; Tamminga, 1992). Urea hydrolysis is rapid and usually complete within 24 hours depending on the temperature (Varel, 1997), whereas protein degradation in the feces is a slower process (Lee et al., 2011; Whitehead and Raistrick, 1993). The TN in these BP likely originated from fecal N.

The impact of storage length and depth on nitrification was evident and dependent upon the slow growth of these organisms and the availability of required substrates. In soil studies, nitrifying bacteria started nitrate production five days after beef manure was added to the soil (Meyer et al., 2002) because nitrifying bacteria in the soil required time to establish and grow even after substrates (ammonium in the manure) became available. We also observed an increase in NAP with time and attributed it to the slow growth of the nitrifying organisms. Woodbury et al. (2001) observed higher NAP in the unconsolidated surface matter of a feedlot soil, while NAP mostly decreased with depth below the feedlot surface which was likely related to increased compaction of the soil. The NAP was low in the bottom zones of our BP because those areas were likely compacted, wet, and under anoxic condition, thus inhibiting nitrification activity. Middle zones had assumedly more aerobic areas because they were drier than bottom zones. In addition, NH_4-N concentration increased once a middle or bottom zone developed and may have promoted nitrifying activity in the these zones.

Zone was not significant as a main effect and not included in any of the two or three-way interactions of DEA. Woodbury et al. (2001) reported decreases in DEA with depth (unconsolidated surface material, 0-0.10 m, 0.10-0.20 m). However, the soil density was almost three times higher in 0.10 to 0.20 m depth compared to the unconsolidated surface (Woodbury et al., 2001) which may explain the lower DEA. The difference in material density and compaction between zones in our study was most likely not as extreme and may explain why DEA did not vary as noticeable in different depth as in the feedlot soil studies. Also denitrifying microorganisms possess a versatile metabolism and can thrive aerobically or fermentatively using oxygen or organic compounds, respectively, as a terminal electron acceptors.

Overall, most of the variables showed no clear distinction across zones. Only MC was significantly different for all three zones in Hot and Cold treatments, while temperatures across zones varied only in the Cold treatments. The BP developed two major zones with different NH_4-N concentrations for cold treatments and two major zones with different TN and TK concentrations for Cold and Hot treatments where concentrations were similar in the middle and bottom zones but lower in the top zone. The NAP was similar across zones in Cold treatments, whereas in the Hot treatments, NAP was similar in top and middle zones but lower in the bottom zone. Total N and C, pH and DEA were all similar across zones in the Hot and Cold treatments.

4.4.4 Manure Management Decisions

All physical, biological and chemical properties were affected by the storage temperature, as were the gaseous releases of NH_3, carbon dioxide, methane and nitrous oxide concentration reported in our companion paper (Ayadi et al., 2015c). The bedding material impacted MC, TN, TC, NH_4-N and TK concentration. All measured variables except TC changed with maturity, while MC, NH_4-N and TK concentration varied across all or some of the different assigned zones.

The seasonal choices producers make on bedding material and manure removing frequencies impact the nutrient/fertilizer value and the weight/volume of the manure. According to the results obtained from this lab-scale experiment, manure management decisions may be affected in the following ways:

- During the hot summer season (temperatures approaching 40°C with dryer air), the MC of the bedded manure will decrease compared to the moderate season (around 10°C with humid air). In addition, the MC will decrease with storage length at high temperatures and MC is expected to be higher when using CS compared to SB. Manure with lower MC may decrease transportation cost per unit of nutrient. Knowing the MC helps estimate the volume that is required for storage of the bedded manure.
- With warmer season, TN and NH_4-N concentration in the BP are expected to decrease, whereas TP and TK concentration will increase towards the bottom of the BP. Thus, thoroughly sampling the BP from top to the bottom is needed to obtain accurate estimates of the nutrient value. This is also true when sampling the manure for TN, NH_4-N and TK concentration during all seasons.
- Total K and NH_4-N concentration are anticipated to be higher when CS is applied as the bedding material compared to SB, whereas TP and TN will not vary between CS and SB bedded manure.
- Maintaining a bedded manure pack leads to higher TN concentration with longer storage, while NH_4-N and TK concentration should not vary with longer storage time.

Depending on the nutrient to be managed, decisions on manure removing frequencies may be more crucial in the summer, while the choice of the bedding material appears to be important year round. The available space for storage of removed manure needs to be considered when making decisions on cleaning frequencies.

4.5 Future Work

As the next step, a process-based model will be developed that involves correlation analyses of the data of the manure constituents reported in this study with the gas concentration data reported in the companion paper (Ayadi et al., 2015c). Nutrient mass balances will provide verification and bounds to develop a process-based model using the BP nutrient and gaseous loss measurements. This model will describe the combined processes occurring within a bedded beef barn system with respect to different bedding material, BP storage length, manure removal frequencies and storage temperature impacts. The process-based model will serve as a tool to predict NH_3 and N_2O emission, and to estimate the quantity produced and N-P-K value of BP from confined beef cattle systems.

4.6 Conclusions

Temperature impacted all measured variables in this study, while most of the physical, biological and chemical parameters in the simulated bedded manure packs changed with storage length and bedding source. The following conclusions were made:

- With the higher storage temperature and dryer environment, moisture content, total N, and denitrification enzyme activity decreased, whereas short-term nitrification activity potential increased and total N, K and P increased towards the bottom of the bedded manure packs.

- As the bedded packs matured, total N, short-term nitrification activity potential, and denitrification enzyme activity increased, whereas the moisture content in the packs decreased only at 40°C.
- At 10°C and 40°C, the moisture content, total N, ammonium N and total K concentration increased towards the bottom of the packs and short-term nitrification activity potential was higher in middle zones, while ammonium N and total P concentration increased with depth only at 10°C and 40°C, respectively.
- Corn stover treatments had higher total ammonium N, moisture content, and total K concentration than treatments with soybean stubble.
- The findings of temperature, bedding, and storage time impacts on physical, biological and chemical parameters help explain nutrient movements and transformations in and from the bedded manure to optimize nutrient and moisture management practices. The data will be used to develop a process-based model that estimates quantity, quality and the fertilizer value of beef bedded manure packs in confined systems.

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CHAPTER 5

PROCESS-BASED NUTRIENT MODELING FOR THE BEDDED MANURE PACK OF CONFINED BEEF CATTLE FACILITIES

Synopsis

Results from Chapters 3 and 4 were used to develop a process-based model that simulates NH_3 and N_2O emission and N, P and K concentrations in the bedded manure pack of confined beef facilities. Data used for calibration and validation were used from the experiments in Chapters 3 and 4.

5.1 Introduction

Modeling can describe the processes occurring in manure and predict the fate of nutrient compounds. A mathematical model uses equations that describe the behavior of a system. Mechanistic or process-based models are based on mathematical models that analyze the whole system with respect to the sub-systems and their interactions with each other (France, 1988). The advantage over an empirical model, which is based on observation and experimental data is that a process-based model can also be applied for conditions that diverge from the original data which was used to develop the model (France, 1988). With help from the model, physical, chemical and biological nutrient transformations and movements in and from manure can be understood. Manure management can then be adjusted to optimize manure quality and reduce gaseous emission.

Until recently, most researchers focused mainly on modeling only NH_3 or GHG to mitigate emission from cattle operating systems (Beukes et al., 2011; Crosson et al., 2011; Moral et al., 2012; Petersen & Sommer, 2011; Schils et al., 2005). The Manure-DNDC (Li et al. (2012) and the IFSM (Rotz et al. (2015) are two available models that predict GHG and NH_3 emissions from livestock farms relating to environmental factors. In addition, the IFSM predicts whole-farm balances of N, P, K, and C. Most of these accessible models lack prediction capabilities for manure nutrient quality and quantity from confined beef housing systems that apply a BP for manure and moisture management within the barn. The IFSM includes a BP component but has not been verified yet with data from commercial BP barns. A model is needed that describes the combined processes occurring within a bedded beef barn system with respect to both different bedding material and manure removal frequencies to predict manure quantity and quality.

5.2 Existing Models

5.2.1 Water Movement Models

The Richards equation is often used to model vertical water movement in soil (Filipović et al., 2014; Selle et al., 2011; Šimůnek et al., 2003; Svoboda et al., 2013; Vereecken et al., 1991). However, when using the Richards Equation, boundary conditions may be difficult to define and a large data set may lead to numerical instabilities causing the model to not converge (Nelson & Parsons, 2007). In addition, the Richards equation model requires soil hydraulic and crop specific parameters obtained from intensive field and laboratory measurements (Nelson & Parsons, 2007; Selle et al., 2011). If the Richards equation would be applied for BP, the specific parameters would have to be determined for the BP since BP texture and structure differs from soil.

Previous research with simulated beef cattle BP demonstrated that water-soluble P and K accumulated toward the bottom of the packs with water movement (Ayadi et al., 2015d). Petersen et al. (1998b) reported that N leaching constituted 1-4% of total N, whereas NH_3 losses constituted 4-5% from stock-piled dairy cattle manure. Results showed that N concentration, expressed with reference to the initial dry matter, increased towards the bottom of stock-piled manure during the three months of storage (Petersen et al., 1998). Thus, a water movement model would be useful to estimate nutrient composition throughout the different layers of a BP.

Water percolation is often modeled in soil studies (Arnold et al., 2012; Chen & Hu, 2004; Verseghy, 1991). One available model that simulates vertical water movement in lab-scale static compost piles (52-cm, 2.6-cm diameter) considers internal and external evaporation, based on reference evaporation, liquid and vapor diffusion using Fick's law, and percolation following Darcy's law as the main processes (Seng et al., 2012). However, the model was not tested under full-scale conditions and did not account for additional water inputs. The IFSM (Rotz et al. (2015) simulates water movement through bedded manure. The modified IFSM models water movement through a 4-layer BP by considering evaporation from the two most upper layers. It also accounts for saturated (drain) and unsaturated flow. The model includes water addition in the form of urine.

5.2.2 Nitrogen Transformation and Movement Models

Nitrogen losses through NH_3 volatilization from liquid livestock manure have been extensively studied. Comprehensive models that describe N emission from cattle manure on a process-based level are Manure-DNDC (Li et al., 2012) and the IFSM (Rotz et al., 2015).

The Manure-DNDC model:

- estimates N and carbon transformations and movements in manure systems of livestock farms based on biochemical and geochemical processes in relation to environmental factors (Li et al., 2012);
- core processes and transformations are decomposition, hydrolysis, nitrification, denitrification, ammonia volatilization, and fermentation and are based on the Denitrification-Decomposition model (Li et al., 2011) to predict gas emissions (NH_3, CO_2, N_2O, NO, N_2, VOC, and CH_4), N leaching and N and P content in and from the manure; and

- was not designed to predict manure quantity and fertilizer concentration based on bedding materials and cleaning frequencies in beef cattle deep-bedded barns.

The IFSM:

- predicts emissions of NH_3, GHG and hydrogen sulfide as well as P losses in livestock farms including manure handling system;
- core processes are ammonia volatilization, leaching, anaerobic digestion, nitrification, denitrification processes, and anaerobic decomposition;
- considers all major farm components from animal performance, feed use, crop production and manure handling including the bedded manure;
- predicts NH_3 and N_2O emission and water movement for BP as well as temperature in BP.
- has not been validated for total N, P and K concentrations for BP of commercial beef barns.

5.2.3 Phosphorus Movement Models

Phosphorus can be leached from manure if land applied (Sharpley & Moyer, 2000) and moves when attached to particles or dissolved in water. Phosphorus leaching is described as the product of water flux and inorganic P concentration (Nelson & Parsons, 2007).

Most soil P models consider only dissolved inorganic P in the leaching process because of the complex organic P cycles and vertical P transport (Nelson & Parsons, 2007). Water-extractable P (WEP) can serve as an indicator for dissolved P and consists of inorganic P (dissolved inorganic P and dissolved minerals; Toor et al. (2006)) and organic P (monoester and diester P and DNA; He et al. (2009)). In livestock manure, around 60 to 90% of the P typically exists in the inorganic form (Sharpley & Moyer, 2000) which is highly plant-available (Eghball et al., 2002). Inorganic P forms detected in beef cattle manure are orthophosphate, pyrophosphate, and polyphosphate, with orthophosphate as the major inorganic P form (Turner, 2004). Turner and Leytem (2004) determined that feedlot cattle manure consists of 42% orthophosphates and 57% organic P. Organic P forms quantified in beef cattle manure are phytate, DNA, phospholipids, and other orthophosphate monoesters and diesters (Turner, 2004; Turner & Leytem, 2004). Using the Hedley fractionation procedure, total P discovery for P from beef cattle manure was 79%; only 11% of P was recovered in the water extract (Turner & Leytem, 2004).

The Soil and Water Assessment Tool (SWAT; Arnold et al. (2008)) and the modified Groundwater Loading Effects of Agricultural Management Systems (GLEAMS; Leonard et al. (1986)) are existing models that predict P movement and transformation in the manure.

The model by Vadas et al. (2011)

- simulates P transformations and P losses in runoff from grazing cattle;
- predicts decomposition of organic matter and physical assimilation into soil as a function of air temperature and fecal moisture and simulates water-extractable inorganic and organic P and non-water extractable inorganic and organic P;
- assumes only the water-extractable P can be leached from manure with the addition of precipitation;

- successfully predicted P runoff and leaching from grazing cattle feces and would be more suitable for soil than P movements and transformations in the BP because of differences in soil structure and decomposition and assimilation of fecal material in soil.

GLEAMS has been used to predict P movement from field-scale agricultural systems (Shirmohammadi et al., 1998). Nelson & Parsons (2006) modified GLEAMS to:

- predict P transport on long-term subsurface P leaching in waste-amended soils based on water percolation rates in the soil profile;
- simulate dissolved P concentrations for long-term predictions;
- Phosphorus concentrations for short-time periods of less than a year were not accurately predicted and this time window would be necessary to estimate P concentration in the bedded manure.

The SWAT model:

- was developed to assess the impact of management and climate on water quality in watersheds and large river basins on a daily time step (Arnold et al., 1998);
- considers diffusion as the main process of P movement in soil and estimates leaching of soluble P only from the top 10 mm of soil into the first layer of soil (Chaubey et al., 2006); and
- Phosphorus losses were only estimated from soil P pools instead of losses from the manure and a high number of parameters are required to run model simulations.

There are no existing studies available that model P transformation and movement through the total depth of a BP in confined beef cattle facilities.

5.2.4 Potassium Movement Models

Most current models to predict transformations and movements focus on K release and K leaching in soil. Phillips (2004) used the models CHEMFLO^{TM}-2000 and Soil Water Infiltration Models (SWIMv2) to predict potassium chloride leaching in sandy soils with:

- both models using a similar approach by simulating one-dimensional water flow using the Richards equation (Verburg et al., 1996) and chemical movements using the convection-dispersion equation in unsaturated soils (Nofziger & Wu, 2003);
- results showing that neither CHEMFLO^{TM}-2000 nor SWIMv2 accurately predicted K movement in unsaturated soil. Potassium concentrations were overestimated by both models whereas soil-water distribution was predicted very closely (Phillips, 2004).

Fortin et al. (2015) developed a software tool that:

- simulates daily seasonal dynamics of N and K leaching under potato crop;
- considers rainfall using a series of least squares support vector machine;
- predicts water loss using the Canadian Land Surface Scheme (CLASS) model (Verseghy, 1991) which uses the Green-Ampt infiltration model and the Darcian equation for one-dimensional flow (Verseghy, 1991);
- accurately modeled K leaching for sandy soil cropped to potato (Fortin et al., 2015).

Sandy soil has low water content and the prediction capability of the model developed by Fortin et al. (2015) would likely not perform accurately for K movement in the bedded manure.

5.2.5 Objective

The objective of this study was to develop a process-based model that estimates manure quantity, nutrient content, fertilizer (N-P-K) value, and gaseous emission (NH_3, N_2O) for the bedded manure mixture. The model simulates the physical, chemical and biological transformations and movements of N, P and K within and NH_3 and N_2O volatilization from the BP surface with respect to different manure storage time, bedding material, and ambient air temperature. The processes were modeled separately and then incorporated and linked together in the overall model. The final process-based model is a system of equations that describes and predicts the NH_3 and N_2O emission and N-P-K value of the BP from a confined beef cattle system. Using the process-based approach, the model is open for further expansion and refinement. Ultimately, producers will have a tool that estimates value, quality, quantity, and air emission by changes in manure management.

5.3 Model Development

5.3.1 Water Movement Model

5.3.1.1 Distribution of Layers

The IFSM water routine (Rotz et al., 2015) was applied and modified to predict water movement through a four-layer BP considering evaporation, saturated (drainage;

considers only matrix flow), and unsaturated flow (Table 5.1). The following assumptions were made:

- following the IFSM model, there are four layers in a BP, and depths of layers 1 and 2 were fixed at 7 and 8 cm, respectively;
- at times of material addition, BP material was pushed down and material
- redistributed. Boundaries of layers 3 and 4 moved upward and increased in height based on the assumption that depth of layers 1 and 2 remained constant (Figure 5.2);
- based on MC observed in simulated BP (Ayadi et al., 2015d) 30% of the added urine including nutrients, flows through macropores (macropore flow) of the BP straight through layers 3 and 4, 10% remains in layer 1, while most of the urine water (60%) was absorbed by layer 2.

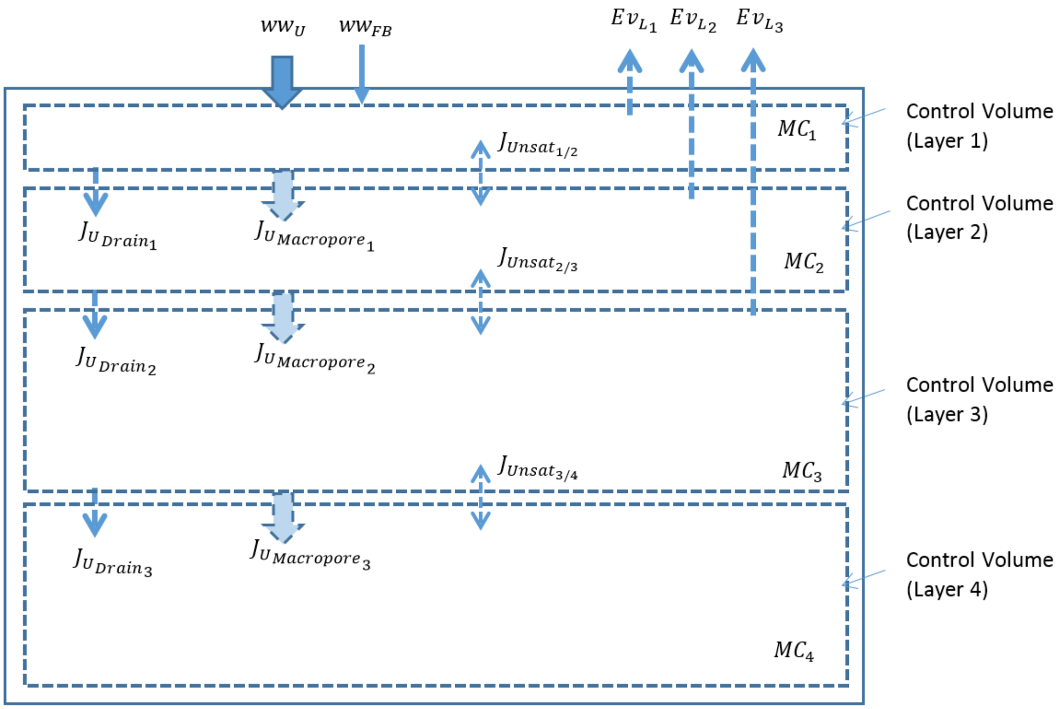


Figure 5.1. Diagram of water movement through a bedded manure pack with four layers.

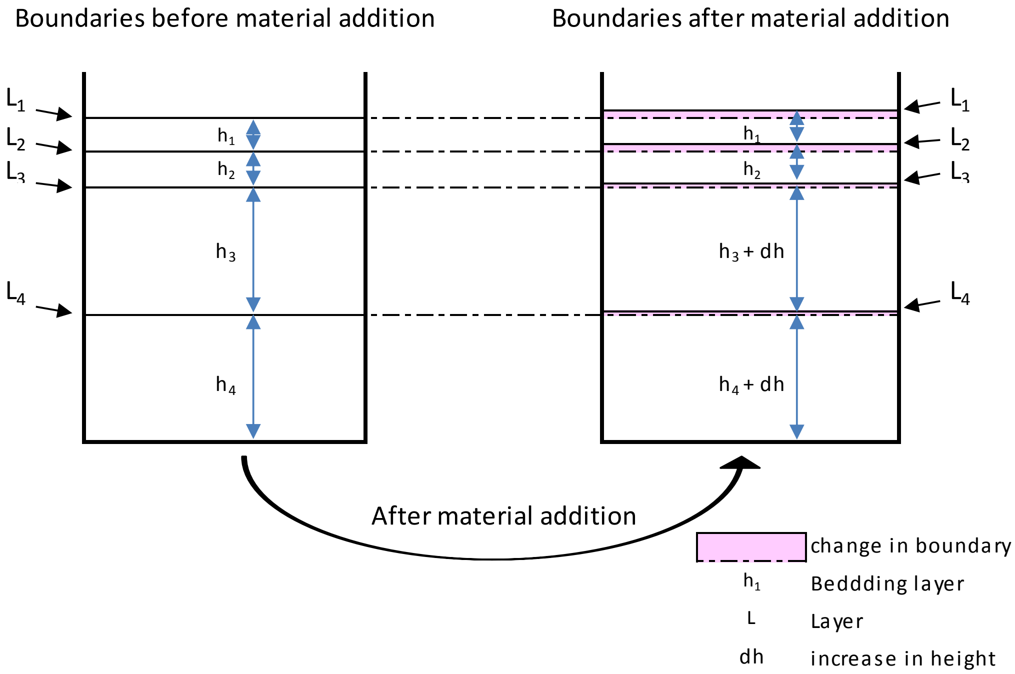


Figure 5.2 Diagram showing how boundary layers are moved after material addition.

Total depth of the BP was calculated using an empirical equation based on BP depth and weight data with respect to age from previous BP studies (Ayadi et al., 2015d).

$$d_{BP} = 8.75 \cdot \ln\left[max\left(1.3, ww_{U_{Tot}} + ww_{FB_{Tot}}\right)\right] + 2.8 \tag{5.1}$$

where d_{BP} = the total depth of BP (cm); $ww_{U_{Tot}}$ = the total urine water in BP (kg); and $ww_{FB_{Tot}}$ = the total wet weight of bedding/feces mixture (kg).

Depths of layers 3 and 4 were calculated based on total depth of the BP as follows:

$$d_L = \frac{d_{BP} - 15}{2} \tag{5.2}$$

where d_L = the depth of layer (cm).

Input variables to the model were temperature, BP area, average wind speed, amount and type of bedding material, and urine and fecal material added. Dry matter (DM) content of the bedding/feces mixture (FB) and the urine and N, P and K concentrations were based from BP analysis of previous studies (Ayadi et al., 2015d). Initial MC and DM conditions for BP were set at the start of the simulation. For fresh packs, the model calculated initial MC based on the mass of added urine, mass of water added through the FB and the wet weight mass (ww) of FB. Initial MC of layers 1, 2, 3, and 4 for 3-6 week old BP, were set at 52%, 58%, 70%, and 74% and the initial MC of FB was set at 50% as observed in simulated BP (Ayadi et al., 2015d).

With this information the distribution of the urine mass in each layer (1 through 4) was calculated as:

$$ww_{U_{L_{t=0}}} = \frac{ww_{FB_{L_{t=0}}} \cdot MC_{L_{t=0}} - W_{FB_{L_{t=0}}}}{(1 - MC_{L_{t=0}})} \tag{5.3}$$

where $ww_{U_{L_{t=0}}}$ = urine water in layer L at time t=0 (kg); $ww_{FB_{L_{t=0}}}$ = wet weight of FB in layer L (kg); $MC_{L_{t=0}}$= initial total BP moisture content (kg water kg^{-1} wet weight of layer L) at time t=0; and $W_{FB_{L_{t=0}}}$= water mass in bedding and feces mixture at time t=0 (kg).

Moisture content was calculated from urine and FB. However, urine water was separated from FB water because only nutrients in urine were assumed to move with water movement since water (including nutrients) in the fecal material was considered hygroscopic. In addition, NH_3 emissions were calculated from urine. The urine (ww_U) and the “free/unbound” water from the FB mixture in layers 1 and 2 were considered as the available water that has the potential to evaporate.

5.3.1.2 Evaporation

The evaporation rate was estimated from previous experiments (Ayadi et al., 2015d) as the average water loss of simulated BP over one week of observation. The weekly rate was then converted to a daily rate. The free water available from the FB mixture for evaporation was set at a maximum of 77% of the water mass in these layers, based on observations in previous studies (Ayadi et al., 2015d) where the MC in the most upper zone did not decrease below 23%. At times of low evaporation, less water evaporates than is available from the ww_U and more water would be available for drainage. At higher evaporation rates, if more ww_U in layer 1 evaporates, the unbound water in ww_{FB} from layer 1 then has the potential to evaporate, followed by the ww_U in layer 2, and finally the water in ww_{FB} from layer 2.

$$ww_{U_{1_t}} = \max\left(0, ww_{U_{1_t}} - Ev_{L_1}\right)$$

$$W_{Ex_1} = \max\left(0, Ev_{L_1} - ww_{U_{1_t}}\right)$$

$$W_{FB_{1_t}} = \max\left(minW_{FB_{1_t}}, ww_{U_{1_t}} - W_{Ex_1}\right)$$
$$W_{Ex_2} = \max\left(0, W_{Ex_1} - \left(W_{FB_{1_t}} - minW_{FB_{1_t}}\right)\right)$$
$$ww_{U_{2_t}} = \max\left(0, ww_{U_{2_t}} - W_{Ex_2}\right)$$
$$W_{Ex_3} = \max\left(0, W_{Ex_2} - ww_{U_{2_t}}\right) \qquad (5.4)$$
$$W_{FB_{2_t}} = \max\left(minW_{FB_{2_t}}, ww_{U_{2_t}} - W_{Ex_3}\right)$$
$$W_{Ex_4} = \max\left(0, W_{Ex_3} - \left(W_{FB_{2_t}} - minW_{FB_{2_t}}\right)\right)$$
$$ww_{U_{3_t}} = \max\left(0, ww_{U_{3_t}} - W_{Ex_4}\right)$$
$$W_{Ex_5} = \max\left(0, W_{Ex_4} - ww_{U_{3_t}}\right)$$

where $ww_{U_{L_t}}$= urine water in layer (L) after material addition (kg); W_{Ex_L}= excess water; depending on evaporation rate either added or subtracted to layer (kg); and $minW_{FB_{L_t}}$ = bound water in the bedding/feces mixture that cannot evaporate (kg).

The actual evaporated water from layers 1 (Ev_{L_1}) and 2 (Ev_{L_2}) was:

$$Ev_{L_1} = W_{Ex_1} - W_{Ex_2}$$
$$Ev_{L_2} = W_{Ex_3} - W_{Ex_4} \qquad (5.5)$$
$$Ev_{L_3} = W_{Ex_4} - W_{Ex_5}$$
$$Ev_{act} = Ev_{L_1} + Ev_{L_2} + Ev_{L_3}$$

5.3.1.3 Saturated and Unsaturated Flow

For saturated (drainage) and unsaturated flow, the IFSM approach was followed. In IFSM, drainage was calculated based on soil water balance from the CERES-MAIZE model used for cropland soils based on relationships described by Jones & Kiniry (1986). Excess water drained to the next lower layer and was estimated on water content differences between the simulated and lower layer, saturation level and depth of the simulated layer and on the moisture content. Unsaturated flow was modeled with the moisture content differences between adjacent layers, and the unsaturated hydraulic conductivity was predicted using an empirical equation from data of dairy cattle manure by Sutitarnnontr et al. (2014) as a function of moisture content. Since fresh BP consisted only of one layer, saturated and unsaturated flow were not estimated for fresh BP.

5.3.1.4 Average Moisture Content and Nutrient Concentrations from Experimental Data

Average MC and TN, TP and TK concentrations were calculated based on water masses in each layer and simulated for BP with only one, two and three different layers for 0-3, 3-6 and 6-9 week old BP, respectively. The decreased number of BP was chosen because the simulated data was evaluated with experimental data from BP that were sampled from not more than three layers (Ayadi et al., 2015c, 2015d). Once per week, right before material addition, all BP (n = 3) were sampled approximately 2 cm below the surface, 3-6 and 6-9 week old BP were sampled approximately 2 cm above the bottom, and 6-9 week old BP were sampled from the approximate middle. The most upper layer (considered as layer 1 (bedding) in the model) was moved when sampling during the bench-scale experiments, and then sampled from 1, 2 and 3 different layers, respectively, depending on BP age. Thus, for the 6-9 week old BP, the model predictions for layers 2, 3, and 4 were compared with top, middle and bottom zones, respectively (Figure 5.3). For 3-6 week old BP, layers 2 and the average MC of layers 3 and 4 were compared to top and bottom zones of the experimental treatments (Figure 5.4). For 0-3 week old BP, also referred to as fresh packs, the model considered only one layer.

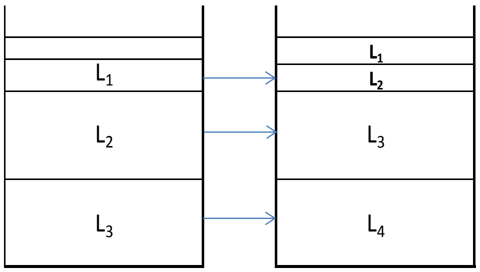


Figure 5.3 Layers of treatment and model of 6-9 week old bedded manure packs

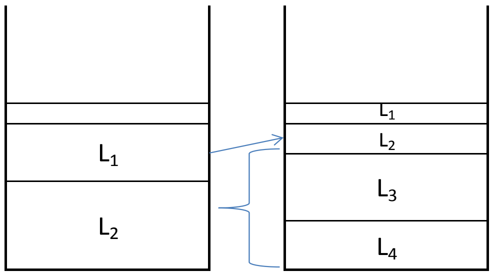


Figure 5.4 Layers of treatment and model of 3-6 week old bedded manure packs

Thus, the total MC of each age treatment was estimated as follows:

$$MC_{Age} = \frac{W_{Tot}}{ww_{Tot}} \tag{5.6}$$

with

$$\begin{aligned} W_{Tot_{0-3wk}} &= ww_1 * \frac{MC_1}{100} \\ W_{Tot_{3-6wk}} &= ww_1 * \frac{MC_1}{100} + ww_2 * \frac{MC_2}{100} + ww_3 * \frac{MC_3}{100} \\ W_{Tot_{6-9wk}} &= ww_1 * \frac{MC_1}{100} + ww_2 * \frac{MC_2}{100} + ww_3 * \frac{MC_3}{100} \end{aligned} \tag{5.7}$$

where ww_n = wet weight in assigned layer (n=1, 2, 3; kg).

Total N, P and K concentrations for the three age treatments were estimated with the following equations. Depending on the age either one, two or three layers were accounted for calculating total nutrient concentrations.

$$c_{TN,TP.TK} = \frac{c_{TN_1,TP_1,TK_1} \cdot ww_1 \left(1 - \frac{MC_1}{100}\right) + c_{TN_2,TP_2,TK_2} \cdot ww_2 \left(1 - \frac{MC_2}{100}\right) + c_{TN_3,TP_3,TK_3} \cdot ww_3 \left(1 - \frac{MC_3}{100}\right)}{ww_{Tot} - W_{Tot}} \tag{5.8}$$

where c_{TN_n} = N concentration in assigned layer (n=1, 2, 3; g kg^{-1}, DM); where c_{TP_n} = P concentration in assigned layer (n=1, 2, 3; g kg^{-1}, DM); c_{TK_n} = N concentration in assigned layer (n=1, 2, 3; g kg^{-1}, DM); and MC_n = moisture content in assigned layer (n=1, 2, 3; %).

5.3.2 Nitrogen Model Development

5.3.2.1 Nitrogen Balance

Nitrogen is the only nutrient that can be transformed via mineralization, immobilization, nitrification, denitrification, leaching, and NH_3 volatilization (Petersen et al., 1998b). Manure N may be lost through NH_3 and N_2O volatilization, leaching, and runoff (Cabrera & Gordillo, 1995; Oenema et al., 2005).

The N balance for the bedded manure pack can be used to determine N leaching and N volatilization. Since different processes occur in the different layers, the N mass balances are defined for all four layers (Figure 5.5):

Layer 1:

$$\begin{aligned} c_{TN_{1,t+1}} \cdot DM_{1,t+1} &= c_{TN_{1,t}} \cdot DM_{1,t} + c_{TN_{FB_a}} \cdot DM_{FB_a} + c_{TN_{UM_a}} \cdot DM_{UM_a} \cdot 0.10 - E_{NH_3} \cdot A_{BP} \\ &\quad \cdot t - E_{N2O} \cdot A_{BP} \cdot t - c_{NH_4^+ + NO_3^+ \, 1} \cdot DRAIN_1 \cdot A_{BP} \cdot \rho_{H2O} \cdot (1 - MC_{urine}) \\ &\quad - \frac{c_{TN_{FB_{a,3}}} \cdot DM_{FB_a}}{2} - \frac{c_{TN_{FB_{a,4}}} \cdot DM_{FB_a}}{2} \end{aligned} \tag{5.9}$$

Layer 2:

$$\begin{aligned} c_{TN_{2,t+1}} \cdot DM_{2,t+1} = c_{TN_{2,t}} \cdot DM_{2,t} + c_{NH_4^+ + NO_3^+ \, 1} \cdot DRAIN_1 \cdot A_{BP} \cdot \rho_{H2O} \cdot \\ (1 - MC_{urine}) - c_{NH_4^+ + NO_3^+ \, 2} \cdot DRAIN_2 \cdot A_{BP} \cdot \rho_{H2O} \cdot (1 - MC_{urine}) + c_{TN_U} \cdot DM_U \cdot 0.60 \end{aligned} \tag{5.10}$$

Layer 3:

$$c_{TN_{3,t+1}} \cdot DM_{3,t+1}$$

$$= c_{TN_{3,t}} \cdot DM_{3,t} + \frac{c_{TN_{FB_{a,3}}} \cdot DM_{FB_a}}{2} + c_{NH_4^+ + NO_3^+ {}_2} \cdot DRAIN_2 \cdot A_{BP} \cdot \rho_{H2O} \cdot (1 - MC_{urine}) - c_{NH_4^+ + NO_3^+ {}_3} \cdot DRAIN_3 \cdot A_{BP} \cdot \rho_{H2O} \cdot (1 - MC_{urine}) + c_{TN_U} \cdot DM_U \cdot 0.15 \quad (5.11)$$

Layer 4:

$$c_{TN_{4,t+1}} \cdot DM_{4,t+1}$$

$$= c_{TN_{4,t}} \cdot DM_{4,t} + \frac{c_{TN_{FB_{a,4}}} \cdot DM_{FB_a}}{2} + c_{NH_4^+ + NO_3^+ {}_3} \cdot DRAIN_3 \cdot A_{BP} \cdot \rho_{H2O} \cdot (1 - MC_{urine}) + c_{TN_U} \cdot DM_U \cdot 0.15 \quad (5.12)$$

where $c_{TNUrine}$ = N concentration in added urine (g kg^{-1}); and c_{TNfec} = N concentration in added FB (g kg^{-1}); $c_{NH_4^+ + NO_3^+ {}_n}$ = Ammonium-N and nitrate concentration in assigned layer (n=1, 2, 3; g kg^{-1}); DM = dry matter (%); E_{NH3} = N lost through ammonia emission (kg m^{-2} d^{-1}); *DRAIN* = drained water (cm water); A_{BP} = area of BP (m^2); and ρ_{H2O} = density of water (kg m^{-3}).

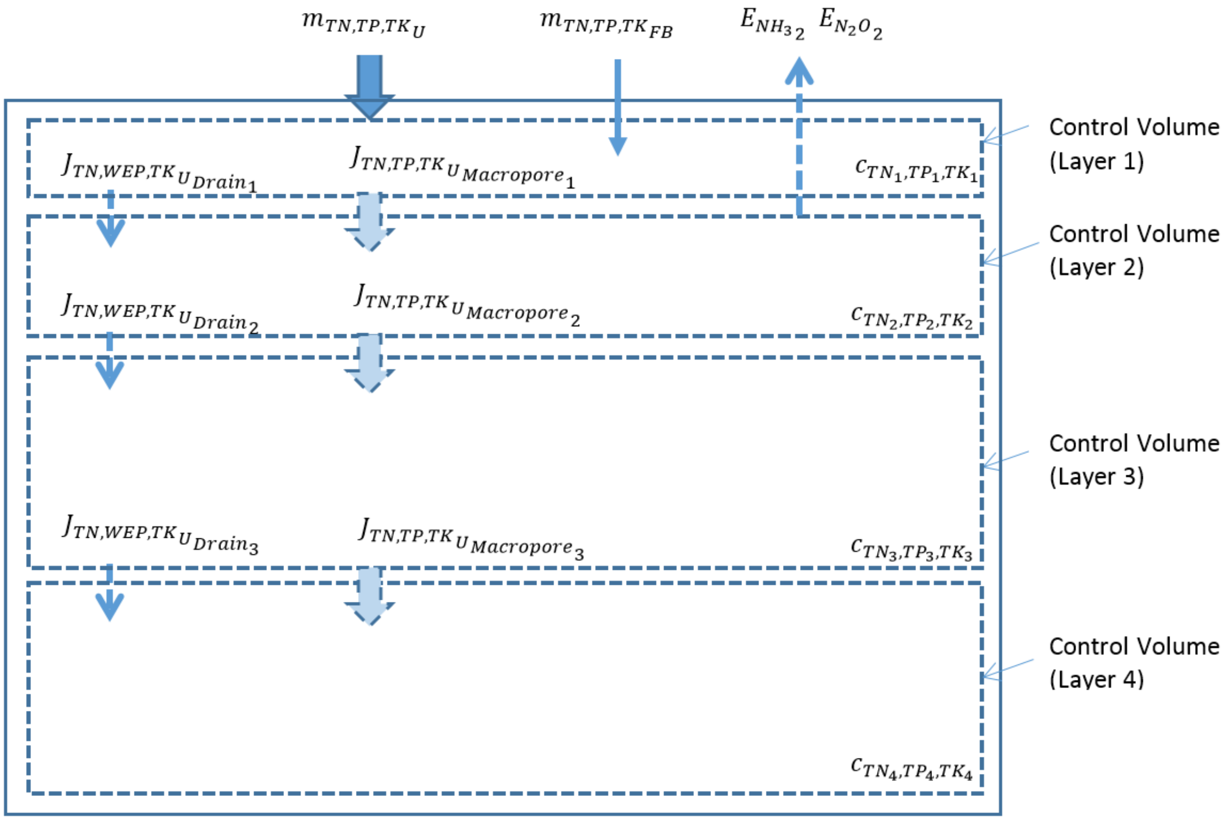


Figure 5.5. Mass balance diagram for total nitrogen, total phosphorus, and total potassium. J refers to flow (either macropore or saturated flow (Drain)).

5.3.2.2 NH₃ Volatilization

A core process to estimate fate of nutrients in the BP is to determine gas volatilization, which in turn, depends on substrate concentrations, temperature, surface pH, air stream, disturbances, and differences in physicochemical properties (Blanes-Vidal et al., 2010; Ni et al., 2009). The majority of N losses from the manure can be lost through NH_3 volatilization (Dewes, 1995; McGinn & Sommer, 2007; Sommer et al., 2006) which depends on the surface area of the bedded manure that is exposed to the surrounding air flow, temperature of the manure (Rotz, 2004), pH, NH_3 concentration (Muck & Steenhuis, 1982), depth and BP material. In order for gases to move into the atmosphere, three steps have to be completed: gas production, release, and emission (Ni et al., 2009). The majority of the ammonia production is based on urea degradation which is temperature dependent (Muck, 1982). It has been shown for cattle manure that these N losses predominantly originate from urea degradation (Ayadi et al., 2015a; Lee et al., 2011) whereas in fecal material, the production of NH_3 is slower but continues with the degradation of the manure through microorganisms under both aerobic and anaerobic conditions (EPA, 2004). Once urea ($CO(NH_2)_2$)) is exposed to both heat and the enzyme urease, it decomposes to NH_3 and CO_2 (Eq. 5.13) (Simpson et al., 1998).

$$CO(NH_2)_2 + H_2O \xrightarrow{Heat\ or\ Urease} 2NH_3 + CO_2 \tag{5.13}$$

Ammonia dissolved in water, forms the positively charged ammonium cation (NH_4^+) and free ammonia (NH_3 (aq)), both together also referred to as total ammoniacal N (TAN). McGinn & Sommer (2007) reported that the majority of inorganic N in stockpiled beef cattle manure (one and nine months old) occurred as TAN, whereas in composted beef manure (three months old), nitrate was dominant as inorganic N. Only free NH_3 (aq) can be released to the atmosphere. Gas release from manure occurs by transport across the liquid-air boundary through a partial pressure gradient between dissolved and gaseous compounds (Blanes-Vidal et al., 2010).

Ammonia volatilization depends on air flow and the gas concentration gradient between the free air near the manure surface and in the manure surface. Thus, under steady-state conditions, NH_3 emission equals NH_3 volatilization whereas under transient state, air flow and concentration gradient governs emission. Ammonia movement within the manure is caused by diffusion and governed by concentration and temperature differences (Ni et al., 2009). Ammonia emissions were estimated based on the IFSM model (2014). Changes were made to predict hourly emission for the times when NH_3

concentrations were measured in the experiments. Assumptions were made that at times of material addition TAN concentration was zero, whereas the urea concentration was 80% of TN concentration added through the material. The change in urea concentration with time to TAN was based on the model by Muck (1982) which uses the Michaelis-Menten equation:

$$\frac{dC_{urea}}{dt} = -\frac{V_{max} \cdot c_{urea}}{K_M + c_{urea}} \tag{5.14}$$

with V_{max} = maximum urea transformation rate, depends on temperature (kg urea kg^{-1} wet material h^{-1}); c_{urea} = urea concentration (kg urea m^{-3} urine); and K_M = Michaelis-Menten constant (kg urea m^{-3} wet material).

The TAN concentration therefore depends on the change in urea degradation minus NH_3 emission. Since 1 mol of urea hydrolyzes to 2 mols of NH_3, the TAN concentration is increasing with urea degradation:

$$\frac{dC_{TAN}}{dt} = -2\left(-\frac{dC_{urea}}{dt}\right) - \frac{E_{NH_3} \cdot A_{BP}}{V_U} \tag{5.15}$$

The transfer mechanism of ammonia from the BP surface to the ambient air is described as convective mass transfer:

$$E_{NH_3} = K \cdot (F \cdot c_{TAN} - H \cdot c_{Air}) \cdot 3600 \cdot A_{BP} \tag{5.16}$$

with E_{NH3} = ammonia emission (kg m^{-2} h^{-1}); K = mass transfer coefficient (s m^{-1}); F = ammonia fraction of TAN in BP (-); c_{TAN} = TAN concentration in BP (kg m^{-3} urine); H = Henry constant (-); c_{Air} = ammonia concentration in surrounding air (kg N m^{-3} air); A_{BP} = BP surface area (m^2); and V_U = urine volume (m^3). The K, F and H equations are described in Rotz et al. (2014).

Assuming that the NH_3 concentration in the surrounding air is negligible compared to the TAN concentration in the BP surface because of the constant air exchange, c_{Air} was neglected in our model.

5.3.2.3 Denitrification/Nitrification contributing to N_2O Losses

Besides gaseous N losses through ammonia, manure N can be reduced to the atmosphere as nitrous oxide (N_2O) via nitrification and/or denitrification (Maeda et al., 2013). Denitrification is an anaerobic process that requires a C-source where NO and N_2O are products of the stepwise reduction of NO_3^- to N_2 when optimum conditions are met (Groenestein & VanFaassen, 1996; Li et al., 2012). Nitrous oxide can also be produced during nitrification as a byproduct of hydroxylamine oxidation (Kool et al., 2011; Wrage, 2001). Maeda et al. (2013) reported that significant N_2O emission from dairy manure compost occurred immediately after pile turning events by the reduction of nitrite and nitrate and suggested that the N_2O is produced by denitrifying microorganisms including nitrifiers for nitrifier denitrification. In previous studies, we found that N_2O release occurred as a pulse immediately after material was added to the BP. In contrast to nitrifying communities, denitrifying bacteria are ubiquitous facultative anaerobes (Michotey et al., 2000) that were likely present throughout the BP as was suggested by no differences in DEA across zones. Since NAP was 1000-fold lower than DEA and nitrite was found in the bedding material, the pulse N_2O releases were likely a results of denitrification (Ayadi et al., 2015b). The DEA did not differ with BP depth, whereas NAP was higher in middle zones. Middle zones had assumedly more aerobic areas because they were drier than bottom zones. In addition, NH_4-N concentration increased once a middle or bottom zone developed and may have promoted nitrifying activity in these zones. In cattle farmyard manure, the highest N_2O production was observed in the middle and surface zone while higher N_2 proportions were found in the wetter bottom zone (Moral et al., 2012). The cattle farmyard manure was 110 cm deep. The surface zone was 0 – 25 cm deep and the middle zone was 25 – 60 cm below the surface (Moral et al., 2012).

Nitrous oxide emissions were calculated based on the assumption that losses only occurred via microbial denitrification. The equations were taken from IFSM and can be found in Table 5.1.

5.3.2.4 Nitrogen Leaching

Nitrogen leaching models exist for soil profiles (Beauchamp & Paul, 1989; Chambers et al., 1999; Hansen et al., 2000). Losses via N leaching in soils are calculated based on the readily available N remaining after NH_3 volatilization (Chambers et al., 1999). Nitrogen lost through leaching is typically in the form of nitrate in soil amended with manure (Baker, 2001; Murphy et al., 2000; Svoboda et al., 2013; Ulén, 1993). Since the majority of N in stored manure is either organic N or TAN (McGinn & Sommer (2007), N leaching in the form of nitrate is neglected in the model.

5.3.3 Phosphorus Model Development

Kleinman et al. (2002) reported a positive correlation between WEP concentration and dissolved-reactive P concentration in surface runoff losses in soils amended with livestock manure. The scientists concluded that greater dilution of manure dry matter increased the WEP (Kleinman et al., 2002). The mass balance for P were based under the assumption that no aerial losses occur (Sommer, 2001) and that only WEP moves downward through macropore flow. At times of material addition, 60% of the TP added through urine remained in layer 2, while 20% moved through macropore flow to layer 3 and 20% to layer 4. Total P (TP) for each layer in the BP can be expressed as the following mass balances:

Layer 1:

$$c_{TP_{1,t+1}} \cdot DM_{1,t+1} = c_{TP_{1,t}} \cdot DM_{1,t} + c_{TP_{FB_a}} \cdot DM_{FB_a} \cdot (1 - WEP) + c_{TP_{UM_a}} \cdot DM_{UM_a} - \frac{c_{TP_{FB_{a,3}}} \cdot DM_{FB_a} \cdot (1 - WEP)}{2} - \frac{c_{TP_{FB_{a,4}}} \cdot DM_{FB_a} \cdot (1 - WEP)}{2} \tag{5.17}$$

Layer 2:

$$c_{TP_{2,t+1}} \cdot DM_{2,t+1} = c_{TP_{2,t}} \cdot DM_{2,t} + c_{TP_{UM_a}} \cdot DM_{UM_a} \cdot 0.60 \tag{5.18}$$

Layer 3:

$$c_{TP_{3,t+1}} \cdot DM_{3,t+1} = c_{TP_{3,t}} \cdot DM_{3,t} + c_{TP_U} \cdot DM_U \cdot 0.20 + \frac{c_{TP_{FB_{a,3}}} \cdot DM_{FB_a} \cdot (1 - WEP)}{2} \tag{5.19}$$

Layer 4:

$$c_{TP_{4,t+1}} \cdot DM_{4,t+1} = c_{TP_{4,t}} \cdot DM_{4,t} + c_{TP_U} \cdot DM_U \cdot 0.20 + \frac{c_{TP_{FB_{a,4}}} \cdot DM_{FB_a} \cdot (1 - WEP)}{2} \tag{5.20}$$

where WEP = water-extractable P (%); $c_{TPUrine}$ = P concentration in added urine (g kg^{-1}); and c_{TKFB} = P concentration in added FB (g kg^{-1}).

5.3.4 Potassium Model Development

Potassium losses occur faster than P losses, since K occurs predominantly in the dissolved form and is leached out rapidly from manure compared to P or other cations

(Öborn et al., 2005; Sommer, 2001). In compost studies with dairy cow manure, Sommer (2001) reported up to 16% of initial K concentration was lost through leaching. In a previous study, we measured up to 80% of total K (TK) existed in the urine portion of material added to simulate beef bedded manure packs (Ayadi et al., 2015d). Similarly, in dairy manure more than 70% of the K is from urine and exists in the dissolved form (COESA-Report, 1998). Thus, the model considers K content from urine as the water-soluble K that moves with water in the BP and treats K in feces and bedding as the non-soluble K. As shown in TP balance, at times of material addition, 60% of the TK added through urine remained in layer 2, while 20% moved through macropore flow to layer 3 and 20% to layer 4. The TK concentration of each layer can be estimated with the following mass balances:

Layer 1:

$$c_{TK_{1,t+1}} \cdot DM_{1,t+1} = c_{TK_{1,t}} \cdot DM_{1,t} + c_{TK_{FB_a}} \cdot DM_{FB_a} + c_{TK_{UM_a}} \cdot DM_{UM_a} - \frac{c_{TK_{FB_{a,3}}} \cdot DM_{FB_a}}{2} - \frac{c_{TK_{FB_{a,4}}} \cdot DM_{FB_a}}{2} \tag{5.21}$$

Layer 2:

$$c_{TK_{2,t+1}} \cdot DM_{2,t+1} = c_{TK_{2,t}} \cdot DM_{2,t} + c_{TK_{UM_a}} \cdot DM_{UM_a} \cdot 0.60 \tag{5.22}$$

Layer 3:

$$c_{TK_{3,t+1}} \cdot DM_{3,t+1} = c_{TK_{3,t}} \cdot DM_{3,t} + c_{TK_U} \cdot DM_U \cdot 0.20 + \frac{c_{TK_{FB_{a,3}}} \cdot DM_{FB_a}}{2} \tag{5.23}$$

Layer 4:

$$c_{TK_{4,t+1}} \cdot DM_{4,t+1} = c_{TK_{4,t}} \cdot DM_{4,t} + c_{TK_U} \cdot DM_U \cdot 0.20 + \frac{c_{TK_{FB_{a,4}}} \cdot DM_{FB_a}}{2} \tag{5.24}$$

where $c_{TKUrine}$ = K concentration in added urine (g kg^{-1}); and c_{TKFB} = K concentration in added FB (g kg^{-1}).

5.3.5 Calculations and Model Input

A survey with beef producers and consultant/planners in Minnesota, South Dakota, Iowa, and Nebraska was conducted to identify the most useful format of input and output parameters to and from the model. Survey responses showed the interest of the participants and proved the utility of the future model: 69% of consultants and planners and 63% of producers found the concept of the manure nutrient calculator useful. Only 24% of the consultants and planners and 13% of the producers found it not useful. The majority of beef producers stated that yearly estimates of the amount of manure produced are needed while consultants/planners answers varied. The survey showed that the most important output of the model is the N-P-K value of the manure followed by the monetary fertilizer value. Responses also indicated that producers found model estimates of gaseous emission not important and needed only yearly estimates.

The computation process used to simulate N_2O emission, NH_3 emission, TN, TP and TK concentrations is illustrated in the flow chart in Figure 5.6. The model assumes that temperature, wind speed, evaporation rate, bedding, added urine and fecal MC, TN, TP and TK composition are constant during the simulation process. The simulations were performed using Microsoft Visual Basic for Applications 7.1 to allow multiple calculations within a short time. The calculations used in the program can be found in Table 5.1.

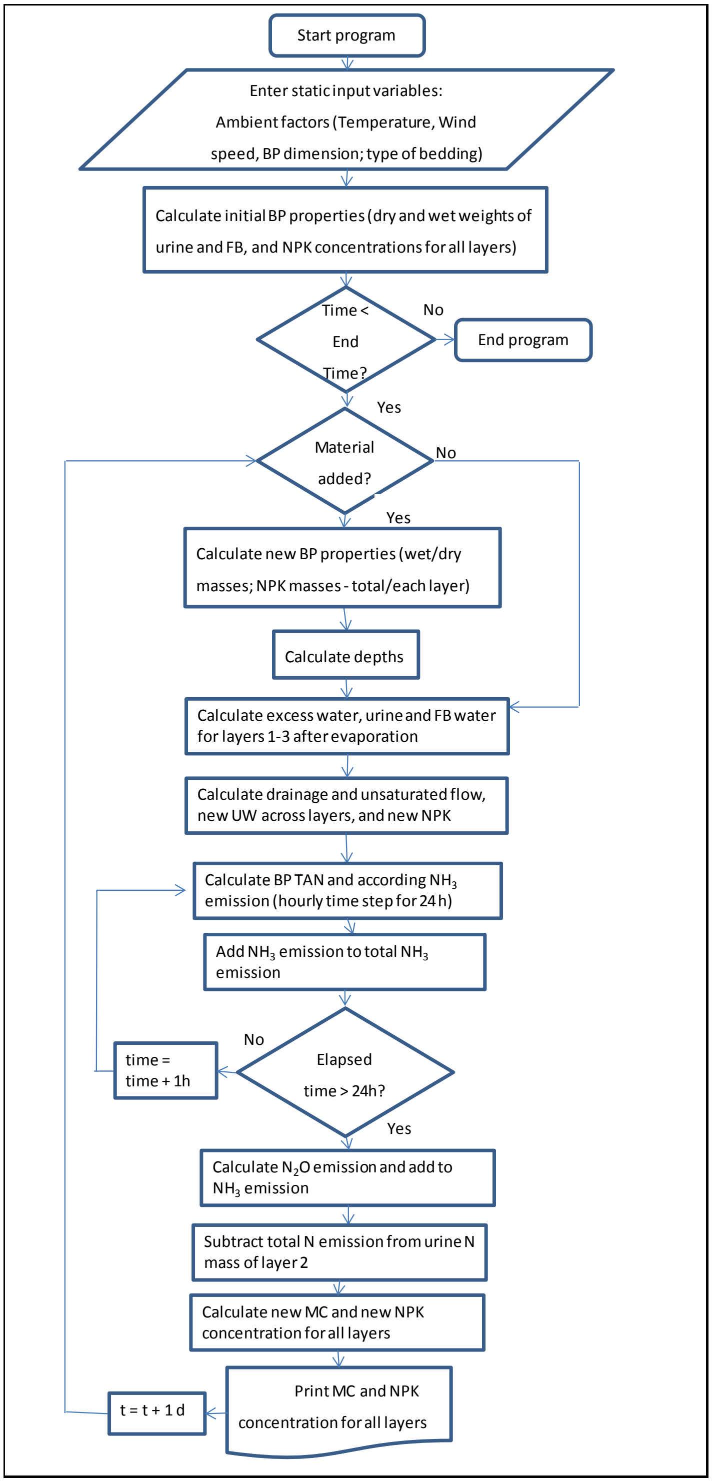


Figure 5.6. Flowchart for the water and nutrient model

5.3.6 Model Equations

Table 5.1. Model process equations

Process	***Variable***	**Calculations**
START		
Set initial Values		BP conditions: Dry density (ρ_{dry} = 0.1 g cm^{-3}) Particle density (PD = 1.5 g cm^{-3}) Water-extractable P (WEP = 11%) Surface pH (10°C) = 8.3; surface pH (40°C)=8.7 Resistance to mass transfer through manure (10°C: R_m=3*10^5 s m^{-1}, 40°C: 12.6*10^5 s m^{-1} (IFSM, 2015) Nitrate concentration (N_{NO3}=40 µg N g $soil^{-1}$) C_{CO2} = soil CO2 flux, µg C g^{-1} soil day^{-1} Water-filled porosity (W_{wfps} = 0.5) Air-filled porosity (GS = 0.4; Ayadi et al., 2015d) Total porosity (PS_{Tot} = 0.55) Dry matter urine (DM_U = 7%) Dry matter feces (DM_F = 80%) Nutrient conc. added material: TN feces (CTN_F = 23 g kg^{-1} DM) TP feces (CTP_F = 10 g kg^{-1} DM) TK feces (CTK_F = 6.4 g kg^{-1} DM) TN urine (CTN_U= 203 g kg^{-1} DM) TP urine (CTP_U= 23 g kg^{-1} DM) TK urine (CTK_U = 73 g kg^{-1} DM)

Enter values	Ambient factors: Temperature (T, °C) Wind speed (WS, m s^{-1}) Relative humidity (RH, -)	BP conditions: Bedding material added (kg d^{-1}) Type of bedding added (CS/SB)	
Assign based on input data:			Dry matter bedding (DM_B, %) CS = 23% DM; SB = 13% DM TN (C_{TNB}): CS = 8.3; SB = 7.5 g kg^{-1} DM TP (C_{TPBed}): CS = 1.4; SB = 1.3 g kg^{-1} DM TK (C_{TKBed}): CS = 13; SB = 11 g kg^{-1} DM
Calculate initial variables		Initial total wet weight (WW), water & dry weight of bedding & feces portion ($CNONH2O$, $H_2O_{CNONH2O_{added}}$ $DM_{CNONH2O\_added}$, kg)	
		Dry matter (DM) of layers 1 and 2 ($DM_{FB}(1)$, $DM_{FB}(2)$, kg)	
		Daily urine (U) & feces (F) production (kg)	
		TN , TP and TK mass (g) in FB and U on a DM basis	
	Based on IFSM	$TN_{FB_a}, TP_{FB_a}, TK_{FB_a}$	
	Saturation point (-)	TN_U, TP_U, TK_U	
	Field capacity		
	Area BP (m^2)		
		$SAT = 1 - \frac{\rho_{dry}}{PD}$ (IFSM, 2015)	
		$DUL = SAT * 0.5$	
		$A_{BP} = L_{BP} \cdot W_{BP}$	
	Max. air moisture by volume (%)	*This part of the model might be more useful for estimating the potential for evaporation rates for outdoor barns in contrast to our simulated lab-scale studies.*	

Evaporation rate	Urine moisture by volume (%) Air moisture by volume (%) Surface humidity ratio (mm H_2O/mass dry air) Air humidity ratio (mm H_2O/mass dry air) Saturation pressure (Pa) (Vladilo et al., 2013) Partial pressure for surface water vapor (Pa) Partial pressure for air water vapor (Pa) Partial pressure for surface dry air (Pa) Partial pressure for dry air (Pa) Density surface dry air (kg m^{-3}) Density of dry air (kg m^{-3}) Specific surface air volume (m^3 kg^{-1}) Specific air volume (m^3 kg^{-1})	$MC_{Air_{max}} = \min\left(100, 0.50806 \cdot e^{0.02525\cdot(1.8\cdot T+32)}\right)$ $MC_{Air_{Sur}} = MC_{Air_{max}}$ $MC_{Air} = \frac{RH}{100} \cdot MC_{Air_{Sur}}$ $HR_{Sur} = 0.622 \cdot \frac{MC_{Air_{Sur}}}{100 - MC_{Air_{Sur}}}$ $HR_{Air} = 0.622 \cdot \frac{MC_{Air}}{100 - MC_{Air}}$ $p_{sat} = \frac{e^{77.345+0.0057\cdot(T+273.15)-\frac{7235}{T+273.15}}}{(T+273.15)^{8.2}}$ $p_{Sur} = p_{sat}$ $p_{Air} = \frac{RH}{100} \cdot p_{sat}$ $p_{dry_{Sur}} = 101325 - p_{Sur}$ $p_{dry} = 101325 - p_{Air}$ $\rho_{dry_{Sur}} = \frac{p_{dry_{Air}}}{R_{Air} \cdot (T+273.15)}$ $\rho_{dry} = \frac{p_{dry}}{R_{Air} \cdot (T+273.15)}$ R_{Air} is the specific gas constant for air $V_{Sur} = \frac{1}{\rho_{dry_{Sur}}}$

	Air moisture content near surface (kg H_2O m^{-3} of dry air) Air moisture content (kg H_2O m^{-3} of dry air) Viscosity (Pa s) Diffusivity (m^2 s^{-1}) Density (kg m^{-3}) Schmidt number (-) Water mass transfer coefficient in gas phase based on data of Mackay & Yeun (1983) (m s^{-1}) Evaporation rate (kg m^2 d^{-1}) (Black et al., 2013)	$V_{Air} = \frac{1}{\rho_{dry}}$ $C_{MC_{Sur}} = \frac{HR_{Sur}}{V_{Sur}}$ $C_{MC} = \frac{HR_{Air}}{V_{Air}}$ $\mu = 0.3768^{-6} \cdot (T + 273.15)^{0.683}$ $D = 1.139^{-9} \cdot (T + 273.15)^{1.75}$ $\rho = \frac{353}{T + 273.15}$ $Sc = \frac{\mu}{D \cdot \rho}$ $K_{g_{H2O}} = 0.00684^{0.08794 \cdot 0.5 \cdot WS} \cdot Sc^{-0.67}$ $Ev = K_{g_{H2O}} \cdot (MC_{Air_{Sur}} - MC_{Air})$			
Calculate initial variables		Layer 1	Layer 2	Layer 3	Layer 4
	Feces/bedding mixture (FB)	$ww_{FB\,L_{t=0}} = \frac{dm_{FB\,L_{t=0}}}{0.5}$ Assume DM an initial FB is 50% in all layers.		$ww_{FB\,3_{t=0}} = \frac{ww_{FB_{Tot_{t=0}}} - ww_{FB_{1_{t=0}}} - ww_{FB_{2_{t=0}}}}{2}$	$ww_{FB\,4_{t=0}} = ww_{FB\,3_{t=0}}$

		$dm_{FB_L} = A_{BP} \cdot d_2 \cdot \rho_{dry} \cdot 10$ $dm_{FB_L} = ww_{FB_{L_{t=0}}} \cdot 0.5$
		$W_{FB_{L_{t=0}}} = ww_{FB_{LYR_{t=0}}} \cdot 0.5$
		$minW_{FB_L} = WW_{FB_{L_{t=0}}} \cdot 0.23$ Bound moisture in layers 1 and 2 that cannot evaporate.
		$ww_{UW_{L_{t=0}}} = \frac{ww_{FB_{L_{t=0}}} \cdot MC_{L_{t=0}} - W_{FB_{L_{t=0}}}}{(1 - MC_{L_{t=0}})}$ $ww_{UW_{Tot_{t=0}}} = \sum_{L=1}^{4} ww_{UW_{L_{t=0}}}$
	Initial Nutrients	
	Feces/bedding mixture	$m_{TN_{FB_{L_{t=0}}}} = dm_{FB_{L_{t=0}}} \cdot C_{TN_{FB_i}} \cdot 0.90$ Assume 10% of TN mass in FB volatilized. $m_{TP_{FB_{L_{t=0}}}} = dm_{FB_{L_{t=0}}} \cdot C_{TP_{FB_i}} \cdot (1 - WEP)$ $m_{TK_{FB_{L_{t=0}}}} = dm_{FB_{L_{t=0}}} \cdot C_{TK_{FB_i}}$
	Urine	$m_{TN_{UW_{L_{t=0}}}} = dm_{UW_{L_{t=0}}} \cdot C_{TN_{UW_i}} \cdot 0.40$ Assume 60% of TN mass in U volatilized. $m_{TP_{UW_{L_{t=0}}}} = dm_{UW_{L_{t=0}}} \cdot C_{TP_{UW_i}} + dm_{FB_{L_{t=0}}} \cdot C_{TP_{FB_i}} \cdot WEP$ $m_{TK_{UW_{L_{t=0}}}} = dm_{UW_{L_{t=0}}} \cdot C_{TK_{UW_i}}$
Loop 1	Is material added on this day?	
		If no material is added:

	Proceed with code for depth calculations			
	$dm_{FB_{1_{t+1}}} = dm_{FB_{1_t}} +$ $dm_{FB_a} - \frac{dm_{FB_a}}{2} - \frac{dm_{FB_a}}{2}$	$dm_{FB_{2_{t+1}}} = dm_{FB_{2_t}}$ $W_{FB_{L_{t+1}}} = W_{FB_{LYR_t}}$	$dm_{FB_{L_{t+1}}} = dm_{FB_{L_t}} + \frac{DM_{FB_a}}{2}$ $W_{FB_{L_{t+1}}} = W_{FB_{L_t}} + \frac{W_{FB_a}}{2}$	
	$ww_{FB_{1_{t+1}}} = ww_{FB_{L_t}} +$ $ww_{FB_a} - \frac{ww_{FB_a}}{2} - \frac{ww_{FB_a}}{2}$ The volume of layer 1 that moves to layer 2 is simplified to as the mass that moved which is equivalent to the ww mass of material added.	$ww_{FB_{Tot_{t+1}}} = \sum_{L=1}^{4} ww_{FB_{L_{t+1}}}$	$ww_{FB_{L_{t+1}}} = ww_{FB_{L_t}} + \frac{ww_{FB_a}}{2}$	
	$ww_{UW_{1_{t+1}}} = ww_{UW_{1_t}} +$ $ww_{U_a} \cdot 0.70$	$ww_{UW_{2_{t+1}}} = ww_{UW_{2_t}}$ $ww_{UW_{Tot_{t+1}}} = \sum_{L=1}^{4} ww_{UW_{L_{t+1}}}$	$ww_{UW_{3_{t+1}}} = ww_{UW_{3_t}} + ww_{U_a} \cdot 0.10$	$ww_{UW_{4_{t+1}}} = ww_{UW_{4_t}} + ww_{U_a}$ $\cdot 0.20$
Nutrients after material addition in each layer in FB	$m_{TN_{FB_{1_{t+1}}}} = m_{TN_{FB_{1_t}}} +$ $m_{TN_{FB_a}} - \frac{m_{TN_{FB_a}}}{2} - \frac{m_{TN_{FB_a}}}{2}$	$m_{TN_{FB_{2_{t+1}}}} = m_{TN_{FB_{2_t}}}$	$m_{TN_{FB_{3_{t+1}}}} = m_{TN_{FB_{3_t}}} + \frac{m_{TN_{FB_a}}}{2}$	$m_{TN_{FB_{4_{t+1}}}} = m_{TN_{FB_{4_t}}} + \frac{m_{TN_{FB_a}}}{2}$ $\cdot 0.90$
	$m_{TP_{FB_{1_{t+1}}}} = m_{TP_{FB_{1_t}}} +$ $m_{TN_{FB_a}} \cdot (1 - WEP) -$ $\frac{dm_{FB_a} \cdot c_{TP_{FB_{3_t}}}}{2} - \frac{dm_{FB_a} \cdot c_{TP_{FB_{4_t}}}}{2}$	$m_{TP_{FB_{2_{t+1}}}} = m_{TP_{FB_{2_t}}}$ Immediately after material addition, nutrient concentrations are not changing in layers 2 to 4 since material is just redistributed by pushing material down.	$m_{TP_{FB_{3_{t+1}}}} = m_{TP_{FB_{3_t}}} +$ $\frac{dm_{FB_a} \cdot c_{TP_{FB_{3_t}}}}{2}$ However, dry masses (DM) are changing and thus masses of nutrients as well.	$m_{TP_{FB_{4_{t+1}}}} = m_{TP_{FB_{4_t}}} +$ $\frac{dm_{FB_a} \cdot c_{TP_{FB_{4_t}}}}{2}$

		$m_{TK_{FB_{1_{t+1}}}} = m_{TK_{FB_{1_t}}} + m_{TK_{FB_a}} - \frac{dm_{FB_a} \cdot C_{TK_{FB_{3_t}}}}{2} - \frac{dm_{FB_a} \cdot C_{TK_{FB_{4_t}}}}{2}$	$m_{TK_{FB_{2_{t+1}}}} = m_{TK_{FB_{2_t}}}$	$m_{TK_{FB_{3_{t+1}}}} = m_{TK_{FB_{3_t}}} + \frac{dm_{FB_a} \cdot C_{TK_{FB_{3_t}}}}{2}$	$m_{TK_{FB_{4_{t+1}}}} = m_{TK_{FB_{4_t}}} + \frac{dm_{FB_a} \cdot C_{TK_{FB_{4_t}}}}{2}$
	Nutrients after material addition in each layer in urine	$m_{TN_{UW_{1_{t+1}}}} = m_{TN_{UW_{1_t}}} + m_{TN_{UW_a}} \cdot 0.70$	$m_{TN_{UW_{2_{t+1}}}} = m_{TN_{UW_{2_t}}}$	$m_{TN_{UW_{3_{t+1}}}} = m_{TN_{UW_{3_t}}} + m_{TN_{UW_a}} \cdot 0.10$	$m_{TN_{UW_{4_{t+1}}}} = m_{TN_{UW_{4_t}}} + m_{TN_{UW_a}} \cdot 0.20$
		$m_{TP_{UW_{1_{t+1}}}} = m_{TP_{UW_{1_t}}} + 0.70\left(m_{TP_{UW_a}} + m_{TK_{FB_a}} \cdot WEP\right)$	$m_{TP_{UW_{2_{t+1}}}} = m_{TP_{UW_{2_t}}}$	$m_{TP_{UW_{3_{t+1}}}} = m_{TP_{UW_{3_t}}} + 0.10\left(m_{TP_{UW_a}} + m_{TK_{FB_a}} \cdot WEP\right)$	$m_{TP_{UW_{4_{t+1}}}} = m_{TP_{UW_{4_t}}} + 0.20\left(m_{TP_{UW_a}} + m_{TK_{FB_a}} \cdot WEP\right)$
		$m_{TK_{UW_{1_{t+1}}}} = m_{TK_{UW_{1_t}}} + m_{TK_{UW_a}} \cdot 0.70$	$m_{TK_{UW_{2_{t+1}}}} = m_{TK_{UW_{2_t}}}$	$m_{TK_{UW_{3_{t+1}}}} = m_{TK_{UW_{3_t}}} + m_{TK_{UW_a}} \cdot 0.10$	$m_{TK_{UW_{4_{t+1}}}} = m_{TK_{UW_{4_t}}} + m_{TK_{UW_a}} \cdot 0.20$
Depths (cm)		$d_{BP}(10°C) = 3.7 \cdot \ln\left(ww_{UW_{Tot}} + ww_{FB_{Tot}}\right) + 23.6$ $d_{BP}(40°C) = 4.3 \cdot \ln\left(ww_{UW_{Tot}} + ww_{FB_{Tot}}\right) + 19.4$ empirically determined			
		$d_L = \frac{d_{BP} - 15}{2}$			
Evaporation	**only Layer 1**	$ww_{UW_{1_t}} = \max\left(0, ww_{UW_{1_t}} - Ev \cdot A_{BP}\right)$			

	$W_{Ex_1} = \max\left(0, Ev \cdot A_{BP} - ww_{UW_{1_t}}\right)$		
Layers 1-3	(i) $W_{FB_{1_t}} = \max\left(minW_{FB_{1_t}}, W_{UW_{1_t}} - W_{Ex_1}\right)$ $W_{Ex_2} = \max\left(0, W_{Ex_1} - \left(W_{FB_{1_t}} - minW_{FB_{1_t}}\right)\right)$	(ii) $ww_{UW_{2_t}} = \max\left(0, ww_{UW_{2_t}} - W_{Ex_2}\right)$ $W_{Ex_3} = \max\left(0, W_{Ex_2} - ww_{UW_{1_t}}\right)$ $W_{FB_{2_t}} = \max\left(minW_{FB_{2_t}}, ww_{UW_{2_t}} - W_{Ex_3}\right)$	(iii) $W_{Ex_4} = \max\left(0, W_{Ex_3} - \left(W_{FB_{2_t}} - minW_{FB_{2_t}}\right)\right)$ $ww_{UW_{3_t}} = \max\left(0, ww_{UW_{3_t}} - W_{Ex_4}\right)$ $W_{Ex_5} = \max\left(0, W_{Ex_4} - ww_{UW_{3_t}}\right)$
	$Ev_1 = W_{Ex_1} - W_{Ex_2}$	$Ev_2 = W_{Ex_3} - W_{Ex_4}$	$Ev_3 = W_{Ex_5}$
Drainage **(IFSM, 2014)**	$SW_L = \frac{ww_{UW_L}}{10 \cdot A_{BP} \cdot d_L}$ $W_D = \max(0, (SW_L - DUL)) \cdot 0.6 \cdot d_L)$ If $SW_{L1} \geq SAT$ Then $W_D = 0$ $If\ \frac{SW_{L+1} + W_D}{d_L} \geq SAT$ Then $W_D = SAT - SW_{L+1} \cdot d_L$ $SW_L = \frac{SW_L - W_D}{d_L}$		

		$SW_{L+1} = \frac{SW_{L+1} + W_D}{d_{L+1}}$ $SW_L = \frac{ww_{UW_L}}{10 \cdot A_{BP} \cdot d_L}$ $W_D = max(0, (SW_L - DUL) \cdot 0.6 \cdot d_{BP_L})$ $W_{D_L} = 10 \cdot W_D$ $m_{TN_{UW_{L_t}}} = m_{TN_{UW_{L_t}}} - \frac{W_D \cdot A_{BP} \cdot 10 \cdot dm_U \cdot C_{TN_U}}{d_L}$ $m_{TN_{UW_{L+1_t}}} = m_{TN_{UW_{L+1_t}}} + \frac{W_D \cdot A_{BP} \cdot 10 \cdot dm_U \cdot C_{TN_U}}{d_{L+1}}$ $m_{TP_{UW_{L_t}}} = m_{TP_{UW_{L_t}}} - \frac{W_D \cdot A_{BP} \cdot 10 \cdot dm_U \cdot C_{TP_U}}{d_L}$ $m_{TP_{UW_{L+1_t}}} = m_{TP_{UW_{L+1_t}}} + \frac{W_D \cdot A_{BP} \cdot 10 \cdot dm_U \cdot C_{TP_U}}{d_{L+1}}$ $m_{TK_{UW_{L_t}}} = m_{TK_{UW_{L_t}}} - \frac{W_D \cdot A_{BP} \cdot 10 \cdot dm_U \cdot C_{TK_U}}{d_L}$ $m_{TK_{UW_{L+1_t}}} = m_{TK_{UW_{L+1_t}}} + \frac{W_D \cdot A_{BP} \cdot 10 \cdot dm_U \cdot C_{TK_U}}{d_{L+1}}$
Unsaturated Flow (IFSM, 2015)		$SW_{LYR} = \min(SW_{LYR}, SAT)$ $BPH2O_{LYR} = SW_{LYR} \cdot d_{LYR} \cdot A_{BP} \cdot 10$
	Water conc. in each layer (kg m^{-3})	$C_{H2O_{LYR}} = \frac{BPH2O_{LYR}}{A_{BP} \cdot \frac{d_{LYR}}{100}}$ $C_{H2O_{LYR+1}} = \frac{BPH2O_{LYR+1}}{A_{BP} \cdot \frac{d_{LYR+1}}{100}}$
	Unsaturated flow (kg m^{-3})	$F_{unsat} = C_{H2O_{LYR+1}} - C_{H2O_{LYR}}$

Moisture fraction in each layer (-)	For negative (downward) flow: $WB_{LYR} = \frac{BPH2O_{LYR}}{BPH2O_{LYR} + WW_{CNONH2O_{LYR}}}$
Hydraulic conductivity (m s^{-1})	$K_h = \frac{e^{-1752 \cdot WB_{LYR}{}^{6} + 5884 \cdot WB_{LYR}{}^{5} - 8098 \cdot WB_{LYR}{}^{4} + 5864 \cdot WB_{LYR}{}^{3} - 2380 \cdot WB_{LYR}{}^{2} + 540 \cdot WB_{LYR} - 61}}{24 \cdot 3600 \cdot 100}$
Water flow (kg)	$F_{H2O} = min(BPH2O_{LYR}, 3600 \cdot 24 \cdot K_h \cdot (-F_{unsat}) \cdot A_{BP})$ If F_{H2O} is added to the next lower layer and the $BPH2O_{LYR}$ would be higher than the corresponding *SAT* value than $F_{H2O} = SAT \cdot d_{LYR+1} \cdot A_{BP} \cdot 10 - BPH2O_{LYR+1}$ $BPH2O_{LYR} = BPH2O_{LYR+1} + F_{H2O}$ $BPH2O_{LYR+1} = BPH2O_{LYR+1} - F_{H2O}$ $DRAIN = \frac{F_{H2O}}{A_{BP} \cdot 10}$ $F_{Leach\ LYR} = F_{Leach\ LYR} + 10 \cdot DRAIN$ For positive (upward) flow: $WB_{LYR+1} = \frac{BPH2O_{LYR+1}}{BPH2O_{LYR+1} + WW_{CNONH2O_{LYR+1}}}$ $K_h = \frac{e^{-1752 \cdot WB_{LYR}{}^{6} + 5884 \cdot WB_{LYR}{}^{5} - 8098 \cdot WB_{LYR}{}^{4} + 5864 \cdot WB_{LYR}{}^{3} - 2380 \cdot WB_{LYR}{}^{2} + 540 \cdot WB_{LYR} - 61}}{\frac{24 * 3600}{100}}$ $F_{H2O} = min(BPH2O_{LYR+1}, 3600 \cdot 24 \cdot K_h \cdot F_{unsat} \cdot A_{BP})$ If F_{H2O} is added to the next upper layer and the $BPH2O_{LYR}$ would be higher than the corresponding *SAT* value than $F_{H2O} = SAT \cdot d_{LYR} \cdot A_{BP} \cdot 10 - BPH2O_{LYR}$

		$BPH2O_{LYR} = BPH2O_{LYR} + F_{H2O}$ $BPH2O_{LYR+1} = BPH2O_{LYR+1} - F_{H2O}$ $DRAIN = -\frac{F_{H2O}}{A_{BP} \cdot 10}$ $F_{Leach\ LYR+1} = F_{Leach\ LYR+1} + 10 \cdot DRAIN$
NH_3 emission (IFSM, 2015)	Ammonia dissociation constant (Montes et al., 2009)	$K_a = 0.74 \cdot 10^{\left(0.05 - \frac{2788}{T}\right)}$
	Ammonia fraction of TAN (Stumm & Morgan, 1996)	$F = \frac{1}{1 + \frac{10^{-pH}}{K_a}}$
	Henry's Law constant for NH_3 (Montes et al., 2009)	$H = \frac{0.2138}{T} \cdot 10^{6.123 - \frac{1825}{T}}$
	Air dynamic viscosity (kg m^{-1} s^{-1}) (Arogo et al., 1999)	$\mu = 0.3768 \cdot 10^{-6} \cdot T^{0.683}$
	Air density assuming dry air (kg m^{-3}) (Arogo et al., 1999)	$\rho = \frac{353}{T}$
	Ammonia diffusivity in air (m^2 s^{-1}) (Cussler, 1997)	$D = 1.139 \cdot 10^{-9} \cdot T^{1.75}$

	Air friction velocity (m s^{-1}) (Mackay & Yeun, 1983)	$v = 0.02 \cdot v_a^{1.5}$
	Schmidt number (-) (Perry et al., 1999)	$Sc = \frac{\mu}{\rho \cdot D}$
	Mass transfer coefficient (Mackay and Yeun, 1983)	$K_g = 0.001 + 0.0462 \cdot v \cdot Sc^{-0.67}$
	Liquid mass transfer coefficient (m s^{-1}) (Datta, 2002)	$K_l = 1.417 \cdot 10^{-12} \cdot T^4$
	Overall mass transfer coefficient (m s^{-1})(Datta, 2005)	$K = \frac{1}{\frac{H}{K_g} + \frac{1}{K_l} + R_m}$
	Max. reaction velocity (kg N m^{-3} h^{-1}) in IFSM based on Muck	$V_{max} = 3.915 \cdot 10^9 \cdot e^{-\frac{6463}{(T+273.15)}}$
	Michaelis-Menten coefficient (kg N m^{-3}) in IFSM based Muck	$K_m = 3.371 \cdot 10^8 \cdot e^{-\frac{5941}{(T+273.15)}}$
Loop 2	From 0 to 24 h in $\Delta = 1$ h increments	

Initial urea concentration in urine (kg m^{-3})	$C_{Urea_{t=0}} = 0.80 \cdot 13.6$ Cole et al. (2005) and Petersen et al. (1998a) reported urinary N consisted of 67 – 91% (beef cattle) and 64-94% (dairy cattle) urea-N depending on the crude protein content of the diet. With the urine from our experiments (1.36% N in urine, as is) assume urea is 80% of TN.
Initial TAN conc. (kg m^{-3})	Assume $C_{TAN_{t=0}} = 0$ at day 7 after material addition
Ammonia manure conc. (Cm_{t+h} kg m^{-3}) (Montes et al., 2009)	$C_{NH3_{BP}} = F \cdot C_{TAN}$
Ammonia emission (kg h^{-1})	$E_{NH3} = K(C_{NH3_M} - H \cdot C_a) \cdot 3600 \cdot A_{BP}$
N lost through Nh3 emission (kg)	$m_{NH3} = \sum_{h=1}^{24} E_{NH3} \cdot \Delta t$ with Δt = 1 hour
Urea transformation rate (kg m^{-3} h^{-1}) based on Muck (1982)	$\frac{dC_{Urea}}{dt} = -\frac{V_{max} \cdot C_{Urea}}{K_m + C_{Urea}}$
	Two moles of ammonia are produced for every mole of urea hydrolyzed. The change in TAN includes the N that is volatilized through $E_{NH3.}$
TAN conc. (TAN_{t+h}, kg m^{-3} h^{-1}) (Elzing & Monteny, 1997)	$\frac{dC_{TAN}}{dt} = -2 \cdot \left(-\frac{dC_{Urea}}{dt}\right) - \frac{E_{NH_3} \cdot A_{BP}}{V_1}$; TAN is the sum ammonium ions (NH_4^+) and free ammonia (NH_3 (aq)) in the urine. Total N in the urine consists of organic N and TAN (reference).
	Repeat Loop 2
N_2O emission (IFSM, 2015)	

Soil nitrate conc. effect (μg N g^{-1} soil day^{-1}) (Parton et al., 2001)	$F_{NO3} = 1.15 \cdot N_{NO3}{}^{0.57}$
Effect of soil respiration	$F_{CO2} = 0.1 \cdot C_{CO2}{}^{1.3}$
Gas diffusivity (-) (Millington, 1959)	$D_{fc} = \left(\frac{GS}{PS_{total}}\right)^2 \cdot PS_{total}{}^{4/3}$
Soil moisture and respiration interaction(-)	$M = 0.145 - 1.25 \cdot \min(0.113, D_{fc})$ $a = 0.90 - M \cdot C_{Co2}$
Factor soil moisture effect (-) (Parton et al., 2001)	$F_{WFPS} = 0.45 + \frac{arctan\left[0.6 \cdot \pi\left(0.1 \cdot W_{wfps} - a\right)\right]}{\pi}$
Intercept of $F_{r,NC}$	$K_l = max\left[1.7, \left(38.4 - 350 \cdot D_{fc}\right)\right]$
Ratio N_{NO3} to C_{CO2}	$r = ratio\ N_{NO3} to\ C_{CO2}$
Ratio of electron donor (NO_3) to substrate (CO_2) (-) (DAYCENT)	$F_{r,NC} = max[(0.16 \cdot K_l), (K_l e^{-0.8r})]$
Soil moisture effect (DAYCENT)	$F_{r,wfps} = max\left[0.1, \left(0.015 \cdot W_{wfps} - 0.32\right)\right]$

Ratio of N_2 to N_2O emission (µg N g^{-1} µ^{-1} N)	$R_{Nratio} = F_{r,NC} \cdot F_{r,W_{wfps}}$	
Nitrous oxide emission from denitrification (kg/d)	$E_{N2O} = \frac{\min(F_{NO3},F_{CO2}) \cdot F_{WFPS}}{1+R_{Nratio}} \cdot \rho_{BP} \cdot d_{BP} \cdot F_{mass} \cdot \frac{1\ ha}{10000\ m^2} \cdot A_{BP}$ with $F_{mass} = 0.157$	
Total MC in each layer L (%)	$MC_L = \frac{ww_{UW_L} + W_{FB_L}}{ww_{UW_L} + ww_{FB_L}} \cdot 100$	
Total N concentration in each layer L (g nutrient kg^{-1} DM BP)	$C_{TN_1} = \frac{m_{TN\,\mathrm{U}\,1} + m_{TN\,\mathrm{FB}\,1} - E_{NH3} \cdot 1000 - E_{N2O} \cdot 1000}{(ww_{UW_1} + ww_{FB_1}) \cdot (1 - MC_1)}$ $C_{TN_{L+1}} = \frac{m_{TN\,\mathrm{U}\,L+1} + m_{TN\,\mathrm{FB}\,L+1}}{(ww_{UW_{L+1}} + ww_{FB_{L+1}}) \cdot (1 - MC_{L+1})}$	
Total P concentration in each layer L (g nutrient kg^{-1} DM BP)	$C_{TP_L} = \frac{m_{TP\,\mathrm{U}\,L} + m_{TP\,\mathrm{FB}\,L}}{(ww_{UW\,L} + ww_{FB_L}) \cdot (1 - MC_L)}$	
Total K concentration in each layer (g nutrient kg^{-1} DM BP)	$C_{TK_L} = \frac{m_{TK\,\mathrm{U}\,L} + m_{TK\,\mathrm{FB}\,L}}{(ww_{UW\,L} + ww_{FB_L}) \cdot (1 - MC_L)}$	
	0-3 week old BP	**3-9 week old BP**
Total MC (%) and N,P,K (g kg^{-1}) for each age treatment		

	$MC_{0-3\,wk} = \frac{ww_{UW_1} + W_{FB_1}}{ww_{UW_1} + ww_{FB_1}} \cdot 100$ $C_{TN_{0-3\,wk}} = \frac{m_{TN\,\mathrm{U}\,1} + m_{TN\,\mathrm{FB}\,1} - E_{NH3} \cdot 1000 - E_{N2O} \cdot 1000}{(ww_{UW_1} + ww_{FB_1}) \cdot (1 - MC_1)}$ $C_{TP_{0-3\,wk}} = \frac{m_{TP\,\mathrm{U}\,1} + m_{TP\,\mathrm{FB}\,1}}{(ww_{UW\,1} + ww_{FB_1}) \cdot (1 - MC_1)}$ $C_{TK_{0-3\,wk}} = \frac{m_{TK\,\mathrm{U}\,1} + m_{TK\,\mathrm{FB}\,1}}{(ww_{UW\,1} + ww_{FB_1}) \cdot (1 - MC_1)}$	$MC_{3-9\,wk} = \frac{ww_{UW_2} + W_{FB_2} + ww_{UW_3} + W_{FB_3} + ww_{UW_4} + W_{FB_4}}{ww_{UW_2} + ww_{FB_2} + ww_{UW_3} + ww_{FB_3} + ww_{UW_3} + ww_{FB_3}} \cdot 100$ $C_{TN\,3-9\,wk} = \frac{m_{TN\,\mathrm{U}\,2} + m_{TN\,\mathrm{FB}\,2} + m_{TN\,\mathrm{U}\,3} + m_{TN\,\mathrm{FB}\,3} + m_{TN\,\mathrm{U}\,4} + m_{TN\,\mathrm{FB}\,4}}{\left(ww_{UW_2} + ww_{FB_2} + ww_{UW_3} + ww_{FB_3} + ww_{UW_3} + ww_{FB_3}\right) \cdot (1 - MC_{3-9\,wk})}$ $C_{TP\,3-9\,wk} = \frac{m_{TP\,\mathrm{U}\,2} + m_{TP\,\mathrm{FB}\,2} + m_{TP\,\mathrm{U}\,3} + m_{TP\,\mathrm{FB}\,3} + m_{TP\,\mathrm{U}\,4} + m_{TP\,\mathrm{FB}\,4}}{\left(ww_{UW_2} + ww_{FB_2} + ww_{UW_3} + ww_{FB_3} + ww_{UW_3} + ww_{FB_3}\right) \cdot (1 - MC_{3-9\,wk})}$ $C_{TN\,3-9\,wk} = \frac{m_{TK\,\mathrm{U}\,2} + m_{TK\,\mathrm{FB}\,2} + m_{TK\,\mathrm{U}\,3} + m_{TK\,\mathrm{FB}\,3} + m_{TK\,\mathrm{U}\,4} + m_{TK\,\mathrm{FB}\,4}}{\left(ww_{UW_2} + ww_{FB_2} + ww_{UW_3} + ww_{FB_3} + ww_{UW_3} + ww_{FB_3}\right) \cdot (1 - MC_{3-9\,wk})}$
Print results	Print results	
	Repeat Loop 1	
End		

5.3.7 Statistical Analyses / Model Evaluation

As suggested by Chang & Hanna (2004) different performance measures should be applied to evaluate any model since each measure has its advantages and disadvantages and no single measure is perfect for all conditions. ASTM (2003) provides a standard guide with statistical performance measures for an indoor air quality model which were used to evaluate model predictions during the calibration and validation process. Depending on the evaluated measurand (either predicted nutrient concentration or gaseous emission), proposed performance measures include the correlation coefficient, the line of regression, and the normalized mean square error (ASTM, 2003). The fractional bias and the variance bias were measures used to assess bias.

5.3.7.1 Correlation Coefficient

The Pearson's correlation coefficient (r-value) explains the proportion of the total variance in the experimental data that can be explained by the model. The r-values near 1 indicate a strong positive relationship between observed value (C_{Oi}) and predicted value (C_{Pi}). The r-values near -1 indicate a strong negative inverse relationship, while values near 0 indicate little or no relationship (Kutner et al., 2005). The coefficient of determination only evaluates the linear relationship between observed and predicted means and variances. Outliers or extreme data can significantly impact the model (Legates & McCabe, 1999). The correlation coefficient is defined as:

$$r = \frac{\sum_{i=1}^{n}\left(C_{O_i} - \overline{C_O}\right)\left(C_{P_i} - \overline{C_P}\right)}{\sqrt{\sum_{i=1}^{n}\left(C_{O_i} - \overline{C_O}\right)^2 \cdot \sum_{i=1}^{n}\left(C_{P_i} - \overline{C_P}\right)^2}} \tag{5.25}$$

where $\overline{C_O}$ = average of observed values; $\overline{C_P}$ = average of predicted values; and n = number of observed values.

Line of Regression

The slope of the regression line (b) is also referred to as the linear regression coefficient and represents the change in observed data per unit of change in predicted data. Thus, the unit of the measured value is crucial. The regression line indicates how well the simulation data is in accordance with the observed data and has a value of 1 for the optimal slope. The equation for the regression line is given by

$$b = \frac{\sum_{i=1}^{n}\left(C_{O_i} - \overline{C_O}\right)\left(C_{P_i} - \overline{C_P}\right)}{\sum_{i=1}^{n}\left(C_{O_i} - \overline{C_O}\right)^2} \tag{5.26}$$

with the regression intercept (a) ideally of 0

$$a = \overline{C_P} - (b \cdot \overline{C_O}) \tag{5.27}$$

5.3.7.2 Normalized Mean Square Error

The normalized mean square error measures the mean relative random scatter and is an estimator for the overall deviation between predicted and observed values. Smaller NMSE-values (< 0.25; ASTM, 2003) indicate better agreement between C_P and C_O (ASTM, 2003), while a perfect model would have a value of 0. For example, if C_P and C_O differ by 50%, the NMSE would be 0.2. The NMSE is defined as:

$$NMSE = \frac{\sum_{i=1}^{n}\left(C_{P_i} - C_{O_i}\right)^2}{n \cdot \overline{C_O} \cdot \overline{C_P}} \tag{5.28}$$

5.3.7.3 Fractional Bias

The fractional bias (FBS) is an indicator only for systematic errors which refers to the arithmetic difference between C_P and C_O and is based on a linear scale compared to the NMSE which measures both systematic and unsystematic (random) errors (Chang & Hanna, 2004). Fractional bias indicates if the model over- or under-predicts. For example, a FBS value of 0.67 suggests that the model over predicts by a factor of 2. The FBS should be within values of -0.25 and 0.25 (ASTM, 2003) and is defined as:

$$FBS = \frac{2 \cdot (\overline{C_P} - \overline{C_O})}{\overline{C_P} + \overline{C_O}} \tag{5.29}$$

5.3.7.4 Variance Bias

The variance bias (FS) relates to the bias based on the variance parameters between observed and predicted values and should lie between -0.5 and 0.5 (ASTM, 2003) and is defined as:

$$FS = \frac{2 \cdot \left(\sigma_{C_P}^2 - \sigma_{C_O}^2\right)}{\sigma_{C_P}^2 + \sigma_{C_O}^2} \tag{5.30}$$

where σ^2_{CO} = variance of the observed data; and σ^2_{CP} = variance of the predicted data.

5.3.7.5 Model Calibration and Validation

During the calibration process, model predictions (output) for a given set of conditions were compared with observed data for the same condition from previous lab-scale experiments (Ayadi et al., 2015c; Ayadi et al., 2015d). Model parameters (evaporation, WEP, and pH) were then adjusted to maximize agreement between model outputs with the observed value. Model validation detects the accuracy of the model performance with respect to the experimental data. After the model was calibrated, the model was then tested against the validation data set.

5.3.7.5.1 Data Sets

Data from previous bench-scale studies (Ayadi et al., 2015c, 2015d) of 0-3, 3-6, and 6-9 week old BP (total of nine weeks) were used to calibrate and validate the model. Thirty-six lab-scale BP were constructed (n = 3 per treatment) and then monitored over a three-week period with fresh feces, urine, and bedding additions weekly. The data set consisted of NH_3 and N_2O concentration measurements on temperature x age x bedding treatments with the BP bin as the experimental unit. Static flux chambers were used to measure duplicate (n = 2) NH_3 concentrations at 0, 5, 9, 23, 34, 46, and 144 h and N_2O concentration at 0, 24, 46, and 144 h after weekly manure and bedding material addition for three consecutive weeks for 24 BP. Nutrient concentrations of the different zones consisted of temperature x age x bedding x zone treatment combination with the different zones nested in the BP.

There were 24 data sets, each with 21 and 12 data points for NH_3 and N_2O concentration, respectively, and 4 data points for each nutrient and MC for each layer. The observed data set was split into twelve data sets for calibration and validation. Data sets were not randomly assigned which may have biased the calibration and/or validation. Half of the data sets which consisted of half of the duplicates were used for calibration and the other half of the duplicates were used for validation. The time step for the model was on an hourly and weekly basis for gas and nutrient concentrations, respectively. The units for gas concentrations (observed) were in ppm for observed values and the units for emission (predicted) were in kg h^{-1} for predicted values. Moisture content was in %, and nutrients were in and g of nutrient (kg DM)$^{-1}$. The model was tested only against 0 to 9 week old BP.

5.4 Results and Discussion

The relative steady-state behavior of many of the nutrients in the BP could be addressed through regressive type models. However, this model sets a framework for incorporating processes that are material, time and moisture-based for a larger variety of scenarios and helps in understanding the underlying processes and their impacts. Equations for unsaturated and saturated flows were calculated based on soil water models. Since the model did not predict any unsaturated or saturated (drainage) flows, the soil water models used to predict saturated and unsaturated flows should be adjusted to be more applicable for BP material. This may be explained by the soil texture which is more compact and denser than a manure/bedding mixture. Hence, macropore flow through the BP was added to the model which is described as the water (urine) that flows through larger pores in the BP. Macropore flow was considered as another dominant method of water movement besides evaporation. Water movement through macropore flow was calculated only as a percentage of the added urine. For more accurate predictions, an empirical or mathematical equation should be used to improve model prediction capability.

For nutrient (TN, TP and TK) concentrations, the NMSE and FBS were chosen as the most appropriate statistical measures to evaluate model predication capabilities. Since there was low variability for MC and nutrients between observed and predicted values, the r-value, the regression slope and the intercept were not representative measures for the model prediction capability. The FS was not appropriate either to analyze model behavior because some of the predicted concentrations had no variance. The R, line of regression and FS evaluations are not suitable for data with low variance, and the results are misleading regarding the model's capabilities.

The model predicts NH_3 and N_2O as gaseous emission (kg h^{-1}), whereas data obtained from experimental results were measured as concentration (ppm). Ammonia and N_2O concentration would show trends for emissions since they were intermittently measured under similar conditions with static flux chambers for a short time interval and thus used to calibrate and validate the dynamics of the model. The r-value can give conclusions about the strength of the linear relation between observed and predicted NH_3 and N_2O data and was thus considered a valid measure to evaluate model behavior for emission prediction.

In addition to the BP data observed week to week (referred to as layer-based observations), the model was also evaluated against the total amount of P and K added through urine, feces and bedding, assuming no losses of these materials occurred (referred to as total material added data).

5.4.1 Model Calibration

5.4.1.1 Evaporation Rate

The evaporation rate was estimated from previous experiments (Ayadi et al., 2015d), based on weight losses of the simulated BP that occurred between material additions. The difference in weight was assumed to result from water reduction through evaporation. Since BP were stored in buckets, no other losses besides aerial emission occurred. The estimated evaporation rate was taken as an average for all ages with a value of 0.3 kg m^{-2} d^{-1} at 10°C and 1.07 kg m^{-2} d^{-1} at 40°C. During the calibration process, the evaporation rate was increased by 20% (0.36 kg m^{-2} d^{-1} at 10°C, 1.28 at 40°C) and decreased by 20% (0.24 kg m^{-2} d^{-1} at 10°C, 0.86 at 40°C). If these changes would improve model prediction capability, the parameter would be adjusted.

Based on the NMSE and FBS, predictions for MC, TP and TK, were more sensitive compared to TN. However, NMSE and FBS were still within acceptable ranges (< 25%). Increasing the evaporation rate by 20% resulted in less accurate model performance for MC, TP, and TK based on NMSE and FBS (Figure 5.7), whereas decreasing the evaporation rate by 20% did not appear to impact predictions of TN, TP and TK concentration. Since a lower evaporation rate decreased model accuracy and higher rates did not impact predictions, the initial evaporation rates were deemed adequate.

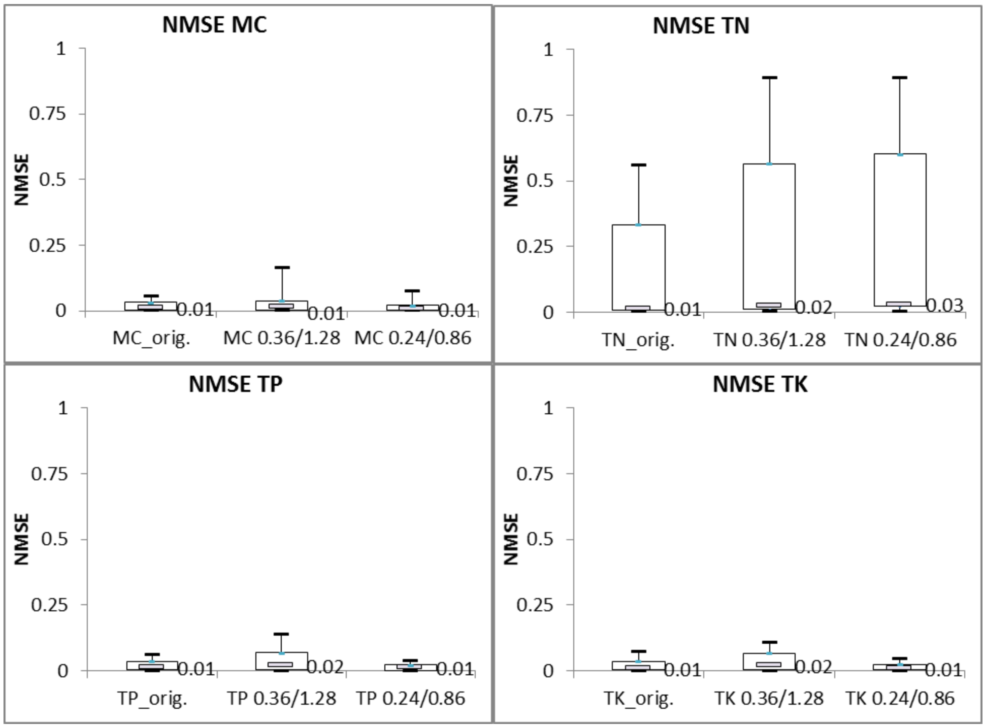


Figure 5.7. Normalized mean square error (NMSE) between average layer-based predicted and observed average moisture content (MC), total nitrogen (TN), total phosphorus (TP), and total potassium (TK) illustrated as box plots.

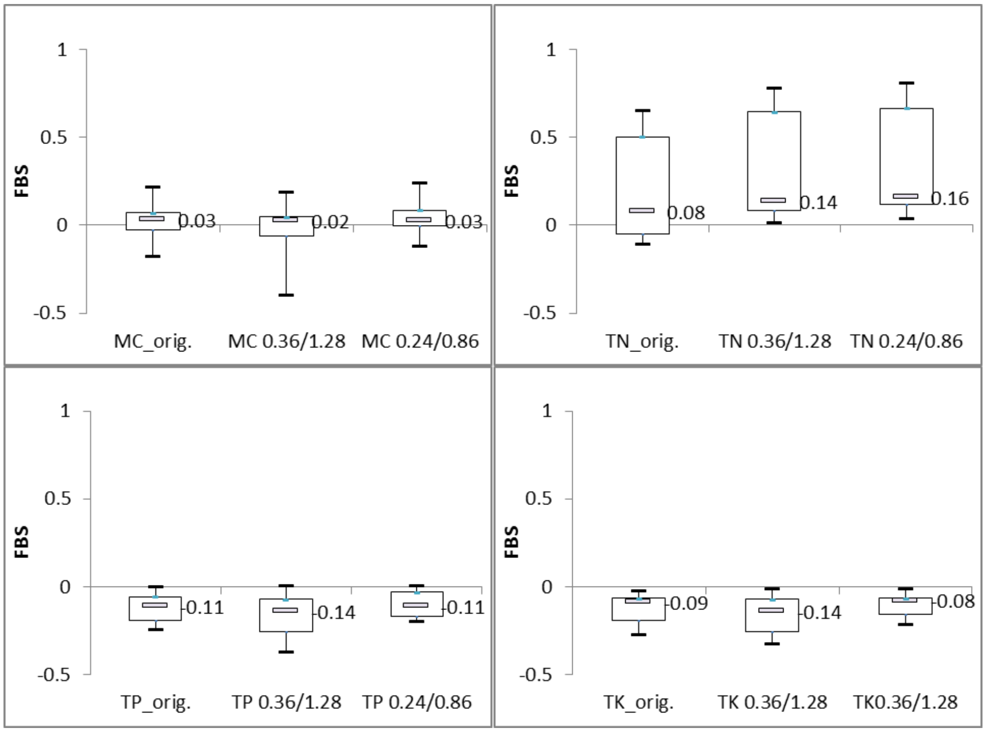


Figure 5.8. Fractional bias (FBS) between average layer-based predicted and observed average moisture content (MC), total nitrogen (TN), total phosphorus (TP), and total potassium (TK) illustrated as box plots.

5.4.1.2 pH

The pH values used to predict NH_3 emission, were taken from surface measurements of simulated BP in previous experiments (Ayadi et al., 2015c). Model performance of NH_3 emission and TN concentration were tested with pH values 20% lower (6.64 at 10°C and 6.96 at 40°C) and 20% higher (9.96 at 10°C and 10.4 at 40°C) than observed surface pH (8.3 at 10°C and 8.7 at 40°C). For lower surface pH, r-values decreased for predicted NH_3 emission (Figure 5.9) and increased NMSE and FBS for predicted TN concentration (Figure 5.10) and thus resulted in decreased model performance. With the higher pH, model performance did not appear to be affected. The pH has a significant impact on NH_3 release (Ni, 1999) and increases NH_3 concentration by up to 10 fold per unit increase in pH up to pH 9 (Vlek & Stumpe, 1978) which explains why there were no differences between the original pH and the higher pH. Since model performance was not impacted by a higher pH and a lower pH lead to a lower model performance, the original pH values (8.3 at 10°C and 8.7 at 40°C) were kept.

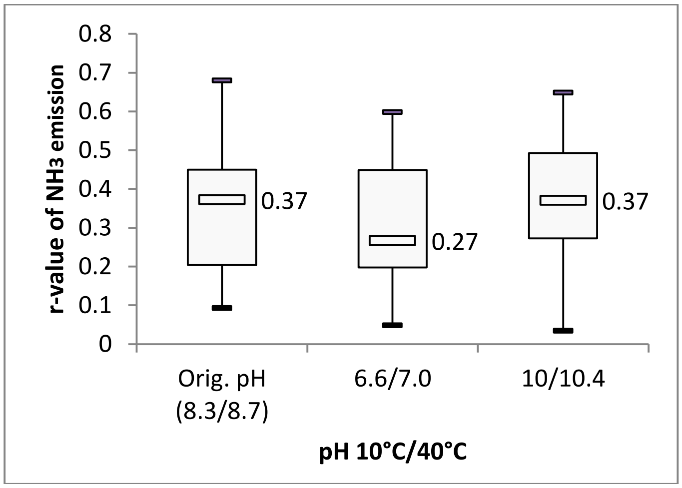


Figure 5.9. The r-values of ammonia emission (NH_3) for different pH values shown as box plots.

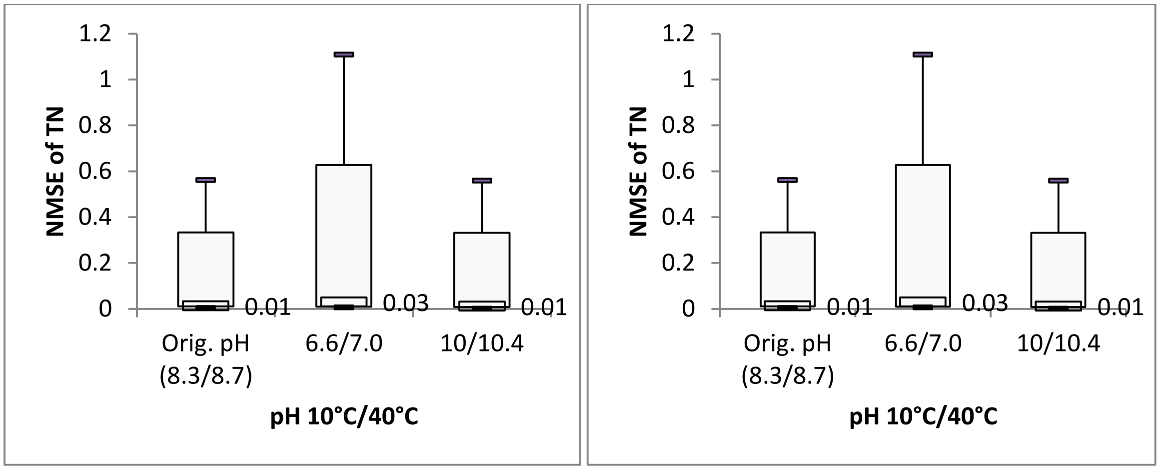


Figure 5.10. Normalized mean square error (NMSE) and fractional bias (FBS) between average predicted ammonia (NH_3) emission and observed NH_3 concentration.

5.4.1.3 Hydraulic Conductivity and Water-Extractable Phosphorus

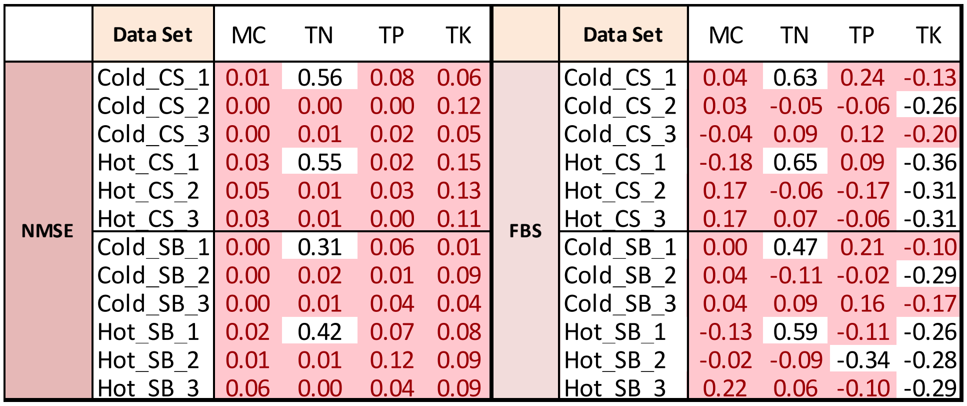
Input variables for the hydraulic conductivity and WEP were also modified to calibrate the model. Because hydraulic conductivity was used to estimated unsaturated flow and in the simulations no unsaturated flow occurred (values resulted in zero flow), model performance was not affected by these changes. The model was also not impacted by changes in WEP. This was expected since P remained in the BP and was not expected to change forms. Thus, WEP and hydraulic conductivity were not changed.

5.4.2 Model Evaluation

5.4.2.1 Simulations for Total Nitrogen, Phosphorus and Potassium

Table 5.2 and 5.3 show the statistics for the calibration and validation data set. None of the tested parameters (evaporation rate, pH, WEP, or hydraulic conductivity) were changed during the calibration process since no improvements were found when predicting TN, TP and TK concentrations, thus the performance of the baseline model (Table 5.2) mimics the final model. Both tables show that the model did not accurately predict TN concentration for 0-3 week old BP. The FBS values indicate that those concentrations were over-predicted by the model. Moisture content and TP concentration appeared to be accurately simulated by the model, whereas TK concentration appeared to be under-predicted according to the FBS values.

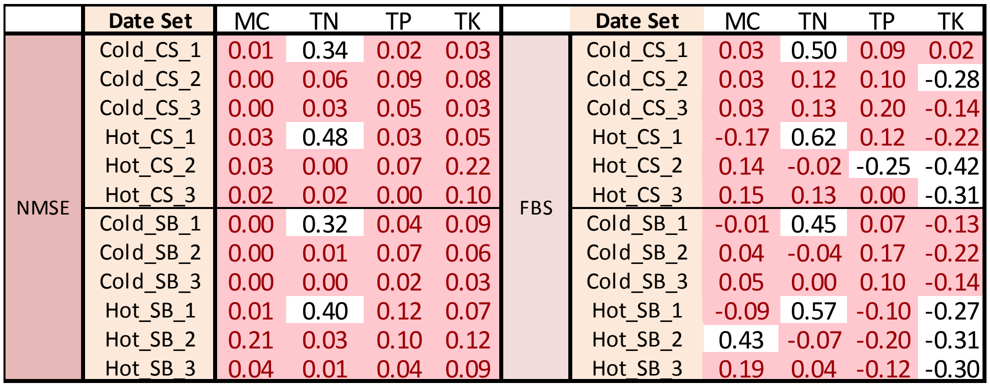
Table 5.2. Normalized mean square error (NMSE) and fractional bias (FBS) of the predicted and observed data for the calibration data set.[*]



	Data Set	MC	TN	TP	TK		**Data Set**	MC	TN	TP	TK
NMSE	Cold_CS_1	0.01	0.56	0.08	0.06	**FBS**	Cold_CS_1	0.04	0.63	0.24	-0.13
	Cold_CS_2	0.00	0.00	0.00	0.12		Cold_CS_2	0.03	-0.05	-0.06	-0.26
	Cold_CS_3	0.00	0.01	0.02	0.05		Cold_CS_3	-0.04	0.09	0.12	-0.20
	Hot_CS_1	0.03	0.55	0.02	0.15		Hot_CS_1	-0.18	0.65	0.09	-0.36
	Hot_CS_2	0.05	0.01	0.03	0.13		Hot_CS_2	0.17	-0.06	-0.17	-0.31
	Hot_CS_3	0.03	0.01	0.00	0.11		Hot_CS_3	0.17	0.07	-0.06	-0.31
	Cold_SB_1	0.00	0.31	0.06	0.01		Cold_SB_1	0.00	0.47	0.21	-0.10
	Cold_SB_2	0.00	0.02	0.01	0.09		Cold_SB_2	0.04	-0.11	-0.02	-0.29
	Cold_SB_3	0.00	0.01	0.04	0.04		Cold_SB_3	0.04	0.09	0.16	-0.17
	Hot_SB_1	0.02	0.42	0.07	0.08		Hot_SB_1	-0.13	0.59	-0.11	-0.26
	Hot_SB_2	0.01	0.01	0.12	0.09		Hot_SB_2	-0.02	-0.09	-0.34	-0.28
	Hot_SB_3	0.06	0.00	0.04	0.09		Hot_SB_3	0.22	0.06	-0.10	-0.29

* 1, 2, and 3 refer to 0-3, 3-6 and 6-9 week old simulated bedded manure packs; Cold and Hot refer to treatments stored at 10°C and 40°C; and CS and SB refers to treatments with corn stover or soybean stubble bedding. NMSE values < 0.25 indicate better model performance and are highlighted in red. FBS values indicate if the model over- or under-predicts and should lie between -0.25 and +0.25 (highlighted in red).

Table 5.3. Normalized mean square error (NMSE) and fractional bias (FBS) of the predicted data and observed validation data set.[*]



	Date Set	MC	TN	TP	TK		**Date Set**	MC	TN	TP	TK
NMSE	Cold_CS_1	0.01	0.34	0.02	0.03	FBS	Cold_CS_1	0.03	0.50	0.09	0.02
	Cold_CS_2	0.00	0.06	0.09	0.08		Cold_CS_2	0.03	0.12	0.10	-0.28
	Cold_CS_3	0.00	0.03	0.05	0.03		Cold_CS_3	0.03	0.13	0.20	-0.14
	Hot_CS_1	0.03	0.48	0.03	0.05		Hot_CS_1	-0.17	0.62	0.12	-0.22
	Hot_CS_2	0.03	0.00	0.07	0.22		Hot_CS_2	0.14	-0.02	-0.25	-0.42
	Hot_CS_3	0.02	0.02	0.00	0.10		Hot_CS_3	0.15	0.13	0.00	-0.31
	Cold_SB_1	0.00	0.32	0.04	0.09		Cold_SB_1	-0.01	0.45	0.07	-0.13
	Cold_SB_2	0.00	0.01	0.07	0.06		Cold_SB_2	0.04	-0.04	0.17	-0.22
	Cold_SB_3	0.00	0.00	0.02	0.03		Cold_SB_3	0.05	0.00	0.10	-0.14
	Hot_SB_1	0.01	0.40	0.12	0.07		Hot_SB_1	-0.09	0.57	-0.10	-0.27
	Hot_SB_2	0.21	0.03	0.10	0.12		Hot_SB_2	0.43	-0.07	-0.20	-0.31
	Hot_SB_3	0.04	0.01	0.04	0.09		Hot_SB_3	0.19	0.04	-0.12	-0.30

[*] 1, 2, and 3 refer to 0-3, 3-6 and 6-9 week old simulated bedded manure packs; Cold and Hot refer to treatments stored at 10°C and 40°C; and CS and SB refers to treatments with corn stover or soybean stubble bedding. NMSE values < 0.25 indicate better model performance and are highlighted in red. FBS values indicate if the model over- or under-predicts and should lie between -0.25 and +0.25 (highlighted in red).

5.4.2.2 Ammonia and Nitrous Oxide Emission

The hourly NH_3 emission simulated by the model were not in accordance with the observed concentrations. The linear relationship between observed NH_3 and N_2O concentrations and predicted NH_3 and N_2O emission were low with r-values between -0.11 and -0.68 indicating only low agreement between observed and simulated NH_3 data (Table 5.4). The graphs in Figure 5.11 and 5.12 illustrate the reverse relationship between observed NH_3 concentration (blue curves) and predicted (red curves) NH_3 emission at times. At 10°C, predicted NH_3 emission showed a peak after material addition and then quickly decreased with time, whereas the observed concentrations peaked after material addition (days 0, 7, and 14), then decreased and then slowly increased again until the next time material was added to the simulated BP. At 40°C, predicted NH_3 emission peaked quickly after material addition, whereas NH_3 concentration peaked one to two days post material addition.

Table 5.4. The r-values for ammonia (NH3) and nitrous oxide (N2O)*

Data Set	r-value	
	NH_3	N_2O
Cold_CS_1	-0.15	0.25
Cold_CS_2	-0.11	-0.09
Cold_CS_3	0.38	0.38
Hot_CS_1	-0.36	0.25
Hot_CS_2	**-0.68**	-0.02
Hot_CS_3	-0.46	0.01
Cold_SB_1	-0.14	0.09
Cold_SB_2	0.25	0.25
Cold_SB_3	0.23	0.45
Hot_SB_1	-0.40	0.29
Hot_SB_2	-0.45	0.15
Hot_SB_3	-0.58	0.12

* 1, 2, and 3 refer to 0-3, 3-6 and 6-9 week old simulated bedded manure packs; Cold and Hot refer to treatments stored at 10°C and 40°C; and CS and SB refers to treatments with corn stover or soybean stubble bedding.

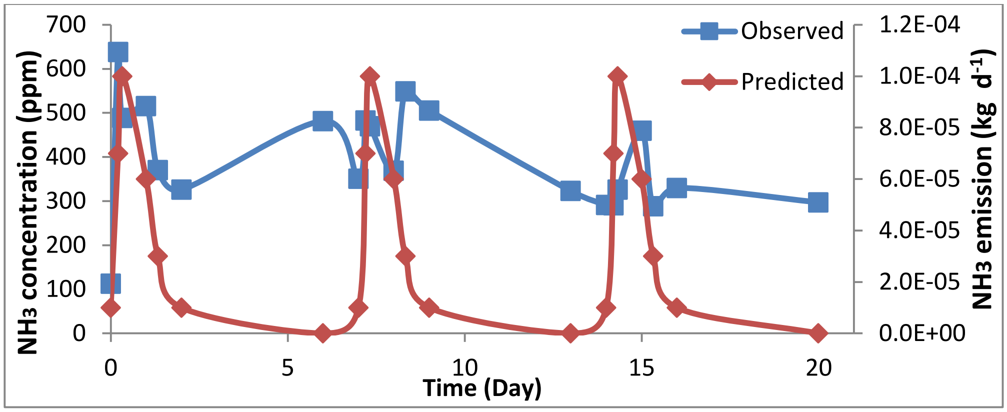


Figure 5.11 Example comparison of simulated ammonia (NH_3) emission (red) and observed (blue) NH_3 concentration for 6-9 week old bedded manure packs with corn stover at 10°C.

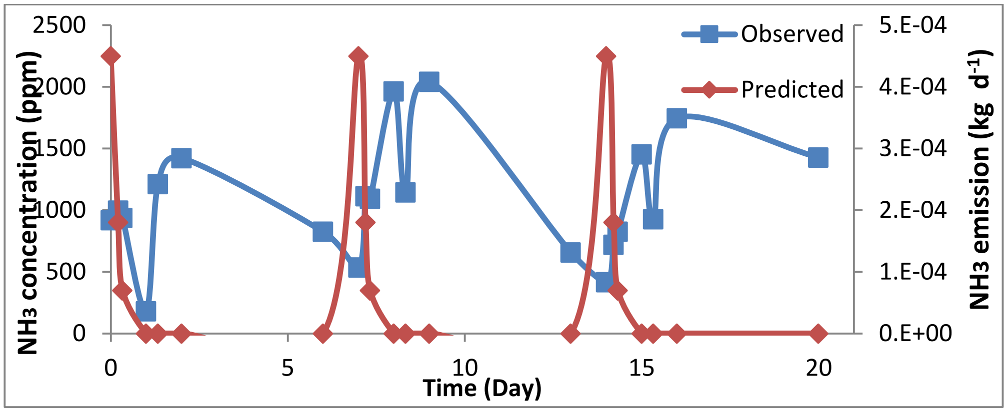


Figure 5.12 Example comparison of simulated ammonia (NH_3) emission (red) and observed (blue) NH_3 concentration for 6-9 week old bedded manure packs with corn stover at 40°C.

Simulated hourly N_2O emissions were in agreement with the observed data except for times of material addition. The model did not capture pulse concentration that were observed for simulated BP at times of material addition. Simulated N_2O emissions were not different between the different temperature treatments as was also measured for observed concentrations. Nitrous oxide emissions were modeled based on microbial denitrification processes. The pulse concentrations at times of material addition most likely caused by incomplete denitrification from pulse nitrate concentrations available in the dried bedding material. Since the nitrate concentration in the model was set as a constant value, the pulse N_2O emissions were not captured at time of material addition.

Nitrate transformations are not being accounted for in the model and should be adjusted in the future model. However, ignoring the peak concentrations that were attributed to material addition, the model mimics steady state emission behavior.

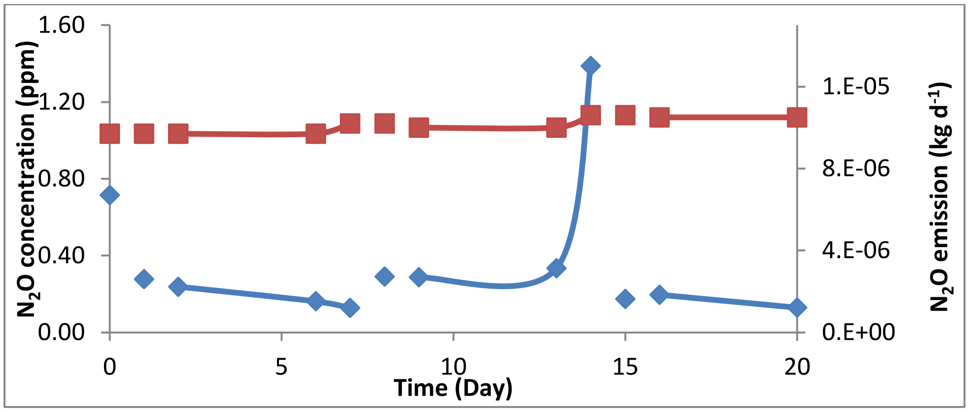


Figure 5.13. Example comparison of simulated nitrous oxide (N_2O) emission (red) and observed (blue) N_2O concentration for 6-9 week old bedded manure packs with corn stover at 10°C.

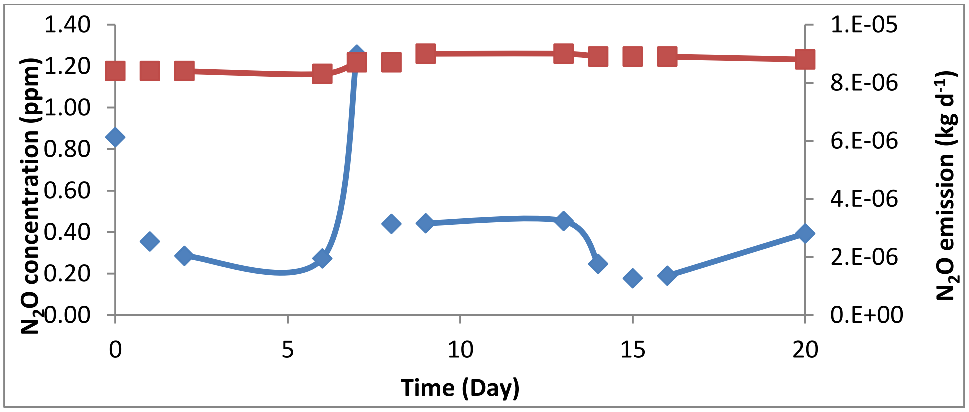


Figure 5.14. Example comparison of simulated nitrous oxide (N_2O) emission (red) and observed (blue) N_2O concentration for 6-9 week old bedded manure packs with corn stover at 10°C.

5.4.2.3 Total Masses of Phosphorus and Potassium

The layer-based observations relied on measured concentrations, but were calculated estimates based on BP layer masses. Thus, the error in predicted TP and TK concentrations could be attributed to layer mass distribution in addition to nutrient movements. An alternative evaluation method was performed by comparing predicted nutrient levels to the total P and K masses added in the formation of the BP. Figure 5.15 shows that observed P masses were lower than predicted and total material added for Cold treatments but higher for Hot treatments, whereas simulated P masses did not vary with temperature and were similar to added masses. Similarly, observed K masses were also higher for Hot treatments than predicted and added nutrient masses through material addition. In addition, total K masses were higher for 6-9 week old BP at 10°C and 0-3 week old CS treatments after three weeks and 3-6 week old CS treatments during week 2 and 3 of monitoring. By comparing the layer-based TK observations with the TK concentration from the material added data, the bias of the model improved from an average of -25% to an average of -12% (Table 5.2 and Table 5.4). The bias for TP concentration was between -34% and 24% for layer-based observations (Table 5.5) compared to predicted values and decreased to 0% to -24% when comparing layer-based observations with predictions.

Table 5.5. Normalized mean square error (NMSE) and fractional bias (FBS) of the predicted data and total material added data set for the calibration data set. [*]

	Data Set	TP	TK		**Data Set**	TP	TK
NMSE	Cold_CS_1	0.01	0.00	**FBS**	Cold	-0.11	-0.06
	Cold_CS_2	0.03	0.03		Cold	-0.18	-0.18
	Cold_CS_3	0.00	0.00		Cold	0.00	-0.02
	Hot_CS_1	0.01	0.00		Hot_	-0.11	-0.06
	Hot_CS_2	0.05	0.05		Hot_	-0.22	-0.21
	Hot_CS_3	0.00	0.00		Hot_	-0.02	-0.04
	Cold_SB_1	0.01	0.01		Cold	-0.11	-0.09
	Cold_SB_2	0.05	0.06		Cold	-0.21	-0.24
	Cold_SB_3	0.00	0.01		Cold	-0.04	-0.08
	Hot_SB_1	0.01	0.01		Hot_	-0.11	-0.09
	Hot_SB_2	0.06	0.08		Hot_	-0.24	-0.27
	Hot_SB_3	0.00	0.01		Hot	-0.06	-0.10

* 1, 2, and 3 refer to 0-3, 3-6 and 6-9 week old simulated bedded manure packs; Cold and Hot refer to treatments stored at 10°C and 40°C; and CS and SB refers to treatments with corn stover or soybean stubble bedding. NMSE values < 0.25 indicate better model performance and are highlighted in red. FBS values indicate if the model over- or under-predicts and should lie between -0.25 and +0.25 (highlighted in red).

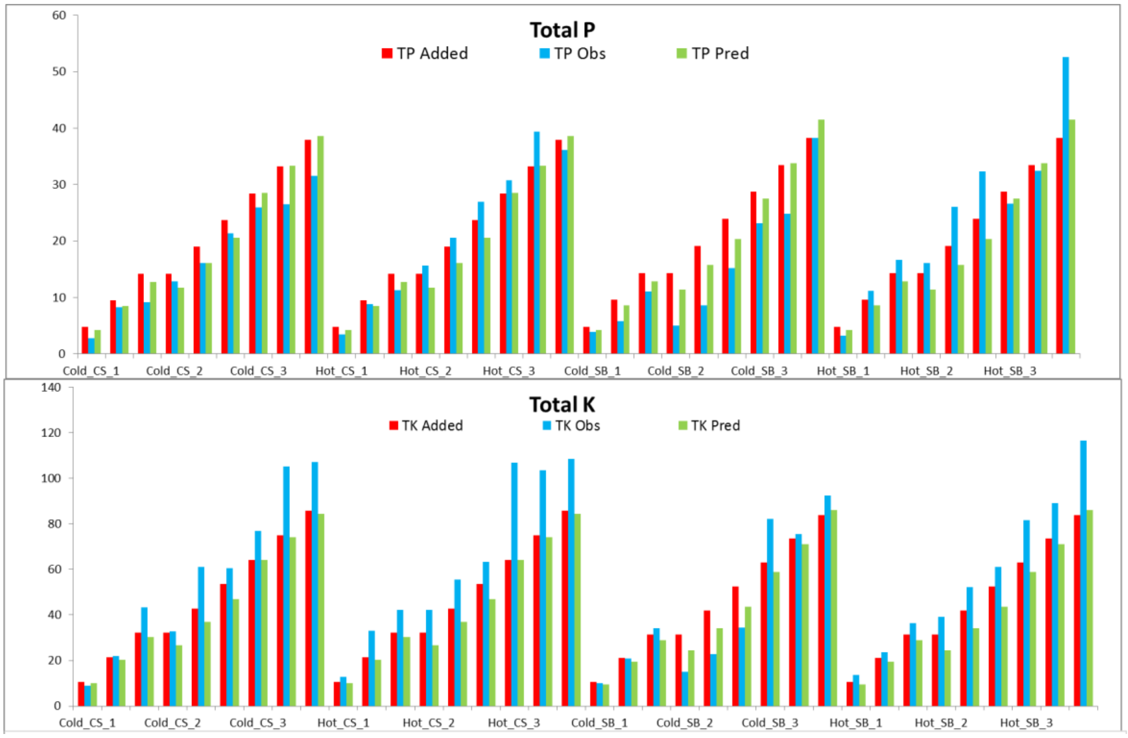


Figure 5.15. Total phosphorus and potassium masses for the bedded manure pack treatments of total nutrients added through material addition (TP Added and TK Added), layer-based observed (TP Obs and TK Obs), and predicted (TP Pred and TK Pred) date.

5.4.3 Total Nitrogen, Phosphorus and Potassium Masses for each Layer

Given the variable distribution of layers in BP, both in simulations and reality, another evaluation approach was performed to understand the predictability of nutrient levels in the different layers, particularly for TK concentrations. Nutrient concentrations of each layer were used to calculate nutrient masses for each layer for observed data and predicted data using predicted dry masses. Figure 5.16 reveals that observed K masses were particularly higher than predicted K masses for middle and bottom zones and increased with weeks for 0-3 week old treatments. The K masses for fresh packs increased up to two and three-fold more than the K mass added though material (10 g TK per material addition).

The graphs (Figure 5.16) show that the model over-predicted TN for the top layer particularly for fresh BP, whereas TN for middle and bottom layer resulted in similar TN masses as for predicted and observed data. The masses of TP for the bottom layer of 6-9 week old Hot treatments were higher for observed values than simulated values. Observed TK masses were higher for middle and bottom layer than the predicted values. The graphs (Figure 5.15) of total material added data showed that observed TK masses were higher than the masses that were added. This was also true for N masses that were added. However, the graph does not account for gaseous N losses.

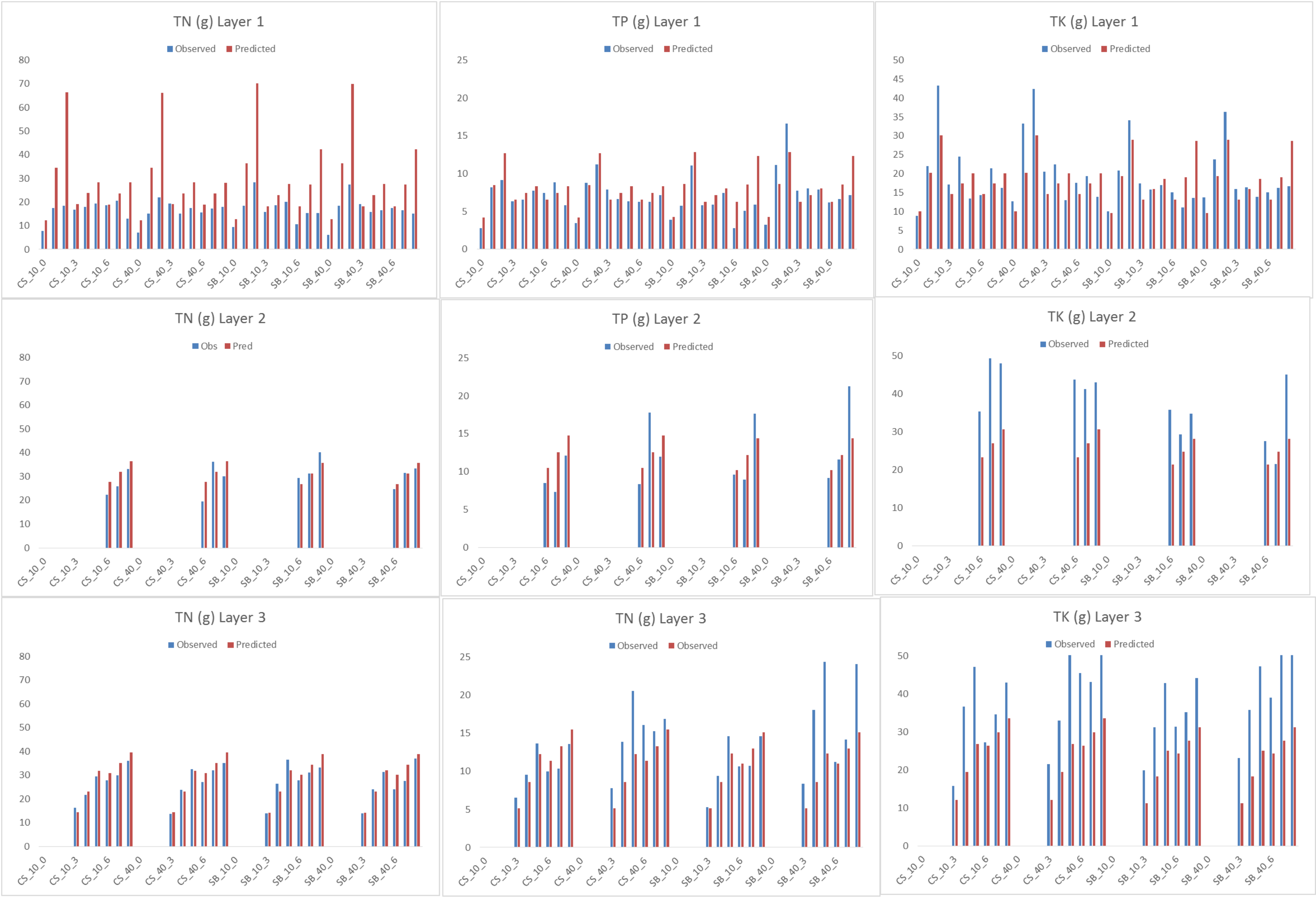


Figure 5.16. Total nitrogen, phosphorus and potassium masses for all three layers and different ages for observed (Observed) and predicted (Predicted) data.

5.5 Conclusions

Overall, the results of the study showed that MC, TP, TK and TK concentrations can be simulated with the developed model if input parameters such as age of the bedded pack, amount and type of bedding, feces and urine addition are known. Except at times of material addition, predicted N_2O emissions showed a steady state relationship with time, similar to observed N_2O concentrations. Ammonia hourly emission conditions were not accurately captured by the model. However, this did not impact prediction of TN concentration. The model performed well for NH_3 emission immediately after material addition. Since urine and fecal material are continuously added in real-life barns, the model will capture these changes. Future studies should validate the model with nutrient concentrations from field-scale bedded beef barns to confirm model accuracy. The model would benefit from adding a temperature component to the N_2O emission sub-model as well as a factor that accounts for N_2O pulse concentration through incomplete denitrification that occur at times of material addition. The latter component would account for nitrate addition and/or nitrate production at times of material addition that fuel the denitrification process. In addition, another sub-model should be included that describes the processes and conditions affecting macropore flow, which appeared to be another important measure for water flow within the bedded manure.

CHAPTER 6

GENERAL DISCUSSION

Synopsis

The final chapter of this dissertation discusses the major findings and implications of the research described in the previous chapters. Uses and applications of the developed model are discussed. Future work is proposed to solve unanswered questions with respect to nutrient movement and transformation in the bedded manure pack.

6.1 Introduction

Manure management including aerial nutrient losses to the environment is of growing concern for beef cattle producers and the general public. However, the manure and manure/bedding mixture is a valuable fertilizer. A tool that would help beef cattle producer estimate manure quantity, fertilizer value, and gaseous emission would thus be of great advantage. To develop a model that predicts amount and volume of bedded manure produced as well as fertilizer (N-P-K) concentration and gaseous N (NH_3 and N_2O) emission, nutrient transformations and movements within and from the BP have to be understood. Bedding material, storage time (BP age), and ambient conditions (such as temperature and wind speed) impact the processes occurring in the bedded pack and thus have to be considered in the decision-making process. This final chapter of this dissertation discusses the findings from the previous chapters and deliberates ideas on how to address manure management concerns and proposes future work to further improve the model.

6.2 Overall Summary

Two studies were conducted to gain a better understanding of nutrient transformation and movement in beef cattle bedded manure packs. The first study evaluated the source of volatilized NH_3-N in beef cattle slurry comprised of beef cattle feces and synthetic urine with ^{15}N-labeled urea during a 15-day bench-scale storage experiment. Results showed that 84% NH_3-N losses originated from urinary urea. At the same time, over 34% of aerial N losses were not captured as NH_3-N suggesting that other N gas emission, likely N_2 or N_2O, occurred from the slurry mixture.

A second lab-scale experiment was conducted to understand how manure handling impacts nutrient flow and transformations in the bedded manure. The headspace above simulated BP were evaluated for NH_3, CO_2, N_2O and CH_4 concentrations based on storage time (0-3, 3-6 and 6-9 week old BP), bedding material (CS or SB), temperature (10°C and 40°C) and depth within the pack. The simulated BP were analyzed for MC, free air space, ammonium-N, total N, total P, and total K concentration and enzyme activity from one, two, or three different depths for 0-3, 3-6 and 6-9 week old BP. Short-term nitrification activity potential, and DEA from BP were measured as indicators of N transformation within the BP.

The IFSM was adapted to predict water movement, and NH_3 and N_2O emission rates. Ammonia, N_2O, TN, TP and TK concentration from bench-scale BP were used to evaluate model performance. Depending on BP age, average MC, TN, TP and TK concentrations showed good agreement with observed data. Overall, the simulations showed that the model can be used to predict N-P-K fertilizer concentration for BP. Hourly changes for NH_3 and N_2O emission were not adequately reflected by the model.

6.3 What did we learn from this research?

The results from this research improve the understanding of NH_3 losses from beef manure and elucidate how storage temperature, storage length, depth of BP, and choice of bedding material affect NH_3 and greenhouse gas concentration, and nutrient content over time for the bedded manure. It is generally assumed that the majority of NH_3 losses occur through the degradation of urea once urine is exposed to fecal enzymes and/or exposure to high temperatures. To make accurate predictions on N volatilization losses from beef BP, it is important to understand how and where major gaseous N losses occur. Findings from the first experiment confirmed that major NH_3-N losses originated from urinary urea and were highest during the first two to four days, when fresh material was added daily. In a commercial deep-bedded barn, major NH_3 volatilization losses were observed within the first four hours after excretion (Spiehs et al., 2011). The model predicted peak NH_3 emission at 10°C and 40°C one and nine hours after material addition, respectively, which is in accordance to reported NH_3 losses in real-life barns. The first experiment revealed that over 34% of aerial N was not captured. Similar observations of uncaptured NH_3 losses were made by Lee et al. (2011). These uncaptured losses were likely N_2O and/or N_2 and assumedly originated all from urinary urea. This means that the model likely over-predicted NH_3 emission since all urea is being converted to NH_3 emission in the model, while other N losses (N_2O and/or N_2) from the urinary urea were ignored. Future research should determine which other N losses occur from the urine and the model should be adjusted accordingly. Ammonia concentrations are expected to be higher when using CS compared to SB bedding in hot summer months (approaching 40°C). Soybean stubble could be used as the bedding instead of CS to reduce NH_3 concentration in warmer seasons. During a cooler more humid season with lower evaporation, CS could be applied to keep the BP drier because CS has a higher water absorption capacity than SB bedding. Nutrient content varies also with season because of the difference in MC in the BP. During cooler seasons, with higher moisture in the pack, TP and TK concentration will be lower on a wet mass basis compared to a drier pack, whereas TN concentration is expected to be higher.

Seasonal management is expected to impact gas production in the bedded packs. During hot, dry summer months, BP are expected to be drier and have less N content because of increased gaseous N losses. Bedded packs with lower MC may decrease transportation cost per unit of nutrient. In addition, knowing the MC helps producers estimate the volume that is required for storing bedded manure since extra manure storage space may be needed for BP with higher moisture content.

The data from the lab-scaled experiments was used to develop a process-based model to facilitate beef cattle producers' work, reduce nutrient losses to the environment, and increase profitability by improving manure monetary value and manure management practices in confined beef cattle barns. Moisture content, TP, TK and TK concentrations can be simulated with the developed model if input parameters such as BP age, amount of bedding, feces and urine addition are known. However, to improve the model prediction capability for BP nutrient concentration, 1) TN, TP and TK concentration and MC measurements from the whole simulated BP should be taken on a weekly basis. This would confirm no P and K losses from the BP occurred and help to better understand how nutrients were distributed throughout BP depth; 2) the compaction throughout a BP should be understood to determine different layers within a BP; the MC (measured with a moisture sensor) can help in understanding the compaction; 3) all nutrient and MC measurements should be validated with measurements from layers in commercial bedded manure pack barns; 4) experiments should be conducted for more than nine weeks; bedded packs, each with at least four replicates should be observed and sampled from start of construction until at least 16 week of age; 5) water movement in the BP should be analyzed in the form of macropore flow and unsaturated and saturated flow should be specifically described for the BP versus the soil matrix; and 6) the model should be tested against a full-scale bedded manure pack barns to verify its applicability for real-life situations. The model did not adequately capture observed hourly conditions for NH_3 and N_2O conditions. To improve model prediction capabilities, hourly measurements of NH_3 and N_2O concentration should be taken with at least three replicates to ensure accuracy of sampling.

The model still needs improvement to make it adaptable for producer and/or consultants and planners application. Components that should be added are:

- Predictions should be based on input variables including dry matter intake of cattle, crude protein content of feed, amount of bedding applied, amount of bedding and manure removed during cleaning that allow the model to make more precise predictions
- The model outputs should include monetary manure fertilizer value and manure storage volume
- The program was written in Microsoft Visual Basic for Applications 7.1 but a user-friendly interface is required that only shows the input parameters and the results without exposing the complete code

6.4 Where do we go from here?

The model was designed to be used by beef cattle producers who raise cattle in confined facilities under a roof and build a bedded manure pack to manage manure. The model will also be a great tool for consultants/planners to estimate manure N-P-K concentration as well as NH_3 and N_2O emission for the bedded packs of confined beef cattle facilities. Further field-scale studies should validate the utility of the model for N_2O emission and N-P-K concentration from different depths of confined beef bedded manure systems. The model should be extended for different bedding materials and a wider temperature range (between 0°C and 40°C) so that it would be more applicable for regions where bedded manure pack barns are applied. Other options, such as economic estimates that allow producers to calculate manure monetary value for bedded packs with different bedding materials at different temperatures would also improve the model. To enhance prediction capabilities, it would be of great advantage if the model estimated both fecal and urinary N, P and K concentrations based on the diet of the animal and the animal breed. This would increase accuracy of predictions specifically assigned to the individual barn. Application of computational fluid dynamics (CFD) would be another way to model water movement in the BP. In CFD, boundary conditions are defined and control volumes can be divided into finite sets (mesh).

Further research should elucidate whether NH_3 and N release from fecal material is warranted and to determine the identity of the uncaptured N losses from urine-feces mixture. Besides making predictions for the bedded manure of beef cattle barns, in the future, the model can be adapted for use in other animal facilities such as dairy cattle, hog, sheep and goat barns.

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