Compartmental Process-based Model for Estimating Ammonia Emission from Stored Scraped Liquid Dairy Manure

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Keywords: Compartmental process-based model, dairy manure, ammonia, biogeochemistry, heat and mass transfer, manure storage

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Abstract

The biogeochemical processes responsible for production and emission of ammonia from stored liquid dairy manure are governed by environmental factors (e.g. manure temperature, moisture) and manure characteristics (e.g. total ammoniacal nitrogen concentration, pH). These environmental factors and manure characteristics vary spatially as a result of spatially heterogeneous physical, chemical, and biological properties of manure. Existing process-based models used for estimating ammonia emission consider stored manure as a homogeneous system and do not consider these spatial variations leading to inaccurate estimations. In this study, a one-dimensional compartmental biogeochemical model was developed to (i) estimate spatial variation of temperature and substrate concentration (ii) estimate spatial variations and rates of biogeochemical processes, and (iii) estimate production and emission of ammonia from stored scraped liquid dairy manure.

A one-dimension compartmentalized modeling approach was used whereby manure storage is partitioned into several sections in vertical domain assuming that the conditions are spatially uniform within the horizontal domain. Spatial variation of temperature and substrate concentration were estimated using established principles of heat and mass transfer. Pertinent biogeochemical processes were assigned to each compartment to estimate the production and emission of ammonia. Model performance was conducted using experimental data obtained from National Air Emissions Monitoring Study conducted by the United States Environmental

Protection Agency. A sensitivity analysis was performed and air temperature, manure pH, wind speed, and manure total ammoniacal nitrogen concentration were identified as the most sensitive model inputs. The model was used to estimate ammonia emission from a liquid dairy manure storage of a dairy farm located in Rockingham and Franklin counties in Virginia. Ammonia emission was estimated under different management and weather scenarios: two different manure storage periods from November to April and May to October using historical weather data of the two counties. Results suggest greater ammonia emissions and manure nitrogen loss for the manure storage period in warm season from May to October compared to the storage period in cold season from November to April.

Keywords: Compartmental process-based model, dairy manure, ammonia, biogeochemistry, heat and mass transfer, manure storage

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General audience abstract

Dairy manure is a byproduct of dairy farming that can be used as a fertilizer to provide essential plant nutrients such as nitrogen, phosphorus, and potassium. However, manure can only be applied to crop lands in a certain time of the year during growing seasons. Further, discharge of dairy manure into natural environment is prevented by the environmental regulations. Therefore, manure storage structures are used to store liquid dairy manure until time permits for land application or use for other purposes. During the storage, liquid dairy manure goes through biological, chemical, and physical processes and release manure gases that are linked to deteriorate human and animal health and contribute to environmental pollution. Ammonia is one of the manure gases released to atmosphere from stored liquid dairy manure. Furthermore, release of ammonia from stored manure reduce nitrogen content and reduce fertilizer value of stored manure. Implementing control measures to mitigate ammonia emission is necessary to prevent ammonia emission and reduce nitrogen loss from stored manure. Deciding and applying of appropriate control measures require knowledge of the rate at which ammonia emission occurs and when ammonia emission occurs.

Use of process-based models is one of the less expensive and reliable method for estimating ammonia emission from stored liquid dairy manure. Process-based model is a mathematical model that simulates processes related to ammonia production and emission from stored manure. Even though, there are several process-based models available for estimating

ammonia emission from stored liquid dairy manure, these models do not fully represent the actual processes and conditions relevant to production and emission of ammonia. For instance, spatial variation of temperature and total ammoniacal nitrogen concentration within stored manure is not considered in existing process-based models. Therefore, in this study a new compartmental process-based model was developed for estimating these spatial variations and production and emission of ammonia from stored liquid dairy manure. The model uses weather data and manure management information as inputs for estimating ammonia emission and nitrogen loss.

The performance evaluation of the compartmental process-based model revealed that air temperature, manure pH, wind speed, manure total ammoniacal nitrogen concentration are important model inputs for estimating ammonia emission from stored liquid dairy manure. The model was used to estimate ammonia emission from a dairy farm located in Rockingham and Franklin counties in Virginia. Results suggest greater ammonia emissions and manure nitrogen loss for the manure storage period in warm season from May to October compared to the storage period in cold season from November to April.

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I dedicate this dissertation to my parents, aunts and all my teachers.

Table of contents

List of abbreviations

1D	One-dimensional
3D	Three-dimensional
AFO	Animal feeding operation
C	Carbon
CAFO	Concentrated animal feeding operation
CH_4	Methane
CO_2	Carbon dioxide
DairyGEM	Dairy gas emissions model
DOC	Dissolved organic carbon
FBS	Fractional bias
FEM	Farm emissions model
FS	Variance bias
GHG	Greenhouse gas
GSA	Global sensitivity analysis
H_2S	Hydrogen sulfide
IFSM	Integrated farm system model
ManureDNDC	Manure denitrification-decomposition model
N	Nitrogen
N_2	Dinitrogen gas
N_2O	Nitrous oxide
NAEMS	National air emissions monitoring study

NCEP	National centers for environmental prediction
NH_3	Ammonia
NH_4^+	Ammonium ion
NMP	Nutrient management plan
NMSE	Normalized mean square error
NO	Nitric oxide
ON	Organic nitrogen
P	Phosphorus
PBAEM	Process-based ammonia emission model
PBM	Process-based model
pH	Negative log of hydrogen ion concentration
r	Correlation coefficient
RH	Relative humidity
RMSE	Root mean square error
RSA	Relative sensitivity analysis
S	Sulfur
SA	Sensitivity analysis
TAN	Total ammoniacal nitrogen
VOC	Volatile organic compound

List of figures

List of Tables

1. Introduction

1.1 Background

In general, the focus of animal feeding operations (AFOs) has been to maintain and/or improve production efficiency to increase profitability. However, there is an increasing public, stakeholder, and government regulation that demands for accountability and demonstration of sustainability. Many AFOs are revaluating their approach to production. Improving sustainable production practices requires concurrent consideration of environmental, social, and profitability issues and would be vastly enhanced by the use of appropriate models. The dairy industry, for example, through The Innovation Center for U.S. Dairy (www.usdairy.com), has launched an effort to improve the sustainability of dairy production systems by supporting the development of process-based models (PBMs) and life cycle assessment (LCA) to identify components or processes that need improvement to reduce their negative impact on the environment along with profitability and related social issues.

PBMs also known as mechanistic models, combine mathematical modeling and experimental data to simulate mass and energy transfer through a system (NRC, 2003; Cuddington et al., 2013; USEPA, 2009). Usually, in a PBM, the behavior of a system is depicted using mathematical equations derived from theoretical knowledge of what is understood as the physical, chemical, and/or biological processes that describe the system (Cuddington et al., 2013; USEPA, 2009). PBMs are used in a wide range of ecological and environmental applications, for example, estimating ammonia (NH_3) and greenhouse gases (GHGs) emissions from AFOs (Li et al., 2012; Rotz et al. 2014), estimating GHG emission from agroecosystems (Gabrielle et al., 2006; Li et al. 2001), estimating GHG emission from lakes (Tan and Zhuang, 2015), modeling carbon and water fluxes of forests (Kramer et al., 2002), and simulating hydrological processes in catchments (Shen and Phanikumar, 2010). Specific to AFOs, PBMs have been developed and used to estimate NH_3, GHGs, and other manure gases from the whole farm or sub units of the farm, such as animal buildings, manure storage, and land application of manure. These PBMs estimate the production and emissions of carbon (C), nitrogen (N), and sulfur (S) based volatile compounds using the principles of mass balance, thermodynamics, and reaction kinetics (NRC, 2003; Li et al., 2012).

Emissions of gases from diary manure storages has been estimated using direct measurement Kaharabata et al., 1998; Van der Weerden et al., 2014; VanderZaag et al., 2014), emission factors (VanderZaag et al., 2011; IPCC, 2006), and mathematical models (Li et al., 2012; Rotz et al., 2016a). Direct measurement methods use technologies such as, gas chromatography (GC), infrared spectroscopy (IR), open path Fourier transform infrared spectroscopy (OP-FTIR), tunable diode laser absorption spectroscopy (TDLAS) to quantify concentration of gases released directly from the source (Powers and Capelari, 2016; Borhan et al., 2012). The emission factor is an average emission rate developed using the observations of the direct measurements. Mathematical models, namely empirical and process-based models, simulate emissions based on the theoretical knowledge of the biogeochemical processes. Direct measurement methods for estimating emissions are the most desirable, but downside of the method is that it can be challenging and expensive depending on the site because of the equipment and skill level required to setup and conduct the measurements (NRC, 2003; Borhan et al., 2012; Heber et al., 2001; Arogo et al., 2003; Larios et al., 2016). Emission factor depends on empirical studies and is sometimes unreliable due to variability of manure management practices in farms where experiments are conducted, as well as environmental factors that govern the emissions (NRC, 2003). To be meaningful, the development of emissions factors and empirical models requires a substantial number of observations and measurements to represent the vast and non-uniform field conditions (e.g., weather, manure management practices, animal productivity etc.) that could affect gas emissions from a manure storage. Given these challenges, the National Research Council (NRC) recommended using PBMs as an alternative and more meaningful approach to estimate aerial emissions from AFOs (NRC, 2003).

Currently, the PBMs used to estimate aerial emissions from stored liquid dairy manure include, Manure Denitrification-Decomposition (Manure-DNDC) model (Li et al., 2012), Integrated Farm System Model (IFSM) (Rotz et al., 2016a), Dairy Gas Emissions Model (DairyGEM) (Rotz et al., 2016b), Process-Based Ammonia Emission Model (PBAEM) (Zhang et al., 2005), and Farm Emissions Model (FEM) (Pinder et al., 2004). The inputs to these models are readily available information such as weather, farm characteristics, and manure management, making them adaptable and amenable for use under various climatic conditions and different management scenarios. For example, Manure-DNDC model has been used to: (1) estimate NH_3 emission in different geographical locations including, Jasper County, IN (Deng et al., 2015) and Coastal plains of North Carolina (Li et al., 2012); (2) assess NH_3, N_2O, and CH_4 emissions from various management scenarios such as comparing manure storages with or without surface cover (Li et al., 2012); and (3) estimate NH_3, N_2O, CH_4, and CO_2 emissions for farm-based life cycle assessment (Stackhouse-Lawson et al., 2012).

1.2 Accurate estimation of aerial emissions from manure storage

First, the knowledge of production and release of manure gases from storage is required to inform better selection and implementation of an appropriate emission mitigation technology. On average, mature lactating dairy cow excretes 31 to 47 kg (69 to 103 lbs) of manure per day for every 454 kg (1,000 pounds) of body weight (Bickert, 2000), leading to handling large quantities of manure on a farm daily, depending on the number of animals raised. Manure includes urine, feces, animal bedding, wasted feed, milking center effluent, and precipitation. Typically, manure is held in storage (in some areas for periods up to six months) to ensure (i) use of manure nutrients (N and phosphorus (P)) as fertilizer for crop and pasture production at the right time, (ii) decrease handling costs, and (iii) minimize the potential to pollute the environment (Muck et al. 1984; Kellogg et al., 2000; Rotz, 2004). During storage, manure continuously undergoes a series of microbial and biogeochemical reactions. Depending on the microbial communities present, changes in the quality and quantity of manure as well as formation of gaseous constituents of N, C, and S will occur. The resulting gaseous compounds of N (e.g., NH_3, nitrous oxide (N_2O), nitric oxide (NO), and dinitrogen gas (N_2)), C (e.g., methane (CH_4), carbon dioxide (CO_2), and volatile organic compounds (VOC)), and S (hydrogen sulfide (H_2S)) produced during storage are typically lost to the atmosphere if the storage is not covered (NRC, 2003; Amon et al. 2006; Berges and Crutzen, 1996; Husted, 1994; Laubach et al., 2015; Smith et al., 2008; Wood et al., 2014). Some of the emitted gases from stored manure are reactive, for example, reactive nitrogen (Nr) compounds NH_3 and N_2O (Galloway et al., 2003; Aillery et al., 2005; Pitesky et al., 2009). If poorly managed, Nr emitted from stored manure present the potential to pollute the environmental and cause human health problems and at the same time, decrease the fertilizer (N content) and economic value of manure (Erisman et al., 2013; FAO, 2006; Galloway et al., 2008; Oenema et al., 2007; Vaddella et al., 2011; Muck and Steenhuis, 1982). Management practices that have been used to mitigate emission of NH_3 and GHGs from stored manure include physical methods (covers, location of inlet of manure into storage - bottom vs top loading) (Muck et al., 1984; Muck and Steenhuis, 1982; VanderZaag et al., 2008; Clanton et al., 1999; Clanton et al., 2001), chemical methods (chemical manure additives) (McCrory and Hobbs, 2001), and biological methods (microbial manure additives) (Zhu, 2000; Kim et al., 2014). Therefore, quantifying production and emission of NH_3 and GHGs is vital for developing effective mitigation strategies that address air quality and manure nutrient loss on dairy farms (NRC, 2003; Eilerman et al., 2016).

Secondly, the knowledge of and ability to estimate aerial emissions from manure storages is also vital for developing and designing safe and healthy work environment for farm workers and livestock. For example, manure gases released in confined areas could lead to oxygen-deficient, toxic, or explosive conditions (NIOSH, 1990). Manure gases can displace oxygen in any space. Depletion of oxygen below 19.5% presents undesirable situations where there is not enough oxygen to support life, leading to asphyxiation, and sometimes, death (NIOSH, 1990). The presence of manure gases such as CH_4 and NH_3 can result in explosive atmospheres, especially, if their concentrations reach 5% and 15% (the lower explosive limit) by volume, respectively NIOSH, 2015). Exposure to toxic manure gas such as NH_3 and H_2S may lead to various health issues including skin and eye irritations and respiratory and cardiovascular illnesses. Some studies have reported that short-term exposure to high concentrations of NH_3 and H_2S gases can be lethal (Casey et al., 2006; Copeland, 2014; Mitloehner and Calvo, 2008). Safety standards that govern safe working environments have been established by institutions such as the National Institute for Occupational Safety and Health (NIOSH) and Occupational Safety and Health Administration (OSHA). For humans, NIOSH guidelines stipulate that NH_3 exposure should not exceed 25 ppm for a 10-hour workday during a 40-hour work week while Occupational Safety and Health Administration (OSHA) recommends the exposure not to exceed 50 ppm during any 8-hour workday during a 40-hour work week (NIOSH, 2015; Mitloehner and Calvo, 2008;

OSHA, 2017). For H_2S, the permissible level is 10 ppm for an indoor 8-hour day (Casey et al., 2006; OSHA,2017). Thus, accurate and scientifically credible estimates of manure gases are required for the development of safety procedures to meet these safety standards (Copeland, 2014).

1.3 Improving accuracy of current PBMs

A review of current PBMs (presented in Chapter 2) suggested that these models have several shortcomings that limit the accurate model predictions, thus further development and refinement is necessary to improve or increase the accuracy of PBMs. These limitations include

(i) inadequate consideration of the spatial variation of manure temperature and substrate concentration within a manure storage

(ii) partial use and consideration of pertinent biogeochemical processes and/or explicit implementation in the model simulation

(iii) under representation of definitive mechanistic approach that typifies PBM, for instance use of singular or combination of emissions factors and empirical equations to describe biogeochemical processes.

To overcome these limitations, the PBMs can be implemented as compartmental models that consider the spatial heterogeneity within the manure storage. Further they can be improved via a more comprehensive modeling approach that incorporates the missing processes and uses stoichiometric and biokinetic parameters that are more relevant to biogeochemical processes in manure storage. This study focuses on the compartmental model approach to improve the PBM.

1.4 Study objective

The overall objective of this study was to develop a one-dimensional compartmental process-based model that estimates production and emission of ammonia from stored scraped liquid dairy manure in a circular storage tank. The overall objective of this study was achieved though completing following specific objectives.

i. Developing a one-dimensional compartmental process-based model to simulate material balance in a circular storage tank, heat transfer, ammonia production, ammonia diffusion, and nitrogen balance within stored liquid dairy manure, and ammonia volatilization from the surface of stored liquid dairy manure
ii. Comparing performance of the one-dimensional compartmental process-based model with the performance of a zero-dimensional non-compartmental process-based model
iii. Estimating ammonia emission from stored scraped liquid dairy manure in a circular storage tank under different management and weather scenarios

2 Literature review

This chapter presents a description of the PBMs currently used for estimating emissions from manure storage, and performs a critical evaluation of PBMs being used to estimate NH_3 and GHGs emissions from AFOs, with a focus on stored liquid dairy manure. The focusing question(s) guiding the review was to discern the basis and vetting used in the development of these models. The specific objectives are to: (1) assess the PBMs against a defined evaluation criteria based on structure, function, and behavior of models; (2) identify the strengths and weaknesses of the models in estimating emissions; and (3) propose novel approaches to improve accuracy of the models.

2.1 Description of process-based models for estimating aerial emissions from stored manure

Five PBMs were identified from published literature as being used to estimate NH_3, GHGs, H_2S, and VOC from liquid manure storages in AFOs, and are listed in Table 2.1. These are whole-farm models with specific sub-models to simulate various farm component e.g., feedlot, housing, manure storage structures, and field. In this review, we only evaluated the manure storage sub-model. Also, listed in Table 2.1 are the gases quantified by the manure storage sub-model, computational platform, and links to the software developed for the models (if available).

Table 2.1: Process-based models for estimating aerial emissions from manure storages

Model	Estimated gases	Computational platform	Reference
Manure Denitrification-Decomposition (Manure-DNDC) model	NH_3, CO_2, CH_4, N_2O, NO, and N_2	Coded in Visual C++ 6.0; Executable software (Microsoft Windows based) available at http://www.dndc.sr.unh.edu	Li et al., 2012
Integrated Farm System Model (IFSM)	NH_3, CO_2, CH_4, N_2O, H_2S, and VOCs	Executable Microsoft Windows based software is available at https://www.ars.usda.gov/northeast-area/up-pa/pswmru/docs/integrated-farm-system-model/	Rotz, 2016a
Dairy Gas Emissions Model (DairyGEM)	NH_3, CO_2, CH_4, N_2O, H_2S, and VOCs	Executable Microsoft Windows based software is available at https://www.ars.usda.gov/northeast-area/up-pa/pswmru/docs/dairy-gas-emissions-model/	Rotz, 2016b
Process-Based Ammonia Emission Model (PBAEM)	NH_3	Coded in MATLAB and not available in the public domain	Zhang et al., 2005
Farm Emissions Model (FEM)	NH_3	No information about the computational platform and software is available	Pinder et al., 2004

2.1.1 Manure Denitrification- Decomposition (Manure-DNDC) model

Manure-DNDC model was developed by Li et al. (2012). It simulates C and N transformation during the lifecycle of manure in a livestock farm. The model adopted known and established biogeochemical processes previously demonstrated and proven in the simulation of soil organic matter transformation in a model called Denitrification-Decomposition (DNDC) (Li et al., 1992; Li, 2000). In general, the manure-DNDC model comprises sub-models for feeding lot (barns or outdoor corrals), manure storage facilities (lagoon, tank), treatment facilities (compost facility, anaerobic digester), and crop fields where manure is applied. The manure storage sub-model simulates biogeochemical processes of liquid manure in a lagoon or slurry tank. Model inputs include (1) properties of manure storage structure such as storage capacity, surface area opens to atmosphere, type of coverage, and storage period; (2) daily weather data (i.e., air temperature, precipitation, wind speed); and (3) manure management data (i.e., daily quantities, manure C:N ratio, manure dry matter, urea, waste water, and percentage of manure removed from storage for land application). The biogeochemical processes included in the manure storage sub-model are driven by environmental factors and manure characteristics such as temperature, moisture, pH, substrate concentration, and redox potential (Figure 1.1). These factors change during the manure storage period based on daily weather data, characteristics of the storage structure, and manure management practices.

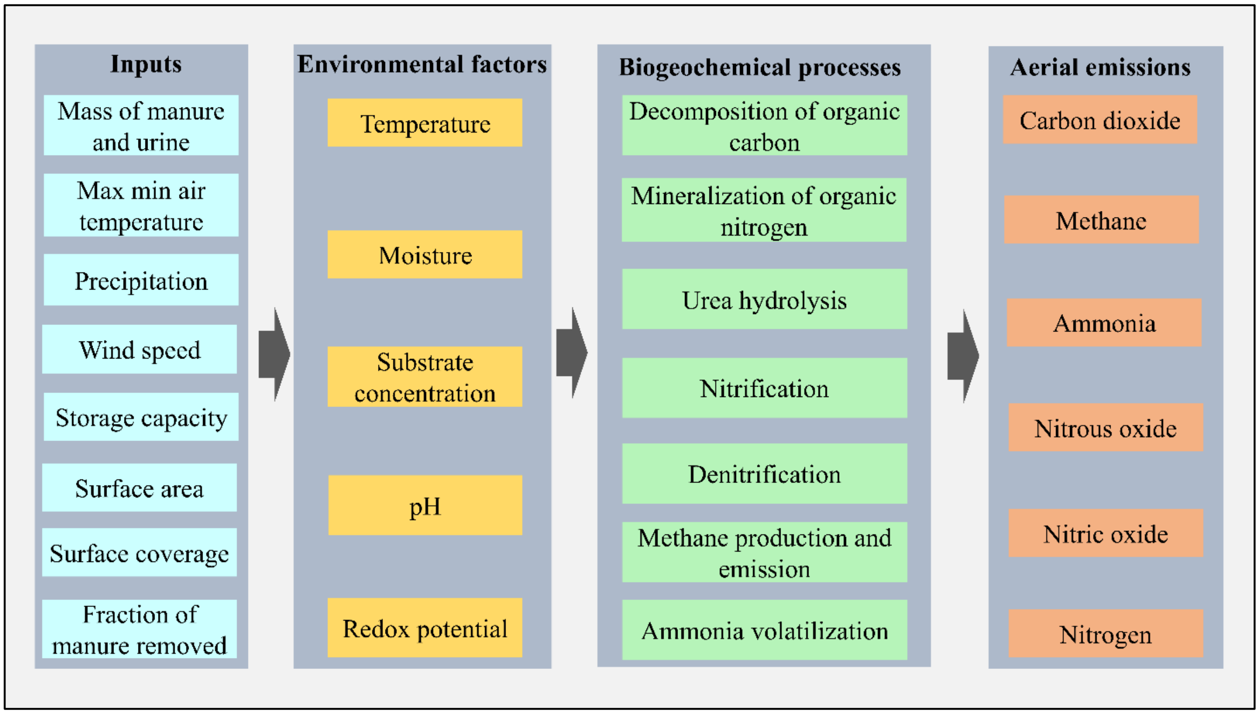

Figure 2.1: The general structure of the Manure-DNDC storage sub-model (adapted from Li et al. (2012))

2.1.2 Integrated Farm System Model (IFSM)

The IFSM has been used to simulate crop, dairy, and beef production systems to assess environmental impacts and economics of farms (Rotz, 2016a). It was developed by expanding the Dairy Forage System Model (DAFOSYM) to include planting operations, tillage, and manure handling components (Rotz et al., 1989; Borton et al., 1995; Harrigan et al., 1996). The latest version of the IFSM model (version 4.2) includes nine sub-models that represent major activities on a farm: tillage and planting, crop and soil, crop harvest, crop storage, grazing, herd and feeding, manure handling, machinery, and economic analysis (Rotz, 2016a). The manure storage sub-model is nested within the manure handling. It simulates biogeochemical processes of stored slurry/liquid manure and estimates emissions of NH_3, N_2O, CH_4, CO_2, H_2S, and VOC. The storage sub-model includes several types of long-term manure storage structures: above-ground steel tank, below-ground concrete tank, and earthen retention ponds. Model inputs include: (1) characteristics of the storage structure (i.e., type, capacity, surface area, surface cover, and storage period; (2) weather data (i.e., air temperature, precipitation, wind speed); and (3) manure management data (i.e., dairy herd characteristics, manure bedding characteristics, manure collection method, and fraction of manure removed). A summary of the biogeochemical processes simulated and the structure of IFSM storage sub-model are summarized in Figure 2.2.

2.1.3 Dairy Gas Emissions Model (DairyGEM)

The DairyGEM was developed to estimate NH_3, CH_4, CO_2, N_2O, H_2S, and VOC emissions from dairy barns, manure storages, and field applied manure (Rotz et al., 2016b). The model consists of four major sub-models: feed availability, the herd, manure handling, and gas emissions. Manure storage sub-model, contained within manure handling similar to that of IFSM, estimates gaseous emissions from slurry/liquid manure storage structures (e.g., tanks or earthen retention ponds). The DairyGEM storage sub-model uses the same processes and model algorithm embedded in the IFSM storage sub-model. Therefore, the review of biogeochemical processes, inputs and outputs, equations, and performance evaluation of the IFSM model is assumed to be valid for the DairyGEM.

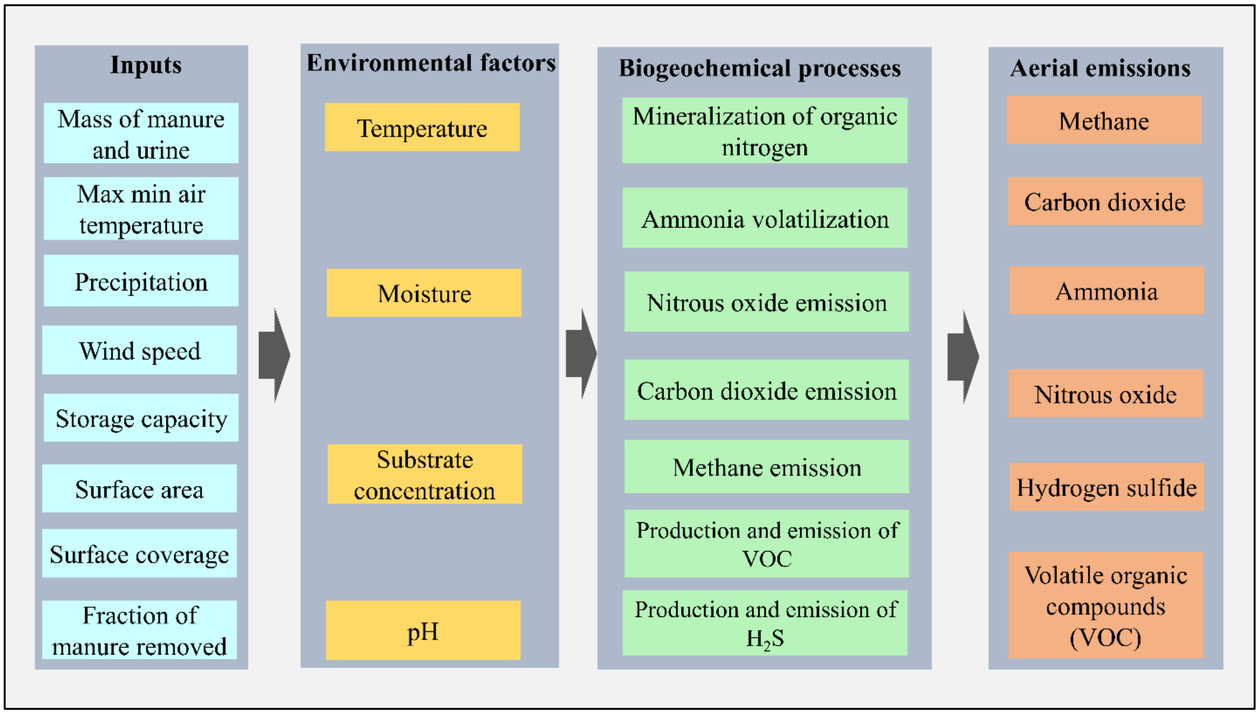

Figure 2.2: Structure of the IFSM and DairyGEM manure storage sub-model (adapted from Rotz et al (2016a, 2016b))

2.1.4 Process-Based Ammonia Emission Model (PBAEM)

Zhang et al. (2005) developed a process-based NH_3 emission model applicable for dairy, beef, swine, and poultry feeding operations. This model includes five sub-modules i.e., manure excretion, confinement housing emission, feedlot emission, liquid manure storage emission, and land application emission. The liquid manure storage emission sub-module estimates NH_3 emissions by simulating the biogeochemical processes relevant to manure N transformation (Figure 1.3). These processes are governed by environmental factors and manure characteristics such as moisture content, pH, temperature, wind speed, and relative humidity.

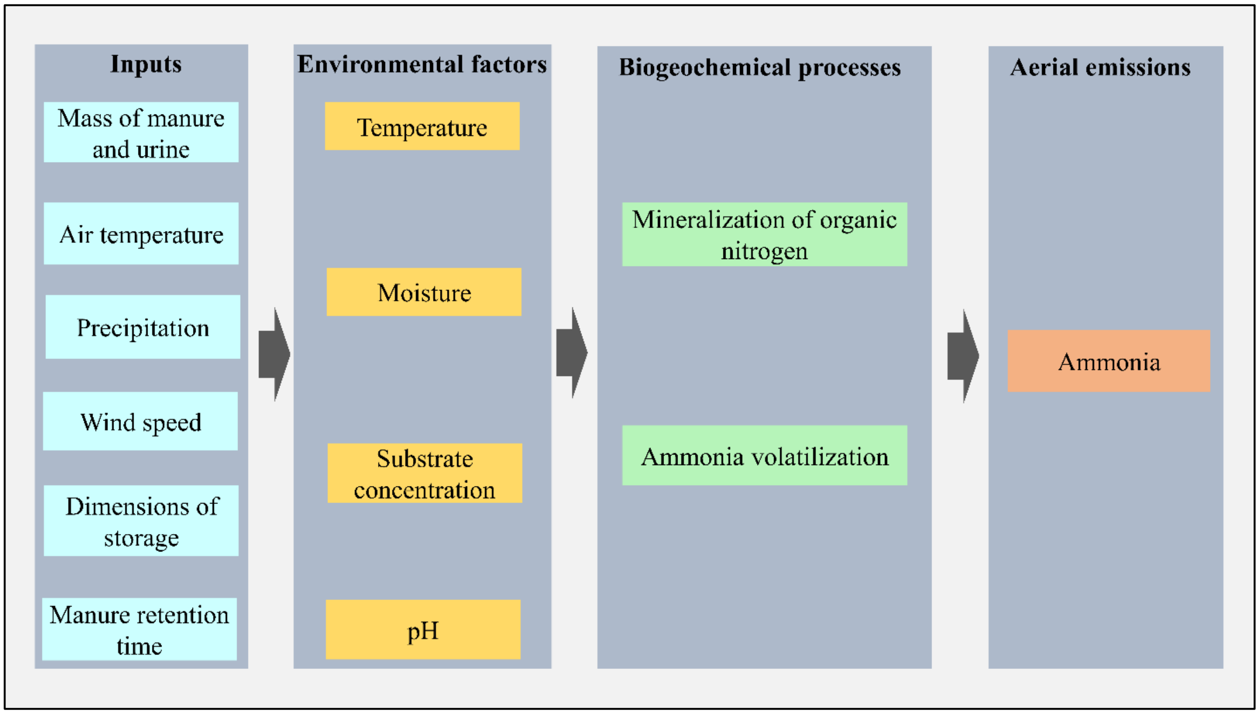

Figure 2.3: Structure of the PBAEM manure storage sub-model (adapted from Zhang et al. (2005))

2.1.5 Farm Emissions Model (FEM)

The FEM, developed by Pinder et al. (2004), tracks N flow through different stages of manure management in a dairy farm by using sub-models for housing, storage, application, and grazing to estimate NH_3 emissions. The storage sub-model considers three different types of manure storage structures: lagoon, earthen basin, and a slurry tank. The sub-model includes biogeochemical processes related to NH_3 production and emission from stored manure. The biogeochemical processes, relevant environmental factors, and manure characteristics are illustrated in Figure 2.4.

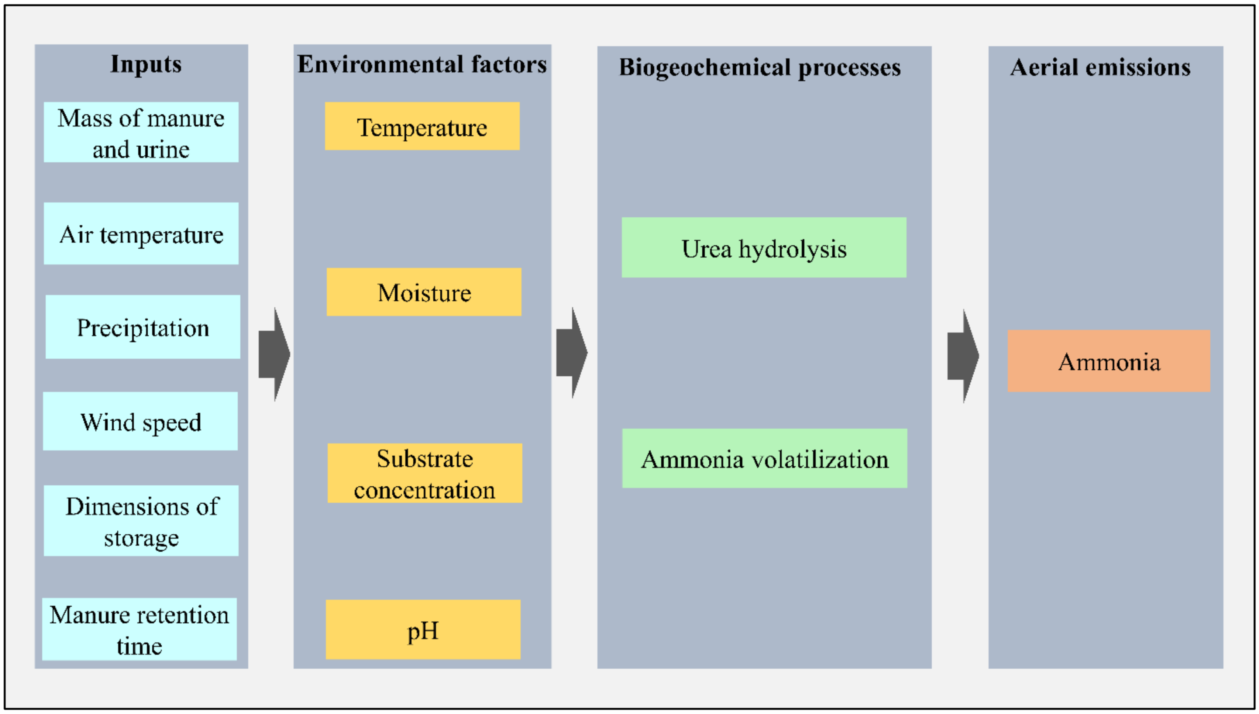

Figure 2.4: Structure of the FEM manure storage sub-model (adapted from Pinder et al. (2004))

2.2 Process-based model evaluation criteria

In general, PBMs can be described based on their structure, function, and behavior (Knüpfer et al., 2013). To provide context for the purposes of this review, structure refers to the model components and their connectivity; function is the intended use of the model; and behavior is the dynamics of the model. The PBMs considered in this review used a variety of inputs, model equations, and mechanisms to simulate production and emissions of NH_3 and GHGs. Our evaluation was based on the following criteria: (i) biogeochemical processes simulated, (ii) equations and parameters used, (iii) inputs and outputs, and (iv) evaluation of model performance as described below.

2.2.1 Biogeochemical processes simulated

Biogeochemical processes that occur in manure during storage are complex but generally include combinations of chemical, biological, and physical processes. Biogeochemical processes are mandatory in a PBM and explicit representation to fully describe and account for all activities occurring in manure during storage is desirable to obtain meaningful and accurate emission estimates. Specific to NH_3 and GHGs emissions, it is important that biogeochemical processes relevant to manure C and N transformation during storage are included as part of simulations of a PBM. It should be noted that C and N transformation processes are closely related to S transformation (Reddy and DeLaune, 2008; Gu et al., 2012; Bridgham et al., 2013). Therefore, comprehensive PBMs simulating C and N transformations should also include S transformation to better represent the actual and/or realistic conditions in stored manure. Stored liquid manure experiences both aerobic and anaerobic conditions. Aerobic conditions occur near the surface of stored manure while anaerobic conditions prevail below the surface. These different environmental conditions along with the complex composition of manure lead to the existence of diverse microbial communities in stored manure (McGarvey et al., 2007; Dungan and Leytem, 2013). Regardless of the complexity of microbial communities and the biogeochemical processes in anaerobic systems, such as liquid stored manure, wastewater, and wetlands, they are commonly modeled using a set of fundamental processes that describe C, N, and S transformations (Reddy and DeLaune, 2008; Grady et al, 1999). A list of some of the prevalent biogeochemical processes relevant to NH_3, GHGs, and H_2S emissions are presented in Table 2.2. In this study, the PBMs were evaluated based on the extent and detail to which these biogeochemical processes were considered in the model simulation.

Table 2.2: Biogeochemical processes relevant to ammonia, greenhouse gas, and hydrogen sulfide emission

Nutrient	Biogeochemical processes	Description	Gaseous products	Reference
Carbon	Decomposition	Microbial conversion of complex manure organic C (e.g., cellulose, lignin, carbohydrates, fats) into simple organic molecules i.e., dissolved organic carbon (DOC) (e.g., sugars and organic acids)	CO_2	Reddy and DeLaune, 2008; Maier et al., 2009
	Respiration	Microbial oxidation of organic C to CO_2 $CH_2O + O_2 \rightarrow CO_2 + H_2O$ (2.1)	CO_2	Madsen, 2011; Zeebe, 2007
	Fermentation	Microbial conversion of organic polymers (e.g., carbohydrates, fats, proteins) and monomers (e.g., glucose) into volatile fatty acids, alcohols, H_2, and CO_2	H_2 CO_2	Reddy and DeLaune, 2008
	Methanogenesis	Microbial conversion of hydrolysis products (e.g., H_2, CO_2, methanol, acetate) to CH_4 under anaerobic conditions $4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$ (2.2)	CH_4	Reddy and DeLaune, 2008; Maier et al., 2009

Nutrient	Biogeochemical processes	Description	Gaseous products	Reference
	Aerobic methane oxidation	Microbial oxidation of CH_4 to CO_2 under aerobic conditions $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ (2.3)	CO_2	Maier et al., 2009; Madsen, 2011
	Anaerobic methane oxidation	Microbial oxidation of CH_4 to CO_2 under anaerobic conditions $5CH_4 + 8NO_3^- \rightarrow 5CO_2 + 6H_2O + 4N_2 + 8OH^-$ (2.4) $CH_4 + SO_4^{2-} + H^+ \rightarrow CO_2 + HS^- + 2H_2O$ (2.5)	CO_2 N_2	Madsen, 2011; Modin et al., 2007
Nitrogen	Mineralization or Ammonification	Microbial conversion of manure organic N into NH_4^+	-	Reddy and DeLaune, 2008; Grady, 1999
	Urea hydrolysis	Conversion of urea (CO $(NH_2)_2$) into NH_4^+ $CO(NH_2)_2 + 3H_2O \rightarrow 2NH_4^+ + HCO_3^- + OH^-$ (2.6)	-	Li et al., 2012; Udert et al., 2003
	Nitrification	Microbial conversion of NH_4^+ to NO_3^- through an oxidation process, N_2O is produced as an intermediate product $NH_4^+ + O_2 \rightarrow NO_2^- + 4H^+ + 2e^-$ (2.7) $NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ + 2e^-$ (2.8)	N_2O	Li et al., 2012; Reddy and DeLaune, 2008; Maier et al., 2009

Nutrient	Biogeochemical processes	Description	Gaseous products	Reference
	Denitrification	Microbial conversion of NO_3^- to NO, N_2O, N_2 though a sequential reduction process $NO_3^- + 2e^- \rightarrow NO_2^- + e^- \rightarrow NO + e^- \rightarrow N_2O + NO_2^- \rightarrow N_2$ (2.9)	NO N_2O N_2	Li et al., 2012; Reddy and DeLaune, 2008; Robertson and Groffman, 2007; Wrage et al., 2001
	Immobilization	Microbial assimilation of inorganic N compounds (e.g., NO_3^-) into organic N compounds (e.g., protein)	-	Reddy and DeLaune, 2008; Robertson and Groffman, 2007
	Ammonia volatilization	Produced $NH_4^+{}_{(aq)}$ is in an equilibrium with $NH_{3(aq)}$ in manure liquid $NH_{4(aq)}^+ \rightleftarrows NH_{3(aq)} + H^+$ (2.10) Diffusion of NH_3 from manure liquid to bulk air depending on the NH_3 concentration gradient	NH_3	Li et al., 2012; Reddy and DeLaune, 2008

Nutrient	Biogeochemical processes	Description	Gaseous products	Reference
	Anaerobic ammonia oxidation (anammox)	Microbial oxidation of NH_4^+ to N_2 under anaerobic conditions $5NH_4^+ + 3NO_3^- \rightarrow 4N_2 + 9H_2O + 2H_4^+$ (2.11) $NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O$ (2.12)	N_2	Reddy and DeLaune, 2008; Kartal et al., 2011; Hu et al., 2011; Kuenen, 2008
Sulfur	Mineralization	Microbial conversion of manure organic S into inorganic forms (e.g., H_2S)	H_2S	Reddy and DeLaune, 2008; Robertson and Groffman, 2007
	Oxidation	Microbial conversion of elemental S and sulfide (S^{2-}) to sulfate (SO_4^{2-})	-	Reddy and DeLaune, 2008; Maier et al., 2009

Nutrient	Biogeochemical processes	Description	Gaseous products	Reference
	Reduction	Microbial conversion of SO_4^{2-} to S^{2-}	H_2S	Reddy and DeLaune, 2008; Maier et al., 2009
	Immobilization	Microbial assimilation of inorganic S compounds (e.g., SO_4^{2-}) into organic S compounds (e.g., protein)	-	Reddy and DeLaune, 2008; Maier et al., 2009
	H_2S volatilization	$H_2S_{(aq)}$ is in an equlibrium with $H_2S_{(g)}$ $H_2S_{(aq)} \rightleftarrows H_2S_{(g)}$ (2.13) $H_2S_{(aq)}$ forms a weak diprotic acid in manure liquid $H_2S_{(aq)} \rightleftarrows H^+ + HS^-$ (2.14) $HS^- \rightleftarrows H^+ + S^{2-}$ (2.15)	H_2S	Reddy and DeLaune, 2008; Arogo et al., 1999

2.2.2 Model equations and parameters

The underlying biogeochemical processes governing aerial emissions from stored manure have been modeled using one or combinations of emission factors, empirically-based equations, or equations based on the known theoretical or mechanistic principles. Models that use a mechanistic approach are considered pure PBMs, while models that combine mechanistic, empirical relationships, and emission factors can be categorized as hybrid PBMs (Cuddington et al., 2013; Mäkelä et al., 2000). Although empirical models are based on observational or experimental data, their application is limited and may only reduce the uncertainty of the model outputs for the defined range of inputs used in the conduct of the experiments (Mishra et al., 2013). Additionally, the exclusion of underlying mechanisms of processes in a system when empirical models are used could result in inaccurate model predictions (Adams et al., 2013). The knowledge of the dynamics of the numerous biogeochemical processes occurring in manure is vital to fully uncover the driving mechanisms of NH_3 and GHGs production and emissions, as well as, designing meaningful and effective mitigation strategies. Thus, the equations used to build a robust PBM should be based on well-known chemical reaction kinetics (e.g., Michaelis–Menten equation for enzymatic reactions), microbial growth kinetics (e.g., Monod equation for the growth of microorganisms), and physical laws (e.g., Fourier's law for heat conduction and Fick's law for diffusion) (Shuler and Kargi, 2001; Nellis and Klein, 2009; Cussler, 1997). It is well understood that one way of reducing uncertainties in model output is to use appropriate model parameters (Reyer et al., 2016). Thus, where possible and when available, the stoichiometric and biokinetic parameters specific to the source or material being modeled, e.g., dairy manure, should be used in the equations describing the biogeochemical processes to represent the PBMs more accurately. Our evaluation of the PBMs was based on the type of mathematical equations and the parameters used to describe the mechanisms of the biogeochemical processes.

2.2.3 Inputs and outputs

The type and quality of input data are important for obtaining meaningful outputs during PBM simulations (Grassini et al., 2015). It is desirable to have input data that is easy to access, for example, weather data (e.g., air temperature, precipitation, relative humidity, wind speed from sources such as, National Climatic Data Center (www.ncdc.noaa.gov/cdo-web/)) and farm information (e.g., number of animals, dimensions of the storage, storage period). Model outputs vary depending on the gases (e.g., CH_4, CO_2, NH_3, N_2O, N_2, H_2S) included. The temporal resolution of model outputs will vary depending on the context of the model. In general, a model output with a higher temporal resolution can describe the dynamics of a process in short time intervals. PBMs with high temporal resolution outputs use more refined and detailed biogeochemical processes and process dynamics compared to those with lower temporal resolution. The temporal resolution of output is important consideration not only for gas emission inventory but also for developing health and safety guidelines for farm workers and animals. In this review, I consider the input parameters used, gases (especially, related to C and N transformations) estimated, and the temporal resolution of inputs and outputs.

2.2.4 Model performance

Models are not perfect in representing systems; there is always a knowledge gap between real and simulated systems. As such, it is important to evaluate the performance of any model we develop. Evaluation of model performance unveils the degree of accuracy and precision of the model predictions (Larocque et al., 2016; Tedeschi, 2006; Willmott et al., 1985). Evaluating model performance involves conducting model calibration, verification, and sensitivity analysis (Larocque et al., 2016; Tedeschi, 2006; Willmott et al., 1985; Shaeffer, 1980). Model verification assesses the accuracy of the output by comparing with the measured data from a real system (Larocque et al., 2016; Rykeil, 1996). Model calibration, also known as model tuning, is conducted to improve the accuracy and precision of model simulation by estimating and adjusting model parameters against measured data of a real system ((Larocque et al., 2016; Rykeil, 1996; Oreskes et al., 1994).

The lack of precise knowledge or information to wholly and comprehensively describe characteristics or behavior of a system can simply be defined as uncertainty (Refsgaard et al., 2007; Uusitalo et al., 2015; Walker et al., 2003). The uncertainty of model output could be related to context, structure, technical implementation, inputs, parameters, and outputs of a model (Refsgaard et al., 2007; Walker et al., 2003). Sensitivity analysis (SA) is one of the several methods that have been used to assess the uncertainty of models. SA measures the contribution of model input parameters to the variance of model output (Saltelli et al., 2006; Saltelli et al., 2010). Therefore, it can be used to identify important input parameters to which the model outputs are the most sensitive (Saltelli, 2000). Two classes of SA have been described in the literature; local sensitivity analysis (LSA) and global sensitivity analysis (GSA) (Saltelli et al., 1999; Campolongo and Saltelli, 1997). LSA can further be divided into absolute (ASA) and relative (RSA) sensitivity analysis. Because of its simplicity, RSA has been used in many studies.

Typically, RSA is performed by changing one parameter at a time over a defined range while fixing the rest of the parameters at their mean values, and does not include factor or parameter interactions. On the other hand, GSA tests the effects of all the input parameters and their interactions on the model output (Baroni and Tarantola, 2014). Therefore, GSA is preferred for SA of ecological and environmental models given the complex processes and interactions in these environments (Baroni and Tarantola, 2014; Harper et al., 2011; Makler-Pick et al., 2011). However, GSA is computationally intensive, an issue that may not be a problem anymore with the development of powerful and fast computing technologies (Smith, 2014). In this review, I seek evidence of model verification, calibration, and sensitivity analysis of the PBMs.

2.3 Evaluation of selected process-based models

2.3.1 Biogeochemical processes simulated

The number and the type of biogeochemical processes used in the selected PBMs vary depending on the type of manure gas estimated. The Manure-DNDC, IFSM, and DairyGEM include transformations of manure C and N to estimate production and emissions of CO_2, CH_4, NH_3 and N_2O. However, the IFSM, and DairyGEM estimate the emission of H_2S as well. The PBAEM and FEM simulate only the transformation of manure N to estimate NH_3 emission. Of note, PBAEM includes N mineralization and NH_3 volatilization, while FEM includes urea hydrolysis and NH_3 volatilization.

In Manure-DNDC model, degradation of manure organic matter (MOM) is presented in greater detail compared to other models. Four major pools of MOM (residual litter, microbial, humads, and passive humus) are defined depending on the C:N ratio. The MOM in each pool decomposes independently and contributes to the overall dissolved organic carbon (DOC) in manure. Each MOM pool has a specific decomposition rate, adopted or derived from published literature for soil organic matter decomposition (Gilmour et al., 1985; Knapp et al., 1983; Molina et al., 1983). The DOC is used as an input variable for microbial reactions (e.g., nitrification, denitrification, methanogenesis etc.) in both the C and N transformation. In contrast, in IFSM and DairyGEM, there is no evidence of partitioning and decomposing MOM into DOC, instead, C transformation processes are related to manure volatile solids (VS) content, for instance, CH_4 production during methanogenesis.

The handling of CO_2 emission from manure is also different for the models that described it. Mechanistically, CO_2 is a product of microbial respiration, aerobic CH_4 oxidation, anaerobic CH_4 oxidation or combination of these. In Manure-DNDC, CO_2 emission is estimated using both microbial respiration and aerobic methane oxidation process-based approaches, while IFSM and DairyGEM use emission factor to estimate CO_2 emission, an approach that does not adequately represent its underlying processes.

In Manure-DNDC model, N mineralization occurs simultaneously with the decomposition of manure organic C, an attempt to reflect realistic interactions of biogeochemical processes occurring in stored manure. For instance, the C:N ratio of the substrate will influence decomposition of organic C and mineralization of organic N, while, concurrently, both the decomposition and mineralization processes alter C:N ratio. In contrast, in IFSM, DairyGEM, and PBAEM, N mineralization is simulated as an individual process without involving processes related to transformation of manure C. In the FEM, it is assumed that the effect of N mineralization on total ammoniacal nitrogen (TAN) pool of stored manure is negligible (Haynes and Williams, 1993).

In Manure-DNDC, nitrification and denitrification processes occur simultaneously with manure C decomposition and ammonia volatilization as these processes share common microbial metabolites (e.g., DOC, NH_4^+). In contrast, IFSM and DairyGEM use an emission factor to describe N_2O emission which is a product of both nitrification and denitrification processes. In Manure-DNDC model, hydrolysis of urea is implemented concurrently with decomposition of manure C. The FEM simulates urea hydrolysis assuming it is the only process that contributes to TAN pool of stored manure. However, urea hydrolysis is not considered in other models, based on the assumption that the hydrolysis of urea to TAN is complete by the time manure reaches the storage. All PBMs include NH_3 volatilization and this process is described based on the TAN content of manure.

The IFSM and DairyGEM are the only models that estimate emission of H_2S from stored manure, presenting an attempt to account for manure S. The models simulate volatilization of H_2S based on dissociation of $H_2S(aq)$ in manure liquid and diffusion of $H_2S_{(g)}$ from manure liquid to the bulk air. However, other relevant processes to comprehensively describe S transformation are not included.

In summary, the Manure-DNDC, IFSM and DairyGEM models estimate emissions of the multiple and similar gases (NH_3, CO_2, CH_4, and N_2O) and present more relevant and relatively comprehensive biogeochemical processes desirable in process based models. None of the models consider anaerobic methane oxidation and anammox processes, which may lead to inaccurate prediction of CH_4 and CO_2 emissions. The relatively simpler models, PBEAM and FEM, developed for estimating NH_3 emission, do not include biogeochemical processes (nitrification, anammox) that could influence quantities and dynamics of NH_3 volatilization. Nonetheless, PBEAM and FEM may reduce computational demand as well as model uncertainty. All the PBMs evaluated do not include the interrelations among the C, N, and S transformations comprehensively. The Manure-DNDC only considers C and N transformations simultaneously.

2.3.2 Model equations and parameters

The equations used to describe the biogeochemical processes related to NH_3 and GHGs emissions vary across the models. Manure-DNDC, PBAEM, and FEM use mechanistic equations, while the IFSM and DairyGEM use a mixture of emission factors and empirical and mechanistic equations. In Manure-DNDC it is assumed that the decomposition rate of manure organic C follows first-order kinetics and is affected by manure temperature and moisture content as described by Molina et al. (1983). Further, CO_2 emission during microbial decomposition is described as a function of DOC. In IFSM and DairyGEM, CO_2 emission from open manure storage is modeled using an emission factor of 0.04 kg CO_2 m^{-3} day^{-1} (Junbluth et al., 2001; Sneath et al., 2006).

Manure-DNDC model uses mechanistic equations to describe methanogenesis. CH_4 production is presented as a function of DOC, CO_2, and activity of methanogenic micro-organisms. The activity of methanogens is controlled by manure temperature, pH, and redox potential (Eh). Methane oxidation rate depends on temperature, Eh, and CH_4 concentration of manure. Manure pH is specified as a dynamic function that depends on the production and consumption of H^+ based on initial values set for each manure type (e.g., 7.0 for dairy cow manure). Even though, the Eh of stored manure varies with time and space (Miller, 2002), a constant redox potential (-300 mV) for stored liquid manure is used (Li et al., 2012). The IFSM and DariyGEM describe CH_4 emission using an empirical model developed by Sommer et al. (20004) that includes an Arrhenius based temperature corrections and the CH_4 emission rate is calculated based on VS content and manure temperature.

All the models except FEM simulate N mineralization using mechanistic approaches. However, the equations are adopted from different sources. The Manure-DNDC model simulates

N mineralization using first order kinetics concurrently with manure C decomposition (Molina et al., 1983). In IFSM, DairyGEM, and PBAEM, N mineralization is defined as a function of organic N and manure temperature.

Nitrification and denitrification processes in Manure-DNDC are developed based on microbial kinetics. The nitrification process in Manure-DNDC is implemented using Michaelis–Menten kinetics based on Blagodatsky and Richter (Blagodatsky and Ritcher, 1998). The reaction rate relies on the concentration of: DOC and NH_4^+, manure temperature, moisture, Eh, and pH. A detailed description of denitrification is provided and the process algorithm is developed after Leffelaar and Wessel (1988). Denitrification is modeled using first-order rate equations (for microbial biomass production), Double-Monod equations (for relative growth rate of denitrifiers), and the Pirt equation (for electron acceptor and substrate consumption) (Leffelaar and Wessel, 1988). In IFSM and DairyGEM, N_2O emission from manure storage is determined using an emission factor. Based on a study by Olesen et al. (2006), an average emission rate of 0.8 g N_2O m^{-3} day^{-1} is used for the bottom-fed uncovered slurry tank.

Urea hydrolysis is considered only in the Manure-DNDC model and FEM. The rate of urea hydrolysis in Manure-DNDC model is described based on the activity of urease enzyme and the concentration of urea in manure. The activity of urease enzyme is set as a function of temperature and DOC. In contrast, hydrolysis of urea to TAN is calculated based on a rate constant in the FEM.

All the PBMs use mechanistic equations in simulating NH_3 volatilization. The dissociation of NH_4^+ ($NH_{3(aq)}$/ NH_4^+ equilibrium) is described using dissociation constant of NH_3 (K_a) and dissociation constant of water (K_w). Both K_a and K_w are calculated as functions of temperature. The transfer of $NH_{3(aq)}$ in bulk liquid to bulk air ($NH_{3(g)}$) is described using a two-film model. In that, NH_3 transfer from interface manure liquid to bulk air is calculated using a mass transfer coefficient of NH_3, Henry's law constant (K_H) of NH_3, and the concentration of NH_3 in the air and in manure liquid. The mass transfer coefficients are defined as a function of wind speed, and air temperature while K_H constant is defined as a function of manure temperature. However, the equations and the parameter values vary depending on the original study from which the equations and parameter values were adopted, for instance, De Visscher et al. (2002). for Manure-DNDC, Montes et al. (2009) for IFSM and DairyGEM, Arogo et al. (2003) for PBAEM, and Hutchings et al. (1996) for FEM.

Engineered or naturally formed (crust) surface covers over stored manure affect dynamics of gas emissions. Considerations for the effect of surface cover/crust on gas emission is presented in all the models except in PBAEM. These models use a resistance parameter for each type of surface cover or crust. For instance, in the IFSM and DairyGEM, it is assumed that crust formation does not occur if manure is fed from the top, manure dry matter content (DM) is less than 8%, and a cover is used (Rotz et al., 2016a). If manure storage meets any of the above criteria, the emission factor of N_2O is set to zero. When a crust is formed, this value was considered to be 0.8 g N_2O $m^{-2}day^{-1}$.

Manure solids and water balance of stored manure is important as manure volume influences the concentration of soluble microbial metabolites (e.g., DOC, TAN), thereby the occurrence and the rate of biogeochemical reactions. Mass and volume of manure in a storage change continuously due to precipitation, evaporation, and infiltration (Ham, 1999). Manure volume changes are taken into account in the PBMs on daily basis except in IFSM and DairyGEM.

Environmental factors (e.g., temperature, pressure) and manure characteristics (e.g., moisture, pH, Eh, nutrients and solids concentration, and manure gas concentration) known to affect biogeochemical reactions, vary in space and time (Li, 2007). Further, these spatial variations affect the transfer and emission of produced gases in stored manure. It should be noted that most PBMs do not consider these spatial variations, except the Manure-DNDC storage sub-model which includes the spatial variation of temperature in model simulations. Nonetheless, Manure-DNDC storage sub-model does not rigorously simulate the distribution of manure temperature based on well-established heat equations. Instead, it uses a simplified heat transfer formula to estimate the temperature at different depths of the stored manure based on air temperature and the lagoon slurry depth. The estimated temperature values are then used in the biogeochemical reactions. Other models estimate liquid manure temperature using measures of correlation between ambient air temperature above the surface of the stored manure and manure temperature. For example, PBAEM calculates liquid temperature based on the average daily ambient air temperature using a correlation equation developed by Stefan and Preud'Homme (1993); IFSM and DairyGEM specify the liquid temperature as the average ambient temperature over the previous 10 days.

All PBMs considered in this review did not adequately represent the diffusion of gases within stored manure or use well-established diffusion equations to model gas diffusion. These models simulate the diffusion of NH_3 only in the upmost layer (liquid air interface) of stored manure. Further, in Manure-DNDC model, a simplified diffusion equation based on CH_4 concentration gradient, temperature, and air-filled porosity is used to estimate CH_4 diffusion. The foregoing review suggests that, all the models include well-developed mechanistic approaches for estimating NH_3 volatilization. This may be owing to the progress of the studies on NH_3 emission from liquid manure (De Visscher et al., 2002; Montes et al., 2009; Ni, 1999). With respect to estimating CH_4, CO_2, N_2O emissions, Manure-DNDC model includes well-established chemical and microbial kinetics while IFSM and DairyGEM consist with empirical equations and emission factors. Spatial variation of environmental factors and manure characteristics are vital for accurate model predictions; however, these spatial variations are underrepresented in the PBMs.

2.3.3 Inputs and outputs

The storage sub-models in the PBMs considered in this review are a part of much bigger whole-farm models. Other than the specifications of the storage structure (e.g., dimensions, surface cover), the input data are not specifically assigned for the storage sub-model but are derived from what is required for the whole-farm model. Input data required to run the PBMs vary but can be divided into four categories: (1) storage structure (storage type, dimensions, capacity, surface cover); (2) livestock and manure (animal numbers, feed rate, composition of feed, bedding type, bedding quantity and frequency of application); (3) manure management data (frequency and fraction of manure fed to storage, retention time in the storage, and fraction of manure removed from storage); (4) weather data (air temperature, precipitation, wind speed, RH). Depending on the context of the model, each PBM produces different outputs of aerial emissions at different temporal resolutions.

In Manure-DNDC model, each type of storage (lagoon and tank) is characterized by its capacity, surface area, type of cover (none, loose, and tight), storage time of manure, and quantity of manure removed from the storage. This model uses daily weather data including maximum and minimum air temperature, precipitation, and wind speed. Output of the storage sub-model include daily fluxes of CH_4, N_2O, NH_3, NO, N_2, and CO_2. Emission of CO_2 and CH_4 are estimated in kg C ha^{-1} day^{-1} while NH_3, N_2O, NO, and N_2 are estimated in kg N ha^{-1} day^{-1}. The IFSM and DairyGEM model consider more storage types (aboveground steel tank, a belowground concrete tank, or a clay or plastic-lined earthen retention pond) compared to other PBMs. Further they simulate two options based on manure loading (top or bottom) into storage not included in other models. As in Manure-DNDC, IFSM and DairyGEM models use local weather data. Output of these two models includes emission of NH_3, N_2O, CH_4, CO_2, H_2S, and VOC. The emission of NH_3, H_2S, and VOC are modeled in hourly time steps in the model algorithm. However, emission of each gas in model output is summed up and reported as mass per day (kg day^{-1}).

Developed for estimating NH_3 emission, both PBAEM and FEM use typical input parameters as other models. However, PBAEM does not include options for surface covers, therefore it is unable to estimate the effect of surface covers on NH_3 emission. The FEM model is simulated in one-day time steps and the daily NH_3 emission is given in kg N cow^{-1}. In contrast, the PBAEM model is simulated in one second time steps and emission of NH_3 is estimated in kg $m^{-2}s^{-1}$ or kg day^{-1} cow^{-1}.

Overall, the PBMs use a suite of input data in four categories that are easily accessible, and estimate various aerial emissions from manure storage. Most of the PBMs (except PBAEM) include options for gas emission mitigation methods, thus, facilitate manure management decisions of a dairy farm. The PBMs nest the manure storage sub-model within the whole-farm model which focus more on long-term effects of nutrient cycling based on the daily routines in a dairy farm. Therefore, most of the PBMs estimate the gas emissions in daily basis. However, refined models with finer temporal resolution in output are desirable.

2.3.4 Model performance

All PBMs met at least one criteria of model performance evaluation we defined, i.e., calibration and verification. The IFSM and PBAEM performed SA, while Manure-DNDC used scenario analysis to identify the effects of different management scenarios on NH_3 and GHG emissions. Pinder et al. (2004) calibrated the surface resistance parameters of FEM using empirical results from previous studies (Sommer et al., 1993; Xue et al., 1999). In Manure-DNDC, IFSM, DairyGEM, and PBAEM, equations and parameters in the storage sub-model are adopted from models that are already been calibrated. For instance, the Manure-DNDC model adopted most of the biogeochemical processes from the original DNDC model which has been calibrated several times (Giltrap et al., 2010). The Manure-DNDC model has been verifed against the experimental data collected from a swine farm in North Carolina by Harper et al. (2004). The data included fluxes of NH_3, N_2O, and N_2 gases from a manure lagoon. Local weather data and farm management data were used as inputs for the simulation. Model predictions were reported to be closely related to the observed values in general, despite some discrepancies. Predicted N_2 from the lagoon was 34% less than the observed value while predicted NH_3 was 28% higher than the observed. Similarly, Deng et al. (2015) verified Manure-DNDC storage sub-model using NH_3 emission data collected from a dairy lagoon located in Jasper County, IN (Grant and Boehm, 2010a). The predicted and observed daily NH_3 fluxes from lagoon showed a strong correlation ($P<0.001$) with a correlation coefficient (r) of 0.82.

Rotz et al. (2014) verified the IFSM for NH_3 emissions under different dairy manure storage types (single stage and three-stage lagoon), storage covers (no cover, natural crust cover, enclosed structure with a lid, and other covers including oil and peat), manure types (slurry manure, digested slurry, and liquid manure), and geographical regions (Indiana, Ohio, and

Wisconsin in US and Denmark). The NH_3 emission data for the verification were obtained from the National Air Emissions Monitoring Study (NAEMS) (Grant and Boehm, 2010a; Grant and Boehm, 2010b) and published data from other studies (Sommer et al. 1993; Harper et al., 2009; Sommer, 1997; Zhao et al., 2007). The authors concluded that the IFSM simulation results were well correlated with measured NH_3 emissions for the different management types considered. Further, the same model has been verified for CH_4 emission data from Husted (1994) for a slurry manure storage tank (Chianese et al., 2009). The authors concluded that the IFSM storage sub-model predicts CH_4 emissions within 12% of measured emissions. The DairyGEM includes the same model components and algorithm as of IFSM, therefore the results are valid for both the models.

Pinder et al. (2004) ran the FEM model for an open liquid manure storage, and compared the predicted output with experimental data from Sommer (1997). The authors reported a lower prediction error for the storage sub-model (RMSE = 0.0154). So far, the storage sub-model of PBAEM has not been verified for a liquid dairy manure. However, Zhang et al. (2005) simulated this sub-model for a swine manure storage tank located in Davis, CA and compared with the NH_3 emissions from Arogo et al. (2003). The authors found that the NH_3 emission rates predicated from the storage sub-model are consistent with the results of Arogo et al. (2003).

Sensitivity analysis has been reported for PBAEM and IFSM. The SA for the PBAEM storage sub-model was performed by Ogejo et al. (2010) and included both RSA and GSA. The results from both RSA and GSA showed that the lagoon liquid pH, liquid temperature, wind speed above the lagoon surface, and the concentration of TAN in the lagoon were the most important model input parameters. In addition, GSA uncovered relationships that could not be detected by RSA. For example, GSA discovered that about two-thirds of the model output variance was attributed to the interactions between model parameters i.e., interaction between pH and temperature, wind speed and total TAN had more influence on variance of the model output than individual parameters.

Chianese et al. (2009) performed a RSA for the storage sub-model in the IFSM. The authors tested the sensitivity of the model to 10 parameters including Arrhenius parameter, mass of manure, and manure temperature. The Arrhenius parameter is an established constant for the model, however, authors changed that parameter by ±25% in the SA. They found that the model output was significantly affected by the Arrhenius parameter, and suggested that additional studies are required for further evaluations of this parameter.

Evidence of systematic SA of Manure-DNDC model as defined in this review was not available in the literature searched. However, Li et al. (2012) reported conducting scenario analysis for Manure DNDC. To a certain extent, a scenario analysis is similar to SA; except it compares the effect of input combinations on output rather than a systematic analysis of the effects of individual model parameters on model outcome (Giltrap et al., 2004). The scenario analysis of Manure-DNDC model by Li et al. (2012) investigated the effect of different farm management practices on NH_3 and GHGs emissions. The management practices used in the simulations are typical for dairy farms in the U.S., located in northern New York with: freestall barn, manure lagoon, and crop field. Four management scenarios were considered: (i) reduced crude protein (CP) concentration of feed from 18% to 15%, (ii) use of surface cover on manure lagoon, (iii) plant high-yielding alfalfa in the field, (iv) combination of all above management practices (Li et al., 2012). The change of aerial emissions from manure lagoon with respect to the baseline case was calculated for each management scenario. The results showed that decreasing CP concentration in feed reduced emissions of NH_3 and N_2O in lagoon by 18% and 48%

respectively; surface cover on lagoon reduced NH_3 emission by 58%, and increased CH_4 emission by 106%. The increase of CH_4 emission was attributed to increased anaerobic conditions caused by lagoon surface cover. Planting high-yielding alfalfa in the field did not have any impact on aerial emissions from the lagoon. The fourth scenario reduced emissions of NH_3 and N_2O in lagoon by 60% and 48% respectively, and increased CH_4 emission by 84%. The scenario analysis revealed that the lagoon surface cover and CP concentration of feed contribute significantly to the outputs of the storage sub-model. Even though the CP concentration of feed is not a direct input parameter of the storage sub-model, it changes the composition of manure (C:N ratio) coming to the lagoon, thereby affects the production and emission of NH_3 and GHGs.

2.4 Limitations and suggestions to improve process-based models

Model evaluation criteria identified differences across the PBMs depending on which gases predicted and what approach used to represent the biogeochemical processes in stored liquid dairy manure. Several limitations of the PBMs that may affect the accuracy of model predictions were identified and suggestions to improve the PBMs are discussed below.

2.4.1 Spatial distribution of manure characteristics

Studies have reported (1) spatial manure temperature variability (Masse et al., 2008; Park and Wagner-Riddle, 2010); (2) stratification of solids in manure lagoons and pits affects the distribution of manure solids (Ndegwa et al., 2002; Nordstedt and Baldwin, 1975; Zhu et al., 2003); and (3) layered stratification of manure nutrients (C, N, P, S) and trace minerals (Al, Ca, Fe, Mg) that may cause spatial changes in the structure of the microbial communities (Lovanh et al., 2009; McLauhlin et al., 2014), in manure during storage. However, the PBMs reviewed neither documented spatial variation of temperature and material concentrations in manure storage nor established them adequately in their description. Omission of these details may lead to inaccurate predictions by the models. One way to cover the full spectrum of spatial variation of environmental factors and biogeochemical processes, is to use compartmental modeling approach (Sharifi et al., 2015). In compartmental modeling, manure storage is divided into small homogeneous units. Then, using well-established heat and mass transfer equations, manure temperature and substrate concentration are estimated for each compartment (Nellis and Klein, 2009; Cussler, 1997). These, estimates are used to simulate the biogeochemical processes relevant to aerial emissions. In this manner, compartmental models can improve the accuracy of estimation of spatially varying parameters (Godfrey, 1983).

2.4.2 Use of empirical equations

Aerial emissions during the transformation of manure C and N involves a series of biogeochemical processes. Use of empirical equations or emissions factors to estimate these emissions inadequately represents the relevant underlying mechanisms, contributing to inaccurate predictions by these models. For example, N_2O is produced in both the nitrification and denitrification processes (Wrage et al., 2001). However, some models do not consider these processes and use an emission factor to estimate N_2O emission from stored manure. Process-based approach can be used instead to better represent the complex biogeochemical processes.

2.4.3 Missing pertinent processes

Under anaerobic conditions, a group of bacteria oxidizes NH_4^+ into nitrogen gas using nitrite as the electron acceptor. This process is called anammox (Kartal et al., 2011; Rich et al., 2008). Both the anammox and denitrification processes occur simultaneously under anaerobic conditions, despite the fact that the growth rate of anammox bacteria is slow compared to denitrifiers (Molinuevo et al., 2009). Therefore, it is important to consider and include these processes in estimating gaseous emissions from manure storages. None of the PBMs consider anammox in model simulations.

Methane oxidation is a process that oxidize CH_4 into CO_2 under aerobic (Maier et al., 2009) or anaerobic conditions (Modin et al., 2007). Under anaerobic conditions, CH_4 is oxidized to CO_2, while nitrate is reduced to N_2 (Modin et al., 2007) and sulfate is reduced to HS^- (Vavillin, 2013). Methane oxidation under aerobic conditions is considered only in the Manure-DNDC model. Anaerobic methane oxidation process is not simulated in any of the models. These missing processes related to C and N transformation need to be considered in future PBMs to obtain more accurate emissions estimates.

Finally, there is a potential to improve the biogeochemical processes already existing in these models to better understand the dynamics of manure C and N transformation. For example, fermentation can be described comprehensively via the processes of hydrolysis, acetogenesis, hydrogenogenesis, homoacetogenesis; methanogenesis can be described by hydrogenous methanogenesis, and acetic methanogenesis (Haung et al., 2010). The PBMs that I considered could be refined by simulating the biogeochemical processes in stored manure in such detail.

2.4.4 Stoichiometric and biokinetic parameters

Stoichiometric and biokinetic parameters used in PBMs are generally derived from established values from studies in soil microbiology and waste water management. These parameter values may not be directly related to the biogeochemical processes in stored manure.

Although, these parameters may be well established justifying or extrapolating their use for non-similar materials may be questionable. Gujer (2011) noted that using parameters derived from experiments with no sufficient relationship to the situation at hand may be a major source of model error even with calibration and verification process. Further, Gujer (2011) reiterated the important need for a good understanding of the growth characteristics of the microbial communities as well as their environment for the simulated biogeochemical processes to be meaningful. With the recent advances in knowledge and tools in biotechnology, we should be able to better understand complex microbial systems, uncover and elucidate the processes that lead to production of aerial pollutants at the farm scale level where the production N based gases of NH_3 and N_2O, the release of CH_4 and CO_2 occur under normal operating conditions.

2.4.5 Sensitivity analysis

Conducting a SA is an integral part of the development of a process-based model. A few studies have performed SA to evaluate the storage sub-models, and most of these studies applied LSA. However, in practice, manure storage sub-models are applied under diverse conditions which involve numerous variables and their interactions. Even though GSA is computationally intensive, it is indispensable to perform a GSA to identify the most significant input parameters for each particular setting. On the other hand, developing models with process-based (or mechanistic) equations will demand a large number of parameters that may increase the magnitude of uncertainty of the model output (Adams et al., 2013). This also highlights the importance of sensitivity analysis.

2.5 Summary

The PBMs described in this review are different from each other based on the structure and mechanisms used. Evaluation of each storage sub-model against the defined criteria revealed their strengths and weaknesses with respect to the estimation of aerial emissions from stored liquid dairy manure. The general conclusions from this evaluation are as follows.

- All models consider and use some form of biogeochemical processes but not to the fullest extent that occurs in manure storage pits.
- Comprehensive consideration of interactions among the C, N, and S transformations are not represented in the PBMs and should be included to reflect the realty of interdependence of these elements in reactions that occur in manure.
- None of the models sufficiently simulated the spatial heterogeneity of environmental factors and manure characteristics within a manure storage. All models considered the storage pit as a single compartment with uniform manure characteristics.
- Models need to use GSA to systematically asses the model performance, only one model attempted GSA.
- The Manure-DNDC, IFSM and DairyGEM models present a more comprehensive approach to estimate NH_3 and GHGs from stored liquid dairy manure. However, based on our evaluation, the Manure-DNDC may be more desirable because of the extent of use of the biogeochemical processes.
- Implementing compartmental modeling approach will allow (1) estimate spatially varying environmental factors and manure characteristics, (2) capture spatial variability of biogeochemical processes, and (3) improve accuracy of model estimations.

- Each manure storage sub-model considered in this review is part of an integrated whole-farm model. The accuracy of storage sub-models is important not only for estimating emissions from manure storage but also for subsequent farm components/operations in manure management. To achieve better representation of processes in a manure storage, these PBMs need to be addressed for their limitations. Using current knowledge of biogeochemistry and mass and energy transfer, these models can be improved to have a higher accuracy.

3 Materials and methods

The review of PBMs in chapter 2 identified that the current PBMs need to be improved to capture spatial variation of environmental factors and manure characteristics in stored manure. The purpose is to accurately estimate spatial variation of biogeochemical processes pertinent to production and emission of ammonia. A spatial compartmental model can be used to represent this spatial heterogeneity.

This chapter presents details of developing the compartmental process-based model that incorporate the spatial variation of manure temperature and TAN concentration in stored manure. First, it provides a summary of the model and the model algorithm. Then the heat and mass transfer equations related to the biogeochemical process expected to occur in stored manure along with the application of the compartmental approach to simulate these processes are described. The last section of this chapter describes the methods and data used in model calibration, verification, sensitivity analysis and scenario analysis.

3.1 Biological, chemical, and physical processes occur in liquid manure storage

Stored liquid dairy manure is a dynamic system that involves biological, chemical, and physical processes. The processes related to ammonia production and emission considered in the compartmental PBM are: (1) material balance in manure storage, (2) heat transfer in stored manure, (3) mineralization of organic N, (4) diffusion of TAN in stored manure, and (5) ammonia volatilization (Figure 3.1). Each process is described in detail in the following sections.

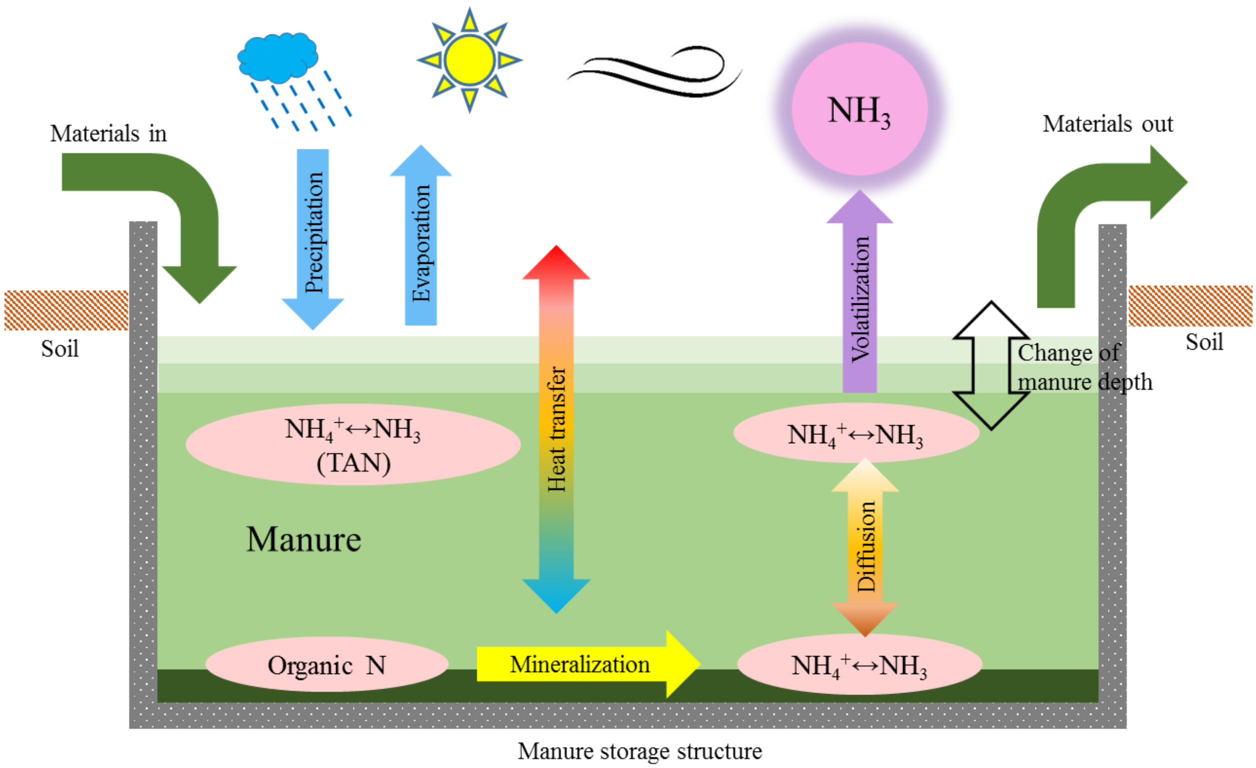

Figure 3.1: Biological, chemical, and physical processes pertinent to ammonia production and emission from stored liquid dairy manure that are considered in compartmental process-based model

3.2 Model development

3.2.1 Compartmental model description

The compartmental process-based model was developed with six (6) sub models: storage size, manure volume/depth change, heat transfer, manure TAN, ammonia transfer, and ammonia volatilization. Inputs of the model include weather, manure management practices, herd, and manure characteristics data (Table 3.1). The processes simulated in the compartmental model are illustrated in Figure 3.2. Figure 3.2 shows the model algorithm, in which the sub models are embedded in a loop to estimate daily emission of NH_3 from stored manure. Sections from 3.2.2 to 3.2.7 describe each sub model and processes in detail.

Table 3.1: Compartmental model input data

Data category	Input	Units
Weather (daily)	Average air temperature	°C
	Total precipitation	cm
	Average wind speed	ms^{-1}
	Average relative humidity	percent
	Standard height at which wind speed is measured	m
	Wind speed correction height	m
Herd and manure management (daily)	Manure storage period	days
	Number of animals	count
	Mass of manure produced per animal	kg
	Mass of bedding used per animal	kg
	Density of manure	kg m^{-3}
	Density of bedding	kg m^{-3}
Dimension of the storage	Total depth/height	m
	Surface area open to air	m^{-2}
	Depth of residual manure	m
Manure characteristics	Initial organic nitrogen concentration	kg m^{-3}
	Initial TAN concentration	kg m^{-3}
	pH	

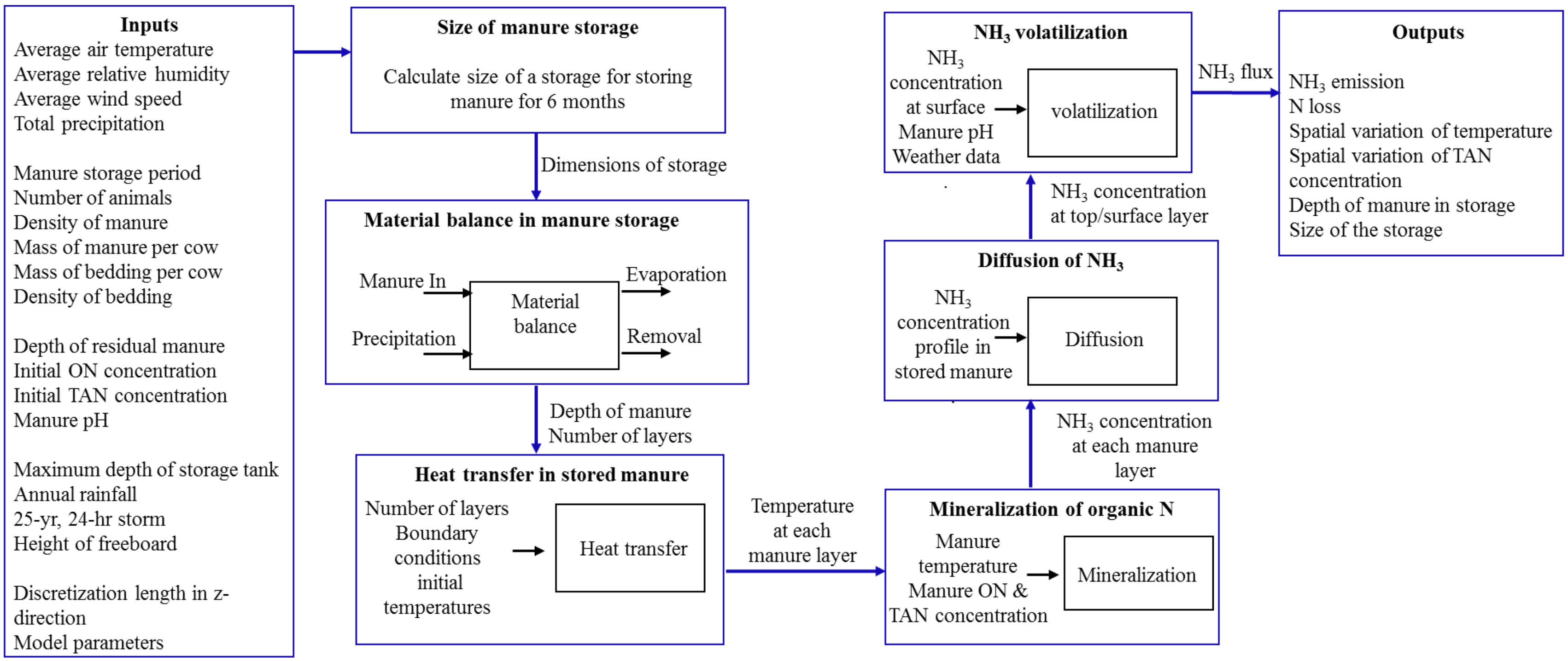

Figure 3.2: Schematic diagram of the processes simulated in the compartmental process-based model

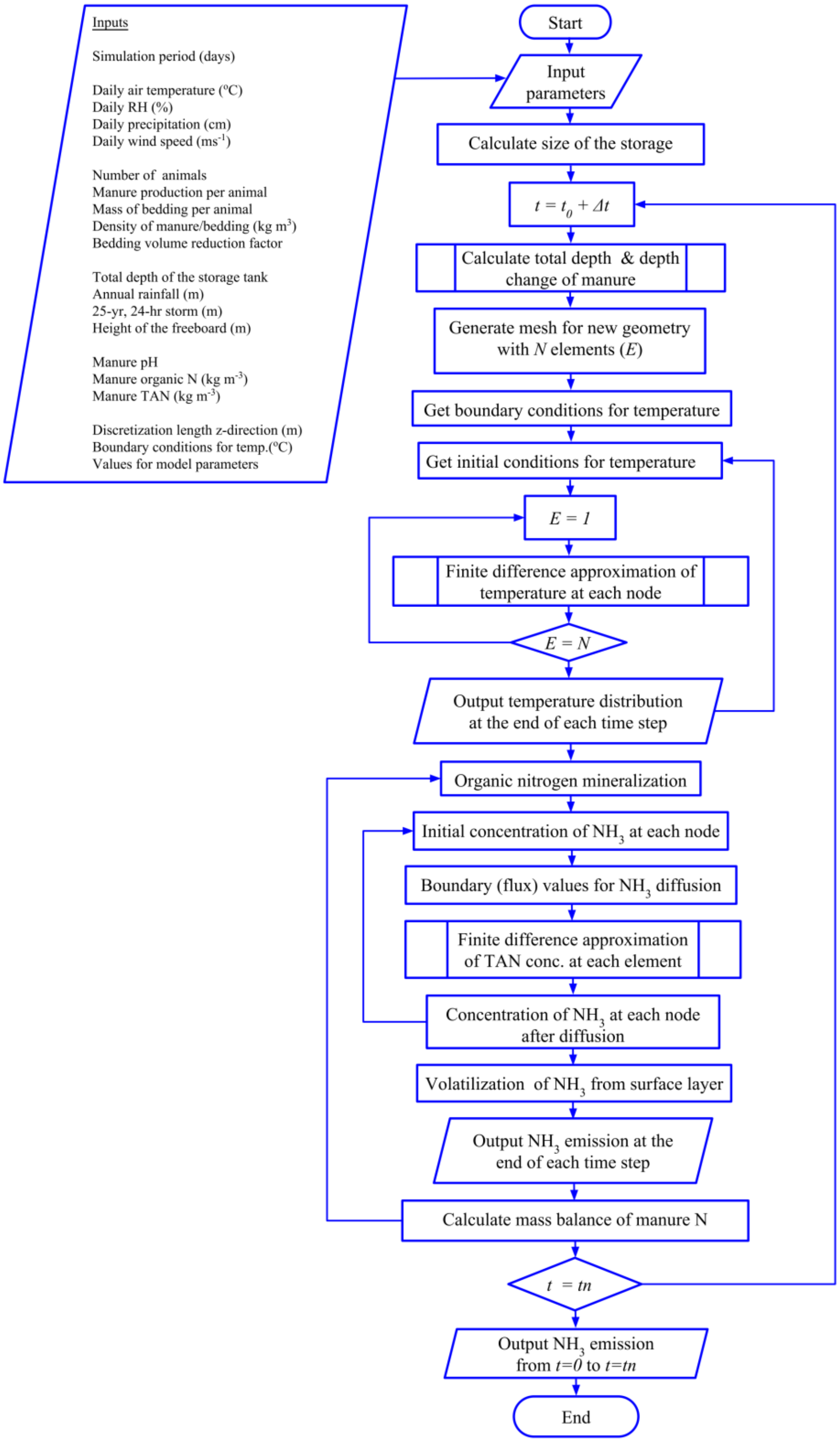

Figure 3.3: Flowchart for the compartmental process-based model algorithm

3.2.2 Sizing a manure storage structure

Figure 3.4 shows the cross section of a circular below ground liquid manure storage structure. The dimensions of manure storage structure determine the surface area of manure exposed to the atmosphere. The surface area of manure exposed to atmosphere can be given as an input if that information is available, otherwise, it can be calculated based on the geometry of the storage structure. In the compartmental model, the surface area of the storage tank exposed to the atmosphere was calculated using equation (3.1) (ASABE, 2013; MWPS, 2001). It was assumed that some form of an impermeable liner is used to minimize or stop seepage from the storage.

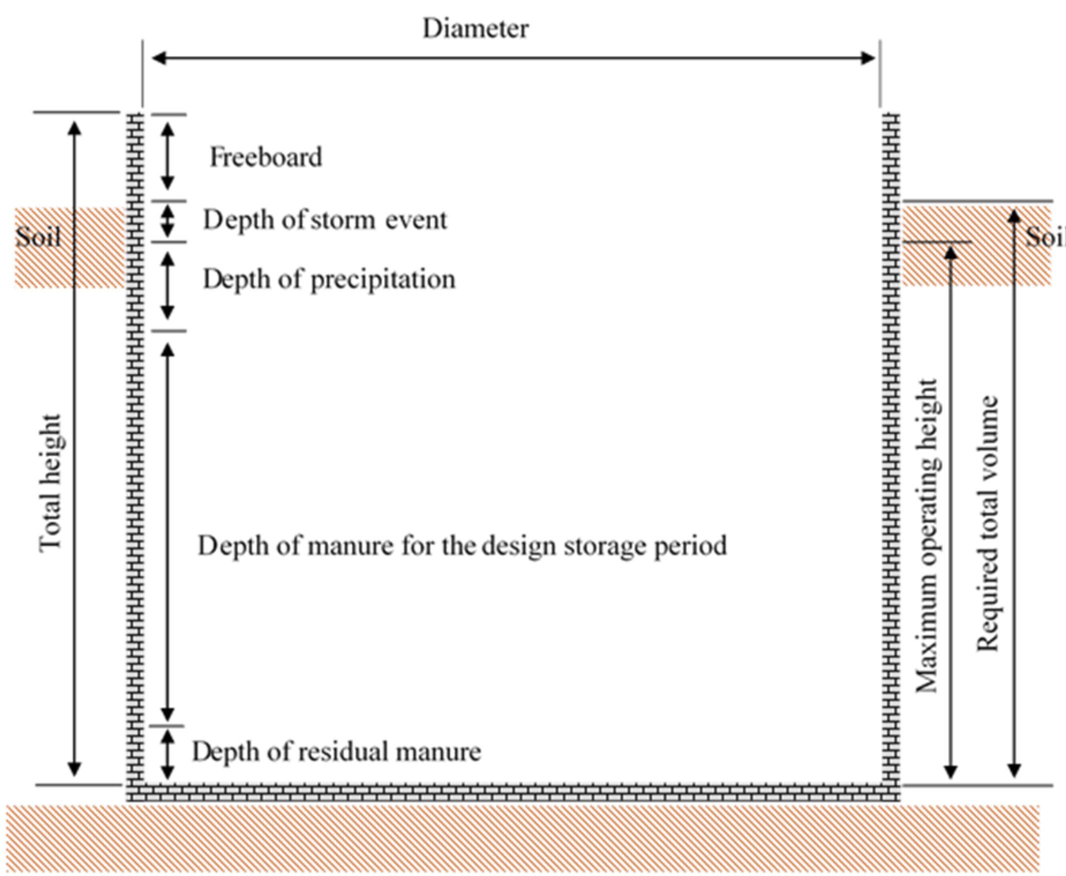

Figure 3.4: Cross section of a circular below ground liquid manure storage structure

$$A_s = \frac{\left(\frac{MW * N}{MD} + \frac{VR * B * N}{BD}\right) D + \left(R_a + S_{25y}\right) Area_{runoff}}{\left(D_T - R_a - E_a - H_{FB}\right)} \qquad (3.1)$$

where,

A_s	Surface area of stored manure exposed to the atmosphere (m^2)
N	Number of animals
MW	Mass of manure produced per animal per day (kg day^{-1})
MD	Density of manure (kg m^{-3})
VR	Volume reduction factor (range, 0.3 to 0.5)
B	Mass of bedding use per cow (kg day^{-1} cow^{-1})
BD	Loose bedding density (kg m^{-3})
D	Number of days of storage (days)
R_a	Annual rainfall of the selected location (m)
S_{25y}	25-year, 24-hour storm of the selected location (m)
$Area_{runoff}$	Land area exposed to runoff (m)
D_T	Total depth/height of the storage tank (m)
E_a	Annual evaporation of the selected location (m)
H_{FB}	Height of the freeboard of the storage tank (m)

3.2.3 Volume and depth change of stored manure

Material balance in a manure storage depends on the quantity of manure and water coming into the storage and quantity of manure, water, and manure gas going out of the storage. Daily material balance in stored manure was estimated using a mass balance equation (3.2) following Zhang et al. (2005). Processes contributing to mass balance vary in magnitude as well as with time. Seepage, mass loss through volatilization of biological gases (e.g. CH_4, CO_2, NH_3, H_2S) and recycling of wash water were excluded. It was assumed that the bottom and side walls of the storage tank were impermeable so that the seepage is zero. The mass loss through biological gases is relatively small (Zhang et al., 2005), therefore it was not considered in the mass balance calculations. Further, the model was developed for scraped dairy manure, therefore, the recycling of wash water was not considered in the calculation.

$$\frac{dM}{dt} = \dot{M}_{Manure\ in} + \dot{M}_{wastewaterin} + \dot{M}_{rain} - \dot{M}_{evap} - \dot{M}_{landapp} \tag{3.2}$$

where,

M	Mass of manure in the storage (kg)
t	Length of time step (day)
$\dot{M}_{Manurein}$	Mass flow rate of manure flowing into storage from housing (kg day^{-1})
$\dot{M}_{wastewaterin}$	Mass flow rate of fresh wash water flowing into storage (kg day^{-1})
$\dot{M}_{rain}$	Rate of precipitation onto top surface of storage (kg day^{-1})
$\dot{M}_{landapp}$	Mass flow rate of manure removed for land application (kg day^{-1})
$\dot{M}_{evap}$	Rate of evaporation from top surface of storage (kg day^{-1})

It was assumed that the manure is not removed from storage pit during the simulation period, therefore the $\dot{M}_{landapp}$ is zero. Evaporation rate ($\dot{M}_{evap}$) was calculated using semi-empirical equations (3.3) to (3.7) following Ham (1999). Ham (1999) compared four meteorological models to experimental evaporation data obtained from swine waste lagoon, and found that the equations (3.3) used here, showed the most promising results.

$$\dot{M}_{evap} = EA_s$$

$$E = \frac{0.622}{R_d(T_s + 273.15)}(e_s^* - e_a)U_r C_e \tag{3.3}$$

where,

- A_s Surface area of storage (m^2)
- E Evaporation flux (kg m^{-2} day^{-1})
- R_d Gas constant (287.04 J kg K^{-1})
- T_s Temperature of the liquid surface (°C)
- e_s^* Saturation vapor pressure at the temperature of the water surface (Pa)
- e_a Vapor pressure of air (Pa)
- U_r Average wind speed at reference height (m day^{-1})
- C_e Bulk aerodynamic transfer coefficient for vapor transport

The bulk transfer coefficient, C_e depends on the measurement height of the U_r and e_a. Ham (1999) used 2.81×10^{-3} for the bulk transfer coefficient that was calculated using U_r measured at 2 m height. The same value was used in this model. U_r was adjusted to the reference height of 2 m using an empirical equation (Albright, 1990).

$$U_r = u_z \left(\frac{2}{z}\right)^a \tag{3.4}$$

where,

- u_z Wind speed (ms^{-1}) at anemometer height (z)
- a Parameter depending on surrounding terrain.

A value of $a = 14$ typical to a smooth terrain such as the surface of a lake was used in the model.

The vapor pressure of air e_a was calculated using the following equations (3.5) and (3.6) (Ham,1999).

$$e_s^* = 0.61078\, exp\left(\frac{17.269 T_S}{237.3 + T_S}\right) \tag{3.5}$$

$$e_a = RH \times e_s^*(T_a) \tag{3.6}$$

where,

RH Relative humidity (%)

T_a Air temperature (°C)

A correlation equation was used to calculate the liquid surface temperature (T_s) base on air temperature (Stefan and Preud'Homme, 1993).

$$T_s = 5.0 + 0.75 T_a \tag{3.7}$$

Quantity as well as depth of manure influence heat transfer in a manure storage. Depth of manure in a storage changes depending on material balance of the storage. Daily change of manure depth was calculated using manure mass, density of manure, and surface area of manure storage. It was assumed that the density of manure does not change over time and side walls of the storage are perpendicular to ground surface.

$$\frac{dh}{dt} = \frac{dM}{dt}\frac{1}{\rho SA} \tag{3.8}$$

where,

h Depth of manure in storage (m)

ρ Density of manure in the storage (kg m^{-3})

t Time (day)

3.2.4 Heat transfer and temperature distribution in stored manure

The governing equation for transient heat conduction with heat generation for a Cartesian coordinate system can be expressed as (Nellis and Klein, 2009):

$$\frac{\partial}{\partial x}\left(k\frac{\partial T}{\partial x}\right)+\frac{\partial}{\partial y}\left(k\frac{\partial T}{\partial y}\right)+\frac{\partial}{\partial z}\left(k\frac{\partial T}{\partial z}\right)+Q\ (x,y,z,t)=\rho c\frac{\partial T}{\partial t} \tag{3.9}$$

where,

x, y, z	Cartesian coordinates
k	Thermal conductivity of manure (W m^{-1} °C^{-1})
$Q(x, y, z, t)$	Internal heat generation rate per unit volume (W m^{-3})
ρ	Density of manure (kg m^{-3})
c	Specific heat of manure (J kg^{-1} °C^{-1})
T	Temperature (°C)
t	Time (h)

The values of thermal and physical properties of dairy manure used in this model are presented in Table 3.2.

Table 3.2: Thermal and physical properties of liquid dairy manure

Parameter	Units	Value	Reference
Thermal conductivity (k)	W m^{-1} °C^{-1}	0.0901 - 0.6814	Nayyeri et al., 2009
Specific heat (c)	J kg^{-1} °C^{-1}	1992.5 - 3606	Nayyeri et al., 2009
Density (ρ)	kg m^{-3}	993 - 1009	MWPS, 1997

Following assumptions were made during the development of heat transfer model,

i. Heat transfer occurs only in z direction (z, along depth). Horizontal temperature variations are negligible. Therefore, the temperature distribution in stored manure is one dimension.

ii. Density, heat capacity, and thermal conductivity, internal heat generation of manure are constant with time and space.

Based on the assumptions, the partial differential equation (3.9) for transient heat conduction simplified to,

$$\frac{\partial T}{\partial t} = K\left(\frac{\partial^2 T}{\partial z^2}\right) + \frac{Q\ (z,t)}{\rho c} \tag{3.10}$$

where,

$$K = \frac{k}{\rho c}$$

Finite difference method[1] was used to solve the heat equation (3.10). Governing heat equation (3.10) was discretized as the first step of finding numerical solution to heat transfer in manure storage. In discretization, a grid was constructed with points (nodes) at which the heat equation is intended to be solved. Manure storage was divided into L number of layers with nz number of nodes. Each layer has a thickness of Δz m (Figure 3.5).

[1] Finite difference method was used for discretization of heat and mass transfer equations because of (1) computational tractability (2) the simple geometry of the heat and mass transfer (i.e. one-dimension transient heat and mass transfer).

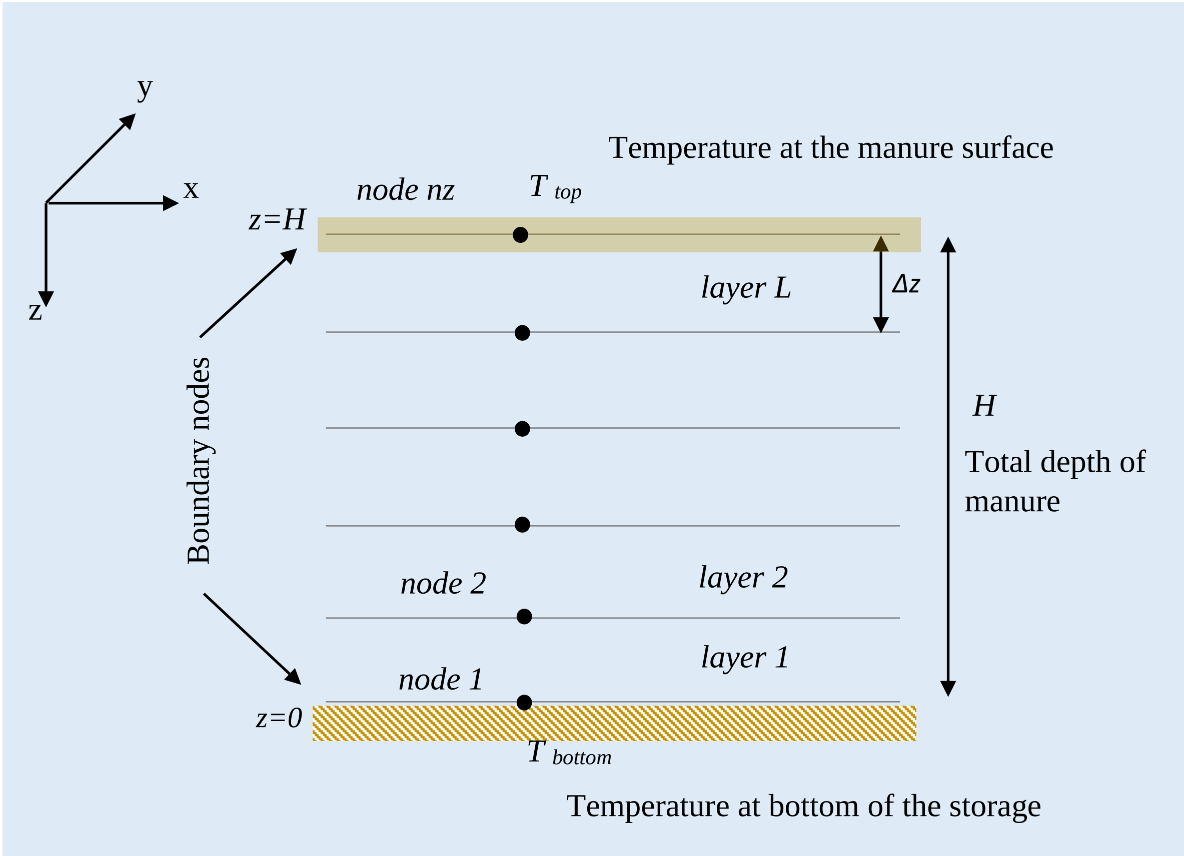

Figure 3.5: Discretization of the domain for heat transfer

Then the continuous derivatives of equation (3.10) were replaced with their finite difference approximations. According to implicit finite difference scheme, equation (3.10) was discretized as follows.

$$\frac{T_i^{n+1} - T_i^n}{\Delta t} = K\left(\frac{T_{i+1}^{n+1} - 2T_i^{n+1} + T_{i-1}^{n+1}}{\Delta z^2}\right) + \frac{Q_i^n}{\rho c} \tag{3.11}$$

where,

n Integer varies from 1 to nt (number of time steps)

i Integer varies from 1 to nz (number of nodes in z-direction)

Q Internal heat generation rate per unit volume (W m^{-3})

$K = \frac{k}{\rho c}$

k Thermal conductivity of manure (W m^{-1} °C^{-1})

ρ Density of manure (kg m^{-3})

c Specific heat of manure (J kg^{-1} °C^{-1})

T Temperature (°C)

Δt Length of a time step (h)

Δz Discretization length/ thickens of a layer (m)

Equation (3.11) was rearranged to bring the unknown terms to one side (left hand) and known terms to the other side (right hand side).

$$-sT_{i-1}^{n+1} + (1+2s)T_i^{n+1} - sT_{i+1}^{n+1} = T_i^n + \frac{Q_i^n \Delta t}{\rho c} \quad (3.12)$$

where,

$$s = \frac{K.\Delta t}{\Delta z^2}$$

Boundary conditions for heat transfer model

The top of storage is open to the air while the bottom is located underground. Temperature at the surface of manure changes with time driven by external factors such as air temperature and wind speed. Equation (3.7) was used to calculate the liquid surface temperature ($T_{surface}$) based on average daily air temperature (Stefan and Preud'Homme, 1993). Soil temperature at bottom of the storage was used as the boundary condition for the first node (T_{bottom}). Soil temperature fluctuation with time is affected by changes in air temperature and solar radiation. In this model, soil temperature at the bottom of the storage was estimated using a sinusoidal function following Hillel (1982). The variation of daily average soil temperature at a given depth was calculated using equation (3.13) (Hillel, 1982).

$$T_{bottom}(t) = T_{soil} + A_0 e^{-z/d} sin\left[\frac{2\pi(t-t_0)}{365} - \frac{z_s}{d} - \frac{\pi}{2}\right] \tag{3.13}$$

$$d = \sqrt{\frac{2D_h}{\omega}}$$

$$\omega = \frac{2\pi}{365}$$

where,

$T_{bottom}(t)$	Soil temperature at bottom of the storage and time t (°C)
T_{soil}	Average soil surface temperature (°C)
z_s	Distance from top to bottom of the storage (m)
A_0	Annual amplitude of the surface soil temperature (°C)
D_h	Thermal diffusivity of soil (m^2 day^{-1})
t	Day of the year in days
t_0	Phase constant (days)

Based on defined boundary conditions above, a system of linear equations was developed for the nodal points.

For 1st node at the bottom,

$$T_{bottom}^{n+1} = T_{bottom}^{n} \tag{3.14}$$

For *i*th node at middle of the storage,

$$-sT_{i-1}^{n+1} + (1+2s)T_i^{n+1} - sT_{i+1}^{n+1} = T_i^n + \frac{Q_i^n \Delta t}{\rho c} \tag{3.15}$$

For *nz*th node at the surface,

$$T_{surface}^{n+1} = T_{surface}^{n} \tag{3.16}$$

The equations (3.14) to (3.16) can be written in matrix form as,

$$\underline{\underline{A}\,x} = \underline{rhs}$$

where,

A Coefficient matrix,

x Solution vector

rhs Right hand side vector

For example, the grid matrix A vectors x and rhs can be written for six-nodes as follows.

$$A = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ -s & (1+2s) & -s & 0 & 0 & 0 \\ 0 & -s & (1+2s) & -s & 0 & 0 \\ 0 & 0 & -s & (1+2s) & -s & 0 \\ 0 & 0 & 0 & -s & (1+2s) & -s \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}$$

$$\underline{x} = \begin{pmatrix} T_1^{n+1} \\ T_2^{n+1} \\ T_3^{n+1} \\ T_4^{n+1} \\ T_5^{n+1} \\ T_6^{n+1} \end{pmatrix}$$

$$\underline{rhs} = \begin{pmatrix} T_{bottom}^{n} \\ T_2^n + \dfrac{Q_2^n \Delta t}{\rho c} \\ T_3^n + \dfrac{Q_3^n \Delta t}{\rho c} \\ T_4^n + \dfrac{Q_4^n \Delta t}{\rho c} \\ T_5^n + \dfrac{Q_5^n \Delta t}{\rho c} \\ T_{surface}^{n} \end{pmatrix}$$

Depth of manure varies as volume of manure in a storage changes with time (eq. 3.8). When depth of manure changes, the geometry used for heat transfer changes as well. Change of the position of manure surface along *z* axis creates a moving boundary. Initially, there is a certain depth of manure in the storage. Then, after every 24-hour period depth of manure in storage changes due to materials coming in and going out of the storage (Figure 3.6). Therefore, the geometry used for heat transfer algorithm was modified for every 24-hour period.

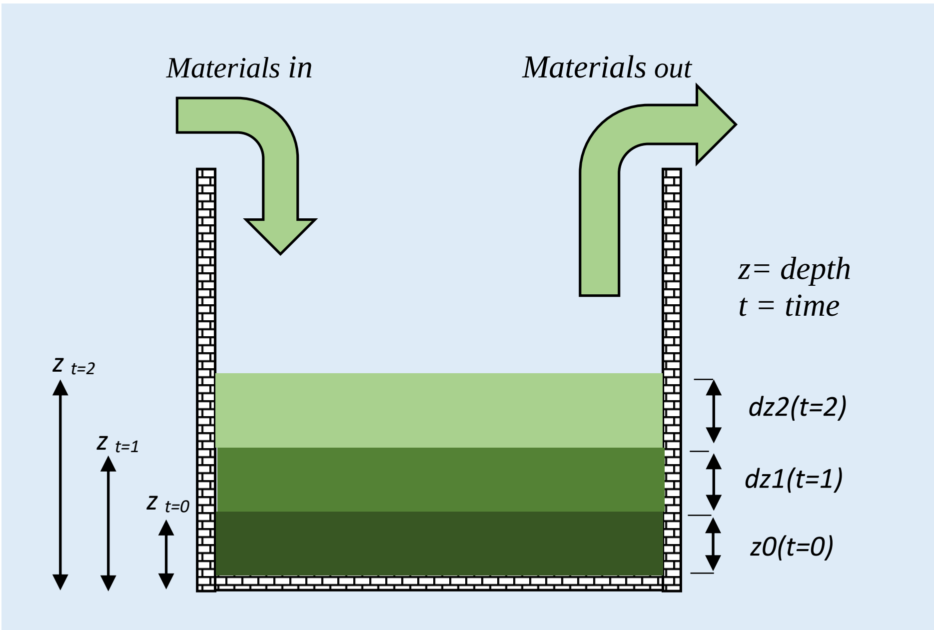

Figure 3.6: Change of manure depth of stored manure over time

Following assumptions were made to develop an algorithm for heat transfer of stored manure.

i. Manure storage is not empty at the beginning (at time zero). There is an initial depth of manure in the storage tank. In the model, the initial depth of manure is 0.3 m.

ii. Depth of manure in the storage changes on daily basis (every 24 hours) and the depth change depends on the material coming in and going out of the storage.

iii. At each time step, there are two different zones in manure storage. Bottom zone that contains manure accumulated up to previous time step and the top zone that contains new manure introduced at current time step.

A new geometry was created by adding the depth of new layer at current time step to the depth of manure at previous time step (Figure 3.7). New grid parameters were given for every 24-hour time period. Air temperature at current time step was given as an initial condition for latest manure layer whereas old temperature field calculated for previous time step was assigned for rest of the domain.

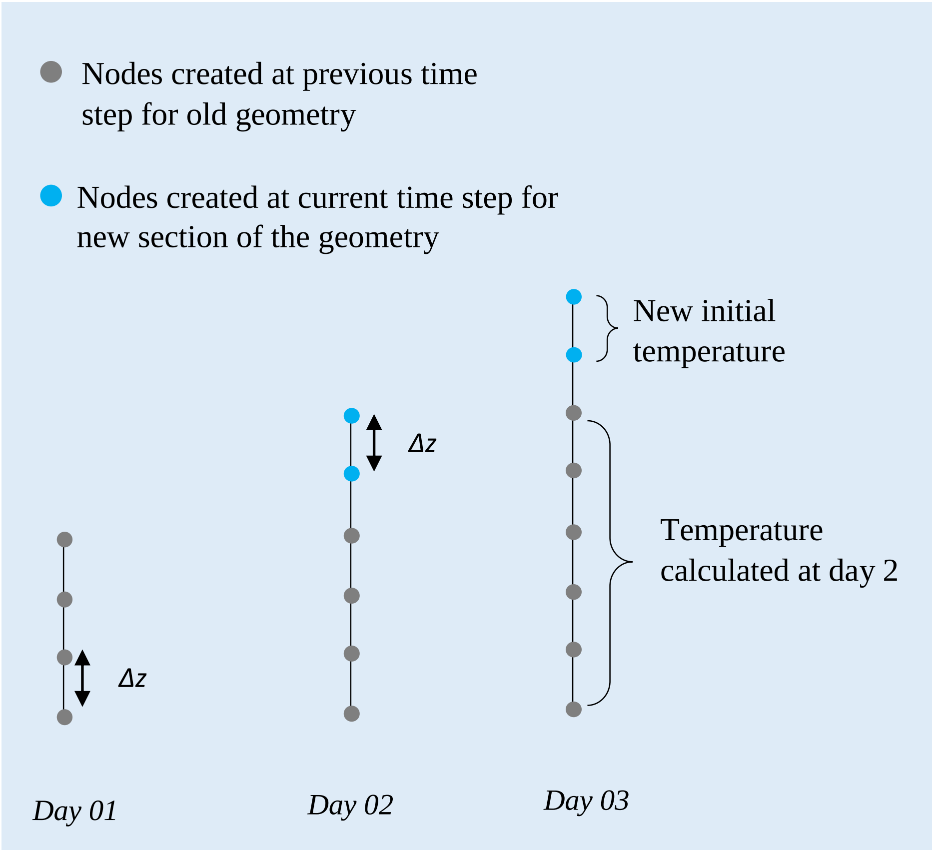

Figure 3.7: Expansion of grid for heat transfer at each time step

3.2.5 Total Ammoniacal Nitrogen in stored manure

Total Ammoniacal Nitrogen (TAN) concentration in each (n^{th}) layer was calculated using equation (3.17). Cross section of manure storage was divided in to L number of layers. Thickness/height of each layer was Δz. It was assumed that the width (W) of the storage tank is constant (straight side walls). Therefore, the volume (ΔzW) of each element/layer is also a constant and mass change of TAN in each element can be expressed as a concentration change.

$$C_{TAN,i}^{n} = C_{TANold,i}^{n-1} + C_{TANgen,i}^{n} dt \qquad (3.17)$$

where,

$C^n_{TAN,i}$ Concentration of TAN in the i^{th} layer at the end of n^{th} time step (kg N m^{-3})

C^n_{TANold} Concentration of TAN in the i^{th} layer at the beginning of n^{th} time step (after diffusion of TAN at the end of previous time step ($n-1$) (kg N m^{-3})

$C^n_{TANgen,i}$ Generation of TAN in the i^{th} layer at n^{th} time step as a result of mineralization of manure Organic Nitrogen (ON) (kg N m^{-3} day^{-1})

dt Length of a time step (day)

The TAN generated by mineralization of manure ON was estimated based on the model developed by Zhang et al. (2005). The concentration of TAN generated was calculated using concentration of manure ON and a rate constant (eq. 3.18).

$$C^n_{TANgen,i} = k_{ON} C^n_{ON,i} \tag{3.18}$$

where

k_{ON} Rate constant at temperature T (day^{-1})

$C^n_{ON,i}$ Concentration of ON i^{th} layer at n^{th} time step

Rate constant of mineralization at 20 °C (k_{ON20}) was corrected for temperatures other than 20 °C using equation (3.19).

$$k_{ON} = k_{ON20} \theta^{(T^n_i - 20)} \tag{3.19}$$

where

θ Temperature coefficient

k_{ON20} Rate constant of mineralization at 20 °C (day^{-1})

T^n_i Temperature of manure in the i^{th} layer at n^{th} time step (°C)

3.2.6 Diffusion of ammonia in stored manure

NH_3 in liquid manure volatilize from the top surface which is generally exposed to atmosphere. Desorption of NH_3 from the top surface creates a lower concentration of NH_3 at the surface than the inside of the stored manure. This concentration gradient of NH_3 drives the diffusion of NH_3 from inside layers to the top surface. Molecular diffusion of NH_3 under unsteady-state can be described by Fick's second law as shown in equation 3.20 below (Cussler, 1995).

$$\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial z^2}\right) \tag{3.20}$$

where,

D Diffusion coefficient of NH_3 ($m^2\, h^{-1}$)

C Concentration of NH_3 (kg N m^{-3})

z Length (m)

t Time step (h)

The following assumptions were made to simplify the modeling of NH_3 diffusion process.

(i) Stored manure has uniform properties in the horizontal direction and NH_3 diffusion occur only in vertical direction.

(ii) Diffusion coefficient of NH_3 is a constant and does not change spatially and temporally.

Finite difference method was used to solve the partial differential equation for unsteady diffusion. The governing equation (3.20) was discretized and a grid was constructed with nodes along z direction. Manure storage was divided into L number of layers with nz number of nodes. Each layer has a thickens of Δz m (Figure 3.8).

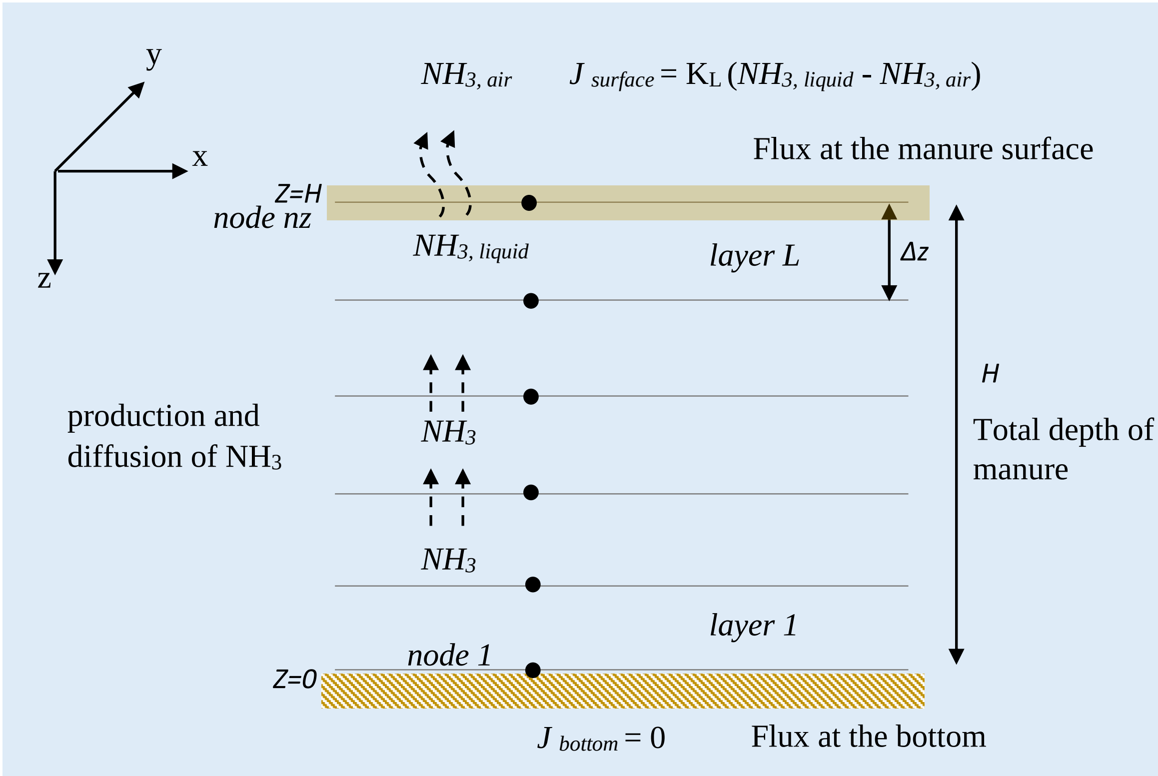

Figure 3.8: Discretization of domain for diffusion of ammonia in stored manure

Using implicit finite difference scheme equation (3.20) was discretized as follow.

$$\frac{C_i^{n+1} - C_i^n}{\Delta t} = D\left(\frac{C_{i+1}^{n+1} - 2C_i^{n+1} + C_{i-1}^{n+1}}{\Delta z^2}\right) \tag{3.21}$$

where,

D Diffusion coefficient of NH_3 ($m^2\ h^{-1}$)

C Concentration of NH_3 (kg N m^{-3})

Δz Discretization length/ thickens of a layer (m)

Δt Length of a time step (h)

where, n and i are integers; n varies from 1 to nt (number of time steps) and i varies from 1 to nz (number of nodes in z-direction).

Equation (19) was rearranged so that the unknown terms are on left hand side and the known terms are on right hand side.

$$-sC_{i-1}^{n+1} + (1+2s)C_i^{n+1} - sC_{i+1}^{n+1} = C_i^n \tag{3.22}$$

where,

$$s = \frac{D\Delta t}{\Delta z^2}$$

Boundary conditions for diffusion model

Following assumptions were made to define boundary conditions for the diffusion model.

(i) The bottom of the storage is impermeable so that no NH_3 diffusion across the boundary.

$$D\frac{dC}{dz} = J_{bottom} = 0 \tag{3.23}$$

(ii) Top surface of manure is open to atmosphere and there is a convective NH_3 transfer across liquid-air phase boundary.

$$D\frac{dC}{dz} = J_{surface} = K_L\,(C_{liquid} - C_{air}) \tag{3.24}$$

Central finite difference approximation for bottom boundary was applied as shown below.

$$\frac{C_2 - C_0}{2\Delta z} = \frac{J_{bottom}}{D} \tag{3.25}$$

C_0 is a fictional boundary point, therefore following steps were applied to derive an expression without C_0.

Equation (3.20) for 1st node,

$$\frac{C_1^{n+1} - C_1^n}{\Delta t} = D\left(\frac{C_2^{n+1} - 2C_1^{n+1} + C_0^{n+1}}{\Delta z^2}\right) \tag{3.26}$$

Using eq. (3.25) derive an explicit expression for C_0^{n+1}

$$C_0^{n+1} = C_2^{n+1} - \frac{J_{bottom} 2\Delta z}{D} \tag{3.27}$$

Substitute C_0^{n+1} in equation (3.26),

$$(1+2s)C_1^{n+1} - 2sC_2^{n+1} = C_{bottom}^{n} - \frac{J_{bottom} 2s\Delta z}{D} \tag{3.28}$$

An expression for the last (nz^{th}) node was derived following the same procedure as for top boundary.

$$-2sC_{nz-1}^{n+1} + (1+2s)C_{nz}^{n+1} = C_{surface}^{n} + \frac{J_{surface} 2s\Delta z}{D} \tag{3.29}$$

The equations (3.22), (3.28), and (3.29) can be written in matrix form as,

$$\underline{\underline{A}}\, \underline{x} = \underline{rhs}$$

where A is the coefficient matrix, x is the solution vector, and rhs is the right hand side vector. For example, the grid matrix A, vectors x and rhs can be written for six-nodes as follows.

$$A = \begin{pmatrix} (1+2s) & -2s & 0 & 0 & 0 & 0 \\ -s & (1+2s) & -s & 0 & 0 & 0 \\ 0 & -s & (1+2s) & -s & 0 & 0 \\ 0 & 0 & -s & (1+2s) & -s & 0 \\ 0 & 0 & 0 & -s & (1+2s) & -s \\ 0 & 0 & 0 & 0 & -2s & (1+2s) \end{pmatrix}$$

$$\underline{x} = \begin{pmatrix} C_1^{n+1} \\ C_2^{n+1} \\ C_3^{n+1} \\ C_4^{n+1} \\ C_5^{n+1} \\ C_6^{n+1} \end{pmatrix}$$

$$\underline{rhs} = \begin{pmatrix} C_{bottom}^{n} - \frac{J_{bottom} 2s\Delta z}{D} \\ C_2^n \\ C_3^n \\ C_4^n \\ C_5^n \\ C_{surface}^{n} + \frac{J_{surface} 2s\Delta z}{D} \end{pmatrix}$$

3.2.7 Volatilization of ammonia

Emission of NH_3 from manure surface to atmosphere is a two-step mass transfer process: (1) diffusion of NH_3 from manure bulk liquid to liquid-gas interface and (2) convective NH_3 transfer from liquid-gas interface to the air (Figure 3.9). The emission of NH_3 from manure surface was modeled using equations (3.30) to (3.41) that were developed based on the two-film theory model (De Visscher et al., 2002).

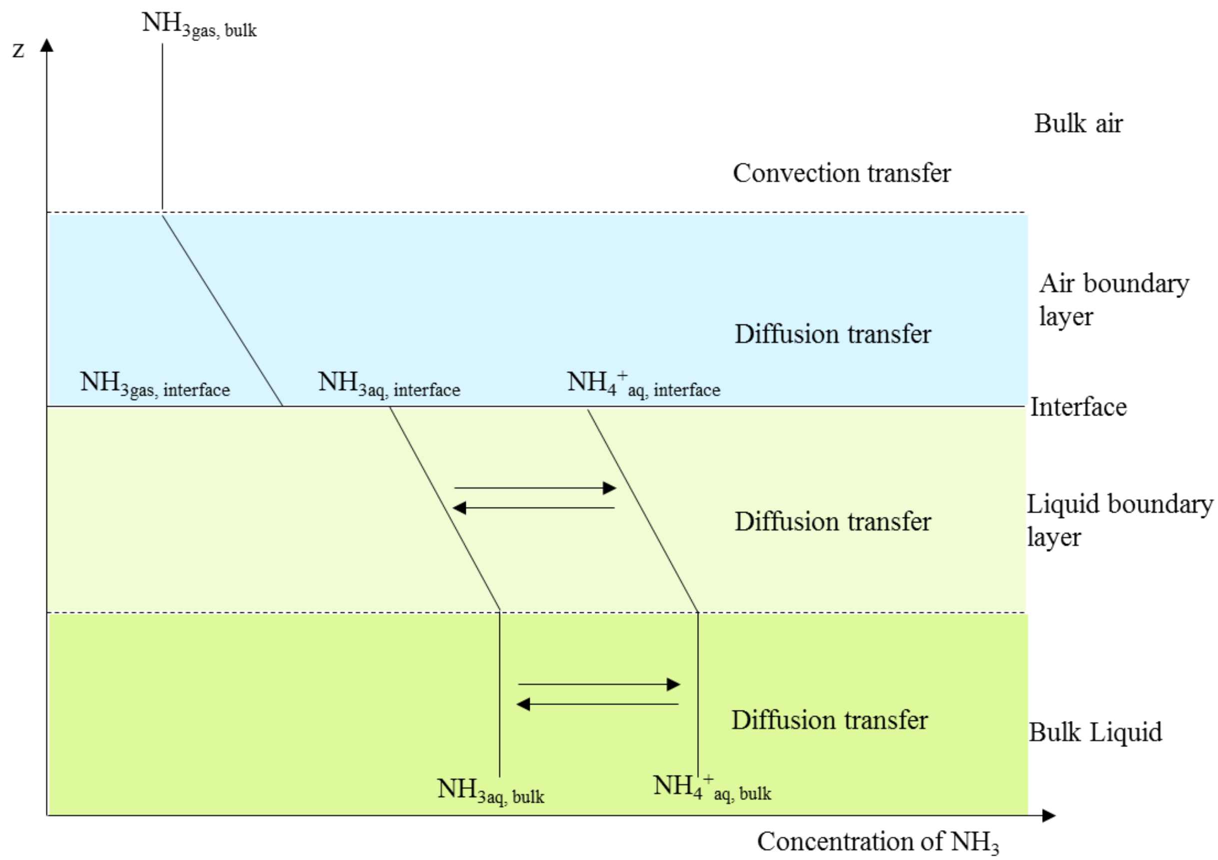

Figure 3.9: Mechanism of ammonia transfer across manure liquid-gas interface in the two-film theory model (adapted from De Visscher et al., 2002)

$$M_{NH3} = J_{surface} = K_L \, (FC_{liquid} - C_{air}) \tag{3.30}$$

where,

M_{NH3}	NH_3 emission flux from manure surface (kg m^{-2} s^{-1})
C_{liquid}	Concentration of TAN in the top layer (nz) of stored manure (kg m^{-3})
C_{air}	Concentration of TAN in the ambient air (kg m^{-3})
F	Fraction of free ammonia presence as TAN
K_L	Mass transfer coefficient (m s^{-1})

Mass transfer coefficient (K_L) was calculated using equation (3.31).

$$K_L = \frac{k_L H k_G}{k_L + H k_G} \tag{3.31}$$

where,

H Henry's constant

k_L Mass transfer efficient in the liquid phase (m s^{-1})

k_G Mass transfer efficient in the gas phase (m s^{-1})

Henry's constant was calculated based on the manure liquid temperature of the top layer (eq. 3.32).

$$H = \frac{2.395 \times 10^{-5}}{T_{liq} + 273.15} e^{\left(\frac{-4151}{T_{liq}+273.15}\right)} \tag{3.32}$$

where, T_{liq} is the manure liquid temperature of the top layer (°C).

Mass transfer of coefficient (k_L) of NH_3 in the liquid phase was calculated using equation (3.33) and mass transfer of coefficient (k_G) of NH_3 in the gas phase was calculated using equation (3.33). These equations were specified as functions of wind speed at 8 m height (U_8), diffusivity of ammonia in water ($D_{H2O,NH3}$), diffusivity of oxygen in water ($D_{H2O,O2}$), diffusivity of ammonia in air ($D_{air,NH3}$), and diffusivity of water vapor in air ($D_{air,H2O}$).

$$k_L = (1.676 \times 10^{-6} e^{-0.236 U_8}) \left[\frac{D_{H2O,NH3}}{D_{H2O,O2}}\right]^{0.57} \tag{3.33}$$

$$k_G = (5.158 \times 10^{-5} + 1.954 \times 10^{-3} U_8) \left[\frac{D_{air,NH3}}{D_{air,H2O}}\right]^{0.67} \tag{3.34}$$

In the model, the wind speed measured at any height was adjusted to 8 m height (eq. 3.35) following Jayaweera and Mikkelsen (1990).

$$U_8 = u_z \frac{ln\left(\frac{8}{z_0}\right)}{ln\left(\frac{z}{z_0}\right)} \tag{3.35}$$

where,

u_z Wind speed (ms^{-1}) at anemometer height (z)

z_0 Roughness height (m)

A value of 8×10^{-5} typical for a water surface was assumed for z_0 (Jayaweera and Mikkelsen, 1990). Diffusivity of NH_3 in air and water, diffusivity of water vapor in air, and diffusivity oxygen in water were calculated using equation (3.36) to (3.39).

$$D_{air,NH3} = \frac{3.0552 \times 10^{-8}(T_{air} + 273.15)^{1.75}}{26.8285 \times P} \tag{3.36}$$

$$D_{air,H2O} = \frac{3.0012 \times 10^{-8}(T_{air} + 273.15)^{1.75}}{25.5231 \times P} \tag{3.37}$$

$$D_{H2O,O2} = \frac{7.2824 \times 10^{-15}(T_{liq} + 273.15)}{e^{\left(\frac{1622}{T_{liq}+273.15} - 12.4058\right)}} \tag{3.38}$$

$$D_{H2O,NH3} = \frac{6.1453 \times 10^{-15}(T_{liq} + 273.15)}{e^{\left(\frac{1622}{T_{liq}+273.15} - 12.4058\right)}} \tag{3.39}$$

where,

T_{liq} Manure temperature at top layer (℃)

T_{air} Ambient air temperature over the manure surface (℃)

The fraction of free ammonia presence as TAN (F) was calculated based on the dissociation constant of NH_3 and manure pH (eq 3.40 to 3.41).

$$F = \frac{1}{1 + \frac{10^{-PH}}{K_a}} \tag{3.40}$$

$$K_a = 10^{\left(0.0897 - \frac{2729}{T_{liq} + 273.15}\right)} \tag{3.41}$$

3.2.8 Description of non-compartmental model

A non-compartmental model was developed for the comparison of compartmental process-based model performance. The non-compartment model was constructed with 4 sub-models: storage size, manure volume/depth change, manure TAN, and ammonia volatilization. Unlike compartmental model, non-compartmental model does not include sub-models (heat transfer and ammonia transfer) that estimate spatial distribution of manure temperature and ammonia. The algorithm of non-compartmental model is shown in Figure 3.10, where sub-models are embedded in a loop to estimate daily emissions of NH_3. Pertinent equations of each sub-model used in the model are similar to that of the compartmental model (see sections from 3.1.2 to 3.1.7). Inputs of the model include weather, manure management practices, herd, and manure characteristics data (Table 3.1).

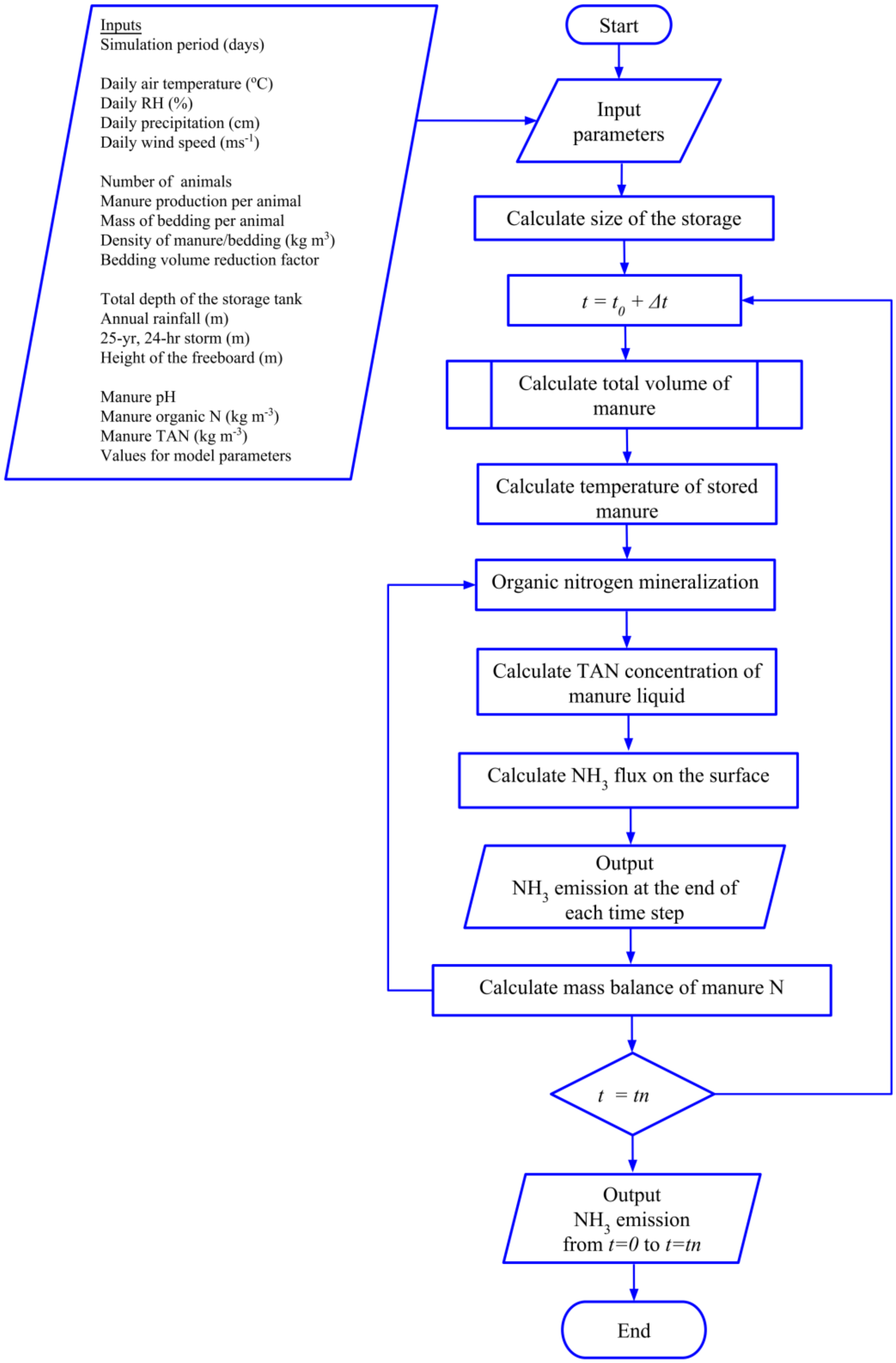

Figure 3.10: Flowchart for the non-compartmental process-based model algorithm

3.3 Model calibration and verification

3.3.1 Model parameters

Parameters used in the model are listed in Table 3.3. For the base model, initial values for these parameters were obtained from the previous studies.

Table 3.3: Parameter values used in the base case compartmental model

Process	Parameter	Value	Units	Reference
NH_3 volatilization	Roughness height (z_0)	8×10^{-5}	m	Jayaweera and Mikkelsen 1990
	Atmospheric pressure (P)	1	atm	Ogejo et al., 2010
Diffusion of NH_3 in manure	Diffusion coefficient of NH_3 (D)	1.24×10^{-9}	$m^2\ s^{-1}$	Muck and Steenhuis, 1982
Organic nitrogen mineralization	Temperature coefficient (θ)	1.036	-	Zhang et al., 2005
	Mineralization rate constant (k_{ON20})	0.007	day^{-1}	Rotz et al., 2014
Temperature variation in manure	Thermal conductivity of manure (k)	0.0901	$W\ m^{-1}\ °C^{-1}$	Nayyeri et al., 2009
	Heat capacity of manure (c)	1992	$J\ kg^{-1}\ °C^{-1}$	Nayyeri et al., 2009

Process	Parameter	Value	Units	Reference
	Internal heat generation of stored manure (Q)	1.2	W m^{-3}	Baral et al., 2013
	Density of manure (ρ)	993	kg m^{-3}	MWPS, 1997 and 2000
	Average soil temperature (T_{soil})	12.95 (Indiana) 14.34 (Virginia)	°C	NIDIS, 2017
	Annual amplitude of surface soil temperature (A_0)	27.66 (Indiana) 25.2 (Virginia)	°C	NIDIS, 2017
	Thermal diffusivity of soil (D_h)	0.03	m^2 day^{-1}	Hillel, 1982
Evaporation	Parameter depend on surrounding terrain (a)	0.14	-	Albright, 1990
	Bulk aerodynamic transfer coefficient (C_e)	2.81×10^{-3}	-	Ham, 1999

3.3.2 Calibration approach

In model calibration process, model performance is evaluated by comparing model predicted NH_3 emission (g m^{-2} day^{-1}) to the experimental data of NH_3 emission (field data). The parameters related to the processes of NH_3 volatilization, NH_3 diffusion within manure, and heat transfer within manure were calibrated. Model calibration was performed manually. For each model parameter three values: low, medium, and high were selected from a given range. Range of parameters used for the calibration were selected based on the literature related to existing PBMs (Table 3.4). The base model had the lowest values for all the selected parameters. Value of each parameter of the base model was changed one at a time and the estimated NH_3 emission was compared with the experimental data. The best value for each parameter was selected based on statistical tests (described below) before calibrating the next parameter.

Table 3.4: Parameter values used for calibration of the compartmental model

Process	Parameter	Range	Units	Reference
NH_3 volatilization	Roughness height (z_0)	8×10^{-5} - 1×10^{-3}	m	Jayaweera and Mikkelsen,1990
Diffusion of NH_3 in manure	Diffusion coefficient of NH_3 (D)	1.24×10^{-9}- 2.5×10^{-9}	m^2 s^{-1}	Ni et al., 1999
Organic nitrogen mineralization	Temperature coefficient (θ)	1.036 - 1.2	-	Zhang et al., 2005 Rotz et al., 2014
	Mineralization rate constant (k_{ON20})	0.007 - 0.06	day^{-1}	Zhang et al., 2005 Rotz et al., 2014

Process	Parameter	Range	Units	Reference
Temperature variation in manure	Thermal conductivity of manure (k)	0.0901 - 0.6814	W m^{-1} °C^{-1}	Nayyeri et al., 2009
	Heat capacity of manure (c)	1992 - 3606	J kg^{-1} °C^{-1}	Nayyeri et al., 2009
	Soil thermal diffusivity (D_h)	0.03 - 0.08	m^2 day^{-1}	Hillel, 1982 Lab, 1982

Model evaluation in the calibration process was conducted using statistical performance measures following the Standard Guide for the Statistical Evaluation of Indoor Air Quality Models (ASTM, 2003). These include Pearson's correlation coefficient, Normalized mean square error, fractional bias, and variance bias. Correlation coefficient (r) was calculated using equation (3.42). The r-values vary from -1 to 1, values near 1 suggest the model performed well showing a strong positive relationship between observed (Y_{O_i}) and predicted (Y_{P_i}) values.

$$r = \frac{\sum_{i=1}^{n}\left(Y_{O_i} - \bar{Y}_O\right)\left(Y_{P_i} - \bar{Y}_P\right)}{\sqrt{\sum_{i=1}^{n}\left[\left(Y_{O_i} - \bar{Y}_O\right)^2\right]\left[\sum_{i=1}^{n}\left(Y_{P_i} - \bar{Y}_P\right)^2\right]}} \tag{3.42}$$

where,

r Correlation coefficient

Y_{O_i} Observed NH_3 emission value

Y_{P_i} Predicted NH_3 emission value

$\bar{Y}_O$ Average of observed values

$\bar{Y}_P$ Average of predicted values

n Number of observed values

Normalized mean square error (*NMSE*) was calculated as shown in equation (3.43). It measures overall deviation between observed and predicted emission values. *NMSE* less than 0.25 indicates adequate model performance. A perfect model would have a *NMSE* of zero (ASTM, 2003).

$$NMSE = \frac{\sum_{i=1}^{n}\left(Y_{P_i} - Y_{O_i}\right)^2}{n.\bar{Y}_O.\bar{Y}_P} \quad (3.43)$$

where,

$NMSE$ Normalized mean square error

Y_{O_i} Observed NH_3 emission value

Y_{P_i} Predicted NH_3 emission value

$\bar{Y}_O$ Average of observed values

$\bar{Y}_P$ Average of predicted values

n Number of observed values

Fractional bias (FBS) is an indicator of the systematic error in terms of arithmetic difference between predicted and observed emission values. It indicates if a model over or under predict. FBS was calculated using the equation (3.44). A well-performing model would have an *FBS* value between -0.25 to 0.25 (ASTM, 2003).

$$FBS = \frac{2(\bar{Y}_P - \bar{Y}_O)}{\bar{Y}_P + \bar{Y}_O} \tag{3.44}$$

FBS Fractional bias

$\bar{Y}_O$ Average of observed values

$\bar{Y}_P$ Average of predicted values

Variance bias (FS) measures the bias based on variance of the observed ($\sigma^2_{Y_O}$) and variance of the predicted ($\sigma^2_{Y_P}$) emission data (eq. 3.45). A *FS* value between -0.5 and 0.5 suggests that the model performs well.

$$FS = \frac{2\left(\sigma^2_{Y_P} - \sigma^2_{Y_O}\right)}{\sigma^2_{Y_P} + \sigma^2_{Y_O}} \tag{3.45}$$

where,

FS Variance bias

$\sigma^2_{Y_O}$ Variance of the observed values

$\sigma^2_{Y_P}$ Variance of the predicted values

3.3.3 Data for model calibration and verification

The NH_3 emission data used in model calibration and verification was for a dairy lagoon located in Jasper County, Indiana (Grant and Boehm, 2010a), which was part of the National Air Emissions Monitoring Study (NAEMS). The data is available at www.epa.gov/afos-air/national-air-emissions-monitoring-study. Grant and Boehm (2010a) measured NH_3 concentrations using Tunable Diode Laser Absorption Spectrometer (TDLAS) open-path instruments and 3-dimensional (3D) sonic anemometers and calculated daily NH_3 emissions rates using radial plume mapping (RPM) and backward Lagrangian Stochastic (bLS) emissions models based on the concentration of NH_3 and meteorological measurements (i.e. barometric pressure, air temperature, relative humidity, solar radiation, and surface wetness). These daily NH_3 emission rates were compared with the output of the compartmental and non-compartmental NH_3 emission models.

Description of the dairy lagoon in Jasper County, Indiana

The dairy farm was located in Jasper County, Indiana. The farm had a capacity of 2600 dairy cows. The manure lagoon was 85 m wide and 116 m long and lined with clay. At maximum capacity, the manure depth was 5 m with a volume of 48212 m^3 and surface area of 9884 m^2. The data reported included daily NH_3 emissions (g m^{-2} d^{-1}), average ambient air temperature, manure pH. A complete data set for daily wind speed, relative humidity, and precipitation was not included in the NAEMS data set, therefore weather data for these input parameters for Jasper County were obtained from NCEP (2017). Model calibration was performed using the emission data collected from May 29, 2009 to August 17, 2009. The data included daily emission for 81 days during this period. Model was verified using the emission data collected for 47 days from March 12, 2009 to April 27, 2009. A summary of data used for the model calibration and verification are given in Table 3.5. The input values used in calibration and the source of the data are listed in the Table 3.6.

Table 3.5: Summary of weather data used for calibration and verification

Weather data	Calibration (May 29 to August 17)			Verification (March 12 to April 27)		
	Average	Min	Max	Average	Min	Max
Temperature (°C)	20.81	14.40	27.30	7.97	-3.80	22.60
RH (%)	74.61	52.15	93.64	79.65	62.97	95.18
Wind speed (ms^{-1})	2.86	1.33	5.46	4.32	1.20	8.49
Total precipitation (cm)	0.36	0.00	4.14	0.47	0.00	3.15

Table 3.6: Input data used for calibration

Input	Units	Value	Data source
Average air temperature	°C	14.4 - 27.3	NAEMS, 2010
Total precipitation per day	cm	0 - 4.14	NCEP, 2017
Average wind speed	ms^{-1}	1.33 - 5.46	NCEP, 2017
Average relative humidity	percent	52.15 - 93.64	NCEP, 2017
Manure storage period	days	81	NAEMS, 2010
Number of animals	count	2600	NAEMS, 2010
Mass of manure produced per animal	kg	67	ASABE, 2005; MWPS,2000
Density of manure	kg m^{-3}	993	MWPS,2000
Total depth/height	m	5	NAEMS, 2010
Surface area open to air	m^{-2}	9744	NAEMS, 2010
Depth of residual manure	m	3	Assumed

Input	Units	Value	Data source
Initial organic nitrogen concentration	kg m^{-3}	1.387	Data for a dairy farm in Virginia obtained via personal communication
Initial TAN concentration	kg m^{-3}	1.089	
pH		7.14	NAEMS, 2010
Standard height at which wind speed is measured	m	1.5	NOAA, 2017

3.4 Sensitivity analysis

A global sensitivity analysis (GSA) was conducted to identify the contribution of input parameters and their interactions on the variance of model output. The GSA was performed following a variance based sensitivity analysis methods (Saltelli, 2002; Saltelli et al., 2004; Saltelli et al., 2008;). The sensitivity coefficient (first order), S_x of an input parameter x was calculated as shown in equation (3.46).

$$S_x = \frac{V\big(E(y|x)\big)}{V_y} \tag{3.46}$$

where,

y	Model output over N Monte Carlo simulations
V_y	Variance of the model output y
$V\big(E(y\|x)\big)$	Variance of the expected value of y given a constant x

Interaction of two model parameters on the model output was described by the second order sensitivity coefficient (eq. 3.47). The summation of all sensitivity indices (first-order, second-order, third-order, etc.) of a model input parameter was defined as the total effect index of the particular model input parameter.

$$S_{x,y} = \frac{V\big(E(y|x,z)\big)}{V_y} - \frac{V\big(E(y|x)\big)}{V_y} - \frac{V\big(E(y|z)\big)}{V_y} \tag{3.47}$$

Sensitivity of the model was evaluated for weather and manure characteristics input parameters (10 parameters). Using Monte Carlo simulation (N =1×10^5), random values for each model parameter were drawn from a uniform distribution within respective parameter range listed in Table 3.7. Using these random values, a “Sample matrix” (M_1) was created allocating one column to each parameter. Using the same procedure another matrix, M_2 (“Re-sample matrix”) was created (See Figure 3.11).

Table 3.7: Input variables and their ranges used for the sensitivity analysis

Input		Units	Range	Reference
Air temperature	T_a	°C	0-30	From weather data
Relative humidity	RH	%	0-100	From weather data
Wind speed	U_z	ms^{-1}	0-8	From weather data
Precipitation	$Rain$	cm	0-6	From weather data
Atmospheric pressure	P	atm	0.876-1.025	Ogejo et al., 2010
Ambient NH_3 concentration	C_{Air}	kg m^{-3}	0-2× 10^{-5}	Ogejo et al., 2010

Input		Units	Range	Reference
Manure pH	pH		6.5-7.5	Li, 2009; Misselbrook et al., 2005
Organic nitrogen concentration	C_{ON}	kg m^{-3}	1.203-4.1	Li, 2009; Sommer et al., 1993
TAN concentration	C_{TAN}	kg m^{-3}	0.66-2.6	Rumberg et al., 2008; Sommer et al., 1993
Density of manure	MD	kg m^{-3}	993-1009	MWPS, 1997

Compartmental process-based model was simulated for a one-time step (one day) using M_1 and M_2 separately to obtain Y_1 and Y_2 output vectors (ammonia (NH_3) emission rates, EM). Unconditional means ($\hat{E}_{Y_1}$ *and* $\hat{E}_{Y_2}$) and variances ($\hat{V}_{Y_1}$ *and* $\hat{V}_{Y_2}$) were calculated for these outputs as shown in equation (3.48) to (3.51).

$$\hat{E}_{Y_1} = \frac{1}{N}\sum_{i=1}^{N} Y_1^{(i)} \tag{3.48}$$

$$\hat{E}_{Y_2} = \frac{1}{N}\sum_{i=1}^{N} Y_2^{(i)} \tag{3.49}$$

$$\hat{V}_{Y_1} = \frac{1}{N-1}\sum_{i=1}^{N}\left(Y_1^{(i)}\right)^2 - \left(\hat{E}_{Y_1}\right)^2 \tag{3.50}$$

$$\hat{V}_{Y_2} = \frac{1}{N-1}\sum_{i=1}^{N}\left(Y_2^{(i)}\right)^2 - \left(\hat{E}_{Y_2}\right)^2 \tag{3.51}$$

where,

$\hat{E}_{Y_1}, \hat{E}_{Y_2}$ Unconditional mean of output Y_1, Y_2

$\hat{V}_{Y_1}, \hat{V}_{Y_2}$ Unconditional variance of output Y_1, Y_2

N Number of Monte Carlo simulations

$$
\begin{array}{cc}
 & \begin{array}{ccccccc} x_1 & x_2 & x_3 & x_4 & x_5 & x_6 & x_7 \end{array} \\
M_1 = & \begin{bmatrix} 9.8 & 6.9 & 0.46 & 7.7 & 0.98 & 35 & 0.01 \\ 23.6 & 7.6 & 0.41 & 3.1 & 0.89 & 1218 & 0.004 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ 30.6 & 7.9 & 0.54 & 5.2 & 0.96 & 345 & 0.008 \end{bmatrix}_{N\times 7}
\end{array}
\rightarrow Y_1 = \begin{bmatrix} 1.2E-4 \\ 2.2E-4 \\ \vdots \\ 3.2E-4 \end{bmatrix}_{N\times 1}
$$

$$
M_2 = \begin{bmatrix} 21.2 & 6.8 & 0.57 & 5.8 & 0.87 & 2400 & 0.006 \\ 15.6 & 7.4 & 0.48 & 10.2 & 0.92 & 885 & 0.0001 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ 29.8 & 8.1 & 0.53 & 11.5 & 1.01 & 478 & 0.07 \end{bmatrix}_{N\times 7} \rightarrow Y_2 = \begin{bmatrix} 1.4E-4 \\ 2.7E-4 \\ \vdots \\ 2.2E-4 \end{bmatrix}_{N\times 1} \vdots
$$

Figure 3.11: Sample matrix (M_1) and re-sample matrix (M_2)

First-order sensitivity of model parameters

For each model input parameter, a new matrix, P was created by taking the respective parameter column from sample matrix, M_1 and all other parameter columns from re-sample matrix, M_2. The output vector (Y_P) was calculated for input parameter values in matrix P as show in Figure 3.12. The variable U_P for each parameter was calculated using Y_1 and Y_P. First-order sensitivity coefficient (S_x) for each input parameter was calculated using U_P, $\hat{E}_{Y_1}$, $\hat{E}_{Y_2}$,and , $\hat{V}_{Y_1}$ as shown in equations (3.52) and (3.53).

$$U_P = \frac{1}{N-1}\sum_{i=1}^{N} Y_1^{(i)} Y_P^{(i)} \tag{3.52}$$

$$S_{x_1} = \frac{U_P - \hat{E}_{Y_1}\,\hat{E}_{Y_2}}{\hat{V}_{Y_1}} \tag{3.53}$$

$$P = \begin{array}{ccccccc} x_1 & x_2 & x_3 & x_4 & x_5 & x_6 & x_7 \\ \end{array}$$

$$P = \begin{bmatrix} 9.8 & 6.8 & 0.57 & 5.8 & 0.87 & 2400 & 0.006 \\ 23.6 & 7.4 & 0.48 & 10.2 & 0.92 & 885 & 0.0001 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ 30.6 & 8.1 & 0.53 & 11.5 & 1.01 & 478 & 0.07 \end{bmatrix}_{N\times 7} \rightarrow Y_P = \begin{bmatrix} 1.1E-4 \\ 3.4E-4 \\ \vdots \\ 3.8E-4 \end{bmatrix}_{N\times 1}$$

From M_1 From M_2

Figure 3.12: Construction of P matrix using components of M_1 and M_2 matrices and calculation of output vector, Y_P

Second-order sensitivity of model parameters

For each interaction, a new matrix, Q was created by taking the respective parameter columns from sample matrix, M_1 and all other parameter columns from re-sample matrix, M_2. The output vector (Y_Q) was calculated for input parameter values in matrix Q (Figure 3.13). Second-order sensitivity coefficient ($S_{x_1 x_2}$) for each two-way interaction was calculated using U_Q, $\hat{E}_{Y_1}$, $\hat{E}_{Y_2}$ and first-order coefficients of x_1 and x_2 (S_{x_1} and S_{x_2}) as shown in equations (3.54) to (3.55).

$$U_Q = \frac{1}{N-1} \sum_{i=1}^{N} Y_1^{(i)} Y_Q^{(i)} \tag{3.54}$$

$$S_{x_1 x_2} = \frac{U_Q - \hat{E}_{Y_1} \hat{E}_{Y_2}}{\hat{V}_{Y_1}} - S_{x_1} - S_{x_2} \tag{3.55}$$

$$Q = \begin{array}{c} \begin{array}{ccccccc} x_1 & x_2 & x_3 & x_4 & x_5 & x_6 & x_7 \end{array} \\ \begin{bmatrix} 9.8 & 6.9 & 0.57 & 5.8 & 0.87 & 2400 & 0.006 \\ 23.6 & 7.6 & 0.48 & 10.2 & 0.92 & 885 & 0.0001 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ 30.6 & 7.9 & 0.53 & 11.5 & 1.01 & 478 & 0.07 \end{bmatrix}_{N\times 7} \\ \begin{array}{cc} \text{From } M_1 & \qquad \text{From } M_2 \end{array} \end{array} \rightarrow Y_Q = \begin{bmatrix} 1.0E-4 \\ 3.8E-4 \\ \vdots \\ 4.3E-4 \end{bmatrix}_{N\times 1}$$

Figure 3.13: Construction of Q matrix using components of M_1 and M_2 matrices and calculation of output vector, Y_Q

Total effect index of model parameters

A new matrix, R was created for each parameter by taking the respective parameter column from re-sample matrix, M_2 and all other parameter columns from sample matrix, M_1 (Figure 3.14). Based on the parameter values in matrix, R the model was simulated N times and the output stored in a new vector, Y_R. The model outputs in vectors, Y_R and Y_1 were used to calculate the variable U_T. Finally, the total sensitivity coefficient (S_T) for each parameter was calculated using U_T, $\hat{E}_{Y_1}$, and $\hat{V}_{Y_1}$ as shown in equations from (3.56) to (3.57).

$$U_T = \frac{1}{N-1}\sum_{i=1}^{N} Y_1^{(i)} Y_R^{(i)} \tag{3.56}$$

$$S_{T(x_1)} = 1 - \left(\frac{U_T - \hat{E}_{Y_1}{}^2}{\hat{V}_{Y_1}}\right) \tag{3.57}$$

$$
R = \begin{array}{c} \begin{array}{ccccccc} x_1 & x_2 & x_3 & x_4 & x_5 & x_6 & x_7 \end{array} \\ \begin{bmatrix} 21.1 & 6.9 & 0.46 & 7.7 & 0.98 & 35 & 0.01 \\ 15.6 & 7.6 & 0.41 & 3.1 & 0.89 & 1218 & 0.04 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ 29.8 & 7.9 & 0.54 & 5.2 & 0.96 & 345 & 0.008 \end{bmatrix}_{N\times 7} \end{array} \rightarrow Y_R = \begin{bmatrix} 4.2E-4 \\ 2.2E-4 \\ \vdots \\ 5.2E-4 \end{bmatrix}_{N\times 1}
$$

From M_2 From M_1

Figure 3.14: Construction of Q matrix using components of M_1 and M_2 matrices and calculation of output vector, Y_R

3.5 Scenario analysis

Scenario analysis for the compartmental model was done for two dairy farms located in Rockingham and Franklin counties, Virginia, using daily average historical (January 01, 1979 to July 31, 2014) weather data. The selected two counties are the top two dairy producers in Virginia as ranked by the USDA (2014) based on the number of Grade A dairy farms (Rockingham County ranked 1 with 236 dairy farms and Franklin County ranked 2 with 72 dairy farms) (Figure 3.15). Each dairy farm consists of 100 milking cows. Each animal weighs 435 kg (1400 lb) and produces 67 kg (150 lb) of manure per day. Manure is scraped from the barn floors and stored in a storage tank. The storage tanks have an approximately 6-month storage capacity. The simulations were done for 2 different periods of 6 months within a year: Period 1. May to October and Period 2. November to April. These periods represent the typical time during which manure is stored.

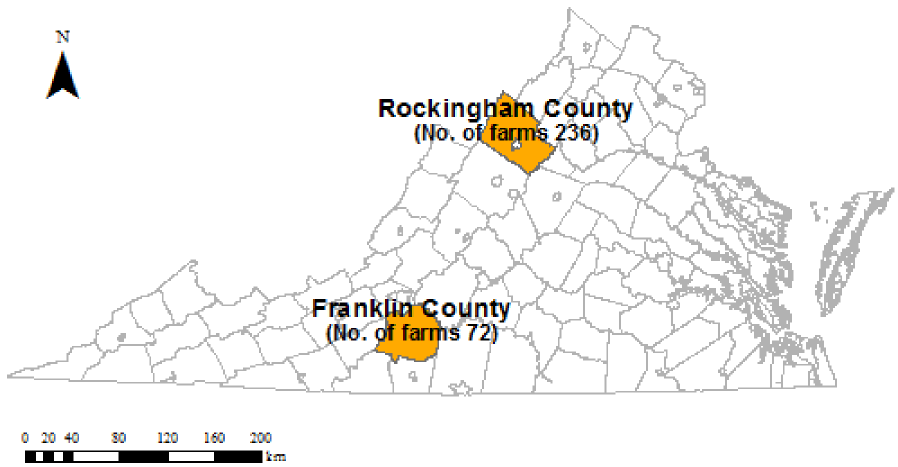

Figure 3.15: Geographical locations of Rockingham and Franklin counties in Virginia, U.S.

Historical weather data

Historical weather data for both the counties were obtained from The National Centers for Environmental Prediction (NCEP, 2017). The weather data for Rockingham County covers a geographical area that includes Harrisonburg, Bridgewater, Dayton, Mt. Crawford, and Grottoes where a majority of dairy farms is located (South Latitude: 38.2393, West Longitude: -79.0528, North Latitude: 38.4794, East Longitude: -78.7109). For Franklin County, weather data covers an area that includes: Rocky Mount, Boones Mill, and Wirtz (South Latitude: 36.9279, West Longitude: -80.0402, North Latitude: 37.1253, East Longitude: -79.7587). The data included daily weather records for average air temperature, average relative humidity, average wind speed, and total precipitation from January 01, 1979 to July 31, 2014. Average daily values were calculated for each weather parameter based on 35 years of weather data. Calculated average daily values were used as the input weather data in the model simulation for different scenario analysis. Historical weather data were divided in to two manure storage periods: (1) cold season from November 01 to April 30 and (2) warm season from May 01 to October 31.

4 Results and discussion

4.1 Weather data

Figure 4.1 and 4.2 show historical weather data used for Rockingham and Franklin counties for two storage periods: (1) from May 01 to October 31 and (2) from November 01 to April 30, respectively. As expected, higher air temperature was observed during manure storage period from May 01 to October 31 compared to November 01 to April 30 for both the counties. During the warm season (May 01 to October 31), air temperature gradually increased and came to a maximum at the end of July and then decreased. During the cold season (November 01 to April 30), it gradually decreased and came to a minimum at the end of January and then increased. Average air temperature of Franklin County was higher by 0.4 ℃ and 0.91 ℃ during warm and cold seasons respectively compared to Rockingham County (see Appendix A). Franklin County receives more precipitation than Rockingham County. Franklin County had a 64.3 cm of total precipitation during May 01 to October 31 and 62.2 cm during November 01 to April 30 compared to that of 45.9 cm during May 01 to October 31 and 50.5 cm during November 01 to April 30 in Rockingham County. Average daily RH and wind speed for both the counties were higher for cold season from November 01 to April 30 compared to May 01 to October 31.

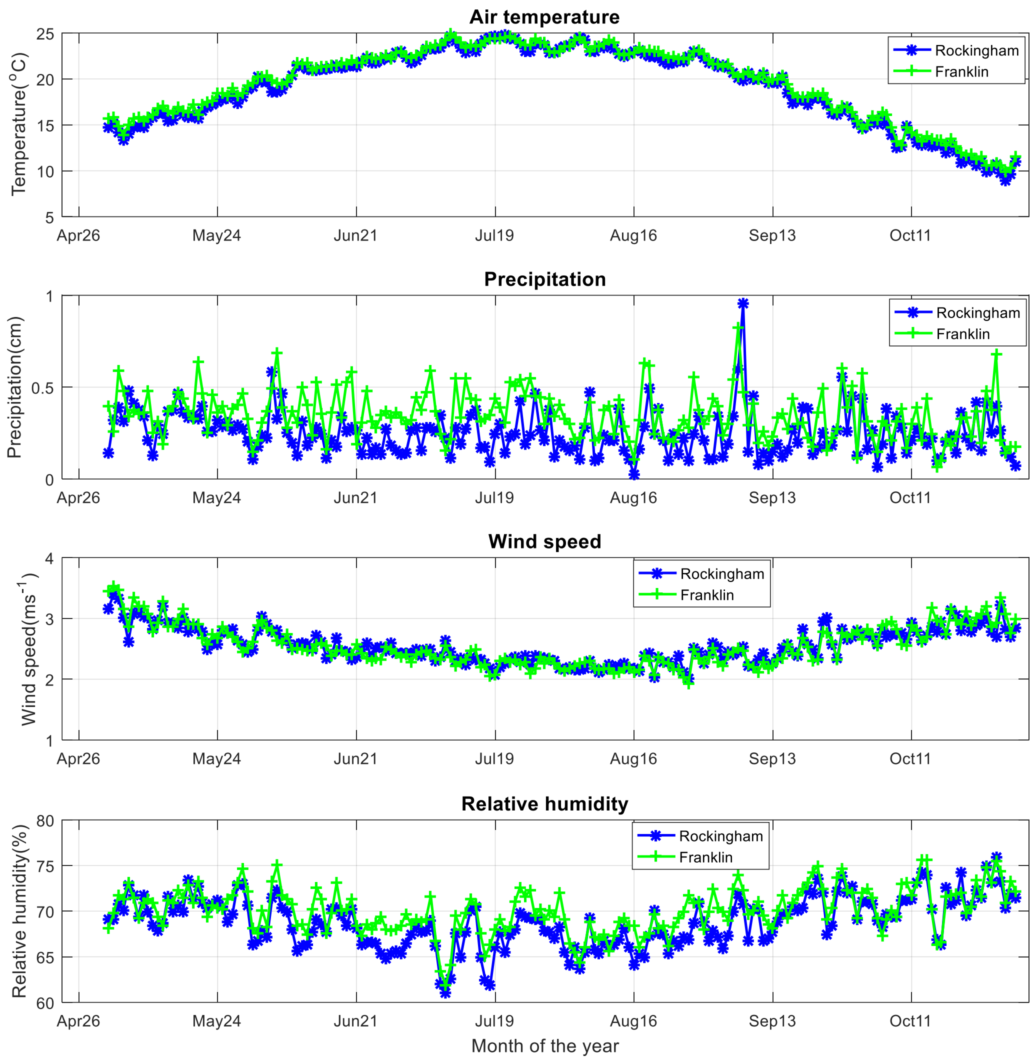

Figure 4.1: Historical average daily air temperature, wind speed, RH, and total daily precipitation of Rockingham (blue) and Franklin (green) counties during manure storage period from May 01 to October 31

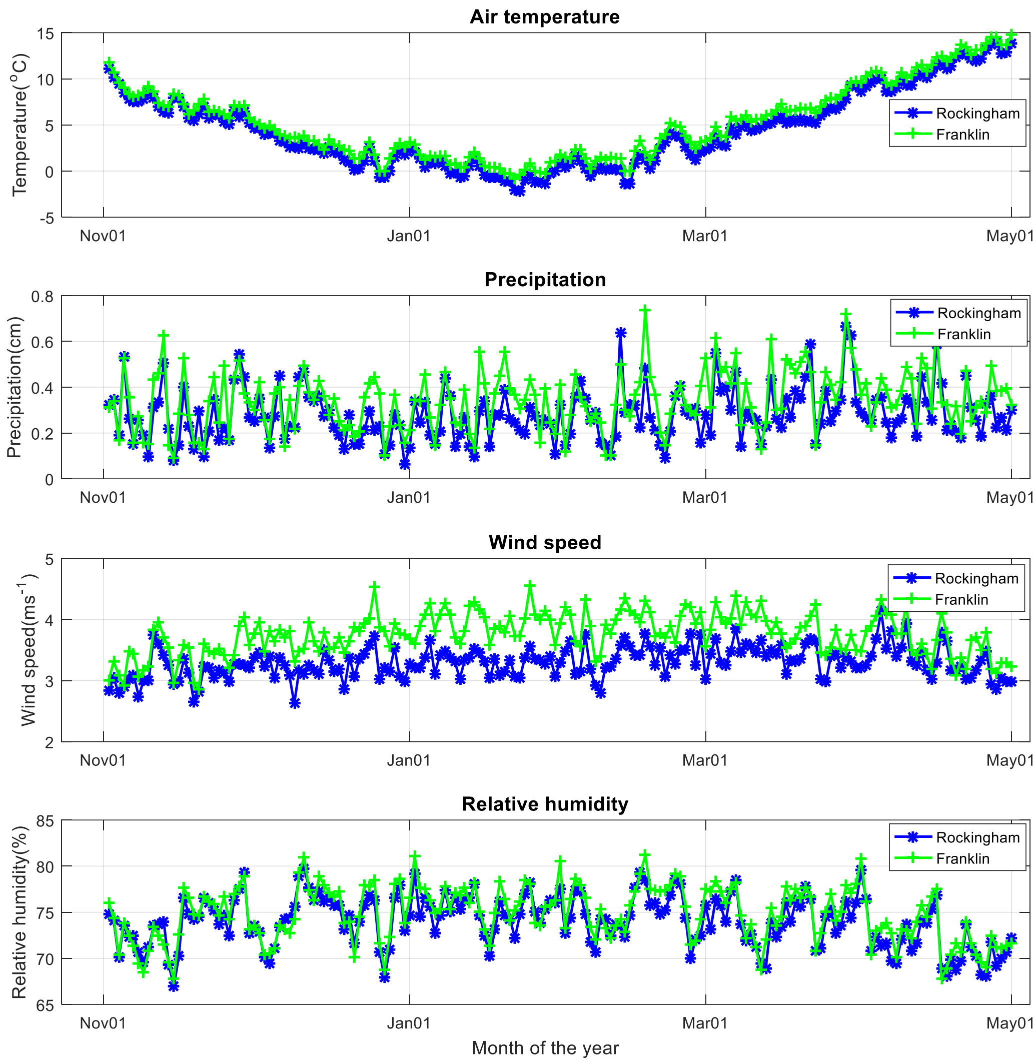

Figure 4.2: Historical average daily air temperature, wind speed, RH, and total daily precipitation of Rockingham (blue) and Franklin (green) counties from November 01 to April 30

4.2 Spatial variation of temperature and manure TAN concentration in stored manure

The base case compartmental model simulation for weather data in Jasper County, Indiana from May 29 to August 17 showed that there was a spatial heterogeneity within stored manure during the simulation period. The daily changes of manure temperature and TAN concentration of stored manure at different manure depths are illustrated in Figure 4.3. Manure depth consistently increased overtime depending on the materials coming in and going out of the storage. In the initial periods manure temperature and manure TAN concentration were more or less homogeneous across the compartments. Temperature in stored manure increased overtime, however, temperature of the upper layers of stored manure was greater than that of bottom layers. In contrast, TAN concentration of stored manure increased in bottom layers. The TAN concentration changes are qualitatively similar to the computer simulation and laboratory results reported by Muck and Steenhuis (1982), who reported that the TAN concentration of stored manure increased with depth and reach maximum at approximately 30 cm.

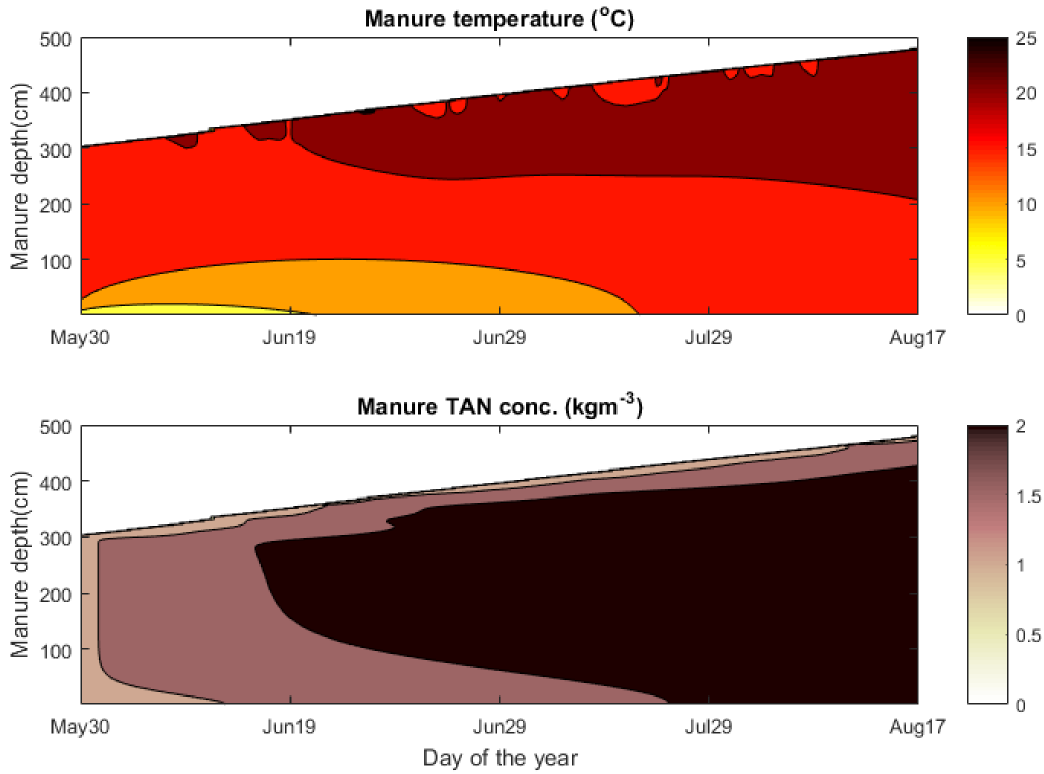

Figure 4.3: Spatial (along y-axis) and temporal (along x-axis) distribution of manure temperature and TAN concentration of stored manure of a dairy lagoon in Jasper County, IN from May 29, 2009 to August 17, 2009

4.3 Model calibration results

The calibration and model evaluation results for selected parameter combinations are given in Table 4.1 below. The base case had the lowest values from the parameter ranges specified in Table 3.4. For the base case, the correlation coefficient was 0.203, and NMSE was 1.118. The FBS and FS suggested that the base case under predicts the NH_3 emissions. When parameter values were increased from their respective base case levels, except for heat capacity of manure, the model performance increased. According to the model performance statistics in the Table 4.1, the case H with the lowest NMSE of 0.740 performed the best, therefore, the parameter values from case H were used in the final compartmental model.

Table 4.1: Compartmental model calibration statistics

Case	Parameter							Average NH_3 emission		Model performance statistics			
	Roughness height (m)	Diffusion coefficient of NH_3 (m^2s^{-1})	Temperature coefficient	Mineralization rate (day^{-1})	Thermal conductivity of manure ($W\ m^{-1}\ °C^{-1}$)	Heat capacity of manure ($K\ kg^{-1}\ °C^{-1}$)	Soil thermal diffusivity (m^2day^{-1})	Measured ($g\ m^{-2}day^{-1}$)	Predicted ($g\ m^{-2}day^{-1}$)	r	NMSE	FBS	FS
Base case	8×10^{-5}	1.24×10^{-9}	1.036	0.007	0.0901	1992	0.03	4.023	1.855	0.203	1.118	-0.738	-1.220
A	1×10^{-3}	1.24×10^{-9}	1.036	0.007	0.0901	1992	0.03	4.023	1.972	0.199	1.003	-1.105	-1.105
B	1×10^{-3}	1.81×10^{-9}	1.036	0.007	0.0901	1992	0.03	4.023	2.049	0.201	0.929	-0.650	-1.317
C	1×10^{-3}	2.5×10^{-9}	1.036	0.007	0.0901	1992	0.03	4.023	2.081	0.204	0.899	-0.636	-1.085
D	1×10^{-3}	2.5×10^{-9}	1.2	0.007	0.0901	1992	0.03	4.023	2.087	0.204	0.894	-0.634	-1.073
E	1×10^{-3}	2.5×10^{-9}	1.2	0.06	0.0901	1992	0.03	4.023	2.313	0.209	0.741	-0.540	-0.852
F	1×10^{-3}	2.5×10^{-9}	1.2	0.06	0.6814	1992	0.03	4.023	2.316	0.210	0.740	-0.539	-0.842
G	1×10^{-3}	2.5×10^{-9}	1.2	0.06	0.6814	3606	0.03	4.023	2.314	0.209	0.741	-0.539	-0.845
H	1×10^{-3}	2.5×10^{-9}	1.2	0.06	0.6814	1992	0.08	4.023	2.316	0.210	0.740	-0.539	-0.842

r=Correlation coefficient, NMSE=Normalized mean square error, FBS=Fractional bias, FS= Variance bias

Ideally, the calibration of compartmental model should be performed using experimental data that represent spatial variation of manure temperature and TAN concentration as well as NH_3 emission. For instance, temperature and TAN concentration at different depths of stored manure are required to calibrate parameters relevant to “heat transfer” and “ammonia transfer” sub-models which are the main focus of compartmental model. However, in this study such experiments were not performed and such data were not found in searched literature. Therefore, instead of calibrating each sub-model separately, the whole model was calibrated focusing on the final output (NH_3 emission) of the model. The reported uncertainty of NH_3 emission data used for the calibration (NAEMS data) was 24% (Grant and Boehm, 2010a, Rotz et al., 2014). Therefore, lack of relevant data and using less accurate data for calibration of the compartmental model may have produced suboptimal parameter estimates.

4.4 Model Verification

The compartmental model was verified using NH_3 emission data collected for March 12, 2009 to April 27, 2009 from a dairy lagoon located in Jasper County, IN. The model simulation outputs from the compartmental and non-compartmental models were compared with the observed emission. Predicted daily NH_3 emissions from these models and the weather data used for the simulation are given in Figure 4.4. A summary of model evaluation statistics is given in Table 4.2. The compartmental model performed better than the non-compartmental model in predicting NH_3 emission as indicated by the lower NMSE and reduced bias (FBS and FS) of the compartmental model. This indicates that model prediction error is smaller when the spatial heterogeneity of manure temperature and TAN concentration is incorporated into the model via compartmental approach. However, on average, the compartmental model under predicted the

NH_3 emissions by 30% while non-compartmental model over predicted by 11.5%. The data used for the verification has 24% of uncertainty similar to the data used in calibration (Grant and Boehm, 2010a, Rotz et al., 2014), this may have been caused the under prediction observed in the compartmental model.

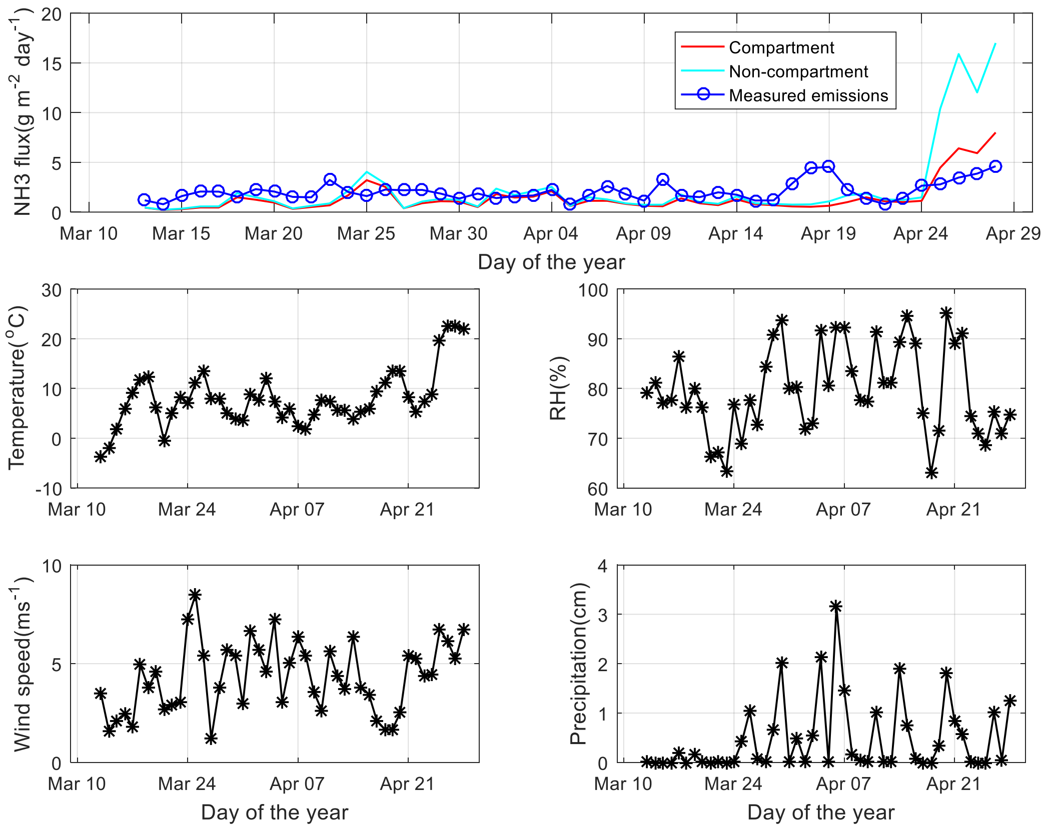

Figure 4.4: Comparison of estimated ammonia emission of compartmental model (red) and non-compartmental model (cyan) with measured emissions (blue) from dairy lagoon in Jasper County, IN from March 12, 2009 to April 27, 2009

Table 4.2: Compartmental and non-compartmental model verification statistics

Model	R	NMSE	FBS	FS
Non-compartmental	0.533	2.230	0.108	1.758
Compartmental	0.497	0.775	-0.355	0.998

r=Correlation coefficient, NMSE=Normalized mean squared error, FBS=Fractional bias, FS= Variance bias

Figure 4.5 and Figure 4.6 below respectively illustrate the estimated daily values of temperature and TAN concentration of stored manure via the compartmental and non-compartmental models. The estimates from the compartmental model indicated that the temperature and TAN concentration of stored manure changed spatially as well as temporally (Figure 4.5). However, the non-compartmental model showed only temporal variations of temperature and TAN concentration (Figure 4.6). Unlike the compartmental model, the non-compartmental model assumes stored manure as a homogeneous unit. Therefore, it is not capable of estimating the spatial variation of environmental factors and manure characteristics of stored manure.

Previous studies have shown that manure temperature (Masse et al., 2008; Park and Wagner-Riddle, 2010), manure characteristics (Ndegwa et al., 2002; Nordstedt and Baldwin, 1975; Zhu et al., 2003), and microbial communities (Lovanh et al., 2009; McLauhlin et al., 2014) in stored manure varies spatially. These spatial variations affect occurrence and rate of biogeochemical processes that are related to production and emission of NH_3 from stored manure. Similar to the non-compartmental model used in this study, most of the process-based models (IFSM, DairyGEM, PBAEM, and FEM) available for estimating NH_3 emission assume stored manure as a homogeneous unit (Rotz et al., 2016a; Rotz et al., 2016b; Zhang et al., 2005; Pinder et al., 2004), thus may not represent the actual conditions in manure storage. The compartment model is capable of estimating spatial variations of manure temperature and manure TAN concentration. Therefore, the compartmental model provides a platform that can further be improved to represent an actual manure storage.

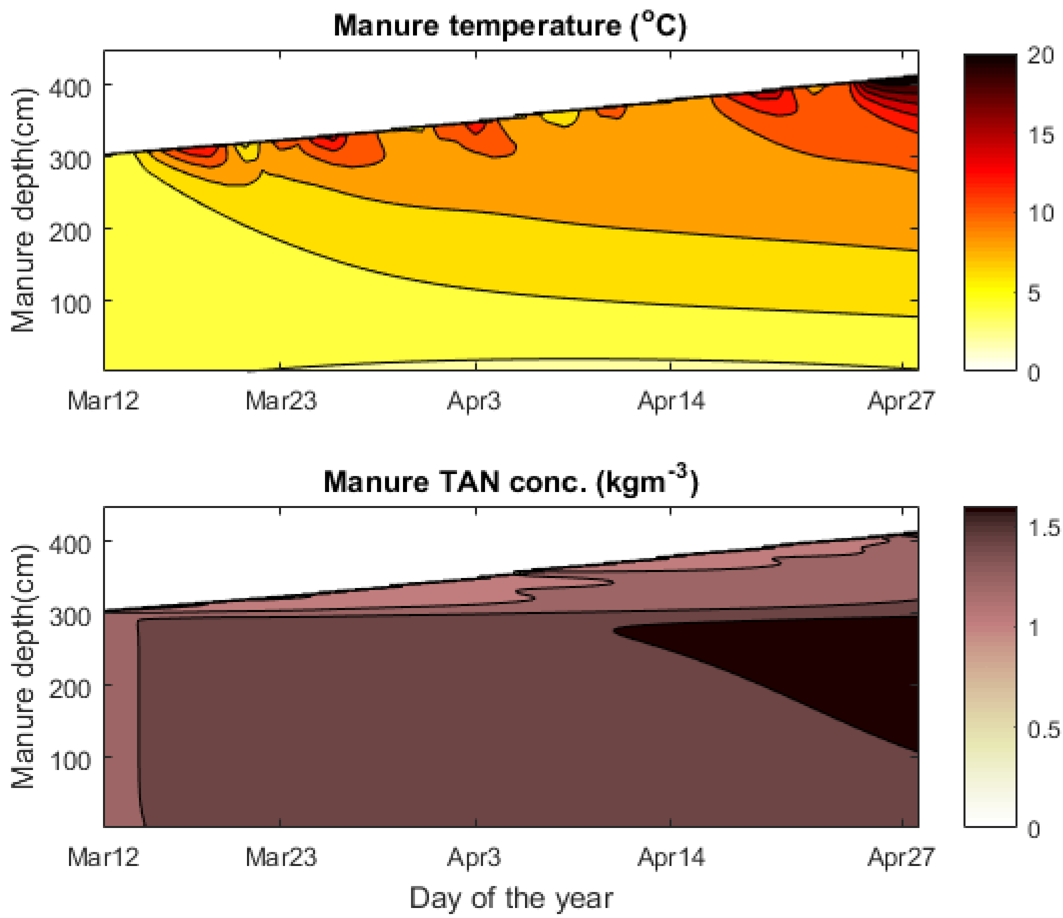

Figure 4.5: Compartmental model estimate of manure temperature and TAN concentration of stored manure of a dairy lagoon in Jasper County, IN from March 12, 2009 to April 27, 2009

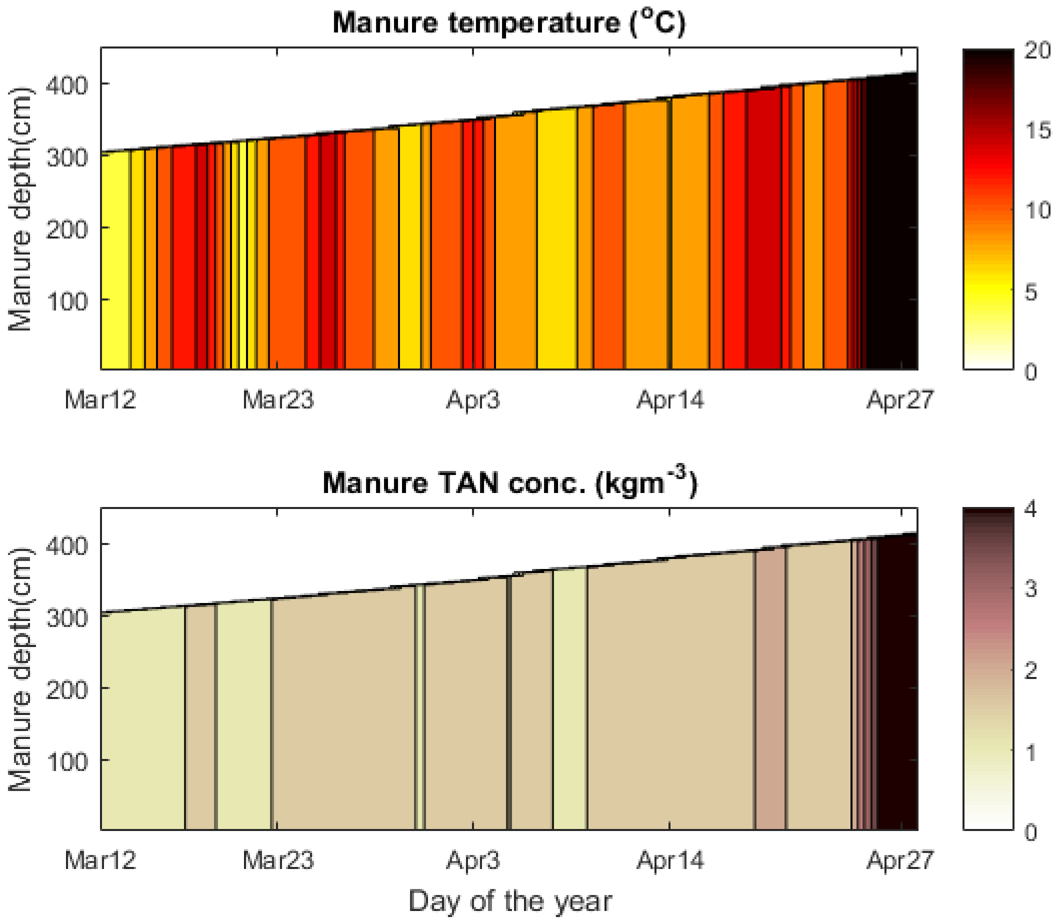

Figure 4.6: Non-compartmental model estimate of manure temperature and TAN concentration of stored manure of a dairy lagoon in Jasper County, IN from March 12, 2009 to April 27, 2009

4.5 Sensitivity analysis

According to the results of GSA (Table 4.3), first-order sensitivity coefficients explained 67%, second-order model parameter interactions explained 28%, and higher-order parameter interactions explained 5% of variance in model output. Air temperature (T_a) gave the highest first-order coefficient and explained 23% of model output variance. Manure pH, wind speed (U_z), and TAN concentration of manure (C_{TAN}) contributed 19%, 18%, and 5% respectively to the variance of model output. Interaction of air temperature and pH ($T_a.pH$), air temperature and wind speed ($T_a . U_z$), and wind speed and pH ($U_z . pH$) had more influence on variance of model output than other second-order interactions. Similar results have been reported by Ogejo et al. (2010) from a GSA conducted for a process-based ammonia emission model. In that study, GSA showed that the manure pH, temperature, wind speed, and the concentration of TAN in the lagoon were the most important model input parameters. In contrast to the results from this study, Ogejo et al. (2010) reported that about two-thirds of the model output variance was attributed to the second-order and higher-order interactions between model parameters.

Table 4.3: Sensitivity coefficient of model input parameters calculated using global sensitivity analysis

Input Parameter	Coefficient
First-order coefficients	
T_a	0.230
pH	0.194
U_z	0.180
C_{TAN}	0.048
C_{ON}	0.004
$Rain$	0.003
C_{AIR}	0.003
MD	0.003
RH	0.003
P	0.003
Total	**0.671**

Input Parameter	Coefficient
Second -order coefficients	
$T_a.pH$	0.086
$T_a.U_z$	0.084
$U_z.pH$	0.066
$U_z.C_{TAN}$	0.014
$pH.C_{TAN}$	0.014
$T_a.C_{TAN}$	0.013
Total	**0.277**
Higher-order coefficients	
Total	**0.052**

[a] 45 second-order coefficients were calculated, however, coefficient values closer to zero are not included in this table.

Total effect index of a parameter was defined as the summation of first-order, second-order, and higher order sensitivity coefficients. According to the sensitivity analysis (Table 4.4), air temperature was the most sensitive model input parameter followed by pH wind speed and TAN concentration of manure. All other input parameters considered in this analysis were not that significant in explaining the variance of the model output.

Table 4.4: Total effect indices of input model parameters

Input parameter	Total effect index
T_a	0.474
pH	0.418
U_z	0.402
C_{TAN}	0.118
C_{ON}	0.006
P	0.001
C_{AIR}	0.001
RH	0.001
$Rain$	0.001
MD	0.001

4.6 Scenario analysis

NH_3 emission estimates for the scenario analysis with historical weather data averaged over the simulation period are given in the Table 4.5. On average, both the compartmental and non-compartmental models estimated higher NH_3 emission rates during Period 1 (May to October) and lower NH_3 emission during Period 2 (November to April). For a given period, the Non-compartmental model estimated relatively higher NH_3 emissions. For example, emission estimates of non-compartmental model for Rockingham County were 51% and 39% higher than those of the compartmental model respectively during the Period 1 and 2. The results were qualitatively similar for the Franklin County.

Estimated ammonia emission fluxes (kg m^{-2} day^{-1}) of both the compartmental and non-compartmental models were less than the values reported in literature (McGinn et al., 2008; Misselbrook et al., 2005; Rumberg et al., 2008; Smith et al., 2007; Sommer et al., 1993; Zhao et al., 2007; Flesch et al., 2009). This discrepancy may have occurred because of the suboptimal parameters of the model and differences between the values of manure characteristics (e.g. TAN concentration and pH of manure) used in this model and the observed values during experiments. For instance, at constant temperature, manure pH controls the equilibrium between $NH_4^+{}_{(aq)}$ and $NH_{3(aq)}$ in manure liquid. Higher pH, typically above 7, favors production of $NH_{3(aq)}$ in the equilibrium increasing potential for NH_3 volatilization (Hristov et al., 2010). Under actual conditions, the pH of stored manure may vary with time. However, in the compartmental model, the pH was held constant at 7 throughout the storage period. This may have influenced the predicted emissions from the compartment model.

Comparison of the results in Table 4.5 across the two counties suggests that, on average, the daily NH_3 emission from a manure storage designed for 100 milking cows in Franklin County is higher than that of Rockingham County. For example, in Franklin County, liquid manure storage emitted 599 g of ammonia per day during warm seasons (May to October) and 264 g of ammonia during cold season (November to April). In contrast, a manure storage in the Rockingham County produced 586 g of NH_3 and 212 g of NH_3 per day during warm and cold seasons respectively. According to the United States Department of Agriculture 2012 census report (USDA, 2014), Rockingham County has more dairy cows (25139) than Franklin County (9802). As implied by above emission estimations for the model farms with 100 cows, Rockingham County is more likely to produce higher county-wide ammonia emission compared to the Franklin County.

Figure 4.7 and Figure 4.8 illustrate the estimated daily NH_3 emissions and weather data in Rockingham County for Period 1 and 2 while Figure 4.9 and Figure 4.10 show the NH_3 emissions and weather data for Franklin County. The results indicated that the NH_3 emissions increased with higher temperature during the period from May to October. This could be because of the elevated biogeochemical activities in stored manure at higher temperature. Table 4.6 presents the association between historical weather data and predicted emissions from the compartmental and non-compartmental models. On average, a higher correlation (Pearson correlation coefficient (r) over 0.9) was observed between the estimated NH_3 emissions and the air temperature above manure surface. A similar observation has been reported by McGinn et al. (2008) who observed a Pearson correlation coefficient (r) of 0.69 between measured NH_3 emissions and surface temperature of a dairy lagoon located in Lethbridge, Alberta during summer (mid-June to mid-September). Differences in the association between the estimated NH_3 emissions and the historical data for the compartmental and non-compartmental models were also noted; most of the weather parameters had a lower correlation with the predicted values from the non-compartmental model and during the colder season.

Table 4.5: Comparison of estimated ammonia emissions with reported values in literature

Source/ Model	NH_3 emission from manure storages						Manure characteristics				Time period	Storage type	Location
	g animal^{-1} day^{-1}			g m^{-2}day^{-1}									
	Ave.	Min	Max	Ave.	Min	Max	Tot N (mgL^{-1})	NH_4-N (mgL^{-1})	TS (%)	pH			
Compartmental model	5.92	2.61	8.94	0.91	0.40	1.37	2476	1089	5.5	7	May 01 to Oct. 31	slurry tank	Rockingham County, VA
	2.16	1.21	4.44	0.33	0.19	0.69	2476	1089	5.5	7	Nov. 01 to Apr. 30	slurry tank	Rockingham County, VA
	6.08	2.85	8.94	0.93	0.44	1.37	2476	1089	5.5	7	May 01 to Oct. 31	slurry tank	Franklin County, VA
	2.63	1.52	5.18	0.41	0.24	0.80	2476	1089	5.5	7	Nov. 01 to Apr. 30	slurry tank	Franklin County, VA
Non-compartmental model	8.97	2.60	16.19	1.37	0.40	2.48	2476	1089	5.5	7	May 01 to Oct. 31	slurry tank	Rockingham County, VA
	3.00	1.31	8.94	0.46	0.20	1.38	2476	1089	5.5	7	Nov. 01 to Apr. 30	slurry tank	Rockingham County, VA
	8.74	2.66	15.59	1.34	0.41	2.38	2476	1089	5.5	7	May 01 to Oct. 31	slurry tank	Franklin County, VA
	3.60	1.60	10.01	0.56	0.25	1.55	2476	1089	5.5	7	Nov. 01 to Apr. 30	slurry tank	Franklin County, VA
McGinn et al., 2008	-	-	-	5.1	0	16	-	831	-	-	June to Sep.	lagoon	Alberta, Canada
Misselbrook et al., 2005	-	-	-	5.9	2.1	10.4	2500	800	-	6.8	July to Oct	slurry tank	Devon, United Kingdom
Rumberg et al., 2008	-	-	-	-	2.6	13	-	439	-	7.8	Year around	lagoon	Pullman, WA
Smith et al., 2007	-	-	-	1.155	0.01	2.81	2750	1000	4	-	-	Slurry tank	Midlands, United Kingdom
Sommer et al., 1993	-	-	-	-	4.2	6.6	4100	2600	-	7.7	July to September	slurry tank	Denmark
Zhao et al., 2007	-	-	-	6.2	0.5	15	-	-	2.2	7.7	Apr. to Nov.	lagoon	Columbus, Ohio
Flesch et al., 2009	-	-	-	6.5	-	-	-	-	-	-	Summer	Lagoon	Wisconsin

Apr. = April, Sep. = September, Oct. = October, Nov. = November

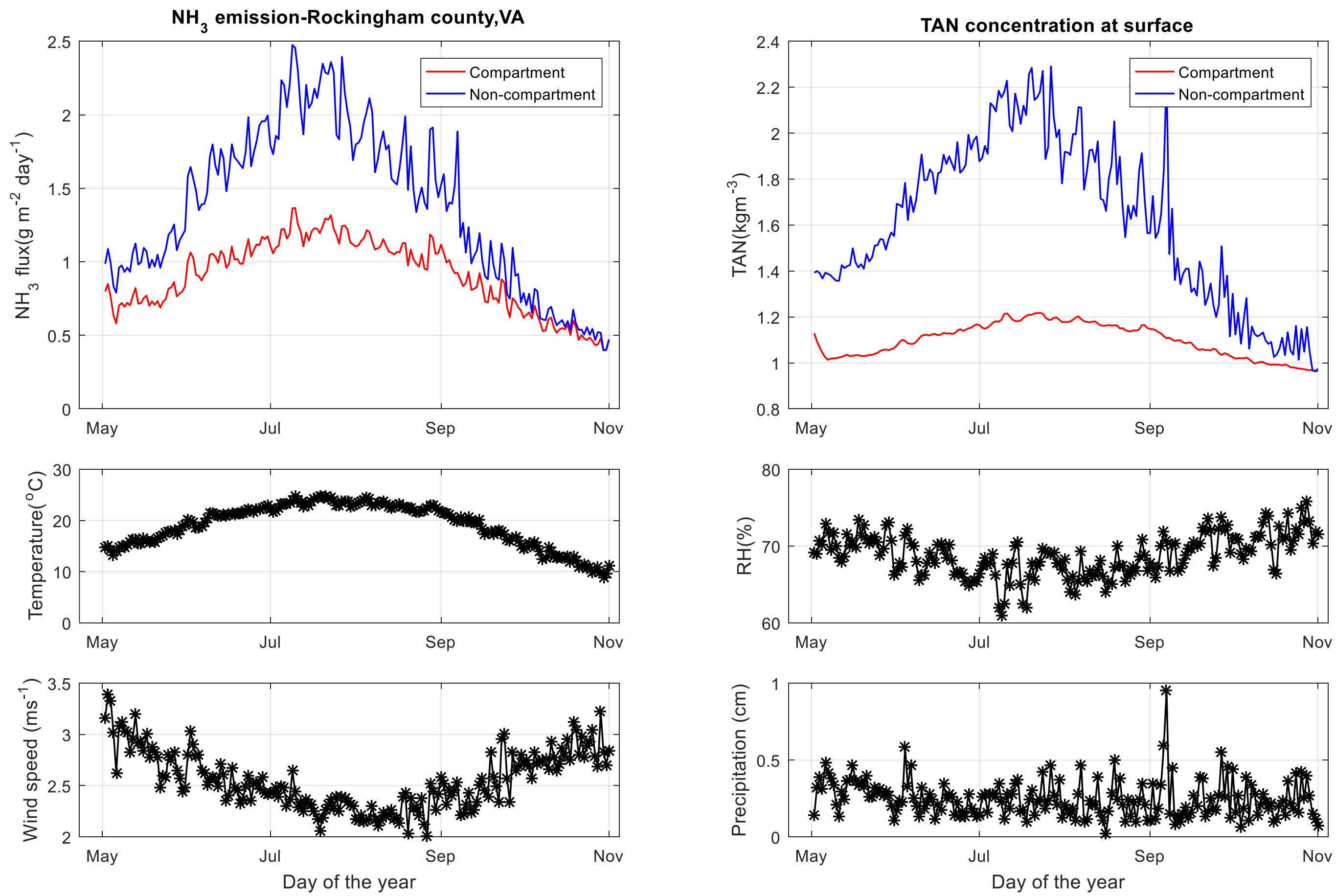

Figure 4.7: Comparison of estimated ammonia emission of compartmental model (red) and non-compartmental model (blue) from dairy storage tank in Rockingham County, VA from May 01 to October 31

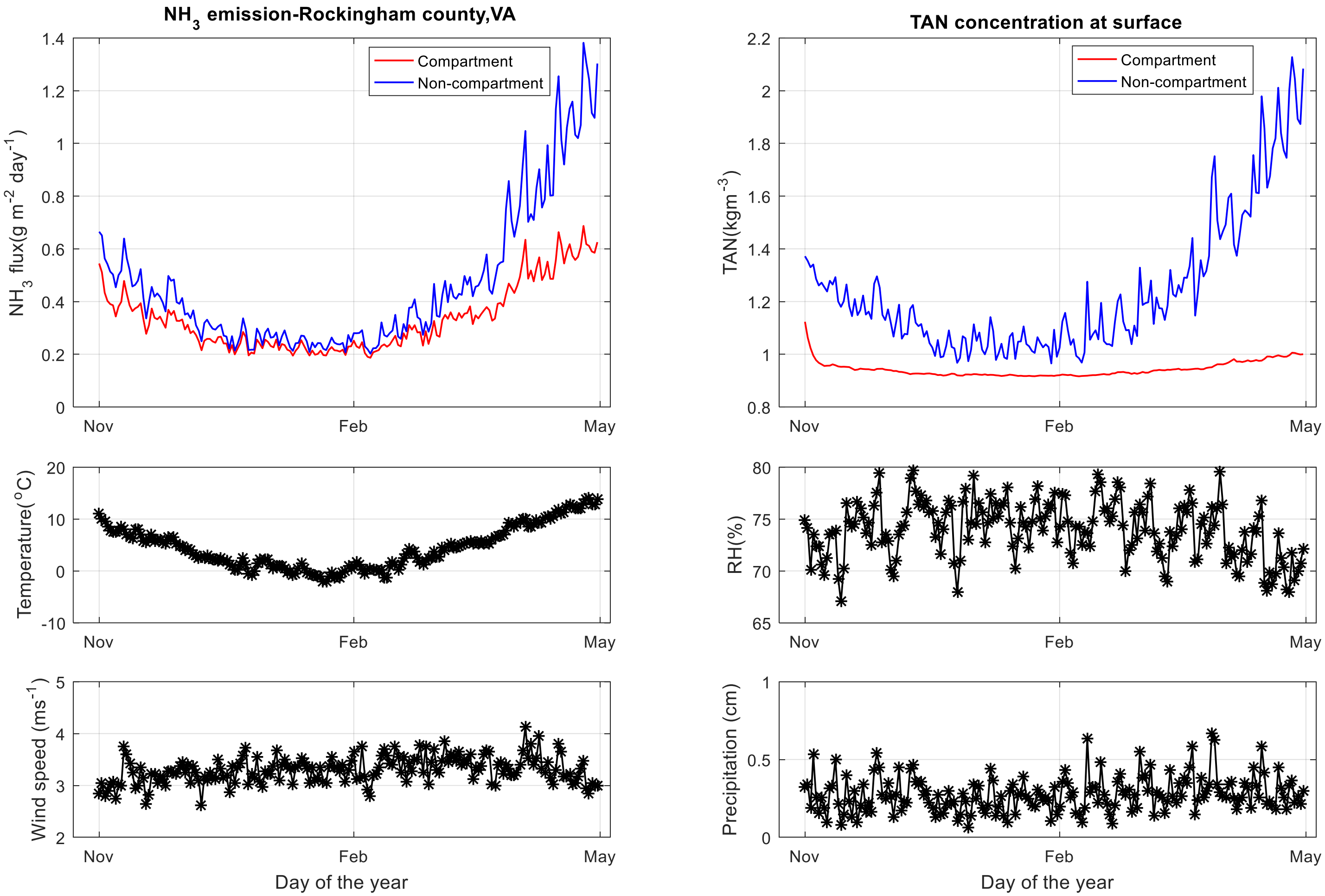

Figure 4.8: Comparison of estimated ammonia emission of compartmental model (red) and non-compartmental model (blue) from dairy storage tank in Rockingham County, VA from November 01 to April 30

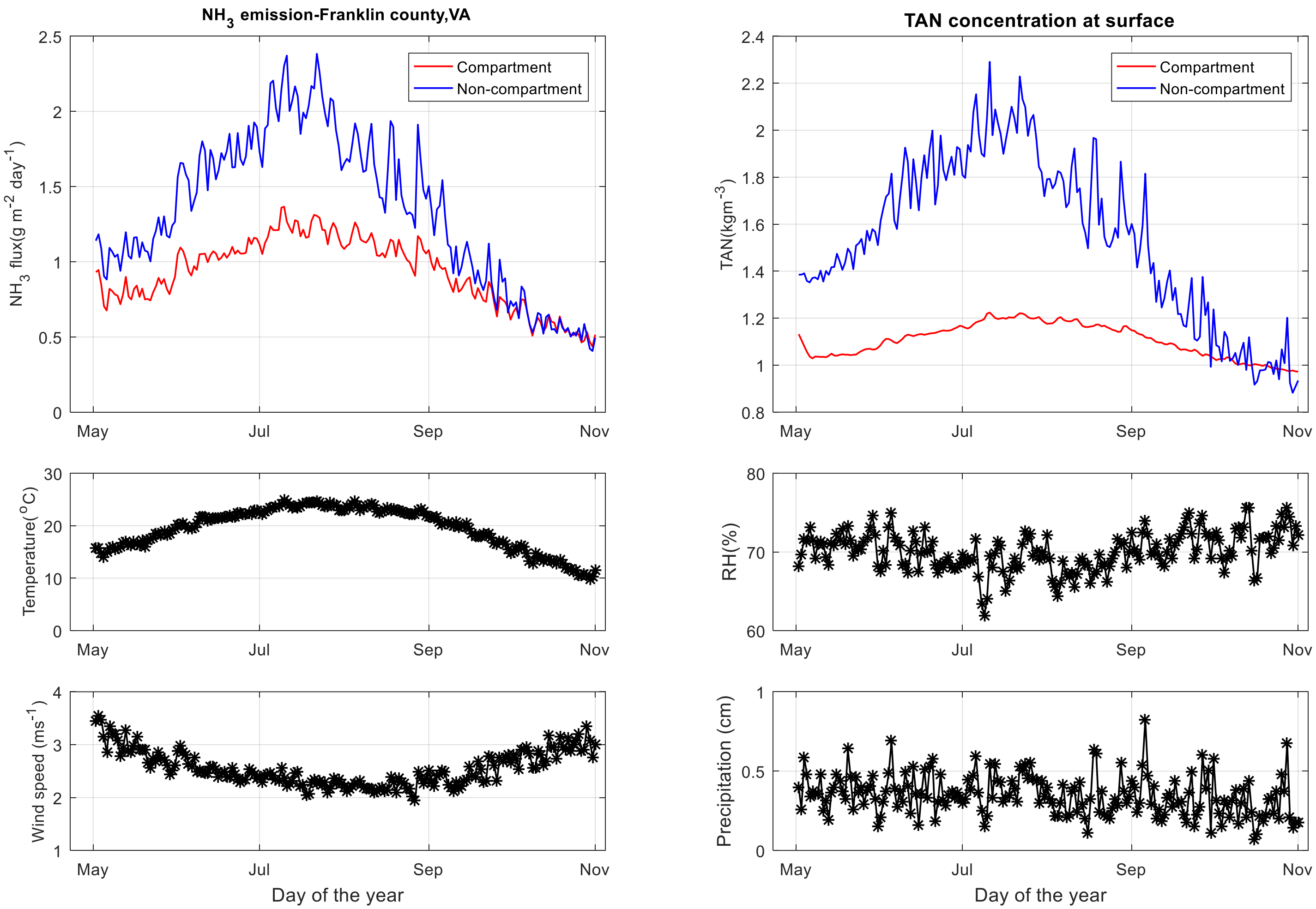

Figure 4.9: Comparison of estimated ammonia emission of compartmental model (red) and non-compartmental model (blue) from dairy storage tank in Franklin County, VA from May 01 to October 31

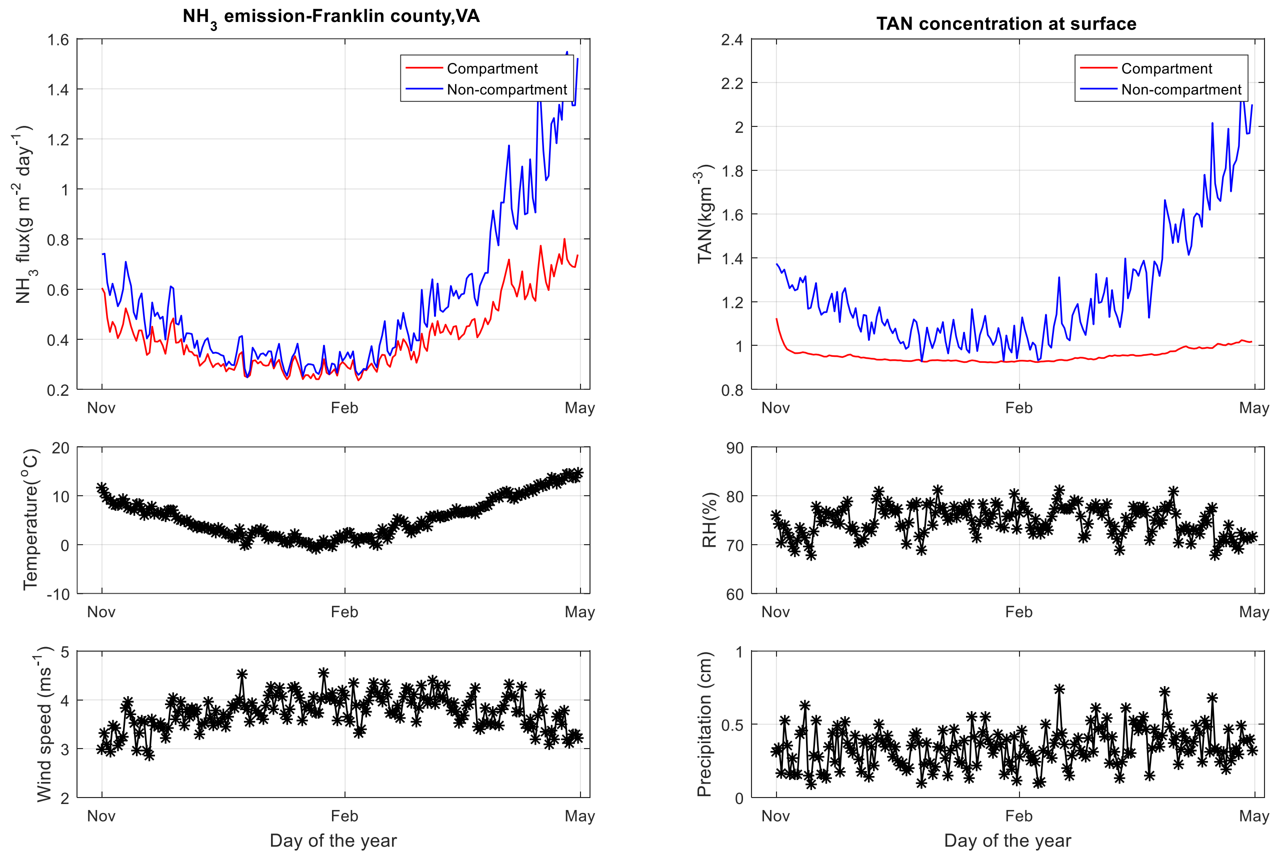

Figure 4.10: Comparison of estimated ammonia emission of compartmental model (red) and non-compartmental model (blue) from dairy storage tank in Franklin County, VA from November 01 to April 3

Table 4.6: Correlation (r) between historical weather data and estimated ammonia emissions

County	Weather data	May 01 to Oct 31		Nov 01 to April 30	
		COMP	NON-COMP	COMP	NON-COMP
Rockingham	Temperature (°C)	0.97	0.94	0.96	0.92
	RH (%)	-0.72	-0.67	-0.43	-0.40
	Wind speed (ms^{-1})	-0.64	-0.62	0.08	0.04
	Total precipitation (cm)	-0.09	0.03	0.04	0.25
Franklin	Temperature (°C)	0.96	0.92	0.95	0.92
	RH (%)	-0.58	-0.50	-0.39	-0.35
	Wind speed (ms^{-1})	-0.62	-0.58	-0.22	-0.26
	Total precipitation (cm)	0.21	0.34	0.18	0.24

COMP = Compartmental model, NON-COMP = Non-compartmental model

Spatial distribution of temperature and TAN concentration of stored dairy manure during two simulation periods from the compartmental and non-compartmental models for the two counties are illustrated in Figure 4.11 and Figure 4.12. The compartmental model for the Rockingham County showed that manure stored during warm season (from May to October) had a homogeneous temperature distribution at the beginning (Figure 4.11). Then the temperature in manure surface layers increased while bottom layers remained at lower temperatures. At the end of the season, temperature of the bottom layers increased while surface temperature decreased. During this simulation period, air temperature reached maximum in mid-season (August) and then decreased. The surface layers of manure followed a similar trend as air temperature, however, it took several weeks for the bottom layers to reach higher temperature. In cold season, from November to April, opposite temperature effects are observed (Figure 4.12). The lag effect of temperature could be attributed to the slower rate of heat transfer in manure. This thermal phenomenon has been observed in manure lagoons by Hamilton and Cumba (2000) and Smith and Franco (1985). The surface temperature of manure follows the mean air temperature, however, slightly lags behind the air temperature (Smith and Franco, 1985). Hamilaton and Cumba (2000) reported that there is about two-month lag between the heating cycles of the upper and lower layers of stored manure.

Figure 4.11 and 4.12 also indicate that TAN concentration within the stored manure vary spatially and seasonally in Rockingham County. On average, the TAN concentration was higher in bottom layers and this pattern was consistent across time within a given season. This result is qualitatively similar to the computer simulation and laboratory results reported by Muck and Steenhuis (1982). Further, the TAN concentration of manure increased during the warmer season compared to cold season. Figure 4.13 and 4.14 show the results for Franklin County for the warmer and colder storage seasons. The observed spatial and temporal patterns were similar to the those of Rockingham County.

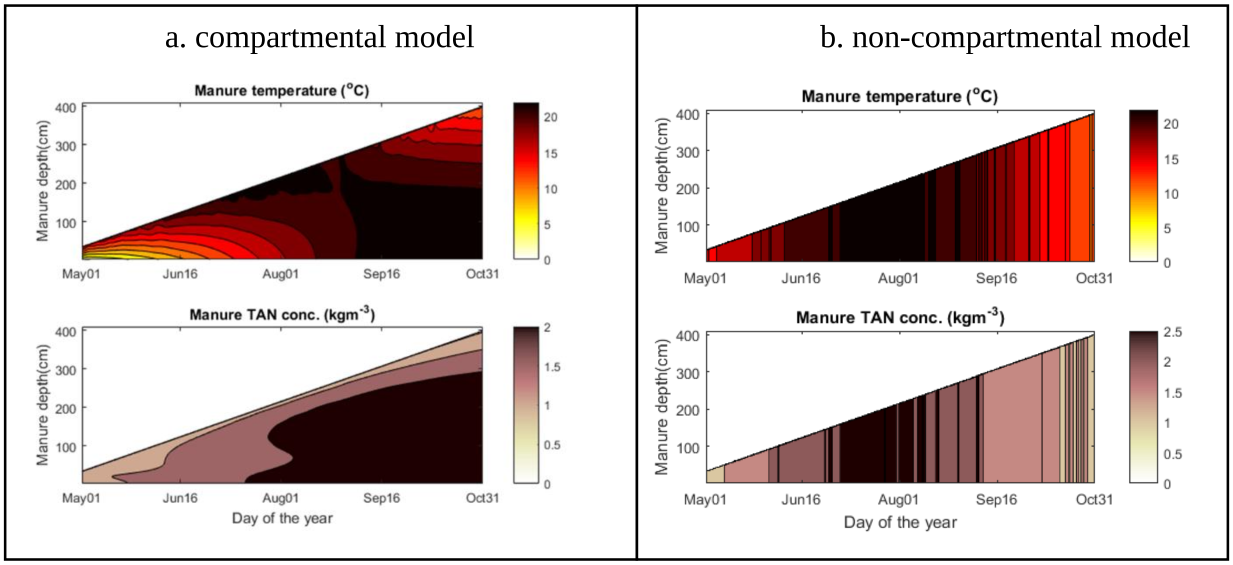

Figure 4.11: Compartmental model (a) and non-compartmental model (b) estimate of manure temperature and TAN concentration of stored manure of a dairy lagoon in in Rockingham County, VA from May 01 to October 31

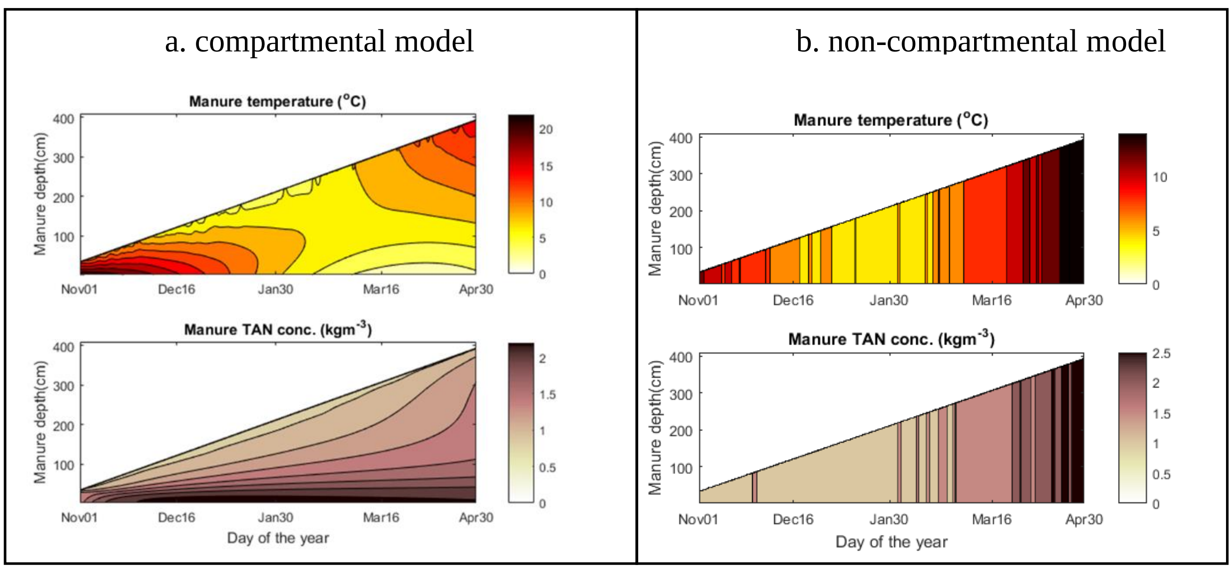

Figure 4.12: Compartmental model (a) and non-compartmental model (b) estimate of manure temperature and TAN concentration of stored manure of a dairy lagoon in in Rockingham County, VA from November 01 to April 30

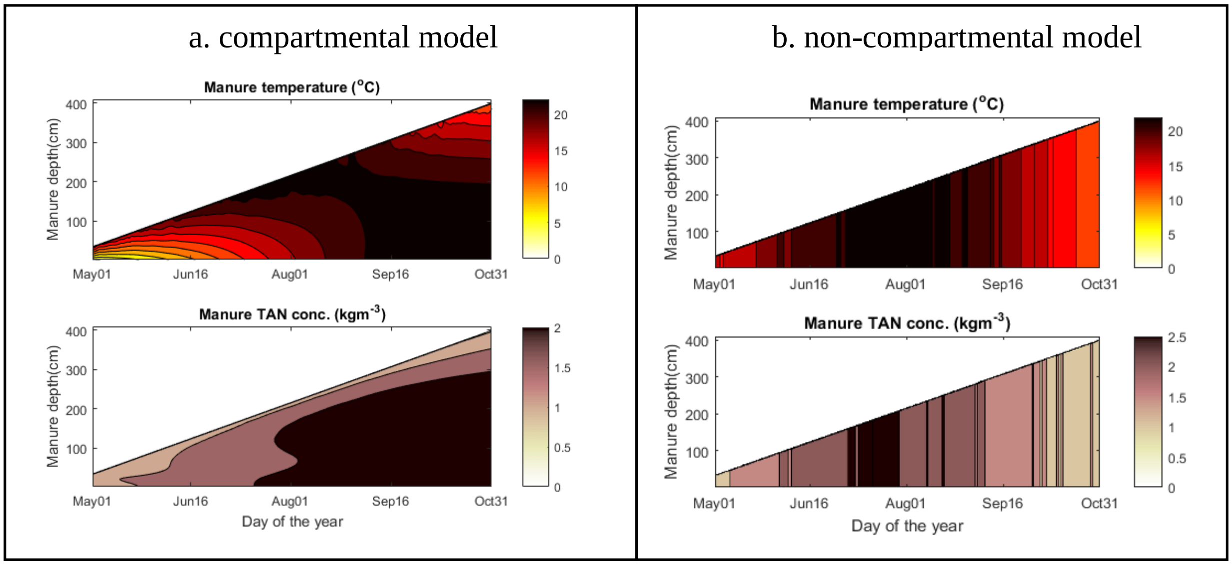

Figure 4.13: Compartmental model (a) and non-compartmental model (b) estimate of manure temperature and TAN concentration of stored manure of a dairy lagoon in in Franklin County, VA from May 01 to October 31

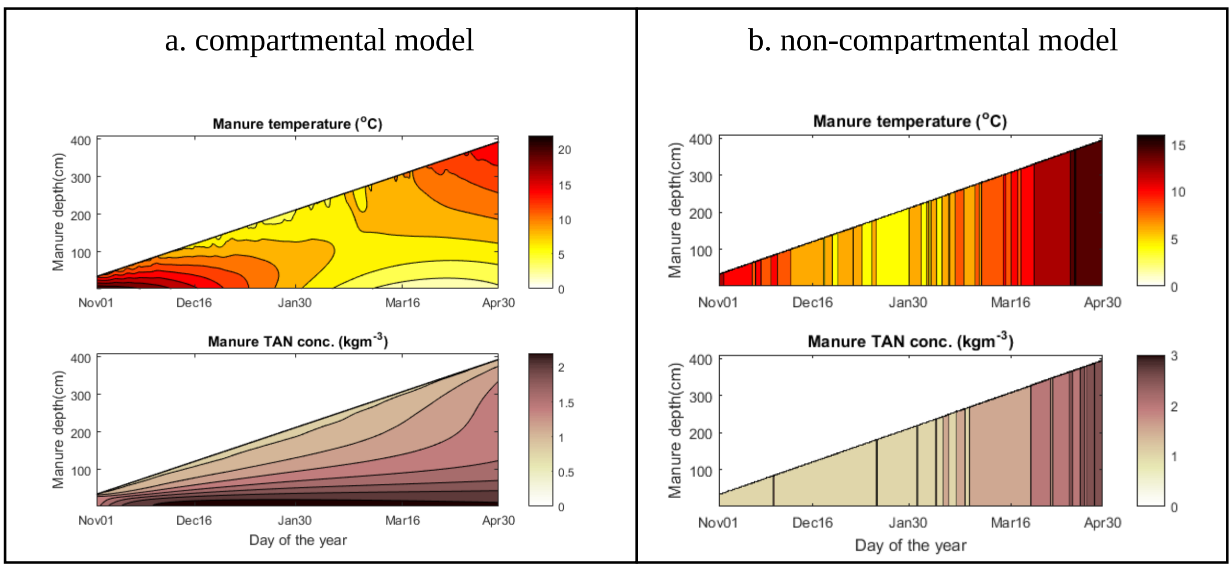

Figure 4.14: Compartmental model (a) and non-compartmental model (b) estimate of manure temperature and TAN concentration of stored manure of a dairy lagoon in in Franklin County, VA from November 01 to April 30

4.7 Studying the effect of model inputs on ammonia emission

The sensitivity analysis revealed that air temperature, manure pH, wind speed and initial manure TAN concentration were the most influential input variables on the estimated ammonia emissions. In model simulations described above, daily values of the air temperature and wind speed were used, thus the effect of these variables were captured in the model output. In contrast, manure pH and initial TAN concentration were held constant throughout the simulation period. In order to study how these two inputs affect the model dynamics, the simulations were performed at various levels of pH and TAN concentration, and the results from this exercise is given in following sections.

4.7.1 Effect of manure pH on ammonia emission

Based on the sensitivity analysis manure pH was the second most influential input variable in the compartmental model. A constant manure pH of 7.0 was used for different weather and management scenario analysis in section 4.6. However, the pH of scraped liquid dairy manure may vary from 6.5 to 7.5 (Li, 2009; Misselbrook et al., 2005). To study the effect of manure pH on model output, ammonia emission was estimated at manure pH 6.5, 7.0, and 7.5 during warm and cold seasons in Rockingham County using historical weather data (Figure 4.15 to 4.16).

Daily ammonia emission from stored liquid manure increased with rising manure pH in both cold and warm storage seasons. The non-compartmental model estimated higher ammonia emission from stored manure at different manure pH. Compared to the compartmental model, the estimated NH_3 emission of non-compartmental model was 91%, 78%, and 36 % higher during the warm season and 67%, 64 %, and 49 % higher during the cold season at manure pH of 6.5, 7.0, and 7.5, respectively. Estimated average daily ammonia emission for cold and warm seasons at different manure pH showed that ammonia emission increased exponentially with increasing manure pH (Figure 4.17 to 4.18). Manure pH is a variable of equation (3.40) in the model that calculates fraction of free aqueous ammonia (*F*) occurring as TAN in manure. The fraction of free aqueous ammonia is directly proportional to the ammonia volatilization (eq. (3.30)) and it increases exponentially when manure pH rises. Therefore, estimated ammonia emission increased exponentially when manure pH increased.

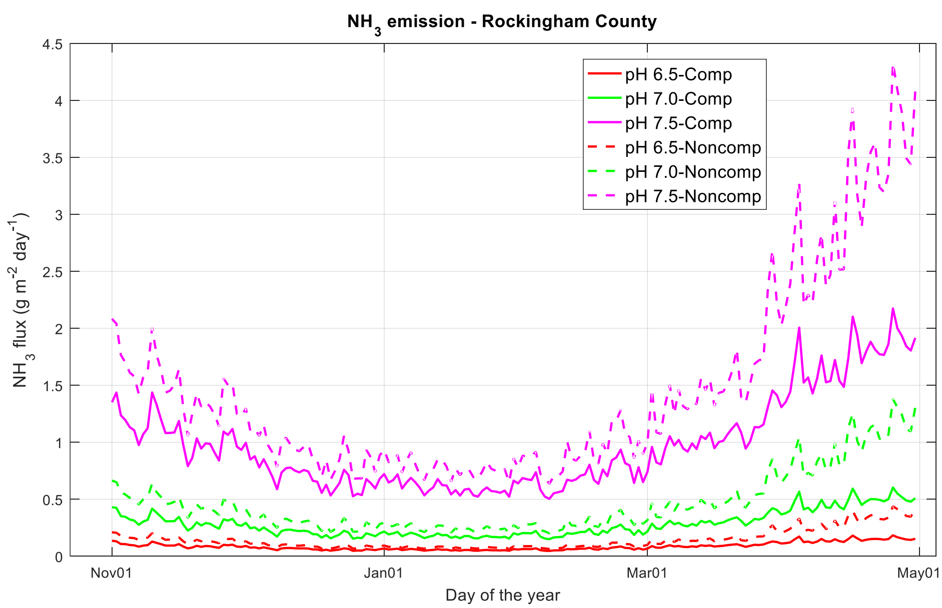

Figure 4.15: Comparison of ammonia emission estimated using the compartmental model (Comp) and non-compartmental model (Noncomp) at different manure pH of stored manure in a dairy lagoon located in Rockingham County, VA from November 01 to April 30

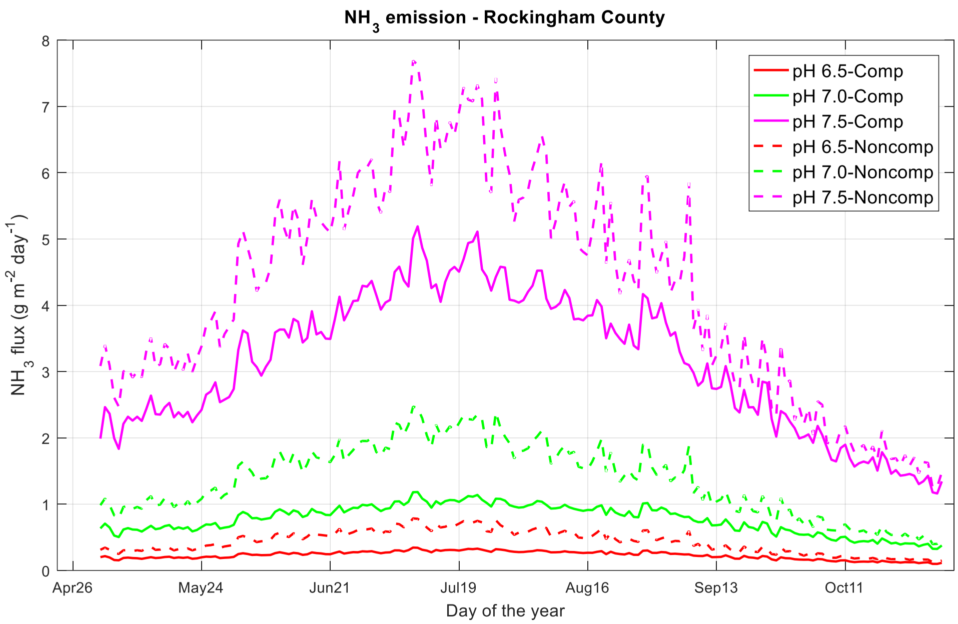

Figure 4.16: Comparison of ammonia emission estimated using the compartmental model (Comp) and non-compartmental model (Noncomp) at different manure pH of stored manure in a dairy lagoon located in Rockingham County, VA from May 01 to October 31

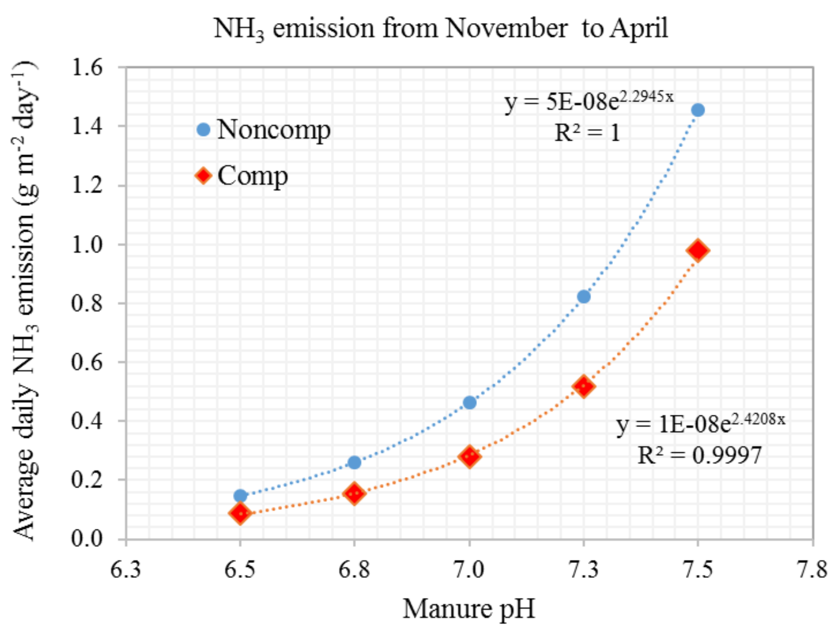

Figure 4.17: Average daily ammonia emission estimated using the compartmental model (Comp) and non-compartmental model (Noncomp) at different manure pH of stored manure in a dairy lagoon located in Rockingham County, VA from November 01 to April 30

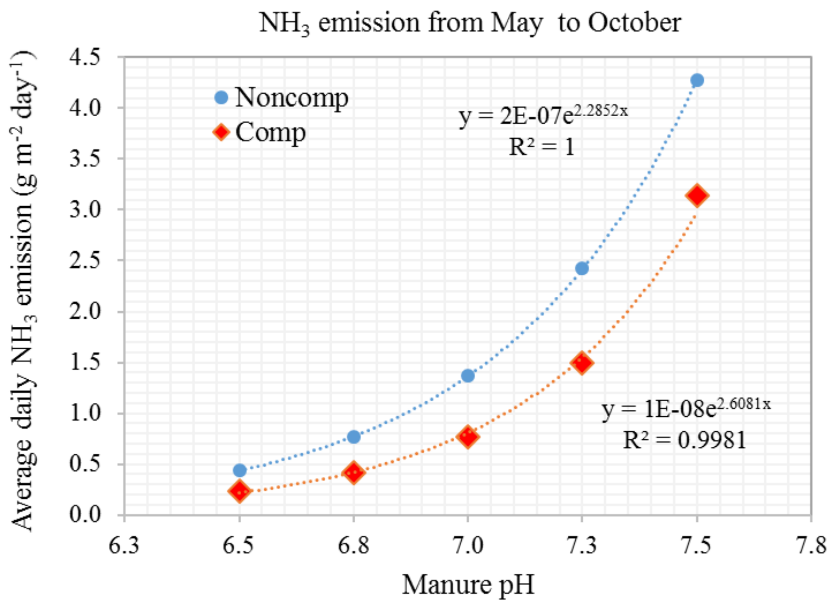

Figure 4.18: Average daily ammonia emission estimated using the compartmental model (Comp) and non-compartmental model (Noncomp) at different manure pH of stored manure in a dairy lagoon located in Rockingham County, VA from May 01 to October 31

4.7.2 Effect of manure TAN concentration on ammonia emission

Initial TAN concentration of manure is another input variable that has higher influence on variance of model output. Sensitivity analysis showed that initial manure TAN concentration is the fourth most influential input variable of the model. The initial manure TAN concentration used in scenario analysis was 1.089 kg m^{-3}. As per literature, the initial TAN concentration of scraped manure may change from 0.44 kg m^{-3} to 2.6 kg m^{-3} (Rumberg et al., 2008; Sommer et al., 1993). The effect of initial TAN concentration of manure on model output was studied via estimating ammonia emission at initial TAN concentrations of 0.5 kg m^{-3}, 1.5 kg m^{-3}, and 2.5 kg m^{-3} (Figure 4.19 to 4.20).

Daily ammonia emission from stored liquid manure increased with rising initial TAN concentration in both cold and warm storage seasons. The non-compartmental model estimated higher ammonia emission from stored manure at different initial manure TAN concentrations. Compared to the compartmental model, the estimated NH_3 emission of non-compartmental model was 150%, 57%, and 32 % higher during the warm season and 115%, 36 %, and 20 % higher during the cold season at initial manure TAN concentration of 0.5 kg m^{-3}, 1.5 kg m^{-3}, and 2.5 kg m^{-3}, respectively. The average daily ammonia emission for cold and warm seasons at different initial TAN concentrations showed that ammonia emission increased linearly with increasing initial TAN concentration of manure (Figure 4.21 to 4.22). TAN concentration of incoming manure contributes to the TAN available in the stored manure. Equation (3.30) shows that the concentration of TAN in stored manure is directly proportional to the ammonia flux from stored manure. Therefore, estimated ammonia emission increased linearly as initial manure TAN concentration increased.

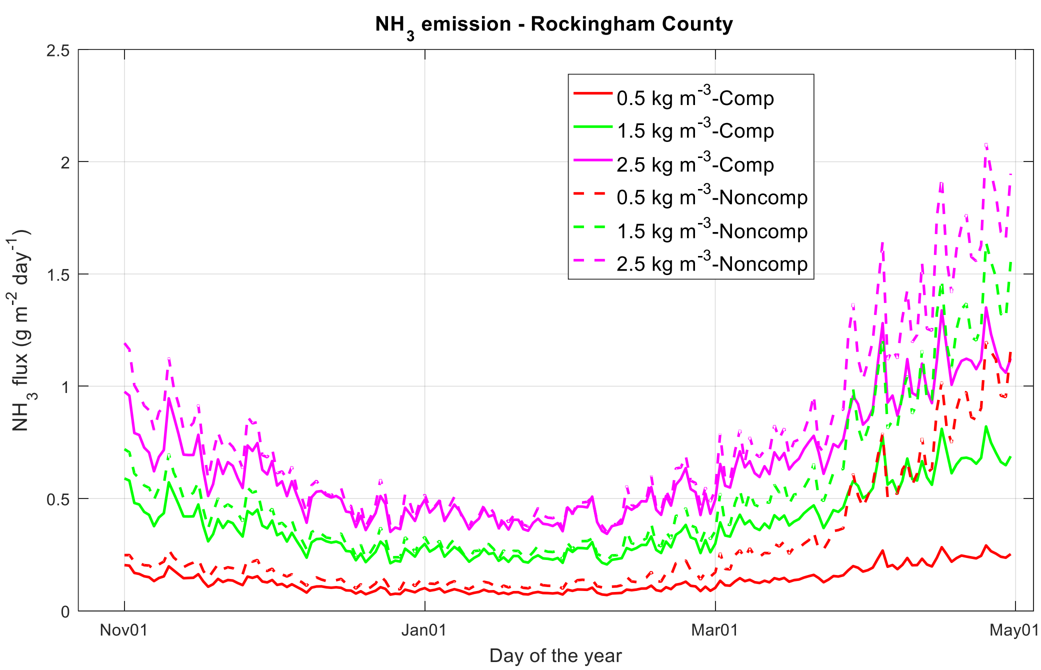

Figure 4.19: Comparison of ammonia emission estimated using the compartmental model (Comp) and non-compartmental model (Noncomp) at different initial manure TAN concentrations of stored manure in a dairy lagoon located in Rockingham County, VA from November 01 to April 30

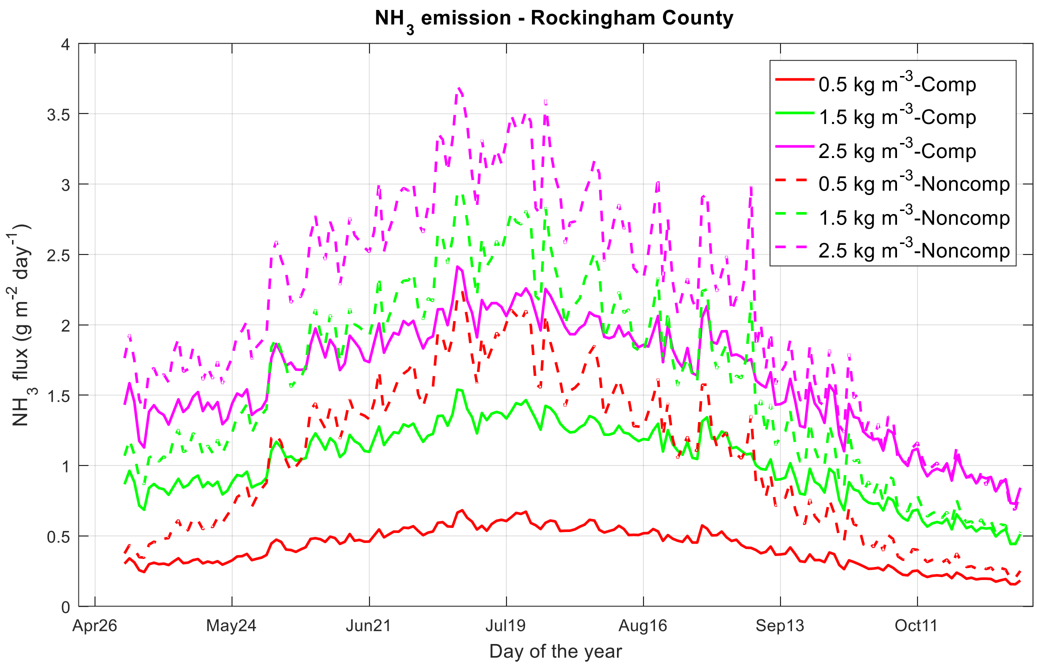

Figure 4.20: Comparison of ammonia emission estimated using the compartmental model (Comp) and non-compartmental model (Noncomp) at different initial manure TAN concentrations of stored manure in a dairy lagoon located in Rockingham County, VA from May 01 to October 31

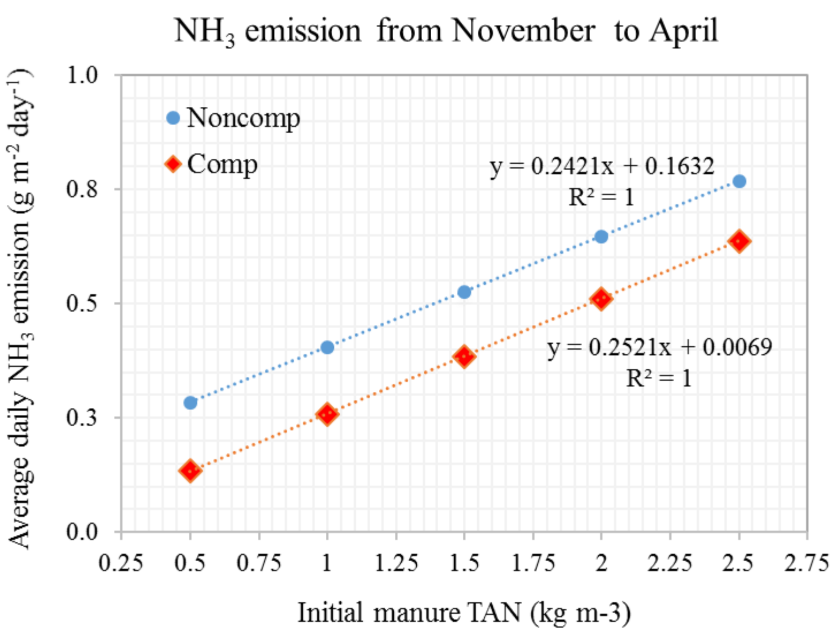

Figure 4.21: Average daily ammonia emission estimated using the compartmental model (Comp) and non-compartmental model (Noncomp) at different initial manure TAN concentrations of stored manure in a dairy lagoon located in Rockingham County, VA from November 01 to April 30

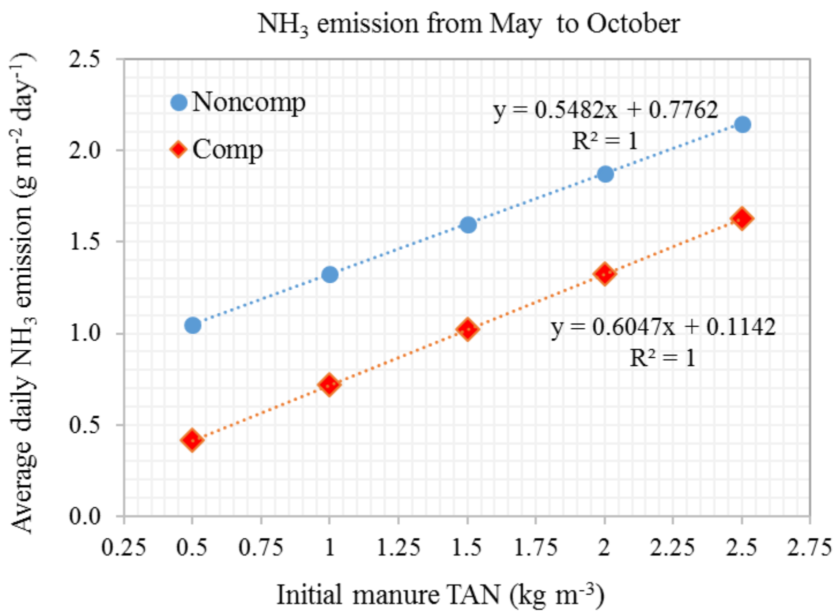

Figure 4.22: Average daily ammonia emission estimated using the compartmental model (Comp) and non-compartmental model (Noncomp) at different initial manure TAN concentrations of stored manure in a dairy lagoon located in Rockingham County, VA from May 01 to October 31

4.8 Uncertainty of future ammonia emission predictions

How much of ammonia is produced per dairy cow depends on numerous factors. For example, (1) mass of manure produced and the amount of nitrogen excreted, (2) composition of feed, (3) environmental factors affecting biogeochemical reactions related to NH_3 emission, and (4) manure management practices. In this study, the compartmental model evaluated how ammonia emission varied with environmental factors, manure characteristics, and manure management. All above predictions were obtained assuming that a dairy cow weighing 635 kg produces 67 kg of manure per day (ASABE, 2005; MWPS, 2000); and the initial total nitrogen concentration of manure is 2.5 kg m^{-3}. However, these assumptions may not hold in real conditions and in future times as advancement of animal breeding and genetic improvement programs produce dairy animals with high feed conversion and nitrogen use efficiency (FAO, 2006a; Thornton, 2010).

Another source of uncertainty comes from the future management decisions in relation to herd management. Based on the predictions of Food and Agriculture Organization of the United Nations (Alexandratos and Bruinsma, 2012) annual per capita consumption of milk in both the developed and developing countries will increase up to 222 kg and 76 kg respectively by 2050. To meet this increasing demand, dairy farms need to use highly productive animals and/or increase number of dairy cows. Depending on which management changes are adopted in future, ammonia emissions from a given dairy farm may vary.

4.9 Applications of compartmental process-based model

4.9.1 Implementation of control measures to mitigate ammonia emission

Understanding the dynamics of biogeochemical processes occurring in stored liquid dairy manure is crucial to implement control measure to mitigate ammonia volatilization and reduce nitrogen loss. The compartmental process-based model provides a platform that can be further improved to study the effect of control measures in mitigating ammonia emission from sored liquid dairy manure. The control measures can mainly be divided into three categories: physical methods (eg. covers, location of inlet of manure into storage - bottom vs top loading), chemical methods (eg. chemical manure additives), and biological methods (eg. microbial manure additives).

The ability of compartmental model to predict spatial variation of temperature and manure characteristics can be used to study the effect of physical methods. Use of surface covers reduce exposed surface area of stored manure for ammonia volatilization as well as increase resistance for ammonia transfer from manure liquid to the atmosphere. Manure-DNDC model uses a reduction factor that varies from 0 to 1 based on the type of surface cover (Li et al., 2012). Similarly, the compartmental model can be modified by including a simple emission reduction factor. For more accuracy, a mechanistic approach imposing resistance to mass transfer through a storage cover can be used. Location of inlet of manure at the bottom of the storage is another physical method that can be used to reduce ammonia volatilization and conserve manure nitrogen. Muck and Steenhuis (1982) found out that under laboratory conditions, bottom-loaded manure storages provide better nitrogen conservation than top-loaded manure storages. The current compartmental model simulates a top-loaded manure storage and adds a new manure layer at the top of stored manure at each time step. However, the model can be modified to simulate a bottom-loaded manure storage by adding a new manure layer at the bottom of stored manure.

Use of chemical additives such as strong acids (e.g. sulfuric and hydrochloric) (Frost et al., 1990; Husted et al., 1991) and salts (e.g. alum and calcium chloride) (Ndegwa et al., 2008) decreases manure pH thereby reduce ammonia volatilization. The simulation results in section 4.7.1 showed that decrease of manure pH variable in compartmental model reduces estimated ammonia emission. Therefore, the model can be used to study the effectiveness of different chemical treatments in reducing ammonia emission. Nitrogen concentration of incoming manure is another key factor that affects ammonia emission from the stored manure. In the compartmental model, initial concentration of manure TAN and organic nitrogen are given as input variables. Estimated ammonia emission under different initial manure TAN concentrations in section 4.7.2 showed that decrease of initial TAN concentration in manure by 1 kg m^{-3} reduces ammonia emission flux by 0.6 g m^{-2} day^{-1} and 0.25 g m^{-2} day^{-1} in warm and cold seasons, respectively. Nitrogen concentration of manure coming to storage can be reduced by dietary changes (e.g. reduce crude protein content of feed) and separation of urine from manure solids (Sparks et al., 2011; Ndegwa et al., 2008). These management practices can be incorporated into the compartmental model algorithm to study these effects on ammonia emissions.

In biological method, microbial processes are used to assimilate volatile nitrogen or transform volatile nitrogen into non-volatile inorganic nitrogen in stored manure (Ndegwa et al., 2008). Nitrification is one of the microbial oxidation process that converts manure TAN into nitrite and nitrate. The rate of nitrification process in stored manure can be increased by aeration. Currently, the compartmental model consists with only one microbial process (mineralization). However, other microbial processes (e.g. nitrification, denitrification, anammox) related to manure nitrogen transformation and can be incorporated to study the effect of different biological treatment methods.

4.9.2 Estimating storage requirement

Discharge of livestock manure and wastewater from concentrated animal feeding operations (CAFOs) is regulated under Clean Water Act by Environmental protection Agency (EPA). EPA estimated in 2003, that these regulations would decrease release of 110 million pounds of N and 56 million pounds of P in to natural ecosystems annually (USEPA, 2012). Nutrient management plan (NMP) is an integral part of a CAFO permit, and helps farmers effectively manage manure to meet crop nutrient requirement while minimizing environmental impact on water and air quality. EPA identified nine minimum requirements that should be included in an NMP (USEPA, 2003 and 2012). The first and the foremost requirement is ensuring adequate storage for manure, litter, and process water and operation and management of that facility. Therefore, capacity of a manure storage structure is a crucial factor in manure management in a dairy farm.

The size of the structure needed to store manure depends on the storage period, volume of manure stored and removed during the storage period, and weather conditions (e.g. rain, temperature). The compartmental process-based model estimated that a circular storage tank with 4.6 m (15 ft) height would be 28.6 m (94 ft) in diameter to store scraped liquid dairy manure from 100 cows for 6-month period in Rockingham or Franklin County, VA (Figure 4.23). Using the same storage size, different scenarios were simulated with historical weather data. Further it was assumed that, for a given storage season, amount of manure produced by dairy cows was constant across different model scenarios. However, the results indicated that the final volume of manure at the end of each storage season varies from one scenario to another (Figure 4.24). These changes in manure depth at the end of each storage season may attribute to the weather conditions during that season, especially total precipitation received during that period. However, none of the scenarios reached the designed maximum operational height (3.85 m) of the storage.

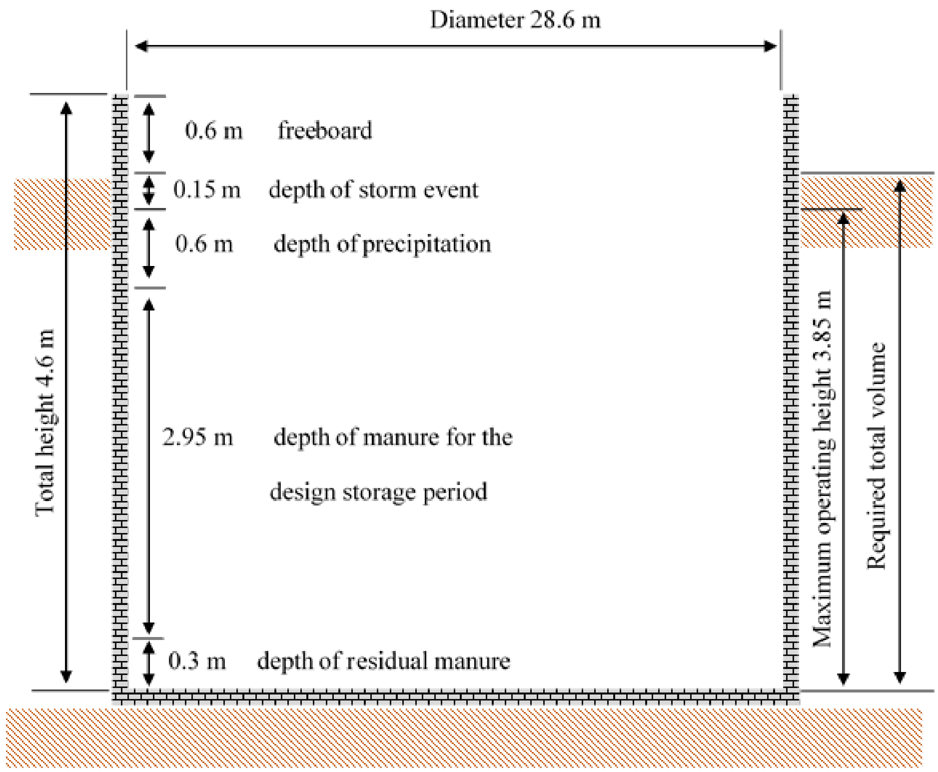

Figure 4.23: Dimension of below ground circular storage tank for storing scraped liquid manure of 100 dairy cows for 6-month period in Rockingham or Franklin County in Virginia

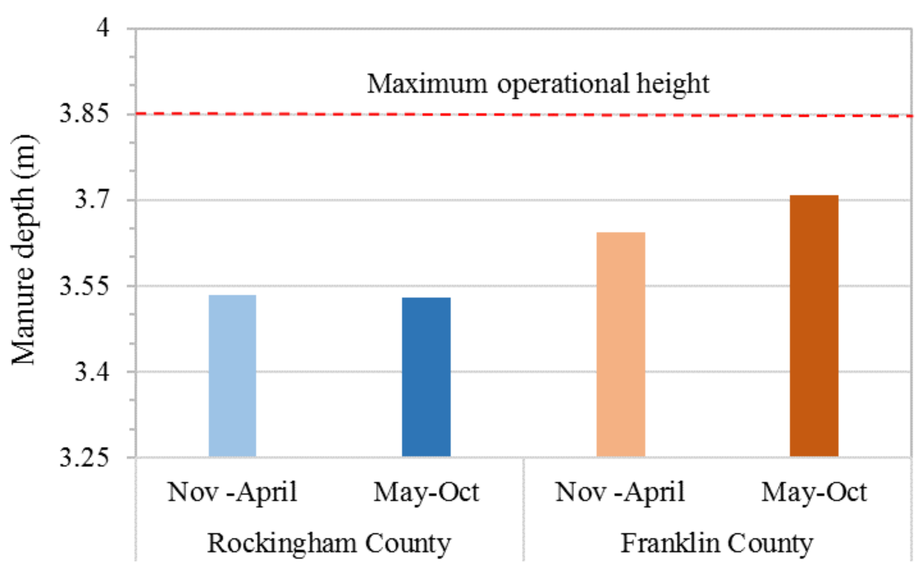

Figure 4.24: Comparison of final depth of manure in the storage tank at the end of each storage period for historical weather data in Rockingham and Franklin Counties, Virginia

4.9.3 Estimate nitrogen loss from stored manure

Volatilization of ammonia during storage of liquid dairy manure decreases nitrogen content of stored manure thereby reduce fertilizer value of manure. In the compartmental model, total nitrogen concentration of manure coming to the storage was 2.476 kg m^{-3}. Thus, the stored manure of a 100-dairy cow farm collects 3074 kg and 3024 kg of nitrogen (total N) during manure storage period from May 01 to October 31 and November 01 to April 30, respectively. However, due to ammonia volatilization, the nitrogen content of stored manure decreased at the end of each storage season. The compartmental model simulation results for historical weather data showed that ammonia volatilization decreased 3.5 % and 3.6 % of nitrogen in stored manure during the warm season and 1.3 % and 1.6 % of nitrogen in stored manure during the cold season in Rockingham and Franklin counties, respectively (Figure 4.25). Knowing nitrogen loss of stored liquid dairy manure helps implementing control measures to reduce nutrient loss. Conserved manure nitrogen can be used as a valuable crop nutrient.

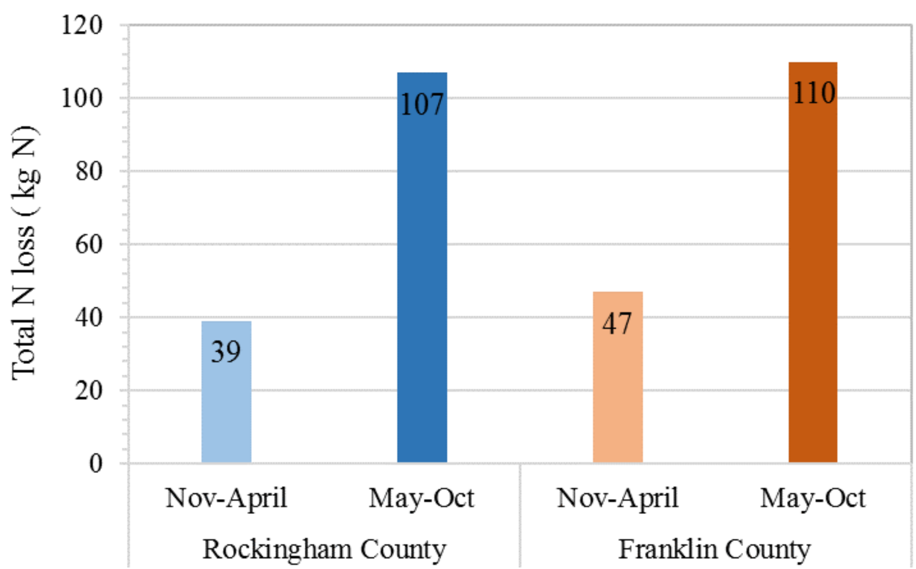

Figure 4.25: Estimated nitrogen loss of liquid dairy manure in Rockingham and Franklin Counties, Virginia

5 Summary and conclusion

Processed-based biogeochemical models are used to estimate production and emission of ammonia from stored liquid dairy manure. The biogeochemical processes responsible for these gaseous emissions are governed by environmental factors and manure characteristics. These factors vary with space and time in a manure storage. However, a review of published literature on process-based models currently used for estimating NH_3 emissions revealed that the spatial heterogeneity is not adequately represented in these models. This study developed a compartmental process-based model to estimate NH_3 emissions from stored liquid dairy manure for improving the model accuracy by incorporating the spatial heterogeneity of environmental factors, manure characteristics and biogeochemical reactions.

The compartmental model was calibrated using published experimental data. Performance of the calibrated model was evaluated by comparing the model estimate with experimental data and simulation output from a non-compartmental model. This evaluation suggested that the compartmental process-based model performs better. A global sensitivity analysis was conducted for 10 input model parameters and air temperature, manure pH, wind speed, and manure TAN concentration were identified as highly influential model inputs. Moreover, model was simulated for a storage tank in a dairy farm with 100 cows located in Rockingham and Franklin counties in Virginia for 6-month storage period under different management and weather scenarios.

The simulation results suggested greater NH_3 emissions for the manure storage period of May to October compared to the period from November to April. The estimated NH_3 emissions showed a higher correlation with air temperature. Further, the model predicted that the final manure volume collected at the end of the storage period increases during the warmer season and decreased in the cold season.

6 Recommendations for future studies

1. Performance evaluation of the compartmental model revealed that it is required to have proper experimental data for calibration and verification of the model. The data used in model calibration and verification were incomplete: the data did not include information on manure characteristics and several weather parameters (e.g. wind speed, RH, precipitation). The missing information were substituted with data obtained from other sources. Therefore, a full-scale experiment to collect a complete data set should be done and the model needs to be calibrated and verified in future studies.

2. For simplicity, current compartmental model simulates the heat and mass transfer in stored manure using a 1D model. However, environmental factors and manure characteristics vary spatially within the manure storage. A 3D model is required to comprehensively capture these variations in full spectrum and produce more accurate emission estimates.

3. Currently the compartmental model only estimates NH_3 emissions. The model can be further improved in future studies to incorporate biogeochemical reactions related to, C, N and S transformations to estimate production and emission of CH_4, CO_2, N_2O, NO, N_2 and H_2S in addition to NH_3.

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Appendices

Appendix A. Summary of historical weather data for Rockingham and Franklin counties

Storage period	Weather data	County					
		Rockingham			Franklin		
		Average	Min	Max	Average	Min	Max
May 01 to October 31	Daily air temperature (℃)	19.11	8.96	24.73	19.51	9.91	24.92
	Daily RH (%)	68.82	61.02	75.87	70.10	61.87	75.58
	Daily Wind speed (ms^{-1})	2.56	2.00	3.40	2.55	1.94	3.54
	Daily precipitation (cm)	0.25	0.02	0.96	0.35	0.07	0.82
	Total precipitation for the period (cm)	45.88			64.35		
November 01 to April 30	Daily air temperature (℃)	4.47	-2.15	13.99	5.38	-0.78	14.83
	Daily RH (%)	73.96	67.02	79.67	74.80	67.74	81.18
	Daily Wind speed (ms^{-1})	3.30	2.62	4.13	3.75	2.86	4.56
	Daily precipitation (cm)	0.28	0.06	0.67	0.34	0.09	0.74
	Total precipitation for the period (cm)	50.51			62.22		

Appendix B. Weather data and measured ammonia emission data used for model calibration

Date	Day	Temperature (°C)	Relative Humidity (%)	Wind speed (m s^{-1})	Precipitation (cm)	Measured NH_3 emission (g m^{-2} day^{-1})
5/29/2009	1	16.9	80.23	3.25	0.67	1.25
5/30/2009	2	16.6	74.27	2.36	0.39	6.88
5/31/2009	3	17.8	65.00	2.29	0.10	3.14
6/1/2009	4	19.8	69.99	4.48	0.46	4.21
6/2/2009	5	18.3	91.47	3.30	0.45	1.55
6/3/2009	6	15.1	86.24	2.94	1.13	3.32
6/4/2009	7	14.4	72.94	2.37	0.00	5.01
6/5/2009	8	16.6	67.14	1.71	0.00	3.25
6/6/2009	9	20	70.95	2.74	0.00	5.80
6/7/2009	10	21.2	75.70	2.73	0.59	3.91
6/8/2009	11	22.6	83.86	4.34	0.83	5.48
6/9/2009	12	20.4	87.69	2.47	0.20	2.60
6/10/2009	13	17.8	85.96	2.47	1.53	4.55
6/11/2009	14	19.3	92.09	3.35	4.14	2.41
6/12/2009	15	18.7	75.64	2.63	0.03	4.29
6/13/2009	16	19.6	80.59	1.49	0.31	3.45
6/14/2009	17	20.4	79.72	2.18	0.07	3.81
6/15/2009	18	21.7	70.84	2.56	0.00	6.65
6/16/2009	19	20	82.15	3.83	1.32	4.64
6/17/2009	20	20.9	86.98	3.64	0.10	4.10
6/18/2009	21	19.2	79.76	2.44	0.00	2.76
6/19/2009	22	25.5	82.97	4.92	0.76	4.48
6/20/2009	23	24.3	73.38	4.01	0.00	2.89
6/21/2009	24	25.1	73.95	1.42	0.00	3.89
6/22/2009	25	24.6	80.86	2.20	1.22	5.10
6/23/2009	26	25.8	70.15	1.56	0.01	4.88
6/24/2009	27	26.2	70.24	1.96	0.22	7.97
6/25/2009	28	27.3	80.02	2.32	1.57	5.36
6/26/2009	29	27.2	73.85	2.79	0.78	10.53
6/27/2009	30	23.8	61.41	1.88	0.00	5.56
6/28/2009	31	25.2	66.56	4.74	0.04	4.03
6/29/2009	32	21.7	72.59	4.74	0.19	2.06
6/30/2009	33	18.5	83.75	3.36	0.16	4.02
7/1/2009	34	16.8	92.44	2.33	0.33	2.51

Date	Day	Temperature (°C)	Relative Humidity (%)	Wind speed (m s^{-1})	Precipitation (cm)	Measured NH_3 emission (g m^{-2} day^{-1})
7/2/2009	35	17.1	86.44	2.73	0.14	2.83
7/3/2009	36	20.4	84.61	1.94	0.02	4.17
7/4/2009	37	18.4	89.51	2.60	1.16	2.29
7/5/2009	38	20.2	79.53	2.10	0.01	6.07
7/6/2009	39	21.6	74.10	2.47	0.03	5.56
7/7/2009	40	21.3	70.53	2.15	0.02	7.08
7/8/2009	41	19.4	70.97	2.60	0.57	4.90
7/9/2009	42	20.3	80.36	2.88	0.47	3.79
7/10/2009	43	22	71.74	2.35	0.00	3.97
7/11/2009	44	23.8	81.72	2.68	1.28	4.60
7/12/2009	45	20.9	64.74	2.17	0.00	5.37
7/13/2009	46	19.9	61.31	1.71	0.00	6.13
7/14/2009	47	18.1	55.48	2.81	0.00	5.36
7/15/2009	48	21.1	61.93	4.32	0.00	3.04
7/16/2009	49	22.4	73.68	3.18	0.12	3.53
7/17/2009	50	19.3	83.40	3.49	0.32	2.90
7/18/2009	51	16.3	88.81	2.28	0.40	1.68
7/19/2009	52	18	93.64	1.33	0.85	3.45
7/20/2009	53	18.4	74.57	1.73	0.01	2.60
7/21/2009	54	20	68.49	2.16	0.03	3.70
7/22/2009	55	18.4	85.62	2.19	0.20	3.45
7/23/2009	56	20.3	86.12	2.37	0.40	0.39
7/24/2009	57	19.7	73.56	2.93	0.01	7.52
7/25/2009	58	21.4	72.08	4.71	0.12	3.98
7/26/2009	59	20.9	83.85	3.35	0.35	2.08
7/27/2009	60	21	77.80	2.88	0.12	5.35
7/28/2009	61	21.9	72.42	3.34	0.37	6.24
7/29/2009	62	20.8	71.86	2.73	0.28	1.99
7/30/2009	63	18.6	62.78	1.93	0.00	2.96
7/31/2009	64	20.3	70.82	2.52	0.00	0.00
8/1/2009	65	19.2	79.39	3.07	0.32	5.65
8/2/2009	66	19.7	70.25	2.77	0.00	0.88
8/3/2009	67	19.4	62.54	5.00	0.00	7.69
8/4/2009	68	22.6	76.43	2.92	0.01	4.45
8/5/2009	69	21.5	59.34	2.62	0.00	2.95
8/6/2009	70	19	52.15	2.18	0.00	0.95
8/7/2009	71	17.7	59.83	2.96	0.10	2.64
8/8/2009	72	23.1	61.34	5.46	0.01	5.32

Date	Day	Temperature (°C)	Relative Humidity (%)	Wind speed (m s^{-1})	Precipitation (cm)	Measured NH_3 emission (g m^{-2} day^{-1})
8/9/2009	73	27.1	61.02	5.02	0.52	7.72
8/10/2009	74	26.1	65.49	3.83	0.10	4.73
8/11/2009	75	23.3	83.29	2.51	0.53	4.22
8/12/2009	76	19.9	68.36	2.93	0.01	3.08
8/13/2009	77	21.4	64.41	1.41	0.00	2.96
8/14/2009	78	21.9	58.41	2.24	0.00	2.96
8/15/2009	79	22.6	59.98	2.87	0.00	1.87
8/16/2009	80	25.5	64.47	4.41	0.46	2.70
8/17/2009	81	24.4	83.05	3.22	1.90	1.77

Appendix C: Weather data and measured ammonia emission data used for model verification

Date	Day	Temperature (°C)	Relative Humidity (%)	Wind speed (m s^{-1})	Precipitation (cm)	Measured NH_3 emission (g m^{-2} day^{-1})
3/12/2009	1	-3.80	79.05	3.47	0.00	1.18
3/13/2009	2	-2.00	81.16	1.61	0.00	0.79
3/14/2009	3	1.90	77.20	2.10	0.00	1.61
3/15/2009	4	6.00	77.80	2.47	0.00	2.06
3/16/2009	5	9.20	86.53	1.80	0.20	2.06
3/17/2009	6	11.80	76.32	4.93	0.00	1.55
3/18/2009	7	12.30	80.13	3.79	0.16	2.31
3/19/2009	8	6.30	76.25	4.56	0.00	2.06
3/20/2009	9	-0.40	66.38	2.67	0.00	1.53
3/21/2009	10	5.10	67.27	2.94	0.00	1.49
3/22/2009	11	8.30	63.35	3.04	0.00	3.23
3/23/2009	12	7.00	76.88	7.26	0.01	2.02
3/24/2009	13	11.10	68.86	8.49	0.42	1.61
3/25/2009	14	13.50	77.76	5.43	1.04	2.26
3/26/2009	15	7.90	72.78	1.20	0.06	2.19
3/27/2009	16	7.90	84.28	3.77	0.00	2.23
3/28/2009	17	4.90	90.79	5.67	0.65	1.86
3/29/2009	18	3.80	93.66	5.44	2.01	1.37
3/30/2009	19	3.60	80.04	2.94	0.01	1.87
3/31/2009	20	8.70	80.19	6.68	0.49	1.41
4/1/2009	21	7.80	71.91	5.71	0.01	1.60
4/2/2009	22	12.00	72.85	4.57	0.53	1.67
4/3/2009	23	7.30	91.75	7.21	2.12	2.23
4/4/2009	24	4.30	80.64	3.07	0.01	0.78
4/5/2009	25	5.90	92.21	5.02	3.15	1.70
4/6/2009	26	2.50	92.26	6.33	1.45	2.63
4/7/2009	27	1.70	83.51	5.39	0.15	1.80
4/8/2009	28	4.60	77.57	3.58	0.04	1.14
4/9/2009	29	7.60	77.35	2.64	0.01	3.25
4/10/2009	30	7.50	91.25	5.61	1.00	1.63
4/11/2009	31	5.70	81.08	4.35	0.00	1.50
4/12/2009	32	5.50	81.16	3.68	0.01	1.99
4/13/2009	33	3.90	89.40	6.38	1.90	1.75
4/14/2009	34	5.20	94.72	3.81	0.75	1.17
4/15/2009	35	5.90	89.06	3.45	0.07	1.18

Date	Day	Temperature (°C)	Relative Humidity (%)	Wind speed (m s^{-1})	Precipitation (cm)	Measured NH_3 emission (g m^{-2} day^{-1})
4/16/2009	36	9.30	74.95	2.12	0.00	2.88
4/17/2009	37	11.20	62.97	1.68	0.00	4.42
4/18/2009	38	13.60	71.48	1.68	0.34	4.54
4/19/2009	39	13.50	95.18	2.54	1.80	2.26
4/20/2009	40	8.30	89.17	5.40	0.83	1.32
4/21/2009	41	5.20	90.95	5.23	0.57	0.81
4/22/2009	42	7.40	74.59	4.35	0.03	1.43
4/23/2009	43	8.90	70.97	4.42	0.00	2.65
4/24/2009	44	19.60	68.71	6.74	0.00	2.78
4/25/2009	45	22.60	75.25	6.12	1.01	3.47
4/26/2009	46	22.60	71.00	5.23	0.05	3.87
4/27/2009	47	22.00	74.79	6.70	1.26	4.61

Appendix D: Estimated ammonia emission for historical weather data

Period	County	Storage period	NH_3 emission					
			g animal^{-1} day^{-1}			g m^{-2} day^{-1}		
			Avg.	Min	Max	Avg.	Min	Max
1979 to 2014	Rockingham	Nov 01- Apr 30	2.15	1.20	4.43	0.33	0.19	0.69
		May 01- Oct 31	5.83	2.57	8.80	0.91	0.40	1.37
	Franklin	Nov 01- Apr 30	2.62	1.52	5.16	0.41	0.24	0.80
		May 01- Oct 31	5.99	2.81	8.80	0.93	0.44	1.37

Appendix E. MATLAB source code of the compartmental process-based model

```
%==========================================================================
% "ManureEmission"- simulates heat transfer, biochemical reactions,
% mass transfer and emission of ammonia gas from a manure storage tank
%
% The driver performs following tasks
%    1. assign all the inputs to the model
%       i. herd and manure management data
%      ii. weather data from a external excel file
%     iii. manure characteristics
%      iv. initial conditions
%    2. Call following functions
%      i. storagesize - calculates volume & surface area of manure storage
%     ii. manuredepth - calculates depth of manure in the storage
%    iii. FDsolver1Dheat - 1D Finite Difference Solver for Heat Transfer
%     iv. manureTAN - calculates concentration of TAN at each element
%      v. FDsolver1Dmass - 1D Finite Difference Solver for Mass Transfer
%     vi. ammoniaemission - calculates NH3 emission (flux) from the manure
surface
%
%==========================================================================
clear
close all
clc
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% INPUTS
% Storage period
numday  = 181;% 181 (Nov to Apr) , 184 (May to Oct) Number of days[days]

t1      = 305:1:365; % Julian day of the year (from Nov 01 to Dec 31)
t2      = 1:1:120;   % Julian day of the year (from Jan 01 to Apr 30)
Jt      = [t1,t2];   % Julian day for soil temperature estimate (from Nov
                       %%% to Apr)
% Jt      = 121:1:304;   % Julian day of the year for soil temperature
                       %%% estimate (from May to Oct)
t0      = 36.4;        % Time lag from the starting date[days]

%---------------------------------------------------------------------------
%% Herd and manure management

NAU     = 100;  % dairy cows, each weighing 635 kg ( 1 animal unit = AU)
MW      = 67 ;  % manure produced per cow,[kg/day](MWPS,2000, MWPS-7)

B       = 3.78; % chopped straw per cow, [kg/day] (MWPS,1993, MWPS-18)
WW      = 0;    % wash per cow,[kg/day]
MD      = 993;  % density of manure, [kg/m^3](MWPS,2000, MWPS-7)
BD      = 128;  % density of bedding, [kg/m^3](MWPS,2000, MWPS-7)
WD      = 1000; % density of water, [kg/m^3]
%---------------------------------------------------------------------------
%% dimensions and properties of the storage
Totalheight= 4.6;  % total depth allocated for the storage [m]
Depth0     = 0.3;  % initial depth of manure in storage [m]
Freeboard  = .6;   % Freeboard (24 inch)
% Area       = 9744; % Surface area open to atmosphere [m^2]
Soildepth  = 4.6;    % soil depth from surface to bottom of the tank(m)
```

```
Rain       = 0.6;     % annual rainfall [m]
S25y       = 0.154;   % 25-year, 24-hour storm [m]
Runoffarea = 4046;    % runoff area, [m^2]% approx. 1 acre 4046
sdays      = 180;     % number of days manure is stored [days]
%---------------------------------------------------------------------------
%% Initial conditions/ manure characteristics
mONnew    = 1.387;    % initial ON conc. in manure, [kg/m^3]
mTANnew   = 1.089;    % initial TAN conc. in manure, [kg/m^3]
pH        = 6.5;      % manure pH

CAIR      = 0;        % Ammonia conc. in air,[kg/m^3]
J         = 0;        % initial NH3 flux[kg/m^2/s]
%---------------------------------------------------------------------------
%% Create input data vectors for simulation period

dayManure  = NAU*(MW);  % kg, total mass of manure moved to storage
dayBedding = NAU*(B);   % kg, total mass of bedding material moved to storage
ManureIN   = dayManure*ones(numday,1); % manure
BeddingIN  = dayBedding*ones(numday,1);% bedding material
WaterIN    = WW*ones(numday,1);        % waste water
ManureLA   = 0;                        % manure removed from the storage(%)

%% Load weather data from an external excel file
%--------------------------------------------------------------------------
% WEATHER DATA
% filename   = 'weatherdata-JC-IN.xlsx';    % Daily weather data
% filename   = 'weatherdataSUMMER-RC-VA.xlsx';    % Daily weather data
filename   = 'weatherdataWINTER-RC-VA.xlsx';      % Daily weather data
% filename   = 'weatherdataSUMMER-FC-VA.xlsx';    % Daily weather data
% filename   = 'weatherdataWINTER-FC-VA.xlsx';    % Daily weather data

Tair1      = xlsread(filename,'C:C'); % Average temperature: unit [C]
RH         = xlsread(filename,'D:D'); % Relative humidity: unit [%]
Wind       = xlsread(filename,'E:E'); % Average wind velocity: unit [m/s]
PRECIP     = xlsread(filename,'F:F'); % Total precipitation: unit [cm]

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%
%--------------------------------------------------------------------------
% Parameters for heat and mass transfer of stored manure
%--------------------------------------------------------------------------
% Size of mesh dz
dz            = 0.01; % y-direction discretization length: unit[m]

% Physical and thermal properties of manure

Thermalparam  = [0.6814 MD 1992 1.2];
% Thermalparam(1) = Thermal conductivity, [W/m/C],(Nayyeri et al., 2009)
% Thermalparam(2) = Density, [kg/m^3],(MWPS, 1997)
% Thermalparam(3) = Heat capacity, [J/kg/C],(Nayyeri et al., 2009)
% Thermalparam(4) = Internal heat generation, [W/m^3],(Baral et al., 2013)

Diffusionparam = 2.5*10^-9;%
% Diffusionparam(1) = Diffusion coefficient of ammonia [m^2/s^-1] (Muck and
Steenhuis, 1982)

% Boundary conditions: Top boundary/ surface temperature
```

```
Tair        = max(0.01,Tair1);
Tsurface1  = 5.0 + 0.75*Tair;      % Surface temperature of manure:
unit[C],(Preud' homme and Stefan, 1993),based on daily air temperature
Told        = Tsurface1(1);         % Initial temperature value for "Told"
variable: unit[C],("Told"-old temperature profile of manure)

% Boundary conditions: Bottom boundary/ bottom temperature
% Parameters for soil temperature calculations
soilparam = [13 28 0.08];
% soilparam(1) = Ta, average soil temperature (C)
% soilparam(2) = A0, annual amplitude of the surface soil temperature (C)
% soilparam(3) = Dh, thermal diffusivity of soil (m^2/day)

% Control parameters for solver (FDSolver1Dheat & FDSolver1Dmass)
dt     = 3600;  % Size of a time step in seconds: unit [sec]
nt     = 24;    % Number of time steps
Store  = 24;    % store data for every 24 steps,

%%
%-------------------------------------------------------------------------
% Parameters for organic nitrogen mineralization
%-------------------------------------------------------------------------

Mineralizationparam = [1.2 0.06];
% Mineralizationparam(1)= Temperature coefficient (Zhang etal.,2005)
% Mineralizationparam(2)= Mineralization rate constant [1/day] (Zhang
etal.,2005)

%-------------------------------------------------------------------------
% Parameters for NH3 emission
%-------------------------------------------------------------------------

z0    = 1*10^-3; % roughness height [m]
P     = 1;       % atmospheric pressure [atm]
WindH = 1.5;     % anemometer height at which wind speed was measured [m]
%-------------------------------------------------------------------------
% Input parameters for evaporation
%-------------------------------------------------------------------------
Evaporationparam = [0.14 WindH 2.81e-3];

% Evaporationparam(1)  = parameter depends on surrounding terrain
% Evaporationparam(2)  = standard height at which wind speed is measured,[m]
% Evaporationparam(3)  = bulk aerodynamic transfer coefficient (Ham, 1999)

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%------------------------------------------------------------------------
%% initialize matrices/vectors for storing data

maxznode     = 4000;                 % max # of nodes on z direction
zMark        = zeros(1,numday);        % contains # of z-nodes for each day
(z-nodes change every day)
Tstore       = zeros(maxznode,numday); % matrix to store Temp data for each
day
Cstore       = zeros(maxznode,numday);
NH3flux      = zeros(numday,1);
NH3fluxgN    = zeros(numday,1);
NH3emission  = zeros(numday,1);
```

```
CTANsurf      = zeros(numday,1);
MHeight       = zeros(numday,1);
Tbottom       = zeros(numday,1);
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%
% Call storage size function
[Area]=
storagesize(Rain,Freeboard,S25y,Runoffarea,WW,sdays,NAU,MW,MD,B,BD,WD,Depth0,
Totalheight);

%% Day loop
for i=1:numday

% Call manuredepth function
    [depth,Depth,dVrem,dhdt,WaterEVAP]=
manuredepth(Area,MD,BD,WaterIN,ManureIN,BeddingIN,ManureLA,PRECIP,Tair,Wind,R
H,Depth0,Evaporationparam,dz);

    Height   = Depth(i);    % Total height of manure at ith time step (at ith
day)
    Htdelta  = depth(i);    % Height change of manure at ith time step (at
ith day)
    Tsurface = Tsurface1(i);% Manure surface temperature at ith time step (at
ith day)

% Call soiltemperature function
    t     = Jt(i);

    [Tbot]    = soiltemperature(Soildepth,t,t0,soilparam);
    Tbottom(i)=Tbot;
% Call aFDSolver function

    [T,nz,nznew]   =
FDsolver1Dheat(Height,Htdelta,dz,Thermalparam,Tbot,Tsurface,dt,nt,Store,Told)
;


    zMark(i) = nz;      % # of z-nodes for each day
    Told     = T;       % Temperature profile of manure at end of the ith
time step
    Tstore(1:nz,i) = T; % Store temperature profile of manure into a 2
dimension matrix

%  %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

    numnodes = nz; % maximum number of nodes per ith time step
%  disp(numnodes)
 if i==1
     mTANold = mTANnew; % kg N/m^3
     mONold  = mONnew;  % kg N/m^3
 end

     Ntemp = T; % Temperature at each node

 for j=1:numnodes
```

```
     [mTAN,ON] =
manureTAN(mTANold,mTANnew,Ntemp,mONold,mONnew,nz,nznew,Mineralizationparam);

 end
     mONold = ON;
     Cold   = mTAN;

% Call FDsolver1Dmass function
    [C,Cdata] = FDsolver1Dmass(Height,dz,Diffusionparam,Cold,J,dt,nt,Store);
     mTANold   = C;
    Cstore(1:nz,i) = C;
% Call ammoniaemission function
    WindS    = Wind(i);
    Tliq     = T(end); % manure temperature of the surface layer/element
    CTAN     = C(end); % TAN concentration of the surface layer/element
    Tai      = Tair(i);

    [NH3em,Ka,F] = ammoniaemission(Tliq,Tai,P,pH,CTAN,WindS,WindH,z0,CAIR);

    J = NH3em; % NH3 flux [kg N/m^2/s]

% NH3 emission from the manure surface

%      NH3flux(i)     = NH3em;              % NH3 flux [kg N/m^2/day]
    NH3fluxgN(i)    = NH3em*84000*10^3;           % NH3 flux (g N/m^2/day)
    NH3emission(i) = NH3em*84000*Area*10^3/NAU; % NH3 emission (g
N/animal/day)
    CTANsurf(i)     = CTAN;
    MHeight (i)     = Height ;
end
%==========================================================================
```

Sub-module “Storagesize”

```
function[Area]=
storagesize(Rain,Freeboard,S25y,Runoffarea,WW,sdays,NAU,MW,MD,B,BD,WD,Depth0,
Totalheight)
%==========================================================================
% "storagesize" calculates the required storage volume & surface area of
% manure storage
%
%==========================================================================

% NAU    = number of cows
% MW     = mass of manure produced per com per day[kg/day/cow]
% sdays  = number of days manure is stored [days]
% WW     = wash water per day [m^3/day]
% WWV    = Waste water volume [m^3]
% ROV    = runoff volume[m^3]
% Rain   = total precipitation for 6 months [m]
% MD     = manure density [kg/m^3]
% BV     = bedding volume
% VR     = volume reduction factor (range, 0.3 to 0.5)
% B      = mass of bedding use per day per animal [kg/day/cow]
% BD     = loose bedding density [kg/m^3]
```

```
VR   = 0.3;

ROV  = S25y*Runoffarea;      % Runoff volume [m^3]
BV   = VR*(NAU*B*sdays)/BD; % Bedding volume [m^3]
WWV  = WW/WD*sdays;         % Waste water volume [m^3]

S    = NAU*MW*sdays/MD+WWV+BV+ROV; % Total storage volume [m^3]
Manureheight = Totalheight - Depth0-Rain-Freeboard;

Area = S/Manureheight;        % surface area of the tank [m^2]
end
```

Sub-module "manuredepth"

```
function[depth,Depth,dVrem,dhdt,WaterEVAP]=
manuredepth(Area,MD,BD,WaterIN,ManureIN,BeddingIN,ManureLA,PRECIP,Tair,Wind,R
H,Depth0,Evaporationparam,dz)
%=========================================================================
% "manuredepth" function calculates depth of manure in storage using
%   1. Weather data - rainfall, air temperature, relative humidity and wind
speed
%   2. Management data - Mass of manure, mass of bedding material, mass of
wash water
%   3. Properties of manure storage - initial depth of manure, surface area
%=========================================================================
% Area = surface area of a rectangular manure storage: unit [m^2]

% INPUT data

% WaterIN    - mass of water used to wash manure: unit [kg/day]
% ManureIN   - mass of manure (urine + feces) produced by 100 dairy cows:
unit [kg/day]
% BeddingIN  - mass of bedding material produced by 100 dairy cows: unit
[kg/day]
% AvgPRECIP  - average precipitation: unit [cm/day]
% Tair       - air temperature: unit [C]
% Wind       - wind speed: unit [m/s]

%% From Zhang et al., 2005 ; Development of an Improved Process Based Ammonia
Emission Model, Lake Michigan Air Directors Consortium

a  = Evaporationparam(1) ; % parameter depends on surrounding terrain
h0 = Evaporationparam(2);  % standard height at which wind speed is measured:
unit [m]
Ce = Evaporationparam(3);  % bulk aerodynamic transfer coefficient for vapor
transport using Wing speed @ 2 m (Ham, 1999)
Rd = 287.04;               % gas constant: unit [J kg/K]

Ur         = Wind*(2/h0).^a;                     % wind speed at height hx
above ground: unit [m/s]
Ts         = 5.0+Tair.*0.75;                      % temperature of the
liquid surface: unit [C]
eTa        = 0.61078*exp((Tair*17.269)./(237.3+Tair));
ea         = RH.*eTa/100;                        % vapor pressure of air:
unit [kPa]
```

```
es         = 0.61078*exp((17.269*Ts)./(237.3+Ts)); % saturation vapor pressure
at the temperature of the water surface: unit [kPa]

E          = 0.622/(Rd*(Ts+273.15))*(es-ea)*Ur*Ce; % evaporation flux: unit
[kg/m^2/s]
WaterEVAP = E*Area*86400;                          % converting kg/s to kg/day
(kg/s*86400 = kg/day)
%%
% dV     - change of manure volume per day
% dhdt   - change of manure depth per day
% Depth0 - initial depth of manure
% MD     - density of manure
% BD     - density of bedding material
% WD     - density of water

dV         = ((ManureIN/MD)+(BeddingIN/BD)+(WaterIN/1000)+(PRECIP*Area/100)-
(WaterEVAP/1000)); % unit [m^3/day]
dVrem      = dV-dV*ManureLA/100;    % volume of manure remain after removal of
manure [m^3/day]
dhdt       = (dVrem/Area);          % unit [m/day]
if dhdt<dz
    error('Daily depth change is less than dz, Decrease dz')
end
[depth]    = round(dhdt*1/dz)/(1/dz);  % roundup depth change to find number
of dz layers

Depth      = Depth0 + cumsum(depth);   % Cumulative depth of manure in
storage: unit [m]

if Depth>4.6
    error('Manure depth exceed max. height, manure overflow')
end
end
```

Sub-module “soiltemperature”

```
function[Tbot]= soiltemperature(Soildepth,t,t0,soilparam)
%===========================================================================
% "soiltemperature" calculates the soil temperature at bottom of the
% storage
% Hillel, 1982. Introduction to Soil Physics, Academic Press, New York.
%===========================================================================
% Ta         = average soil temperature (C)
% A0         = annual amplitude of the surface soil temperature (C)
% Soildepth  = soil depth from surface to bottom of the tank(m)
% d          = damping depth (m)
% Dh         = thermal diffusivity of soil (m^2/day) = k/Cs
% Tbot       = temperature at bottom of the manure storage
% t          = time [days], e.g., starting from Jan 1
% t0         = time lag from the starting date[days]

Ta = soilparam(1);
A0 = soilparam(2);
Dh = soilparam(3);
```

```
omega = 2*pi/365;          % 1/day
d     = (2*Dh/omega)^1/2;
Tbot  = Ta + A0*(exp(-Soildepth/d))*sin((2*pi*(t-t0)/365)-(Soildepth/d)-
(pi/2)); % C
end
```

Sub-module "FDsolver1Dheat"

```
function
[T,nz,nznew]=FDsolver1Dheat(Height,Htdelta,dz,Thermalparam,Tbot,Tsurface,dt,n
t,Store,Told)

%   1D Finite Difference Solver for Heat Transfer in a manure storage
%   This function takes following inputs
%==========================================================================
%   Height     -- Total depth of manure in tank, [m]
%   Htdelta    -- Depth of newly added manure layer, [m]
%   dz         -- z-direction discretization length, [m]
%   Qg         -- Heat generation of stored manure, [W/m^3]
%   Parameters -- Array of manure parameters
%   Tbot       -- Temperature at bottom of the storage, [C]
%   Tsurface   -- Surface temperature of manure, [C]
%   Told       -- Initial value for old temperature field, [C]
%   dt         -- Size of time step, [sec]
%   nt         -- Number of time step computed, [days]
%==========================================================================

% Initial uniform temperature profile
% Physical and thermal properties of manure
kappa   = Thermalparam(1); % Thermal conductivity: unit [W/m/C]
density = Thermalparam(2); % Density : unit [kg/m^3]
cp      = Thermalparam(3); % Heat capacity: unit [J/kg/C]
Qg      = Thermalparam(4); % Internal heat generation, [W/m^3]

% Numerical parameters
nz    = round(Height/dz)+1; % Number of nodes in z-direction
nznew = round(Htdelta/dz);  % Number of new nodes in z-direction

q   = Qg;     % Uniform heat generation [W/m^3]
rec = Store; % Steps for storing data


% initial uniform temperature profile
Tint = Tsurface;

% construction of coefficient matrix A
s = kappa*dt/dz^2/density/cp;

A  = sparse(nz,nz);

for i = 2:nz-1
    A(i,i-1) = -s;
    A(i,i)   =(1+2*s);
```

```
    A(i,i+1) = -s;
end

 % Bottom boundary: fixed temperature
 A(1,1)  = 1;

 % Top boundary: fixed temperature

 A (nz,nz)= 1;

 % Set ICs for the simulation

T     = zeros(nz);
Tdata = zeros(nz,nt/rec);
% T(1:nz) = Told;


 if i==1
     T(2:nz-1) =Tint;
 else
     T(1:nz-nznew) = Told;       % portion of the matrix with old T
     T((nz-nznew)+1:end)= Tint; % portion of the matrix with new T
 end

 % Solve the matrix for different time step
 time = 0;    % starting time

 for n = 1:nt,
     % compute rhs for center domain
     rhs = zeros(nz,1);
     for i=2:nz-1,
         rhs(i)= T(i)+q/density/cp*dt;
     end
  % top and bottom
 rhs(1)  = Tbot;        % Fixed temperature at bottom
 rhs(end)= Tsurface;    % Fixed temperature at surface
% compute temperature at new time step

T_vector = A\rhs;

Tnew = T_vector;

% Store the temperature field for each 'rec' time step
if rem(n,rec)== 0,
    Tdata(:,n/rec)= T;
end

% Update the T field
T = Tnew;

% increase time

 time = time+dt;
```

```
 end
```

Sub-module "manureTAN"

```
function[mTAN,ON]=
manureTAN(mTANold,mTANnew,Ntemp,mONold,mONnew,nz,nznew,Mineralizationparam)
%===========================================================================
% "manureTAN" calculates concentration of TAN at each node
%
% 1. Mineralization of organic N to TAN
% 2. Remaining organic nitrogen after mineralization
% 3. Concentration TAN at each node
%===========================================================================
% kON   -- rate constant at any temperature T (1/day)
% theta -- temperature coefficient
% kON20 -- rate constant at temp 20C (1/day)
% Temp  -- manure temperature (C)
% mON   -- concentration of organic nitrogen in manure(kg/m^3)
% mTANold-- conc. of TAN remaining at end of previous day (kg/m^3)
% mTANgen-- conc. of TAN generated by new manure (kg/m^3)
% mTAN   -- conc. of TAN generated
%---------------------------------------------------------------------------
% Parameters for organic nitrogen mineralization
theta = Mineralizationparam(1); %
kON20 = Mineralizationparam(2); % 1/day

% Create vecotors for creating new mON and TAN concentration profile
mON    = zeros(nz,1); % concentration of organic nitrogen in manure
TANtot = zeros(nz,1); % concentration of total TAN in manure

% Create vecotors for creating new concentration profile
mON(1:nz-nznew) = mONold ;       % portion of the vector with old mON
mON((nz-nznew)+1:end)= mONnew;   % portion of the vector with new mON

% Create vecotors for creating new concentration profile
TANtot(1:nz-nznew) = mTANold;      % portion of the vector with old TAN
TANtot((nz-nznew)+1:end)= mTANnew;% portion of the vector with new TAN

kON         = kON20*theta.^(Ntemp-20);% correction of rate of mineralization
for temperature
mTANgen     = kON.*mON;                % TAN produced from [kg N/m^3]
mTAN        = TANtot + mTANgen;        % Total TAN after mineralization [kg
N/m^3]
ON          = mON-mTANgen;             % Organic Nitrogen remaining after
mineralization [kg/m^3]
end
```

Sub-module "FDsolver1Dmass"

```
function
[C,Cdata]=FDsolver1Dmass(Height,dz,Diffusionparam,Cold,J,dt,nt,Store)
%   1D Finite Difference Solver for Mass Transfer in a manure storage
```

```
%   This function takes following inputs
%==========================================================================
%   Height     -- Total depth of manure in tank, [m]
%   Htdelta    -- Depth of newly added manure layer, [m]
%   dz         -- z-direction discretization length, [m]
%   Parameters -- manure parameters
%   Cold       -- Initial values for old concentration field, [kg/m^3]
%   dt         -- Size of time step, [sec]
%   nt         -- Number of time step computed
%==========================================================================
% Initial uniform temperature profile

% Numerical parameters
nz    = round(Height/dz)+1;    % Number of nodes in z-direction
% nznew = round(Htdelta/dz);   % Number of new nodes in z-direction

rec = Store; % Steps for storing data

% Physical properties of manure
D   = Diffusionparam; % Diffusion coefficient [m^2/s^-1]

% A coefficient matrix
s = D*dt/dz^2;

A  = sparse(nz,nz);

for i = 2:nz-1
    A(i,i-1) = -s;
    A(i,i)   =(1+2*s);
    A(i,i+1) = -s;
end

 % Bottom boundary: zero flux
 A(1,1) = 1+2*s;
 A(1,2) = -2*s; % -2*s

 % Top boundary: changing flux
 A(nz,nz) = 1+2*s;
 A(nz,nz-1) = -2*s; % -2*s

%  A(nz,nz)= 1;

 % Set ICs for the simulation

C    = zeros(nz);
Cdata = zeros(nz,nt/rec);
% C(1:nz-1) = Cold;
C (1:nz)    = Cold;

% Solve the matrix for different time step
 time = 0;   % starting time

 for n =1:nt,
     % compute rhs for center domain
```

```
     rhs = zeros(nz,1);
     for i=2:nz-1, % i=2:nz-1
         rhs(i)= C(i);
     end
% top and bottom of right hand side vector

 rhs(1)   = C(1)-(0*2*s*dz/D);     % at bottom node
 rhs(end)= C(end)+(J*2*s*dz/D);   % at surface node

% compute concentration at new time step

C_vector = A\rhs;

Cnew = C_vector;

% Store the concentration field for each 'rec' time step
if rem(n,rec)== 0,
    Cdata(:,n/rec)= C;
end

% Update the C field
C = Cnew;

% increase time

time = time+dt;

 end
```

Sub-module “ammoniaemission”

```
function [NH3em,Ka,F] =
ammoniaemission(Tliq,Tai,P,pH,CTAN,WindS,WindH,z0,CAIR)
%=========================================================================
% "ammoniaemission" function calculates NH3 emission (flux) from the manure
% surface
%
%=========================================================================
%
% z  = height of the anemometer (m) 1.5
% uz = wind speed at an anemometer height (ms^-1)
% z0 = roughness height (m)

uz  = WindS;
z   = WindH;

U8 = uz*(log(8/z0))/log(z/z0);           % wind speed at 8m height;
Ka = 10.^(0.0897-(2729/(Tliq+273.15)));  % Dissociation constant for NH3
Jayaweera and Mikkelsen (1990)
F  = 1/(1+(10.^-pH)/Ka);                 % Fraction of free ammonia

Dh2oo2 = (7.28236*(10.^-15)*(Tliq+273.15))/(exp((1622/(Tliq+273.15))-
12.40581)); %Diffusivity of oxygen in water (m2/s)
```

```
Dairh2o =(3.00123*(10.^-8)*(Tai+273.15).^1.75)/(25.5231*P); % Diffusivity of
water vapor in air (m2/s)
Dh2onh3 = (6.14526*(10.^-15)*(Tliq+273.15))/(exp((1622/(Tliq+273.15))-
12.40581));%Diffusivity of NH3 in water(m2/s)
Dairnh3 = ((3.05519*10.^-8)*(Tai+273.15).^1.75)/(26.8288*P); % Diffusivity of
ammonia in air (m2/s)

kL =((1.6761*10^-6)*exp(0.236*U8))*(Dh2onh3/Dh2oo2)^0.57;     % Mass transfer
coefficient in the liquid phase(m/s)

kG =((5.1578*10^-5)+ (2*10^-3)*U8)*(Dairnh3/Dairh2o)^0.67;    % Mass transfer
coefficient in the gas phase (m/s)

H =((2.39*10.^5)/(Tliq+273.15))*exp(-4151/(Tliq+273.15));% Henry's constant

KL =(kL*H*kG)/(H*kG+kL);                % overall mass transfer coefficient
(m/s)

NH3em = KL*(F*CTAN-CAIR);               % ammonia flux (kg/m^2/s)
end
```

Appendix F. MATLAB code for sensitivity analysis

```
%#########################################################################
% Following program simulates the compartmental process-based NH3 emission
model and analyses the sensitivity of its input parameters
% Sampath A Karunarathne
% 03/12/2017
%#########################################################################
clear; close all; clc


nmax=1e4; % number of simulations

% model input parameters

% Sample matrix M1
Ta1   = unifrnd(0,30,nmax,1);      % random values of air temperature
RH1   = unifrnd(0,100,nmax,1);     % random values of relative humidity
Uz1   = unifrnd(0,8,nmax,1);       % random values of wind speed
Rain1 = unifrnd(0,6,nmax,1);       % random values of precipitation
P1    = unifrnd(0.876,1.025,nmax,1);% random values of atmospheric pressure
CAIR1 = unifrnd(0,2e-5,nmax,1);    % random values of ambient NH3 conc.
pH1   = unifrnd(6.5,7.5,nmax,1);  % random values of pH
CON1  = unifrnd(1.203,4.1,nmax,1);% random values of manure organic N
CTAN1 = unifrnd(0.66,2.6,nmax,1); % random values of manure TAN
MD1   = unifrnd(993,1009,nmax,1); % random values of manure density

% Re-sample matrix M2
Ta2   = unifrnd(0,30,nmax,1);
RH2   = unifrnd(0,100,nmax,1);
Uz2   = unifrnd(0,8,nmax,1);
Rain2 = unifrnd(0,6,nmax,1);
P2    = unifrnd(0.876,1.025,nmax,1);
CAIR2 = unifrnd(0,2e-5,nmax,1);
pH2   = unifrnd(6.5,7.5,nmax,1);
CON2  = unifrnd(1.203,4.1,nmax,1);
CTAN2 = unifrnd(0.66,2.6,nmax,1);
MD2   = unifrnd(993,1009,nmax,1);

% arrays to store MC output
Y1 = []; % results matrix Y1
Y2 = []; % results matrix Y2

% first-order results matrices:
YTa   = [];
YRH   = [];
YUz   = [];
YRain = [];
YP    = [];
YCAIR = [];
YpH   = [];
YCON  = [];
YCTAN = [];
YMD   = [];
```

```
% second-order results matrices
YTaRH=[];YTaUz=[];YTaRain=[];YTaP=[];YTaCAIR=[];YTapH=[];YTaCON=[];
YTaCTAN=[];YTaMD=[];YRHUz=[];YRHRain=[];YRHP=[];YRHCAIR=[];YRHpH=[];
YRHCON=[];YRHCTAN=[];YRHMD=[];YUzRain=[];YUzP=[];YUzCAIR=[];YUzpH=[];
YUzCON=[];YUzCTAN=[];YUzMD=[];YRainP=[];YRainCAIR=[];YRainpH=[];
YRainCON=[];YRainCTAN=[];YRainMD=[];YPCAIR=[];YPpH=[];YPCON=[];
YPCTAN=[];YPMD=[];YCAIRpH=[];YCAIRCON=[];YCAIRCTAN=[];YCAIRMD=[];
YpHCON=[];YpHCTAN=[];YpHMD=[];YCONCTAN=[];YCONMD=[];YCTANMD=[];

% total sensitivity coefficient
YTat   = [];
YRHt   = [];
YUzt   = [];
YRaint = [];
YPt    = [];
YCAIRt = [];
YpHt   = [];
YCONt  = [];
YCTANt = [];
YMDt   = [];


for i=1:nmax
    [EM1] =
ManureEmission(Ta1(i),RH1(i),Uz1(i),Rain1(i),P1(i),CAIR1(i),pH1(i),CON1(i),CT
AN1(i),MD1(i));
    Y1    = [Y1,EM1];
end

for i=1:nmax
    [EM2] =
ManureEmission(Ta2(i),RH2(i),Uz2(i),Rain2(i),P2(i),CAIR2(i),pH2(i),CON2(i),CT
AN2(i),MD2(i));
    Y2    = [Y2,EM2];
end

Eum1 = 1/nmax*(sum(Y1)); % Estimated unconditional mean matrix M1
Eum2 = 1/nmax*(sum(Y2)); % Estimated unconditional mean matrix M2

Euv1 = (1/(nmax-1))* sum((Y1.^2)-(Eum1.^2)); % Estimated unconditional
variance1
%Euv2 = (1/(nmax-1))* sum((Y2.^2)-(Eum2.^2)); % Estimated unconditional
variance2

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% first-order sensitivity coefficient of Air Temperature (Ta)
for i=1:nmax
    [EM3] =
ManureEmission(Ta1(i),RH2(i),Uz2(i),Rain2(i),P2(i),CAIR2(i),pH2(i),CON2(i),CT
AN2(i),MD2(i));
    YTa    = [YTa,EM3];
end
UPTa =(1/(nmax-1))*sum(Y1.*YTa);
STa =(UPTa-(Eum1*Eum2))/Euv1;
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
```

```
% figure
% bar (Ta1,YTa);
% xlabel('T_A_i_r(^oC)')
% ylabel('NH_3 gm^-^2day^-^1')
% disp(STa)

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Second-order sensitivity coefficient of Ta & RH
for i=1:nmax
    [EM13] =
ManureEmission(Ta1(i),RH1(i),Uz2(i),Rain2(i),P2(i),CAIR2(i),pH2(i),CON2(i),CT
AN2(i),MD2(i));
    YTaRH    = [YTaRH,EM13];
end
UPTaRH =(1/(nmax-1))*sum(Y1.*YTaRH);
STaRH =((UPTaRH-(Eum1*Eum2))/Euv1)-STa-SRH;
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Total effect coefficient of air temperature (Ta)
for i=1:nmax
    [EM58] =
ManureEmission(Ta2(i),RH1(i),Uz1(i),Rain1(i),P1(i),CAIR1(i),pH1(i),CON1(i),CT
AN1(i),MD1(i));
    YTat   = [YTat,EM58];
end
UPTat = (1/(nmax-1))*sum(Y1.*YTat);
STat  = 1-((UPTat-(Eum1*Eum2))/Euv1);
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
```