Title Page

DAIRY GAS EMISSIONS MODEL

Reference Manual

Version 3.2

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EXECUTIVE SUMMARY

The Dairy Gas Emissions Model (DairyGEM) is a software tool for estimating ammonia, hydrogen sulfide, greenhouse gas (GHG), and volatile organic compound (VOC) emissions of dairy production systems as influenced by climate and farm management. A dairy production system generally represents the processes used on a given farm, but the full system may extend beyond the farm boundaries. A production system is defined to include emissions during the production of all feeds whether produced on the given farm or elsewhere. It also includes GHG emissions and energy use that occur during the production of resources used on the farm such as machinery, fuel, electricity, and fertilizer. Manure is assumed to be applied to cropland producing feed, but any portion of the manure produced can be exported to other uses external to the system.

DairyGEM uses process level simulation to predict ammonia, hydrogen sulfide, and VOC emissions from manure in the housing facility, during long term storage, following field application and during grazing. Process-based relationships and emission factors are used to predict the primary GHG emissions from the production system. Primary sources include the net emission of carbon dioxide plus all emissions of methane and nitrous oxide. All emissions are predicted through daily simulations of feed use and manure handling. Daily emission values of each gas are summed to obtain annual values.

Ammonia emissions occur from the barn floor, during manure storage, following field application, and during grazing. Barn floor emissions are determined separately for cow and replacement heifer facilities. For each facility, hourly emission rates are a function of the type of housing facility, the nitrogen level in excreted manure, temperature, air velocity, and other factors. When long term manure storage is used, ammonia emissions continue from the storage facility as a function of manure nitrogen and solids content, storage design, temperature, and wind velocity. Following field application of manure, ammonia is rapidly emitted unless it is incorporated by a tillage operation or directly injected into the soil. For grazing animals, ammonia is emitted from urine and fecal excretions where the emission rate is again a function of temperature and wind velocity.

Hydrogen sulfide emissions are predicted using a process-based model similar to that used for ammonia. Since hydrogen sulfide is created under anaerobic conditions, most of this emission occurs during anaerobic storage of manure. The barn floor or drylot may also be an important source with minor emissions following field application and during grazing. Emissions from the barn floor are related to the sulfide content of the manure, manure pH, air temperature, and air velocity. These same factors influence emissions during long-term storage where the anaerobic conditions are conducive to sulfide production. When stored manure is broadcast on fields, any sulfide remaining in the manure is quickly lost and further formation ceases under these aerobic conditions. Very small amounts of hydrogen sulfide are produced and released from feces deposits on pasture as influenced by temperature.

VOC emissions are predicted from silage and manure sources. Silage sources include the face of an open silo, the feed mixer, and the feed bunk. Manure sources are the barn floor, during long term storage, following field application, and during grazing. Process simulation is used to predict emissions form each source for major compound groups. These group values are weighted by their reactivity in the atmosphere and summed to get a total emission in potential smog forming units.

Carbon dioxide emissions include the net annual flux in feed production and daily values from animal respiration and microbial respiration in manure on the barn floor and during storage. The annual flux in feed production is that assimilated in the feed minus that in manure applied to cropland. Emission of carbon dioxide through animal respiration is a function of animal mass and daily feed intake, and that from the floor is a function of ambient or barn temperature and the floor surface area covered by manure. Emission from a manure storage is predicted as a function of the volume of manure in the storage using an emission factor. Finally, carbon dioxide emission from fuel combustion in farm engines is calculated from the amount of fuel used in the production and feeding of feeds and the handling of manure.

Methane emissions include those from enteric fermentation, the barn floor, manure storage, and feces deposited in pasture. Emission from enteric fermentation is a function of the metabolizable energy intake and the diet starch and fiber contents for the animal groups making up the herd. Daily emissions from the manure storage are a function of the amount of manure in the storage and the volatile solids content and temperature of the manure. Emissions following field application of manure are related to the volatile fatty acid content of the manure and the amount of manure applied. Emissions during grazing are proportional to the amount of feces deposited on the pasture; that emitted in the barn is a function of the amount of manure deposited in the barn, barn temperature, and the floor area covered by the manure.

Nitrous oxide emissions are that emitted from crop and pasture land during the production of feeds with minor emissions from the manure storage and barn floor. An emission factor approach is used to estimate annual emissions in feed production where the emission is 1% of the fertilizer and manure N applied to cropland and 2% of that applied to pastureland. Emission from the crust on a slurry manure storage is a function of the exposed surface area.

Total greenhouse gas emission is determined as the sum of the net emissions of the three greenhouse gases where methane and nitrous oxide are converted to carbon dioxide equivalent units (CO2e). The net GHG emission and total energy use are determined through a partial life cycle assessment (LCA) of the production system including both primary and secondary sources. Primary emissions are those emitted from the farm or production system during the production process. Secondary emissions are those that occur during the manufacture or production of resources used in the production system. These resources include machinery, fuel, electricity, fertilizer, pesticides, plastic, and any replacement animals not raised on the farm. Secondary emissions from the manufacture of equipment are apportioned to the feed produced or manure handled over their useful life. By totaling the net of all annual emissions from both primary and secondary sources and dividing by the annual milk produced (corrected to 3.5% fat and 3.1% protein), a carbon footprint is determined in units of CO_2e per unit of energy corrected milk.

INTRODUCTION

Support for the Clean Air Act has increased pressure on regulatory agencies to address airborne emissions from animal feeding operations (**NRC, 2003**). Ammonia emitted in livestock production is of particular interest because of the potential environmental impact and the loss of nitrogen, a valuable nutrient that needs to be replaced with costly petroleum based fertilizers. Ammonia in the atmosphere can precipitate in acid rain contributing to surface water eutrophication and over-fertilization of ecosystems; it can also contribute to the development of small particulate matter in the atmosphere, which is a human health concern (**NRC, 2003; Arogo et al., 2003; Renard et al., 2004**).

Hydrogen sulfide is another toxic chemical that is regulated under the Clean Air Act. Hydrogen sulfide is produced as manure decomposes anaerobically, resulting from the mineralization of organic sulfur compounds as well as the reduction of oxidized inorganic sulfur compounds by sulfur-reducing bacteria (**Blunden et al., 2008**). Potentially, hazardous hydrogen sulfide levels can be produced in confined manure storage areas, while nuisance emissions can be generated in several other areas on a farm Chronic and acute exposure to certain levels of hydrogen sulfide can cause respiratory distress syndrome or pulmonary edema (**Predicala et al., 2008**), and fatalities have occurred with exposure to this poisonous gas. Aside from the health issues, hydrogen sulfide contributes to odor, one of the main public relation issues between dairy farmers and surrounding populations. Hydrogen sulfide also causes corrosion and deterioration of the concrete used in farm facilities. Considering the odorous, toxic and corrosive nature of this gas a variety of approaches aimed to control the production and emission of this compound in livestock facilities are being investigated (**Predicala et al., 2008**).

Volatile organic compound (VOC) emissions are a growing concern in some regions due to their potential role in smog formation (**Hafner et al., 2013**, **Howard et al., 2010**). Silage has been identified as a significant source of VOC emissions from farms, but manure also contributes. Very limited measured data on VOC emissions from farms are available. A process model was developed to predict emissions, but to this point the limited measured data available has not permitted a complete evaluation of the model. Model predictions related to VOC emissions should be considered as preliminary.

Greenhouse gas (GHG) emissions have also become a national and international concern. Important GHGs emitted by animal agriculture includecarbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O). Anthropogenic emissions have increased atmospheric concentrations of GHGs throughout the twentieth century, and this is thought to be contributing to an increase in the surface temperature of the earth and other climatic disturbances (**IPCC, 2001; 2007**). As a result, scientists and policymakers have focused on both quantifying and reducing anthropogenic emissions of GHGs world-wide.

Agriculture is believed to contribute about 6% of total GHG emissions in the U.S. with about half of this emission from livestock and manure sources (**EPA, 2005**). Although this contribution represents only a small percentage of CO_2 emissions, agriculture is the largest emitter of N_2O and the third largest emitter of CH_4, accounting for 75% and 30% of their respective national total emissions (**EIA, 2006**). The FAO (**FAO, 2006**) has reported that, world wide, agriculture contributed more GHG emissions than the transportation sector but in the U.S. emissions from all of agriculture are about 25% of that released through the combustion of transportation fuel (**EPA, 2008a**). Although

there is still uncertainty in specific numbers, agriculture appears to have a significant role in this international issue. Within agriculture, plant production is generally a net sink for carbon (C) in the production of food, feed, and fiber products. In livestock agriculture though, animals, particularly ruminants, release GHGs during feed digestion with further emissions during the handling of their manure.

With the growing concern over GHG emissions, a need has developed for expressing the total emission associated with a product or service. A term that has come to represent this quantification is the C footprint. This term originated from a methodology known as the 'ecological footprint' (**Kitzes et al., 2008**). This footprint was defined as the area of biologically productive land needed to produce the resources and assimilate the waste generated using prevailing technology. The term C footprint refers specifically to the biologically productive area required to sequester enough C to avoid an increase in atmospheric CO_2. This was originally calculated as the required area of growing, non-harvested forest land. Today, a more practical definition of C footprint is the net GHG exchange per unit of product or service. This net emission is best determined through a life cycle assessment that includes all important emission sources and sinks within the production system as well as those associated with the production of resources used in the system.

Measuring the assimilation and emission of gaseous compounds from farms is difficult, relatively inaccurate, and very expensive. Emissions are also very dependent upon farm management, so large differences can occur among farms. The various factors affecting emissions interact with each other as well as with the climate, soil, and other components, requiring a comprehensive evaluation to predict their overall impact. All individual factors and their interactions must be analyzed to identify cost-effective management practices that minimize net farm emissions. The National Research Council's Ad Hoc Committee on Air Emissions from Animal Feeding Operations identified the limitation of available methodologies to estimate national emissions from animal agriculture and recommended that the U.S. EPA develop a process-based modeling approach incorporating nutrient mass balance constraints and appropriate component emission factors (**NRC, 2003**). Mechanistic models representing volatilization processes as influenced by production and environmental conditions provide robust tools for evaluating management influences on emissions (**Ni, 1999**).

Model Scope

The Dairy Gas Emissions Model (DairyGEM) provides a relatively simple tool for predicting ammonia, hydrogen sulfide, and volatile organic compound (VOC) emissions and the integrated net global warming potential of all GHG emissions from dairy production systems. Secondary GHG emissions from the production of farm inputs such as machinery, fertilizer, fuel, electricity, and chemicals are also included to determine overall carbon carbon and water footprints for the milk produced. Our objective is to create a relatively simple and easy to use software tool that includes a simulation model that predicts each of the major gaseous emissions. Model development is being done in collaboration with basic research on gaseous formation and emission and whole farm monitoring work to evaluate model predictions. As such, the model will continue to evolve as new information is developed. This version of the model is provided as a tool for estimating net emissions and major environmental footprints of dairy production systems. As the model is further developed, improved accuracy in prediction is anticipated, but large changes in overall predictions are not expected.

DairyGEM is designed to estimate emissions of dairy production systems. This production

system generally represents a farm, but the system boundaries may be different than that of the physical farm (**Figure 1.1**). The boundaries of the production system include the production of all feeds used to maintain the herd. All manure nutrients are assumed to be returned and used in crop production unless a portion or all of the manure is designated as exported from the production system. Likewise, emissions during the production of all feed crops are included whether those feeds are produced on the same farm with the animals or they are purchased from another farm. This approach provides a comprehensive evaluation of the full milk production system that looks beyond the specific boundaries of the farm. A more complex tool, the Integrated Farm System Model, is available that evaluates emissions and footprints along with other nitrogen and phosphorus losses and farm economics (available at http://www.ars.usda.gov/Main/docs.htm?docid=8519).

Model Overview

DairyGEM includes a process based simulation of gaseous emissions from dairy barns, manure storages, following field application of manure and during grazing. These major processes that create gaseous emissions are simulated through time over many years of weather to obtain long term estimates of maximum and average emissions. The major components of the model include available feeds, animal intake and manure production, and manure handling. The feeds available and their nutrient contents are provided through user input. Balanced rations are prepared for each animal group on the farm and their feed intake is determined to meet their energy and protein requirements. Based upon feed intake, growth and milk production, the nutrient output in manure is predicted. From this nutrient excretion, emissions are predicted as a function of weather conditions and management practices.

Model Input

Input information is supplied to the program through two data files: farm and weather parameter files. The farm parameter file contains data that describe the farm facilities. This includes feeds and pasture available, number of animals at various ages, housing facilities, and manure handling strategies. These parameters are quickly and conveniently modified through the menus or dialog screens in the user interface. Any number of files can be created to store parameters for different farms for later use in other simulations.

The weather data (location) file contains daily weather for many years at a particular location. Files for each state in the U.S. are provided with the model. All files are in a text format so they can be easily created or edited with a spreadsheet program or text editor. When creating a new weather file, the exact format for the weather data file must be followed. The first line contains a site code, the latitude and longitude for the location, the atmospheric carbon dioxide level, and a parameter set to zero for the northern hemisphere and one for the southern. The remainder of the file contains one line of data for each day. The daily data includes the year and day of that year, solar radiation (MJ/m²), average temperature (°C), maximum temperature (°C), minimum temperature (°C), total precipitation (mm), and wind velocity (m/s). Only 365 days are allowed each year, so one day of data must be removed from leap years.

Model Algorithm

The model is a structured program that uses various objects or subroutines to represent processes on the farm. There are four major submodels that represent the major component processes. These major components are: feed availability, the herd, manure handling, and gas emissions. The functions, relationships, and parameters used in each of these submodels are described in detail in the

following sections of this reference manual. The emphasis of this section is to describe the linkage and flow of information for the overall model.

The model begins by gathering input information. All parameters stored in the requested farm parameter file are read. The model user can modify most of these parameters by editing the displayed values in the input menus and dialog boxes. If the file is saved, the modified values become permanently stored in the file or new files can be created using different names.

After the input parameters are properly set, a simulation can be performed. The first step in any simulation is to initialize various arrays of information in the model. This initialization sets all simulation variables to their starting condition.

The simulation is performed on a daily time step over each weather year. Weather data is read for the 365 days of the first year from the weather file. Each of the major farm processes is simulated through those weather conditions, and then the next year of weather data is read. This continues until 15 years are simulated.

In a given year, the simulation begins with feed utilization and herd production. Feed allocation, feed intake, milk production, and manure production are predicted for each animal group making up the herd. Most often these processes are simulated on an annual time step, where feed rations for all animals are formulated for the year based upon the feeds available (See **Dairy Herd** section). If pasture or a seasonal calving herd is used, feeding and herd production processes are simulated on a monthly time step. The pasture available on a given month and the stored feeds available that year are used to feed the animal groups each month. Supplemental feeds are purchased to meet protein and energy requirements of the herd.

Following the herd simulation, the manure produced is tracked through the scraping, storage, and application processes to predict gas emissions and the balance of nutrients around the maintenance of the herd (See **Manure and Nutrients** section). Manure production is predicted from the feed dry matter (*DM*) consumed and the digestibility of those feeds. Emissions during manure handling processes are then simulated on a daily time step as influenced by manure characteristics, temperature, rainfall, and solar radiation.

Following the simulation of manure handling processes, the simulation proceeds to the next weather year and the process is repeated. This annual loop continues until 15 years or a lesser number of years in the weather file are completed. After the simulation is complete, all performance and emission information is organized and written to output files.

Model Output

The model creates output in four separate files. Following a simulation, the files requested appear in overlaying windows within the primary DairyGEM window where they can be selected and viewed. The four output files are the summary output, the full report, optional output, and parameter tables. The summary output provides the option for two tables that contain the average feed use and gaseous emissions over the simulated period. Values include the mean and maximum daily emission over all simulated years. The more extensive full report includes these values and more. In the full report, values are given for each simulated year as well as the mean and variance over the simulated years.

Optional output tables are available for a closer inspection of how the components of the full simulation are functioning. These tables include a breakdown of animal rations and feed use. Optional output is best used to verify or observe some of the more intricate details of a simulation. This output can become lengthy and as such is only available when requested.

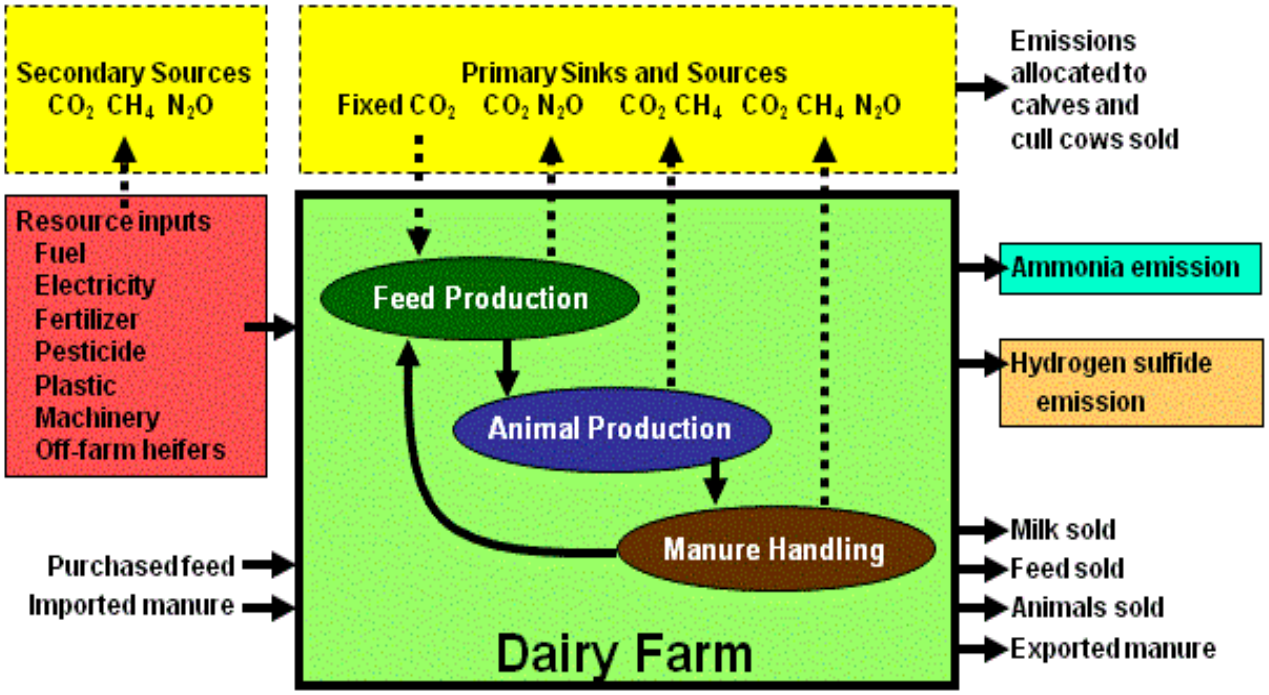
Parameter tables can also be requested. These tables summarize the input parameters specified for a given simulation. Any number of tables can be requested where tables are grouped for major sections of model input. These sections include: available feed, grazing, herd and facility, and manure handling parameters. These tables provide a convenient method for documenting the parameter settings for specific simulations.

The DairyGEM software can plot several components of the model output. These include the daily emissions of ammonia, hydrogen sulfide, methane, carbon dioxide, and total GHG (CO_2e) from the barn and manure storage, as well as the whole farm over a full year. These plots can be viewed on the monitor and printed on a compatible printer.

At the completion of a simulation, a bar graph is provided summarizing the predicted emissions. Three bars represent average annual emissions of ammonia, hydrogen sulfide, and total GHG emissions. Each bar is divided to show the emission occurring from the barn, manure storage, feed producing fields, and grazing animals. A pie chart is also available representing the carbon footprint of the production system. The chart provides a breakdown of the emissions from animal production, manure handling, engine operation, and the secondary (embodied) emissions from the production of farm inputs. Pie charts are displayed both including and excluding biogenic carbon dioxide sources and sinks.

Figure 1.1 - Production System Boundaries and Components

Important components, sources, and sinks considered in the emission of ammonia, hydrogen sulfide, greenhouse gases and the life cycle assessment determining the carbon footprint of dairy production systems.



AVAILABLE FEEDS

The model user specifies the amount of various forages and high moisture grain typically available for feeding the dairy herd. This should represent the average annual amounts of these feeds normally produced on the farm. For farms that rely heavily upon purchased forage, these values can represent average annual amounts purchased.

Concentrate feeds available for feed supplementation are also specified. These include protein and energy supplements. The amounts of each used are the total of that required to meet the protein and energy requirements of all animal groups making up the herd. These amounts are determined by the herd component of the model (See **Feed Characteristics** section).

The nutritive contents of each available feed are also set by the user. Although nutritive contents may vary, particularly within forage types, the values set must reflect average expected values. Forages can be set for both high and lower quality categories. High quality forage will normally be used in formulating rations for early lactating cows while lower quality forages will be used for older heifers, dry cows and late lactating cows depending upon how much is available (See **Dairy Herd** section).

Assigned nutritive contents for each available feed include: crude protein (*CP*), protein degradability, acid detergent insoluble protein (*ADIP*), net energy for lactation (*NEL*), and neutral detergent fiber (*NDF*). Concentrate feeds can also include a feeding limit. This limit controls the maximum amount of that feed that can be included in the ration of early lactating animals. When this limit is met, other available feeds must be used to meet remaining nutrient requirements of that animal group (See **Dairy Herd** section).

Pasture Use

A portion of the forage can be fed directly to animals through the use of grazing. The model user sets the average annual amount of pasture DM available to the herd and the number of months during the year when pasture is available. The amount of pasture available can vary within the grazing season. For simplicity, this variation is set within the model to reflect typical within season variation in pasture availability.

Predicting the nutritive content of grazed forage is very difficult since animals are selective in what they consume. Grazing animals tend to eat the plants and the plant parts that are highest in nutritive value. Therefore, prediction of the nutritive content of the whole crop is not relevant. For simplicity, the nutritive contents of pasture are assigned with different values during the various months of the grazing season. Assigned nutritive contents include: *CP*, protein degradability, *ADIP*, *NEL*, and *NDF*. In addition, the calculation of fill and roughage units (See **Feed Characteristics** section) requires values for the portion of the crop that is large particles and the *NDF* content of those large particles. Different values are assigned for each of the following time periods: April through May, June, July through August, and September through October.

Nutritive content information is assigned in the farm parameter file. Although these values can be changed, the values assigned represent a well managed pasture in the northern U.S. that uses rotational grazing (**Fales et al., 1995**). Crude protein is set at 26% in the spring with a drop to 23% in the summer and a rebound to 26% in the fall. Net energy for lactation starts at 1.57 in the spring and

slowly decreases to 1.42 in the fall. Neutral detergent fiber starts at 52% in the spring, increases to 55% in the summer, and drops to 53% in the fall. For lack of better information, the portion of a grass-based pasture that is large particles is set at 80% and the *NDF* content of this portion of the crop is set equal to the *NDF* of the whole crop. The rumen degradability of protein is set at 80% of *CP* and the *ADIP* content is set at 2% of *DM*.

Fill and roughage units for the pasture are determined as a function of the fill or roughage factors, *NDF* contents of small and large particles, and the portion of the crop in small and large particle pools (See **Feed Characteristics** section). Assigned fill factors for pasture are 1.2 for the large particle pool and 0.5 for the small particle pool. Roughage factors are 1.0 and 0.7 for large and small particles, respectively.

A grazing strategy is defined by the animal groups placed on pasture and the amount of time they have access to the pasture. Nine options are available for defining the animals on pasture: older heifers, older heifers and dry cows, all heifers, all heifers and dry cows, dry cows, lactating cows, all cows, older heifers and all cows, and all animals. Within these options, older heifers are defined as those over one year of age. The amount of pasture allocated to each animal group depends upon the number of animal groups allowed on the pasture and the time each day they are on pasture. Animals can be on pasture quarter days (4-5 hours per day) during the grazing season, half days (9-10) hours per day during the grazing season, full days (16-18 hours per day) during the grazing season, or full days (18-20 hours per day) all year. All year grazing implies that the animals are maintained outdoors year around even though pasture growth may not be available during several months of the year. When not on pasture, animals are maintained in the selected housing facility. If they are on pasture all year, a housing facility is not needed.

Pasture is allocated along with other available feeds to meet the nutrient needs of each animal group in the herd while making best use of the available pasture. This is done by developing a partial total mixed ration that best compliments the quantity and nutrient content of the pasture consumed (See **Dairy Herd** section). The pasture consumed by a given animal group is limited by either that available, grazing time, or the maximum amount of pasture forage that can be consumed by that animal. The maximum consumption is the maximum amount of this forage that can be included in the animal diet along with the available supplemental feeds while maintaining the desired production level (or as close to this level as can be obtained). Diets of each animal group are formulated with a linear program set to maximize forage use in rations (See **Dairy Herd** section).

Determining the amount of pasture forage available to each animal group requires proper allocation among the different groups of grazing animals. This allocation is done by comparing the available roughage from pasture with roughage available from other forages on the farm and the roughage requirement of the herd. Allocation is done each month to make best use of the pasture available that month, and stored feed inventories are modified to prepare for the allocation next month. The goal in the allocation each month is to use as much of the available pasture as possible, and to use stored forages at an appropriate rate so that stocks last most of the year. For example, if both alfalfa and corn silage are fed along with pasture, both forages are used each month at a rate where they will not be depleted much before the last simulated month of the year (See **Dairy Herd** section).

For any given month, the roughage available from pasture and other forages is the concentration of roughage units in each forage times the amount of that forage available. The

roughage requirement for meeting the forage needs of the herd is estimated as a function of the number of animals in each feeding group times their average body weight times their fiber intake constraint summed over all six animal groups (See **Dairy Herd** section). When animals are on pasture for less than full days, the amount of roughage that can be obtained from pasture is reduced in proportion to their time on pasture.

Rations are balanced for each of the six animal groups each month of the year. The portion of the total forage fed to each animal group that comes from pasture is set comparing available roughage to that required. If a surplus of pasture forage exists on the farm, all of the forage in the ration is provided by pasture for all animal groups that are grazed. For months when forage must be supplemented to meet herd needs, pasture is allocated first to grazing heifers and dry cows. Any remaining pasture is combined with available hay and silage or purchased hay to meet the roughage needs of the lactating cows. The ratio of pasture forage in the ration to that from hay and silage is set based upon the quantity of roughage available from each compared to that required to meet the animal's needs. Although pasture use is set to distribute available pasture across all animal groups using that pasture, the full amount of available pasture forage can be depleted. In any month where the available pasture is depleted before all animals are fed (and months when pasture is not available), any remaining animals are fed using hay and silage.

The amount of pasture consumed each month is limited by that available. The amount consumed is also limited by the forage requirement of all animal groups grazed. Any excess forage (available pasture forage minus that consumed) is considered lost. The model does not allow for pasture forage to be carried over from a given month to the next; therefore, forage available during a given month must be used during that period.

Feed Characteristics

Feed characteristics required to balance rations and predict feed intake include crude protein (*CP*), rumen digestible protein (*RDP*), acid detergent insoluble protein (*ADIP*), net energy of lactation (*NEL*) or net energy of maintenance (*NEM*), and neutral detergent fiber (*NDF*). The total digestible nutrients (*TDN*) content is also used to predict manure excretion. Typical or average parameters for major feeds can be found in **Rotz et al. (1999a)**. The NEM concentration in each feed is determined by converting NEL content of the feed to TDN, then converting TDN content to metabolizable energy (ME), and finally converting ME to NEM (**NRC, 2000**).

Two limitations of the *NRC* (**NRC, 1989**) system were revised to create a more flexible ration formulation routine. The first limitation was intake prediction; the *NRC* system only provided the dry matter intake (*DMI*) required for an animal to obtain adequate *NEL*. A maximum forage intake implies that ruminal fill is at the maximum that the cow will tolerate and still maintain a target milk production. A theoretical fill unit (*FU*) is defined to represent the filling effects of forages and concentrates based on their *NDF* concentration, fraction of particles that are large or small, and filling factors for large and small particle *NDF*. The *FU* concentration in each feed is determined by:

$$FU_i = (FFL_i)(NDFL_i)(LP_i) + (FFS_i)(NDFS_i)(SP_i) \qquad [2.1]$$

where FFL_i = fill factor of large particles in feed *i*,

$NDFL_i$ = *NDF* concentration of large particles in feed *i* (fraction of *DM*),

LP_i = large particles (e.g. alfalfa stem or corn stover) in feed *i* (fraction of *DM*),
FFS_i = fill factor of small particles in feed *i*,
$NDFS_i$ = *NDF* concentration of small particles in feed *i* (fraction of *DM*),
SP_i = small particles (e.g. alfalfa leaves or corn grain) in feed *i* (fraction of *DM*)
= $1.0 - LP_i$
and NDF_i = *NDF* concentration in feed $_i$ (fraction of *DM*).

$$= (NDFL_i)(LP_i)(NDFS_i)(SP_i) \quad [2.2]$$

Large and small particle fractions in forages are related to physical characteristics of the crop. For alfalfa and grass, stems are defined as large, slow degrading particles that occupy more space in the rumen. The small particles are leaves that rapidly degrade in the rumen and thus have less filling effect. For corn and small grain silages, 85% of the stover is defined to be large particles with the remainder of the plant being small particles. For grass forages, 70% of the crop is assumed to be large particles with the *NDF* concentrations in large and small particles being equal. For other forages, the proportion of large and small particles and their *NDF* concentrations vary with growing, harvest, and storage conditions.

Fill factors serve as weighting factors for increasing or decreasing the effect that the *NDF* in feed particle size pools has on rumen fill. Values are assigned that are inversely related to the digestibilities of those particles, i.e., a greater value represents a lower fiber digestibility and thus greater fill. Initial values were selected considering the relative fiber digestibilities of feed constituents with 1.0 being the average of all feeds. Large particles were defined to have over three times the filling effect of small particles in alfalfa and corn silage with less difference between the particle pools for grass, small grain, and pasture forages. Grain, high-moisture corn without cobs, and protein and fat supplements were assumed to be all small particles with a fill factor similar to that of alfalfa leaves and the grain in corn silage. Initial values were tested and refined in the model. The final values selected (**Table 2.1**) give equivalent milk production using each forage in diets balanced to similar *NDF* concentrations.

The second limitation of the *NRC* system for formulating rations is related to the minimum fiber requirement. A minimum fiber level in the diet is recommended to prevent the *NEL* density from going too high, which results in health disorders and milk fat depression. Reducing the particle size of fiber can reduce or eliminate its ability to meet the minimum fiber requirement.

A roughage unit (*RU*) system is used to ensure that adequate forage is included in rations. In addition, there is the option of selecting rations that minimize forage use when forage is not available or when it is expensive. Roughage units are then used to define the minimum forage allowed in lactating cow rations.

The *RU* system again considers particle size and the *NDF* concentration of feeds. The equation used to estimate *RU* for each feed is:

$$RU_i = RFL_i\,(NDFL_i)\,(LP_i) + (RFS_i)\,(NDFS_i)(SP_i) \quad [2.3]$$

where RFL_i = roughage unit factor of large particles in feed *i*,
and RFS_i = roughage unit factor of small particles in feed *i*.

Values for *RFL* and *RFS* are assigned to represent the relative physical effectiveness of the *NDF* in the two particle size pools. The effectiveness of *NDF* in long grass hay was assigned a value of 1.0, and chewing activity was used to estimate the relative physical effectiveness of the *NDF* in other forages. Large particles in all forages are assigned a roughage factor of 1.0. Factors for small particles are assigned so that the weighted average of the two particle pools provided values similar to the physically effective *NDF* values assigned by **Mertens (1997).**

Fill and roughage units vary with the characteristics of the feed. This is particularly true for forages where large particle content (stem or stover portion) and *NDF* concentration in those particles vary with growing, harvest, and storage conditions (**Rotz et al., 1989**). Typical *FU* and *RU* values for feeds can be found in **Rotz et al. (1999a)**. Although fill and roughage factors may be influenced by crop maturity and harvest method, this is not considered in the present model. For simplicity, assigned factors represented typical or normal conditions.

DAIRY HERD

A dairy herd consists of growing heifers, lactating cows, and nonlactating cows. The model is organized in five sections. First, the characteristics of the major animal groups are established. Next, available feeds are allocated to the animal groups. Each group's requirements for fiber, energy, and protein are then determined, and a linear program is used to find the lowest cost, nutritionally balanced mix of feeds to meet these requirements. Finally, based upon the diet fed, the quantity and nutrient content of the manure produced is determined.

Animal and Herd Characteristics

The herd is described as six animal groups: young stock under one year old, heifers over one year old, three groups of lactating cows, and nonlactating cows. There is flexibility in how the three groups of lactating cows are divided, but generally they represent early, mid, and late lactation cows. All cow groups are further subdivided between primiparous and multiparous animals with the portion of each set by the user as the replacement rate of the herd. The seven available animal types are large Holstein, average Holstein, small Holstein, Brown Swiss, Ayrshire, Guernsey, and Jersey.

Five characteristics are used to describe each animal group: potential milk yield, milk fat content, body weight (*BW*), change in *BW*, and fiber ingestive capacity. For cows, continuous functions are used to describe each characteristic over a full lactation (**Table 3.2**). A modified infinite Gamma function is used as the base model for each. This function has the following form:

$$Y = \left[A(w+s)^{b}\right] / \left[e^{c(w+s)}\right] \qquad [3.1]$$

where A = the intercept,
w = week of lactation,
s = shift factor (in weeks),
b = exponent of time,
and c = the exponential rate of change.

Parameters b and c define the shape of the curve and parameter A determines the peak. A scaler is used to adjust these relationships for different animal breeds and sizes (**Rotz et al., 1999a**).

Although the feeding groups can be modified, the normal procedure is to assume that 16% of the cows are in early lactation, 23% in mid lactation, 46% in late lactation, and 15% are nonlactating. Following a standard lactation cycle, this implies that the four groups represent weeks 0 to 9, weeks 10 to 22, weeks 23 to 48, and weeks 49 to 56, respectively. The animal characteristic functions are integrated over the appropriate weeks of the lactation cycle for a given group to determine the average characteristic over that period. The change in *BW* is the average daily change in *BW* over the period. Each characteristic of the group is then determined as the average of the primiparous and multiparous subgroups weighted by the number of animals in each subgroup. The herd is normally modeled with a 56 wk lactation cycle, but feed intake and milk production are totaled for the calendar year.

If a seasonal calving strategy is selected, the lactation cycle is set to a calendar year. Seasonal

calving places all cows on the same lactation cycle to better match their forage demand with available pasture forage. Either spring or fall calving cycles can be used. For a spring cycle, all cows are assumed to calve in March and they are dry during January and February. With fall calving, lactation begins in October and ends in July.

Feed Allocation

A feed allocation scheme is used to represent a producers approach to making the best use of feeds. This scheme uses decision rules to prioritize feed use. The feeds potentially available for feeding include any combination of: high-quality silage, low-quality silage, high-quality hay, low-quality hay, grain crop silage, high-moisture grain, and dry grain. Purchased feeds include corn grain, dry hay, a *CP* supplement, an *RUP* or oil seed supplement, and an animal or vegetable-based fat supplement. Because over feeding ingredients such as animal fat, blood meal, and meat and bone meal could result in unpalatable diets, user-specified limits prevent excessive inclusion of these feeds in rations.

The preferred forage for lactating cows is a mix of grain crop silage, high-quality alfalfa/grass silage, and high-quality hay. For nonlactating cows and growing heifers, preferred forages are grain crop silage, low-quality alfalfa/grass silage, and low-quality hay. Alternative forages are used when preferred forage stocks are depleted. If grain crop silage is not available, alfalfa or grass provides the forage. If high-quality hay or silage is preferred but unavailable, low-quality hay or silage is used and vice versa. When stocks of farm-produced forage are depleted, purchased forage is used.

A priority order for allocation is used to match forage quality with the animal groups that best use the available nutrients. Feeds are allocated first to animals with low nutrient requirements (nonlactating cows and heifers) using low-quality forage. After that, the high-quality forage is allocated to the early lactation cows to maximize their production. Feeding the lower producing cows last allows low-quality forage to be used by animals with lower nutrient requirements when stocks of high-quality forage are depleted. Similarly, feeding younger heifers after nonlactating cows and older heifers assures that, if a shortage of low-quality forage exists, animals with higher requirements receive the better feed.

The portion of each forage used in rations is based upon the amount of each forage type available and an estimate of the total forage requirement for the herd. Both available forage and forage requirement are modeled using fill units (*FU*). Total forage *FU* requirement for the herd is proportional to the sum of the maximum *FU* requirements of the individual animal groups:

$$ARF = \sum FR_j(FIC_j)(BW_j)(365/yr)(\textit{number of animals in a group}) \qquad [3.2]$$

where AFR = annual forage requirement for the herd, FU/yr,
FIC_j = fiber ingestive capacity for animal group j, FU/kg of BW/d,
BW_j = average BW in animal group j, kg,
and FR_j = portion of the maximum FU that normally comes from forage for animal group j.

Values of FR_j vary among animal groups and with the amount of forage used in diets. Average

values for nonlactating cows, older heifers, and young heifers are 0.80, 0.80, and 0.98, respectively. For maximum forage rations, values of FR_j for early, mid and late lactation groups are 0.83, 0.90, and 0.93, respectively. For minimum forage rations, these values are 0.80, 0.68, and 0.57.

The objective in proportioning forage is to give first priority to pasture and second priority to silage. The lowest priority is given to dry hay because it is the easiest to market. Total fill units available from each forage source are determined as the product of the available forage *DM* and the *FU* concentration in that forage. When available, grazed forage is used to meet as much of the annual forage requirement as possible. The portion of grazed forage permitted in the diet is limited to that available in the pasture when distributed among the grazed animal groups.

A portion of each forage is mixed to meet the remaining forage requirement set by the ratio of the *FU* available in that forage to the total *FU* of all available forages. After the portions of pasture and ensiled feeds in the ration of a given animal group are set, the remaining forage requirement is met with dry hay. This procedure maximizes the use of ensiled feeds, so that excess forage is normally dry hay.

Once a ration is formulated, the final step is to determine the number of animals in the group that can be fed that ration for a given time period from current feed stocks. The period is a full year for confined feeding systems, but a one-month period is used for grazing animals. If feedstocks do not allow all animals in the group to be fed the given ration for the full period, as many animals as possible are fed. Remaining animals of the group are fed rations balanced with alternate feeds. If milk production within the group is different because different rations are used, a weighted average milk production is computed for the group. Remaining feed quantities are updated each time a group of animals is fed.

Animal Nutrient Requirements

Rations for a representative animal of each animal group are formulated to meet four nutrient requirements: a minimum roughage requirement, an energy requirement, a minimum requirement of *RDP*, and a minimum requirement of *RUP*. The minimum roughage requirement stipulates that the total roughage units in the diet must meet or exceed 21% of the total ration *DM* (**Mertens, 1992** and **1997**). This assures that roughage in the formulated ration is adequate to maintain proper rumen function.

The energy and protein requirements for each animal group are determined using relationships from the Cornell Net Carbohydrate and Protein System, level 1 (**Fox et al., 2004**). The total net energy (*NE*) requirement is the sum of the requirements for maintenance, lactation, pregnancy, and growth. The maintenance energy requirement is determined as influenced by shrunk body weight (*SBW*), lactation, activity, and ambient temperature (**Fox et al., 2004**). The lactation effect on maintenance is determined using a thermal neutral maintenance requirement for fasting metabolism of 0.073 Mcal/day-$SBW^{0.75}$.

Activity is modeled as the sum of the daily requirements for standing, changing position, and distance traveled (**Fox et al., 2004**). Hours spent standing are set at 12, 14, 16, and 18 h/d for confinement, half-day intensive grazing, full-day intensive grazing, and continuous grazing, respectively. Distances traveled for these four options are 0.5, 0.8, 1.0, and 2.0 km/d, respectively. A

temperature effect and the resulting potential for heat stress are a function of the current and previous month's average temperature and the current relative humidity, wind speed, and hours of exposure to sun light (**Fox et al., 2004**). For simplicity, the relative humidity and wind speed are set at average values of 40% and 1.6 km/h, respectively. Exposure time is set at 0, 5, and 10 h/day for confinement, half-day, and full-day grazing systems. Cold stress effect is modeled considering an average hide thickness and hair coat (**Fox et al., 2004**), but this effect seldom occurs using temperatures averaged over a monthly time step.

Cows also include an energy requirement for lactation, and both cows and replacement heifers include a gestation requirement during pregnancy. Metabolizable energy requirement for lactation is proportional to milk yield as influenced by milk fat content (**Fox et al., 2004**). The gestation requirement is a function of the number of days pregnant and calf birth weight (**Fox et al., 2004**). Energy and protein requirements for lactation are increased by a lead factor to ensure that the requirements of a greater than average portion of the cows in each group are met. A lead factor of 12% is used for the early lactation group, and 7% is used for the mid and late lactation groups. Diets are formulated using these increased requirements, but feed consumption is determined to meet the original requirements.

Energy required for growth is a function of average daily gain (*ADG)* and equivalent empty body weight (**Fox et al., 2004**). To determine an equivalent empty body weight, a standard reference weight is assumed. This standard reference weight is 478 kg for cows and older replacement heifers and 462 kg for heifers less than 1 yr old.

Maintenance energy is based upon an animal in its third or higher lactation cycle. The total net energy requirement is adjusted by the multiple of maintenance of the animal group to model the efficiency of energy use as influenced by *DM* intake. The multiple of maintenance is the ratio of the total *NE* requirement to that needed for maintenance (**Table 3.3**). The total *NE* requirement is reduced by 4% for each multiple of maintenance less than three and increased by 4% for greater multiples of maintenance (**NRC, 1989**). Although increased intake actually affects the amount of energy extracted from the feed, this effect is included on the requirement side of the constraint equation to simplify the linear programming matrix (**Table 3.3**).

Finally, the *NE* requirement is increased to include an energy cost for excess protein in the diet. Each kilogram of excess protein requires 0.7 Mcal of *NE* to convert this protein to urea for excretion (**Tyrrell et al., 1970**). Excess protein is computed to include both *RUP* and *RDP* (**Table 3.3**). Excess *RDP* is that greater than the amount useful for making microbial *CP* (based on non-fat energy intake). Intake of *RUP* that causes total metabolizable protein to exceed the metabolizable protein requirement is considered excess.

The metabolizable protein requirement of each animal group is the sum of the maintenance, lactation, pregnancy, and growth requirements. The maintenance requirement is a function of *SBW*, lactation requirement is proportional to milk yield and milk protein content, gestation is a function of calf birth weight and days pregnant, and the growth requirement is related to *ADG* and the net energy required for growth (**Fox et al., 2004**). The metabolizable protein requirement is divided between *RDP* and *RUP* requirements. The *RDP* requirement is the microbial crude protein (*MCP*) requirement divided by 0.9 where *MCP* is defined as 0.13 times the digestible *DM* intake. Only energy coming from sources other than added fat is considered useful for making *MCP*. Added animal or vegetable fat helps meet the energy requirement, but this added energy does not yield bacterial cells.

The *RUP* requirement is the total metabolizable protein requirement minus the digestible microbial protein and the unavailable protein in the diet (**Table 3.3**). The digestible microbial protein is *MCP* multiplied by a conversion efficiency of 64% (**NRC, 1989**). Unavailable protein in the diet is set at 70% of the *ADIP* in forages and 40% of that in concentrates (**Weiss et al., 1992**). Because some of the *ADIP* of feeds is not included in the *RUP*, the ratio of digestible *RUP* to total *RUP* is set to 0.87 instead of the 0.8 recommended by the **NRC (1989).**

Feed Intake and Milk Production

Animal diets and performance are modeled using a linear program that simultaneously solves five constraint equations in a manner that maximizes herd milk production with minimum cost rations. The constraints include a limit on ruminal fill and constraints for each of the four requirements described above. The ruminal fill limit is the product of the fiber ingestive capacity and the average animal weight for the given animal group (**Mertens, 1987**). Thus, the sum of the fill units of the feeds in the ration must be less than or equal to this maximum ingestive capacity (**Table 3.3**). The second constraint is the roughage requirement. As described above, the sum of the roughage units of all feeds in the diet must be greater than 21% of the ration *DM* (**Table 3.3**).

The third constraint equation is that the energy consumed must equal the energy requirement. An equality is used to ensure that an energy balance is maintained and that intake and feed budgets are accurate for each animal group. The total *NE* from all feeds in the ration minus the energy cost of excess dietary protein must equal the requirement (**Table 3.3**). The energy cost of excess protein places some feed characteristic terms on the requirement side of the equation. To simplify the linear programming matrix, the equation is rearranged so that all feed characteristics are on the left side of the constraint equation.

The last two constraints specify the minimum protein requirement in the ration. The *RUP* constraint requires that 87% of the sum of the *RUP* in all feeds must be greater than or equal to the *RUP* requirement (**Table 3.3**). The *RDP* constraint requires that the sum of the *RDP* contents of feeds plus the rumen influx protein (15% of feed *CP*) be greater than or equal to the rumen available protein requirement (**Table 3.3**).

The five constraint equations are simultaneously solved with the objective of minimizing ration cost. Ration cost is determined using relative prices of feed ingredients. For grain and concentrates, the relative price is the long-term average price set by the model user. For forages, the relative price is set to zero for maximum forage diets. With a low relative price, the model uses as much forage as possible in ration formulation. Another user-specified option allows a minimum forage diet for lactating animals. For this option and these animal groups, the price of forage is set high relative to concentrates forcing a minimum amount of forage in rations.

The constraint equations are solved for each of the six animal groups making up the herd. Each solution provides a ration that meets the minimum roughage, minimum protein, and energy requirements without exceeding the limit for intake. If a feasible solution is not found for early lactating animals, the milk production goal for the group is reduced by 0.5% and the procedure is repeated until a feasible solution is found. For later lactation groups, milk yield predicted by the functions of **Table 3.2** is reduced in proportion to the decrease found in early lactation. A set of feasible solutions for all animal groups, therefore, gives both balanced rations and a herd production

level. In this case, milk production is the maximum that can be achieved considering the nutritional value of available forage and the type and amount of concentrates fed.

An option is available for balancing rations based upon crude protein content rather than protein fractions. With this option, the degradable protein constraint is replaced with a crude protein constraint. The feed protein available becomes the DM of each feed consumed times its protein content and the requirement becomes the set crude protein level times the total DM intake. An equality is used to force the fed protein to equal the set requirement. If a feasible solution is not found, a warning message is given. This indcates that the specified crude protein content is too low or too high to be met with the available feeds. The set crude protein content must be adjusted to allow a feasible solution.

The average annual milk production of the herd is also converted to fat and protein corrected milk using a standard milk fat content of 4.0% and milk protein content of 3.3% (**IDF, 2010**). A correction factor is determined as:

$$FPCF = 0.2534 + 0.1226\ (MF) + 0.0776\ (MP) \qquad [3.3]$$

where $FPCF$ = fat and protein correction factor
MF = milk fat content, %
MP = milk protein content, %

Average milk fat content is a user defined parameter, and milk protein is defined as a function of the fat content:

$$MP = 1.7 + 0.4\ (MF) \qquad [3.4]$$

Annual milk production is multiplied by FPCF to obtain fat and protein corrected milk.

Manure DM and Nutrient Production

Manure production includes fecal *DM*, urine *DM*, bedding, and feed lost into manure. Fecal *DM* is the total quantities of all feeds consumed by each animal group multiplied by the fraction of indigestible nutrients (1 - *TDN*) of each feed. The *TDN* values are reduced 4% for the low production group and 8% for the medium and high production groups to account for the reductions in digestibility under multiple increases of intake over maintenance intake. Urine production (kg/day) is predicted as a function of *DM* intake, *CP* intake, and milk production (**Fox et al., 2004**):

$$URINE = (3.55+0.16(DMIA) + 6.73(CPIA) - 0.35(MILKA))\ SBW / 454 \qquad [3.5]$$

where $DMIA$ = *DM* intake per 454-kg animal unit, kg/day,
$CPIA$ = *CP* intake per 454-kg animal unit, kg/day,
$MILKA$ = milk production per 454-kg animal unit, kg/day.

Urinary *DM* is set as 5.7% of total urine mass. Manure *DM* is increased by the amount of bedding used and by an additional 3% of the feed *DM* intake to account for feed lost into the manure. The quantity of wet manure is determined as manure *DM* divided by a user-specified value for manure

DM content.

The nutrients in fresh manure are determined through a mass balance of the six animal groups. Manure nutrients excreted equals nutrient intake minus the nutrients contained in milk produced and animal tissue growth. Nitrogen intake is determined from the protein content of the feeds consumed (*CP* / 6.25). Fractions of the N contained in milk and body tissue are set as average values for the herd: 0.53% for milk and 2.75% for body tissue. Body tissue produced is based upon animal mass exported from the herd, not the change in body weight of individual animals during their annual cycle. Although these nutrient concentrations may vary with animal and feeding conditions, average values provide an acceptable level of detail for this model.

Manure *N* is partitioned between organic *N* and ammoniacal *N*. Organic *N* is assumed to come primarily from feces. Fecal *N* is fecal protein divided by 6.25 where fecal protein is the sum of the indigestible bacterial protein, the indigestible nucleic protein, the indigestible undegraded protein, and the metabolic fecal protein (**NRC, 1989**). Manure organic *N* also includes *N* from feed lost into manure and *N* contained in bedding. Feed loss is assumed to be 3% of the total *N* intake, and the *N* from organic bedding materials is 0.69% of the bedding *DM*.

Fecal *N* from the herd is the product of the excretion for each feeding group, the number of animals in the group, and the length of the feeding period summed over all animal groups. Urinary *N* excretion is then assumed to be the total *N* excreted by all animal groups minus the fecal *N*. All urine *N* is considered to be urea, ammonium, or another form that can readily transform to ammonia following deposition. Organic *N* is considered stable during manure handling, and ammonia *N* is susceptible to volatile loss.

Table 3.1 - Fill and Roughage Factors

Fill and roughage factors assigned to large and small particle pools of each feed type.

	Fill Factors		**Roughage Factors**	
	Large Particles	Small Particles	Large Particles	Small Particles
Alfalfa hay and silage	1.35	0.4	1.0	0.6
Grass hay and silage	1.50	0.8	1.0	0.8
Pasture	1.40	0.5	1.0	0.7
Corn silage	1.45	0.4	1.0	0.7
Small grain silage	1.55	0.6	1.0	0.8
Grain and concentrates	---	0.4	---	0.4

Table 3.2 - Animal Characteristics

Functions used to describe dairy cow characteristics through a 56 wk lactation cycle.

Characteristics	Animal Type	Function
Milk Yield, kg/d	Primiparous cows	$MY_1(w^{0.178})(e^{-0.021w})$
	Multiparous cows	$MY_2(w^{0.2218})(e^{-0.034w})$
Milk Fat, %	Primiparous cows or Multiparous cows	$MF(w^{-0.24})(e^{0.016w})$
Body weight, kg	Primiparous cows	$BW_1(w+1.71)^{-0.0730}[e^{0.00869(w+1.71)}]$
	Multiparous cows	$BW_2(w+1.57)^{-0.0803}[e^{0.00720(w+1.71)}]$
Fiber ingestive capacity FU/(kg of BW)/d	Primiparous cows	$FIC_1(w+0.857)^{0.360}[e^{-0.0186(w+0.857)}]$
	Multiparous cows	$FIC_2(w+3.000)^{0.588}[e^{-0.0277(w+3.00)}]$

[1]MY = milk yield parameter, MF = milk fat content parameter, BW = body weight parameter, FIC = fiber ingestive capacity parameter, w = week in the lactation cycle, 1 to 56, and FU = fill units.

Table 3.3 - Ration Constraints

Constraints and associated equations used to develop dairy animal rations.

Constraint Equations		
Physical fill	$\sum x_i (FU_i)$	$\leq FIC_j (BW_j)$
Effective fiber	$\sum x_i (RU_i\text{-}0.21)$	≥ 0
Energy requirement	$\sum x_i (NE_i)$	$= [NED_j + 0.7 (ECP_j)] AMM_j$
Rumen degradable protein	$\sum x_i (CP_i) (RPD_i + 0.15)$	$\geq MCP_i / 0.9$
Rumen undegradable protein	$\sum x_i\ 0.87 (AUP_i)$	$\geq MPR_j - 0.64 (MCP_i)$

Associated Equations	
Adjustment for multiple of maintenance	$AMM_j = 0.92 / [1\text{-}0.04 (NER_j / NEM_j - 1)$
Available undegraded protein	$AUP_i = CP_i [1\text{-}RPD_i - UF_i (ADIP_i)]$
Microbial crude protein	$MCP_j = 0.13 (TDND_j) (DMI_j)$
Excess protein	$ECP_j = \sum x_i (CP_i) [RPD_i + 0.15 + 0.87 (1 - RPD_i - UF_i (ADIP_i)] - 0.7\ MPR_j + 0.47 (MCP_j)]$

$ADIP_i$ = acid detergent insoluble protein concentration in feed i (fraction of CP)

AMM_j = adjustment factor for multiple of maintenance in lactating animal group j

AUP_i = available RUP in feed i, fraction of DM

BW_j = body weight of animal group j, kg

CP_i = CP concentration in feed i, fraction of DM

RPD_i = rumen degradability of protein in feed i, fraction of CP

DMI = DMI estimate which resolves NEm intake with NEm and NEg requirements, kg/d

ECP_j = excess protein consumption, kg/d

FIC_j = fiber ingestive capacity, kg NDF/kg SBW/d

FU_i = fill units (NDF adjusted for particle size and digestibility; **Rotz et al., 1999a**) of feed i, fraction of DM

MCP_j = microbial crude protein production in animal group j, kg/d

MPR_j = metabolizable protein requirement of animal group j, kg/d

NE_i = NEm concentration in feed i, MCal/kg DM

$NEMD$ = diet NEm which resolves NEm intake with NEm and NEg requirements, MCal/kg DM

NEM_j = net energy requirement for maintenance of animal group j, MCal

NER_j = net energy requirement of animal group j, MCal

RU_i = roughage units (NDF adjusted for particle size and digestibility; **Rotz et al., 1999a**) of feed i, fraction of DM

$TDND_j$ = total digestible nutrient concentration of the diet, fraction of DM

UF_i = unavailable fraction of ADIP (0.7 for forages and 0.4 for concentrates).

x_i = amount of feed i in the diet, kg DM/d

$1\sum$ means the summation over all feeds in the ration

MANURE AND NUTRIENTS

The manure component simulates a variety of options in manure handling including methods of manure collection, storage, transport, and application. Collection methods include hand scraping or gutter cleaner, an alley scraper or tractor mounted scraper, and a flush system. Storage methods include a stack for dry manure, a cement pad and buck wall for short-term storage of semi-solid material and tanks or earthen retention ponds for slurry or liquid manure storage. Transport and application is done with spreaders or irrigation equipment with manure spread on field surfaces, injected into the soil, or irrigated.

The model allows the user to specify up to two manure collection methods used on the farm. For each collection method, the user must assign appropriate inputs that include manure type, storage method, and machinery for field application of manure.

All N flows through the dairy herd are tracked to determine a nutrient balance. Nitrogen intake is that consumed in feeds. Nutrient levels in feeds are set by the user where *N* concentration is protein content divided by 6.25. Nutrient outputs include milk, animal tissue, and manure. Nutrient levels in milk and animal tissue are those given above in the **Dairy Herd** section. The efficiency of N use is the N obtained in milk and animal tissue divided by the total consumed in feed. A similar but simpler procedure is used to predict excretions of phosphorus, potassium and carbon. Typical contents are assumed in the milk produced and growth tissue and the remainder is excreted in manure.

Manure Handling

The quantity and nutrient content of the manure produced by the animals on the farm is a function of the feeds fed as described in the **Dairy Herd** section above. In each manure collection method, the total quantity of manure handled is a function of the amount and type of bedding used, the amount of water contained in the manure, and the percentage of total manure handled (assigned by the user). Bedding options include manure solids, straw, sawdust, and sand. For each collection method, the user can select the bedding type and specify the amount of bedding used per mature animal in the herd. The quantity of bedding used is determined by calculating the number of animal units on the farm with the mass of an animal unit being the average mass of a mature cow in the herd. This animal mass varies with the animal breed selected. The number of animal units thus reflects the total animal mass on the farm (including young stock) expressed in units of mature animals. Bedding use is the product of mature animal units and the use per animal unit.

The quantity of wet manure handled is determined from total manure *DM* and the user selected manure type. Manure types are dry, solid, semisolid, slurry, and liquid. Total manure *DM* includes that excreted by animals plus that of bedding and feed lost into the manure. Total manure handled is manure *DM* handled divided by *DM* content. Although *DM* content can be adjusted, preset values are 70, 20, 13, 8, and 5% for dry, solid, semisolid, slurry, and liquid manures, respectively. Dry manure is manure removed from dry lots, which is typically very dry when removed. Solid manure is that from packed beds, and semi-solid represents fresh manure plus bedding. Slurry manure typically includes milking facility wastewater and additional water from rain runoff from animal holding areas. For liquid manure, additional water from rain or other sources such as flush water is assumed and a liquid/solid separator may be used.

Two different manure handling systems can be used on a simulated farm. The first, designated

as the primary system, would normally be the system handling most of the manure. If a secondary system is used, a designated portion of the total manure dry matter is handled with this system and the remainder is handled in the primary system. Manure nutrients entering the two systems are split in proportion to the excreted dry matter handled by each. Both systems are simulated through the same processes except that an anaerobic digester can only be associated with the primary system.

Storage

Manure storage options include long-term storage in tanks or clay- or plastic-lined earthen retention ponds. Essentially any storage size can be selected by setting an average diameter and depth for the structure. The type and size of storage selected controls the amount of manure that can be stored, and it influences the amount of volatile loss that occurs from storage.

Storage options include short-term, four-month, six-month, and twelve-month storages. With short-term storage, manure must be hauled each day. This option can also be used to represent short-term storage on a slab or in a small pit. With a four-month storage, manure is emptied three times each year in the spring, summer, and fall. With a six-month storage, manure is emptied twice each year in the spring and fall. For twelve-month storage, it is emptied once a year in the spring. For either of the two long-term storage options, the manure produced during that period of time each year is compared to the storage capacity. If the storage is too small to hold the manure produced, the simulation continues but a warning message is given that the user should consider increasing the storage size.

When stored in a concrete or steel tank, manure can be added to the top or bottom of the tank. Top loading represents scraping or pumping of the manure onto the top surface; whereas, bottom loading represents the pumping of manure into the bottom. With bottom loading, a crust can form on the manure surface. This crust helps seal the surface, reducing volatile loss from the storage facility.

Covered or enclosed tanks can also be used for manure storage to reduce volatile losses. A covered storage is defined to have some type of cover that is relatively effective in preventing volatile loss. An enclosed tank is more effective with a sealed top that is vented to prevent pressure buildup within the tank. Thus, volatile emissions are minimal with an enclosed top, but small amounts still escape through the vent. A flare is used to burn the escaping biogas to reduce methane emission.

Application

Manure deposited during grazing is applied to the grazed crop, and this portion is not included in the value for total manure handled, i.e. the manure handled is the total produced minus that deposited during grazing. The amount applied during grazing is proportional to the time the animals spend in the pasture. When animals are maintained on pasture year around, about 85% of the total manure produced is deposited during grazing. For seasonal grazing, this value is about 40%.

Manure application is simulated on a daily time step. For daily hauling (or short-term storage) of manure, hauling and application occur each day with that applied being that produced on the given day. When a storage facility is emptied, manure is applied each day suitable for field operations until the storage is emptied. The amount applied each day is the total manure accumulated during the storage period divided by the days available for field application.

Manure Import and Export

Manure can be brought into the production system or exported to another use. This affects the nutrient balance of the farm and the predicted emissions. When manure is imported, the farm owner provides a service to the manure producer by supplying land for disposal of the manure. The farm can also obtain benefit from the use of the added nutrients. Any emissions following land application are attributed to the production system receiving the manure.

When fresh manure or separated manure solids are exported, that portion of the nutrients are removed from the production system and any emissions following land application are not attributed to the farm. When manure is exported in the form of compost, that portion of the nutrients are again removed, but emissions during the composting process are attributed to the farm.

Nutrient Import

When manure is carried onto the farm, the amount of manure imported and the dry matter and nutrient contents of that manure are provided by the model user. The amount of manure dry matter applied to cropland is the sum of that produced on the farm and that imported. Likewise, the total quantity of *N* is the sum of that produced and that imported.

The flow, transformation, and loss of the added manure nutrients follows the same relationships used for the farm-produced manure. The manure carried onto the farm has volatile losses following field application, but losses that occur in the barn or during storage and handling are not included. These losses have occurred before the manure is brought onto the farm, which should be considered when setting the *N* content of the imported manure. The *N* volatilization rate following field application is set at the same rate as that for manure produced on the farm. This is a function of the total ammoniacal *N* content of the manure and the time between spreading and incorporation of the manure. The fraction of *N* that is in a volatile form is set to be the same as that produced on the farm. If no manure is produced on the farm, the volatile *N* content of the manure is set at 40% of the total *N* in the imported manure.

Nutrient Export

Manure nutrients can leave the farm as fresh manure, separated solids, or compost. Similar but somewhat different relationships are used to model the effect of each type of export. The manure dry matter exported is set as a portion of the total manure dry matter produced on the farm. This can be anywhere from 0 to 100% of the manure solids produced.

When the export is fresh manure, the nutrients removed are the nutrient contents of the manure following storage (or following barn scraping if no storage exists) times the manure dry matter removed from the farm. The *N* content is that determined after volatile losses occur in the barn and during storage (if manure storage is used). For the portion of the manure exported from the farm, the *N* loss that would have occurred following land application are eliminated.

When separated manure solids are removed from the farm, the nutrient removal is the dry matter removed times the nutrient contents of the removed solids. By default in the program, the *N*, *P*, and *K* contents in organic bedding material (straw or sawdust) are set at 1.4, 0.3, and 0.4%, respectively (**Chastain et al., 2001**; **Meyer, 1997**). With sand bedding, fewer nutrients are retained in the solids, so the *N*, *P*, and *K* contents are set at 0.8, 0.15, and 0.4% respectively (**Van Horn et al., 1991**; **Harrison, unpublished data).** The nutrient contents of the removed solids can also be set in

the farm parameter file. When values are set, the default values in the program are overwritten by the user specified values.

The amount of manure handled and the nutrients in the remaining manure are adjusted for the solids removed. The solids removed are assumed to contain 40% *DM*. The manure applied to feed producing cropland is that produced minus the solids removed and the moisture contained in those solids. The *DM* content of the remaining manure is the original *DM* minus that exported divided by the remaining quantity of manure. Nutrients remaining in the production system following separation are those in manure received from the barn minus that leaving in separated solids. Nutrient losses during storage and following land application are reduced in proportion to the amount removed.

The remaining option is to remove manure and nutrients in the form of compost. The manure removed as compost reduces the amount of manure stored and applied to cropland. When a portion of the manure is exported as compost, the nutrient content of the manure removed is that following barn scraping. The portion removed reduces *N* losses during storage and field application in proportion to that removed. There are *N* losses during the composting process, which are included as loss from the farm. The portion of the *N* lost by volatilization during composting is assumed to be the volatile *N* content in the manure following scraping plus 25% of the organic *N* content (**Sommer, 2001**; **Ott et al., 1983)**. This *N* loss is added to that that occurs during the storage of farm-produced manure increasing the total volatile *N* loss from the farm.

Anaerobic Digestion

Anaerobic digestion of manure on farms, particularly dairy farms, is becoming more common. The major incentives are energy recovery, odor reduction, and reductions in greenhouse gas emissions. In an anaerobic digester, volatile solids in manure are decomposed by microorganisms in a warm anaerobic environment to produce biogas. Biogas generally contains about 60% methane (the main component of natural gas) and 40% carbon dioxide on a volumetric basis. Biogas can be burned to create heat or used as stationary engine fuel, normally to power generators for creating electricity. Burning of the biogas converts methane to carbon dioxide, a less potent greenhouse gas. The energy produced is primarily used on the farm, but it can also be sold to power and natural gas companies for resale as “green” energy. The anaerobic digester is modeled in three major components: energy production, energy use, and effects on manure.

Energy production

Biogas is produced through the microbial degradation of volatile solids in the manure. The rate of volatile solids flow into the digester is determined from the manure dry matter produced and loaded into the digester and the volatile solids content of that dry matter:

$$Q_{vs} = C_{vs} \; Q_m \qquad [3.1]$$

where

Q_{vs} = flow rate of volatile solids into digester, kg/d

C_{vs} = volatile solids concentration in manure influent, fraction

Q_m= loading rate of manure dry matter, kg/d

The manure loading rate is the amount of manure excreted and collected from barns (See the **Manure**

and Nutrient Production section). The volatile solids content of the manure is primarily a function of the animal groups that produced the manure (see **Table 4.3**).

The amount of methane produced is a function of an assigned productivity and a conversion efficiency:

$$CH4 = Q_{vs}\ (E_{vs})\ (CH4_{yld})\ /\ 100 \qquad [3.2]$$

where

$CH4$ = methane production rate, kg/d

E_{vs} = efficiency of volatile solids conversion, %

$CH4_{yld}$ = methane productivity per unit of volatile solids destroyed, kg CH_4/kg VS

The methane productivity from volatile solids is dependent on characteristics of the manure, and is not expected to vary substantially. The methane productivity is set at 0.35 kg CH_4/kg VS, based on predicted and measured values reported by **Hill (1984)** and measured values given in **Converse et al. (1977)** and **Moller et al. (2007).** Over all studies, reported values range from 0.23 to 0.39 kg CH_4/kg VS. The conversion efficiency is a user defined characteristic of the digester, and may range from about 20% to 45% for dairy manure, with typical values close to 30% (**Converse, 1977; Hill, 1984; Moller et al., 2004**). A similar relationship is used to predict carbon dioxide production where the productivity is 0.9 kg CO_2/kg VS. In practice, carbon dioxide productivity also varies. Values calculated from the data in **Converse et al. (1977)** range from 0.74 to 0.98 kg/kg, but this parameter has only a small effect on greenhouse gas emissions.

The power available in the biogas produced is a function of the energy content (lower heating value) of methane:

$$P_{bg} = E_{CH4}\ (1 - L_{BG}\ /\ 100)\ (CH4)\ /\ 3.6 \qquad [3.3]$$

where

P_{bg} = power available in the biogas produced, kW-h/d

E_{CH4} = lower heating value of methane, 50 MJ/kg CH_4 (**Masters, 2004**)

L_{BG} = biogas leakage rate, %

3.6 = conversion from MJ to kW-h

The biogas leakage rate is assigned by the model user; a typical value is 1% (**EPA, 1999**).

Biogas use

The total power in the biogas produced can be used to heat water in a boiler, generate electricity, or burned in a flare. The amount used to heat water is set by the model user as a portion of the total available:

$$P_{BLR} = BLR_{use}\ (P_{bg})\ /\ 100 \qquad [3.4]$$

where

P_{BLR} = biogas power used in the boiler, kw-h/d

BLR_{use} = portion of biogas used to heat water, %

All remaining biogas power is available to generate electricity. Electricity production is a function of the efficiency of electrical generation and the capacity of the generator. The amount of electricity produced each day is limited by either the capacity of the generator and the time it is operating or the amount of biogas available:

$$ELECT = \min (24\, F_{run}\, (CAP_g),\ E_g\, (P_{bg} - P_{BLR}) / 100) \qquad [3.5]$$

where

$ELECT$ = electricity produced, kW-h/d

F_{run} = portion of time engine-generator sets are running, %

CAP_g = electric generation capacity, kW

E_g = efficiency of electric generation, %

The portion of time the engine-generator sets are running, the generation capacity, and the generation efficiency are all set by the model user to represent the characteristics of the system modeled. The efficiency of the engine-generator varies with the type and age of the equipment used, but will generally be about 25%. The goal is to keep the engine-generator sets running most of the time, but maintenance, repairs, and other shut downs reduce this time.

Any remaining biogas that is not used for electric generation and water heating is burned in a flare. The power disposed of in the flare (P_{flr}) is determined as:

$$P_{flr} = P_{bg} - P_{BLR} - ELECT / (E_g / 100) \qquad [3.6]$$

Burning the methane converts the lost carbon to carbon dioxide, which reduces the global warming potential of the emission (see the **Methane Emission** section). This power represents a loss of energy, and thus should be minimized.

Effects on manure effluent

A major benefit from anaerobic digestion of manure is a reduction in the volatile solids content in the effluent. The effluent is normally stored in a tank or basin, the same as that used to store raw manure without digestion. Because of the reduction in volatile solids, the odor and methane produced from this storage is less than that occurring from untreated manure.

The effluent dry matter leaving the digester is reduced to account for volatile solids converted to methane and carbon dioxide:

$$Q_e = Q_m - E_{vs}\, (Q_{vs}) \qquad [3.7]$$

where

Q_e = digester effluent dry matter entering long term storage, kg/d

The volatile solids leaving the digester are determined as the amount entering minus that decomposed in the digester. Total volatile solids can be separated into degradable and slow degrading or non

degradable fractions. The more degradable volatile solids in the effluent are determined as:

$$VS_d = (B_o / E_{CH4pot} - E_{vs})\, Q_{vs} \qquad [3.8]$$

where

VS_d = degradable volatile solids in effluent, kg/d

B_o = achievable emission of methane during anaerobic digestion, g/kg VS

E_{CH4pot} = potential methane productivity during storage of the manure, g/kg VS

The achievable emission of methane and potential methane productivity are assigned characteristics of the raw manure; typical assigned values are 0.2 and 0.48, respectively (**Sommer et al., 2004**; see the **Methane Emission** section). The slow degrading or non degradable volatile solids in the effluent are determined as:

$$VS_{nd} = (1 - B_o / E_{CH4pot})\, Q_{vs} \qquad [3.9]$$

where

VS_{nd} = nondegradable volatile solids in effluent, kg/d

The remaining volatile solids in the manure control the methane emission rate of the stored digester effluent (see the **Methane Emission** section).

The digestion process also affects the nitrogen fractions in the manure. A portion of the organic N in the raw manure is decomposed to TAN. Based upon data collected by **Gooch et al. (2007)**, the amount of TAN in effluent entering long term storage is modeled as 15% greater than that entering the digester. This increase in TAN potentially increases the ammonia emissions from the storage and field applied effluent (see the **Ammonia Emissions** section).

AMMONIA EMISSIONS

Research over the past century has developed a good understanding of how volatile compounds in solution form, migrate, react, and ultimately volatilize to the atmosphere. Mathematical models have been developed and validated that accurately represent these processes. Through adaptation of these relationships, emissions such as ammonia from manure can be predicted for livestock farming systems. Predicted emissions from each important source are summed to determine the total farm emission.

Formation and Emission Processes

Total manure *N* consists of organic *N* and ammoniacal *N* (See the **Dairy Herd** section) where only the ammoniacal form is readily volatilized during manure handling. Immediately upon excretion, about 95% of cattle manure *N* is in an organic form (**Muck, 1982**). Depending on how the cattle are fed, about 40-50% of this organic *N* is in the form of urea excreted in urine (**Nennich et al., 2006**). Excess protein *N* fed to cattle generally ends up in the urine, increasing the concentration of urea in the manure mixture of feces and urine. The primary source of ammoniacal *N* in manure is through the transformation of urea by the urease enzyme present in the feces. A portion of the organic fecal N can also transform to ammoniacal *N* during extended storage periods.

Immediately following excretion, ammonia emission from a manure surface involves five important processes: urea hydrolysis, dissociation, diffusion, aqueous-gas partitioning, and mass transport away from the manure surface to the atmosphere. Upon excretion, urea comes in contact with urease enzymes present in feces or on floor and soil surfaces. Enzymatic hydrolysis quickly decomposes the urea to aqueous un-ionized ammonia, *NH3 (aq),* as shown in Reaction (4.1) (**Mobley and Hausinger, 1989**).

$$CO\,(NH_2)_2 + 2H_2O \rightarrow 2NH_3 + H_2CO_3 \qquad [4.1]$$

In solution, $NH_3\ (aq)$ exists in equilibrium with ammonium, NH_4^+, as shown in Reaction (4.2).

$$NH_4^+ \leftrightarrow NH_3\ (aq) + H^+ \qquad [4.2]$$

The sum of $NH_3\ (aq)$ and NH_4^+ is referred to as total ammoniacal *N* or *TAN*.

The rate of urea hydrolysis is dependent on temperature, pH, and the concentration of urea in the manure solution. **Muck (1982)** found that over 95% of the urea in dairy cattle manure decomposed within 6 h of excretion at 30°C and within 24 h at 10°C. Therefore, up to 50% of the total *N* excreted (all of the urea *N*) can be transformed to *TAN* in the housing facility when manure is removed once a day or less frequently. **Muck (1982)** found that Michaelis-Menten kinetics provided a model to describe the degradation of urea by the urease present in feces. The maximum reaction velocity (V_{max}) and the Michaelis-Menten coefficient (K_{mc}) increased with temperature between 10 and 40°C, and the activity decreased linearly on both sides of a pH range of 6.8 to 7.6. Since the pH of fresh cattle manure normally falls within an optimum range for urease activity (**Sommer et al, 2006**), pH has little influence in this model.

The transformation of urea to *TAN* is modeled on an hourly time step as a function of temperature and urea concentration in manure (**Muck, 1982**):

$$RUC = Vmax\ C_U / (K_{mc} + C_U) \quad [4.3]$$

where

RUC = rate of urea transformation to TAN via Eq. (1), kg/m^3-h

C_U = urea concentration in urine, kg/m^3

V_{max} = maximum rate of urea conversion, kg N/m^3 wet feces-h

$$= 3.915 \times 10^9\ e^{-6463/T} \quad [4.4]$$

K_{mc} = Michaelis-Menten coefficient, kg N/m^3 mixture

$$= 3.371 \times 10^8\ e^{(-5914/T)} \quad [4.5]$$

T = temperature, K

The distribution of TAN between ammonia (NH_3) and ammonium (NH_4^+) in a solution such as manure, i.e. TAN dissociation, is modeled using thermodynamic equilibrium principles (**Stumm and Morgan, 1996**). The ammonia fraction of TAN in a manure solution is a function of pH and a dissociation constant (K_a) that increases exponentially with temperature (Montes et al., 2009):

$$F = 1 / (1 + 10^{-pH} / K_a) \quad [4.6]$$

where

$$K_a = 10^{(0.05 - 2788/T)} \quad [4.7]$$

pH = surface pH of manure or urine

Therefore, ammonia formation is very sensitive to pH and temperature. Below pH 8, a one unit increase in pH increases the ammonia fraction by about an order of magnitude, and this fraction approximately doubles with each 10°C increase in temperature. As the ammonia fraction in a solution increases, the potential emission rate increases.

Henry's Law relates the ammonia in a solution to that in a gas phase equilibrium with the solution. The Henry's Law constant, defined as the ratio of ammonia concentration in a solution in equilibrium with gaseous ammonia concentration in air, is exponentially related to temperature. A number of equations have been used to represent this relationship with a wide range in predicted values (**Montes et al., 2009; Ni, 1999**). A model developed by **Montes et al. (2009)** based upon thermodynamic principles is used:

$$H = (T/0.2138) \times 10^{(1825/T - 6.123)} \quad [4.8]$$

where

H = Henry's Law constant for ammonia, dimensionless aqueous:gas.

Because ammonia concentration is so sensitive to pH, knowing the pH at the surface of the manure is critical for accurate prediction of emission rate. Surface pH is difficult to measure and model. When manure is exposed to air, dissolved carbon dioxide is released more rapidly than ammonia due to a lower solubility. The rapid loss of carbon dioxide leads to an increase in manure

surface pH, while the pH of the bulk of the manure remains relatively constant (**Montes et al., 2009; Sommer et al., 2006; Blanes-Vidal et al., 2009**). Measurements and model predictions of manure pH suggest that surface pH may be on the order of 0.5 to more than 1.0 pH unit greater than the bulk pH (**Chaoui et al., 2009; Ni et al., 2009; Blanes-Vidal et al., 2009; Montes et al., 2009**). The magnitude of the pH increase is expected to depend on solution chemistry, manure depth, and environmental properties. On a barn floor with constant animal movement, there is continuous mixing of the manure, so the surface pH likely varies across a manure covered floor surface.

Equations 4.7 and 4.8 represent ammonia formation in an infinitely dilute solution. For a substance such as manure, ions in the solution affect the equilibrium of NH_3 and NH_4^+ and thus the overall emission rate. In this mixed electrolyte solution, the interaction with other ions affects chemical activity. This effect can be estimated from the concentrations of these species in solution multiplied by their corresponding activity coefficients where the activity coefficients are a function of ionic strength (**Montes et al., 2009**). Ionic strength in cattle manure depends on manure composition and DM content, but is fixed at 0.35 in our model (**Chaoui et al. 2009**), which gives an activity coefficient of 0.74 for NH_4^+, based on the Davies equation (**Montes et al., 2009**). Since NH_3 has no charge, its activity coefficient will be close to 1.0. To account activity corrections, K_a from equation 4.7 is multiplied by 0.74.

The movement of ammonia away from the manure surface into the surrounding atmosphere is described in the model using a mass transfer coefficient (Eq. 4.14). The rate of transfer is a function of the air velocity over the surface, temperature of the manure and air, and the geometry of the surface in relation to air movement (**Montes et al., 2009**). A number of empirical relationships have been used to predict ammonia transfer from manure (**Ni, 1999**), but most are based on conditions different from that of a flat manure covered surface (**Montes et al., 2009**).

Principles are again well established for deriving the mass transfer coefficient based upon a two film model and the properties of the emitted compound and air as the transfer media (**Montes et al., 2009**). In our model, the mass transfer coefficient is a function of the air friction velocity and the Schmidt number (**Mackay and Yeun, 1983**):

$$K_g = 0.001 + 0.0462\, U\, (SC^{-0.67}) \qquad [4.9]$$

where

K_g = mass transfer coefficient through gaseous layer, m/s

U = air friction velocity near surface, m/s

$$= 0.02\, V_a^{1.5} \qquad [4.10]$$

V_a= ambient air velocity measured at a standard anemometer height of 10 m

SC = Schmidt number (**Perry et al., 1997**), dimensionless

From the review by **Ni (1999),** the mass transfer coefficient through the liquid film layer (K_l) is modeled as:

$$K_l = 1.417 \times 10^{-12}\, T^4 \qquad [4.11]$$

This coefficient has relatively little effect on the mass transfer of ammonia.

A remaining process that must be considered is mass transfer of *TAN* within the bulk material below the liquid film. For manure in a thin layer, such as on a free stall barn floor, this process is assumed to not limit emission and is thus neglected. In a large volume of manure such as in a storage tank, aqueous phase mass transfer within the tank becomes important. As the ammonia is emitted, there is a drop in the concentration of *TAN* at the surface. This forms a gradient in concentration from the bulk material to the surface, and the *TAN* migrates from the high concentration at lower depths toward the lower concentration at the surface. The rate of this migration is dependent on the distance *TAN* migrates and the degree of mixing of the manure. With no mixing, *TAN* will move by diffusion only, leading to a low rate of migration. With mixing due to manure addition, wind, or temperature gradients, migration is more accurately described as convection, and can be much greater than that by diffusion (**Cussler, 1997; Incropera, 2006**). This effect is modeled as a resistance to mass transfer which is the sum of the resistance to movement through the manure and the resistance of any cover material over the manure:

$$R_m = R_s + R_c \qquad [4.12]$$

where

R_m = resistance to mass transfer, s/m

R_s = resistance to mass transfer through the manure, s/m

R_c = resistance to mass transfer through a storage cover, s/m

The overall mass transfer coefficient is the reciprocal of the sum of the three resistances to mass transfer:

$$K = 1 / (H / K_g + 1/K_l + R_m) \qquad [4.13]$$

The hourly rate of emission is then a function of the overall mass transfer rate and the difference in ammonia concentration between the manure and surrounding atmosphere:

$$J = 3600\, K (C_m - H (C_a)) \qquad [4.14]$$

where

J = ammonia flux, kg/m^2-s

C_m = concentration of ammonia in manure, kg/m^3

C_a = concentration of ammonia in ambient air, kg/m^3

Ammonia concentration in the ambient air is assumed to be negligible, and is thus set to zero. The ammonia concentration in the manure is calculated from the bulk *TAN* concentration and *F* from Eq. 4.6.

$$C_m = F \times C_{TAN} \qquad [4.15]$$

where

C_{TAN} = concentration of *TAN* in the manure solution, kg/m^3

By linking models for the emission processes, emission rates are predicted for each of the major ammonia sources on farms. The four sources are housing facilities, manure storage, field applied manure, and direct deposits on pasture. The principles and relationships described above are used to predict emissions from each with some differences as described in the following sections.

Animal Housing

A major difference among housing facilities is the area soiled by the manure. As manure is spread over more area, the ammonia emission rate per animal increases. Exposed manure surface area is set considering typical designs for cattle housing. The soiled areas assigned to tie stall, free stall, and bedded pack facilities are 1.2, 3.5 and 5.0 m^2 per cow or finishing beef animal, respectively. For growing animals, the areas are 1.0, 2.5 and 3.0 m^2 per head. These areas are fixed for the duration of a simulation.

Free Stall and Tie Stall Barns

The mass of *N* on the floor of the housing facility is a function of the time animals spend in the facility, the amount excreted, the manure removal rate, and rates of urea hydrolysis and ammonia emission. These processes occur simultaneously in our model with a fixed time step of one hour. During the day, urea *N* accumulates in proportion to time and the excretion rate. When animals spend a portion of their time on pasture, the amount of manure deposited in the housing facility is proportional to their time in that facility. Urine and fecal production and *N* excretion are functions of animal size, feed intake, protein intake, and milk production (See the **Dairy Herd** section). The amount of urea *N* excreted is set at 70% of the total urine *N* and 9% of the fecal *N* with 1% of the urine *N* excreted as ammoniacal *N* (**Bristow et al., 1992, Rotz, 2004**). All remaining *N* is in a more stable organic form that does not affect emissions from the housing facility. Removal rate is a function of housing type. Removal factors, or the fraction of the manure removed each day are 0.98, 0.98, 0.9 and 0.0 for tie stall, flushed free stall, scraped free stall, and bedded pack facilities, respectively. The portion not removed remains on the exposed surface where emissions can continue. As the urea accumulates, the rate of urea *N* conversion to *TAN* is determined using equation 4.3, and the *TAN* emission rate is predicted using equations 4.6 to 4.15. Emission rates are determined separately for the lactating cow and growing animal facilities due to differences in manure excretion, composition, and management.

When manure is removed by flushing, three parameters are adjusted to account for differences compared to scraped manure. Following a scraping operation, a very thin layer of manure is spread over the surface. This causes increased carbon dioxide emission, which increases surface pH. Following flushing, a cleaner and wetter floor surface follows that removes this effect on surface pH. This is modeled by setting the surface pH equal to that of the bulk manure pH for the first hour following flushing. As noted above, the removal factor is also increased to 0.98 to represent a cleaner floor immediately following removal. The third factor is that the urinary *N* deposited following flushing is diluted by increasing the volume of solution on the floor by 20%.

Important parameters for predicting housing emissions are temperature, air velocity, and manure pH. For naturally ventilated facilities, temperature is set to that of the ambient air. For enclosed, mechanically ventilated barns, air temperature in the barn is modified as a function of the ambient air temperature:

$$T = \max(-5.0, 0.63\ T_a + 6.0) \quad [4.16]$$

where

T_a = ambient air temperature, ^oC

Hourly temperatures are estimated from daily maximum and minimum temperatures using a hyperbolic tangent fitting algorithm (**USAF, 1991**):

$$T_a = H_x(T_{max} - T_{min})/2 + (T_{max} + T_{min})/2 \quad [4.17]$$

where

$$H_x = -\tanh((H + 3.5)/3.5) \quad \text{for } H \leq 4 \quad [4.18]$$

$$H_x = \tanh((H - 9.5)/2.5) \quad \text{for } 4 < H \leq 14$$

$$H_x = -\tanh((H - 21.5)/3.5) \quad \text{for } H > 14$$

H = hour of the day from 1 to 24

For bedded pack facilities, the air speed near the manure surface is set equal to the ambient wind speed. For naturally ventilated barns, this speed is set at half the ambient wind speed. For mechanically ventilated barns, the air velocity in the barn (V_a) is determined as a function of ambient temperature with an increase in ventilation rate as temperature increases:

$$V_a = \max(0.3, 0.1\ T_a) \quad [4.19]$$

where

V_a = air velocity in barn, m/s

As described above, manure pH is influenced by the characteristics of the manure and environmental conditions. The pH of excreted cattle manure is about 7 for feces and 8 for urine. The mixture has a pH of about 7.5, which is assumed to be the bulk pH of the manure laying on the floor or in the bedded pack. Since the ammonia concentration at the surface controls emission rate, the pH at the surface is most important. Based upon experimental data (**Chaoui et al., 2009; Ni et al., 2009; Blanes-Vidal et al., 2009**), the surface pH for manure in all housing facilities is set 0.7 units greater than the average bulk pH of the excreted manure.

Hourly emissions from each animal facility are totaled to obtain a daily emission. For barns where manure is removed on a daily basis, the mass of *TAN* removed is all urea and ammoniacal *N* in the excreted manure minus the *TAN* emitted during the day. This provides the mass placed into storage or that applied to fields through a daily application strategy.

Open Lots

For open lot facilities, the exposed manure surface area is based on typical animal densities for dairy and beef operations. Animal densities of 60.0 and 25.0 m^2 per head are assigned to represent the surface areas for dairy open lots and beef open lots, respectively. These areas are fixed for the duration of a simulation.

The mass of *N* on the open lot is a function of the amount of urine excreted, the time spent by animals on open lots, and manure pack conditions, such as moisture content and the amount of

organic matter present (see **Nitrous Oxide** section). For open lots, effects of processes such as urine infiltration and ammonium adsorption on ammonia emissions are considered. These processes are modeled simultaneously on an hourly time step.

For open lot facilities, manure harvesting is normally done after several months of operation. As an example, manure harvesting at beef feedyards is performed at the end of each feeding cycle, which can last for 180 days. Until the manure pack is harvested, organic forms of *N* in the urine excreted on open lots can undergo decomposition into urea *N* or other forms of *N* that can transform into ammoniacal *N* (**Bristow et al., 1992**). Depending on soil/manure temperature, open lots have the capacity to hydrolyze all urea *N* due to urease activities in both fresh and non-fresh manure areas. As stated previously, over 95% of urea decomposed within 6 h at 30°C and within 24 h at 10°C (**Muck,1982**). Assuming a manure N content of 7,000 mg N/kg feces for cattle manure (**Lorimor et al., 2000**), an expression is derived for estimating the fraction of urine *N* (urea *N*, ammoniacal *N* and other organic *N*) excreted on open lots that hydrolyzes within 24 h:

$$F_{ur} = min\ (1,\ 0.4232 \text{ x } e^{0.0901 T_{s,avg}}) \qquad [4.20]$$

where

F_{ur} = fraction of urine *N* that hydrolyzed, 0.0 to 1.0

$T_{s,avg}$ = daily average manure temperature, ^{o}C

Applying equation 4.20, all urine *N* hydrolyzes within 24 at manure temperatures above 10°C. Below 10°C, the fraction of urine *N* that hydrolyzes within 24 h decreases exponentially with manure temperature. The daily average manure temperature is the average of daily maximum and minimum manure temperatures approximated using relationships presented by **Parton (1984)**.

When excreted on the open lot, a portion of the urine infiltrates the manure pack while the remaining stays on or near the surface and becomes available for ammonia volatilization. The degree of urine infiltration depends on the moisture content of the manure pack. A dry manure pack has a capacity to hold more moisture and thus leads to higher infiltration whereas a wet manure pack will not hold much additional moisture reducing infiltration. The fraction of urine infiltrating into the manure pack (*IR*) is computed as a function of the runoff curve number (*CN*):

$$IR = 1 - CN / 100 \qquad [4.21]$$

For open lots, *CN* is computed daily and estimated from the initial abstraction of the manure pack (**USDA, 2005**). As initial abstraction is the amount of moisture needed to exceed field capacity (**Dahlke et al., 2012**), the initial abstraction (I_a) for the manure pack on open lots is:

$$I_a = max(0,\ FC - MC)\ D \qquad [4.22]$$

where

FC = field water holding capacity of the manure pack, cm H_2O/cm soil

MC = water content of the manure pack, cm H_2O/cm soil

D = depth of the manure pack, 5 cm

CN is then calculated from I_a using:

$$CN = 36.486 I_a^2 - 89.571 I_a + 96.895 \quad [4.23]$$

A regression equation derived using I_a - *CN* values presented in Table 2-4 of the Engineering Field Handbook (**USDA, 2012**).

The moisture content of the manure pack is predicted using a soil water model adapted from relationships described by **Jones and Kiniry (1986)**. Moisture is predicted in layers considering the water entering (i.e., precipitation minus runoff, urine), moving through (i.e., moisture flow among the soil layers) and leaving the manure pack or soil profile (i.e., evaporation and leaching). The open lot soil profile is modeled in four layers, with the top 3 layers of 3.0- (surface), 4.5- and 7.5-cm depths representing the manure pack and a fourth layer with 100-cm depth representing the underlying soil. Prediction of the moisture content requires several parameters such as porosity, field capacity and saturation moisture content. In calculating the total porosity for open lots, a particle density of 1.89 g/cm^3 (**Pepple et al., 2011**) and bulk density of 1.7 g/cm^3 (**Mielke et al., 1974**) are used. Equations developed for calculating field capacity and saturation moisture content for open lots are:

$$SAT = PO + 0.4\ OM_{mp} \quad [4.24]$$

$$FC = 0.5\ SAT \quad [4.25]$$

where

SAT = water content at saturation, cm H_2O/cm soil

FC = water content at the drained upper limit, cm H_2O/cm soil

PO = porosity, fraction

OM_{mp} = organic matter content of the manure pack, fraction

Stage 2 water evaporation (**Ritchie, 1972**) starts at a water-filled pore space of 30%, which is under dry/near dry conditions for feedyard soils (**Razote et al., 2006**).

As manure lays on the open lot until removal, ammonia can be emitted from fresh and non-fresh manure areas. Hourly ammonia emission rates from fresh manure are determined using equations 4.6 to 4.11 and 4.13 to 4.15, with the resistance to mass transfer (R_m in equation 4.13) equal to the inverse of the manure pack's hydraulic conductivity (equations 4.28 to 4.30). The same equations are used in estimating hourly ammonia emission rates from non-fresh manure areas. However, instead of using equation 4.6, ammonium adsorption is considered in calculating the ammonia fraction in *TAN* for non-fresh manure areas due to its higher degree of organic matter decomposition. As organic matter decomposes, the adsorption capacity of the manure pack increases (**Bernard et al., 2009; Waldrip et al., 2012**), which then gives more sites to adsorb cations that can include ammonium. The ammonia fraction in *TAN* (*F*) is computed by:

$$F = 1 / [1 + (10^{-ph_f}/K_a) + (K_f C_s 10^{-ph_n}/K_a)] \quad [4.26]$$

where

K_a = dissociation constant, computed using equation 4.7

pH_f = pH of fresh manure, 8.0

pH_n = pH of non-fresh manure, 7.5

K_f = reference linear partitioning coefficient for ammonium adsorption

= 10 L/kg (**Waldrip et al., 2012**)

C_s = concentration of solids available for ammonium adsorption, kg solids/L

An equation for predicting C_s is derived using the manure pack characteristics reported in previous studies (**Mielke et al., 1974; Razote et al., 2006**):

$$C_s = [\,(OM + F_{clay})/OM_{ref}\,]\,(\rho_{s,avg}/WFP) \qquad [4.27]$$

where

OM = organic matter content of the manure pack, fraction, 0.38

F_{clay} = clay content of the manure pack, fraction, 0.06

OM_{ref} = organic matter content at which K_f was measured, 0.70

$\rho_{s,avg}$ = average density of the whole manure pack layer, 1.25 g/cm^3

WFP = water-filled pore space of the manure pack, fraction

Important parameters for predicting ammonia emissions from open lots are air velocity, temperature of the manure pack, and mass transfer resistance through the manure pack. Hourly manure pack temperatures are estimated from daily maximum and minimum manure temperatures calculated using relationships presented by **Parton (1984)**. Effects of solar radiation on the manure pack temperature is accounted for in the daily maximum manure temperature computation. Similar to hourly ambient air temperatures, hourly manure temperatures are calculated from daily maximum and minimum values using a hyperbolic tangent fitting algorithm (**USAF, 1991**) (equations 4.17 to 4.18).

The resistance to mass transfer in the soil is the inverse of its hydraulic conductivity (**SSDS, 1993**). For fresh manure, the mass transfer resistance is based on its saturated hydraulic conductivity assuming that fresh manure is at 100% saturation. For non-fresh manure areas, the mass transfer resistance is based on its unsaturated hydraulic conductivity to account for effects of lower moisture on the flow of ammonia solution through the manure pack. The saturated hydraulic conductivity is estimated from the clay and silt contents using the relationship (R^2 = 0.95) derived by **Delgado-Rodriguez et al. (2011)**:

$$K_{hc,sat} = 0.101176\ FINES^{-1.62}/(24 \times 3600) \qquad [4.28]$$

where

$K_{hc,sat}$ = saturated hydraulic conductivity, m/s

$FINES$ = average of clay and silt contents combined, fraction

$FINES$ is calculated from clay and silt contents of the manure pack layer, 6 and 32%, respectively (**Razote et al., 2006**), and the underlying soil layer, which are available as input through the soil

characteristics menu of IFSM. Assuming that the particle density remains constant throughout the manure pack, the calculated saturated hydraulic conductivity, $K_{hc,sat}$, is adjusted to account for the lower porosity at the surface using the Kozeny-Carman equation (**USDOE, 2009**):

$$K_{hc,adj} = K_{hc,sat}\,(f_{sur}^{3}/(1-f_{sur})^{2})((1-f_{mp})^{2}/f_{mp}^{3}) \qquad [4.29]$$

where

$K_{hc,adj}$ = adjusted saturated hydraulic conductivity, m/s

f_{sur} = porosity of the surface, fraction

f_{mp} = porosity of the manure pack, fraction

Mass transfer resistance for fresh manure is the inverse of the adjusted saturated hydraulic conductivity, $K_{hc,adj}$. For computation of the mass transfer resistance for non-fresh manure, the unsaturated hydraulic conductivity is estimated from the adjusted saturated hydraulic conductivity based on manure pack moisture content and texture. The relationships used in calculating the unsaturated hydraulic conductivity are based on **Saxton and Rawls (2006)**:

$$K_{hc,unsat} = K_{hc,adj}\,(WFP/100)^{(3+2/\gamma)} \qquad [4.30]$$

where

$K_{hc,unsat}$ = unsaturated hydraulic conductivity, m/s

WFP = manure pack water-filled pores space, %

γ = slope of the logarithmic tension-moisture curve

The variable γ is a function of soil texture as computed using equations 1, 2, 15 and 18 of **Saxton and Rawls (2006)**.

Similar to computations for other facilities, hourly emissions from open lots are summed to obtain the daily emission. At the end of each day, remaining *TAN* either infiltrates the manure pack or stays on or near the surface for potential volatilization the next day depending upon the infiltration characteristics of the surface for that day.

Bedded Pack Barns

For bedded pack barns, there are three general ways of managing the bedded manure pack (i.e., manure pack with bedding): 1) the bedded manure pack, or just bedded pack, is scraped and removed at regular short intervals from daily to every few weeks; 2) the bedded pack is allowed to accumulate; and 3) the bedded pack is allowed to accumulate and is aerated through regular stirring or tilling to enhance microbial decomposition. Barns that practice the last two bedded pack management styles are typically called deep-bedded pack barns and compost barns, respectively. In IFSM, bedded pack barns modeled are those that fall under the category of deep-bedded pack.

Animal spacing for bedded pack barns is set at 5.0 m^2 per cow and 3.0 m^2 per growing animal or finishing beef animal. With the presence of a bedded pack, which is similar to the manure pack in open lots, simulation of ammonia emissions for bedded pack barns follows the procedure implemented for open lot facilities (see **Ammonia Emission Open Lot** section above; **Bonifacio et**

al., 2015). The mass of *TAN* for bedded pack barns is calculated based on daily urine excretion, and the amount of organic matter present in the bedded pack (see **Nitrous Oxide** section). Expressions used in simulating processes such as urea hydrolysis (equation 4.20) and ammonia volatilization from fresh (equations 4.6 to 4.11, 4.13 to 4.15) and non-fresh manure areas (equation 4.26) are those used for open lot facilities. Simulation of ammonia emissions is done on an hourly time step and the daily emission is obtained by summing hourly emissions within the day.

Unlike open lots, however, bedded pack barns are structures with sidewalls and a roof resulting in lower air velocity in the barn with negligible effects from solar radiation. As a result, bedded pack barns have wet manure pack conditions throughout the year, with moisture contents ranging from 60% to 75% (**Spiehs et al., 2011**; **NRCS South Dakota, 2011**). To provide drier conditions for cattle, bedding materials such as straw and manure solids are added to the surface of the manure pack to absorb some of the excess moisture. Effects of these manure pack conditions (i.e., wet) and management (i.e., bedding use) on ammonia emissions are modeled for bedded pack barns.

Presence of bedding materials on the pack can reduce ammonia emission by absorbing some urine and immobilizing some of the ammonium (**Misselbrook and Powell, 2005**; **Gilhespy et al., 2009**). In the model, the fraction of urine absorbed by the bedding material is computed as a function of total absorbance capacity of the bedding and the amount of urine excreted:

$$F_{abs} = \min(F_{abs,max}, ABS_{total} / URINE) \qquad [4.31]$$

where

F_{abs} = fraction of urine absorbed
$F_{abs,max}$ = maximum fraction of urine that can be absorbed
ABS_{total} = total absorbance capacity of the bedding material on the surface, kg H_2O
$URINE$ = daily urine production calculated using equation 3.5, kg/day

The setting for $F_{abs,max}$ is 0.50, based on refinement using measurements by **Gilhespy et al. (2009)** and **Misselbrook et al. (2000)**, from which 30%, 73%, and 80% reductions in ammonia emissions were approximated for 3-lb, 10-lb, and 20-lb amounts of straw bedding, respectively. In a simulation performed, the model predicted that application of 3-lb, 10-lb, and 20-lb straw bedding would lead to ammonia emissions lower than those from no bedding by 37%, 76%, and 78%, respectively, with the maximum amount of urine absorbed limited to half of the total excretion.

The ABS_{total} is given by:

$$ABS_{total} = ABS_{unit} \, (BED_{animal}) \, (ANIMALS) \qquad [4.32]$$

where

ABS_{unit} = absorbance per unit mass of bedding, kg H_2O/kg bedding
BED_{animal} = mass of bedding per animal per day, kg bedding/animal-day
$ANIMALS$ = number of animals kept in the bedded pack barn.

Properties, which include ABS_{unit}, for several types of bedding materials (**Misselbrook and Powell,**

2005; **Bickert et al., 2000**) are summarized in **Table 4.1**. The BED_{animal} is a user-defined parameter.

Ammonium adsorption is considered in calculating the ammonia fraction in *TAN* for non-fresh manure areas (equation 4.26). The adsorption capacity of the bedded pack is based on its two components: decomposed/non-fresh manure and bedding. An ammonium adsorption linear partitioning coefficient (K_f) for manure is set to 10.0 L/kg (**Waldrip et al., 2012**) whereas for bedding, it is approximated from the cation exchange capacity of the material used (**Table 4.1**). For both manure and bedding, concentration of solids for ammonium adsorption (C_s in equation 4.26) is calculated from their corresponding dry matter masses and the total volume of bedded pack moisture.

The IFSM water routine for bedded pack barns has been evaluated and found to be applicable in predicting water movement for beef cattle bedded manure packs (**Ayadi et al., 2015a**). The moisture content of the bedded pack is predicted using the soil water component based on relationships by **Jones and Kiniry (1986)**. However, relationships by **Jones and Kiniry (1986)** for simulating water evaporation and calculating water diffusivity do not apply for bedded pack barns due to the absence of solar radiation and significantly wetter pack conditions. For bedded pack barns, the amount of water evaporated is a function of the difference in moisture concentrations between ambient air and the air layer right above the bedded pack surface **(Black et al., 2013)**:

$$EVAP = K_{g,w}\ (C_{sur} - C_{air})\ (\ 3{,}600)\ (24)\ (\ AREA\ ) \qquad [4.33]$$

where

$EVAP$ = amount of water evaporated, kg H_2O/day

$K_{g,w}$ = overall surface mass transfer coefficient of water, m/s

C_{sur} = moisture concentration of the air layer right above the surface, kg H_2O/m^3 dry air

C_{air} = moisture concentration of ambient air, kg H_2O/m^3 dry air

$AREA$ = surface area of the bedded pack, m^2

The $K_{g,w}$ value is calculated using an empirical equation derived using data by **Mackay and Yeun (1983)**. The C_{sur} and C_{air} values are estimated from corresponding relative humidities (i.e., 100% and ambient air relative humidity, respectively) and ambient air temperature (**Black et al., 2013**). The surface area is just the product of animal spacing and total number of animals in the barn. In situations in which *EVAP* exceeds urine excretion (*URINE*), *EVAP* will be limited by the total amount of moisture in the first 3 cm of the bedded pack (i.e., similar to assumption used by **Jones and Kiniry (1986)**).

The water diffusivity used in simulating unsaturated flows (**Jones and Kiniry, 1986**), and also in calculating the resistance to ammonia mass transfer in the manure (R_m in equations 4.12 and 4.13), is estimated using an empirical equation derived using hydraulic conductivity data by **Sutitarnnontr et al. (2014)**. In simulating water movement, the bedded pack profile is modeled in four layers. Depths of 7 and 8 cm are assigned for the first and second layers, respectively. The remaining depth of the bedded pack (i.e., total depth minus 15 cm) is divided equally into third and fourth layers. Saturation moisture and field capacity contents of the bedded pack used in the simulation are calculated using equations 4.24 (i.e., without the OM_{mp} variable) and 4.25, respectively. Simulated total bedded pack depth and assumed particle density are discussed in the **Nitrous Oxide** section.

Manure Storage

When long term storage of manure is used on livestock farms, the storage facility is another important source of ammonia emission. Manure is stored in a liquid, slurry, or solid form depending upon the manure management strategy used. By the time manure is placed into storage, most of the urea has been converted to *TAN*. Any remaining hydrolysis has no effect on ammonia emission, so urea conversion to *TAN* is assumed to be complete once manure is removed from the barn. Bedding and manure solids can be separated from manure to form liquid manure (about 5% DM). This liquid portion, containing most of the *TAN*, is typically stored in an earthen basin or tank. Due to wind-induced mixing and the mixing created when manure is pumped into the storage, this liquid portion remains relatively well mixed. When manure is stored as slurry (7-12% DM), less mixing occurs within the storage structure, so diffusion is more important. If the slurry is pumped into the bottom of the storage tank or basin, a crust can form on the manure surface. This crust provides additional resistance, further reducing the rate of migration to the surface. Manure mixed with bedding material may also be stored as semi-solid or solid manure (greater than 12% DM). In this form, diffusion through the manure becomes a major constraint to the emission rate. For each type of storage, equations 4.6 to 4.15 are used to describe diffusion, dissociation, aqueous to gas partitioning, and mass transport away from the manure surface to predict emission rate. As described below, the difference among storage types is in the diffusion properties of the manure and the constraint they place on the movement of *TAN* to the surface.

On a given day, the amount of *TAN* in storage is that accumulated up to that day minus that lost from the storage between the date loading began and the given date. The accumulated *TAN* is that removed from the barn plus the portion of the organic *N* that mineralizes to an ammoniacal form during long-term storage. Mineralization is calculated on a daily time step where the rate of mineralization is a function of the manure temperature:

$$TAN_o = N_o \min\left(0.007,\ 0.007\left(1.2^{(Tm - 20)}\right)\right) \qquad [4.31]$$

where

TAN_o = rate of organic *N* transformation to *TAN*, kg/d

N_o = organic *N* in storage, kg

T_m = temperature of stored manure, ^{o}C

Manure temperature in the storage is set as the average ambient temperature over the previous 10 days.

The daily emission rate is a function of the exposed surface area, *TAN* concentration, temperature, air velocity, and surface pH. Slurry and liquid manures are assumed to spread across the exposed surface of the storage where the surface area is determined by the storage dimensions set by the model user. Thus in the early stages of loading, manure is in a relatively thin layer with a large surface area per unit volume stored. As the storage fills, this surface area to volume ratio decreases. *TAN* concentration on a given day is the total *TAN* remaining in the storage divided by the liquid mass in the storage. This liquid mass on a given day is the total manure mass in the storage minus the manure *DM* loaded into the storage. Daily changes due to precipitation and evaporation are not specifically modeled, but the total mass includes the long-term moisture added from wash water and

rain. Air friction velocity at the surface is determined using equation 4.10 where the ambient air velocity is the average daily wind velocity.

Manure pH is a function of the solids content of the manure. A relationship was developed to vary the bulk pH of stored cattle manure from 7 with no manure solids to 8.5 with a relatively high solids content:

$$PH = \min(8.5, 15.3 - 8.2(1 - DMC)) \quad [4.32]$$

where

DMC = dry matter content of the stored manure, fraction

PH = pH in the bulk of the manure

Surface pH also varies with solids content. With no solids in the manure, carbon dioxide will not be formed and emitted, so the surface pH will be the same as the bulk pH. With increasing solids, there is greater opportunity for microbial decomposition, formation and emission of carbon dioxide, and thus a greater increase in surface pH relative to bulk pH:

$$PHS = \min(8.5, PH + 8.0 - 8.0(1 - DMC)) \quad [4.33]$$

where

PHS = manure surface pH.

This effect on surface pH is included for stacked manure and top-loaded slurry or liquid storages. For bottom loaded storages, this surface pH effect is not included since fresh manure is not exposed at the surface.

The resistance to ammonia loss is the sum of the resistances to transport through the bulk manure to the surface and from the surface to the free atmosphere (Equation 4.13). The effective resistance of the manure is a function of manure type with assigned values of 3×10^5, 2×10^5, 33×10^3 and 0 s/m for solid, semi solid, slurry, and liquid manure types, respectively. The additional resistance for covered and enclosed manure storages is 2×10^5 and 2×10^6 s/m, respectively.

Daily loss of ammonia N is determined such that the cumulative loss up to a given date cannot exceed the accumulated TAN loaded into the storage. This is particularly important in the early stages of loading when a thin layer of manure on the bottom of the storage creates maximum exposure for the loss of TAN. By summing daily emissions over the full year, an annual storage loss is determined. For storages with a six-month capacity, the storage is emptied in early April and again in early October. With a twelve-month capacity, the storage is emptied only in April. The mass of TAN available for field application is the mass remaining in the manure when the storage is emptied.

Field Application

Manure is applied to fields either through daily hauling or from long-term storage. With a daily strategy, smaller amounts of manure are applied each day. When storage is used, large amounts of manure are applied over a period of several days. The same model is used to simulate each of these approaches. With daily hauling, the manure produced each day is applied the same day. With six-month storage, half of the annual manure produced and stored on the farm is applied to cropland over ten-day periods in early-to mid-April and early-to mid-October. For twelve-month storage systems, all

manure for the year is applied in a ten-day period in April.

Four manure application methods are modeled: broadcast spreading, irrigation, band spreading, and direct injection into the soil (**Rotz et al., 2010**). Some *TAN* is lost as the manure moves through the air in the actual application process. This loss is 1% and 10% of the applied *TAN* for broadcast spreading and irrigation with no loss in band spreading and injection. Thus, the manure *TAN* reaching the field surface is that hauled from the barn or manure storage on a given day minus this loss.

When applied to a soil surface, the manure is applied in a thin layer where remaining *TAN* can readily volatilize as ammonia. Emission from the manure applied on a given day is determined by integrating equations 4.6 to 4.15 over the period until the manure is incorporated by a tillage operation. A maximum of 15 d is set for this period since all *TAN* is normally lost or infiltrated into the soil after this much time on a field surface. Because the emission rate is very rapid when manure is first applied, this integration is done on a 2-hour (0.08 d) time step. Loss during each time step is determined using the average ambient temperature of each day over this period. Manure pH is set to increase to 8.6 immediately following application due to the rapid release of CO_2 (**Sommer et al., 1991**). As the manure lays in the field, the pH decreases at a rate of 0.3 units per day until it reaches a neutral pH of 7.0 (**Sommer et al., 1991**).

The mass of water contained in the manure (M_w) on the field surface varies through time. The initial amount following application is set assuming a manure application rate of 0.3 kg DM/m^2. The contained water is calculated from the application rate and the manure *DM* content (*DM* application rate divided by the manure *DM* content minus the manure *DM*). The remaining manure moisture is adjusted during each time step by subtracting infiltration and evaporation and adding moisture from rain.

Evaporation is predicted as proportional to the incident solar radiation of the day. Daily evaporation (*EV*) varies from 0 to 60% of the available solution mass as solar radiation varies between 0 and a maximum level of 30 MJ/m^2. When rain occurs, the manure solution is increased assuming a uniform rate of rainfall over the daily period.

Infiltration is determined as a function of the manure *DM* content (**Hutchings et al., 1994**):

$$IR = e^{(6.95 - 31.9\ DMC)} \qquad [4.34]$$

where IR = infiltration rate, kg/m^2-d or mm/d

DMC = manure *DM* content, fraction

Daily infiltration is limited to a maximum of 70% of the available manure water content. The remaining mass of water at each time step is M_w minus *EV*. During each time step, the mass of water is reduced by the infiltration and evaporation rates times the length of the time step (0.08 d) and increased by the rainfall rate times the time step length.

Manure *TAN* on the soil surface also varies through time. The initial *TAN* is that reaching the soil following the application process. During each time step, ammonia loss occurs to the atmosphere and *TAN* moves into the soil with the infiltration of moisture. The *TAN* moving into the soil is set in

proportion to the manure solution that infiltrates into the soil, i.e. if *IR* is 10% of M_w, 10% of the available *TAN* is removed from the surface pool and is thus unavailable for volatilization. Ammonia emission is determined for each time step using equations 4.6 to 4.15. This loss is a function of the *TAN* and M_w on the field surface at a given point in time. At the completion of each time step, *TAN* and M_w are adjusted to provide initial values for the next time step.

Ammonia loss is determined by integrating these relationships over the period from application until incorporation into the soil or 15 days. This provides an exponential decline in the emission rate through time as influenced by changes in manure *TAN* content, infiltration rate, and DM content along with the effects of rainfall and ambient air temperature. When manure is incorporated the same day as applied, an average exposure time of 8 h is assumed. When manure is not incorporated, remaining TAN becomes negligible after a few days, and the emission rate approaches zero.

To predict loss from manure directly injected into the soil, a simpler approach is used. Because little manure remains on the surface, the process level simulation of surface emissions is bypassed. Ammonia *N* loss is set at 5% of the *TAN* in manure applied through deep injection into cropland and 8% of the *TAN* in manure applied through shallow injection to grassland. This provides relatively small losses, similar to those measured in field experiments.

Losses occurring from daily applications are summed to determine an annual loss. The total loss includes ammonia volatilized during the application process plus that volatilized from the field surface. Any remaining *TAN* not volatilized is available in the soil for plant uptake along with mineralized organic *N*.

Grazing Deposits

When grazing is used, ammonia emission occurs from fecal and urine deposits in the pasture. The *N* in feces is primarily organic, so about 90% of the ammonia emission occurs from the *N* in urine (**Rotz, 2004**). A portion of the urine (about 30-50%) infiltrates into the soil where the urea hydrolyzes and the resulting *TAN* binds to the soil. The remaining portion settles on plant and soil surfaces where it comes in contact with urease. Urease enzyme activity quickly transforms the urea to *TAN* that can volatilize.

To model ammonia emission from pastures, a similar approach is used as that for field application of manure, but some simplifying assumptions are made. The *TAN* available for volatilization is the urea *N* and *TAN* excreted by grazing animals. Although hydrolysis must occur to transform the urea to *TAN*, this process is relatively fast compared to the time animals are on pasture. Thus hydrolysis is assumed to immediately transform all urea to *TAN*. The *N* excreted is determined by how they are fed (See the **Herd and Feeding** section), and the portion applied to pasture is set proportional to the time each animal group spends on pasture. The amount of *TAN* applied is 71% of the urine *N* plus 9% of the fecal *N* excreted on pasture.

The daily solution mass applied is the total urine from all animals on pasture. Of this total, a portion is assumed to immediately infiltrate into the soil and the remainder infiltrates at a slower rate. The amount remaining on the soil surface immediately after excretion (M_w) varies from about 3 to 7 kg/m^2 (or mm/d) as a function of the moisture-absorbing ability of the soil (**Rotz and Oenema,**

2006):

$$M_w = 16.5 - 0.146\ CN \qquad [4.35]$$

where

CN = the runoff curve number for the user-specified soil.

Of this remaining solution, a portion infiltrates at a daily rate:

$$IR = 1 - 0.55\ M_w / (M_w + RN) \qquad [4.36]$$

where

IR = daily infiltration rate into soil, mm/d

RN = daily rainfall, mm/d

If rainfall occurs on a given day, the manure mass is diluted by the rain, i.e. M_w is increased by the daily rainfall amount. This dilution reduces the concentration of the remaining *TAN* in the solution and increases infiltration. The portion of the *TAN* deposited that infiltrates into the soil is determined by the amount of manure moisture that infiltrates and the concentration of *TAN* in that moisture.

Hourly emission rates are determined using equations 4.6 to 4.15 based upon temperature, air velocity, and manure solution pH. Hourly ambient temperature is set using equation 4.17, and ambient air velocity is the average daily wind speed. The pH is set at 8.5 to reflect an increase that normally occurs in urine patches over the first few days following deposition (**Haynes and Williams, 1992**).

Daily ammonia loss from grazing animals is determined for each day animals are on pasture. When animals are maintained on pastures throughout the winter, a daily loss is determined for each day of the year. Otherwise, losses are integrated over the grazing season set by the model user considering the time each animal group spends on pasture. Calculated losses are summed over the time on pasture to obtain an annual loss. Remaining *N* is available for fertilization of the pasture.

Table 4.1 - Bedding Material Properties

Properties of different bedding materials for bedded pack barns.

Property	Unit	Manure solids	Sand	Sawdust	Straw	Chopped straw
Absorbance capacity[a]	kg H_2O/kg	4.22	0.27	2.63	2.85	2.85
Cation exchange capacity[a]	$cmol_c$/kg	16.0	0.3	3.8	9.7	9.7
C/N ratio[a]	-	12	*no nitrogen*[b]	500	105	105
N content[a]	kg N/kg	0.033	0	0.0011	0.004	0.004
Density[a]	g/cm^3	0.09	1.35	0.07	0.04	0.11[c]
Lignin content[d]	kg lignin/kg	0.14	0	0.40[e]	0.12	0.12

[a] Values from **Misselbrook and Powell (2005)**.

[b] For computation purposes, set to $1x10^6$ in the simulation.

[c] Density for chopped straw from **Bickert et al. (2000)**.

[d] Based on lignin contents used in simulating croplands and open lots.

[e] Setting maximized based on ranges reported by **Spiehs et al. (2014)** and **Changirath et al. (2011)**.

HYDROGEN SULFIDE EMISSIONS

Hydrogen sulfide is a toxic compound that is regulated by the US EPA under the Clean Air Act. In response to the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA; **EPA, 2010**), there is a reporting requirement for any point source that emits more than 100 lb (454 kg) of this compound on any given day. Therefore, it is important for dairy producers to know the amount of this compound emitted from their farms. Normally emissions of hydrogen sulfide from dairy farms are well below this limit.

On dairy farms, hydrogen sulfide is primarily created and emitted from decomposing manure under anaerobic conditions. Major sources include the barn floor and long-term manure storage with minor losses following field application. Hydrogen sulfide is a contributor to the nuisance of manure odor. It is also a toxic compound when the concentration builds up in a confined space such as an enclosed manure storage. Therefore, it can be a threat to human and animal health in poorly ventilated facilities. Hydrogen sulfide is also very corrosive, which can lead to deterioration, greater maintenance, and shortened life of farm facilities.

Formation and Emission Processes

Cattle feeds contain minor amounts of sulfur with most of this sulfur present in the amino acids cystine and methionine. Hard drinking water is another potential source. In the rumen, sulfur in amino acids and sulfate are reduced to sulfide by bacteria (**Van Soest, 1994**). Excess sulfur in the diet is processed by bacteria to hydrogen sulfide, which is transported through the digestive track, absorbed, and oxidized to sulfate in the liver. Sulfate is then excreted in urine or recycled through salivary excretion. Although much of the excreted sulfur is in the form of sulfate, microbial activity in the manure can transform the sulfur to a sulfide form.

Hydrogen sulfide forms a weak diprotic acid that dissociates into hydrogen (H^+), bisulfide (HS^-), and sulfide (S^{2-}) ions when dissolved in an aqueous solution. The following reactions govern the presence of the different forms (**Arogo et. al., 1999**):

$$H_2S_{(aq)} \leftrightarrow H_2S_{(g)} \qquad [5.1]$$

$$H_2S_{(aq)} \leftrightarrow H^+ + HS^- \qquad [5.2]$$

$$HS^- \leftrightarrow H^+ + S^{2-} \qquad [5.3]$$

The fractions of H_2S, HS^-, and S^{2-} (α_0, α_1, α_2, respectively) present in an infinitely dilute solution can be calculated from the pH of the solution and the ionization constants using the following equations (**Snoeyink and Jenkins, 1980**):

$$\alpha_0 = [H^+]^2 / ([H^+]^2 + K_{a,1}[H^+] + K_{a,1} K_{a,2}) \qquad [5.4]$$

$$\alpha_1 = K_{a,1} [H^+] / ([H^+]^2 + K_{a,1}[H^+] + K_{a,1} K_{a,2}) \qquad [5.5]$$

$$\alpha_2 = K_{a,1} K_{a,2} / ([H^+]^2 + K_{a,1}[H^+] + K_{a,1} K_{a,2}) \qquad [5.6]$$

where

$K_{a,1}$ = first ionization constant, $10^{-7.1}$ at 25 °C

$K_{a,2}$ = second ionization constant, 10^{-14} at 25 °C

Figure 5.1 shows the change in concentrations of the different sulfide species in an aqueous solution with respect to pH at 25°C. Only $H_2S_{(aq)}$ can be released from the liquid phase. As the pH changes from basic to acidic, the concentration of molecular hydrogen sulfide in water increases, increasing the potential for $H_2S_{(g)}$ emission. The sulfide anion forms at pH levels above 12. This condition is significantly above the pH of cattle manure, and therefore is ignored in our model.

The ionization constants for H_2S and HS^- are a function of temperature. Based on Van't Hoff's equation (**Snoeyink and Jenkins, 1980**):

$$\ln (K_{T1} / K_{T2}) = \Delta H° (1/T_2 - 1/T_1) / R \qquad [5.7]$$

where

T = temperature, K

K_{T1} = equilibrium constant at temperature T_1, mol/L

K_{T2} = equilibrium constant at temperature T_2, mol/L

$\Delta H°$ = standard enthalpy change, 21673 J/mol

R = universal gas constant, 8.3145 J/K-mol

The hydrogen sulfide dissociation constant ($K_{a,1}$) can be estimated at different solution temperatures (T_L)with:

$$\ln K_{a,1} = \ln (1.26 \times 10^{-7}) - (2606 (1 / (273 + T_L) - 1 / 298)) \qquad [5.8]$$

where

T_L = solution temperature, °C

To determine the hydrogen sulfide emission rate, the $H_2S_{(aq)}$ concentration in the aqueous solution or liquid manure must be known. This cannot be directly measured, but the total sulfide concentration (sum of the three sulfides) is easily measured. At a typical manure pH of 6 to 8, the fraction of S^{2-} is negligible ($\alpha_2 \approx 0$ and $K_{a,1} K_{a,2} = 0$), so a simplified version of equation 5.4 and $C_{T,S}$ can be used to estimate the concentration of $H_2S_{(aq)}$:

$$C_L = C_{TS} (10^{-PH}) / (10^{-PH} + K_{a,1} / 0.7) \qquad [5.9]$$

where

C_L = concentration of hydrogen sulfide in manure solution [$H_2S_{(aq)}$], kg/m^3

C_{TS} = total sulfide concentration in manure solution, kg/m^3

PH = pH of the manure solution, -log H^+]

In Eq. [5.9], the thermodynamic ionization constant calculated from Eq. [5.8] is corrected for the activity coefficient of HS^-, which is taken as 0.7 (see **Ammonia Emissions** section). The activity

coefficient of H_2S was assumed to be unity.

The mass transfer or emission process is often described using the two-layer film model of molecular exchange between water and air (**Figure 5.2**). As described below, this model is a major simplification of the processes thought to control H_2S emission. In our model, we assume that H_2S diffuses from the bulk liquid through the liquid film to the air-liquid interface, where it further diffuses through the air film to the surrounding turbulent air (**Blunden et. al., 2008**). Using this theory, the main body of each fluid is assumed to be well mixed and the main resistance to gas transport is from the gas and liquid interfacial layers, where the gas transfer is by molecular processes (**Liss and Slater, 1974**). The overall flux is represented as (**Liss and Slater, 1974; Cussler 1997; Lewis and Whitman, 1924**):

$$J = K\,(C_L - H\,(\,C_a\,)\,) \qquad [5.10]$$

where

J = emission flux, kg/m^2-s

K = overall mass transfer coefficient, m/s

H = Henry's Law constant, g liquid/g gas

C_a = concentration of hydrogen sulfide in ambient air [$H_2S_{(g)}$], kg/m^3

Equation 5.10 gives the overall emission flux used to estimate hydrogen sulfide mass transfer across the gas-liquid interface, with K being a function of the transfer resistances of the aqueous and gas layers:

$$K = 1\,/\,(H\,/\,k_a + 1\,/\,k_L + R_m\,) \qquad [5.11]$$

where

k_L = mass transfer coefficient through the liquid layer, m/s

k_a = mass transfer coefficient through the gaseous layer, m/s

R_m = resistance to mass transfer created by a cover, s/m

The Henry's Law constant for H_2S is modeled using a function developed by **Blunden et al. (2008)**. For a dimensionless Henry's Law constant (aqueous:gas), this equation is:

$$H = 1\,/\,(-4\text{x}10^{-7}\,T_L^{\,3} + 4\text{x}10^{-5}\,T_L^{\,2} + 0.0067\,T_L + 0.2147) \qquad [5.12]$$

The mass transfer coefficients (k_a and k_L) are related to the properties of the gas and liquid layers. For our model, these are the properties of the air and manure solution. Important properties include the density, viscosity, and diffusivity of both the gas and liquid components. The density of moist air is related to both temperature and relative humidity (**Arogo et al., 1999**):

$$\rho_a = (353\,/\,T_a)\,(760 - 0.3783\,RH\,\mathrm{e}^{(0.0596\,Ta\,-\,14.6135)}\,)\,/\,760 \qquad [5.13]$$

where

ρ_a= density of moist air, kg/m^3

T_a= air temperature, K

RH= relative humidity, fraction

The density of the manure solution is assumed to be that of water. **Holman (1981)** reported values for water density as a function of temperature from 0 to 315°C. These values were fitted to a linear trend line to obtain an equation for the density as a function of temperature:

$$\rho_w = 1033.3 - 0.934\ T_L \qquad [5.14]$$

where

ρ_w = density of water, kg/m^3

The dynamic viscosity of air is estimated as a function of temperature using the following empirical expression (**Jacobson, 1999**):

$$\mu_a = 1.8325\text{x}10^{-5}\ (416.16 / (T_a + 120)\ )\ (T_a / 296.6)^{1.5} \qquad [5.15]$$

where

μ_a = dynamic viscosity of air, kg/m-s

T_a = air temperature, °K

The dynamic viscosity of water is predicted using a relationship from **Xiang et al. (1997):**

$$\mu_w = 4.57\text{x}10^{-5}\ (\ TR\ /647.1)^{-(1.77\ THETA\text{^}-0.25\ +\ 2.95\ THETA)} \qquad [5.16]$$

where

μ_w = dynamic viscosity of water, kg/m-s

$$THETA = (1 - TR)^2 / TR \qquad [5.17]$$

TR = temperature T_L expressed as a fraction of absolute temperature

Based on the **Wilke and Chang (1955)** correlation, the following equation was used to determine the diffusion coefficient for hydrogen sulfide in water.

$$D_w = 0.00074\ (273 + T_L)\ (\varphi\ MW)^{0.5} / (\mu_w\ V^{0.6}\ ) \qquad [5.18]$$

where

D_w = diffusion coefficient of H_2S in water, cm^2/s

φ = solute-solvent interaction factor, 2.6

MW = molecular weight of water, 18.01g/mol

V = molar volume of hydrogen sulfide at the boiling point, 32.9 cm^3/mol

As presented in (**Cussler, 1997**), the diffusivity of hydrogen sulfide in air was derived from:

$$D_a = 10^{-7}\ (\ (273 + T_a)^{1.75}\ (1/\text{MW}_1 + 1/\text{MW}_2)^{1/2}\ )\ /\ P\ (\ \text{V}_{i1}^{1/3} + \text{V}_{i2}^{1/3}\ )^2 \qquad [5.19]$$

where

D_a = diffusivity of H_2S in air, m^2/s

MW_1 = molecular weight of H_2S, 34 g/mol

MW_2 = molecular weight of air, 29 g/mol

V_{i1} = diffusion volume of H_2S, 20.96 cm^3/mol at 1 atm

V_{i2} = diffusion volume of air, 20.1 cm^3/mol at 1 atm

P = atmospheric pressure, 1 atm

The mass transfer coefficients were obtained from existing mass transfer correlations that are recommended as generally applicable for compounds including hydrogen sulfide **(EPA, 1994)**. The gas and liquid mass transfer coefficients are functions of wind speed at a reference height of 10 meters, kinematic viscosity, and diffusivity. The air mass transfer coefficient equation was taken from **Mackay and Yeun (1983)**:

$$k_a = 0.001 + 0.0462\ (U_*)\ S_{ca}^{-0.67} \qquad [5.20]$$

where

k_a = air mass transfer coefficient, cm/s

U_* = friction velocity, m/s

$$= 0.02\ U^{1.5} \qquad [5.21]$$

U = wind speed at reference height of 10 m

S_{ca} = Schmidt Number in air, dimensionless

$$S_{ca} = \mu_a\ /\ (\ \rho_a\ /\ D_a\ ) \qquad [5.22]$$

The liquid mass transfer coefficient equations were obtained from **Springer et al. (1984)** as applied by the **EPA (1994)** :

For $U < 3.25$

$$k_L = 2.78 \times 10^{-6}\ (\ D_w\ /\ D_{ether}\ )^{2/3} \qquad [5.23]$$

For $U > 3.25$

$$k_L = (2.6 \times 10^{-9}\ \mathrm{FD} + 1.277 \times 10^{-7})\ \mathrm{U}^2\ (\ D_w\ /\ D_{ether}\ )^{2/3} \qquad [5.24]$$

where

k_L = liquid mass transfer coefficient, m/s

D_{ether} = diffusion coefficient for ethyl ether in water, cm^2/s

FD = linear distance across surface over depth

S_{cw} = Schmidt Number in the liquid, dimensionless

$$= \mu_w\ /\ (\ \rho_w\ /\ D_w\ ) \qquad [5.25]$$

The diffusion coefficient for ethel ether (D_{ether}) is determined using equation 5.18 with a molar volume for ether of 107 cm^3.

This model has some potential shortcomings in representing the full emission process for hydrogen sulfide. First, our model only includes diffusion of hydrogen sulfide in the liquid film. Diffusion of HS^- is expected to also transport sulfide through the liquid film, but is not included. The

assumption of a well-mixed bulk solution below a liquid film may not be an accurate description of manure in storage, where a gradient in redox potential may cause a gradient in total sulfide. Moreover, liquid phase diffusion may not be the only mechanism responsible for transferring sulfide to the manure surface, since biogas bubbles emitted from manure may be a significant mechanism of hydrogen sulfide transport (**Ni et al., 2009**). Despite these shortcomings, our model is able to match measured emission rates of hydrogen sulfide from farms, suggesting that the model is a reasonable approximation, or contains compensating errors. Simulation results suggest that hydrogen sulfide emission is limited by sulfide production. Therefore, accurate predictions of hydrogen sulfide emission will ultimately require a better understanding of sulfide production in manure.

Enteric Emission

A potential source of emission on dairy farms is direct emission from the cattle through belching or flatulence. Microorganisms in the digestive tract produce gases during the digestion of feed, particularly during fermentation in the rumen (**Dewhurst et al., 2001**). Therefore, enteric and other direct emissions of hydrogen sulfide from the animals must be considered.

Hydrogen sulfide, methyl sulfide, and dimethyl sulfide are the predominant sulfur containing gases present in the rumen headspace of dairy cows (**Dewhurst et. al., 2001**). As stated by **Dewhurst et al. (2001)**, neither **Elliot-Martin et al. (1997)** or **Mottram et al. (2000)** found hydrogen sulfide above 2 mg/kg in expired breath, confirming that most of the hydrogen sulfide is absorbed via the lungs and detoxified (**Bird, 1972**). Studies by **Dewhurst et al. (2001)** confirmed significant production of dimethyl sulfide in the rumen. Although the dimethyl sulfide levels were 10-fold lower than hydrogen sulfide in rumen gas, only dimethyl sulfide was detected in the cows' breath (**Mottram et al., 2000**). Therefore, enteric hydrogen sulfide emission was assumed to be insignificant and is ignored as an emission source.

Housing Floor

Manure on the floor of housing facilities is another potential source of hydrogen sulfide emission. This hydrogen sulfide may form from sulfide in the manure excreted by the animal or it may be formed through microbial decomposition of sulfate in the manure. Floor emission is predicted on an hourly time step using the two-layer thin film model described above. The hourly emission is a function of temperature, air velocity, sulfide content in the manure, and manure pH. Hourly air temperature is predicted as a function of the daily maximum and minimum temperatures using equations 4.17 and 4.18. When the cattle are in an enclosed barn, the indoor temperature is a function of outdoor temperature (Eq. 4.16). Manure temperature is set to the average daily temperature. Air velocity in outdoor facilities is set equal to the mean daily wind velocity measured at a 10 m height as obtained from the weather input file. When animals are in an open barn, this velocity is reduced by 50%. For an enclosed barn with mechanical ventilation, the velocity is set as a function of the outdoor temperature (Eq. 4.19) to reflect an increase in ventilation rate with temperature.

Little information is available on the sulfide content of freshly excreted dairy manure on a barn floor or open lot surface. Data reported by **Zhao et al. (2007)** and **Finke and Jorgensen (2008)** indicate that sulfate reduction to sulfide increases exponentially from $0^{o}C$ to around $35^{o}C$ and then declines. Based upon the work of **Zwietering et al. (1991)**, the following relationship was developed to predict the sulfide concentration that results from microbial activity in excreted manure laying on the barn floor:

$$C_{TS} = C_S\,(0.0033\,(T_L + 5)\,)^2\,(1 - e^{(0.75\,(TL\,-\,45)\,)}\,) \qquad [5.26]$$

where

C_S = total sulfur concentration in excreted manure, kg/m^3

C_{TS} = total sulfide concentration in manure solution, kg/m^3

This sulfur concentration is a function of the diet fed with a value of 0.625 kg m^{-3} when the sulfur requirement for the herd is met (**ASABE, 2010**). This value is increased or decreased in proportion to the amount of sulfur fed above or below the requirement. As temperature increases, increased microbial activity leads to greater decomposition of sulfate in the manure to sulfide.

When a flushing system is used for manure removal, manure solids are typically removed from the manure liquid, and the liquid portion is recycled as the flushing solution. With this process, the sulfide concentration in the liquid increases and becomes less influenced by temperature:

$$C_{TS} = C_S\;(0.125 + 0.0074\,(T_L)\,) \qquad [5.27]$$

This relationship was also developed based upon data collected in the National Air Emissions Monitoring Study (**EPA, 2011**)

As illustrated in **Figure 5.1**, manure pH has a strong influence on the amount of hydrogen sulfide formed. The pH controlling volatilization is that at the manure surface or the interface between the liquid and gas phases. This surface pH is influenced by the rates of volatilization of carbon dioxide and ammonia (see **Ammonia Emission** section). For a freshly disturbed manure surface, the volatilization of carbon dioxide is greater than that of ammonia causing an increase in pH. For manure on a barn floor, this surface pH is set at an average value of 0.7 units greater than the bulk manure pH, which is set at 7.5.

Hourly emissions are summed to obtain a total emission for each day. This emission is proportional to the amount of time the animals spend in the housing facility assuming that the amount of manure excreted is proportional to the time spent in the barn or open lot. Daily emissions are summed to obtain the annual emission from the housing facility.

Manure Storage

When long term manure storage is used on the farm, this storage is typically the largest source of hydrogen sulfide emission. Stored manure emissions are modeled on an hourly time step as a function of manure and air temperatures, air velocity, sulfide concentration, manure pH, and the amount of manure in the storage. Manure temperature is predicted as the average ambient temperature over the previous 10 days. Hourly air temperature is predicted as a function of the daily maximum and minimum temperatures using equations 4.17 and 4.18. Air velocity is the reported mean daily wind velocity obtained from the weather input for the model.

The pH controlling the sulfide emission process is that at the manure surface, which can be greater than that within the storage. Bulk pH is determined as a function of the solids content of the manure using equation 4.32. For top loaded slurry storages or manure stacks, the surface pH can be greater than that of the bulk pH (See **Ammonia Storage Emissions** section). This increase is predicted as a function of the manure solids content using equation 4.33.

The amount of manure in the storage on a given day is the sum of that removed from the

housing facility since the manure storage was last emptied. The sulfide accumulated in the manure is the balance between that added through sulfate decomposition and that emitted. That added on a given day is proportional to the sulfur content of the manure in the storage as influenced by temperature:

$$TS = C_S\,(\,M_m\,)\,(\,\max(0.,\,0.00032 + 0.000073\,T_L)\,) - E_{H2S} \qquad [5.28]$$

where

C_S = total sulfur concentration in manure, 0.625 kg/m^3

TS = total sulfide contained in manure on a given day, kg

M_m = mass of manure in storage, m^3

E_{H2S} = hydrogen sulfide emitted, kg

Sulfur concentration is that remaining in the manure removed from the barn. The temperature effect on sulfide production is modeled based upon data from various sources (ex. **Finke and Jorgensen, 2008; Zhoa et al., 2007**) indicating an increase in hydrogen sulfide production with increasing temperature within the normal range of temperature for stored manure. This reflects greater microbial activity and reduction of sulfate with increasing temperature.

When a natural crust forms on the manure surface or a cover is used over the stored manure, a resistance is added to the transfer of sulfide to the surface (Equation 5.11). Resistances for the natural crust, unsealed cover and fully enclosed storage were 4.6 x 10^5, 9.2 x 10^6, and 9.2 x 10^7 s/m.

When the storage is emptied, the model is reset and the storage begins to fill. As the storage fills, the potential emission of hydrogen sulfide increases in proportion the amount of manure in the storage and the sulfide contained in that manure. As described, the amount emitted in a given hour is a function of the manure and environmental conditions of that hour. Predicted hourly emissions are summed to obtain the daily emission, and daily emissions are summed to get an annual emission.

Field Applied Manure

When manure is spread on a field surface, the thin layer applied is exposed to aerobic conditions. Under these conditions, sulfide is not expected to form. Therefore, that emitted is that contained in the applied manure. The amount of sulfide applied is that remaining in the manure removed from the storage. Considering that the transformation of sulfide to hydrogen sulfide is very fast, we assume all sulfide will transform and be emitted. This hydrogen sulfide is assumed to quickly emit on the day that it is applied. Daily emissions are then summed to obtain an annual emission.

If manure is applied using a daily haul strategy, the assumption is made that no sulfide exists in the manure. Without long term storage of the manure under anaerobic conditions, no further sulfide forms. Therefore, any hydrogen sulfide from excreted manure would be emitted as it lies on the barn floor, and that emitted following application is negligible.

Grazing Animals

Little data exists on hydrogen sulfide emissions from the excretion of grazing animals. This is a minor source, but some emission is expected from fecal deposits on the pasture.

The emission from grazing animals is modeled similar to that from animal housing floors except that only feces deposits are considered as an emission source. Hydrogen sulfide is not expected to form under the more aerobic conditions of urine deposits, but sulfide excreted in feces can be emitted. As the feces decompose, further emission may occur. The feces is assumed to decompose within 60 days with no further sulfide formation after this period.

Emissions are predicted on an hourly time step as a function of temperature, air velocity, pH, and the sulfide concentration in the feces. Hourly temperature of the feces and air are assumed to be equal. This temperature is predicted as a function of daily maximum and minimum temperatures using equations 4.17 and 4.18. Air velocity is set as the mean daily wind velocity at a 10 m height as obtained from input weather data. The pH of the feces is set at a constant value of 7.0, and the sulfide concentration is set at a constant value of 1 g/m^3. Hourly emissions are summed to obtain the total daily emission and daily emissions are summed over the time animals are on the pasture to obtain total annual emissions. This emission source is typically very small relative to other farm sources of hydrogen sulfide, so the simplifying assumptions in this component of the model are justified.

Figure 5.1 - Hydrogen Sulfide Species

Fractions of sulfide species present in aqueous solution as a function of pH at 25°C (**Blunden and Aneja, 2008; Snoeyink and Jenkins, 1980**).

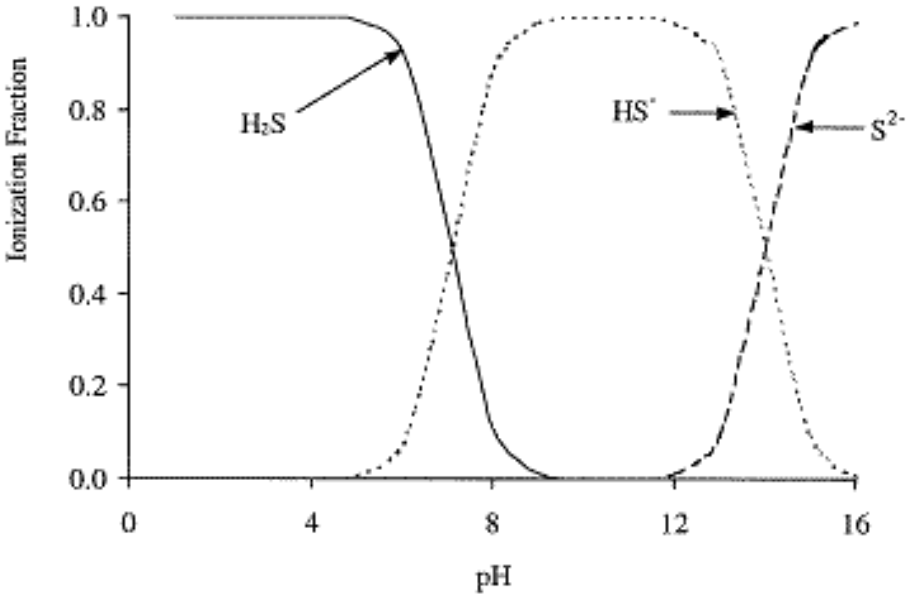
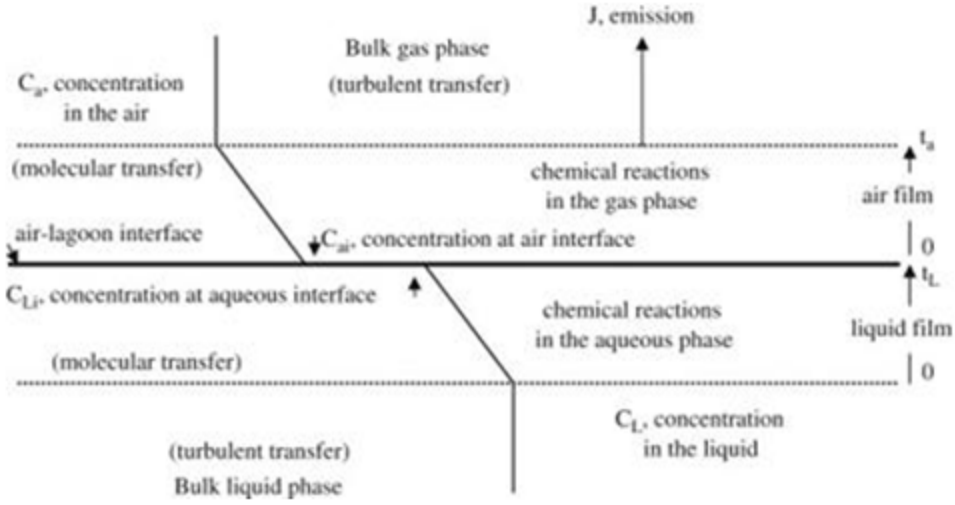


Figure 5.2 - Gas-Liquid Interface

Two-layer model of a gas-liquid interface (**Blunden et al., 2008**)



GREENHOUSE GAS EMISSIONS

Important greenhouse gases (GHG) emitted from dairy farms are carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O), with various sources and sinks of each throughout the farm. A major CO_2 sink occurs through the fixation of carbon in crop growth with emission sources including plant respiration, animal respiration, and microbial respiration in the soil and manure. Major sources of methane include enteric fermentation and the long term storage of manure with minor sources being the barn floor, field applied manure, and feces deposited by grazing animals. Nitrous oxide is a product of nitrification and denitrification processes in the soil and these processes can also occur in the crust on a slurry manure storage or during the storage of solid manure in a bedded pack or stack.

A comprehensive evaluation of production systems is obtained by considering the integrated effect of all sources and sinks of the three gases. Various processes affecting emissions interact with each other as well as with the climate, soil, and other components. Therefore, all individual processes and their interactions must be integrated in a comprehensive whole-farm analysis to determine the net result.

Carbon Dioxide

Multiple processes emit CO_2 from dairy farms. The major source is animal respiration, followed by less significant emissions from manure storages and barn floors. Cropland assimilates CO_2 from the atmosphere through fixation during crop growth and emits CO_2 through plant and soil respiration. Typically, over the course of a full year, croplands assimilate C from CO_2. In other words, the plants capture more CO_2 through photosynthesis than is emitted through respiration.

Cropland Emissions

A relatively simple but robust approach is used to predict net CO_2 emission from feed production in cropland. The long term carbon balance for the cropland producing feeds is assumed to be zero. Therefore, the sum of all carbon leaving the cropping system in feed and emissions is equal to that assimilated during the growth of the crop (i.e., the capture of CO_2 through photosynthesis) plus any other C entering the cropping system. Emissions of CO_2 from cropland include that from plant respiration (autotrophic) and soil respiration (heterotrophic), as well as microbial respiration during the decomposition of manure. The primary source of non photosynthetic C entering the system is land applied manure.

A carbon balance is determined considering all flows in and out of cropland during the production of feeds used in the dairy production system. By enforcing a long term balance, the net difference between that fixed during crop growth and that emitted through plant and soil respiration must equal the C removed in harvested feed minus that applied to the cropland in manure. Applied manure is that excreted by the animals minus all C lost in the barn, during manure storage, and following land application plus any C in manure imported to the farm and minus that exported from feed production. Therefore, the net flux of C in feed production is determined as:

$$C_{net} = C_{feed} - (C_{exc} - C_{CH4} - C_{CO2} - C_{exp} + C_{imp}) \qquad [6.1]$$

where C_{net} = net flux of C assimilated in feed production minus plant and soil respiration, kg
C_{feed} = C in feed produced plus that in bedding minus that in excess feed, kg
C_{exc} = C in manure excreted by animals on the farm, kg
C_{CH4} = C lost as CH_4 from barn floor, during storage, and following land application, kg
C_{CO2} = C lost as CO_2 from the barn floor and manure storage, kg
C_{exp} = C in manure exported from feed production, kg
C_{imp} = C in manure imported to farm, kg

The C content of most feeds is set at 40% of DM, but that in high protein concentrates is set at 45% of DM and that in added fat is set at 70%. The C in manure excreted by the animals is determined using a C balance of the herd where the C intake must equal the C output. Therefore, the C excreted is equal to that consumed in feed minus that emitted by the animals in CH4 and CO_2 and that contained in the milk and animal weight produced. Carbon in exported manure is determined as the user-defined portion of manure exported times the C remaining in excreted manure after storage. Imported manure is assumed to have a C content of 40% of DM. Emissions of CH4 and CO_2 are as defined in the following sections.

Since the net flux of C in feed production, C_{net}, represents a net exchange of CO_2 with the atmosphere, it can be converted to units of CO_2. A conversion is done by multiplying the units of C by the ratio of the molecular weight of CO_2 (44 g/mol) to that of C (12 g/mol). Therefore, there are 3.67 kg of CO_2 assimilated or released per kg of C.

Lime is often used to neutralize the acidity of soil and this provides an additional carbon source for emission as CO_2. Lime use is determined as a function of soil acidity and the crops grown following the agronomic guidelines for Pennsylvania (**Penn State, 2011**). For alfalfa and soybean crops, the calcium carbonate equivalent requirement is:

$$R_{CACO3} = 1121 \cdot EA \cdot A_{crop} \qquad [6.2]$$

where R_{CACO3} = lime requirement in calcium carbonate equivalents, kg
EA = exchangeable acidity of the soil
A_{crop} = crop area, ha.

For all other crops and when the soil exchangeable acidity is greater than or equal to 4, the calcium carbonate requirement is:

$$R_{CACO3} = 942 \cdot EA \cdot A_{crop} \qquad [6.3]$$

If the exchangeable acidity is less than 4 and the soil pH is less than 6.5:

$$R_{CACO3} = 2242 \cdot A_{crop} \qquad [6.4]$$

For a soil pH of 6.5 or greater and an exchangeable acidity of 4 or greater, the calcium carbonate equivalent requirement is zero. By totaling the requirements for all crop areas, a total requirement is

determined. Since this requirement is normally applied every three years, the total is divided by 3 to obtain an average annual requirement.

Over the three year period following lime application, most of the added carbon transforms to carbon dioxide that is volatilized to the atmosphere. We assume that 10% of the total applied will be lost through leaching, runoff or other non volatile means; therefore, 90% is lost through CO_2 volatilization. This primary emission of CO_2 is determined considering that there are 0.12 units of CO_2 carbon emitted per unit mass of calcium carbonate equivalent applied (**IPCC, 2006**).

$$E_{CO2,lime} = 0.12 \cdot 44/12 \cdot 0.9 \cdot A_{CACO3} \qquad [6.5]$$

where $E_{CO2,lime}$ = CO_2e emitted from applied lime, kg
A_{CACO3} = Average annual application of calcium carbonate equivalent, kg.

It is important to note that this approach does not allow for long term sequestration or depletion of soil C. By forcing a long term balance, it is assumed that there is no net change in soil C content over time. If major changes in tillage and cropping practices are made, soil C levels can change over a number of years until the soil again reaches an equilibrium level. An example of this type of change is the conversion of row cropland to perennial pasture. Substantial amounts of soil C can be sequestered over 25 to 50 years until equilibrium soil conditions are maintained. Another example is the conversion of conventional tillage to reduced tillage or no tillage practices. Such conversions can increase the net flux of C into feed production, i.e. reduce net CO_2 emission. Our model does not account for this potential change in soil C, but this change can be added or subtracted from the net value determined by DairyGEM. To obtain values for quantifying long term changes in soil C, we recommend the COMET-VR model available at http://www.comet2.colostate.edu/. COMET-VR provides a relatively easy to use tool for quantifying potential changes in soil C with changes in production practices. Values obtained can be used to adjust values predicted by DairyGEM.

Animal Respiration

Carbon dioxide emission through animal respiration is sometimes ignored as a GHG emission source (**IPCC, 2001** and **2007**). This respired CO_2 is part of the C cycle that initially begins with photosynthetic fixation by plants. When the animals consume the crop (fixed C in the plant material), they convert it back to CO_2 through respiration (**Kirchgessner et al., 1991**; **IPCC, 2001**). On a farm, animal respiration of CO_2 is a major source relative to other CO_2 emissions. In the overall farm balance, the CO_2 released largely offsets the CO_2 assimilated in the plant material. However, some of the feed intake of C is converted and released as CH_4 and some is in the milk and animals produced. To obtain a full accounting and balance of all C flows through the farm, all sources of C emissions, including animal respiration, are considered.

A relationship developed by **Kirchgessner et al. (1991)** relating CO_2 emissions to DMI is used to predict animal respiration. Respired CO2 is determined as:

$$E_{CO2,resp} = -1.4 + 0.42 \cdot M_{DMI} + 0.045 \cdot M_{BW}^{0.75} \qquad [6.6]$$

where $E_{CO2,resp}$ = emission of CO_2 from animal respiration, kg CO_2/head/day
M_{DMI} = daily intake of feed dry matter for each animal, kg DM/head/day
M_{BW} = animal body weight, kg.

The DMI and body weight for each animal group are available from the herd component. Dry matter intake is determined based upon the nutrient requirements (fiber, energy and protein) of a representative animal for each group within the herd and the amount and nutrient content of available feeds including pasture (See **Dairy Herd** section). Body weight is determined based upon animal breed, as specified by the model user, and the age and stage of lactation as simulated in the herd component.

Barn Floor Emissions

Floors of housing facilities can be a source of CO_2 emissions due to decomposition of organic matter in manure deposited by animals. Although not a major source, barn floor emissions are included to obtain a comprehensive simulation of farm-level CO_2 emissions from all sources.

Published models to predict CO_2 emissions from barn floors were not found. Using emissions data measured from manure covered floors in a free stall barn at the Penn State dairy facility (**Wheeler et al., 2008**), an equation was developed through regression analysis relating CO_2 emission to the ambient temperature in the barn and the manure covered floor area ($R^2 = 0.74$).

$$E_{CO2,floor} = \max(0.0, 0.0065 + 0.0192\,T)\,A_{barn} \qquad [6.7]$$

where $E_{CO2,floor}$ = daily rate of CO_2 emission from the barn floor, kg CO_2/day
T = ambient temperature in the barn, °C
A_{barn} = floor area covered by manure, m^2

Equation 6.7 represents the best available information describing CO_2 emissions from barn floors. As a function of temperature, this relationship provides a simple process-based model that predicts reasonable emission rates over a full range in potential ambient barn temperatures. Because barn floor emissions are so small compared to other sources, development of a more sophisticated model was not justified at this time.

Manure Storage

Compared to other farm sources, slurry storages emit relatively low amounts of CO_2. Because of this minimal contribution to whole-farm emissions, there were no models and few data available quantifying CO_2 emissions from storages. Lack of available data, as well as the relative importance of this loss to overall farm emissions did not support the development of a detailed model. Therefore, a constant emission factor represented the best available method for predicting this emission. To determine an emission factor, emission rates were obtained from two published studies and the average was used as our emission rate (**Table 6.1**).

The average emission rate of 0.04 kg CO_2/m^3-day is applicable to uncovered slurry storages. Covers are sometimes used to reduce gaseous emissions, but no data were available documenting the effect of covers on CO_2 emissions. To model this effect, we assumed that CO_2 emissions are reduced

by a similar proportion when using a cover as found for more important gases such as ammonia. For ammonia, a cover reduces emission by about 80%, depending upon the storage dimensions (**Rotz et al., 2015**). Therefore, to simulate CO_2 emissions from a covered storage, the emission rate was reduced to 0.008 kg CO_2/m^3-day. To represent a sealed storage where biogas is burned, the loss of CO_2 was eliminated. However, the total emission from this type of storage includes the CO_2 created through the combustion of CH_4 (see the following section on CH_4 emission).

Engine Combustion

During the operation of tractors and other engine powered equipment, C in fuel is transformed to CO_2, which is released in engine exhaust. The amount of CO_2 produced is proportional to the amount of fuel consumed. The emission factor used is 2.637 kg CO_2e/liter of diesel fuel consumed (**Wang, 2007**). Fuel consumption is estimated using fuel use factors for each feed produced and the amount of manure handled (see section on **Energy Use**). Total fuel use is the sum of .that used for producing and feeding each feed and that used in manure handling.

Methane

Methane is a strong GHG with a global warming potential around 25 times that of CO_2 (**IPCC, 2007**). Multiple processes emit CH_4 from dairy farms. The majority of CH_4 is created through enteric fermentation, followed by emissions from manure storages (**EIA, 2006; Chianese et al., 2009a**). In addition to these major sources, smaller emissions result from field-applied manure and manure deposited by animals inside barns or on pasture. Most field studies report croplands as a negligible source, or very small sink, of CH_4 over full production years. However, field-applied manure can result in significant emissions for a few days after application. In DairyGHG, emissions from cropland are neglected except for this small emission that occurs immediately after manure application.

Enteric Fermentation

Ruminant animals subsist primarily on forages. Like most animals, ruminants do not have the enzymes necessary to break down cellulose. Instead, enteric methanogens, which exist in a symbiotic relationship with other microorganisms in the rumen, break down and obtain energy from cellulose. During this process, hydrogen is produced and can build up in the rumen, leading to acidosis, a health problem in dairy cows. However, these methanogens decrease the amount of hydrogen in the rumen by using the excess to reduce CO2 to CH_4, preventing this health effect. The CH_4 produced is released to the atmosphere by eructation and respiration. The amount of CH_4 produced from enteric fermentation is impacted by various factors including animal type and size, digestibility of the feed, and the intake of dry matter, total carbohydrates, and digestible carbohydrates (**Monteny et al., 2001**; **Wilkerson et al., 1995**).

After considering the various mechanistic and empirical models available to predict enteric fermentation emissions (**Wilkerson et al., 1995; Benchaar et al., 1998**; and **Mills et al., 2003**), a relatively simple approach is used, which uses the Mitscherlich 3 (Mits3) equation developed by **Mills et al. (2003)**. Mits3 is a simplified process model that is well suited for use in whole-farm simulation. The model is based on dietary composition and is capable of accounting for management practices that alter the animal's intake and diet. Mits3 is process-based, relating CH_4 emissions to dietary intake

as well as animal type and size. When compared to data from the U.S., Mits3 has yielded a regression slope of 0.89 with an intercept of 3.5 and a square root of the mean square prediction error (MSPE) of 34% (**Mills et al., 2003**). In addition, Mits3 predicts realistic emissions at the extremes of the parameter ranges. With zero feed intake, the model predicts zero CH_4 production; at the other extreme of very high feed intake, the nonlinear model predicts that CH_4 emission approaches a maximum. Thus, the model can be applied to conditions outside those for which it was originally developed without predicting unreasonable emissions.

Three model inputs are required: starch content of the diet, acid detergent fiber (ADF) content of the diet, and metabolizable energy intake. These inputs are readily obtained from the feed and animal components of DairyGHG. Through these inputs, CH4 production is directly related to diet and indirectly related to animal size and type. This allows prediction of changes in CH_4 production as affected by changes in animal nutrition and management. A detailed description of the selected model can be found in **Mills et al. (2003)**.

Enteric emission of CH_4 is predicted as:

$$E_{CH4,ent} \; [\, E_{max} \; - \; E_{max} \exp(-c \cdot M_{EI}\,)\,]\; F_{kgCH4} \qquad [6.8]$$

where $E_{CH4,ent}$ = emission due to enteric fermentation, kg CH_4 /head-day
E_{max} = maximum possible emission, MJ CH4 /head-day
c = shape parameter for how emissions change with increasing $M_{EI,}$ dimensionless
M_{EI} = metabolizable energy intake, MJ/head-day
F_{kgCH4} = conversion of MJ to kg of CH4, 0.018 kg CH_4 /MJ

From **Mills et al. (2003),** the maximum possible emission is defined as 45.98 MJ CH4 / head-day. This maximum possible emission is constant for all animals; the effect of animal size and type is indirectly provided through the value of M_{EI}. The shape parameter, c, is calculated as:

$$c = -0.0011 \cdot (\, Starch \,/\, ADF) + 0.0045 \qquad [6.9]$$

where $Starch$ = starch content of the diet, fraction
ADF = acid detergent fiber content of the diet, fraction

Equation 6.4 models the observed trend of increased CH_4 emission with high fiber diets and decreased emission with high starch diets.

To use the above equations, values are needed for the starch and ADF contents of diets and the metabolizable energy intake of animal groups making up the herd. The herd component determines the ration that each animal group is fed based upon a representative animal's nutritional requirements and the available feeds (See **Herd** and **Feed** Sections). This information includes the required energy content of the diet [MJ/kg DM], the total dry matter intake [kg DM/day/head], and the amount of each feed used. The first two parameters are used to calculate M_{EI}. The ADF contents of feeds are determined assuming a linear relationship with neutral detergent fiber (NDF) for each feed type (**Table 6.2**). These relationships were developed using feed composition data from the National Research Council (**NRC, 2001**). The starch contents of feeds are determined assuming a linear

relationship with the amount of non fiber carbohydrate (NFC) in the feed (**Table 6.2**). The fraction of NFC is determined as:

$$F_{NFC} = 1 - (F_{NDF} + F_{CP} + F_{fat} + F_{ash}) \quad [6.10]$$

where F_{NFC} = fraction of NFC in the diet
F_{CP} = fraction of crude protein (CP) in the diet
F_{fat} = fraction of fat in the diet
F_{ash} = fraction of ash in the diet.

The fractions of NDF and CP are available in the herd component; typical fractions of fat and ash (**Table 6.2**) were obtained from the National Research Council (**NRC, 2001**). A given animal group is typically fed a mixture of feeds making up the whole diet. A weighted average of the individual feed characteristics in the ration is used to determine the starch and ADF contents of the full ration fed to each of the six possible animal groups making up the herd.

Barn Emissions

Manure on housing facility floors is also a small source of CH_4. No published model or data were found for this emission source. Therefore, unpublished CH_4 emission data measured from free stall barn floors (**Wheeler et al., 2008**) were used to develop an empirical equation relating CH_4 emission to the ambient temperature in the barn ($R^2 = 0.48$). The resulting model is:

$$E_{CH4,floor} = \max(0.0,\ 0.13\ T) \cdot A_{barn} / 1000 \quad [6.11]$$

where $E_{CH4,floor}$ = daily rate of CH_4 emission from the barn floor, kg CH_4 /day
T = ambient barn temperature, °C
A_{barn} = area of the barn floor covered with manure, m^2

This relationship represents the best available information describing CH_4 emissions from free stall and tie stall barn floors. The temperature dependence of CH_4 production is well-documented (**Zeikus and Winfrey, 1976**; **van Hulzen et al., 1999**). This simple relationship predicts reasonable emission rates for ambient temperatures of 0°C and greater.

When manure is allowed to accumulate into a bedded pack, CH_4 emissions are increased. For this management option, an adaptation of the tier 2 approach of the IPCC (2006) is used. Emission on a given day is determined as a function of the ambient barn temperature and a methane conversion factor (MCF).

$$E_{CH4,floor} = VS\,(B_m)\,(0.67)\,(MCF) / 100 \quad [6.12]$$

where $E_{CH4,floor}$ = daily CH_4 emission, kg CH_4 /day
VS = volatile solids excreted in manure, kg VS
B_m = maximum CH_4 producing capacity for dairy manure, 0.24 m^3 CH_4 /kg VS
0.67 = conversion factor of m^3 CH_4 to kg CH_4

MCF = CH_4 conversion factor for the manure management system, %.

MCF is modeled as an exponential function of ambient barn temperature through a regression of the data provided by the **IPCC (2006)**:

$$MCF = 7.11\ e^{0.0884(T_b)} \qquad [6.13]$$

where T_b = ambient barn temperature, ^oC
MCF is limited to a minimum value of 0 and maximum of 80.

In warm dry climates, animals are often housed in open, non vegetated areas normally referred to as open lots. Manure typically accumulates on the soil surface for weeks or months before being removed. To predict emissions from this surface, the tier 2 approach of **IPCC (2006)** is again used. Based upon the IPCC (2006) data, MCF was modeled as a linear relationship with ambient outdoor temperature:

$$MCF = 0.0625\ T_a - 0.25 \qquad [6.14]$$

where T_a = ambient temperature, ^oC.
MCF is limited to a minimum value of 0. In systems that combine free stall and open lot housing, the assumption is made that half of the manure is deposited in free stall allies with the remainder deposited on the open lot. The total emission is then the sum of the two sources modeled using the appropriate relationships.

Manure Storage

During manure storage, CH_4 is generated through a reaction similar to that described for enteric fermentation. The cellulose in the manure is degraded by microbes, with products of this process serving as substrates for methanogenesis. Temperature and storage time are the most important factors influencing CH4 emissions from stored manure because substrate and microbial growth are generally not limited (**Monteny et al., 2001**). Although the processes are similar, there are important differences between the rumen and manure storage. The temperature in the storage varies, in contrast to the relatively constant temperature in the rumen, and the manure in storage is more heterogeneous (e.g., the substrate is less well mixed and some carbohydrates are already partially decomposed) as compared to the consistency of the rumen (**Monteny et al., 2001**).

As with enteric fermentation, both mechanistic and empirical models have been developed to predict CH_4 emissions from manure storages. Unlike some of the empirical enteric fermentation models that simply use statistical correlations, the majority of empirical manure storage models are biologically based. After considering two mechanistic (**Hill, 1982**; and **García-Ochoa et al., 1999**) and four empirical models (**Chen and Hashimoto, 1980**; **Hill, 1991**; **Zeeman, 1994**; and **Sommer et al., 2004**), the model of **Sommer et al. (2004)** was selected as the most appropriate approach for our application. Their model employs commonly used empirical relationships (e.g., Arrhenius relationship) that are more general and thus more applicable to conditions outside of which they were developed. Additionally, this is a more recent model, incorporating more recent developments and data. Unlike most of the other models, the model of **Sommer et al. (2004)** was developed for more general application to either digested or untreated slurry manure.

The model of **Sommer et al. (2004)** simulates the production and emission of CH_4 from manure storages based upon the degradation of volatile solids (VS). Additional factors affecting CH_4 production are temperature and storage time. Some extension of their model was done to better fit the needs of our simulation. Whereas their model was developed to predict emission based upon the volatile solids entering storage, we modified the relationship to determine the emission rate as a function of the volatile solids contained in the manure storage on any given day. The emission rate from a slurry storage with a crust on the surface is given by:

$$E_{CH4,man} = 0.024\ VS_T \cdot \left(VS_d \cdot b_1 + VS_{nd} \cdot b_2\right) \cdot \exp\left[\ln(A) - \left(E/RT\right)\right] \qquad [6.15]$$

where $E_{CH4,man}$ = emission of CH_4 from the storage, kg CH_4 /day

VS_T = VS contained in the storage on a given day, kg

VS_d and VS_{nd} = degradable and nondegradable VS fractions in the manure, kg/kg VS

b_1 and b_2 = rate correcting factors, dimensionless

A = Arrhenius parameter, g CH_4 /kg VS-h

E = apparent activation energy, J/mol

R = gas constant, J/K/mol

T = temperature, ^oK

Values used for these parameters are listed in **Table 6.3**.

The portion of degradable volatile solids in the storage is the difference between that loaded into the storage and that lost from the storage where all of that lost is assumed to be in a degradable form. From **Sommer et al. (2004)**, the degradable fraction of the VS can be determined from the potential methane yield and the achievable emission:

$$VS_d = VS_{in}\,(B_o / E_{CH4,pot}) - VS_{loss}) / VS_T \qquad [6.16]$$

where VS_{in} = VS loaded into the storage up to the given day, kg

VS_{loss} = VS lost from the storage up to the given day, kg

B_o = achievable emission of CH_4 during anaerobic digestion, kg CH_4/kg VS

$E_{CH4,pot}$ = potential CH_4 yield of the manure, kg CH_4/kg VS

$E_{CH4,pot}$ can be estimated using Bushwell's equation and the carbohydrate, fat, and protein content of the manure. For cattle slurry, **Sommer et al. (2004)** defined B_o as 0.2 kg CH_4 / kg VS and $E_{CH4,pot}$ as 0.48 kg CH_4 / kg VS.

Total VS in the manure storage at any point in time is the difference between that entering the storage and that lost from the storage up to that point. The amount entering is determined from the manure mass removed from the barn and the total solids and VS contents of that manure:

$$VS_T = M_{manure} \cdot P_{TS} \cdot P_{VS} - VS_{loss} \qquad [6.17]$$

where M_{manure} = accumulated mass of manure entering the storage, kg

P_{TS} = total solids content in the manure, kg TS / kg manure
P_{VS} = fraction of VS in the total solids, kg VS / kg TS (**Table 6.3**)
VS_{loss} = accumulated VS loss, kg.

To obtain a similar rate of VS loss as that reported by **Sommer et al. (2004)**, this loss was predicted as three times the methane loss from the stored manure. The fraction of nondegradable volatile solids is determined using a mass balance:

$$VS_{nd} = VS_T - VS_d \qquad [6.18]$$

The inputs required are the mass and temperature of the manure in storage. The amount of manure in storage is the accumulation of that produced by the herd while in the barn with daily manure excretion determined in the animal component (See **Manure DM and Nutrient Production** section). The temperature of the manure in storage on a given simulated day is estimated as the average ambient air temperature over the previous ten days.

This predicted storage emission is for an uncovered, bottom-loaded storage of slurry (7 - 12% DM) manure where a crust forms on the surface. For a top-loaded tank or with manure containing less DM, this emission rate is increased 60% (**IPCC, 2006**). Storage covers are sometimes used to reduce emissions. With a non-sealed cover, the emission rate is reduced to 50% of that occurring from the open storage. A more tightly sealed cover or enclosed storage can be used where the biogas produced is burned to convert the emitted CH_4 to CO_2. This technique greatly reduces the emission of CH_4, although it does increase the emission of CO_2 through the combustion of CH_4. To simulate this storage treatment, the emission of CH_4 from an enclosed manure storage is calculated as:

$$E_{CH4,cov} = E_{CH4,man} \cdot (1 - \eta_{eff}) \qquad [6.19]$$

where $E_{CH4,cov}$ = CH_4 emitted from the enclosed manure storage, kg CH_4 /day
$E_{CH4,man}$ = CH_4 emission from the storage with no cover using equation 6.11, kg CH_4 /day
η_{eff} = efficiency of the collector, dimensionless

The efficiency of the collector and flare is assumed to be 99% (**EPA, 1999**). The subsequent flaring of the captured CH_4 releases CO_2, which adds to the overall farm emission of this gas. Assuming complete combustion, the additional emission of CO_2 from the combustion of CH_4 is calculated as:

$$E_{CO2,flare} = E_{CH4,cov} \cdot 2.75 \qquad [6.20]$$

where $E_{CO2,flare}$ = emission of CO_2 from the combustion of captured CH_4, kg CO_2 /day
2.75 = ratio of the molecular weights of CO_2 and CH_4.

Semi-solid (8-14% DM) and solid manure (>15% DM) can be stored in stacks. Methane emission from this type of storage is modeled through an adaptation of the tier 2 approach developed by the **IPCC (2006)**. Emission on a given day is determined as a function of the total volatile solids placed into the storage and the methane conversion factor:

$$E_{CH4} = VS\,(B_m)\,(0.67)\,(MCF)\,/\,100 \qquad [6.21]$$

where E_{CH4} = daily CH_4 emission, kg CH_4 /day

B_m = maximum CH_4 producing capacity for dairy manure, 0.24 m^3 CH_4 /kg VS

0.67 = conversion factor of m^3 CH_4 to kg CH_4

MCF = CH_4 conversion factor for the manure management system, %.

Using the recommended data of the **IPCC (2006)**, a function was developed to predict *MCF* as a function of the temperature of the stored manure:

$$MCF = 0.201\ T_m - 0.29 \qquad [6.22]$$

where T_m = manure temperature, ^oC.

MCF is set at a minimum of zero, and the manure temperature is the average ambient temperature over the previous 10 days.

Field-Applied Manure

Research has shown that field-applied slurry is a source of CH_4 for several days after application, emitting between 40 to 90 g CH_4/ha-day (**Sommer et al., 1996**; **Chadwick and Pain, 1997**; **Sherlock et al., 2002**). Emissions drastically decrease within the first few days, and the soils return to a neutral source of CH_4 by 11 days (**Sherlock et al., 2002**).

Sherlock et al. (2002) related CH_4 emissions from field-applied slurry to the volatile fatty acids (VFAs) concentration in the soil. Because the VFAs in the soil are due to the application of the slurry (**Sherlock et al., 2002**), their model is used to relate CH_4 emissions to the VFA concentration in the slurry. Emission of CH4 from field-applied slurry is predicted using the following derived empirical relationship:>

$$E_{CH4,app} = (0.170 \cdot F_{VFA} + 0.026\,) \cdot 0.032 \cdot A_{man}\ /\ r_{app} \qquad [6.23]$$

where $E_{CH4,app}$ = emission of CH_4 from field-applied slurry, kg CH_4 /day

F_{VFA} = daily concentration of VFAs in the slurry, mmol /kg slurry

A_{man} = amount of manure applied, kg

r_{app} = application rate, kg/ha

Sherlock et al. (2002) found that the daily VFA concentration exponentially decreased in the days following the application of manure slurry and approached background levels within approximately four days. Using this information, we derived a relationship predicting the daily concentration of VFA in the field-applied slurry:

$$F_{VFA} = F_{VFAi}\ e^{-0.6939\ t} \qquad [6.24]$$

where F_{VFA} = daily concentration of VFAs in the slurry, mmol /kg slurry

F_{VFAi} = initial VFA concentration in the slurry at application, mmol /kg slurry

t = time since application with t = 0 representing the day of application, day

Paul and Beauchamp **(1989)** developed an empirical model relating the pH of manure slurry to VFA and total ammoniacal nitrogen (TAN) concentrations:

$$pH = 9.43 - 2.02 - [F_{VFAi} \ / \ F_{TAN}] \qquad [6.25]$$

where pH = pH of the manure slurry, dimensionless

F_{TAN} = concentration of TAN ($NH_4^+ + NH_3$) in the slurry, mmol /kg slurry

Rearranging Equation 6.21, we obtained an equation to predict the initial concentration of VFAs based on the pH and TAN content of the manure slurry:

$$F_{VFAi} = [F_{TAN} \ / \ 2.02] \ (9.43 - pH) \qquad [6.26]$$

To predict emissions from field applied manure, equation 6.22 was used to determine an initial VFA concentration and equation 6.20 was used to track the VFA concentration through time following field application. Using this concentration, an emission rate was determined until the remaining VFA concentration approached zero.

Grazing Animals

On farms that incorporate grazing for at least a portion of the year, freshly excreted feces and urine are directly deposited by animals on pastures. Studies have shown that feces are a small source of CH_4 and that emissions from urine are not significantly different from background soil emissions (e.g., **Jarvis et al., 1995**; **Yamulki et al., 1999**). Because animal-deposited feces contribute only minimally to overall farm CH_4 emissions, there are few data quantifying these emissions.

Due to the lack of supporting data and the relatively low importance of this emission source, a constant emission factor is used to predict CH_4 from the feces deposited by grazing animals. To determine this emission factor, emission rates were obtained from four published studies and the average (0.086 g CH_4 /kg feces) was used for our emission rate (**Table 6.4**). Therefore, for grazing systems, the daily emission of CH_4 is predicted as the product of this emission rate and the daily amount of feces deposited by grazing animals.

Nitrous Oxide

Nitrous oxide is the strongest of all greenhouse gases emitted in agricultural production with a global warming potential 298 times that of CO_2 (**IPCC, 2007**). In 2005, agriculture had the greatest overall impact on N_2O emissions, contributing 78% of the U.S. total (**EIA, 2006**). In fact, this contribution has become increasingly important, with reported emissions increasing by 10% between 1990 and 2005 (**EIA, 2006**). Multiple sources emit N_2O on dairy farms. The majority is emitted from soil, followed by manure storages, with relatively small amounts emitted from manure in bedded pack barns or open lots (**Groenestein and Van Faasen, 1996**; **EPA, 2008**).

Cropland Emissions

Croplands are the largest source of N_2O emitted from dairy farms. Although undisturbed soils

emit N_2O naturally, the rate of emission from cultivated soils is much greater because of the greater N inputs. Two pathways can lead to emissions of N_2O: denitrification and nitrification. Denitrification is the microbial reduction of NO_3 to N_2 under anaerobic conditions, with the production of NO and N_2O as intermediates (**Figure 6.1**).

Historically, denitrification was believed to be the primary source of N_2O emissions; however, scientists have established that nitrification also contributes to emissions (**Sahrawat and Keeney, 1986**). Nitrification is an aerobic process that oxidizes NH_4^+ to NO_3, with the production of NO and N_2O as intermediates (**Figure 6.2**).

The emission of N_2O is thus dependent on both denitrification and nitrification. A conceptual model published by **Davidson et al. (2000)** describes how denitrification and nitrification are connected (**Figure 6.3**). This model, known as the "hole-in-the-pipe" (HIP) model, connects the two pathways and thus links the emission of NO and N_2O (**Davidson et al., 2000**).

To simplify the model, soil processes are not simulated in DairyGEM. Therefore, a relatively simple emission factor approach had to be used to estimate N_2O emissions in the production of feeds. Based upon the recommendation of the **IPCC (2007)**, the N_2O-N emission from cropland is set at 1% of the N applied and that from pasture land is set at 2% of applied N. Since crop production is not simulated, N applied is set as 40% greater than that removed in harvested feed. This approach assumes relatively efficient use of N fertilizer in producing the feed crops. The over application of 40% allows for the loss of N that naturally occurs when N is applied at a recommended rate to meet nutrient removal. To predict N application, the total N in the feed consumed by the herd is determined as the sum of the DM for each feed consumed times the protein content divided by 6.25. This N is increased by 40% and multiplied by the appropriate emission factor and an N to N_2O conversion factor of 1.57. The N deposited in pasture is proportioned by the time animals spend in the pasture, which is a function of the grazing system used. When animals are maintained outdoors all year, 85% of excreted N is applied to pastureland.

This approach was evaluated by comparing predicted emissions from this simple model to those predicted by a more complex process-based approach in the Integrated Farm System Model (**Rotz et al., 2015**). In general, average annual values predicted by the two approaches were similar even though this simple approach did not account for differences in soil type and climate conditions. Development of a more robust model for use in DairyGEM to predict N_2O emission from cropland is planned.

Barn Emissions

Free Stall and Tie Stall Barns

Manure on the floors of free stall and tie stall barns appears to be a negligible source of N_2O emission. Based upon limited available data, the emission of N_2O is modeled as zero from the floors of these facilities where manure is typically removed on a daily basis (**Chianese et al., 2009b**).

Open Lot Facilities

For open lots, prediction of N_2O emissions involves simulation of other processes that affect

the nitrogen balance and forms in the manure pack. These processes include mineralization, nitrification, denitrification and leaching. Urine *N* hydrolyzes and manure organic *N* mineralizes to form NH_4^+. Through nitrification, NH_4^+ is converted to NO_3^-, which can undergo leaching and denitrification. Based on the Nitrate Leaching and Economic Analysis Package (NLEAP) model (**Shaffer et al., 1991**), the mineralization rate of manure organic N is a function of temperature, moisture content and a mineralization rate coefficient. Using the experimental data by **Pratt and Castellanos (1981)**, the derived daily mineralization rate coefficient for cattle manure is 0.052/day. Hydrolyzed urine *N* that infiltrates the manure pack (see **Ammonia Emission - Open lots** section) undergoes nitrification. Modeling of nitrification, denitrification and leaching processes are based on relationshis from the DAYCENT model (**DAYCENT, 2007**).

DAYCENT is process-based, accounting for how management scenarios affect the moisture content, pH, soil ammonium and nitrate concentrations and gaseous *N* emissions for croplands. Detailed documentation of the N_2O module of DAYCENT can be found in **Del Grosso et al. (2000)** and **Parton et al. (2001)**. Some relationships have been modified for open lot predictions. This section provides a brief description of the relationships as incorporated in DairyGEM.

Emission of N_2O from the manure pack is predicted as the sum of nitrification and denitrification losses:

$$E_{N2O,soil} = E_{N2O,soil,N} + E_{N2O,soil,D} \qquad [6.27]$$

where

$E_{N2O,soil}$ = total emission of N_2O from the manure pack, kg N_2O/ha-day
$E_{N2O,soil,N}$ = emission due to nitrification, kg N_2O/ha-day
$E_{N2O,soil,D}$ = emission due to denitrification, kg N_2O/ha-day

Emission from nitrification is predicted as:

$$E_{N2O,soil,N} = K_2 \cdot R_{NO3} \cdot F_{N,conv} \qquad [6.28]$$

where

K_2 = fraction of nitrified N lost as N_2O flux, g N/g N
R_{NO3} = nitrification rate, g N/m^2- day

$F_{N,conv}$ = conversion factor, 15.7 (kg N_2O/ha-day)/(g N/m^2- day)

Parton et al. (2001) defined K_2 as 0.02 g N flux/g N nitrified. The equation used for computing the nitrification rate in the manure pack, R_{NO3}, is:

$$R_{NO3} = K_{max} \cdot N_{NH4} \cdot F_{wfp} \cdot F_{ph} \qquad [6.29]$$

where

K_{max} = maximum fraction of ammonium concentration nitrified
N_{NH4} = ammonium concentration in the manure pack, g N/m^2-day

F_{wfp} = factor for the effect of manure pack moisture, dimensionless
F_{ph} = factor for the effect of manure pack pH, dimensionless

The effects of manure pack moisture and pH on the nitrification rate are computed using relationships described in **Parton et al. (1996)**. Unlike the model described by **Parton et al. (2001)**, the effect of temperature on nitrification is not considered because no relationship has been established between manure pack temperature and nitrification for open lots (**Woodbury et al., 2001**). The K_{max} is set to 0.40 based on a feedyard soil experiment (**Stewart, 1970**). Nitrification is also predicted for the first 3 upper layers only (see **Ammonia Emission - Open lots** section). Because there is no NH_4^+ source for the lower layer (100-cm depth) and NH_4^+ in the upper layers does not leach, it is assumed that no nitrification occurs in the lower layer.

For both upper and lower soil layers, emission of N_2O due to denitrification is predicted as:

$$E_{N2O,soil,D} = \left[\left(min(F_{d,NO3} \cdot F_{d,CO2}) \cdot F_{d,WFPS} \right) \Big/ (1+R_{Nratio}) \right] \cdot \rho_{soil} \cdot d_{soil} \cdot F_{N,mass} \qquad [6.30]$$

where
$E_{N2O,soil,D}$ = emission of N_2O from the manure pack, kg N_2O/ha-day
$F_{d,NO3}$ = factor for the effect of manure pack nitrate concentration, µg N/g soil-day
$F_{d,CO2}$ = factor for the effect of respiration in the manure pack, µg N/g soil-day
$F_{d,WFPS}$ = factor for the effect of manure pack moisture, dimensionless
R_{Nratio} = ratio of N_2 to N_2O emission, µg N/µg N
ρ_{soil} = bulk density of the manure, g/cm^3
d_{soil} = active depth of layer simulated (upper, lower), cm
$F_{N,mass}$ = unit conversion factor, 0.157 (kg N_2O/ha-day) /(µg N/cm^2-day)

Similar to the model of **Parton et al. (1996)**, the effect of nitrate concentration on the N_2O flux due to denitrification, $F_{d,NO3}$, is calculated using an arctangent function (**DAYCENT, 2007**). The nitrate concentration for the upper layer is estimated from the amount of nitrified N (equation 6.29) and for the lower layer, is estimated from the amount of nitrate that leached from the upper layers to the lower layer (equations 6.39 to 6.41). The effect of soil respiration on the N_2O flux due to denitrification, $F_{d,CO2}$, is predicted as (**Parton et al., 2001**):

$$F_{d,CO2} = 0.1 \cdot (C_{CO2})^{1.3} \qquad [6.31]$$

where C_{CO2} = CO_2 flux in the feedyard soil layer, µg C/g soil.

The model of **Parton et al. (2001)** assumes that denitrification does not occur at a soil moisture below approximately 55%. Above 55%, denitrification increases exponentially and asymptotically approaches a maximum as soils approach saturation. This effect is predicted as:

$$F_{d,WFPS} = 0.45 + \arctan [0.6 \cdot \pi (0.1 w_{wfps} - a)] / \pi \quad [6.32]$$

where

w_{wfps} = water-filled pore space, percent

a = factor controlling soil moisture content where denitrification is half the maximum rate

arctan = arctangent function, radians

Parameter a is calculated as:

$$a = 9.0 - M \cdot C_{CO2} \quad [6.33]$$

$$M = 0.145 - 1.25 \cdot \min (0.113, D_{fc}) \quad [6.34]$$

where

M = interaction between soil moisture and respiration, dimensionless

D_{fc} = gas diffusivity coefficient, dimensionless

As in DAYCENT (**Del Grosso et al., 2000**), the ratio of gas diffusivity in the manure pack to gas diffusivity in the air, D_{fc}, is computed using the method described by **Potter et al. (1996)**.

The ratio of N_2 to N_2O, R_{Nratio}, is predicted as:

$$R_{Nratio} = F_{r,NC} \cdot F_{r,WFPS} \quad [6.35]$$

where

$F_{r,NC}$ = ratio of electron donor (NO_3) to substrate (CO_2), dimensionless

$F_{r,WFPS}$ = effect of manure pack moisture on the relative emissions of N_2 and N_2O, dimensionless

DAYCENT uses empirical equations to model $F_{r,NC}$ and $F_{r,WFPS}$. The effect of the ratio of NO_3 to CO_2 is predicted as:

$$F_{r,NC} = \max [(0.16 \cdot K_1), (K_1 e^{-0.8r})] \quad [6.36]$$

$$K_1 = \max [1.7, (38.4 - 350 \cdot D_{fc})] \quad [6.37]$$

where K_1 = intercept of $F_{r,NC}$, dimensionless

r = ratio N_{NO3} to C_{CO2}, g N/g C

The effect of manure pack moisture is predicted as:

$$F_{r,WFPS} = \max [0.1, (0.015 \cdot w_{wfps} - 0.32)] \quad [6.38]$$

Leaching affects the amount of nitrate available for denitrification. The fraction of the total nitrate that leached from a layer is a function of the nitrate concentration, the sand content in the layer,

the amount of water leached, and empirical parameters from DAYCENT:

$$N_{leach} = 0 \qquad \text{when } W_{leach} = 0 \qquad [6.39]$$

$$N_{leach} = N_{NO3} \cdot K_{texture} \cdot F_{leach} \qquad \text{when } W_{leach} > 0$$

$$K_{texture} = 0.6 + 0.2 \cdot F_{sand} \qquad [6.40]$$

$$F_{leach} = \min\left[1.0,\ 1.0 - \left((CF_{leach} - W_{leach}) / CF_{leach}\right)\right] \qquad [6.41]$$

where

N_{leach} = amount of nitrate leached from a layer, g N/m^2- day
W_{leach} = water drained from the manure pack or soil layer, mm
$K_{texture}$ = effect of soil texture on leaching, dimensionless
F_{sand} = sand content, decimal
F_{leach} = leaching intensity, dimensionless
CF_{leach} = critical water flow for nitrate leaching, mm

The WF_{leach} is calculated using the soil water model described for open lots (see **Ammonia Emission - Open lots** section). The CF_{leach} is set to 1.0 mm for the upper layers and to 3.0 mm for the lower layer. In calculating nitrate leaching, the lowest layer (100-cm depth) is subdivided into five sublayers with depths of 10, 15, 15, 30 and 30 cm. The total *N* leaching loss reported by the model is the amount of nitrate that leached through the lowest sublayer.

To implement the above equations, input values are needed for soil bulk density, CO_2 flux, water-filled pore space, air-filled pore space, and total porosity. Soil bulk density and total porosity are both constants for open lot simulation (see **Ammonia Emission - Open lots** section). Water-filled pore space is calculated using the open lot soil water model (see **Ammonia Emission - Open lots** section). Air-filled pore space is calculated from water-filled pore space and total porosity. Relationships have been developed using the Integrated Farm System Model (**Rotz et al., 2015**), which has a component for predicting CO_2 flux based on **DAYCENT (2007)**, to approximate maximum CO_2 fluxes in both upper and lower layers of the manure pack. In the relationships developed, the maximum CO_2 flux is a function of the amount of fecal organic *N* in the manure pack, number of animals, and type of facility (i.e., dairy open lots with 60.0 m^2 per head animal spacing vs. beef feedyards with 25.0 m^2 per head animal spacing). On each simulation day, the flux computed for each layer is multiplied by a factor to account for temperature, moisture and rain effects on respiration (**DAYCENT, 2007**). For the amount of fecal organic *N*, it is assumed that there is an average 3-month accumulation of manure on open lots (based on typical 6-month feeding cycle at beef feedyards).

Bedded Pack Barns

Bedded pack barns are modeled similar to open lots with some important differences. Temperature of the bedded pack is modeled because of its influence on *N* transformations, and consequently N_2O emissions. Even without aeration, microbial decomposition (also referred to as organic matter mineralization) taking place in a deep-bedded pack is high enough to raise bedded pack temperatures above ambient levels. As an example, **Spiehs et al. (2011)** reported average

bedded pack temperatures of 15°C, 19°C, and 29°C for periods with barn air temperatures of < 0°C, 0°C to 20.6^{o}C, and > 20.6^{o}C, respectively, which corresponded to average temperature differences between the bedded pack and barn air of 18°C, 7°C, and 5°C, respectively. Compared to open lots, bedded pack barns have a greater potential for organic C and N mineralization because of wetter conditions and additional carbon from bedding.

In predicting *N* transformations and N_2O emissions for bedded pack barns, the equations for mineralization, nitrification, denitrification, and leaching in soil are used (equations 6.27 to 6.41). Both mineralization (**Shaffer et al., 1991**) and nitrification (equation 6.29) are functions of temperature. Through these two processes, temperature can affect the amount of nitrate *N* available for both denitrification and leaching.

For compost barns, temperature at the surface of the bedded pack is similar to ambient air temperature while temperature within does not vary significantly with depth (**Barberg et al., 2007**). Bedded pack barns would likely have similar temperature profiles. Using simulated 33-cm deep non-aerated bedded packs, **Ayadi et al. (2015c)** reported median temperatures that varied with depth by 1.2^{o}C or less only. Therefore, in modeling temperature, the bedded pack is simulated as two layers: the surface layer (i.e., 1 cm depth) and the rest of the bedded pack. The depth of the bedded pack is approximated from amounts and properties of manure excreted and bedding applied. Similar to open lots, it is assumed that there is a 3-month accumulation of manure and bedding on bedded pack barns throughout the year, and the manure C/N ratio is set at 15.

The temperature model for bedded pack barns is adapted from **Cekmecelioglu et al. (2005)**. On a daily time step, bedded pack temperature is computed by considering heat gain from microbial decomposition and heat losses due to evaporation and convection. As bedded pack barns are covered structures, net heat gain or loss due to radiation is neglected. Calculation of heat gain requires the amount of C respired as CO_2-C. Evaporation heat loss is the product of the amount of water evaporated (equation 4.33) and the latent heat of evaporation (**Cekmecelioglu et al., 2005**). Following **Cekmecelioglu et al. (2005)**, convection heat loss is a function of the temperature difference between the bedded pack and ambient air. But since the model described by **Cekmecelioglu et al. (2005)** is limited to above freezing ambient conditions only, another approach is used in calculating convection heat loss for periods with freezing ambient conditions. In simulating these periods, convection heat loss is estimated through iteration, which involves the following steps: 1) a step heat transfer of 1 MJ from the bedded pack to the surface layer is applied; 2) based on **Barberg et al. (2007)**, heat loss from the surface layer to the atmosphere is simulated until the surface layer temperature is equal to ambient air temperature + 1°C; and 3) the iteration cycle is repeated until the temperature difference between the surface layer and the rest of the bedded pack is less than 20°C. Convection heat loss from this procedure, which is just the sum of all simulated heat losses in step 2, is lower than the corresponding value if based on **Cekmecelioglu et al. (2005)**. The 20°C temperature difference criterion in step 3 is based on temperature observations by **Spiehs et al. (2011)**.

As particle density is an important parameter in modeling moisture contents (**Jones and Kiniry, 1986**), it can affect simulation of bedded pack temperature through amounts of moisture that can be potentially evaporated and calculated thermal properties of the bedded pack. In the absence of published values appropriate for each manure-bedding material combination simulated, particle density used in simulating the bedded pack is calculated on the first day of each simulation year:

$$\rho_p = \rho_{w,i} / (1 - PO_{air}) \quad [6.42]$$

where

ρ_p = particle density, g/cm^3

$\rho_{w,i}$ = initial wet bulk density, g/cm^3

PO_{air} = air-filled porosity, fraction

The $\rho_{w,i}$ value is approximated from amounts of manure, bedding, and moisture in the bedded pack. At the start of a simulation, a 65% wet-based moisture content is assumed based on yearly averages by **Spiehs et al. (2011)** and **NRCS South Dakota (2011)**. The PO_{air} is initially set to 0.45, which is approximated from gas pore measurements by **Ayadi et al. (2015b)** for simulated bedded packs. The computed ρ_p is held constant throughout the simulation year.

Similar to open lots, C balance in bedded pack barns is not completely simulated in DairyGEM - specifically, simulation of CO_2-C respiration is not included in the model. Still, in order to simulate N decomposition/mineralization, the amount of C decomposed is simulated following the procedure in the NLEAP model (i.e., equations 10 to 14 of **Shaffer et al. (1991)**). For bedded packs, daily mineralization rate coefficients for manure and bedding are computed as functions of temperature:

$$K_{manr}, K_{resr} = x_1 [1.066^{(T_{bp}+20)} - 1.21^{(T_{bp}-20)}] \quad [6.43]$$

where

K_{manr}, K_{resr} = mineralization rate coefficients for manure and bedding, respectively, 1/day (**Shaffer et al., 1991**)

x_1 = effectiveness of decomposition rate, dimensionless

T_{bp} = bedded pack temperature, ^oC

Equation 6.43 is based on **Haug (1993)** modified to have the maximum decomposition rate at 30^oC. This modification is made to have simulated bedded pack temperatures agree with measurements by **Spiehs et al. (2011)**. Assuming that the decomposition rate for manure is four times that for bedding, x_1 is set to 1.35 x 10 $^{-3}$ for manure and 3.58 x 10 $^{-4}$ for bedding through refinement using measurements from simulated bedded packs **(Ayadi et al., 2015b)**. Because K_{manr} and K_{resr} already account for effects of temperature on decomposition, the temperature factor (TFAC) in equation 11 of **Shaffer et al. (1991)** is not used in calculating C and N decomposition rates. With a slower decomposition rate for bedding, most of organic N that decomposes comes from manure and is approximated from decomposed manure C using a C/N ratio of 15. In simulating decomposition, a microbial C/N ratio requirement of 23.8 is assumed **(Shaffer et al., 1991)**. Given that microbial C/N ratio is higher than manure C/N ratio (i.e., N microbial requirement < N decomposed), some of decomposed N stays as NH_4^+ and becomes available for nitrification.

Nitrification for bedded packs is computed using equation 6.29 but with another factor accounting for effects of temperature on nitrification (F_{temp}). Adapted from **DAYCENT (2007)**, the

equation for F_{temp}, refined using ammonium concentration data by **Ayadi et al. (2015b)**, is given by:

$$F_{temp} = (-25^{o}C - T_{bp})/(-60^{o}C)^{1.5} \text{ x } exp[(1.5/18)(1-((-25^{o}C - T_{bp})/(-60^{o}C))^{18})] \qquad [6.44]$$

With equations 6.43 and 6.44 incorporated in simulating decomposition (i.e., using NLEAP equations, **Shaffer et al. (1991)**) and nitrification (i.e., equation 6.29 with F_{temp}), respectively, the model was able to predict the profile of ammonium concentration with time for simulated bedded packs at both low (10°C) and high (40°C) ambient temperature conditions **(Ayadi et al., 2015b)**. Assuming that trends of NH_4^+-N/NO_3^--N ratio for bedded packs are comparable to those for compost barns **(Shane et al., 2010)** (i.e., average NH_4^+-N/NO_3^--N ratios of 267 and 608 for summer and winter conditions, respectively), K_{max} in equation 6.29 is set to 2.67 x 10^{-4} for bedded packs.

Denitrification, and leaching are simulated using the same expressions used for open lots (**Bonifacio et al., 2015**). However, the leaching routine is slightly revised for bedded pack barns such that nitrate within the bedded pack can move in both downward and upward directions depending on simulated water movement, and no nitrate leaches out of the bedded pack based on the assumption that the bedded pack barn is built with an impermeable floor (e.g., concrete slab, lining).

Simulation of bedded pack temperatures (i.e., heat generation) and denitrification requires CO_2 flux. Similar to open lots, relationships has been developed in predicting maximum CO_2 fluxes for bedded pack barns. Derived using the Integrated Farm System Model (**Rotz et al., 2015**), a more detailed process-based model, the maximum CO_2 flux is a function of several parameters that include bedding type, bedding amount, total amount of organic C in the bedded pack, and type of facility (i.e., dairy bedded pack barns with 5.0 m^2 per head animal spacing vs. beef bedded pack barns with 3.0 m^2 per head animal spacing). In addition, there are two sets of relationships, one applied for both first and second simulation layers and the other applied for third and fourth layers. For each layer, the computed flux is multiplied by a factor to account for effects of moisture on respiration (**DAYCENT, 2007**).

Enteric Emissions

Limited data indicate that a small amount of enteric N_2O is emitted by the animal (**Hamilton et al., 2010**). Based upon these data and similar experiments conducted at UC Davis, an emission rate of 0.8 g N_2O / kg N intake was established and used to predict this enteric emission from dairy cattle. The *N* intake of each animal group in a given production system is determined in the animal component of the model **(See Feed Intake and Milk Production section)**

Manure Storage Emissions

Manure is stored as a liquid or in stacks. Nitrous oxide emission from slurry or liquid manure is predicted as a function of the exposed surface area of the manure storage and the presence of a crust on the surface. For an open slurry storage tank with a crust, an average emission rate of 0.8 g N_2O /m^2-day determined by **Olesen et al. (2006)** is used to predict N_2O emissions:

$$E_{N2O,manure} = E_{F,N2O,man} \cdot A_{storage} / 1000 \qquad [6.45]$$

where $E_{N2O,manure}$ = emission of N_2O from slurry storage, kg N_2O /day

$E_{F,N2O,man}$ = emission rate of N_2O, 0.8 g N_2O /m^2-day

$A_{storage}$ = exposed surface area of the manure storage, m^2

This relatively simple model is justified given the lack of available information to support a more complex model and because the N_2O emission from this type of manure storage is typically a relatively small portion of the whole farm emission of GHGs (**Olesen et al., 2006**).

The emission factor of 0.8 g N_2O /m^2-day is applicable to bottom-loaded, uncovered slurry storage tanks where a natural crust forms on the manure surface. hen a crust does not form, no N_2O is formed and emitted (**Külling et al., 2003**; **Sneath et al., 2006**). This occurs if the manure DM content is less than 8%, manure is loaded daily onto the top surface of the storage, or an enclosed tank is used. Therefore, when any of these manure handling options are selected, the emission rate is zero.

For stacked manure with a greater DM content, an emission factor of 0.005 kg N2O-N /(kg N excreted) is used (**IPCC, 2006**). The excreted N stored in this manner is multiplied by this factor to predict a daily emission.

Figure 6.1 - Pathway of Denitrification in Soils

Pathway of denitrification in soils (**Parton et al., 1996**).

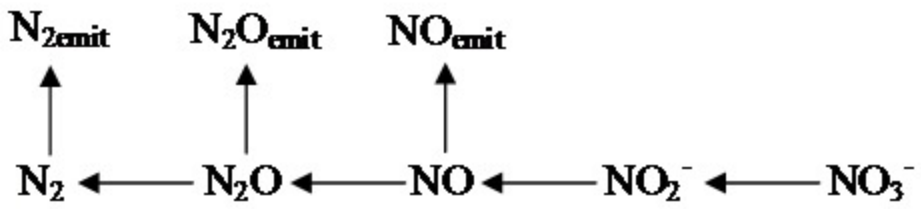


Figure 6.2 - Pathway of Nitrification in Soils

Pathway of nitrification in soils. Dashed lines and square brackets indicate incompletely understood processes and intermediates (**Parton et al., 1996**).

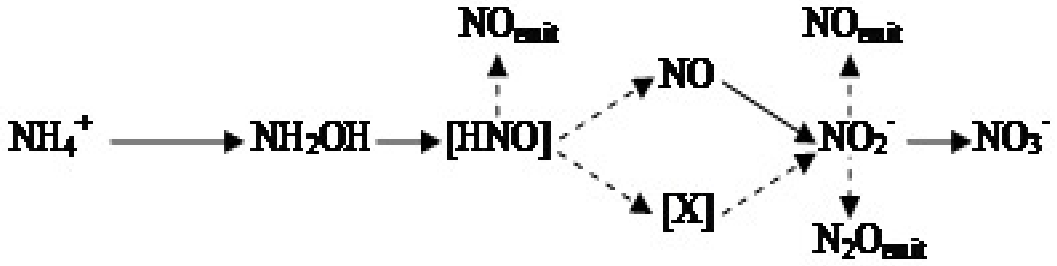


Figure 6.3 - Nitrogen Gas Emissions from Soil

Conceptual model of controls on N gas emissions from soil using the leaky pipe metaphor (**Parton et al., 2001**).

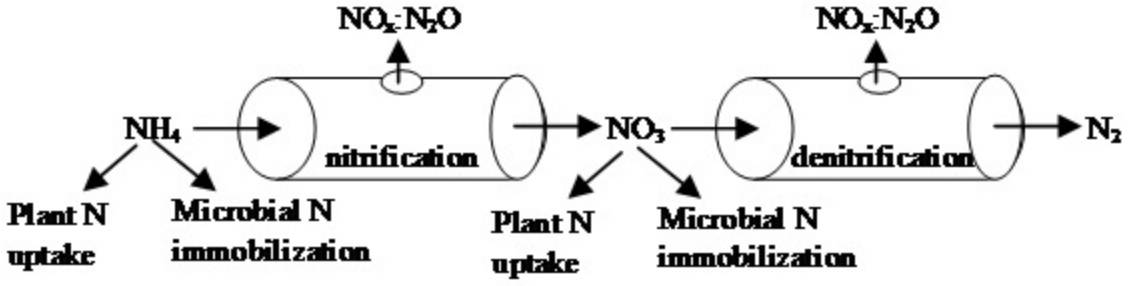


Table 6.1 - Carbon Dioxide from Storage

Published and assigned emission rates of CO_2 emitted from uncovered slurry storages.

Reference	Emission rate [kg CO_2 /m^3-day]
Jungbluth et al. (2001)	0.036
Sneath et al. (2006)	0.041
Assigned	0.04

Table 6.2 - Starch and ADF Contents of Feeds

Relationships used to model starch and ADF contents of feeds.

Feed type	Starch[a] [fraction]	ADF [fraction]
Alfalfa hay	$0.64*(1-F_{NDF}-F_{CP}-0.11)$	$0.78*F_{NDF}$
Alfalfa silage	$0.89*(1-F_{NDF}-F_{CP}-0.12)$	$0.82*F_{NDF}$
Grass hay	$0.45*(1-F_{NDF}-F_{CP}-0.11)$	$0.61*F_{NDF}$
Grass silage	$0.65*(1-F_{NDF}-F_{CP}-0.12)$	$0.64*F_{NDF}$
Corn grain	0.68	0.036
High moisture corn	0.52	0.004
Corn silage	$0.80*(1-F_{NDF}-F_{CP}-0.07)$	$0.62*F_{NDF}$
Perennial grass/legume	$0.48*(1-F_{NDF}-F_{CP}-0.14)$	$0.72*F_{NDF}$
Alfalfa pasture	$0.48*(1- F_{NDF}-F_{CP}-0.14)$	$0.55*F_{NDF}$
Protein supplements	0.0	0.0
Fat additive	0.0	0.0

[a] The last value in the equations developed to predict starch content represents an average total of fat plus ash contents for the given feed. Typical values for fat and ash were obtained from NRC (2001).

Table 6.3 - Manure Storage Emissions Model

Parameters and values for the manure storage emissions model of **Sommer et al. (2004)**.

Parameter	Variable	Value	Units
Volatile solids content[a]	P_{VS}	0.726, 0.698, 0.68[b]	g VS /g TS
Achievable CH_4[c]	B_o	0.2	g CH_4 /g VS
Potential CH_4[c]	$E_{CH4,pot}$	0.48	g CH_4 /g VS
Correcting factors[c]	b_1, b_2	1.0, 0.01	dimensionless
Arrhenius parameter[c]	ln(A)	43.33	dimensionless
Activation energy[c]	E	112,700	J /mol
Gas constant[c]	R	8.314	J /K-mol

[a] From **USDA-SCS (1999).**
[b] Values for heifers, dry cows, and lactating cows, respectively.
[c] From **Sommer et al. (2004)**.

Table 6.4 - Methane from Grazing Animals

Published and assigned emission rates of CH_4 emitted from feces directly deposited by animals on pasture lands**.**

Reference	Emission rate [g CH4 / kg feces]
Jarvis et al. (1995)	0.110
Flessa et al. (1996)	0.130
Holter (1997)	0.068
Yamulki et al. (1999)	0.036
Assigned	0.086

Volatile Organic Compound Emissions

Emissions of volatile organic compounds (VOCs) from farms can contribute to the formation of ground-level ozone and other components of photochemical smog. Silage has been identified as a significant source of VOC emissions from farms, but manure also contributes. Development of emission inventories requires estimates of VOC emissions, but on-farm measurement is difficult and expensive. Simulation of emission processes provides an alternative method for estimating VOC emissions. Integration of VOC emission processes in DairyGEM provides a tool for estimating whole farm emissions and evaluating the effects of alternative management strategies for mitigating those emissions.

The contribution of a particular VOC to ozone formation is determined by the emission rate of the compound and its reactivity in the atmosphere. Following physical and chemical principles, emission rates are controlled by the concentration of VOCs in silage or manure and their volatility (Henry's law constant). A compound's volatility will control emission rate when the concentration is not limiting. When the concentration is limiting, i.e., when cumulative emission approaches the total quantity of a compound present, volatility is less important. These relationships are described in more detail in Hafner et al. (2012) and Hafner et al. (2013).

Very limited data on VOC emissions from farms are available. A process model was developed to predict emissions, but to this point the limited measured data available has not permitted a complete evaluation of the model. This portion of DairyGEM should be considered as preliminary. The effects of management changes on the relative changes in emission levels should be representative of those experienced on real farms. The absolute values predicted should be considered as only a representative level of emissions until further model evaluation can be done with comparisons to measured farm emission data.

Silage Sources

Although many different organic compounds are emitted from silage, alcohols (which can be formed by both bacteria and yeasts) appear to be the most important (**Howard et al., 2010; Hafner et al., 2013**). To represent total VOC emission, we consider four groups of VOCs which have the most potential to contribute to poor air quality: acids, alcohols, esters, and aldehydes (**Hafner et al., 2013**). On farms, VOC emission from silage is determined by the production of VOCs in silage and the fraction of each compound that is volatilized. VOC production can vary greatly among silages, and the sources of this variability are not yet known (**Hafner et al., 2013**). Therefore, in our model, VOC production is set based on typical values for different types of silage. From these fixed initial concentrations, we simulate VOC emissions.

For each VOC group, a given concentration in silage after fermentation is assigned. Emission losses are predicted and the remaining VOC mass is tracked as silage moves through three stages: storage removal (when silage is exposed following daily or more frequent feed removal), feed mixing, and feeding. VOC emission during storage removal and mixing reduces the concentration of VOCs present in the remaining stages. From the storage face and during feeding, cumulative VOC emission is determined over a defined exposure period using a three-pool first-order model, which approximates the behavior of a more complex convection-diffusion model. VOC emission from the mixing stage uses a similar (but simpler) completely-mixed first-order model.

Emission processes

Measurements have shown that silage alcohols partition between aqueous and gas phases and sorption to particles is insignificant. VOC partitioning between aqueous and gas phases is based on Henry's Law:

$$K_H = m/P \quad [7.1]$$

where K_H = Henry's constant, mol/kg-atm

m = molal concentration of VOC, mol/kg

P = partial pressure of VOC in equilibrium with m, atm.

Following the van't Hoff equation, log K_H is inversely proportional to absolute temperature:

$$\log K_H = a + b / T \quad [7.2]$$

where a and b are empirical parameters

T = temperature (K)

Since mass transfer calculations are based on concentrations, it is useful to transform the Henry's law constant into one based on concentrations (i.e., aqueous mol/kg per gaseous mol/m = m^3/kg):

$$H = m/c_g \quad [7.3]$$

$$H = K_H R T \quad [7.4]$$

where H = concentration-based Henry's law constant, m^3/kg

c_g = gas-phase concentration

R = universal gas constant, 8.2057×10^{-5} m^3 atm/K-mol

Silage emissions take place from exposed surfaces. VOC molecules are lost from deeper layers as well, but they must be transported to the surface through dispersion or diffusion (**Hafner et al., 2010; Hafner et al., 2012**). Although models are available for simulating simultaneous VOC transport and emission from all layers (**Hafner et al., 2012**), such approaches are computationally intensive. Instead, we use a simpler three-pool first-order model that simulates diffusion and convection from three discrete layers within silage.

In our three-pool model, each layer has two "films": a gas film, with an effective mass transfer coefficient, and a layer of silage that separates the emitting silage layer from the exposed surface, with an effective diffusion coefficient. These "effective" coefficients are applicable to bulk volumetric concentrations. We assume pools behave independently and there is no transfer between them. Furthermore, we assume that the mass of each compound present in the films is negligible. Therefore, at any time, the flux from the emitting layer and from the exposed surface is equal:

$$\alpha\, c_{s,b} = D / l\, (c_{l,b} - c_{s,b}) \quad [7.5]$$

where α = effective mass transfer coefficient, m/s

D = effective diffusion coefficient, m^2/s

l = distance from the center of the emitting layer to the exposed surface, m

c_b = bulk volumetric concentrations, g/m^3

Subscripts l and s indicate the emitting layer and exposed surface. The left-hand side of Eq. 7.5 is an expression for the flux through the gas film (i.e., the surface flux), while the right-hand side is for flux through the silage "film" (i.e., from the emitting layer). Rearranging 7.5 gives the following expression for the surface concentration:

$$c_{s,b} = (D/l)\, c_{l,b} \,/\, (D/l + \alpha) \qquad [7.6]$$

Substituting Eq. 7.6 into the right-hand side of Eq. 7.5 and rearranging, gives an expression for emission rate based on the concentration within the layer.

$$j = K\, c_b \qquad [7.7]$$

where

$$K = 1 / (1/\alpha + l/D) \qquad [7.8]$$

Effective transport parameters are related to gas-phase values:

$$D = E_{sg} / (H\rho_w w + \Phi) \qquad [7.9]$$

$$\alpha = K_g / (H\rho_w w + \Phi) \qquad [7.10]$$

where E_{sq} = diffusion-dispersion coefficient for VOCs through silage gas pores, m^2/s

K_g = surface mass transfer coefficient, m/s

c_b = bulk volumetric concentration of a VOC group, g/m^3

ρ_w = wet silage density, kg/m^3

w = gravimetric water content of silage, kg/kg

Φ = gas-phase porosity (m^3/m^3)

VOCs in aqueous and gas phases are assumed to be in equilibrium at all times and locations (**Hafner et al., 2012**).

For each of the three pools, the analytical solution for VOC loss by emission over time t is:

$$f_{emis} = 1 - e^{-Kt/L} \qquad [7.11]$$

where f_{emis} = fraction of a given compound from a given layer that has been lost at time t

L = layer thickness, m

t = cumulative exposure time, s

Total emission loss at any time is the sum of the absolute losses from each pool.

For feed mixing, completely-mixed conditions are assumed. Therefore, internal resistance to transport is neglected in the model. Emission of VOCs during mixing of feed appears to be a complex process, and is probably affected by air flow through the mixing material. However, the most obvious route of emission is from silage particles at the upper surface of the material that is being mixed. In our model, we assume that emission only occurs from the upper surface. VOC emission is simulated as a first-order process, where flux is proportional to the gas-phase VOC concentration in the mixed feed.

$$f_{emis} = 1 - e^{-\alpha t A/V} \quad [7.12]$$

Eq. 7.12 is a special case of Eq. 7.11, where l in Eq. 7.8 is zero, and the effective total thickness is calculated from the exposed area of the mixing wagon (A, m^2) and volume of feed in the wagon (V, m^3).

Calculated emissions from the three groups of compounds are aggregated after normalizing emissions based on the ozone formation potential of each group.

$$M_{O3} = r\, M_{VOC} \quad [7.13]$$

where M_{O3} = potential ozone forming emission, kg

r = Equal Benefit Incremental Reactivity, kg O_3 per kg VOC

The Equal Benefit Incremental Reactivity (EBIR) is a measure of the ozone formation potential of VOCs that is more suitable for rural environments than that of the maximum incremental reactivity (MIR).

Emission parameters

Characteristics of each VOC group were assigned based upon available data. With the exception of acids, data on VOC concentrations within silage are limited. Mean VOC concentrations from a compilation of silage data (**Hafner et al., 2013**) are presented in **Table 7.1**. Data for alcohols include ethanol, 1-propanol, methanol, and other alcohols for corn and grass silage, but only ethanol for other feeds. Aldehyde data include acetaldehydes and several others for corn, grass, and alfalfa. Several esters have been measured in corn and grass silage, but not in other types of silage. We estimated concentrations for groups for which data were not available based on measurements for other silages.

The Henry's law constant is based on a single representative compound for each group: acetic acid (CAS number 64-19-7) for acids, ethanol (CAS 64-17-5) for alcohols, ethyl acetate (CAS 141-78-6) for esters, and acetaldehyde (ethanal; CAS 75-07-0) for aldehydes. Parameters for Eq. 7.2 used to calculate Henry's law constants are given in **Table 7.2**.

To determine K_g, we use the same relationship used for ammonia and hydrogen sulfide emission (**see those sections**). For the dispersion-diffusion coefficient, Esg, we use a single value of 3.2 × 10-5 m/s, which is the best-fit value determined from the mass balance trials described in **Hafner et al. (2012)** (using the ethanol data given in Table 4 in that paper).

Equal Benefit Incremental Reactivity values used to aggregate emissions were assigned based upon the work of **Carter (2009)** (**Table 7.3**). The potential ozone formation from each VOC group (MO3) is summed over all groups to give an estimate of the total potential ozone formation from the emitted VOCs.

Gas transport is predicted from three layers on the silage surface. The thicknesses of the first two layers are held constant (**Table 7.4**) while the third and thickest layer varies among emission sources. For the silo face, the thickness is determined by the the amount removed each feeding. The average diffusion distance of gases varies with layer thickness (**Table 7.4**).

Farm processes

VOC emissions are determined for each silo or silage storage facility on the farm each year at the completion of the storage period. Important input parameters are the type and size of silo or other storage facility used, the type of feed stored, the type of barn where animals are fed, and daily weather (average ambient temperature and wind speed). This information is available from other components of DairyGEM.

Daily emissions are determined for each silage facility through 365 days of weather for each simulated year. Emissions of each VOC group are predicted for each day in which silage is being removed, using the emission process relationships described above. Emissions are first determined for the silage face exposed to the ambient atmosphere. The portion of each VOC group emitted is removed from the silage and the mass is moved to the feed mixer. Emissions from the mixer are than predicted, losses of each VOC group are removed, and the remaining mass moves to the feed bunk. Emissions continue from the feed bunk until the feed is consumed. The average time the feed remains in the fed bunk is set to half of the interval between feedings, to approximate the effect of cattle removing feed from the feed bunk through consumption. The temperature of the silage and surrounding air at each stage is the average daily ambient temperature.

Five different types of storage structures are considered: stave tower silo, sealed tower silo, bunker, silage bag, and bale silage. Sealed tower silos are assumed to be open during feed removal for only two hours per day, and the air speed across the face is assumed to be very low (0.01 m/s). The air speed is also set to this low value for bale silage where removal from storage is essentially immediate. For all other cases during silage removal from storage, air velocity at a reference height is set to 70% of the outside wind speed. During feed mixing, this reference air velocity is set to 50% of the outside wind speed. During feeding, when mixed feed is placed in feed lanes, air velocity is set to 50% of the outside wind speed for naturally ventilated barns, and is a function of air temperature for mechanically ventilated barns (see **ammonia emission section**). These reductions were based on the wind profile power law (**Peterseon and Hennessey, 1978**).

$$v_z = v_{z(ref)} \, (z / z_{ref})^{1/7} \qquad [7.14]$$

where v_z = air velocity at height z

$v_{z(ref)}$ = air velocity at reference height z_{ref}

To apply Eq. 7.14 for silage storage, we use a reference height of 10 m and a height of 1 m for the center of the silage pile. For mixed feed, a reference height of 1 m is used with a height of 1 cm for the location of the effective air velocity from the feed surface.

Other information needed to calculate emissions from the silo face are silage density, dry matter content, and the expose surface area. For tower silos, density is calculated as a function of silo height and for bunker silos, density is a function of the moisture content of the silage entering the silo (**Savoie and Jofriet, 2003).** For bagged silage and bale silage, wet densities are 550 and 450 kg/m3, respectively. Silage dry matter contents are set at 320 and 350 g DM/kg silage for bunker and all other silo types, respectively. The model is not sensitive to this parameter, so these general values are adequate. The exposed surface area is calculated from the radius of tower silos and bagged silage or the width and settled depth of bunker silos.

Values for the thickness and depth of each silage pool in the three-pool model are fixed at the values given in Table 7.4. These values were selected to capture the behavior of the natural mass balance trials in **Hafner et al. (2012)** (using the ethanol data from Table 4 in that paper).

Output from the silage VOC submodel includes daily emissions of each of the three VOC

groups (kg of VOC) and daily values of the potential ozone formed (kg ozone, based on EBIR). Daily values are summed to obtain total annual emissions.

Manure Sources

Several VOCs have been measured in cattle manure, and these measured compounds fall within three groups: acids, alcohols, and aromatics (**Table 7.5**). It is not clear if other compounds are present at much lower concentrations or if other compounds simply have not been measured within manure. Emissions of other VOCs have been measured indicating their presence in some form.

In general, volatile fatty acids are the most concentrated VOCs in manure (**Fig. 7.1**). However, their importance for ozone formation is reduced by ionization in solution (which effectively lowers volatility) and low reactivity. Ethanol has been measured at high concentrations in some cases, and is the only alcohol that has been measured in multiple studies. Measurements suggest that concentrations of most aromatic compounds are lower than concentrations of acids and alcohols, although some compounds may be present at high concentrations.

Measurement of VOC concentrations in manure during incubations has shown that production and consumption of organic compounds significantly impact VOC concentrations. In incubations of beef manure at room temperature, **Varel et al. (2010)** found that alcohol concentrations doubled within a few days, and acetic acid concentrations more than doubled over two weeks. Alcohol concentrations began to decline after a week of incubation, and the total alcohol concentration (mostly ethanol) was less than half of the initial concentration after four weeks. Aromatic compounds showed less change over time.

These production processes complicate modeling efforts. The magnitude of changes in VOC concentrations during manure storage are probably dependent on numerous variables, including cattle feed, manure handling and storage, and weather. With only limited data on changes in VOC concentrations over time, it is not currently possible to develop a robust model for predicting these changes, so fixed initial concentrations are used. Since the goal of our model is to predict the impact of manure handling strategies on emissions, initial concentrations are not particularly important as long as reasonable levels are assumed.

Volatility, reactivity, and implications for emission and ozone formation

The principles of volatility and reactivity were incorporated into two indices for estimating the relative importance of VOCs with regard to emission rate and ozone formation. Concentration alone provides an indication of the total mass available for emission, and therefore can serve as an index of relative emission (mass units) when concentrations are limiting. The second index is the product of concentration and Henry's law constant, which indicates the emission rate potential (mass units) when concentration is not limiting.

For manure in the barn, where exposure time is short, the second index (which includes volatility) seems most relevant. For stored manure, where exposure time is long but the depth of manure is high, volatility is also likely controlling, since it is unlikely that emission loss will be high enough for concentrations to be limiting. For field-applied manure, where losses of moderately- to highly-volatile compounds may approach 100%, an index without volatility seems most relevant.

Volatility of the compounds found in manure varies widely (**Table 7.6**). Alcohols have the highest volatility of the compounds considered. Reactivity also varies widely. In general, aromatic

compounds have higher MIR values than alcohols and acids. However, this pattern is not true for EBIR, for which some aromatic compounds have negative values.

Alcohols have the highest emission potential (product of concentration and Henry's law constant), although variability is high, reflecting the variability in concentrations (**Fig. 7.2**). The acid (acetic acid) and aromatic (cresol) with the highest values have mean values about 10% of that of ethanol.

We considered MIR and EBIR to evaluate reactivity and ozone forming potential (**Table 7.6**). The relationship among the compounds differs substantially among the indices; no one compound dominated in all cases. Considering reactivity and concentration, acids are the most important compounds for index 1, but for index 2 (with volatility included) alcohols are most important. Ethanol is the most important alcohol for both indices. Aromatic compounds generally have low values, with some exceptions. For index 1, the aromatic acids approach the values of some acids. For index 2, values of cresol and skatole are within a factor of 10 of the value for ethanol, while the indices of all acids are low.

Assuming that concentration and volatility control emission rates, these results suggest that alcohols, and ethanol in particular, are the most important VOCs emitted from manure, in terms of both mass emitted and ozone formation potential. This conclusion is consistent with emission measurements. Results suggest that some compounds can be ignored, but, unfortunately, numerous compounds in each group have the potential to make a significant contribution to ozone formation.

Based upon concentration, volatility and reactivity, five groups of compounds are defined as important: two groups of acids, one group of alcohols, and two groups of aromatics. Including each individual compound may provide a more accurate model, but given the large uncertainty in concentrations of VOCs in manure, this accuracy would not be realized. Furthermore, a lumped parameter approach provides a more usable model. Bulk concentrations of compounds are fixed as constant, or set at an initial value and allowed to decline due to emission with a fixed time step. Initial VOC concentrations for fresh manure within the barn are set at different levels (typically lower) than for manure in storage, to reflect an accumulation of VOCs over time (**Table 7.5**).

Ethanol is used as the representative compound for alcohols. Two groups are used for acids to capture differences in volatility and reactivity: C2 and C3 acids (group 1), and C4 acids (group 2). Two groups are also used for aromatic compounds: aromatic acids and others, since the acids are generally less volatile than the other aromatic compounds present in manure. Parameter values for these five groups are given in **Table 7.7**.

Emission processes

Emission is modeled using a two-film model with an additional resistance term that incorporates any gradient below the liquid film as well as resistance due to a surface cover or crust:

$$j = K\,c \qquad [7.15]$$

where j = VOC flux, g/m^2- s

K = overall mass transfer coefficient in aqueous phase units, m/s

c = VOC concentration in manure, g/m^3.

This relationship assumes that the VOC concentrations in the ambient air are negligible. The overall mass transfer coefficient is given by:

$$K = 1 / (1/ (H\, k_g) + 1/ k_l + R_m) \quad [7.16]$$

where k = individual mass transfer coefficients for the gas (g) and liquid (l) films, m/s

R_m = additional resistance term, s/m

For the alcohol and aromatic groups, c in Eq. 7.15 is the total aqueous volumetric concentration of each group. For the acid groups, ionization must be considered:

$$RCOOH \leftrightarrow RCOO^- + H^+ \quad [7.17]$$

For a given group of acids, the fraction of the total concentration in the free form (α) is determined as:

$$\alpha = 1 - \gamma_{RCOO}\, K_a / (10^{-pH} + K_a) \quad [7.18]$$

where K_a = dissociation constant, dimensionless

γ_{RCOO} = activity coefficient of the ionized species, dimensionless

pH = solution pH, taken as the activity of H^+

We assume that γ_{RCOO} is 0.7.

The gas phase mass transfer coefficient is related to air velocity near the surface based on the correlation of **MacKay and Yuen (1983),** as is currently used for ammonia and hydrogen sulfide emission components:

$$k_g = 0.001 + 0.0462\, U \cdot SC^{-0.67} \quad [7.19]$$

where U = friction velocity, m/s

Friction velocity is given by:

$$U = 0.02\, V^{1.5} \quad [7.20]$$

Determination of the liquid-phase mass transfer coefficient is more difficult. Correlations have been developed for solutions, but the higher viscosity of manure is expected to increase the thickness of the liquid film. The liquid mass transfer coefficient (k_l, m/s) is determined as a function of temperature:

$$k_l = 1.417 \times 10^{-12}\, (T^4) \quad [7.21]$$

where T = temperature (K).

Farm processes

VOC emissions can occur from manure in the housing facility, during long term storage, following land application and from feces deposited on pasture. Each of these processes is simulated on an hourly or daily time step, and daily emissions from each VOC group are converted to potential ozone forming units using the EBIR. Daily emissions are summed to give an annual emission from each manure source.

Daily VOC emissions from the housing facility are predicted using a procedure similar to that used to predict ammonia emissions (see **ammonia emission section**). Emissions are determined for each hour of the day using Eq. 7.15 to 7.20. Hourly ambient temperature throughout the day is set as a function of maximum and minimum daily temperatures using Eq. 4.17 and 4.18. Air and manure

temperature within barns is determined as a function of the ambient temperature using Eq. 4.16. For outdoor facilities, the temperature is the ambient temperature. The air velocity is equal to the average daily wind speed for outdoor facilities and half the ambient wind speed for open structures. For enclosed barns, air velocity is a function of ventilation rate which is directly related to ambient temperature (Eq. 4.19). Surface pH of the manure is set as determined in the ammonia emission routine. For most barn types, the surface pH is 0.7 units greater than the bulk manure pH.

VOC concentration in the manure decreases each hour following excretion, i.e. the initial concentration is reduced each hour by the amount volatilized. At the end of 24 h, the amount and concentration of each VOC group remaining moves into long term storage or they provide the amount applied through daily spreading of manure.

When long term manure storage is used, emissions of each VOC group are again predicted each hour using Eq. 7.15 to 7.20. Air velocity over the storage is set to the average wind speed of the day. Temperature throughout the day is predicted using Eq. 4.17 and 4.18. Bulk manure pH and surface pH are determined as a function of manure dry matter content using Eq. 4.32 and 4.33. The amount of each VOC group in the storage is tracked by adding that coming into the storage and subtracting that emitted. When the storage is emptied, these amounts are reset. Hourly emissions are totaled to give daily and annual emissions of each VOC group.

Covers are sometimes used on manure storages. To represent cover effects, an additional transfer resistance is included in Eq. 7.16. For lack of better information, resistance values are those used to represent the effect on ammonia emission from covered storages (see **ammonia emission section**).

Emissions following field application are determined on a 2 h time step beginning the day of application and continuing until the manure is incorporated into the soil. With incorporation, all emissions are assumed to cease. Emissions are predicted using Eq. 7.15 to 7.20 and mean daily air temperature and wind velocity. Manure pH increases to 8.6 immediately following application due to the rapid release of CO_2 (See **ammonia emission section**). As the manure dries in the field, the pH decreases at a rate of 0.3 units per time step until it reaches a neutral pH of 7.0. Emissions for each time step are totaled for each VOC group.

Field emissions are also affected by infiltration of the manure into the soil. Following the procedure used to predict ammonia emission, the infiltration rate is a function of the dry matter content of the manure (Eq. 4.34). When rain occurs, the dry matter content is reduced in proportion to the amount of rain, and this increases the infiltration rate (see **ammonia emission section**). The VOCs contained in the portion of the manure that infiltrates into the soil are no longer available for volatilization.

Feces deposits are the only VOC source considered from pasture. This source is tracked on a daily time step for up to 15 days following excretion. Emissions are predicted for each VOC group using equations 7.15 to 7.20. Temperature and air velocity are set to the mean daily ambient temperature and wind speed. Surface pH of the manure pat is set at 0.5 units greater than the bulk pH or about 8.0. As the manure dries, an additional transfer resistance is assumed to increase by 2×10^5 s/m each day, which decreases the potential emission. As with the other sources, daily emissions from each VOC group are converted to potential ozone forming emissions and totaled for the year.

Table 7.1 - VOC Concentrations

Initial VOC concentrations (mg/kg, dry matter basis) used in the model, based on a compilation of literature data. Values in bold are estimates based on measurements in other feeds, and are approximate at best.

Group	Corn silage	Small grain silage	Alfalfa silage	Grass silage	High-moisture corn
Acids	22	27	28	38	**5**
Alcohols	9.7	2.9	3.0	5.6	**2**
Esters	1.9	0.5	**0.5**	0.04	**0.5**
Aldehydes	0.58	0.5	0.020	0.43	**0.1**

Table 7.2 - Henrys Constants

Parameters for calculating Henry's law constants using Eq. (7.2).

Group	Reference compound	a	b	K_H 20°C (mol kg^{-1} atm^{-1})
Acids	Acetic acid	-5.439	2716	6700
Alcohols	Ethanol	-6.852	2713	250
Esters	Ethyl acetate	-6.884	2283	8.0
Aldehydes	Acetaldehyde	-7.524	2573	18

Table 7.3 - EBIR Values

Equal Benefit Incremental Reactivity (EBIR) values used to aggregate emissions (**Carter, 2009**).

Group	Reference compound	EBIR (g/g)
Acids	Acetic acid	0.20
Alcohols	Ethanol	0.57
Esters	Ethyl acetate	0.24
Aldehydes	Acetaldehyde	1.61

Table 7.4 - Depth and Thickness

Depth and thickness of silage layers represented as pools in the three-pool model in meters.

Pool/layer	Mean distance (l)	Thickness (L)
Surface	0.01	0.02
Middle	0.045	0.05
Deep	0.10	Total thickness – 0.07

Table 7.5 - Manure VOCs

Geometric mean concentrations of VOCs present in fresh and incubated manure. See **Fig. 7.1** for information on variability and the number of studies identifying each compound.

			Concentration	(mg/kg DM)
Group	Compound	CAS no.	Initial	Incubation
Acids	Acetic acid	64-19-7	12300	27700
	Propionic acid	79-09-4	6820	11800
	Butyric acid	107-92-6	2730	4300
	Isobutryic acid	79-31-2	1140	1440
	Lactic acid	50-21-5	756	9480
	Valeric acid	109-52-4	519	867
	Hexanoic acid	142-62-1	445	463
	Isovaleric acid	503-74-2	334	423
	Isohexanoic acid	646-07-1	29.9	28.9
	Heptonoic acid	111-14-8	10.2	10.7
	Octanoic acid	124-07-2	1.81	1.81
Alcohols	Ethanol	64-17-5	117	1440
	Propanol	71-23-8	20.9	71.3
	Butanol	71-36-3	10.6	36.2
	Methanol	67-56-1	1	514
	Isobutanol	78-83-1	12.3	13.3
Aromatics	Phenyl acetic acid	103-82-2	1230	
	Benzoic acid	65-85-0	1860	1320
	Phenyl propionic acid	501-52-0	213	
	Cresol	1319-77-3	117	119
	Skatole	83-34-1	8.46	2.98
	Indole	120-72-9	10.2	4.87
	4-ethylphenol	123-07-9	9.5	4.5
	Phenol	108-95-2	15.6	23.8

Data are from: **Miller and Varel (2001), Miller and Varel (2002), Spiehs and Varel (2009), Varel et al. (2010), El-Mashad et al. (2010), and Archibeque et al. (2011)**.

Table 7.6 - Volatiliy and Reactivity

Volatile organic compounds measured in cattle manure and their volatility and reactivity.

			Log 10 Henrys	Incremental	reactivity‡
Group	Compound	Cas no.	law constant (g:aq)*	Maximum (MIR)	Equal benefit (EBIR)
Acids	Acetic acid	64-19-7	-7.33	0.66	0.203
	Propionic acid	79-09-4	-7.13	1.17	0.342
	Butyric acid	107-92-6	-6.86	1.75	0.548
	Isobutryic acid	79-31-2	-7.07	1.15	0.376
	Lactic acid	50-21-5	-9.26		
	Valeric acid	109-52-4	-6.62	2.3§	0.702§
	Hexanoic acid	142-62-1	-6.66	2.86§	0.87§
	Isovaleric acid	503-74-2	-6.58	2.3§	0.702§
	Isohexanoic acid	646-07-1	-6.36	2.86§	0.87§
	Heptonoic acid	111-14-8	-6.35	3.42§	1.04§
	Octanoic acid	124-07-2	-6.18	3.98§	1.21§
Alcohols	Ethanol	64-17-5	-3.67	1.45	0.571
	Propanol	71-23-8	-3.54	2.38	0.792
	Butanol	71-36-3	-3.47	2.76	0.882
	Methanol	67-56-1	-3.74	0.65	0.197
	Isobutanol	78-83-1	-3.36	2.41	0.723
Aromatics	Phenyl acetic acid	103-82-2	-8.45	3.35§	-0.676§
	Benzoic acid	65-85-0	-8.46	2.75§	-0.845§
	Phenyl propionic acid	501-52-0	-8.49	3.86§	-0.537§
	Cresol	1319-77-3	-4.4	2.34	-0.765
	Skatole	83-34-1	-4.2	3.66§	0.999§
	Indole	120-72-9	-4.33	3.66§	0.999§
	4-ethylphenol	123-07-9	-4.44	2.95§	-0.746§
	Phenol	108-95-2	-4.67	2.69	-0.879

*From NIST (measured) or ChemSpider (predicted from structure). For all acids, value was adjusted downward to reflect the fraction of the compound in the free form at pH 6.5.

‡From **Carter (2009)**

§Estimated value, based on extrapolation from smaller analogous compounds, addition of values for smaller compounds, or substitution of the value for a similar compound.

Table 7.7 - Emission Parameters

Parameter values for the manure VOC emission model.

			Henry's law constant (g:aq)		Reactivity (g/g)		Concentrations (g/kg dry matter)	
Group	Representative compound	*pKa*	*a*	*b*	MIR	EBIR	Initial conc.	Storage conc.
C2 & C3 acids	Acetic acid	4.83	3.652	2596	0.90†	0.27†	20	30
C4 and larger acids	Butyric acid	4.84	-4.673	0	1.5†	0.46†	5.0	20
Alcohols	Ethanol	---	5.576	2757	1.45	0.57	0.2	2.0
Aromatic acids	Phenylacetic	4.31	-5.76	0	3.35‡	0	3.0	3.0
Aromatics	Indole	---	-4.33	0	3.0†	0†	0.2	0.2

*Dimensionless constant (g:aq) is calculated by: $\log H = a - b / T$, where T = temperature, K

†Composite value

‡An estimate based on addition of values for individual compounds

Figure 7.1 - VOC Concentrations

Concentrations of VOCs in cattle manure for both fresh manure (initial) and incubated manure (incubations). Points show values from individual studies (including medians, minima, and maxima), while vertical lines show overall geometric means. Numbers in parentheses show the number of studies that data came from.

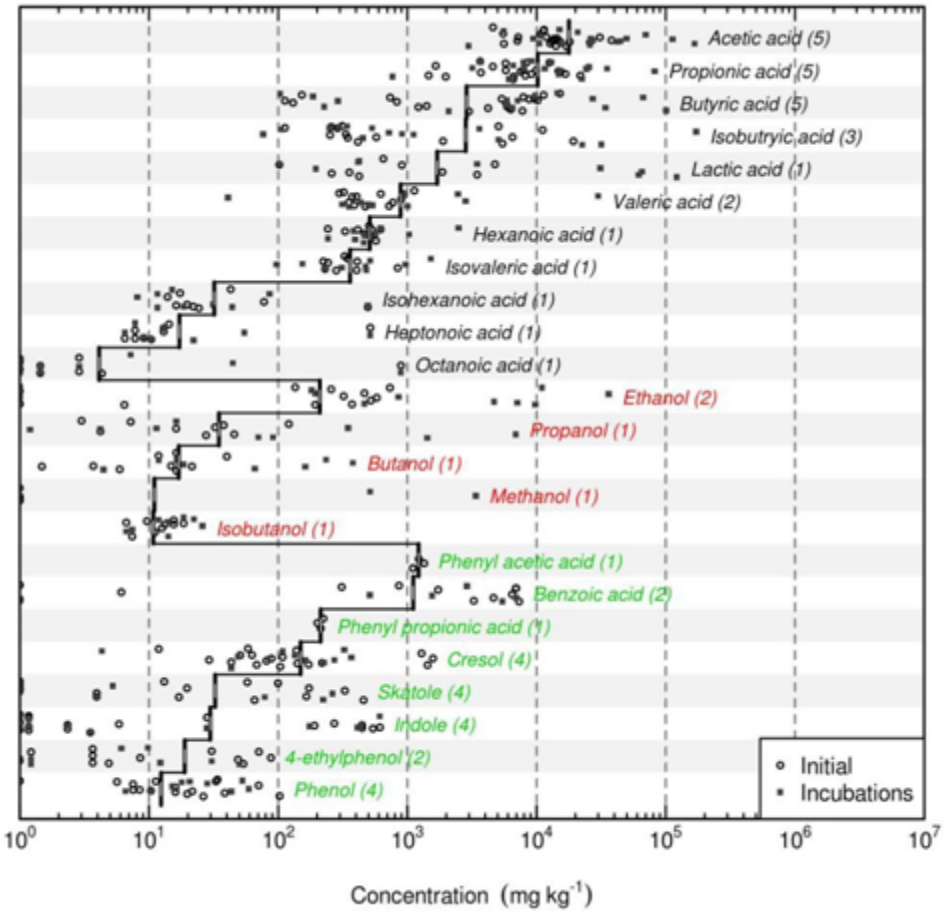
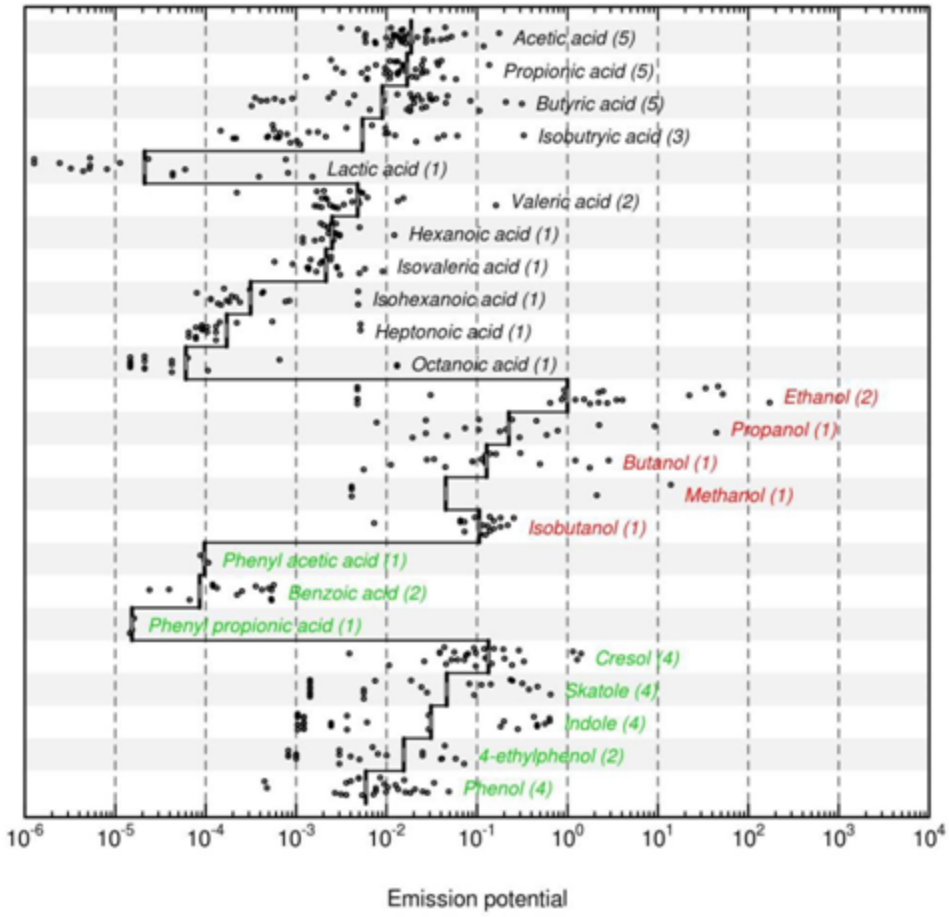


Figure 7.2- Emission Potential

Emission potential (product of concentration and Henry's law constant) for all observations. Values are normalized to ethanol. Vertical lines show overall medians.



ENVIRONMENTAL FOOTPRINTS

Environmental footprints are defined as the effect on the environment expressed per unit of product produced. In DairyGEM, three environmental footprints are assessed: water use, energy use, and carbon emission. Functions or factors are used to estimate values for important uses or sources of each in the production system. This includes the major uses of water and fossil energy and the GHG emissions that occur during the manufacture of resources used in the production system. These secondary uses or sources can include the manufacture or production of fuel, electricity, machinery, fertilizer, pesticides, seed, and plastic used on the dairy farm. Other major secondary inputs include any feed or replacement animals purchased and imported to the production system.

The unit of product produced is fat and protein corrected milk. Following the recommendation of the **International Dairy Federation (IDF, 2010)**, milk is corrected to a fat content of 4% and protein content of 3.3%. A correction factor is determined using equations 2.3 and 2.4 (see the **Feed Intake and Milk Production** section). Milk production is multiplied by this factor to make the correction. In the U.S., milk is often corrected to 3.5% fat and 3.1% protein. Correcting to this lower milk solids content will reduce the footprint by 8%.

Another issue in determining an environmental footprint is the proper allocation of the environmental issue between the milk and co-products produced on the farm. Co-products can include extra feed or crops produced and sold from the farm and animals sold for beef production or other uses. **Cederberg and Stadig (2003)** discuss four options for allocating between milk and co-products in a life cycle assessment: no allocation, economic allocation, physical or biological allocation, and system expansion. With no allocation, all emissions are attributed to milk production with no allocation toward the feed or animals sold. For an economic allocation, whole farm emissions are allocated between the two products based upon the annual income received from each. A number of criteria can be used as a basis for a physical or biological allocation. Suggested approaches are to allocate based upon the mass of each produced or the energy required to produce each. The final option of system expansion avoids allocation by expanding the system to include the alternative method of producing the co-product.

In DairyGEM, a mass-based allocation is used to allocate between unused feed and that used in dairy production. The total resource use or emission associated with all feed production is determined. The portion of this total included in the dairy footprint is determined by subtracting that used to produce feeds not fed on the farm. The water or energy used to produce the unused crop is the total used in feed production times the ratio of feed dry matter not used or exported from the production system over the total produced. Similarly, the GHG emission associated with the unused feed is the total available times the portion of the total dry matter not used.

The animal co-product from dairy farms includes extra calves, heifers and cull cows sold from the farm. Resource use and emissions associated with heifers produced on the farm are included in the total for the production system. The portion of these heifers used as dairy replacements is determined from the replacement rate of the lactating cows and the heifer mortality rate. Any additional heifers raised but not used are exported from the production system. Extra calves and cull cows are also exported from the production system for use in meat production or other products.

Following the recommendation of the **International Dairy Federation (IDF, 2010)**, a biophysical allocation procedure is used to allocate resource use or emissions between milk and

animal products. For heifers produced on the farm, the resource use and emissions associated with the exported heifers is removed from that associated with milk production. That associated with exported heifers is the footprint associated with heifer production (per unit weight) times the heifer liveweight leaving the farm. For calves and cull cows sold, an allocation factor is calculated based upon the physiological feed requirements of the animal to produce milk and meat (**IDF, 2010**). The allocation factor (*AF*) is determined as:

$$AF = 1. - 5.7717\ M_{meat} / M_{milk} \qquad [8.1]$$

where M_{meat} is the annual amount of animal liveweight in calves and cull cows sold (kg) and M_{milk} is the annual amount of milk sold (kg) from the production system. This factor varies among production systems, but generally attributes about 85% of the resource input or net farm emission to milk production with the remainder attributed to the production of the calves and cull cows used for meat production. This allocation factor provides the portion of the total water use, fossil energy use, or GHG emission included in milk production.

Water Use

Water use in agricultural production is becoming an important environmental concern, particularly in drier regions of the country. With a growing demand for water, the amount available for agriculture can be restricted. Knowing the amount required to produce milk and where it is used can be useful in assessing the long term sustainability of production systems.The water use footprint calculated by DairyGEM should be used only as a general estimate of water use. There will be much variability among production systems as affected by climate and production practices, and these differences may not be fully accounted in this model. The predicted water footprint is most useful for evaluating the relative differences obtained through management changes.

The major water requirement is for the production of feed. Other uses include drinking water for the animals, cleaning of the parlor and holding areas, and animal cooling. A footprint is determined by summing the estimates for each of these uses, removing that allocated to other co-products, and dividing by the amount of fat and protein corrected milk produced.

Large amounts of water are required to produce crops. For each feed crop, the amount required is defined as the amount taken up by the crop or emitted through evapotranspiration. That drained through the soil profile is available for other uses, such as well water. Likewise, that running off the field surface contributes to surface waters for recreational and other uses. Therefore, the amount attributable to feed production is that available through precipitation or irrigation minus that removed by drainage and runoff. This amount remains relatively constant over typical growing conditions, but water may be used more efficiently under drought conditions.

In DairyGEM, the amount of water used is determined using a water use factor for each feed crop. By multiplying the amount of each feed produced and used on the farm by the water use factor, a total is estimated. Water use factors were determined by simulating different cropping strategies with the Integrated Farm System Model (**Rotz et al., 2015**) and recording the water use per unit of feed dry matter produced. Simulations were done using both natural rainfall and irrigated crop conditions. Through multiple simulations, average factors were determined for each of the major feed crops. The factors assigned for pasture, grass silage, and alfalfa silage production are 0.8 kg/kg feed DM and that used for grass or alfalfa dry hay is 0.9 kg/kg DM. For corn silage, the factor is 0.6 kg/kg

DM and for high moisture or dry corn grain, the factor is 1.0 kg/kg DM.

Drinking water use by the herd is determined using relationships from the **NRC (2001)** for estimating water requirement. For each group of lactating cows:

$$FWI = 15.99 + 1.58\ DMI + 0.9\ MILK + 0.05\ SI + 1.2\ TMIN \qquad [8.2]$$

where FWI = fresh water intake, kg/cow/d

DMI = feed dry matter intake, kg/cow/d

$MILK$ = milk production, kg/cow/d

SI = sodium intake, g/cow/day

$TMIN$ = average minimum daily temperature, ^{o}C

For nonlactating cows and heifers, the drinking water requirement is determined as:

$$FWI = -10.34 + 0.2296\ \mathrm{DM} + 2.212\ DMI + 0.0394\ CP \qquad [8.3]$$

where DM = dry matter content of diet, %

CP = crude protein content of diet, %

Water intake is determined each month for each animal group making up the herd, and these are summed to obtain the annual requirement. Feed intake, milk production, and feed characteristics are obtained from the animal component of the model (**See Feed Intake and Milk Production section**). Sodium intake is determined using an assigned typical sodium content of 0.18% of *DMI*.

Daily use of water for parlor and equipment cleaning is estimated at 25 kg/cow. This value will vary with parlor type and size and the number of animals milked. Because this water use is relatively small compared to other uses, a more farm specific value or function was not warranted.

Another relatively small water use is that for animal cooling. The amount of water used is primarily a function of the daily temperature. This is modeled by assuming that cooling is used on any day when the maximum daily temperature exceeds 25 ^{o}C. On days when cooling is used, water use is set at 30 kg/cow.

Secondary water use in the production of farm inputs is considered only for purchased feed, animals, and seed. Water used in the production of machinery, fertilizer, pesticides, and plastic is considered to be very small and unimportant. That used for producing feed not produced on the farm is determined using the same procedure as that laid out above for feed produced on the farm. Water use factors are 1.0 kg/kg DM for grain, 0.8 kg/kg DM for forage, 1.0 kg/kg DM for crop based feed supplements and 0 kg/kg DM for byproduct feeds. For heifers imported to the farm, a water footprint of 30 kg/kg live body weight is assigned. This factor was determined by simulating various heifer producing farms using various management strategies. An average value for the water used to produce the animals was divided by the mass of the animals produced to obtain this average footprint.

The remaining secondary water use is in producing seed. A water footprint of 2.0 kg/kg of seed production is assigned based upon the amount of water required to produce grain seed crops.

Energy Use

Another important consideration in the evaluation of the sustainability of production systems is the energy footprint. This is defined as the total energy required to produce the milk except for the solar energy captured by the growing feed crops. This includes all fuel and electricity directly used in the production system as well as the secondary energy used in the production of resources used on the farm.

A major use of energy on dairy farms is the fuel used to operate tractors and other equipment for feed production, feeding, and manure handling. Fuel consumed is estimated through the use of fuel use factors. These factors represent a typical or average amount of fuel used to produce and deliver a unit of feed to the herd or remove a unit of manure. Fuel use factors were determined with the use of the Integrated Farm System Model (**Rotz et al., 2015**). This farm model simulates feed production and use over many years of weather. By simulating various feed production systems, average amounts of fuel use per unit of feed produced and fed were determined for each of the major types of feed used in dairy production (**Table 8.1**). This same approach was used to determine a factor for manure handling of 0.6 liter/t of manure removed from the barn. By summing the products of the fuel use factors and the amount of each feed used or the amount of manure handled, an estimate of total fuel use is obtained. Fuel use is converted to energy units assuming 38.6 MJ per liter of fuel.

Electricity is primarily used for milking, ventilation, and lighting. To estimate electricity consumption, electric use factors were obtained from a survey by Ludington and Johnson (2003). Electricity required for milking activities using a parlor is estimated as 0.04 kW-h/kg of milk produced times the total annual milk production. Electricity use in lighting is 60 for a drylot and 80 kW-h per cow for all other facilities. That used in ventilation is 0, 50, and 120 for drylots, naturally ventilated barns, and mechanically ventilated barns, respectively. When drylot and free stalls are combined, the electrical use is the average of the two facility types. When grazing is used, electrical use for lighting and ventilation are set proportional to the time animals spend in the barn. Electrical use is converted to energy units based upon 3.6 MJ per kWh of electricity.

Energy is also required for heating water that is used in cleaning. This requirement is estimated based upon the amount of milk received. The energy required for water heating is 0.072 MJ per kg of milk production.

Other energy inputs are the secondary energy uses during the production of farm inputs. These resource inputs include fuel, electricity, machinery, fertilizer, pesticides, seed, and plastic. Energy use factors for the production of each of these resources, except seed and plastic, were obtained from the GREET model (**DOE, 2011**). For fuel and electricity, the energy consumed in their production is 7.86 MJ per liter and 9.22 MJ per KWh, respectively. For fertilizers, energy use in production is set at 49.4, 14.13, 8.84 and 8.08 MJ per kg of nitrogen, phosphate, potash and calcium carbonate used, respectively. The secondary energy use for pesticide production is 275 MJ per kg of active ingredient where pesticide use is determined by feed crop using the factors of **Table 8.1**.

Fertilizer use is estimated based upon the nutrient removal of the crop. The N removed in the production of each feed is determined as the protein content times the feed DM fed divided by 6.25. Nitrogen use is then set at 140% of this value to allow for typical N losses in crop production. Phosphate and potash use are set at 110% of that removed in each feed. With these assumptions, a total requirement of each fertilizer is determined. This total is reduced to account for manure nutrients

returned to the cropland producing the feed. The quantities of each of the three major manure nutrients are available from the manure production and handling components of the model (see **Manure and Nutrient** section). This approach represents efficient use of manure and fertilizer nutrients. For manure not returned to cropland producing feed, the model user can specify the portion of the manure exported from the production system. The carbon and other nutrients for this manure are removed and the balance is satisfied through chemical fertilizers and imported manure.

To determine the energy used in manufacturing equipment, the total mass of equipment used in the production system was required. Machinery use factors were derived for the production of each major type of feed using the Integrated Farm System Model (**Rotz et al., 2015**). With this farm model, various production systems were simulated over a wide range in farm sizes. From model output, the total mass of machinery needed to produce each feed was totaled and this total was increased in proportion to the repairs used over the life of each machine. This total mass of machinery was then divided by the total feed produced over the life of the machine to obtain the machine use factor associated with each feed (kg of machinery per t DM of feed). Machinery use factors for a relatively small (100 cow) farm are listed in **Table 8.1**. Using the same procedure, a machine use factor of 0.17 kg per tonne of manure was obtained for manure handling on the small farm.

On larger farms, machines are generally used more efficiently providing some reduction in the machinery required per unit of feed produced. From further simulation data of the Integrated Farm System Model, an adjustment for farm size was determined as:

$$ADJ = 1.06 - 0.0006\ COWNO \qquad [8.4]$$

where ADJ = scaling factor for herd size, fraction

$COWNO$ = number of cows in the dairy herd

Therefore, as herd size increases, the machinery use factor is reduced by this scale adjustment. A lower limit on this scaling factor is set at 0.46, so that herd sizes over 1000 cows provide no further improvement in machinery efficiency. Machinery-use factors are multiplied by the associated use of all feeds during each year. This total, multiplied by an energy use factor of 42.6 MJ per kg of machinery mass, gives an annual value for this secondary energy use, i.e. the embodied energy in the manufacture of agricultural machinery (**DOE, 2011**).

Two relatively minor sources of secondary energy use are seed and plastic production. Seed us is a function of the feed crop produced (**Table 8.1**) and an energy use factor of 85 MJ per kg of seed is assumed. Plastic is used to produce silage in bags, bales or to cover silos. The amount of plastic used is a function of silo type. For simplicity in DairyGEM, bunker silo covering is assumed using 0.3 kg of plastic per tonne of silage used. The energy to produce this plastic is set at 50 MJ per kg of plastic.

When growing heifers or cows are purchased or imported to the farm as replacements for lactating cows, the energy used to produce those animals must be included in the footprint of the production system. This energy use is determined by multiplying the body weight of the imported animals by an energy use factor of 30 MJ per kg. This factor was determined by executing the DairyGEM model for a variety of heifer raising systems and dividing the total energy use by the weight produced. Although this footprint of heifer production varies some among production strategies and size of operation, an average energy use factor is used.

Carbon Emission

With the growing concern over global climate change and the potential impact of GHG emissions, a need has developed for expressing the total emission associated with a product or service. A term that has come to represent this quantification is the carbon footprint (http://en.wikipedia.org/wiki/Carbon_footprint). A carbon footprint is defined in many ways dependent upon the product or service represented. In general though, the carbon footprint is the total GHG emission, expressed in CO_2 equivalent units (CO_2e), associated with that product or service. The conversion to CO_2e is done using the GWP of each greenhouse gas where GWP values used for CH_4 and N_2O are 25 and 298, respectively (**IPCC, 2001**; **EPA, 2007**).

We define the carbon footprint of milk production to be the net of all greenhouse gases assimilated and emitted in the production system divided by the total fat and protein corrected milk produced. This net emission is determined through a partial life cycle assessment of the production system (**Figure 1.1**). All emission sources of the three gases are summed, and the net CO_2 assimilated in feed production is subtracted to give the net emission of the production system. Emissions include both primary and secondary sources. Primary emissions are those emitted from the farm or production system during the production process. Secondary emissions are those that occur during the manufacture or production of resources used in the production system (machinery, fuel, fertilizer, etc.). Secondary emissions such as those in the manufacture of equipment must be apportioned to average annual values. By totaling the net of all annual emissions from both primary and secondary sources and dividing by the annual milk production, a carbon footprint is determined in units of CO_2e per unit of milk produced.

The carbon footprint is first determined as the net emission of the three GHGs including all sources and sinks of CO_2. A carbon balance is enforced, so a portion of the CO_2 assimilated in the feed is in the carbon exported from the system in the milk and animals produced. Although this provides a more complete assessment of the carbon footprint of the production system, this procedure deviates from the more standard protocol followed by most other studies publishing carbon footprints of milk production. The more standard protocol does not consider assimilated CO_2 and includes only the CO_2 emitted by the combustion of fossil fuels (**IDF, 2010**). For comparison, a carbon footprint is also determined following the standard procedure. Use of this protocol increases the footprint about 30-50% compared to the first approach. The difference is in the CO_2 assimilated in the carbon exported from the production system.

Primary Sources

Primary sources of GHG emissions include the net emission of CO_2 plus all emissions of CH_4 and N_2O occurring from the farm production system. Daily emission values of each gas are summed to obtain annual values. Carbon dioxide emissions include the net annual flux in feed production, daily emissions from animal respiration, and daily emissions from microbial respiration in manure on the barn floor and during storage. The annual net exchange in feed production is determined as that assimilated in the feed minus that in manure applied to cropland (**Equation 6.1**). Emission of CO_2 through animal respiration is a function of animal mass and daily feed DM intake (**Equation 6.2**) and that from the barn floor is a function of ambient barn temperature and the floor surface area covered by manure (**Equation 6.3**). Emission from a slurry manure storage is predicted as a function of the

volume of manure in the storage using an emission factor. Finally, CO_2 emission from fuel combustion in farm engines is proportional to the amount of fuel used in the production and feeding of feeds (see **Energy Use** section). The amount of CO_2 released is 2.637 kg per liter of fuel consumed (**DOE, 2011**).

Methane emissions in milk production include those from enteric fermentation, the barn floor, manure storage, and feces deposited in pasture. Daily emission from enteric fermentation is a function of the metabolizable energy intake and the diet starch and fiber contents for the animal groups making up the herd (**Equation 6.4**). Daily emissions from the manure storage are a function of the amount of manure in the storage and the volatile solids content and temperature of the manure (**Equation 6.11**). Emissions following field application of manure are related to the volatile fatty acid content of the manure and the land area covered (**Equation 6.19**). Emissions during grazing are proportional to the amount of feces deposited on the pasture and that emitted in the barn is a function of barn temperature and the floor area covered by manure (**Equations 6.7 and 6.8**).

Nitrous oxide emissions considered in the carbon footprint are that emitted from crop and pasture land during the production of feeds with minor emissions from the manure storage and barn floor. As described above, an emission factor approach is used to estimate annual emissions in feed production. Emissions from the crust on a slurry storage and from a bedded pack barn floor are predicted as functions of the exposed surface area of each (**Equation 6.23**).

Secondary Sources

Secondary sources included in DairyGEM are the production of fuel, electricity, machinery, fertilizer, pesticide, and plastic used in the production of feeds, maintenance of animals, and handling of manure. Also included are the emissions during the production of any replacement animals not raised on the farm. Secondary emissions are all expressed in annual values of CO_2e units. Most of these emissions are in the form of CO_2, but where appropriate CH_4 and N_2O emissions are converted to CO_2e units and included in emission factors.

Emissions during the production of fuel and electricity are set using emission factors derived from the GREET model (**DOE, 2011**). These factors are 0.734 kg CO_2e/litre of fuel and 0.53 kg CO_2e/kWh of electricity used in the production system. As described above, fuel use is estimated as the product of a fuel-use factor for each feed times the amount of feed used summed over all feeds fed in the production system. Electricity use is the total of that used for milking, milk cooling, and related milking activities and that used for barn lighting and ventilation (see **Energy Use** section).

Secondary emissions associated with machinery include both the initial manufacture and the repairs required to maintain the equipment. These emissions are primarily due to the energy used to extract and process steel which accounts for the majority of the mass of agricultural machines (**Bowers, 1992**; **Doering, 1980**; **Fluck, 1992**). Based on this premise, an average GHG emission factor for the production of machinery is set at 3.54 kg CO2e per kg of machinery mass. This emission factor was established based upon available sources of information on embodied energy or emissions in the manufacture of agricultural machinery (**DOE, 2011**; **Wu et al., 2006**; **Farrell et al., 2006**; **Schroll, 1994**; **Lee et al., 2000**; **Graboski, 2002**). Machinery mass required is determined as defined in the **Energy Use section**.

Emissions in the manufacture of fertilizer were obtained from the GREET model (**DOE,**

2011). Factors used for nitrogen, phosphate, and potash fertilizers are 3.307, 1.026, and 0.687 CO_2e /kg of each used in the production of feeds. Fertilizer use is estimated as a function of the nutrients removed in the feed (see **Energy Use** section). Emission during the production of lime is determined using an emission factor of 0.63 kg CO_2e kg^{-1} of calcium carbonate equivalent used (**DOE, 2011**) where lime use is determined as described in the **Carbon Dioxide** section.

Emissions in the manufacture of pesticides are generally small, but they are included. Pesticide use is estimated using a pesticide use factor set for each feed produced (**Table 8.1**). The total pesticide use is this factor times the amount of each feed used summed over all feeds. An average emission factor of 22 CO_2e /kg of pesticide is used to determine emissions during manufacture. This emission factor was set based upon the GREET model (**DOE, 2011**) and other sources (**Bath et al., 1994**; **Dalgaard et al., 2001**; **Patzek, 2004**; **West and Marland, 2002**; **Fluck, 1992**; **Pimentel, 1980**).

Emissions in the production of seed are modeled similar to that of pesticides. Again this emission is small. Seed use factors were derived from typical seeding rates and yields of each crop (**Table 8.1**). Seed use is summed over all feeds fed based upon these typical seeding rates. An emission is determined using an emission factor of 0.3 CO_2e /kg of seed. This factor was estimated considering all the emissions in producing the seed crop minus the carbon contained in the seed (**Graboski, 2002**; **Patzek, 2004**; **Nagy, 1999**; **West and Marland, 2002**; **Schmer et al., 2008**; **Borjesson, 1996**). This value is likely to vary among feed crops, but due to the lack of available information and the relative unimportance of this emission source, this average rate is used.

Plastic is often used in silage production for bags, to cover silos, or to wrap bales. Plastic use factors for tower silos, bunker silos, silage bags, and bale silage are 0.0, 0.3, 1.8, and 3.6 kg / t DM of stored feed for each storage type, respectively (**Savoie and Jofriet, 2003**). The emission factor for plastic production is set at 2.0 kg CO_2e /kg of plastic use (**IPCC, 2006**; **Garrain et al., 2007**; **AMPE, 2008**; **Patel, 1999**). This emission source is normally very small and relatively unimportant compared to other secondary emission sources.

When heifers are purchased and brought onto the farm to replace lactating cows, the emissions associated with their production must be considered as part of the production system. These emissions will vary with the production practices used. To determine an average emission factor for heifer production, the model was used to determine the emissions for producing heifers over a wide range in farm size and feeding strategies including grazing. The range found for this secondary source was 8 to 14 kg CO_2e /kg of body weight produced with the lower values associated with larger farms or grazing production systems. An average emission factor of 11 kg CO_2e / kg of body weight was selected to best represent this source. This secondary emission is determined by multiplying this factor by the net body weight of the livestock purchased to meet the replacement rate of the dairy herd. If all replacements are raised on the farm, this source is eliminated. If extra animals are raised and sold from the farm, secondary emissions are reduced by the amount sold.

Table 8.1 - Resource input factors

Use factors for major resource inputs in feed production.

Feed type	Fuel use liter/t DM feed[a]	Machine use kg/t DM feed[b]	Pesticide use kg ai/t DM feed[c]	Seed use kg/t DM feed[d]
Grazed forage	0.0	0.0	0.05	0.9
Alfalfa or grass silage	25.0	5.5	0.10	0.9
Alfalfa or grass hay	17.0	3.0	0.10	0.9
Corn silage	19.0	5.5	0.30	1.7
High moisture corn	15.0	3.0	0.67	4.0
Corn grain	12.0	1.5	0.67	4.0
Protein supplement	3.5	0.5	0.00	0.0
Fat additive	3.5	0.5	0.00	0.0

[a] Liters of fuel used in the production and feeding of each feed.
[b] Total equipment mass per unit of feed produced over the life of the equipment.
[c] Mass of active ingredient applied per unit of each feed produced.
[d] Mass of seed used per unit of each feed produced.

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