Estimate of changes in agricultural terrestrial nitrogen pathways and ammonia emissions from 1850 to present in the Community Earth System Model

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Abstract. Nitrogen applied to the surface of the land for agricultural purposes represents a significant source of reactive nitrogen (N_r) that can be emitted as a gaseous N_r species, be denitrified to atmospheric nitrogen (N_2), run-off during rain events or form plant useable nitrogen in the soil. To investigate the magnitude, temporal variability and spatial heterogeneity of nitrogen pathways on a global scale from sources of animal manure and synthetic fertilizer, we developed a mechanistic parameterization of these pathways within a global terrestrial model land model, the Community Land Model (CLM). In this first model version the parameterization emphasizes an explicit climate dependent approach while using highly simplified representations of agricultural practices including manure management and fertilizer application. The climate dependent approach explicitly simulates the relationship between meteorological variables and biogeochemical processes to calculate the volatilization of ammonia (NH_3), nitrification and run-off of Nr following manure or synthetic fertilizer application. For the year 2000, approximately 138 Tg N yr-1 is applied as manure and 86 Tg N yr-1 is applied as synthetic fertilizer. We estimate the resulting global NH3 emissions are 21 TgNyr−1 from manure (15% of manure production) and 12 TgNyr−1 from fertilizer (14% of fertilizer application); reactive nitrogen dissolved during rain events is calculated as 11 TgNyr−1 from manure and 5 TgNyr−1 from fertilizer. The remaining nitrogen from manure (106 Tg N yr-1) and synthetic fertilizer (69 Tg N yr-1) is captured by the canopy or transferred to the soil nitrogen pools. The parameterization was implemented in the CLM from 1850 to 2000 using a transient simulation which predicted that, even though absolute values of all nitrogen pathways are increasing with increased manure and synthetic fertilizer application, partitioning of nitrogen to NH_3 emissions from manure is

increasing on a percentage basis, from 14 % of nitrogen applied (3 Tg NH_3 yr^{-1}) in 1850 to 17% of nitrogen applied in 2000 (22 Tg NH_3 yr^{-1}). Under current manure and synthetic fertilizer application rates we find a global sensitivity of an additional 1 Tg NH3 (approximately 3% of manure and fertilizer) emitted per year per degree C of warming. While the model confirms earlier estimates of nitrogen fluxes made in a range of studies, its key purpose is to provide a theoretical framework that can be employed within a biogeochemical model, that can explicitly respond to climate and that can evolve and improve with further observation.

1. Introduction

Nitrogen is needed by all living things for growth. However, it is relatively inert in its most abundant form, diatomic nitrogen (N_2), and needs to be converted to a form of reactive nitrogen (N_r) before it can be used by most plants for growth [Visek, 1984]. Supplying sufficient N_r for maximum crop yield is a major concern in agriculture. In pre-industrial times N_r demand was partly solved with the use of animal manure and seabird guano as well as crop rotation and the use of nitrogen fixing crops [Smil, 2000]. However, by the early 20th century the supply of these N_r sources could not match the demands of an increasing population and a process of creating synthetic N_r was developed; the Haber-Bosch process [Galloway et al., 2004].

The use of N_r to improve crop yield has recently become an environmental concern as N_r in synthetic fertilizer and manure cascades through the soil, water and the atmospheric nitrogen cycles. Plants can readily use applied N_r for plant growth; however, N_r washed off fields or volatilized as gas can reduce ecosystem biodiversity through acidification and eutrophication [Sutton et al., 2013]. Increased N_r in the hydrosphere can lead to the subsequent degradation of riverine and near shore water quality as the water becomes more acidic and the growth of primary producers blooms [Turner and Rabalais, 1991; Howarth et al., 2002], which can alter the local interspecies competition and biodiversity [Sutton et al., 2012]. Reactive nitrogen emissions into the atmosphere impacts air quality through the ozone generation associated with NO emissions [e.g., Hudman et al., 2010] and the contribution of ammonia to aerosol formation [e.g., Gu et al., 2014]. Nitrogen cycling also impacts climate through the stimulation of plant growth and associated increased carbon storage; through the associated emissions of N_2O, a strong greenhouse gas; through emissions of nitrogen oxides and the associated ozone production; and through the emissions of ammonia (NH_3) with its potential to cool the climate through aerosol formation [e.g., Adams et al., 2001].

As a result of their dependency on environmental conditions, N_r pathways following manure or synthetic fertilizer application are likely to change in the future under climate change scenarios. This study describes a biogeochemically consistent process driven parameterization suitable for incorporation into Earth System Models that simulates N_r flow following the surface addition of N_r as manure or synthetic fertilizer. The parameterization is evaluated on both the local and global scales against local measurements and independent global NH_3 flux estimates. The calculated emission estimates for NH_3 and the N_r runoff due to manure and synthetic fertilizer application will be used in ensuing studies in both present and future climates to investigate their impact on nitrogen cycling and climate within the earth system. To our knowledge, no Earth System model has yet to explicitly predict changing nitrogen pathways from manure and synthetic fertilizer in response to climate.

Sources of N_r largely fall into two categories, 'new' sources, created by chemical and biological processes, and those that are 'recycled', such as manure excretion of animals. The largest natural new N_r producers are biological nitrogen fixers, found in the ocean and on land, and as the by-product of lightning estimated at 140 Tg N yr^{-1} ± 50%, 58 Tg N yr^{-1} ± 50 % and 5 Tg N yr^{-1} ± 50 %, respectively [Fowler et al., 2013]. The dominant anthropogenic sources of new N_r are Haber-Bosch derived fertilizer (estimated at 120 Tg N yr^{-1} ±10 % in 2005), the burning of fossil fuels, (30 Tg N yr^{-1} ± 10 % in 2000), and a further 60 Tg N yr^{-1} ± 30 % circa 2005 estimated from biological nitrogen fixers grown for human consumption, such as legumes [Fowler et al., 2013]. Since pre-industrial times, anthropogenic N_r creation has increased from 15 Tg N yr^{-1} to the present estimate of 210 Tg N yr^{-1} [Galloway et al., 2004; Fowler et al., 2013]. Animal manure is used to stimulate plant growth in agriculture. It contains N_r recycled from the soil produced when animals eat plants. A comprehensive increase in livestock population is estimated to have increased global manure production from 21 Tg N yr^{-1} in 1850 to the present estimate of 141 Tg N yr^{-1} [Holland et al., 2005]. It is suggested that this increase in recycled N_r production speeds up the decay and processing of plant biomass, releasing different N_r products to the atmosphere when compared to natural decay processes [Davidson, 2009].

Projections of agricultural activity [Bodirsky et al., 2012] suggest continued increases in the application of synthetic fertilizers until the mid-21st century (and possibly beyond) concurrent with likely increases in manure production [Tilman et al., 2001]. In addition to the increased use of organic and synthetic fertilizers in the future, NH_3 emissions are expected to increase because of changing climate on nitrogen biochemistry [Tilman et al., 2001; Skjoth and Geels, 2013; Sutton et al., 2013].

Current estimates of the direct forcing of nitrate aerosols present as ammonium nitrate encompass the range from -.03 Wm^{-2} to -.41 Wm^{-2} over the ACCMIP (Atmospheric Chemistry and Climate Model Intercomparison Project) [Shindell et al., 2013] and AeroCom Phase II [Myhre et. al., 2013] simulations. With a future reduction in sulfate emissions the relative importance of nitrate aerosols is expected to dominate the direct aerosol forcing by 2100 with a resulting increase in radiative forcing of up to a factor of 8.6 over what it would have been otherwise [Hauglustaine et al., 2014]. These estimates do not consider the temperature dependence of NH_3 emissions. Skjoth and Geels [2013] predict increases in future NH_3 emissions of up to 60% over Europe by 2100 largely due to increased NH_3 emissions with temperature. Sutton et al. [2013] predicts future temperature increases may enhance global NH_3 emissions by up to approximately 40% assuming a 5^o C warming. In addition to future changes in climate-induced NH_3 volatilization from manure and synthetic fertilizer application, future changes in agro-management practices, soil microbiological processes and nitrogen runoff may be expected.

Studies calculating NH_3 emission from manure and synthetic fertilizer have broadly fallen into two categories: models that use empirically derived agriculturally-based emission factors and more complex process-based models. Global emissions have almost been universally estimated using the former approach. Emission factors were used by Bouwman et al. [1997] to estimate global NH_3 emissions in 1990 of 54 Tg N yr^{-1}, with the greatest emission of 21.6 Tg N yr^{-1} from domestic animals [Bouwman et al., 1997]. Beusen et al. [2008] also used emission factors to estimate global NH_3 emission from agricultural livestock (21 Tg N yr^{-1}) and synthetic fertilizers (11 Tg N yr^{-1}) in 2000; Bouwman et al. [2013] estimated emissions of 34 Tg NH_3 yr^{-1} on agricultural land, with 10 Tg NH_3 yr^{-1} from animal housing. A number of more recent global models have included emission factors explicitly as a function of temperature [e.g., Huang et al., 2012; Paulot et al., 2014]. Paulot et al. [2014] estimates global NH_3 emissions of 9.4 Tg yr^{-1} for synthetic fertilizer and 24 Tg yr^{-1} for manure.

Alternatively process-based or mechanistic models have been developed that estimate N_r flows, equilibria and transformations between different nitrogen species as well as nitrogen emissions from synthetic fertilizer and manure. Process models have been used on the field to regional scale, but not on the global scale. These models generally do not simulate the run-off of N_r. For example, Génermont and Cellier [1997] model the transfer of NH_3(g) to the atmosphere after considering the physical and chemical equilibria and transfer of Nr species (NH_3(g), NH_3(aq), NH_4^+(aq)) in the soil. The resulting model is used to calculate the NH_3 emissions from synthetic fertilizer over France within the air quality model, Chimere [Hamaoui-Laguel et al., 2014]. Other examples include Pinder et al. [2004], who describes a process model of NH_3 emissions from a dairy farm, while Li et al. [2013] describes a farm-scale process model of the decomposition and emission of NH_3 from manure.

The overall goal of this paper is to describe and analyze a global model capable of simulating nitrogen pathways from manure and synthetic fertilizer added to the surface of the land under changing climactic conditions to allow a better global quantification of the climate, health and environmental impacts of a changing nitrogen cycle under climate change. The resulting model is of necessity designed for use within an Earth System Model so as to simulate the interactions between the climate and the carbon and nitrogen cycles. Section 2 presents the overall methodology including a detailed description of the process model developed here to calculate climate dependent nitrogen pathways. Section 3 analyzes this model and includes: a comparison of simulated versus site level measurements of NH_3 fluxes; an analysis of the globally heterogeneous nitrogen pathways from applied manure and synthetic fertilizer over a range of climatic regimes; model predictions for changes in nitrogen pathways from 1850 to present and the sensitivity of the results to model parameters. Section 4 gives our conclusions.

2. Methods

In this section we describe a model designed to predict the spatial and temporal variations in the evolution of N_r that results from the application of manure and synthetic fertilizer within the context of an Earth System Model, the Community Earth System Model 1.1 (CESM1.1). The process model developed here simulates the loss major pathways of N_r

following the application of synthetic fertilizer or manure to the Earth's surface: its incorporation into soil organic matter and soil nitrogen pools [Chambers et al., 1999], the volatilization of NH_3 to the atmosphere and the direct runoff of N_r from the surface (Figure 1). The model is global in nature, is designed to conserve carbon and nitrogen and responds to changes in climate. The model developed here is designed provide an interface between the application of manure and fertilizer and the nitrogen cycling developed within the Community Land Model 4.5 (CLM4.5), the land component of the CESM.

Nitrogen pathways subsequent to the application of manure or synthetic fertilizer depend on the complex interaction between both human and natural processes. In particular they depend on the biology and physics of the applied substrate, agricultural practices and climate. Bottom-up emission inventories with specified emission factors that take into account the animal feed, the type of animal housing if any and the field application of the synthetic fertilizer or manure [e.g., Bouwman et al., 1997] are generally used in global chemistry and chemistry-climate applications. For example, this type of emission inventory [e.g. Lamarque et al., 2010] was used in the Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP) [Lamarque et al., 2013a] for assessing historical and future chemistry-climate scenarios as well as in assessing nitrogen deposition [Lamarque et al., 2013b] with implications for impacts on the carbon cycle. However, these inventories include very simplified representations of the effect of climate on emissions, for example, by grouping countries into industrial or developing categories [Bouwman et al., 1997]. A seasonal emission dependence is not implicit in these bottom-up inventories although sometimes an empirical relationship is applied [e.g., Adams et al., 2001; also see Skjøth et al., 2011].

In the first application of the model described here we take the opposite tact here. We have minimized the description of agricultural practices, and instead emphasize representing a physically based climate dependent biogeochemistry of manure and synthetic fertilizer decomposition and the resultant nitrogen pathways. We recognize that we are simplifying many important agro-management processes including: (1) we assume all synthetic fertilizer is urea and the pH of soil is given. Different applied synthetic fertilizers have a strong impact on the pH of the soil-fertilizer mixture with the overall emission factor very dependent on the pH as well as day since application (Whitehead and Raistrick, 1990). Urea is the most commonly used synthetic fertilizer accounting for over 50% of the global nitrogenous synthetic fertilizer usage [Gilbert et al., 2006] and has one of the highest emission factors for commonly used synthetic fertilizers [Bouwman et al., 1997]. Emission factors for other types of fertilizers can be significantly smaller. (2) We do not account for manure management practices. We assume all manure is continuously spread onto fields. In contrast, in a global study Beusen et al. (2008), for example, considered four primary pathways for manure excretion: (i) in animal houses followed by storage and spreading on cropland (accounting for approximately 37% of global manure application), (ii) in animal houses followed by storage and spreading on grassland (accounting for approximately 7% of global manure application) and iii) excreted by grazing animals (accounting for approximately 44% of global manure application), (iv) losses from the system (accounting for approximately 16% of global application). Beusen et al. (2008) estimated that the overall emission factor accounting for all processes including nitrogen losses from the system is 19%; however, the emission factors for the individual pathways vary substantially ranging from 38% for pathway (ii) to 11% for pathway (iii). (3) We do not account for specific fertilizer application techniques. For example, the soil incorporation of manure leads to a 50% reduction in ammonia emissions compared to soil broadcasting (Bowman et al., 2002). We recognize that there are large spreads in all these ranges, that regional practices may alter these numbers and that the above list is by no means exhaustive. We also recognize that large errors may be unavoidable due to insufficient characterization of regional agro-management practices. While our global emission rate of ammonia from manure of 15% of applied manure is within the uncertainty range specified in Beusen et al. (2008) large regional discrepancies may exist.

On the otherhand a physically based geographical and temporal accounting for meteorology, including temperature, turbulence and rainfall is accounted for in the parameterization described below, but is not accounted for in the traditional bottom-up ammonia emission inventories. As with regional differences in agro-management practices, meteorological impacts may also induce large regional and interannual variations in ammonia emissions. For example, increasing the ground temperature from 290o K to 300oK at a pH of 7 increases the ammonia emissions by a factor of 3 (see equation XXX, below). Moreover, the simulation of dynamic ammonia emissions, as described below, with ammonia emissions responding to temperature on the model timestep, allows for a regionally resolved ammonia flux between the land and atmosphere that depends on boundary layer turbulence and explicit bidirectional exchange depending on the canopy compensation point. Of course high spatial heterogeneity may preclude an accurate local representation of these exchange processes on the approximately 2 x 2 ° grid cell used here, but even on similar coarse resolutions Zhu et al. [2015] show the implementation of a bidirectional scheme has significant global and pronounced regional impacts (e.g, approximately a 44% decrease in emissions over China in April). In the present application we do not explicitly simulate this atmosphere-land coupling, but such a step is a fairly simple extension of the parameterization. On the otherhand, bottom-up inventories assume bulk emission rates cannot simulate the bidirectional flux of ammonia or allow for regional and temporal differences in atmospheric turbulence.

In addition, the following specifications are necessary to model ammonia emissions following synthetic fertilizer or manure application within an Earth System Model, specifications that are not included in more traditional formulations. (1) The model must be global in nature to characterize global interactions between applied N_r and climate. (2) The model must conserve nitrogen. In particular the nitrogen associated with manure does not add new nitrogen to the system, but merely represents a recycling of available nitrogen. Artificial sources or sinks of nitrogen may have serious repercussions especially when simulating the global nitrogen cycle on the timescale of centuries. (3) The model must be able to simulate the changing impact of climate on the fate of manure and synthetic fertilizer N_r. In particular, NH_3 emissions are sensitive to both temperature and to the water content of the soil. In addition the runoff of N_r is likely to change under climate change scenarios. For this reason the process model developed here is capable of simulating the physics of changing nitrogen pathways under a changing climate.

An ideal model would incorporate a globally more explicit representation of agro-management practices, including manure treatment (housing, storage and spreading) and fertilizer application [e.g., see Sutton et al., 2013] as well as a more explicit representation of the bidirectional exchange of ammonia between the land and atmosphere. A representation of these processes has been developed elsewhere and are an extension of the model described below. As shown below, the model developed here captures many of the regional and global features seen in models based on emission factors. The truth of the matter, of course, lies somewhere in between.

2.1 Relation between the process model and the CESM1.1

The parameterization developed here acts as the interface between specified manure and fertilizer application and the CESM1.1. The CESM1.1 simulates atmospheric, ocean, land and sea ice processes, linked together using a coupler, and includes a land and ocean carbon cycle [Hurrell et al., 2013; Lindsay et al., 2014]. The CESM participates in the Climate Model Intercomparison Project (CMIP5), and has been extensively evaluated in the literature [see Hurrell et al., 2013]. The land model within the CESM1.1, the CLM 4.5 includes representation of surface energy and water fluxes, hydrology, phenology, and the carbon cycle [Lawrence et al., 2007; Oleson et al., 2008]. The CLM simulations can be forced by meteorology (as done here), or as a part of a coupled-carbon-climate model [Lawrence et al., 2007; Oleson et al., 2008]. The current version of the carbon model is an improved version of the coupled-carbon-climate model used in Keppel-Aleks et al. [2013], Lindsay et al., [2014] and Thornton et al., [2009]. The carbon model includes a nitrogen limitation on land carbon uptake, described in Thornton et al. [2007, 2009]. Further improvements have been made to the below ground carbon cycle, as well as other elements of the land model in order to improve its [e.g. Koven et al., 2013; Lawrence et al., 2012]. The impact of increases in nitrogen deposition (NO_y and NH_x from fossil fuels, fires and agriculture [Lamarque et al., 2010]) have been evaluated [Thornton et al., 2007; Thornton et al., 2009] and extensively compared to observations [e.g. Thomas et al., 2013].   The CLM4 has been extensively tested and evaluated by many studies at the global [Lawrence et al., 2007; Oleson et al., 2008; Randerson et al., 2009] and the site [Stoeckli et al., 2008; Randerson et al., 2009] scale. The CLM4.5 retains the basic properties of CLM4 but with improvements to better simulate: (1) water and momentum fluxes at the Earth's surface; (2) carbon and nitrogen dynamics within soils and (3) precipitation run-off rates [Koven et al., 2013].

As described in Koven et al., [2013], the CLM4.5 simulates the basic flows of N_r within soils following the Century N model [Parton et al., 1996, 2001; Grosso et al., 2000] including the processes of nitrification, denitrification, and emissions of N_r and N_2 and the loss of N_r from leaching and runoff. The CLM4.5 also simulates the transfer of N_r between soils and vegetation, and the loss of N_r from fire. Sources of N_r within the CLM4.5 are from biological nitrogen fixation and from surface deposition. The process model developed here adds an additional source of N_r to the CLM4.5, the addition of synthetic fertilizer. It also adds an additional pathway whereby N_r is recycled: the creation and application of manure (Figure 1).

The relation between nitrogen cycling within the process model developed here and that within the atmospheric, land and river components of the Community Earth System Model (CESM1.1) is given in Figure 1. In this first study the subsequent fate of N_r from fertilizer or manure application as is incorporated into the soil organic matter or the soil nitrogen pools of the CLM4.5 is not considered here (see Figure 1). As described in more detail below fertilizer and manure is not applied to particular plant functional types (pft) (e.g., pasture or grassland) within the CLM4.5. This is because soil related properties including soil nitrogen are not specified at the pft level within the CLM4.5, but instead specified at the column level that includes many pfts. In practice we expect that the impact of this contamination across pfts will be small since the major N-application regions (central US, northern India, eastern China) are not PFT-diverse but contain almost exclusively crop and grass PFTs.

In addition, the fate of N_r emitted into the atmosphere as NH_3 directly from synthetic fertilizer or manure is handled by the atmospheric chemistry component of the CESM (CAM-chem) and is not considered here (Figure 1). The aerodynamic resistances used to compute the flux of ammonia to the atmosphere are calculated with the CLM4.5, but due to the configuration of the CLM are not calculated at the pft level. In addition, the canopy deposition of the ammonia flux is calculated as a global number and not at the pft level. Incorporation of PFT dependent canopy deposition and aerodynamic resistances are among future improvements.

In addition, the fate of reactive nitrogen emitted into the atmospheric model is not further considered here.

Note that as a first approximation the model described here does not simulate the direct emission loss of species other than NH_3. Atmospheric emission losses of N_2O or N_2 (and potentially NO_X) are simulated in the Community Land Model (CLM) 4.5 [Koven et al., 2013], the land component model of the CESM1.1, 'downstream' from the pathways explicitly considered here. The run-off of N_r from manure or synthetic fertilizer nitrogen pools has been coupled to the river transport model (RTM) in [Nevison et al., 2016] (Figure 1), but is not considered here.

2.2 Process model for predicting nitrogen pathways from manure or synthetic fertilizer

A schematic of the overall model analyzed here is given in Figure 1. All the equations and variables used in the model have been collated and are presented in the appendix. The assumptions used in constructing this model are detailed below where appropriate. Sensitivity to model parameters is given in section 3.4. The nitrogen loss pathways are calculated separately for manure and synthetic fertilizer. While this model assumes that synthetic fertilizer application and manure application can take place in the same approximately 2 x 2 ° grid cell, we also assume that manure and synthetic fertilizer are not applied in the exactly the same place. Therefore the NH_3 emissions, the nitrogen incorporation into soil pools, and the nitrogen run-off in rain water are separately calculated for manure and synthetic fertilizer in each column. This means that the Total Ammoniacal Nitrogen (TAN) pools (consisting of NH_3(g), NH_3(aq), NH_4^+) for manure and synthetic fertilizer are discrete and hence the nitrogen pathways are not combined.

The application rate and geographical distribution used for manure and synthetic fertilizer application is taken from the synthetic fertilizer application and manure production datasets developed in Potter et al [2010]. These datasets are valid for circa 2000 for synthetic fertilizer and 2007 for manure [Potter et al., 2010]. Beusen et al. [2008] estimates that 14% of the manure produced is lost from the agricultural system through building materials and other uses. In this first study we do not explicitly account for the fate of this lost manure. We further assume that manure is continuously spread onto fields by-passing the use of animal houses and storage. While most manure is excreted in housing prior to being applied in the field, the emission factors for NH_3 emissions from spreading are not significantly different than from housing and storage: the emission factor for spreading onto grassland is higher and that onto cropland is lower [Beusen et al., 2008]. A more sophisticated analysis could take into account differences in manure treatment, although regional differences in animal housing and storage practices would make a global analysis quite challenging.

To adequately model the conversion timescales of N_r input from animals to TAN, it is necessary to separate the manure into different pools depending on the decomposition timescales (sections 2.2.1 and 2.2.2 and Figure 1). A similar strategy was adopted by Li et al. [2013] for manure and is commonly used in simulating litter decomposition.

Synthetic fertilizer Nr is added to one pool, where after it decomposes into the TAN pool (Figure 1). Once in the TAN pool N_r (1) washes off during rain events [Brouder et al., 2005]; (2) volatilizes to the atmosphere as NH_3 [Sutton et al., 1994; Nemitz et al., 2000]; (3) nitrifies to form nitrate (NO_3^-) [Stange and Neue, 2009]; 4) or is incorporated into the soil nitrogen pools. A number of other smaller loss processes are not explicitly simulated. Nitrate, in turn, becomes incorporated into the soil (Figure 1).

Manure must be added to the model in such a manner as to conserve nitrogen (Figure 1). Here, we assume animals consume carbon and nitrogen from plants and then subsequently excrete this as manure. Within the CLM, carbon and nitrogen in the plant-leaf pool is thus converted to carbon and nitrogen in manure and urine, conserving overall carbon and nitrogen. The conversion rate from carbon and nitrogen in plants to that in manure and urine is set to equal the rate of manure and urine production. The external dataset of Potter [2010] gives the rate of N_r production from animals , and thus allows us to specify the nitrogen flows. The specified C to N ratio in the plant-leaf pool determines the associated carbon flows due to ruminant consumption of plant material. The input manure and urine production rate from animals implicitly includes that produced from transported feed. Thus the subsequent NH_3 emission rate includes the nitrogen contained in transported feed grown elsewhere. Here we make the simplification that the consumption rate of plant matter to balance the manure and urine production is local. That is, we do not explicitly consider the import of animal feed to match the carbon and nitrogen flows associated with manure and urine production. While this is not entirely consistent, the development of the requisite dataset for feedstock flows from

1850-2000 is outside the scope of this study, although such a dataset could be developed in the future. We do not know of an Earth System Model that does consider the anthropogenic import of nitrogen or carbon. This inconsistency could produce cases where there is insufficient local plant material to balance the overall manure and urine production, but this is generally not the case. The parameterization also ignores export of N_r in ruminant products such as milk and protein, which could create an additional source of uncertainty.

2.2.1 Manure and Urine. Prescribed manure (including urine) is input at a constant annual rate ($\alpha_{applied}(m)$) (g m^{-2} s^{-1}) depending on latitude and longitude into the manure nitrogen pools. Nitrogen applied to the land as manure (or synthetic fertilizer) is assumed to be spread uniformly on each grid cell irrespective of plant functional type (pft) or surface type (see discussion in section 2.1). Future development will spread the input into different pfts (e.g., grassland or agricultural land). It is assumed that a fraction (f_u = 0.5) of nitrogen excreted is urine, with the remaining 50 % excreted as faecal matter [Gusman and Marino, 1999]. In practice the fraction of nitrogen excreted as urine is highly variable depending on the type of animal feed amongst other parameters [Jarvis et al., 1989]. The excreted urine is directly added to the TAN pool (g N m^{-2}). This is consistent with urea as the dominant component of urine N and the subsequent rapid conversion to ammoniacal form [Bristow et al., 1992]. Faeces are composed of matter with varying carbon to nitrogen ratios that take different times to decompose depending on how easily they can be digested by microbes. Excreted faeces are assumed to form three different pools (g m^{-2}) depending on their rate of mineralization [e.g., Gusman and

Marino, 1999]**:** (1) we assume a fraction f_{un} =5 % is excreted as unavailable nitrogen ($N_{unavailable}$), the lignin component of manure where the nitrogen remains immobilized by bacteria (C:N ratio > 25:1), (2) a fraction f_r =45% goes to the resistant pool ($N_{resistant}$) which forms the cellulose component of manure (C:N ratio *c.* 15:1) which forms TAN relatively slowly; (3) and a fraction f_a =50% goes to the available pool ($N_{available}$) that is readily available to form TAN ($N_{available}$). In reality the fractions within each of these broadly defined pools will be dependent on the type of animal and the type of feed.

The equations governing the three manure pools (see Figure 1) are:

$$dN_{available}/dt = f_a \ x \ \alpha_{applied}(m) - K_a \cdot N_{available} - k_m \cdot N_{available} \quad (1)$$

$$dN_{resistant}/dt = f_r \ x \ \alpha_{applied}(m) - K_r \cdot N_{resistant} - k_m \cdot N_{resistant} \quad (2)$$

$$dN_{unavailable}/dt = f_{un} \ x \ \alpha_{applied}(m) - k_m \cdot N_{unavailable} \quad (3)$$

where $\alpha_{applied}(m)$ is the amount of manure applied (g m^{-2} s^{-1}); f_a, f_r and f_{un} are the fractions of manure applied to each pool; K_a and K_r (s^{-1}) are temperature dependent mineralization rates and k_m (s^{-1}) is the mechanical loss rate of nitrogen out of these manure pools and into soil nitrogen pools. The decay constants, K_a and K_r are measured as the fast and slow decomposition rates for biosolids added to various soils and incubated at 25^{o} C [Gilmour et al., 2003], where a two-component decay model accurately fit approximately 73% of the samples incubated. The decay timescales for manure are 48 days and 667 days at 25 °C. The temperature dependence of the decay constants is derived from a fit of temperature dependent mineralization rates (see appendix) [Vigil and Kissel, 1995] corresponding to a Q10 value of 3.66. To prevent the manure pools from building up over long-timescales we assume that manure is incorporated into soils with a time constant of 365 days with a mechanical rate constant

k_m. This timescale is consistent with the base bioturbation rate of 1 cm^2 $year^{-1}$ assumed in Koven et al. [2013] and a typical length scale of 1 cm. The sensitivity of the subsequent nitrogen pathways to this timescale is small (section 3.4). Note, that nitrogen in the $N_{unavailable}$ pool does not mineralize and is thus only incorporated into soil organic matter on the timescale determined by k_m. We assume nitrogen prior to conversion to TAN comprises a range of insoluble organic compounds that do not wash away or otherwise volatilize.

2.2.2 Synthetic fertilizer. Synthetic fertilizer nitrogen is added to the $N_{fertilizer}$ pool (g N m^{-2}) (Figure 1) at a rate ($\alpha_{applied}(t)(f)$) (g N m^{-2} s^{-1}) that depends on geography and time. The amount of nitrogen within the synthetic fertilizer pool is subsequently released into the TAN pool with the rate k_f (s^{-1}):

$$dN_{fertilizer}/dt = \alpha_{applied}(f) - k_f \cdot N_{fertilizer} \qquad (4)$$

Here we assume all synthetic fertilizer is urea. Urea is the most commonly used synthetic fertilizer accounting for over 50% of the global nitrogenous synthetic fertilizer usage [Gilbert et al., 2006]. Many other fertilizer types have significantly lower emission factors (see section 2, introduction) depending largely on changes in soil pH due to interactions between the soil and the fertilizer (Whitehead and Raistrick, 1990). We do not simulate this interaction here, but it should be accounted for in future model development. Thus the estimates here for fertilizer ammonia emissions may be considered as an upper estimate. We set the decay timescale of urea fertilizer to be 2.4 days consistent with the decay rate measured in Agehara and Warncke [2005] for temperatures from 15 to 20 °C. In a series of experiments Agehara and Warncke [2005] show that 75% of the urea hydrolyzes in a week at temperatures from 10 to 25 ^{o}C without a significant dependence on temperature especially for temperatures above 15 to 20 ^{o}C.

The timing for synthetic fertilizer application is determined internally within the CLM4.5-CN crop model as the spring planting date for corn. We use corn as the CLM4.5 crop model only specifically includes corn, soybean and temperate cereals and the planting date for corn lies between the earlier planting date for temperate cereal crops and the later planting of soy. The date for fertilizer application is determined for each grid point location using the surface temperature-based criteria developed by Levis et al. [2012] for simulating the planting date of corn: the ten-day running mean temperature, ten-day running mean daily minimum temperature and growing degree days must all surpass fixed threshold values (283.15K, 279.15K and 50 days, respectively) before planting can take place. We do not use the Levis et al. [2012] crop model in this study but use these criteria to determine a planting date for each grid point and assume synthetic fertilizer is applied on this date. Fertilizer application dates can have a large influence on the seasonality of the emissions (e.g., see Paulot et al., 2014) and the nitrogen loss pathways following fertilization (section 3.4). Future applications will assume more complete algorithms for fertilizing the spectrum of crops, as well as multiple fertilizer applications and double cropping. A global accounting of fertilization practices and application techniques (e.g., fertilizer injection) nevertheless remains a considerable source of uncertainty in global modeling of the ammonia emissions from agriculture.

2.2.3 Total Ammonical Nitrogen (TAN). We consider two TAN pools (g N m^{-2}), one for the nitrogen produced from synthetic fertilizer $N_{TAN}(f)$ the other for nitrogen from manure $N_{TAN}(m)$. The budget for the manure and synthetic fertilizer TAN pools respectively is given by:

$$N_{TAN}\ (m)/dt = f_u x\ \alpha_{applied}(\mathrm{m}) + K_r \cdot N_{resistant} + K_a \cdot N_{available}$$
$$-F_{run}(m) - K_D^{NH4} \cdot N_{TAN}(m) - F_{NH3}(m) - F_{NO3}(m) \quad (5)$$

$$N_{TAN}\ (f)/dt = k_f \cdot N_{\boldsymbol{fertilizer}}$$
$$-F_{run}(f)\ \ -K_D^{NH4} \cdot N_{TAN}(f) - F_{NH3}(f) - F_{NO3}(f) \quad (6)$$

Here $F_{run}(m/f)$ (g N m^{-2} s-^{1}) is the loss of nitrogen by runoff from the manure or synthetic fertilizer pool, K_D^{NH4} (s^{-1}) the loss rate of nitrogen to the soil nitrogen pools, $F_{NH3}(m)$ *and* $F_{NH3}(f)$ (g N m^{-2} s-^{1}) the NH_3 emissions from the TAN pool to the atmosphere from the soil manure and synthetic fertilizer pools, respectively, and $F_{NO3}(m)$ *and* $F_{NO3}(f)$ (g N m^{-2} s-^{1}) the loss of nitrogen through nitrification from the manure and synthetic fertilizer pools respectively. The formulation of each of these terms is given below. Inputs into $N_{TAN}\ (m)$ pool are from the fraction (f_u) of applied manure as urine ($\alpha_{applied}$(m)), and from the decomposition of the nitrogen within the available and resistant manure pools. Input into the $N_{TAN}\ (f)$ pool is through decomposition of nitrogen within the synthetic fertilizer pool.

2.2.4 Runoff of nitrogen to rivers. The immediate runoff of fertilizer and manure nitrogen to rivers is derived from the runoff rate of water (R) (m s^{-1}) in the CLM multiplied by concentration of nitrogen in the TAN water pool:

$$F_{run}(m/f) = R \cdot \frac{N_{TAN}(m/f)}{N_{water}(m/f)}. \quad (7)$$

The value of R is calculated within the CLM and is a function of precipitation, evaporation, drainage and soil saturation. The amount of water within the TAN pool ($N_{water}(m/f)$)(m) is needed to convert N_{TAN} (g N m^{-2}) to a concentration (g N m^{-3}). An expression for $N_{water}(m/f)$ is given in 2.2.9. It should be emphasized that this is the immediate runoff of manure and synthetic fertilizer nitrogen from the TAN pools. Subsequent loss of manure and synthetic fertilizer nitrogen from runoff and leaching occurs following the nitrogen transfer to the soil pools. Additional losses will also occur following after ammonia volatilization to the atmosphere followed by subsequent deposition.

Initially, we attempted to use the runoff parameterization based on the global Nutrient Export from Watersheds 2 (NEWS 2) Model [Mayorga et al., 2010] where runoff is also parameterized in terms of R. However, the amount of nitrogen that runs off in NEWS 2 is represented in terms of the annual nitrogen initially applied to the land and thus is not directly related to the amount of nitrogen in the TAN pool.

2.2.5 Diffusion through soil. Nitrogen is assumed to diffuse from the TAN pool to the soil pools. Génermont and Cellier [1997] represent the diffusion coefficient of ammonium through soils as dependent on soil water content, soil porosity, temperature and an empirical diffusion coefficient of ammonium in free water (see appendix). For example, assuming a temperature of 21° C, a soil porosity of 0.5 and a soil water content of 0.2 the resulting diffusion coefficient is approximately 0.03 cm^2 day^{-1}, in reasonable agreement with measurements in Canter et al. [1997]. Here we assume a typical length scale of 1.0 cm to convert the diffusion rate to a timescale. The resulting diffusion of ammonical nitrogen is added to pre-existing nitrogen pools in the CLM4.5.

2.2.6 Flux of Ammonia to the Atmosphere. The flux of NH_3 (F_{NH3}, g m^{-2} s^{-1}) to the atmosphere is calculated from difference between the NH_3 concentration at the surface ($NH_3(g)$, g m^{-3}) of the TAN pool and the free atmosphere NH_3 concentration ($NH_3(a)$, g m^{-3}) divided by the aerodynamic (R_a) and boundary layer (R_b) resistances (Equation 8) [Nemitz et al., 2000; Loubet et al., 2009, Sutton et al., 2013].

$$F_{NH3} = \frac{NH_3(g) - \chi_a}{R_a(z) + R_b} \qquad (8)$$

The calculation of $NH_3(g)$ is given below. For compatibility with the NH_3 emission model we compute average values of R_a and R_b for each CLM soil column, which may contain several PFTs. Continental NH_3 concentrations between 0.1 and 10 μg m^{-3} have been reported by Zbieranowski and Aherne [2012] and Heald et al. [2012]. A background atmospheric NH_3 concentration (χ_a = 0.3 μg m^{-3} in Equation 8) is specified, representative of a low activity agricultural site [Zbieranowski and Aherne, 2012]. This concentration is intermediate between the mean surface concentrations of low to moderate pollution sites as diagnosed in GEOS-chem (Warner et al., 2015). The sensitivity to this parameter is small as $NH_3(g)$ is usually very large (section 3.4). While equation (8) allows for negative emissions ($NH_3(g) < \chi_a$) or deposition of atmospheric

NH_3 onto the soil we currently disallow negative emissions in the current simulations. In future studies the atmospheric concentration of NH_3 will be calculated interactively when the NH_3 emission model is coupled with CAM-chem allowing the dynamics of the NH_3 exchange between the soil, the atmosphere and vegetation to be captured [e.g., Sutton et al., 2013].

A large fraction of the NH_3 emitted to the atmosphere is assumed captured by vegetation. The amount emitted to the atmosphere is given by:

$$F_{NH3_{atm}}(m/f) = (1 - f_{capture})\times F_{NH3}(m/f) \quad (9)$$

where $f_{capture}$ is set to 0.6, where this accounts for the capture of the emitted ammonia by plants. Plant recapture of emitted ammonia is non-negligible. This is often reported to be as high as 75 % (Harper et al., 2000; Nemitz et al., 2000; Walker et al. 2006; Denmead et al., 2008; Bash et al., 2010). Using seabird nitrogen on different substrates (rock, sand, soil and vegetation) inside a chamber Riddick (2012) found ammonia recapture to be 0% on rock, 32% on sand, 59% on soil and 73% on vegetation 73%. We chose a value of 60% as it was in-line with the findings of Wilson et al. (2004) and is mid-way between the value for soil (when the crops are planted) to when they are fully grown. Bouwman et al (1997) also used canopy capture to estimate emissions with the captured fraction ranging from 0.8 in tropical rain forests to 0.5 in other forests to 0.2 for all other vegetation types including grasslands and shrubs. Bouwman et al. (1997) omitted canopy capture over arable lands and intensively used grasslands. Overall, the deposition of NH3 onto the canopy (or even the soil surface) is poorly constrained (e.g., see Erisman and Draaijers, 1995) and often ignored in model simulations. In reality canopy capture is not constant but depends on surface characteristics and boundary layer meteorology. Variations in canopy capture will induce temporal and regional variations in ammonia emissions. Explicitly including the canopy capture fraction allows us to explicitly differentiate between different biogeochemical pathways. In the future when the model is fully coupled with the atmospheric ammonia cycle acompensation point approach would be desirable, but we feel it is outside the scope of the present study.

It is assumed that the nitrogen in the TAN pool is in equilibrium between *$NH_3(g)$* (g m^{-3}), *$NH_3(aq)$* (g N m^{-3}) and *$NH_4^+(aq)$* (g N m^{-3}). The equilibrium that governs the speciation of these species is determined by the Henry's Law coefficient (K_H), where K_H is a measure of the solubility of NH_3 in water, and the disassociation constant of NH_4^+ in water (K_{NH4}) (moles l^{-1}) [e.g., Sutton et al., 1994]

$$NH_3(g) + H_2O \overset{K_H}{\leftrightarrow} NH_3(aq) \tag{10}$$

$$NH_4^+(aq) \quad \xleftrightarrow{K_{NH4}} NH_3(aq) + \ H^+ \tag{11}$$

Combining these two expressions $NH_3(g)$ can be expressed as a function of the total TAN (e.g., Pinder et al. [2004], although note their different units for K_H and K_{NH4})

$$NH_3(g)(m/f) = \ \frac{N_{TAN}\,(m/f)/\,N_{water}(m/f)}{1+K_H+\,K_H[H^+]/K_{NH4}} \qquad (11)$$

where $[H^+]$ is the hydrogen ion concentration in moles/liter. Both K_H and K_{NH4} are temperature dependent. As temperature and pH increase the concentration of $NH_3(g)$ increases. The pH of the solution depends on the type of soil, the exposure of the manure to air and may change with the aging of the manure or synthetic fertilizer TAN pool. In Eghball et al. [2000] the majority of the reported measurements of pH for beef cattle feedlot manure are between 7 and 8, although in one case a pH of 8.8 was measured. The recommended pH for various crops ranges from approximately 5.8 to 7.0 depending on the crop (e.g., http://onondaga.cce.cornell.edu/resources/soil-ph-for-field-crops). For now we simply set the pH of the solution to 7 for both the synthetic fertilizer and manure TAN pools. Sensitivity to pH is explored in section 3.4.

2.2.7 Conversion of TAN to NO_3^-. The flux from the TAN pool to NO_3^- by nitrification (N_{NO3-}, g m^{-2} s^{-1}) was adapted from that derived by Stange & Neue [2009] to describe the gross nitrification rates in response to fertilization of a surface with manure or synthetic fertilizer. In particular Stange & Neue [2009] fit measured gross nitrification rates to an expression using a maximal nitrification rate r_{max}, μg N kg^{-1} h^{-1}) modified by a soil temperature response function (*f(T)*) and a soil moisture response function (*f(M)*) [Stange and Neue, 2009] (see appendix). However, since r_{max} is fit from their experimental data the dependence of the nitrification rate on the ammonium concentration is not explicitly included in the formulation of Stange & Neue [2009]. We have remedied this by setting the maximum nitrification rate (r_{max}) in the formulation of [Stange and Neue, 2009] to $1.16\ 10^{-6}$ s^{-1} consistent with the formulation in Parton et al. [2001]:

$$F_{NO3}(m/f) = \frac{2.\, r_{max} N_{water}(m/f) NH_3(g)(m/f) K_H [H^+]/K_{NH4}}{\frac{1}{f(T)} + \frac{1}{f(M)}} \qquad (12)$$

where f(T) and f(M) are functions of soil temperature and moisture and the ammonium concentration is assumed to be in equilibrium with the other forms of ammoniacal nitrogen and is thus expressed in terms of pH, K_H and K_{NH4} and $N_{TAN}\ (m/f)$.

2.2.8 Nitrate. The rate of change of the nitrate pool is given by:

$$dN_{NO3}(m/f)/dt = F_{NO3}(m/f) - K_D^{NO3} N_{NO3}(m/f) \quad (13)$$

The source of nitrate ions is nitrification from the TAN pool (see Eq. 13). Nitrate is lost to the soil nitrate pool through diffusion. Nitrate leaching is not explicitly taken into account in the current model as the diffusion of nitrate into the soil pools occurs very rapidly. The loss of nitrate through runoff and leaching can, however, occur within the CLM. NO_3^- ions diffuse significantly faster than the NH_4^+ ions because they are not subject to immobilization by negatively charged soil particles [Mitsch and Gosselink, 2007]. Diffusion rates used in this study are derived from the same formulation as assumed for the diffusion of ammonium [e.g., see Jury et al., 1983] with a different base diffusion rate. The summary of measurements given in Canter et al. [1997], where both the diffusion of ammonium and nitrate were measured in the same soil types and wetness suggest the base diffusion rate of NO_3^- is 13 times faster than that of ammonium.

2.2.9 TAN and Manure Water pools. The evolution of the TAN manure and synthetic fertilizer water pools depends on the water added during manure or synthetic fertilizer application and the subsequent evolution of the water in the pools. The equations for the manure and synthetic fertilizer water are:

$$dN_{water}(m)/dt = s_w(m) \times \alpha_{applied}(m) - k_{relax} \times (N_{water}(m) - M_{water}) \quad (12)$$

$$dN_{water}(f)/dt = S_w(f) \times \alpha_{applied}(f) - k_{relax} \times (N_{water}(f) - M_{water}) \quad (13)$$

These equations include a source of water ($s_w(m)$ or $S_w(f)$) added as a fraction of the synthetic fertilizer or manure applied and a relaxation term (k_{relax}, s^{-1}) to the soil water (M_{water}, m) calculated in the CLM for the top 5 cm of soil. The value for M_{water} explicitly takes into account the modification of the water pool due to rainfall, evaporation and the diffusion of water into deeper soil layers. We assume the TAN pool equilibrates with water within the top 5 cm of the soil with a rate of 3 days^{-1}. The solution is insensitive to this parameter within the ranges examined of 1 to 10 days^{-1} (section 3.5). The water content of manure applied to fields depends on the animal, its feedstock and on agricultural practices. Here we assume cattle manure is added as a slurry with a dry fraction of 74.23 g kg^{-1} and a nitrogen content of 1.63 g kg^{-1}, resulting in 5.67 10^{-4} m water applied per gram of manure nitrogen applied [Sommer and Hutchings, 2001]. In the case of synthetic fertilizer we assume urea is added as a liquid spread, where water added is calculated from the temperature dependent solubility of urea in water [UNIDO and FIDC, 1998].

2.3 Model spin up and forcing

Two different type of model simulations were conducted using the CLM4.5: a present day control simulation (1990-2004) and a simulation (1850-2000). The resolution used in these simulations is: 1.9 degrees latitude by 2.5 degrees longitude.

2.3.1 Present day control simulation. This simulation uses the manure and synthetic fertilizer input as given in Potter et al. [2010]. Forcing at the atmospheric boundary is set to the Qian et al. [2006] reanalysis for solar input, precipitation, temperature, wind and specific humidity. The simulation is run for fifteen model years (1990-2004) with the last ten years of the simulation used for analysis. The spinup period allows for the more decomposition resistant N pools to approach a steady state with respect to the loss from mechanical incorporation into the soil.

2.3.2 Historical simulation. The historical simulation uses transient forcing conditions (accounting for changes in atmospheric CO_2, nitrogen deposition, aerosol deposition and land use change forcings) and the Qian et al. [2006] atmospheric forcing dataset. Quality meteorological 6-hourly meteorological datasets for the period prior to 1948 do not exist. Therefore from 1850 to 1973 the CLM4.5 is driven by recycled meteorological data, using meteorological data from the 1948-1973 time period. During this time there is little increase in temperature: the statistically significant changes in temperature (outside of natural variability) occur after 1973. After 1973 the meteorological data is not recycled but is valid for the year applied.

The temporal distribution of manure and synthetic fertilizer application from 1850-2000 is specified by applying the temporal distribution of Holland et al. [2005] to the base values as calculated in Potter et al. [2010]. For lack of detailed information on the geography of historical manure and synthetic fertilizer we use the scaled spatial distribution from Potter et al. [2010]. We assume manure production has changed from

26.3 Tg N yr^{-1} in 1860 to 138.4 Tg N yr^{-1} in 2000 [Holland et al., 2005; Potter et al., 2010], but acknowledge these temporal changes are uncertain Synthetic fertilizer was first used in the 1920s with use increasing to 86 Tg N yr^{-1} in 2000.

3. Results

3.1 Model evaluation

To evaluate model output, measurements of the percentage of applied nitrogen that was emitted as NH_3 (P_v) from literature were compared against corresponding model predictions. The model predictions are obtained from the present day control simulation. The percent-volatilized ammonia was used as a metric because it can be compared across time irrespective of the absolute amount of nitrogen applied to the surface. To be able to compare emissions to published measurements we require field studies with published data on: nitrogen excretion rates, NH_3 emissions, ground temperature, location, and date of measurement. Given all of these requirements we found that only a small selection of publications had enough data.

For the manure emissions, 35 measurements in a range of climates (temperatures from 1.4 °C to 28 °C) and a range of livestock management methods (commercial beef cattle feedyard, dairy cow grazing on ryegrass, beef cattle grazing on ryegrass and dairy cattle grazing on pasture land) were used (Supplementary Table 1). Each P_v reported by the measurement campaign was compared against the P_v at the corresponding grid cell in the model. For the synthetic fertilizer scenario, 10 measurements in a range of latitudes (43 °S to 50 °N) over a range of land use surfaces (pasture, sown crops, turf and forest) were used (Supplementary Table 2). Each total annual P_v reported by the measurement campaign was compared against the annual P_v of the corresponding grid cell.

3.1.1 Nitrogen volatilized as NH_3 from manure. There is a general increase in the percentage of applied manure lost as NH_3 (P_v) with temperature, in both the model and measurements (Figure 2). However, temperature is not the only factor in determining NH_3 emissions where wind speed, water availability and below ground soil properties can also effect NH_3 emission. This is particularly demonstrated by the measurements of Todd et al. [2007] at temperatures less than 5^{o} C where the measured emissions are higher than those predicted at higher temperatures [e.g., Bussink, 1992]. It is also worth noting that the model predicts the emissions of Todd et al [2007] at lower temperatures with relative success.

The agreement between measured and modeled P_v from manure appears reasonable, with an R^2 of 0.78 that is significant at the 99.9% confidence level (p-value - 1.87×10^{-16}). On closer inspection, the model appears to agree best with measurements made on grassland and differs considerably with measurements made by both campaigns for beef cattle feedlots in Texas, where beef cattle feedlots are commercial operations to prepare livestock for slaughter and comprise of thousands of animals contained in a pen [US EPA, 2010]. This is perhaps not surprising, as the parameterization developed here explicitly represents emissions from manure spreading and likely does not represent the more managed conditions in feedlots.

3.1.2 Nitrogen volatilized as NH_3 from synthetic fertilizer. The comparison between measured and modeled annual average P_v from synthetic fertilizer applied to a range of land use types appears weak with an R^2 of 0.2 that is significant at the 90% confidence level (p-value - 0.15) (Figure 3). The lowest emissions in the model and measurements tend to be associated with the higher latitudes of both hemispheres. There does not appear to be any noticeable bias with land use type where the model estimates are both higher and lower than measured values of P_v for surfaces covered in turf, pasture land and crops. The fact that the R^2 for the synthetic fertilizer measurements is lower than the R^2 of the manure measurements is potentially caused by the single application date applied in the model, where actual farming practices may differ from model assumptions.

3.1.3 Nitrogen run-off. Nevison et al. [2016] routes the nitrogen runoff from manure and synthetic fertilizer pools using the River Transport Model (RTM) [Dai and Trenberth, 2001; Branstetter and Erickson, 2003] within the CESM. Nevison et al. [2016] assumes denitrification occurs within the simulated rivers at a rate inversely proportional to the river depth (amounting to approximately 30% of the nitrogen inputs on average) and compares the simulated nitrogen export at the river mouths against the measured nitrogen export [Van Drecht et al., 2003] partitioned into the proportion that is DIN (Dissolved Inorganic Nitrogen) following Global NEWS [Mayorga et al., 2010]. The simulated nitrogen export is nearly unbiased for six identified rivers with high human impact: the Columbia, Danube, Mississippi, Rhine, Saint Lawrence and Uruguay. Explicit comparisons against the Mississippi River show that the amplitude and seasonality of the simulated N_r runoff is in reasonable agreement with the measurements. While the comparison in Nevison et al. [2016] gives confidence the runoff is reasonably simulated, the complications in simulating river runoff preclude tight model constraints.

3.2 Global Nitrogen Pathways: Present Day

3.2.1 Geography of Nitrogen Inputs. Global maps of nitrogen input from synthetic fertilizer and manure application during the present-day simulation are given in Potter et al. [2010] and are not repeated here. Heavy synthetic fertilizer use generally occurs in the upper Midwest of the U.S. (mostly east of 100^o W and north of 40^o N), Western Europe (mostly west of 20^o E and north of 40^o N), the Northern part of India and much of Northeastern and North Central China. High manure usage coincides with the areas of heavy synthetic fertilizer use but is more widespread extending across much of Eastern South America from 20-40^o S and across Africa at approximately 10^o N.

3.2.2 Geography of Nitrogen Losses. There are strong geographical differences in the loss pathways of nitrogen following manure or synthetic fertilizer application. The importance of the various loss pathways from the TAN pool (the amount nitrogen volatilized as NH_3, runoff, nitrified or diffused directly into the soil, Figures 4-8) is dependent on temperature, precipitation and soil moisture. In hot, arid climates, the percentage volatilized is high (Figures 4 and 5). For example, regions of high NH_3 volatilization of applied manure N_r approach 50% across the southwest U.S. and Mexico, Eastern South America, central and southern Africa, parts of Australia, and across southern Asia from India to Turkey (Figure 5). The absolute highest emissions of NH_3 from applied synthetic fertilizer and from applied manure approach 20 kg N ha^{-1} yr^{-1} over hot regions with high applications, e.g. the Indian peninsula and parts of China (Figure 4 and 5). Ammonia emissions from manure are more broadly distributed globally than those of synthetic fertilizer with high NH_3 emissions not only over the synthetic fertilizer hotspots, characterized by heavy application of both synthetic fertilizer and manure, but also over southeastern South America and central Africa. For the most part, the largest synthetic fertilizer NH_3 emissions occur during April-June reflecting the single fertilization used in this study as calculated in the CLM for corn. While Paulot et al. [2014] also show the maximum synthetic fertilizer emissions generally occur from April-June they obtain relatively higher emissions than simulated here during the other seasons. This is likely due to differences in the assumed timing of applied synthetic fertilizer: Paulot et al. [2014] consider three different synthetic fertilizer applications for each crop as well as a wide variety of crops. The seasonal emission distribution of NH_3 emissions from manure is broader than that of synthetic fertilizer but with maximum emissions usually occurring in April-June or July-Sept. The simulated geographical and seasonal NH_3 emission distribution from manure is in broad agreement with Paulot et al. [2014].

Runoff of N_r from applied synthetic fertilizer and manure TAN pools as well as nitrification and diffusion into the soil depend on precipitation and soil moisture (see appendix). High manure and synthetic fertilizer N_r run off from the TAN pools (see Figure 6-7) occur particularly across parts of China, Europe (particularly the Northern parts) and the East central U.S. The global hotspot for simulated N_r runoff from the TAN pools is China where runoff approaches 20 kg N ha^{-1} yr^{-1} for nitrogen applied as either in manure and synthetic fertilizer. However, we do find other regions where the nitrogen input is high but where simulated N_r runoff from the TAN pools is relatively low, for example over India and Spain. In these regions with their high temperatures (and dry conditions) the NH_3 volatilization is the preferred pathway for nitrogen losses from the TAN pool. In general the importance of runoff as a nitrogen loss pathway becomes more important in the wetter and cooler regions. The same holds true for the percent of the TAN pool nitrified or diffused directly into the soil (see Figs 7 and 8). The amount of nitrogen nitrified has an optimal temperature of 28^o C and tends to occur more rapidly under moist conditions; the diffusion of nitrogen into the soil is also promoted under wet conditions (see appendix).

3.2.3 Regional and Global accounting of nitrogen losses. As nitrogen cascades through the environment it can be emitted as ammonia or runoff or leached at many different stages. Here we only examine the losses directly from manure or fertilizer application. Globally, the direct loss of applied nitrogen to the atmosphere as NH_3 is similar for manure and synthetic fertilizer (17% for manure, 20% for synthetic fertilizer; see Figure 9). Our global estimates of manure and synthetic fertilizer volatilized as NH_3 are similar to Bouwman et al. [2002] and Beusen et al. [2008], although our estimate for synthetic fertilizer volatilization as NH_3 is somewhat high. Bouwman et al. [2002] estimates 19-29% of applied manure and 10-19% of applied synthetic fertilizer volatilizes as NH_3; Beusen et al. [2008] concludes 15-23% of applied manure is lost as NH_3 (including losses from housing and storage, grazing and spreading) and 10-18% of applied synthetic fertilizer is lost.

We calculate the global direct run-off from manure or fertilizer TAN pools as 8% for manure N_r and 9% for synthetic fertilizer. Bouwman et al [2013] find that 23% of deposited N_r (comprised of synthetic fertilizer, manure and atmospheric nitrogen deposition) runs off, higher than our estimate. However, our estimate only includes the direct runoff from the TAN pool; further loss of nitrogen due to runoff and leaching may also occur from the soil nitrogen pools or following N_r deposition downstream.

Our simulations assume a large fraction of emitted nitrogen is captured by the canopy, where canopy capture accounts for 25.5% of manure losses and 30% of synthetic fertilizer losses. The nitrogen captured by the canopy may have a number of fates. First, Sparks [2008] posits that since foliar nitrogen uptake is a direct addition of N to plant metabolism it could more readily influence plant growth than uptake from soils. As such it would decrease plant demand on soil uptake and thus conserve the soil nitrogen reservoirs. Secondly, nitrogen uptake by the plants, even if not directly used in plant metabolism, may redeposit onto the surface with litter fall. Finally, it may be emitted back to the atmosphere from plants. The latter process can be represented through a compensation point model between the atmosphere, the ground and stomata [e.g., Massad et al., 2010]. A full accounting of this requires the simulation to be l in a coupled mode with the atmosphere and is beyond the scope of the present study.

In the case of synthetic fertilizer the direct diffusion of TAN N_r into the soil pool (22%) is larger than nitrification (17%); for manure it is just the opposite: the nitrification (29%) is larger than the direct diffusion (14%) (Figure 9). In practice, as simulated here, this makes little difference as the diffusion of nitrate into the soil pool occurs very rapidly, an order of magnitude faster than the diffusion of nitrogen from the TAN pool. Thus NO_3^- is directly incorporated into the soil nitrate pool without any subsequent loss. Recall, also, a small percentage of manure is mechanically stirred into the soil organic nitrogen pools. Accounting for the N_r diffused from the TAN pool into the soil pools, and assuming the NH_3 emissions captured by the canopy, as well as the ammonium nitrified to NO_3^- also end up in the soil pools we find that globally 75% of TAN manure and 71% of TAN synthetic fertilizer ends up in the soil nitrogen or soil organic nitrogen pools. Of course, once in these soil pools there may be subsequent losses of nitrogen due to runoff and leaching or emissions, but these are not calculated in this initial study.

The percentages change appreciably when examined over subsets of countries (Figure 10). For example, over all developed countries the percentage of emissions of manure and synthetic fertilizer TAN as NH_3 [13%] is substantially smaller than for developing countries [21%]. These differences can be largely explained by the fact that developing countries tend to be located in warmer climates than developed countries. Bouwman [2002] took these differences into account when developing emission factors for developing and industrialized countries. Bouwman [2002] calculated NH_3 emission factors for manure of 21% and 26% for developed and industrialized countries, respectively and for synthetic fertilizer of 7% and 18%, respectively. The US and the European Union have N_r emission percentages of 16% and 9%, respectively and runoff percentages from the TAN pools of 9% and 14%, respectively, within a factor of two although nitrogen runoff is favored in the cooler moister climate of Europe. However, note the large contrast between India and China, where for India emissions are 27% of the applied N_r with very little runoff, whereas for China the runoff and emissions are approximately equal (13% and 10%, respectively).

3.2.4 Comparison to other emissions inventories. Figure 11 gives a comparison of manure and synthetic fertilizer NH_3 emissions from our process oriented model and various bottom-up emission inventories. The bottom-up inventories rely on emission factors depending on animal husbandry, types of synthetic fertilizer usage and other details of agricultural practices. Only the NH_3 emission inventory of Huang et al. [2012] for China and Paulot et al. [2014] explicitly account for temperature to modify their emission factors; the inventory of Paulot et al. [2014] also uses wind speed to modify the emission factors. The inventories of Paulot et al. [2014] for 2005-2008, Beusen et al. [2008] for 2000, and EDGAR v4.2 for 2005-2008 are global inventories. The EDGAR inventory does not strictly separate the ammonia emissions into those of manure and synthetic fertilizer so we simply show the overall ammonia emissions. Over the US we also give an estimate for 1995 for synthetic fertilizer NH_3 emissions [Goebes et al., 2003] and for NH_3 emissions from animal agricultural operations the US EPA [2006]. Over China the global NH_3 emission estimates are supplemented by Huang et al. [2012] for 2006 and Streets et al. [2003] for 2000. Over Europe results using the Greenhouse Gas and Air Pollution Interactions and Synergies [GAINS] model are given [Klimont and Brink, 2004] as reported in Paulot et al. [2014]. In this study synthetic fertilizer application dataset is valid circa 2000 and the manure application dataset is valid circa 2007 [Potter et al., 2010].

Globally all inventories give approximately the same overall NH_3 emissions of 30-35 Tg N yr^{-1}. The global apportionment of emissions between manure and synthetic fertilizer in this study in approximately the ratio of 2:1, roughly consistent with that of Paulot et al. [2014] and Beusen et al. [2008]. The apportionment of manure to synthetic fertilizer emissions in the EDGAR inventory (approximately in the ratio 1:3, respectively) is not consistent with the other three inventories presented. The European and Chinese NH_3 emissions estimated here are on the low side of the other inventories, while the U.S. emissions are on the high side. In Europe the current parameterization underestimates the manure emissions compared to the other estimates, while the synthetic fertilizer emissions fall between the Paulot et al. (2014) and GAINS emission inventories and that of EDGAR. In the U.S. the manure NH_3 emissions are close to the estimate of all the inventories except that of EDGAR while the synthetic fertilizer emissions are high compared to all inventories, although the synthetic fertilizer emissions are close to that of EDGAR. In China our synthetic fertilizer emissions are similar to those of Huang et al. [2012], but underestimate the manure NH_3 emissions of all the other inventories except EDGAR. Of the three regions examined all inventories suggest the Chinese emissions are highest. Note, however, there is considerable variation amongst the Chinese inventories for both synthetic fertilizer and manure. Our results appear to match those of Huang et al. [2012] the best.

3.2.5 Site specific simulated pathways. The hourly time series of the fate of applied nitrogen from manure and synthetic fertilizer at a single site better illustrates the relationship between the different pathways and the local meteorology (Fig. 12). This site shown near the Texas panhandle experiences several large rain events and surface temperatures ranging from 0 to 18 degrees Celsius over a period of about two months during the spring season. The response of the NH_3 emissions to the diurnal temperature range is clearly evident. The nitrogen losses of manure TAN due to NH_3 volatilization is initially small, on par with the diffusive loss and somewhat less than the loss due to nitrification. The loss by nitrification and diffusion from the TAN manure pool remain roughly constant through the period examined although both processes show some response to precipitation, particularly the diffusion which reaches a maximum near May 21 presumably due to the increased water content in the soil by the prior rain event. With the rise in temperatures towards the end of the period, the emission loss of manure TAN becomes the dominant loss pathway and the TAN manure pool decreases. Closer inspection suggests, however, that the large increase in the NH_3 emissions towards the end of the period cannot solely be attributed to temperature, but must also be attributed to decreased water in the TAN pool as the soil dries. The latter process increases the concentration of nitrogen species within the TAN pool. The TAN manure pool is punctuated by sharp decline events, associated with precipitation and increased runoff (Fig. 12c). Synthetic fertilizer TAN responds similarly during these events but the different temporal distribution of N application for synthetic fertilizer is clearly evident in these plots. The decrease in the synthetic fertilizer TAN pool occurs on a timescale of approximately a week, consistent with the timescale used in the MASAGE_NH3 model (Paulot et al., 2014).

3.3 Global Nitrogen Pathways: Historical

Historical nitrogen pathways are accessed since 1850 in a simulation with changing climate and changing application amounts. These simulations do not include changing agricultural practices including changes in animal housing and storage, changes in animal diet and explicit changes in landuse, all of which may substantially alter the nitrogen pathways. Thus the results must be treated with caution.

The nitrogen produced as manure increases in the historical simulation from 21 Tg N yr^{-1} in 1850 to 125 Tg N yr^{-1} in 2000 (Figure 13). In 1900 we estimate that 37 Tg N yr^{1} of manure is produced, similar to the Bouwman et al (2011) estimate of 35 Tg N yr^{-1}. Emissions of NH_3 from applied manure increase from approximately 3 Tg N yr^{-1} in 1850 (14.3% of the manure produced) to 22 Tg N yr^{-1} in 2000 (17.6% of the applied manure). On the other hand the percentage of manure nitrogen that is nitrified decreases from 33 to 27% since the preindustrial.

Synthetic fertilizer nitrogen application has increased dramatically since the 1960s with an estimated 62 Tg N yr^{-1} applied as synthetic fertilizer in 2000. We estimate the volatilization of synthetic fertilizer as ammonia is 12 Tg N yr^{-1} in 2000 (19.3% of that applied). The percent of synthetic fertilizer nitrogen volatized to the atmosphere as NH_3 in 1920 was 8%. On the other hand, the percentage of synthetic fertilizer that is lost through runoff decreased since the preindustrial by 8%. It is evident that these percentage changes can be explained by the fact the runoff of synthetic fertilizer acted to completely drain the TAN synthetic fertilizer pool in at the small synthetic fertilizer application rate prior to 1960.

In part the emission increases can also be explained by changes in climate. Climate has warmed by approximately 1^{o} C since the preindustrial. In a sensitivity experiment the temperature was artificially increased by 1^{o} C in the rate equations governing the nitrogen pathways from manure and synthetic fertilizer application. Under current manure and synthetic fertilizer application rates we find a global sensitivity of an additional 1 Tg NH3 emissions amounting to an increase in manure emissions of 4% and an increase in fertilizer emissions of 3%.

3.4 Sensitivity Tests

We have conducted a large number of sensitivity tests to evaluate the effect of changes in individual model parameters on NH_3 emissions. The various parameters may co-vary, of course, with non-linear impacts on the NH_3 emissions; however, we have not attempted to evaluate these effects. The sensitivity tests for manure are given in Table 1, those for synthetic fertilizer in Table 2. The sensitivities tests are labeled with a number denoting the sensitivity parameter perturbed and a letter denoting whether the test is with respect to manure emissions (m) or synthetic fertilizer emissions (f). In each case we give the percent change in NH_3 emissions due to the parameter change and the relative emission change with respect to the relative parameter change (the sensitivity). Rationale for the assumed parameter bounds is given in the supplement. Note that in the test of fertilizer sensitivity we varied the breakdown time of the fertilizer, but not its reaction with the soil column. Thus did not simulate the fertilizer induced pH changes in the soil column.

Except for changes in the canopy capture parameter (EX8m/f, EX9m/f) and changes in the timing or composition of manure or synthetic fertilizer inputs (EX18m, EX19f, EX20f, EX21f), changes in the sensitivity parameters directly change the nitrogen cycling within the TAN pool (as described below). For the most part the synthetic fertilizer and manure TAN pools respond similarly to the parameter changes. Note also, that except for EX18, where the amount of nitrogen input into the TAN pools is reduced, the total input and loss of nitrogen from the TAN pools remain the same for all sensitivity experiments. In general, the sensitivity of NH_3 emissions to the imposed parameter changes are within the range of $\pm20\%$ with many processes within the range of $\pm10\%$. The sensitivity to the mechanical mixing of manure (EX1m, EX2m), the adjustment timescale for the water pool (EX3, EX4), the diffusion rate into the soil (EX14, EX15), the assumed depth of the water pool (EX12, EX13) and the maximum nitrification rate (EX16, EX17) all impact NH_3 emissions by less than 20%. The sensitivity to the assumed background NH_3 concentration is also low (EX10, EX11). The high NH_3 concentration in equilibrium with the TAN pool renders the emissions rather insensitive to the background concentration.

The NH_3 emissions are most sensitive to changes in pH (EX5m/f, EX6m/f, EX7m/f). The ammonia emissions decrease by approximately 60% when the pH is increased from 7 to 8 and increase by 50 to 70% (for manure and synthetic fertilizer, respectively) when the pH is decreased from 7 to 6. We also tested the sensitivity to the spatially explicit pH from ISRIC-WISE dataset [Batjes, 2005], with a global pH average of 6.55. In contrast to assuming a constant pH of 7, the spatially explicit pH changed the manure ammonia emissions by 23% and the fertilizer ammonia emissions by 14%. Changes in pH also have a large impact on nitrification. Increased pH reduces $NH_4^+(aq)$ and thus the rate of conversion of $NH_4^+(aq)$ to NO_3^-. The effect of pH on the rate constant for nitrification is not included in the current parameterization. Parton et al. (2001) suggests this effect is small between a pH of 6 and 8, varying only on the order of 15%. Changes in pH also results in marked changes in the runoff and soil diffusion due to the large changes in emissions and nitrification: low pH's act to increase the flux of nitrogen through these loss pathways, high pH's act to decrease them.

Emissions are also highly sensitive to changes in canopy capture (i.e., the parameter *fcapture)* as shown in EX8m/f, EX9m/f. Decreasing the fraction captured by the canopy by a factor of 2 increases the emissions by approximately a factor of 3. Changes in this fraction modify the fixed ratio between the amount of nitrogen captured by the canopy and that emitted to the atmosphere, but do not impact nitrogen cycling within the TAN pools within the current modeling setup. Of course, further downstream than simulated here, the nitrogen captured in the canopy does impact the overall soil nitrogen budget.

The NH_3 emissions are somewhat sensitive to the depth of the water pool (EX12m/f, EX13m/f), where the water budget is calculated over depth of the water pool. Smaller depths give higher concentrations of all the constituents within the TAN pool resulting in larger NH_3 emissions (equations 7 and 11) and larger nitrogen runoff (section 2.4.1). Larger depths have the opposite effect. The diffusion of nitrogen into the soil is somewhat sensitive to changes in the assumed water depth as the coefficient of diffusion is proportional to the water content to the 10/3 power (see appendix). Increased diffusion at higher depths likely reflects changes in the water content of the soil with depth.

We conducted various sensitivities to synthetic fertilizer applications. Early synthetic fertilizer applications decrease NH_3 emissions due to their strong temperature dependence and increase the susceptibility of the TAN pool to washout. An early fertilization date (set to March 15) decreases the NH_3 emissions by 23% and increases the nitrogen run off from the TAN pool by 62% (EX19f). To investigate the sensitivity to the application rate of synthetic fertilizer, synthetic fertilizer was applied over 20 days as opposed to the single day application assumed in the default version (EX20f). This did not have a significant impact on the emissions. The assumed synthetic fertilizer type in the default version of the model (urea) was replaced with ammonium nitrate fertilizer in EX21f. Whereas urea is converted to NH_3 rather slowly, the conversion of ammonium nitrate is rapid (in the sensitivity test it is assumed to be instantaneously released into the TAN pool). However, the emissions are not particularly sensitive to this change. This is in contrast to differences in volatilization rates of different synthetic fertilizers given in Bouwman (2002). Whitehead and Raistrick (1990) show that one of the primary differences between the addition of urea versus ammonia nitrate as fertilizer is in the effect of the fertilizer on the soil pH, an effect that we do not consider in this first study. In particular urea increases the soil pH and thus the ammonia emissions.

Finally we test the impact of manure composition on the NH_3 emissions (EX18f). The composition of manure nitrogen excreted by animals depends in part on the digestibility of the feed, which can vary in both time and space. To investigate this uncertainty we varied the composition of the manure assumed in the default model version (50% urine, 25% available, 22.5 % resistant and 2.5% unavailable) to the less soluble N excreta from dairy cattle in sensitivity simulation EX18m (41% urine, 21% available, 25% unavailable and 13% resistant [Smith, 1973]). This decreased the NH_3 emissions by 21 percent demonstrating an important sensitivity to the composition of manure and urine.

It is important to emphasize that these sensitivity simulations only test the parameter sensitivity within the imposed model. In particular, the sensitivities to various farming practices are generally extraneous to the model assumptions with some exceptions. The sensitivities to synthetic fertilizer or manure input assumptions are tested in simulations EX18m, EX19f, EX20f, EX21f; sensitivities to the water depth which may crudely represent some of the impacts of plowing manure or synthetic fertilizer into the soil are examined in EX12 and EX13; finally modifications to soil pH are tested in EX5, EX6 and EX7.

4. Discussion and Conclusions

In this paper we develop a process-oriented model that predicts the climate dependent reactive nitrogen pathways from synthetic fertilizer and manure application to the surface of the land. Continued population growth will likely result in an increased application of synthetic fertilizers with concurrent increases in manure production in the future (Davidson, 2012). Climate is an important determinant in the ultimate fate of this applied nitrogen, important in determining the resulting emissions of NH_3 and other reactive nitrogen gases, in the runoff of the applied nitrogen, its nitrification and its incorporation into the soil organic and inorganic pools. The fate of the resultant applied nitrogen may act to acerbate climate change through the formation of N_2O, or perhaps mitigate climate change through increased carbon fertilization and the increased formation of aerosols. On the flip side the impact of a changing climate on agriculture and the resultant pathways for N_r is likely to be significant.

Agricultural NH_3 emissions are an unusual emission source in that both natural and anthropogenic processes control their emissions. Previous global NH_3 emission inventories have exclusively used bottom up emission factors mainly governed by agricultural practices. In many cases the emission factors only implicitly include temperature dependence by using different emission factors for industrial and developing countries [e.g., Bouwman et al. 1997], although recently some inventories have included empirical emission factors that vary with temperature [Paulot et al., 2014; Huang et al., 2012]. Here, however, we take the opposite tact by constructing a model where the N_r pathways and in particular the NH_3 emissions are explicitly driven by climate but where the explicit representation of most agricultural practices are minimized. We find the global emissions of NH_3 due to manure and fertilizer nitrogen sources are similar to other recent inventories, with 21 Tg N yr^{-1} emitted from manure nitrogen and 12 Tg N yr^{-1} emitted from fertilizer nitrogen. Strong regional differences in emissions captured by the bottom up inventories are also simulated. Moreover, we are able to simulate the inter-annual, seasonal and diurnal changes in NH_3 emissions critical for air pollution applications (De Meij et al., 2006). Most previous inventories have included no seasonal dependence of the emissions, although in some cases a seasonal dependence is empirically introduced. It is perhaps important to note that the impact of nitrogen emissions on the global carbon budget has generally made use of these previous inventories without explicit seasonal or diurnal dependence of NH_3 emissions and with a rather minimal representation of the geographic dependence.

The model developed here uses a process level approach to estimate nitrogen pathways from fertilizer and manure application. It is suitable for use within an Earth System model to estimate the resulting NH_3 emissions, nitrogen run-off, and the incorporation of the nitrogen into soil organic and inorganic matter. The modeled N_r pathways dynamically respond to climatic variation: (1) the breakdown timescale of manure and fertilizer into TAN depends on temperature; (2) the formation of NH_3 gas from the TAN pool is highly temperature sensitive with the rate of formation described by the temperature dependence of the thermodynamic Henry and dissociation equilibria for NH_3 [Nemitz et al., 2000]; (3) the rate of nitrification of NH_3 within the TAN pool, determined by the rate at which ammonium ions are oxidized by nitrifying bacteria to form nitrate ions [Abbasi and Adams, 1998] is controlled by environmental factors such as soil temperature and soil moisture; (4) the runoff of N_r is determined by the precipitation. Predictions for direct nitrogen runoff from fertilizer and manure nitrogen pools and the incorporation of nitrogen into soil pools from applied fertilizer and manure nitrogen are some of the first made by a global process-level model. Measurements of nitrogen runoff from rivers heavily impacted by anthropogenic nitrogen input compare favorably with simulated results using the River Transport Model within the CESM [Nevison et al., 2016].

Manure is not a new nitrogen source, but contains recycled N_r from soil nitrogen produced when animals eat plants. Therefore to conserve nitrogen within an earth system model, the application of manure determines the consumption of plant matter byanimals . Specifically, the model calculates the amount of nitrogen and carbon needed for a given manure application and subtracts it from the plant leaf pools within the CLM. The manure production acts to speed up the decay and processing of plant biomass, releasing different N_r products to the atmosphere than natural decay [Davidson, 2009].

The climate dependency incorporated into the model suggests that the pathways of nitrogen added to the land are highly spatially and temporally heterogeneous. An examination of nitrogen loss pathways at a point over Texas shows the variation of the nitrogen pathways on a variety of timescales with changes in temperature, precipitation and soil moisture. Spatially, values for the percentage of manure nitrogen volatilized to NH_3 in this study show a large range in both developing countries (average of 20% (maximum: 36 %)) and industrialized countries (average of 12% (maximum: 39 %)). The model also predicts spatial and temporal variability in the amount of NH_3 volatilized as manure from agricultural fertilizers ranging from 14% [maximum 40 %] in industrialized countries to 22 % [maximum 40 %] in developing countries. As a result of temperature dependency, NH_3 volatilization is highest in the tropics with largest emissions in India and China where application of fertilizer and manure is high. In comparison, the EDGAR database uses the emission factors based on Bouwman et al. (2002), where 21 % and 26 % of manure is converted into NH_3 in industrialized and developing countries, respectively. The respective emission factors for fertilizer application are 7 % in industrialized countries and 18 % in developing countries. Nitrogen run-off from the manure and synthetic fertilizer TAN pools is highest in areas of high Nr application and high rainfall, such as China, North America and Europe. Despite high nitrogen input rates we simulate low nitrogen runoff in India and Spain, for example. We also simulate climate dependent pathways for the diffusion of N_r into the soil inorganic nitrogen pools and the nitrification of ammonium to nitrate.

Historically we predict emissions of NH_3 from applied manure to have increased from approximately 3 Tg N yr^{-1} in 1850 to 22 Tg N yr^{-1} in 2000 while the volatilization of fertilizer reaches 12 Tg N yr^{-1} in 2000. The NH_3 emissions increase by approximately 4% for manure applications and 5% for fertilizer applications over this historical period (1930 to 2000 for fertilizer). However similar increases are not evident in the runoff of nitrogen. Note, however, we do not include runoff and leaching from the mineral nitrogen pools within the CLM in these calculations. The latter may be impacted by plant nitrogen demand such that excess fertilization would act to increase the nitrogen runoff.

The NH_3 emissions appear reasonable when compared to other inventories on the global scale, but also when compared to the local scale measurements of manure and synthetic fertilizer (Figure 2 and 3), although these latter comparisons highlight the difficulty in making global scale assumptions about surface parameters and farming methodology. The biggest disagreement with the manure emission measurements is from beef cattle feedlots in Texas. On the whole the model performs best when estimating NH_3 manure emissions from cows on grassland. Despite the issues described above, this model gives reasonable NH_3 emission predictions given the limited global information available on the grazing land of agricultural animals.

The model described here is capable of predicting global to regional impacts of climate on applied synthetic fertilizer and manure nitrogen. However, given the nature of global modeling described here and simplifying modeling assumptions there are numerous sources of error associated with our model predictions. Parameter sensitivity studies show the largest sensitivity to the assumed pH, consistent with other studies [e.g., Fletcher et al., 2013], and to the canopy deposition. The actual pH likely depends on a complex interaction of soil types, and agricultural and animal husbandry practices. Canopy capture depends on bidirectional exchange models that involve resistances between the plant canopy, the ground and ground emissions [see, e.g., Massad et al., 2010]. In the future these processes will be simulated when the CLM is coupled with a chemistry model, although the conservation of nitrogen in a biogeochemical context may present peculiar challenges. More accurate specification of the NH_3 emissions can be made within an Earth System model by better accounting of synthetic fertilizer and manure application within specific PFTs or explicit incorporation into an agricultural model.

The approach taken here has been rather different from an approach using emission factors to model NH_3 emissions. Perhaps, then, the greatest source of uncertainty in this study is associated with simplifying farming methods. This model uses a single date for synthetic fertilizer application, considers only urea fertilizer, and does not take into account manure storage methods, such as slurry pools or different types of animal manures. It also assumes a fixed depth of manure and synthetic fertilizer application. The use of simplified farming practices may be acceptable in many locations as more complex farming methods are rarely employed in the developing world. The Food and Agriculture Organization [FAO, 2005] suggests over 75 % of the global agricultural land uses traditional farming methods. Still, adapting a hybrid approach as outlined in Sutton et al. [2013] using both emission factors governing animal stockyards and the approach outlined here for manure applied to fields may be the most reasonable. The depth of synthetic fertilizer and manure mixing and a more exact representation of soil water through the vertical discretization of the soil nitrogen pools would also help account for additional agricultural practices.

The increased use of synthetic fertilizer and growing livestock populations has increased N_r emission to both the atmosphere and oceans to unprecedented levels with a marked effect on the environment. We have provided a first estimate of globally distributed temporal changes in nitrogen pathways from manure and synthetic fertilizer inputs in response to climate. This is relevant to current studies investigating the ecosystem effects of N_r, and in particular, how adding synthetic fertilizer to farmland affects the ocean, the atmosphere and impacts climate. The model predicts vastly different nitrogen pathways depending on the region the inputs are applied. Scenarios predicting future synthetic fertilizer use and livestock populations suggest large increases in nitrogen added to the land surface from both sources [Tilman et al., 2001; Skjoth and Geels, 2013]. The climate dependence of the nitrogen pathways suggests these pathways will be sensitive to climate change. The interaction of these changes with climate is not yet clear. The volatilization of NH_3 increases exponentially with temperature suggesting future increases are likely. However, increases in temperature may surpass the optimal temperature at which certain biological processes occur, slowing the process. Washout pathways are also likely to change, not only with climate, but with increases in nitrogen loading. Future applications of this model will investigate the tight coupling between nitrogen, agriculture and climate.

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Appendix A. Description of Model Variables and Equations.

Description	Symbol	Unit	Value Used or Equation	Reference
Prognostic Variables				
Pool of nitrogen from applied manure that easily forms TAN	$N_{available}$	g m^{-2}	$dN_{available}/dt =$ $f_a\ x\ \alpha_{applied}(m)$ $-K\_a \cdot N_{available} - k\_m \cdot N_{available}$	
Pool of nitrogen from applied manure that is resistant to forming TAN	$N_{resistant}$	g m^{-2}	$dN_{resistant}/dt =$ $f_r\ x\ \alpha_{applied}(m) - K\_r \cdot N_{resistant} - k\_m$ $\cdot N_{resistant}$	
Pool of nitrogen from applied manure that does not form TAN	$N_{unavailable}$	g m^{-2}	$dN_{unavailable}/dt =$ $f_{un}\ x\ \alpha_{applied}(m) - k\_m \cdot N_{unavailable}$	

Pool of nitrogen from applied fertilizer	$N_{fertilizer}$	g m^{-2}	$dN_{fertilizer}/dt =$ $\alpha_{applied}(f)$ $-k\_f \cdot N_{fertilizer}$	
Pool of nitrogen in TAN pool from manure	$N_{TAN\ (m)}$	g m^{-2}	$N_{TAN}\ (m)/dt =$ $f_u x\ \alpha_{applied}$(m) $+ K\_r \cdot N_{resistant}$ $+K\_a \cdot N_{available}$ $-K\_w \cdot N_{TAN}(m)$ $-K_D^{NH4} \cdot N_{TAN}(m)$ $-\ F_{NH3}\ (m)$ $-\ F_{NO3}(m)$	

Pool of nitrogen in TAN pool from fertilizer	$N_{TAN\ (f)}$	g m^{-2}	$N_{TAN}\ (f)/dt =$ $+ k\_f \cdot N_{fertilizer}$ $-K\_w \cdot N_{TAN}(f)$ $-K_D^{NH4} \cdot N_{TAN}(f)$ $- F_{NH3}(f)$ $- F_{NO3}(f)$	
Pool of surface NO_3^-	N_{NO3}	g m^{-2}	$dN_{NO3}\ /dt =$ $F_{NO3}(m/f) - K_D^{NO3} \cdot N_{NO3}$	
Pool of manure/fertil-izer water in TAN pool	$N_{water}\ (m)$	m	$dN_{water}\ (m)/dt =$ $s_w(m) \times \alpha_{applied}(m))$ $-k_{relax} \times (N_{water}(m) - M_{water})$	

Pool of manure/ fertilizer water in TAN pool	$N_{water}\ (f)$	m	$dN_{water}\ (f)/dt =$ $S_w(f)\times\alpha_{applied}(f))$ $-k_{relax}\times(N_{water}(f)-M_{water})$	
Variables from CLM				
Ground Temperature	T_g	^oK	Taken from model	
Run-off	R	m s^{-1}	Taken from model	
Aerodynamic resistance	R_a	s m^{-1}	Taken from model	
Boundary Layer resistance	R_b	s m^{-1}	Taken from model	
Water in soil	M	m	Taken from the model (top 5 cm of soil)	

Diagnostic Variables				
Available manure decomposition	K_a	s^{-1}	$K\_a = k_{a1}\, T_R(T_g)$	[Gilmour et al., 2003; Vigil & Kissel, 1995]
Resistant manure decomposition	K_r	s^{-1}	$K\_r = k_{a2}\, T_R(T_g)$	[Gilmour et al., 2003; Vigil & Kissel, 1995]
Temperature dependence for K_a, K_r	T_R	N/A	$T_R(T_g) = t_{r1} \exp\left(t_{r2}\,(T_g - 273.)\right)$	[Vigil & Kissel, 1995]
Surface runoff flux	$F_{run}(m/f)$	g $m^{-2}s^{-1}$	$F_{run}(m/f) = R \cdot \frac{N_{TAN}(m/f)}{N_{water}(m/f)}$	
NH_4^+ loss rate to soil pool	K_D^{NH4}	s^{-1}	$K_D^{NH4} = (1/l^2) \cdot (\Theta_w^{10/3}/\varphi^2)\varkappa_{NH4}^{aq}$	[Génermont and Cellier, 1997]
NO_3^- loss rate to soil pool	K_D^{NO3}	s^{-1}	$K_D^{NO3} = (1/l^2) \cdot (\Theta_w^{10/3}/\varphi^2)\varkappa_{NO3}^{aq}$	[Génermont and Cellier, 1997]

Base vertical diffusion for TAN pool	$\varkappa_{NH4}^{aq}$	m^2s^{-1}	$\varkappa_{NH4}^{aq} = 9.8\ 10^{-10} \cdot 1.03^{(T_g - 273.15)}$	[Génermont and Cellier, 1997]
Base vertical diffusion for NO3 pool	$\varkappa_{NO3}^{aq}$	m^2s^{-1}	$\varkappa_{NO3}^{aq} = 1.3\ 10^{-8} \cdot 1.03^{(T_g - 273.15)}$	[Génermont and Cellier, 1997]
Water Content	Θ_w		$\Theta_{w} = N_{water}(m/f)/\mathcal{H}$	
Flux of nitrogen lost as NH_3 for manure(m) or fertilizer(f)	$F_{NH3}(m/f)$	g m^{-2} s^{-1}	$F_{NH3}(m/f) = \dfrac{NH_3(g)(m/f) - \chi_a}{(R_a(z) + R_b)}$	[Nemitz et al., 2000; Loubet et al., 2009; Sutton et al., 2013]]
Flux of NH3 to atmosphere	$F_{NH3_{atm}}$ (m/f)	g m^{-2} s^{-1}	$F_{NH3_{atm}}(m/f) = (1 - f_{capture}) \times F_{NH3}(m/f)$	[e.g., Wilson et al., 2004]

NH3(g) in equilibrium with the TAN manure (m) or fertilizer (f) pool	$NH_3\ (g)$ (m/f)	g m^{-3}	$NH_3\ (g)(m/f) = \dfrac{N_{TAN}\ (m/f)/\ N_{water}(m/f)}{1 + K_H +\ K_H[H^+]/K_{NH4}}$	Derived from [Sutton et al., 1994]
Henry's Law Constant for NH_3	K_H		$K_H\ = 4.59\ (\ {}^{o}K^{-1}) \cdot T_g \cdot exp^{4092(1/T_g - 1/T_{ref})}$	[Sutton et al., 1994]
Dissociation Equilibrium Constant for NH_3 (aq)	K_{NH4}	mol l^{-1}	$K_{NH4}\ = 5.67\ 10^{-10} exp^{-6286(1/T_g - 1/T_{ref})}$	[Sutton et al., 1994]
Flux of nitrogen from TAN to NO_3^- pool	$F_{NO3}(m/f)$	g m^{-2} s^{-1}	$F_{NO3}(m/f) = \dfrac{2.\ r_{max} N_{water}(m/f) x NH_3\ (g)(m/f) K_H[H^+]/K_{NH4}}{\frac{1}{\Sigma(T_g)} + \frac{1}{\Pi(M)}}$	[Stange and Neue, 2009, Parton et al., 2001]

Soil temperature function	Σ (T_g)		$\Sigma(T_g) = \left(\frac{t_{max} - T_g}{t_{max} - t_{opt}}\right)^{a\,\Sigma} exp\left(a_{\Sigma}\left(\frac{T_g - t_{opt}}{t_{max} - t_{opt}}\right)\right)$	[Stange and Neue, 2009]
Soil moisture response function	*f(M)*		$\Pi(M) = 1 - e^{-\left([(M \cdot \rho_{water})/(h \cdot \rho_{soil})]/m_{crit}\right)^{b}}$	[Stange and Neue, 2009]
Water:N ratio in applied fertilizer	$S_w(f)$	$m^3 g^{-1}$	$S_w(f) = \frac{1 \cdot 10^{-6}}{0.466 \times 0.66 \times e^{0.0239 \times (T_g - 273)}}$	[UNIDO and FIDC, 1998]

Parameters				
Flux of manure nitrogen applied to the surface	$\alpha_{applied}(m)$	g m^{-2} s^{-1}	Spatial distribution from Potter et al. (2010); annual temporal distribution from Holland et al. (2005)	[Potter et al., 2010; Holland et al., 2005]
Flux of fertilizer nitrogen applied to the surface	$\alpha_{applied}(f)$	g m^{-2} s^{-1}	Spatial distribution from Potter et al. (2010); annual temporal distribution from Holland et al. (2005)	[Potter et al., 2010; Holland et al., 2005]
Fractions of nitrogen in manure/urine	f_u, f_a, f_r, f_{un}	N/A	$f_u = 0.5$, $f_a = 0.25$, $f_r = 0.225$, $f_{un} = 0.025$	[Gusman and Marino, 1999]
Mechanical incorporation of manure into soil	k_m	s^{-1}	$k\_m = (365*86400)^{-1}$	see Koven et al. [2013]

Fertilizer Decomp-osition	k_f	s^{-1}	k_f = 4.83 x 10 $^{-6}$	[Agehara and Warncke, 2005]
Water:N ratio in applied manure	$s_w(m)$	$m^3 g^{-1}$	$s_w(m)$=5.67 10^{-4}	[Sommer and Hutchings, 2001]
Relaxation rate of TAN water pool to soil water pool	k_{relax}	s^{-1}	k_{relax} =$(3*86400)^{-1}$	
Empirical factors for K_a, K_r	k_{a1}, k_{a2}	s^{-1}	k_{a1} = 8.94 x 10^{-7} s^{-1} , k_{a2} = 6.38 x 10^{-8} s^{-1}	[Gilmour et al., 2003]
Empirical factors for T_r	t_{r1}, t_{r2}	$^{o}K^{-1}$	t_{r1} = 0.0106 , tr_2 = 0.12979 $^{o}K^{-1}$	[Vigil & Kissel, 1995]
Length Scale	l	m	$l=10^{-2}$ m	

Soil Porosity	φ		φ=0.5	
Depth of Soil Water Pool	$\mathcal{H}$	m	$\mathcal{H} = 5.0\ 10^{-2}$	
Atmospheric NH_3 concentration	χ_a	g m^{-3}	$\chi_a = 0.3 \text{ x } 10^{-6}\text{g m}^{-3}$	[Zbieranowski and Aherne, 2012]
Fraction of ammonia emissions capture by canopy	$f_{capture}$		$f_{capture} = 0.7$	[e.g., see Wilson et al., 2004]
Concentration of Hydrogen Ions	$[H^+]$	mol l^{-1}	$[H^+] = 10^{-7}$	
Reference Temperature	T_{ref}	^{o}K	$T_{ref} = 298.15$	[Sutton et al., 1994]
Maximum rate of nitrification	r_{max}	s^{-1}	$r_{max} = 1.16\ 10^{-6}$	[Parton et al., 2001]

Optimal temperature of microbial activity	t_{opt}	K	$t_{opt} = 301$	[Stange and Neue, 2009]
Maximum temperature of microbial activity	t_{max}	K	$t_{max} = 313$	[Stange and Neue, 2009]
Empirical factor	a_{Σ}		$a_{\Sigma} = 2.4$	[Stange and Neue, 2009]
Sharp parameter of the function	b		$b = 2$	[Stange and Neue, 2009]
Critical water content of soil	m_{crit}	g g^{-1} soil	$m_{crit} = 0.12$	[Stange and Neue, 2009]
Density of soil	ρ_{soil}	kg m^{-3}	$\rho_{soil} = 1050.$	

Table 1. Manure Sensitivity Tests

Exper[1]	Parameter[2]	Value[3]	NH3[4]	Run[5]	Soil[6]	Nitrif.[7]	Canopy[8]	ΔNH3[9] %	Sens.[10] %/%
Control[11]			19.5	10.2	15.2	32.3	29.2		
EX1m	*k_m*	100 d^{-1}	16.6	9.1	13.6	41.8	24.8	-15	.20
EX2m	*k_m*	750 d^{-1}	20.8	10.7	16	25.9	31.2	+7	.06
EX3m	k_{relax}	1 d^{-1}	19.5	10.2	15.3	32.2	29.2	0	0.0
EX4m	k_{relax}	10 d^{-1}	19.4	10.3	15.2	32.4	29.1	+1	0.0
EX5m	pH	6	8.0	16.6	23.9	45.8	12.0	-59	4.1
EX6m	pH	8	29.6	3.7	5.1	23.5	44.4	+52	3.6
EX7m	pH	Dataset[12]	15.0	13.8	18.4	36.8	22.5	-23	
EX8m	$f_{capture}$	0.4	29.2	10.2	15.2	32.3	19.5	+50	-1.3
EX9m	$f_{capture}$	0.8	9.7	10.2	15.2	32.3	38.9	-50	-2.2
EX10m	χ_a	.1 ug m^{-3}	20.0	9.9	14.7	31.8	30.0	+3	-.04
EX11m	χ_a	1 ug m^{-3}	18.2	11.1	16.4	33.5	27.3	-7	-.03
EX12m	H2O Depth	10 cm	16.0	7.7	20.7	37.9	24.1	-18	-.18
EX13m	H2O Depth	2 cm	23.1	13.4	8.2	27.1	34.6	+18	-.31
EX14m	K_D	×0.5	20.7	11.6	9.4	33.8	31.0	+6	-.12
EX15m	K_D	×2.0	17.8	8.5	22.9	30.4	26.8	-9	-.09
EX16m	r_{max}	× 0.5	20.7	11.0	16.7	27.0	31.1	+6	-.12
EX17m	r_{max}	× 2.0	17.5	9.0	13.0	40.5	26.3	-10	-.10
EX18m	*manure comp*[13]		15.4	8.4	12.5	23.8	23.1	-21	

[1]Control Experiment [2]Parameter changed from default values [3]New parameter value [4]NH_3 emissions (Tg N yr^{-1}) [5]Runoff (Tg N yr^{-1}) [6]Diffusion to soil (Tg N yr^{-1}) 7Nitrification (Tg N yr^{-1}) [8] Canopy capture (Tg N yr^{-1}) [9]Percent change in NH_3 emissions due to parameter change (%) [10] Percent change in NH_3 emissions

per % change in parameter value [11]Control simulation [12] Soil pH from the ISRIC-WISE dataset [Batjes, 2005][13]Change in manure composition to urine 41%, available 21%, unavailable 25%, and resistant 13%

Table 2. Fertilizer Sensitivity Tests

Exper[1]	Parameter[2]	Value[3]	NH3[4]	Run[5]	Soil[6]	Nitrif.[7]	Canopy[8]	ΔNH3[9] %	Sens.[10] %/%
Control[11]			10.9	5.3	12.3	9.8	16.3		
EX3f	k_{relax}	1 d^{-1}	11.3	5.6	11.6	9.0	17.0	+4	-.06
EX4f	k_{relax}	10 d^{-1}	10.1	4.7	13.7	10.9	15.1	-7	-.03
EX5f	pH	6	4.4	8.5	17.7	17.5	6.5	-60	+4.2
EX6f	pH	8	18.4	1.5	4.1	2.8	27.6	+69	+4.8
EX7f	pH	Dataset[12]	9.4	6.6	13.5	10.9	14.1	-14	
EX8f	$f_{capture}$	0.4	16.3	5.3	12.3	9.8	10.9	+50	-1.2
EX9f	$f_{capture}$	0.8	5.4	5.3	12.3	9.8	21.7	-50	-2.1
EX10f	χ_a	.1 ug m^{-3}	10.9	5.2	12.3	9.8	16.3	+0	0.0
EX11f	χ_a	1 ug m^{-3}	10.8	5.3	12.4	9.9	16.1	-1	0.0
EX12f	H2O Depth	10 cm	9.0	4.0	15.2	12.9	13.4	-17	-.17
EX13f	H2O Depth	2 cm	12.9	6.8	8.3	7.2	19.3	+18	-.31
EX14f	K_D	×0.5	11.8	6.1	7.6	11.3	17.7	+8	-.17
EX15f	K_D	×2.0	9.6	4.2	18.3	7.9	14.4	-12	-.12
EX16f	r_{max}	× 0.5	11.8	5.8	13.7	5.5	17.7	+8	-.17
EX17f	r_{max}	× 2.0	9.4	4.4	10.3	16.3	14.2	-14	-.14
EX18f	*Fert. Date*[13]		8.4	8.6	15.5	8.6	12.6	-23	
EX19f	*Fert. Rate*[14]		11.3	5.6	11.5	9.1	17.0	+4	
EX20f	*Fert Decomp*[15]		10.5	4.9	12.9	10.5	15.7	-4	

[1]Control Experiment [2]Parameter changed from default values [3]New parameter value [4]NH_3 emissions (Tg N yr^{-1}) [5]Runoff (Tg N yr^{-1}) [6]Diffusion to soil (Tg N yr^{-1}) 7Nitrification (Tg N yr^{-1}) [8] Canopy capture (Tg N yr^{-1}) [9]Percent change in NH_3 emissions due to parameter change (%) [10] Percent change in NH_3 emissions per % change in parameter value [11]Control simulation [12] Soil pH from the ISRIC-WISE dataset [Batjes, 2005]. [13]Change in fertilizer date to Mar 20 (NH) and Sept 20 (SH) [14]Apply fertilizer over 20 days [15]Assume fast release ammonium nitrate decay of fertilizer

Figure Captions.

Figure 1. Schematic of the addition of manure and fertilizer (Process Model) to the CESM nitrogen cycle. Some minor pathways are not shown. Soil nitrogen pools and and plant nitrogen exist in CLM4.5. Urine nitrogen (N_{urine}) is directly input to the TAN pool while fecal matter is split into three parts that decompose into the TAN pool at a rate determined by their C: N ratio ($N_{available}$, $N_{resistant}$, $N_{unavailable}$). Manure nitrogen that does not mineralize ($N_{unavailable}$) is added to the soil organic nitrogen pool. Nitrogen applied as synthetic fertilizer is added to the $N_{fertilizer}$ pool where it decomposes into the TAN pool. Losses from the TAN pool include ammonia (NH_3) emission (into CAM-chem), nitrogen run-off (into the RTM), above ground nitrate (NO_3^-) formation and diffusion to the soil nitrogen pools.

Figure 2. Comparison of model to measurements for percentage of nitrogen lost as NH_3 emissions from manure for a range of studies (see supplementary Table 1). Symbol color measures temperature at which emissions were made; shape gives the study.

Figure 3. Comparison of model to measurements for percentage of nitrogen lost as NH_3 emissions from fertilizer (see supplementary Table 2). Symbol color gives the latitude at which the measurement was made; symbol shape gives the study and type of fertilizer application.

Figure 4. Simulated NH_3 emissions from fertilizer application from 1995-2004 for the present-day control simulation. Simulated emissions (kg N ha^{-1} yr^{-1}) as a) an annual average, c) Jan-Feb-Mar average, d) Apr-May-Jun average, e) Jul-Aug-Sep average, and f) Oct-Nov-Dec average. Simulated emissions as a percent of annual fertilizer application, b).

Figure 5. As in Figure 4 but for manure application.

Figure 6. Simulated runoff of N_r from fertilizer and manure TAN pools for the present-day (1995-2004) control simulation. Simulated runoff (kg N ha^{-1} yr^{-1}) as an annual average for a) fertilizer, c) manure. Simulated as a) percent of annual fertilizer application, d) percent of annual manure application.

Figure 7. As in Figure 6, but for simulated nitrification.

Figure 8. As in Figure 6 but for flux of TAN nitrogen to the soil.

Figure 9. Global Fate of TAN Nr applied as fertilizer (a) or as manure (b). Emissions are split between those to the atmosphere and those captured by the canopy.

Figure 10. As in Figure 9, but fate of TAN nitrogen by country and region. Countries are split between developed countries and developing countries.

Figure 11. Comparison of manure (red) and synthetic fertilizer (blue) ammonia emissions or combined manure and synthetic fertilzer (green) (Tg N yr^{-1}) a**)** globally, b) China, c) Europe and d) US for this study (Riddick) and for other studies as collated by Paulot et al. (2104). Details on other studies in text.

Figure 12. Site specific pathways for nitrogen budget at 35˚N and 100˚W, near the Texas panhandle . Panels show a) the temperature (^{o}C) and precipitation (mm s^{-1}) used to force the CLM, b) the manure (solid) and fertilizer TAN pools (dashed) (gN m^{-2}), and the four major loss pathways from the TAN pools (NH_3 emissions, red; runoff, orange; nitrification, green; diffusion to the soil, blue) (g N m^2 s^{-1}) from c) the manure TAN pool d) the fertilizer TAN pool.

Figure 13. Applied nitrogen and nitrogen losses for the historical simulation in Tg N yr^{-1} for a) manure and c) fertilizer. Nitrogen losses from the TAN pool as a percentage of applied nitrogen for the historical simulation for b) manure and d) fertilizer. The losses from the TAN pool are divided into emission losses of ammonia to the atmosphere (golden diamond), runoff (green diamond) and loss to the soil. Loss to the soil is divided into that due to canopy loss (askerisk) , direct diffusive loss (cross) and nitrification (plus) (see section 3.2.3).

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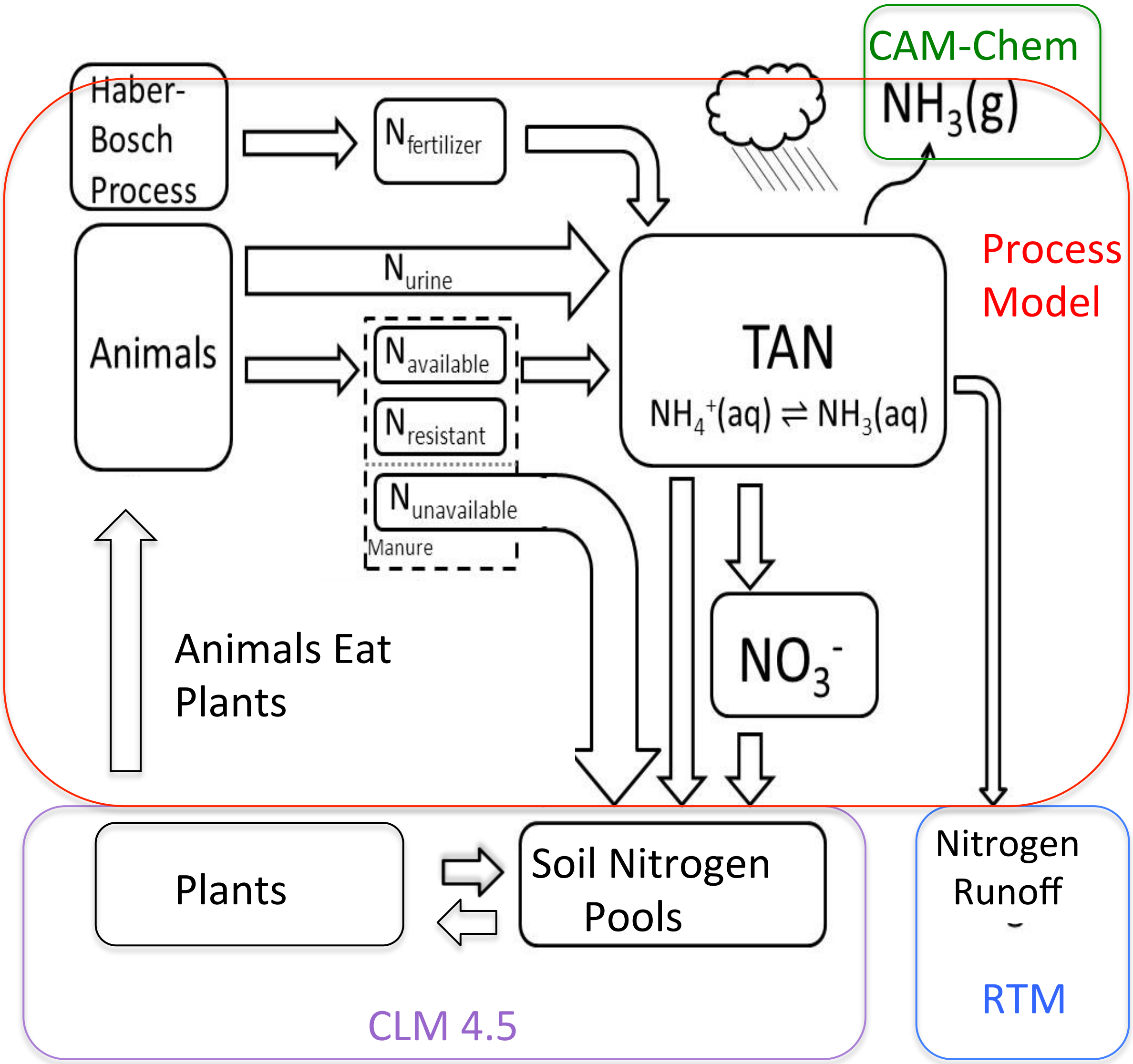


Figure 1. Schematic of the addition of manure and fertilizer (Process Model) to the CESM nitrogen cycle. Some minor pathways are not shown. Soil nitrogen pools and and plant nitrogen exist in CLM4.5. Urine nitrogen (N_{urine}) is directly input to the TAN pool while fecal matter is split into three parts that decompose into the TAN pool at a rate determined by their C: N ratio ($N_{available}$, $N_{resistant}$, $N_{unavailable}$). Manure nitrogen that does not mineralize ($N_{unavailable}$) is added to the soil organic nitrogen pool. Nitrogen applied as synthetic fertilizer is added to the $N_{fertilizer}$ pool where it decomposes into the TAN pool. Losses from the TAN pool include ammonia (NH_3) emission (into CAM-chem), nitrogen run-off (into the RTM), above ground nitrate (NO_3^-) formation and diffusion to the soil nitrogen pools.

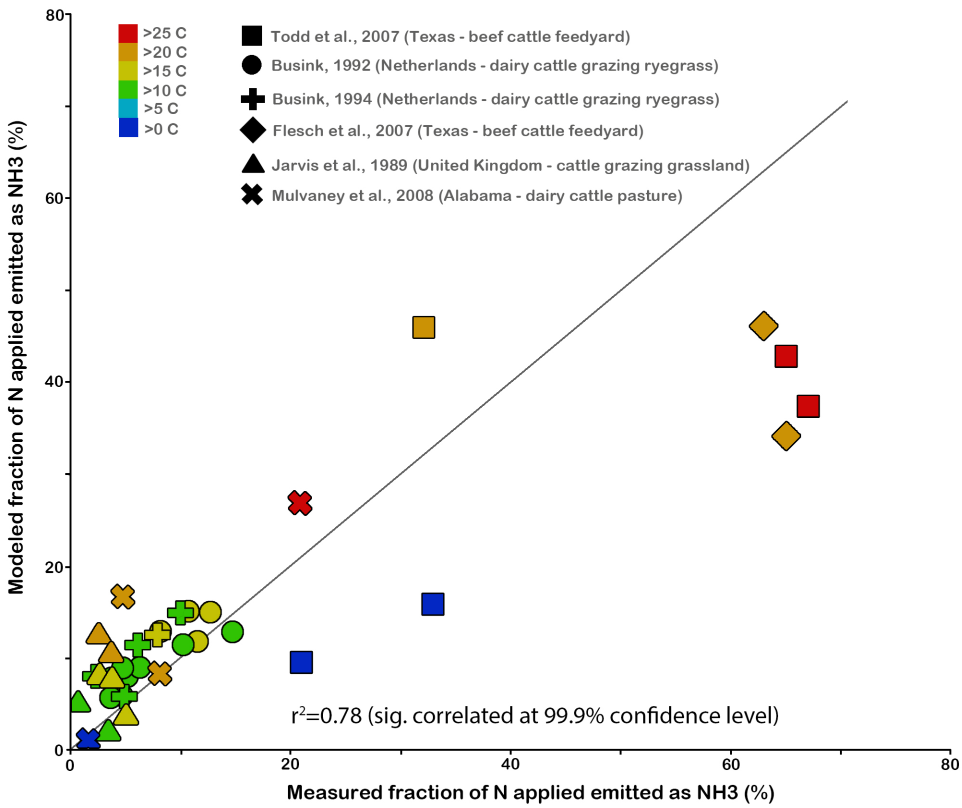


Figure 2. Comparison of model to measurements for percentage of nitrogen lost as NH_3 emissions from manure for a range of studies (see supplementary Table 1). Symbol color measures temperature at which emissions were made; shape gives the study.

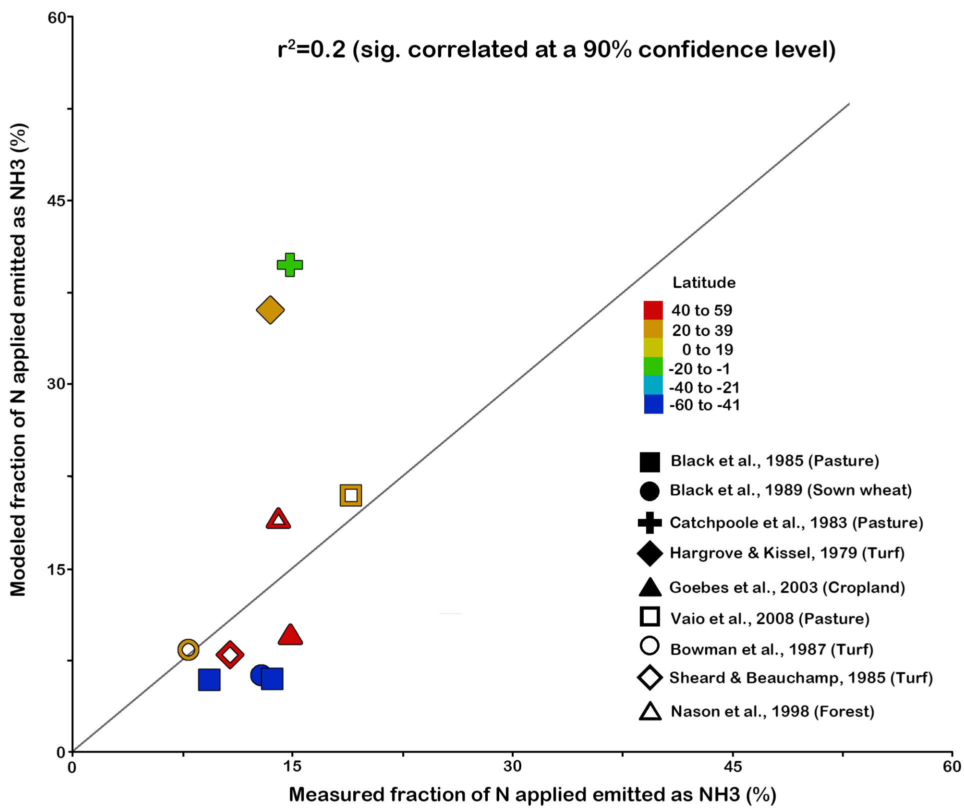


Figure 3 Comparison of model to measurements for percentage of nitrogen lost as NH_3 emissions from fertilizer (see supplementary Table 2). Symbol color gives the latitude at which measurement were made; symbol shape gives the study and type of fertilizer application.

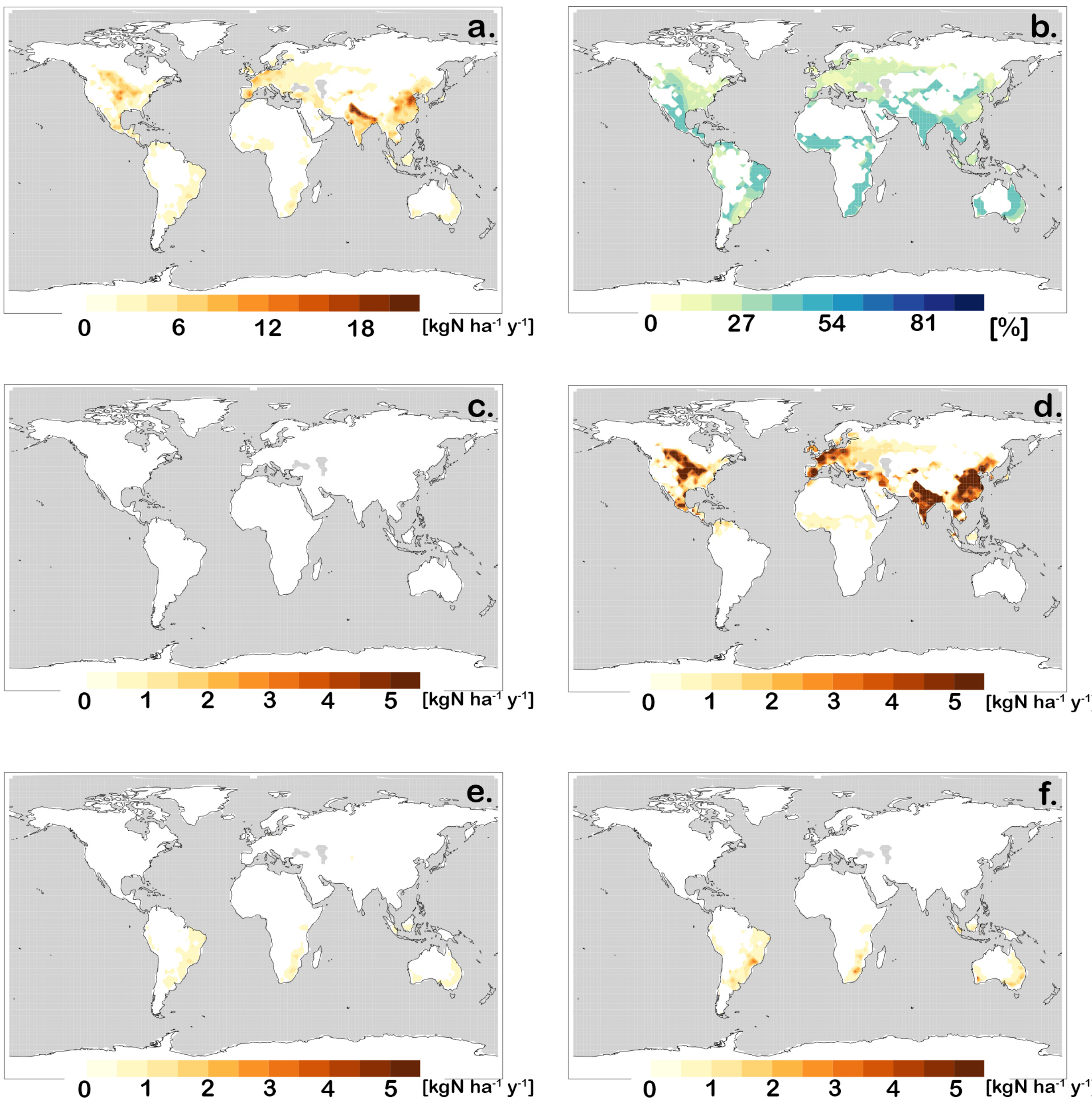


Figure 4. Simulated NH_3 emissions from fertilizer application from 1995-2004 for the present-day control simulation. Simulated emissions (kg N ha^{-1} yr^{-1}) as a) an annual average, c) Jan-Feb-Mar average, d) Apr-May-Jun average, e) Jul-Aug-Sep average, and f) Oct-Nov-Dec average. Simulated emissions as a percent of annual fertilizer application, b).

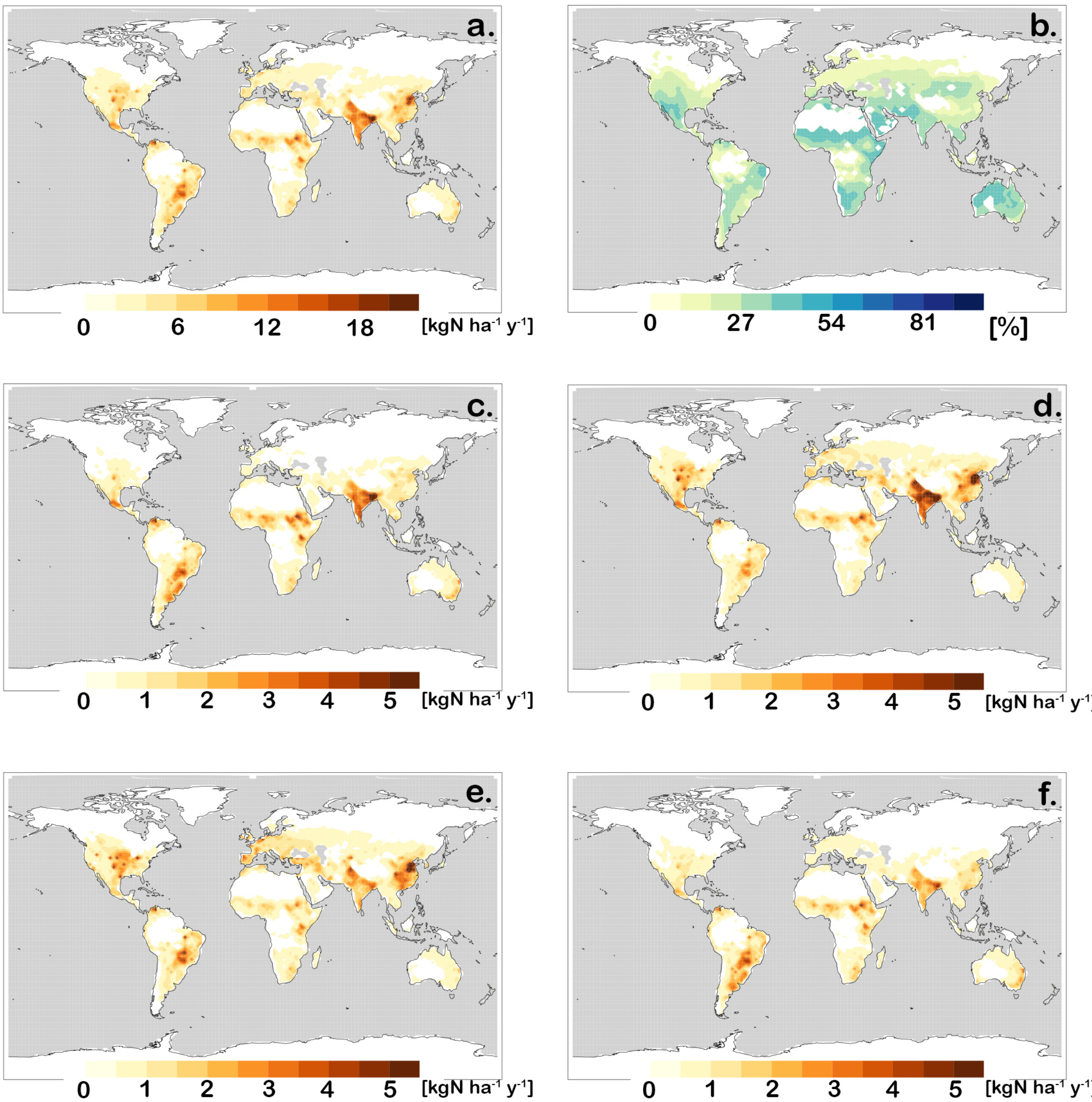


Figure 5. As in Figure 4 but for manure application.

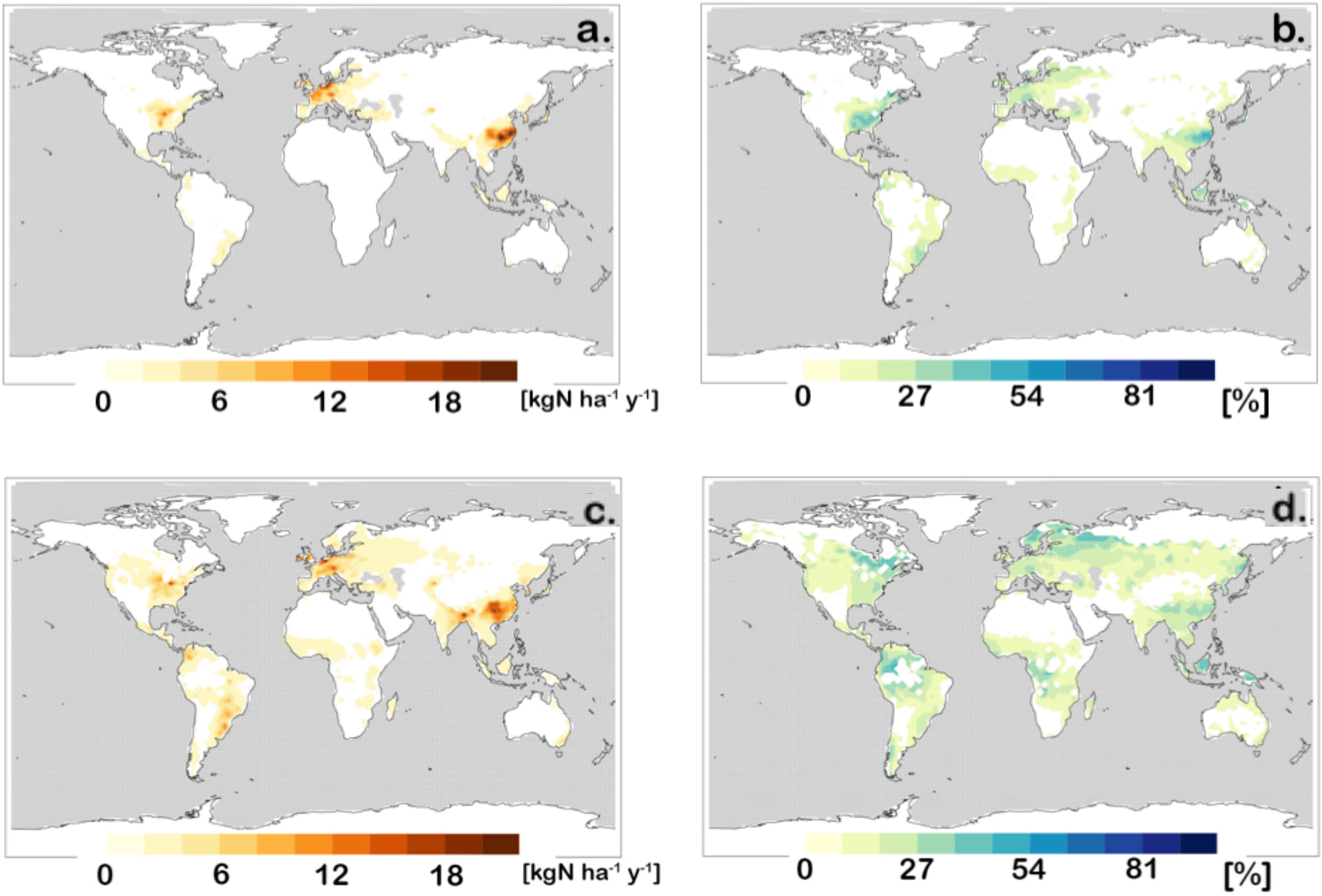


Figure 6. Simulated runoff from fertilizer and manure application from 1995-2004 for the present-day control simulation. Simulated runoff (kg N ha^{-1} yr^{-1}) as an annual average for a) fertilizer, c) manure. Simulated as a) percent of annual fertilizer application, d) percent of annual manure application.

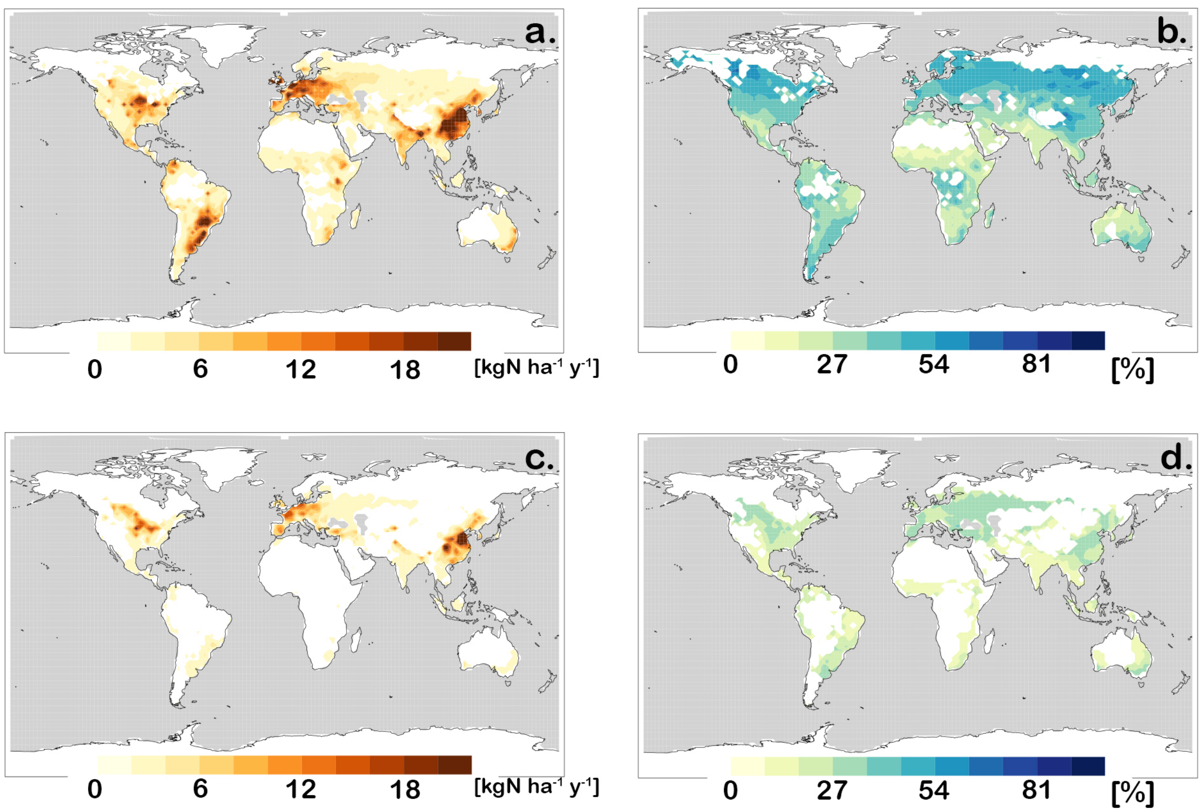


Figure 7. As in Figure 6, but for simulated nitrification.

c.c

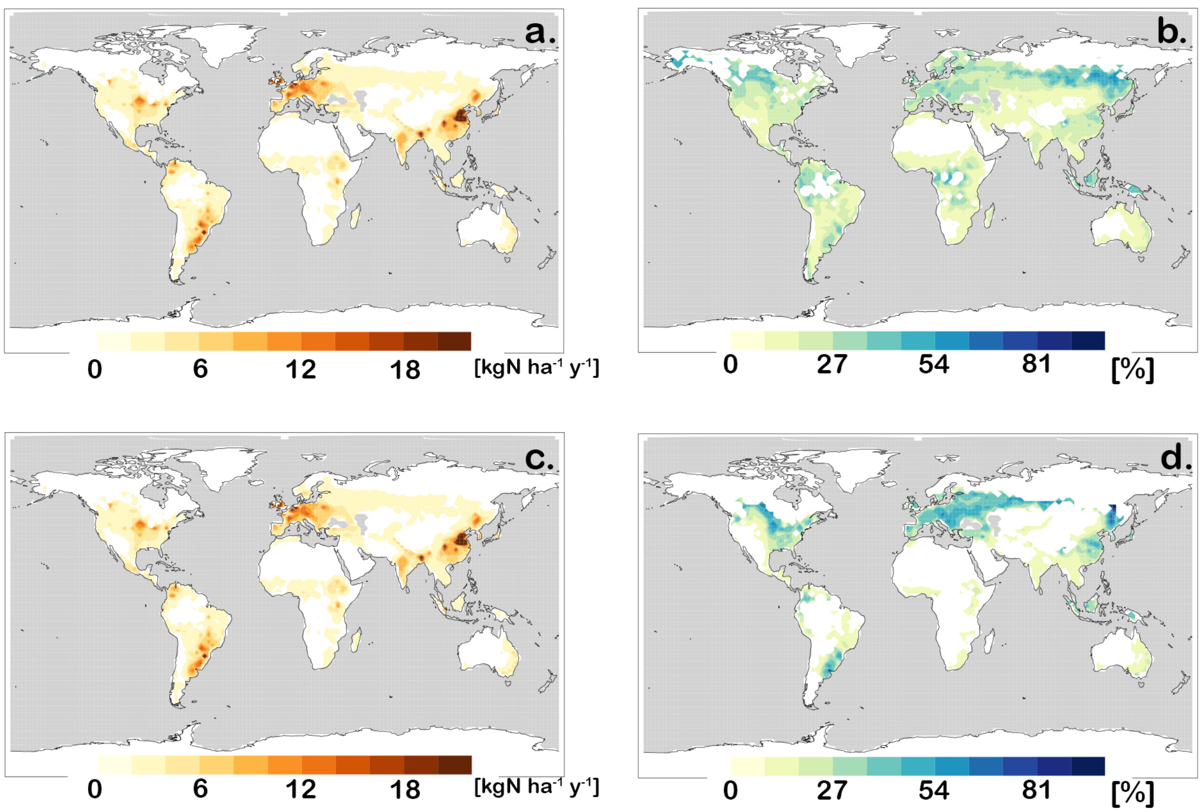


Figure 8. As in Figure 6 but for flux of TAN nitrogen to the soil.

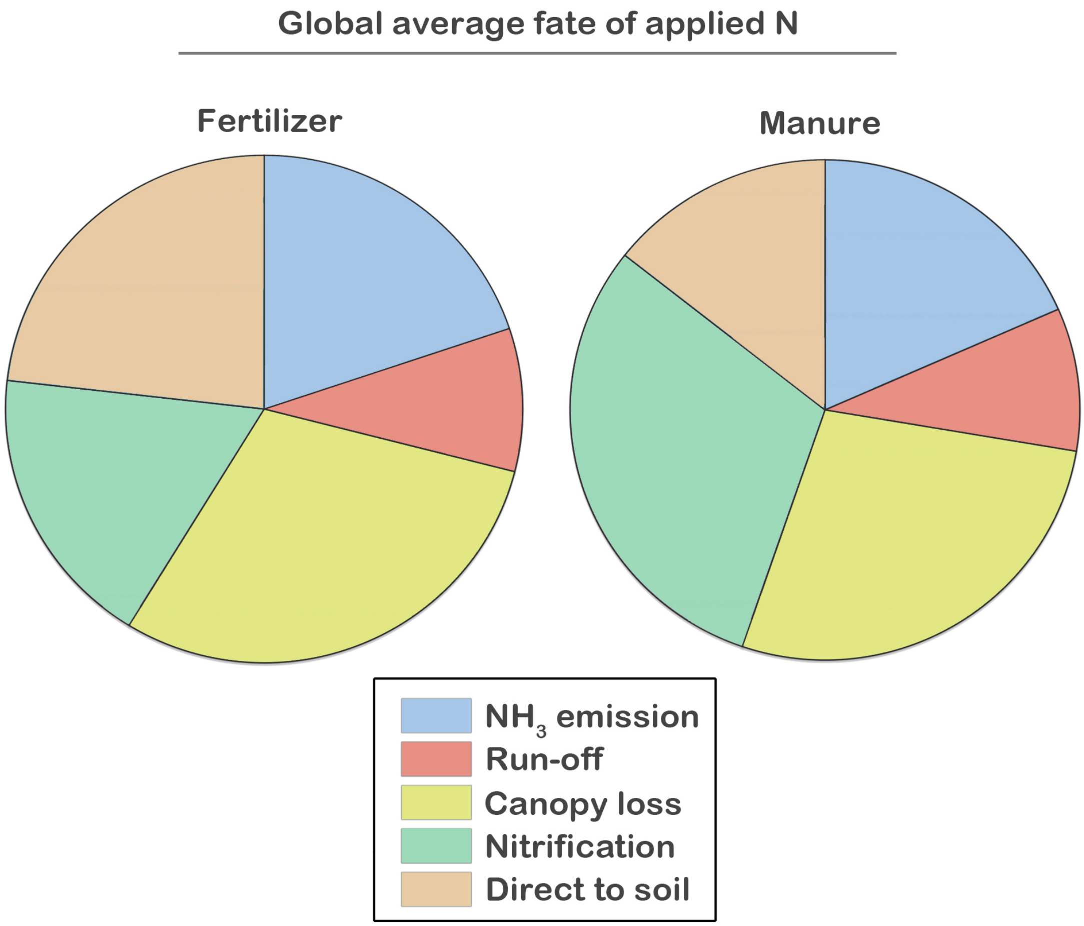


Figure 9. Global Fate of TAN Nr applied as fertilizer (a) or as manure (b). Emissions are split between those to the atmosphere and those captured by the canopy.

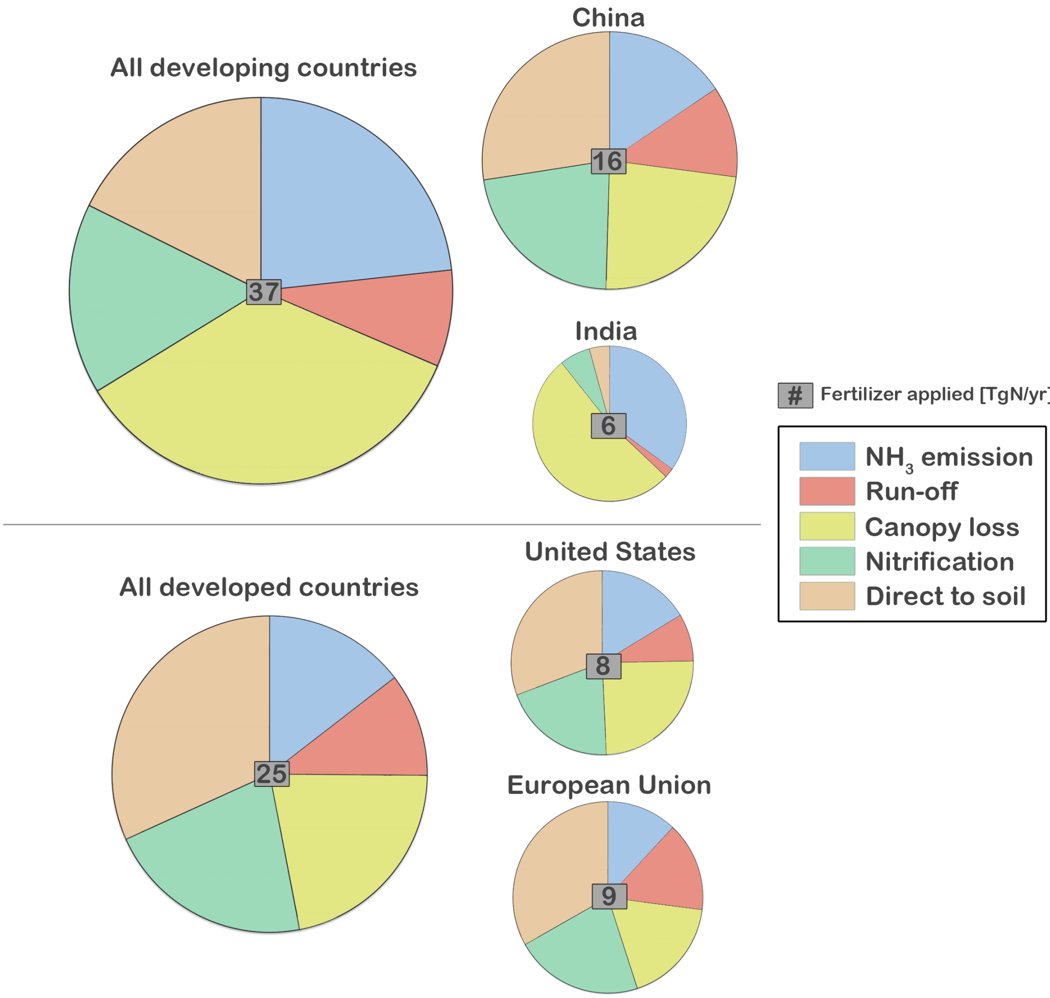


Figure 10. As in Figure 9, but fate of TAN nitrogen by country and region. Countries are split between developed countries and developing countries.

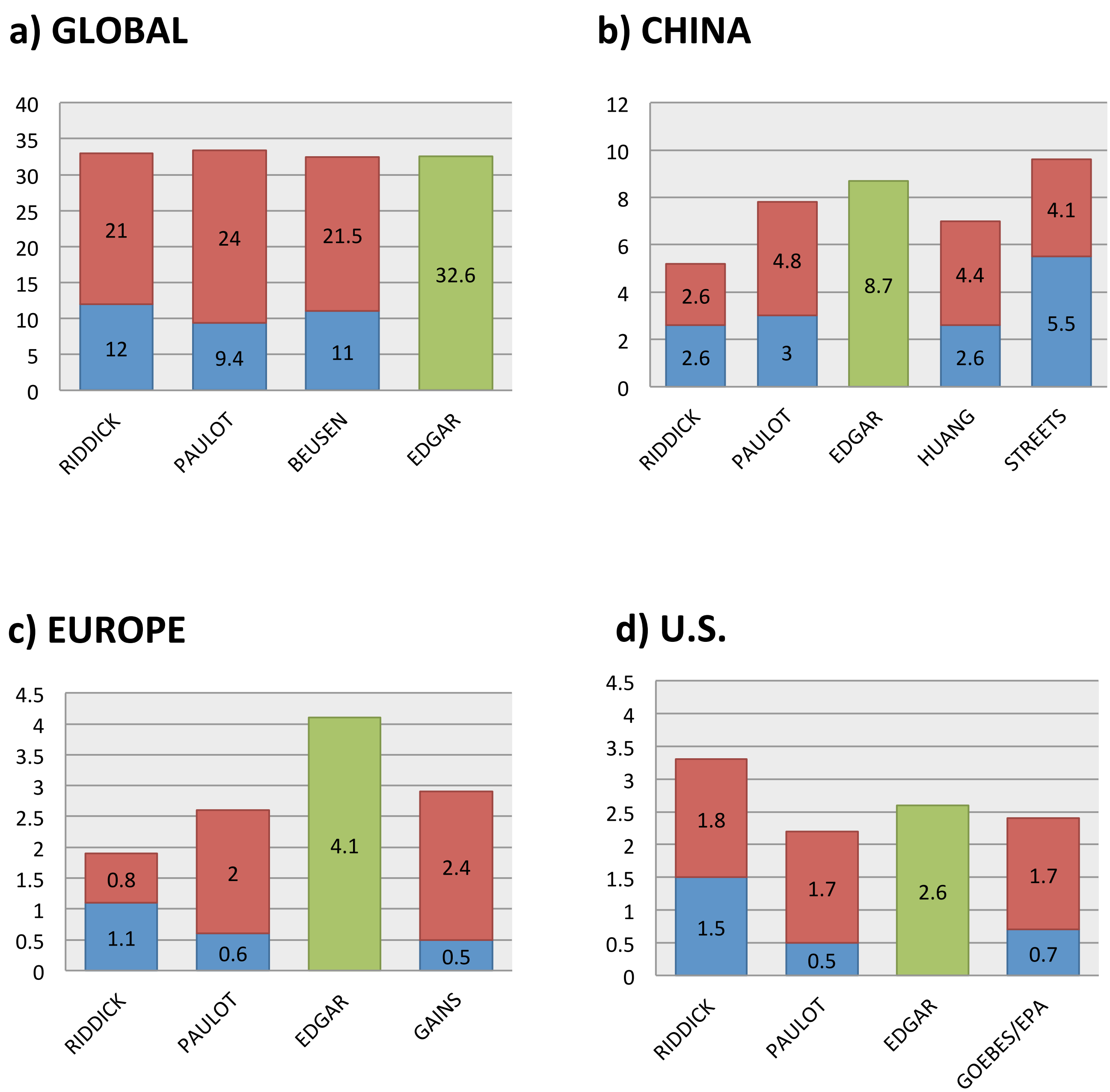
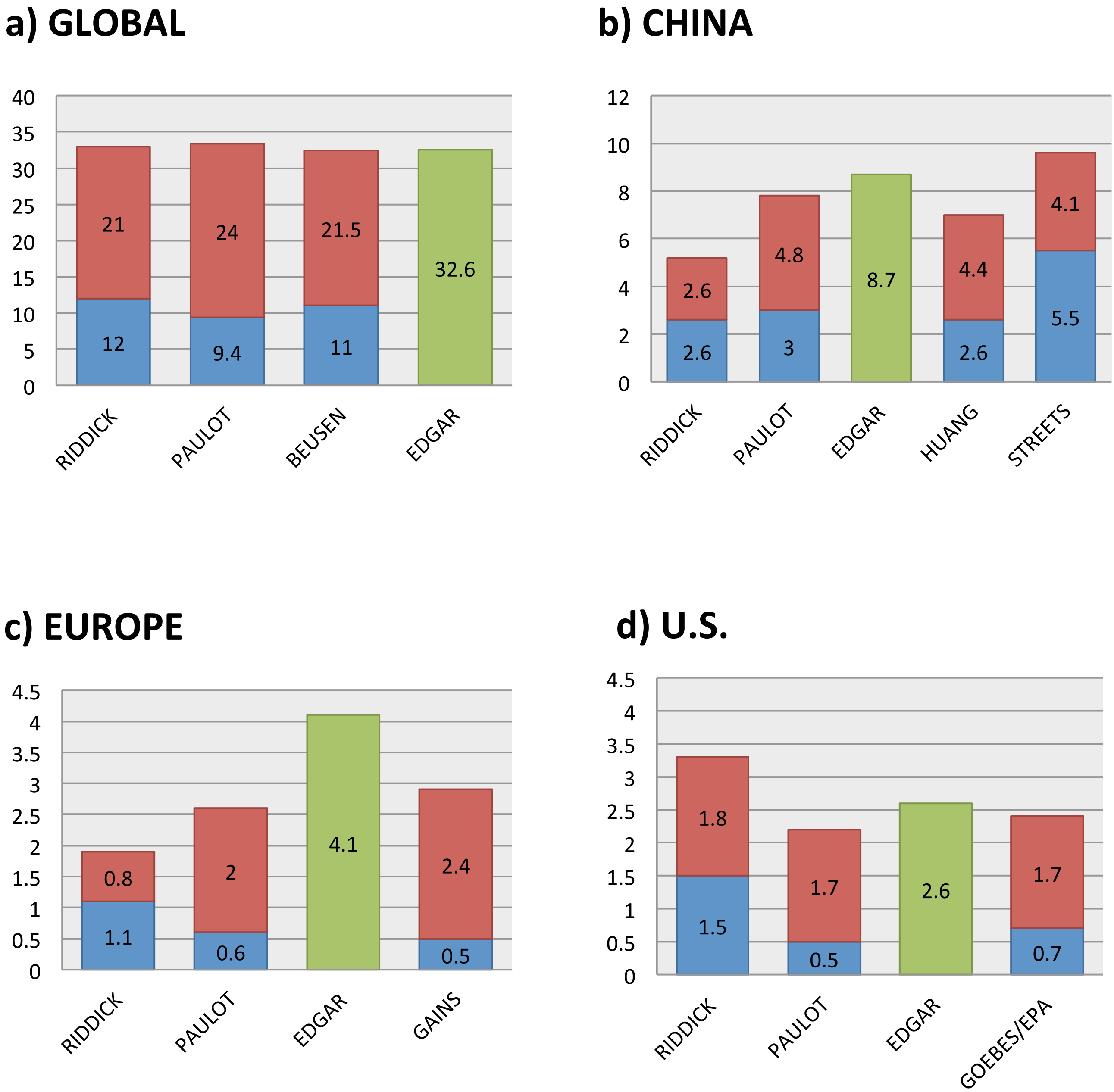
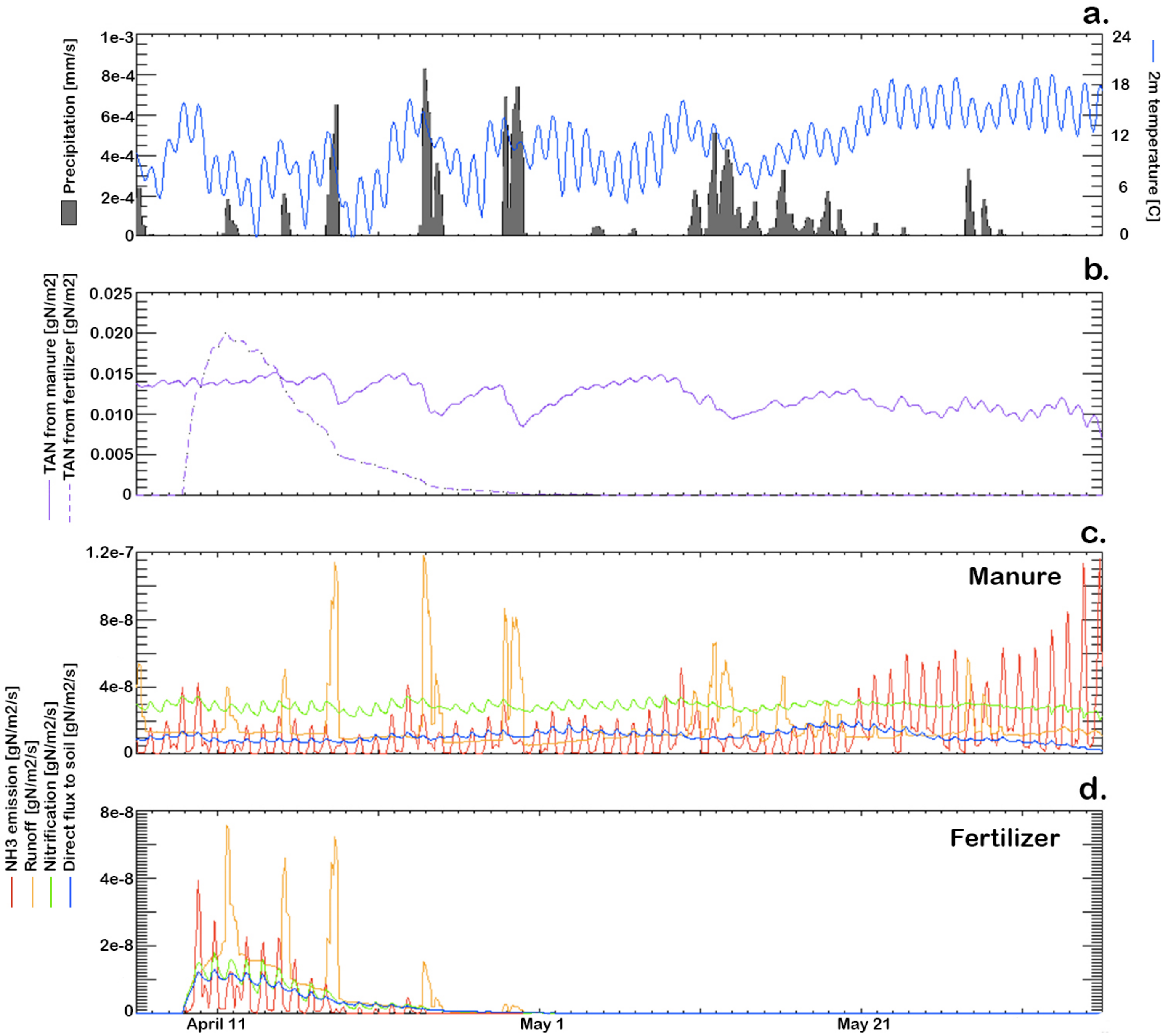


Figure 11. Comparison of manure (red) and fertilizer (blue) or both ammonia emissions (Tg N ha^{-1} yr^{-1}) a) globally, b) China, c) Europe and d) US for this study (Riddick) and for other studies as collated by Paulot et al. (2104). Details on other studies in text.


a) GLOBAL
40
35
30
25
20
15
10
5
0
21
12
24
9.4
21.5
11
32.6
RIDDICK
PAULOT
BEUSEN
EDGAR
b) CHINA
12
10
8
6
4
2
0
2.6
2.6
4.8
3
8.7
4.4
2.6
4.1
5.5
RIDDICK
PAULOT
EDGAR
HUANG
STREETS
c) EUROPE
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
0.8
1.1
2
0.6
4.1
2.4
0.5
RIDDICK
PAULOT
EDGAR
GAINS
d) U.S.
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
1.8
1.5
1.7
0.5
2.6
1.7
0.7
RIDDICK
PAULOT
EDGAR
GOEBES/EPA



12. Site specific pathways for nitrogen budget at 35˚N and 100˚W, near the Texas panhandle . Panels show a) the temperature (^{o}C) and precipitation (mm s^{-1}) used to force the CLM, b) the manure (solid) and fertilizer TAN pools (dashed) (gN m^{-2}), and the four major loss pathways from the TAN pools (NH_3 emissions, red; runoff, orange; nitrification, green; diffusion to the soil, blue) (g N m^2 s^{-1}) from c) the manure TAN pool d) the fertilizer TAN pool.

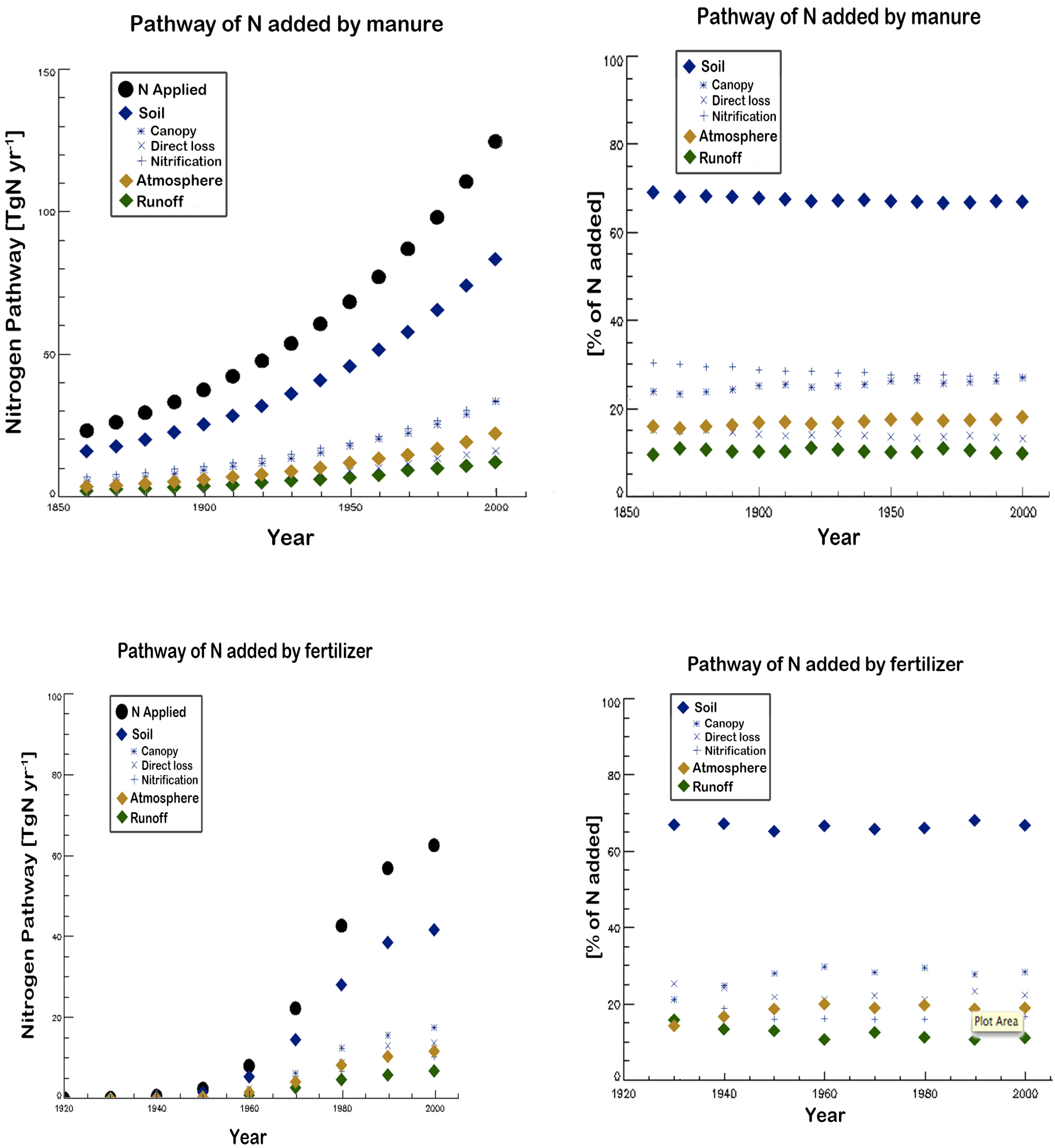


Figure 13: Applied nitrogen and nitrogen losses for the historical simulation in Tg N yr^{-1} for a) manure and c) fertilizer. Nitrogen losses from the TAN pool as a percentage of applied nitrogen for the historical simulation for b) manure and d) fertilizer. The losses from the TAN pool are divided into emission losses of ammonia to the atmosphere (golden diamond), runoff (green diamond) and loss to the soil. Loss to the soil is divided into that due to canopy loss (askerisk) , direct diffusive loss (cross) and nitrification (plus) (see section 3.2.3).