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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. The parameterization uses a climate dependent approach whereby the relationships between meteorological variables and biogeochemical processes are used to calculate the volatilization of ammonia (NH_3), nitrification and run-off of N_r following manure or fertilizer application. For the year 2000, we estimate global NH_3 emission and N_r dissolved during rain events from manure at 21 and 11 $\mathrm{Tg\,N\,yr^{-1}}$, respectively; for synthetic fertilizer we estimate the NH_3 emission and N_r run-off during rain events at 12 and 5 $\mathrm{Tg\,N\,yr^{-1}}$, respectively. The parameterization was implemented in the Community Land Model 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 $\mathrm{Tg\,NH_3\,yr^{-1}}$) in 1850 to 18 % of nitrogen applied in 2000 (22 $\mathrm{Tg\,NH_3\,yr^{-1}}$). 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

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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 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 fertilizer. The parameterization is evaluated on both the local and global scales against local measurements and inde-

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pendent global NH_3 flux estimates. The calculated emission estimates for NH_3 and the N_r runoff due to manure and 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 %), the burning of fossil fuels, (30 Tg N yr^{-1} ± 10 %), and a further 60 Tg N yr^{-1} ± 30 % 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 inorganic 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 future, NH_3 emissions are ex-

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pected 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 −0.03 to −0.41 $W m^{-2}$ 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 5^0 warming. In addition to changes in NH_3 volatilization from manure and fertilizer application, nitrogen runoff will change in a future climate, changes that have not been explicitly considered to date.

Studies calculating NH_3 emission from manure and fertilizer have broadly fallen into two categories: models that use empirically derived emission factors and more complex process-based models. Global emissions have almost been universally estimated using the former approach with specified emission factors taking into account the animal feed, the type of animal housing if any and the field application of the fertilizer or manure (e.g., Bouwman et al., 1997). Very simplified representations of the effect of climate have been taken into account by grouping countries into industrial or developing categories (Bouwman et al., 1997). For example, this type of emission inventory was used in the Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP) (Lamarque et al., 2013) for assessing historical and future chemistry-climate scenarios. The global impact of nitrogen on the carbon cycle as well as on atmospheric chemistry has traditionally been assessed using these type of inventories of NH_3 emissions. 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). 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 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 mineral 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 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 N_r 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 mineral 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 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 vs. site level measurements of NH_3 fluxes; an analysis of the globally heterogeneous nitrogen pathways from applied manure and 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 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 major loss 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 (Fig. 1). The model is global in nature, is designed to conserve carbon and nitrogen and responds to changes in climate.

2.1 Relation between the process model 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 relation between 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 Fig. 1. In this first study the

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subsequent fate of N_r within these other components of the CESM1.1 is not further considered. Thus, this first study does not account for the feedbacks between the applied nitrogen in the fertilizer or manure pools and the carbon cycle. However future studies will consider these effects. In particular, the fate of N_r incorporated into soil organic matter or the soil nitrogen pools of the Community Land Model (CLM) 4.5, the land component model of the CESM1.1, is not considered (see Fig. 1). In addition, the fate of N_r emitted into the atmosphere as NH_3 directly from fertilizer or manure is handled by the atmospheric chemistry component of the CESM (CAM-chem) and is not considered here (Fig. 1). 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 fertilizer coupled has been coupled to the river transport model (RTM) (Nevison et al., 2015) (Fig. 1).

The process model described here strongly interacts with the land component of the CESM1.1, the CLM 4.5. 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 performance (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, 2009) and extensively compared to observations (e.g. Thomas et al., 2013). The CLM4 has

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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; Del 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 (Fig. 1).

2.2 Process model for predicting nitrogen pathways from manure or fertilizer

The following specifications are necessary to model the nitrogen cascade following fertilizer or manure application within an Earth System Model. (1) The model must be global in nature to characterize global interactions between applied N_r and climate. However, as detailed soil types and agricultural practices are not well characterized globally a global picture necessarily sacrifices some of the regional and local details. (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 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.

Nitrogen pathways subsequent to the application of manure or 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 inventories with explicit although still incomplete incorporation of agricultural practices through the use of emission factors tend to minimize the climate dependence of the emissions. As discussed above this type of model has seen extensive use in the climate and chemical modeling communities. We take the opposite tact here. We have minimized the description of agricultural practices, which have not been sufficiently characterized on a global basis, and emphasize the biogeochemistry of manure and fertilizer decomposition and the resultant nitrogen pathways. As shown below, this type of model 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. An ideal model would incorporate both emission factors (temperature and wind dependent) where appropriate (e.g., from animal housing) as well as a more physically based system simulating the physics of applied manure and fertilizer volatilization and runoff as modified by agricultural practices (e.g., see Sutton et al., 2013).

A schematic of the overall model analyzed here is given in Fig. 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 Sect. 3.4. The nitrogen loss pathways are calculated separately for manure and fertilizer. While this model assumes that fertilizer application and manure application can take place in the same approximately $2^{\circ} \times 2^{\circ}$ grid cell, we also assume that manure and 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 fertilizer in each column. This means that the Total Ammoniacal Nitrogen (TAN) pools

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(consisting of NH_3(g), NH_3(aq), NH_4^+) for manure and fertilizer are discrete and hence the nitrogen pathways are not combined.

The application rate and geographical distribution used for manure and fertilizer application is taken from the fertilizer application and manure production datasets developed in Potter et al. (2010). These datasets are valid for circa 2000 for 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 and storage systems 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 (Sects. 2.2.1 and 2.2.2 and Fig. 1). A similar strategy was adopted by Li et al. (2013) for manure and is commonly used in simulating litter decomposition. Fertilizer N_r is added to one pool, where after it decomposes into the TAN pool (Fig. 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 (Fig. 1).

Manure must be added to the model in such a manner as to conserve nitrogen (Fig. 1). Here, we assume ruminants consume carbon and nitrogen from plants and then subsequently excrete this as manure. Within the CLM, carbon and nitrogen in

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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 ruminants, 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 ruminants 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 lateral transport 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 lateral transport 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 ($\alpha_{\text{applied}}(m)$) ($\text{g}\,\text{m}^{-2}\,\text{s}^{-1}$) depending on latitude and longitude into the manure nitrogen pools. Nitrogen applied to the land as manure (or fertilizer) is assumed to be spread uniformly on each grid cell irrespective of plant functional type (pft) or surface type. 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 (urea), with the

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remaining 50 % excreted as faecal matter (Gusman and Marino, 1999). The excreted urine is directly added to the TAN pool ($\mathrm{g\,N\,m^{-2}}$). 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 ($\mathrm{g\,m^{-2}}$) depending on their rate of mineralization (e.g., Gusman and Marino, 1999): (1) we assume a fraction $f_{\mathrm{un}} = 5\,\%$ is excreted as unavailable nitrogen ($\mathrm{N_{unavailable}}$), the lignin component of manure where the nitrogen remains immobilized by bacteria (C : N ratio > 25 : 1), (2) a fraction $f_{\mathrm{r}} = 45\,\%$ goes to the resistant pool ($\mathrm{N_{resistant}}$) which forms the cellulose component of manure (C : N ratio *c.* 15 : 1) resistant to forming TAN; (3) and a fraction $f_{\mathrm{a}} = 50\,\%$ goes to the available pool ($\mathrm{N_{available}}$) that is readily available to form TAN ($\mathrm{N_{available}}$). 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 Fig. 1) are:

$$\mathrm{dN_{available}}/\mathrm{d}t = f_{\mathrm{a}} \times \alpha_{\mathrm{applied}}(m) - K_{\mathrm{a}} \cdot \mathrm{N_{available}} - k_{\mathrm{m}} \cdot \mathrm{N_{available}} \tag{1}$$

$$\mathrm{dN_{resistant}}/\mathrm{d}t = f_{\mathrm{r}} \times \alpha_{\mathrm{applied}}(m) - K_{\mathrm{r}} \cdot \mathrm{N_{resistant}} - k_{\mathrm{m}} \cdot \mathrm{N_{resistant}} \tag{2}$$

$$\mathrm{dN_{unavailable}}/\mathrm{d}t = f_{\mathrm{un}} \times \alpha_{\mathrm{applied}}(m) - k_{\mathrm{m}} \cdot \mathrm{N_{unavailable}} \tag{3}$$

where $\alpha_{\mathrm{applied}}(m)$ is the amount of manure applied ($\mathrm{g\,m^{-2}\,s^{-1}}$); $f_{\mathrm{a}}, f_{\mathrm{r}}$ and f_{un} are the fractions of manure applied to each pool; K_{a} and K_{r} ($\mathrm{s^{-1}}$) are temperature dependent mineralization rates and k_{m} ($\mathrm{s^{-1}}$) is the mechanical loss rate of nitrogen out of these 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 °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 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

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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 $cm^2\,yr^{-1}$ 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 (Sect. 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 Fertilizer

Synthetic fertilizer nitrogen is added to the $N_{fertilizer}$ pool ($g\,N\,m^{-2}$) (Fig. 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 fertilizer pool is subsequently released into the TAN pool with the rate k_f (s^{-1}):

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

Here we assume all synthetic fertilizer is urea. Urea is the most commonly used fertilizer accounting for over 50 % of the global nitrogenous fertilizer usage (Gilbert et al., 2006). 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 °C without a significant dependence on temperature especially for temperatures above 15 to 20 °C.

The timing of the fertilizer application in the model coincides with the spring planting date. This date 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. In Levis et al. (2012) the ten-day running mean temperature, ten-day running mean daily minimum temperature and growing degree days must all surpass fixed threshold

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values (283.15 K, 279.15 K and 50 days, respectively, for corn) 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 fertilizer is applied on this date. Future applications may assume a more complete algorithm for fertilizing the spectrum of global crops.

2.2.3 Total Ammonical Nitrogen (TAN)

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

$$\begin{aligned}\mathrm{N_{TAN}}(m)/\mathrm{d}t &= f_\mathrm{u} x \alpha_\mathrm{applied}(m) + K_\mathrm{r} \cdot \mathrm{N_{resistant}} + K_\mathrm{a} \cdot \mathrm{N_{available}} F_\mathrm{run}(m) \\ &\quad - K_D^{\mathrm{NH_4}} \cdot \mathrm{N_{TAN}}(m) - F_{\mathrm{NH_3}}(m) - F_{\mathrm{NO_3}}(m) \qquad (5)\\ \mathrm{N_{TAN}}(f)/\mathrm{d}t &= k_\mathrm{f} \cdot \mathrm{N_{fertilizer}} - F_\mathrm{run}(f) \\ &\quad - K_D^{\mathrm{NH_4}} \cdot \mathrm{N_{TAN}}(f) - F_{\mathrm{NH_3}}(f) - F_{\mathrm{NO_3}}(f) \qquad (6)\end{aligned}$$

Here $F_\mathrm{run}(m/f)$ ($\mathrm{g\,N\,m^{-2}\,s^{-1}}$) is the loss of nitrogen by runoff from the manure or fertilizer pool, $K_D^{\mathrm{NH_4}}$ ($\mathrm{s^{-1}}$) the loss rate of nitrogen to the soil nitrogen pools, $F_{\mathrm{NH_3}}(m)$ and $F_{\mathrm{NH_3}}(f)$ ($\mathrm{g\,N\,m^{-2}\,s^{-1}}$) the $\mathrm{NH_3}$ emissions from the TAN pool to the atmosphere from the soil manure and fertilizer pools, respectively, and $F_{\mathrm{NO_3}}(m)$ and $F_{\mathrm{NO_3}}(f)$ ($\mathrm{g\,N\,m^{-2}\,s^{-1}}$) the loss of nitrogen through nitrification from the manure and fertilizer pools respectively. The formulation of each of these terms is given below. Inputs into $\mathrm{N_{TAN}}(m)$ pool are from the fraction (f_u) of applied manure as urine ($\alpha_\mathrm{applied}(m)$), and from the decomposition of the nitrogen within the available and resistant manure pools. Input into the $\mathrm{N_{TAN}}(f)$ pool is through decomposition of nitrogen within the fertilizer pool.

2.2.4 Runoff of nitrogen to rivers

The runoff of nitrogen to rivers is derived from the runoff rate of water (R) ($\mathrm{m\,s^{-1}}$) in the CLM multiplied by concentration of nitrogen in the TAN water pool:

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

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 ($\mathrm{N_{water}}(m/f)$)(m) is needed to convert $\mathrm{N_{TAN}}$ ($\mathrm{g\,N\,m^{-2}}$) to a concentration ($\mathrm{g\,N\,m^{-3}}$). An expression for $\mathrm{N_{water}}(m/f)$ is given in 2.2.9. 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 $0.03\,\mathrm{cm^2\,day^{-1}}$, 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_{NH_3}, $g\,m^{-2}\,s^{-1}$) 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 (Eq. 8) (Nemitz et al., 2000; Loubet et al., 2009; Sutton et al., 2013).

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

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 $10\,\mu g\,m^{-3}$ have been reported by Zbieranowski and Aherne (2012) and Heald et al. (2012). A background atmospheric NH_3 concentration ($\chi_a = 0.3\,\mu g\,m^{-3}$ in Eq. 8) is specified, representative of a low activity agricultural site (Zbieranowski and Aherne, 2012). The sensitivity to this parameter is small as $NH_3(g)$ is usually very large. While Eq. (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:

$$F_{NH_{3atm}}(m/f) = (1 - f_{capture}) \times F_{NH_3}(m/f) \tag{9}$$

where $f_{capture}$ is set to 0.6, slightly less than the value of 0.7 assumed in Wilson et al. (2004).

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It is assumed that the nitrogen in the TAN pool is in equilibrium between NH_3(g), NH_3(aq) and NH_4^+(aq). 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_{NH_4}) (e.g., Sutton et al., 1994)

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

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

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_{NH_4})

$$NH_3(g)(m/f) = \frac{N_{TAN}(m/f)/N_{water}(m/f)}{1 + K_H + K_H[H^+]/K_{NH_4}} \tag{12}$$

Both K_H and K_{NH_4} 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 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 fertilizer and manure TAN pools. Sensitivity to pH is explored in Sect. 3.4.

2.2.7 Conversion of TAN to NO_3^-

The flux from the TAN pool to NO_3^- by nitrification ($N_{NO_3^-}$, $g\,m^{-2}\,s^{-1}$) was adapted from that derived by Stange and Neue (2009) to describe the gross nitrification rates in

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response to fertilization of a surface with manure or fertilizer. In particular Stange and Neue (2009) fit measured gross nitrification rates to an expression using a maximal nitrification rate r_{max}, $\mu g\,N\,kg^{-1}\,h^{-1}$) 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 and Neue (2009). We have remedied this by setting the maximum nitrification rate (r_{max}) in the formulation of (Stange and Neue, 2009) to $1.16 \times 10^{-6}\,s^{-1}$ consistent with the formulation in Parton et al. (2001):

$$F_{NO_3}(m/f) = \frac{2 \cdot r_{max} N_{TAN}(m/f) K_H \left[H^+\right] / K_{NH_4}}{\frac{1}{f(T)} + \frac{1}{f(M)}} \tag{13}$$

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, K_{NH_4} and $NTAN_{m/f}$.

2.2.8 Nitrate

The rate of change of the nitrate pool is given by:

$$dN_{NO_3}(m/f)/dt = F_{NO_3}(m/f) - K_D^{NO_3} N_{NO_3}(m/f) \tag{14}$$

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

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

$$\mathrm{dN_{water}}(m)/\mathrm{d}t = s_\mathrm{w}(m) \times \alpha_\mathrm{applied}(m) - k_\mathrm{relax} \times (\mathrm{N_{water}}(m) - M_\mathrm{water}) \tag{15}$$

$$\mathrm{dN_{water}}(f)/\mathrm{d}t = S_\mathrm{w}(f) \times \alpha_\mathrm{applied}(f) - k_\mathrm{relax} \times (\mathrm{N_{water}}(f) - M_\mathrm{water}) \tag{16}$$

These equations include a source of water ($s_\mathrm{w}(m)$ or $S_\mathrm{w}(f)$) added as a fraction of the 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 $\mathrm{day\,s}^{-1}$ (Sect. 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 $\mathrm{g\,kg}^{-1}$ and a nitrogen content of 1.63 $\mathrm{g\,kg}^{-1}$, resulting in 5.67×10^{-4} m water applied per gram of manure nitrogen applied (Sommer and Hutchings, 2001). In the case of 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).

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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 historical simulation (1850–2000). The resolution used in these simulations is: 1.9° latitude by 2.5° longitude.

2.3.1 Present day control simulation

This simulation uses the manure and 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 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 ge-

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ography of historical manure and 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). 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 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 (Supplement Table S1). Each P_v reported by the measurement campaign was compared against the P_v at the corresponding grid cell in the model. For the 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 (Supplement Table S2). 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 (Fig. 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 °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).

3.1.2 Nitrogen volatilized as NH_3 from fertilizer

The comparison between measured and modeled annual average P_v from 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) (Fig. 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 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.

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3.1.3 Nitrogen run-off

Nevison et al. (2015) routes the nitrogen runoff from manure and fertilizer using the River Transport Model (RTM) (Dai and Trenberth, 2001; Branstetter and Erickson, 2003) within the CESM. Nevison et al. (2015) 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. (2015) 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 fertilizer and manure application during the present-day simulation are given in Potter et al. (2010) and are not repeated here. Heavy fertilizer use generally occurs in the upper Midwest of the US (mostly east of 100° W and north of 40° N), Western Europe (mostly west of 20° E and north of 40° N), the Northern part of India and much of Northeastern and North Central China. High manure usage coincides with the areas of heavy fertilizer use but is more widespread extending across much of Eastern South America from 20–40° S and across Africa at approximately 10° N.

3.2.2 Geography of nitrogen losses

There are strong geographical differences in the loss pathways of nitrogen following manure or 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, Figs. 4–8) is dependent on temperature, precipitation and soil moisture. In hot, arid climates, the percentage volatilized is high (Figs. 4 and 5). For example, regions of high NH_3 volatilization of applied manure N_r approach 50 % across the southwest US and Mexico, Eastern South America, central and southern Africa, parts of Australia, and across southern Asia from India to Turkey (Fig. 5). The absolute highest emissions of NH_3 from applied 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 (Figs. 4 and 5). Ammonia emissions from manure are more broadly distributed globally than those of fertilizer with high NH_3 emissions not only over the fertilizer hotspots, characterized by heavy application of both fertilizer and manure, but also over southeastern South America and central Africa. For the most part, the largest 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 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 fertilizer: Paulot et al. (2014) consider three different 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 fertilizer but with maximum emissions usually occurring in April–June or July–September. 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 fertilizer and manure applications as well as nitrification and diffusion into the soil depend on precipitation and soil moisture (see Appendix). High manure and fertilizer N_r run off (see Figs. 6 and 7) occur particularly across parts

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of China, Europe (particularly the Northern parts) and the East central US. The global hotspot for simulated N_r runoff is China where runoff approaches $20\,kg\,N\,ha^{-1}\,yr^{-1}$ for nitrogen applied as either in manure and fertilizer. However, we do find other regions where the nitrogen input is high but where simulated N_r runoff 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 °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

Globally, the loss of applied nitrogen to the atmosphere as NH_3 is similar for manure and fertilizer (17 % for manure, 20 % for fertilizer; see Fig. 9). Our global estimates of manure and fertilizer volatilized as NH_3 are similar to Bouwman et al. (2002) and Beusen et al. (2008), although our estimate for fertilizer volatilization as NH_3 is somewhat high. Bouwman et al. (2002) estimates 19–29 % of applied manure and 10–19 % of applied 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 fertilizer is lost.

We calculate the global run-off as 8 % for manure N_r and 9 % for fertilizer. Bouwman et al. (2011) find that 23 % of deposited N_r (comprised of fertilizer, manure and 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 may also occur from the soil nitrogen pools.

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

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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 run in a coupled mode with the atmosphere and is beyond the scope of the present study.

In the case of 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 %) (Fig. 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 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 or emissions, but these are not calculated in this initial study.

The percentages change appreciably when examined over subsets of countries (Fig. 10). For example, over all developed countries the percentage of emissions of manure and 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

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(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 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 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 fertilizer NH_3 emissions from our process oriented model and various bottom-up emission inventories, as collated by Paulot et al. (2014). The bottom-up inventories rely on emission factors depending on animal husbandry, types of 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. We supplement these estimates over North America with the Goebes et al. (2003) estimate to 1995 for synthetic fertilizer NH_3 emissions and the US EPA (2006) estimate for NH_3 emissions from animal agricultural operations. 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 fertilizer application dataset is valid circa 2000 and the manure application dataset is valid circa 2007 (Potter et al., 2010).

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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 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 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 US emissions are on the high side. In Europe the current parameterization underestimates the manure emissions compared to the other estimates, while the fertilizer emissions fall between the Paulot et al. (2014) and GAINS emission inventories and that of EDGAR. In the US the manure NH_3 emissions are close to the estimate of all the inventories except that of EDGAR while the fertilizer emissions are high compared to all inventories, although the fertilizer emissions are close to that of EDGAR. In China our 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 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 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 °C 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

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show some response to precipitation, particularly the diffusion which reaches a maximum near 21 May 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). Fertilizer TAN responds similarly during these events but the different temporal distribution of N application for fertilizer is clearly evident in these plots. The decrease in the 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

The nitrogen applied as manure increases in the historical simulation from 21 $Tg\,N\,yr^{-1}$ in 1850 to 125 $Tg\,N\,yr^{-1}$ in 2000 (Fig. 13). Emissions of NH_3 from applied manure increase from approximately 3 $Tg\,N\,yr^{-1}$ in 1850 to 22 $Tg\,N\,yr^{-1}$ in 2000. Bouwman et al. (2011) estimates that 35 $Tg\,N\,yr^{-1}$ is produced as manure in 1900 similar to our estimate of 37 $Tg\,N\,yr^{-1}$. The percentage of nitrogen applied as manure that volatilizes to NH_3 increases by 4 % since the preindustrial while the percentage of manure TAN nitrified decreases from 33 to 27 %. Fertilizer nitrogen application has increased dramatically since 1960 from essentially zero to 62 $Tg\,N\,yr^{-1}$ in 2000. Accompanying this increase, the volatilization of fertilizer reaches 12 $Tg\,N\,yr^{-1}$ in 2000.

For fertilizer there is an increase of emissions to the atmosphere and a decrease in nitrogen runoff. Since 1920 the percent of fertilizer nitrogen volatized to the atmosphere as NH_3 increases from 8 to 20 %, while the runoff has decreased by 8 %. It is evident

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that much of this change can be explained by the fact the fertilizer runoff can completely drain the TAN fertilizer pool at the small fertilizer application rate prior to 1960.

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 sensitivity tests for manure are given in Table 1, those for 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 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.

Except for changes in the canopy capture parameter (EX7m/f, EX8m/f) and changes in the timing or composition of manure or fertilizer inputs (EX17m, EX18f, EX19f, EX20f), changes in the sensitivity parameters directly change the nitrogen cycling within the TAN pool (as described below). For the most part the fertilizer and manure TAN pools respond similarly to the parameter changes. Note also, that except for EX17, 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 ±20 % with many processes within the range of ±10 %. 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 (EX13, EX14), the assumed depth of the water pool (EX11, EX12) and the maximum nitrification rate (EX15, EX16) all impact NH_3 emissions by less than 20 %. The sensitivity to the assumed background NH_3 concentration is also low (EX9, EX10). 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). The NH_3 emissions increase by a factor of 3–4 when the pH is changed from 6 to 8. Increased pH pushes the solution towards NH_3(aq) and away from NH_4^+(aq) (Eqs. 10 and 11). As NH_3(aq) is in equilibrium with NH_3(g) increased pH increases the concentration of NH_3(g) and consequently the NH_3 emissions. Decreased pH has the opposite effect. Changes in pH also have a large impact on the nitrification rate. 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 nitrification rate constant 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 EX7m/f, EX8m/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.

The NH_3 emissions are somewhat sensitive to the depth of the water pool (EX11m/f, EX12m/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 (Eqs. 7 and 11) and larger nitrogen runoff (Sect. 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 fertilizer applications. Early 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 15 March) decreases the NH_3 emissions by 23 % and increases the nitrogen runoff by 62 % (EX18f). To investigate the sensitivity to the application rate of fertilizer, fertilizer

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was applied over 20 days as opposed to the single day application assumed in the default version (EX19f). This did not have a significant impact on the emissions. The assumed fertilizer type in the default version of the model (urea) was replaced with ammonium nitrate fertilizer in EX20f. 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 fertilizers given in Bouwman (2002).

Finally we test the impact of manure composition on the NH_3 emissions (EX17f). 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 EX17m (41 % urine, 21 % available, 25 % unavailable and 13 % resistant, Smith, 1973). This decreased the NH_3 emissions by 21 %.

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 fertilizer or manure input assumptions are tested in simulations EX17m, EX18f, EX19f, EX20f; sensitivities to the water depth which may crudely represent some of the impacts of plowing manure or fertilizer into the soil are examined in EX11 and EX12; finally modifications to soil pH are tested in EX5 and EX6.

4 Discussion and conclusions

In this paper we develop a process-oriented model that predicts the climate dependent reactive nitrogen pathways from fertilizer and manure application to the surface of the land. Continued population growth will likely result in an increased application of inor-

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ganic 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 $21\,\mathrm{Tg\,N\,yr^{-1}}$ emitted from manure nitrogen and $12\,\mathrm{Tg\,N\,yr^{-1}}$ 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 in-

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ventories 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 nitrogen runoff 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., 2015).

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 by model ruminants. 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

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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 is highest in areas of high N_r 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 $3\,\mathrm{Tg\,N\,yr^{-1}}$ in 1850 to $22\,\mathrm{Tg\,N\,yr^{-1}}$ in 2000 while the volatilization of fertilizer reaches $12\,\mathrm{Tg\,N\,yr^{-1}}$ 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 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

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and synthetic fertilizer (Figs. 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 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 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 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 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 Orga-

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nization (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 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 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 fertilizer inputs in response to climate. This is relevant to current studies investigating the ecosystem effects of N_r, and in particular, how adding 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 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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Table 1. Manure sensitivity tests.

Exper[1]	Parameter[2]	Value[3]	NH_3[4]	Run[5]	Soil[6]	Nitrif.[7]	Canopy[8]	ΔNH_3[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	0.20
EX2m	k_m	$750\,d^{-1}$	20.8	10.7	16	25.9	31.2	+7	0.06
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	$f_{capture}$	0.4	29.2	10.2	15.2	32.3	19.5	+50	−1.3
EX8m	$f_{capture}$	0.8	9.7	10.2	15.2	32.3	38.9	−50	−2.2
EX9m	χ_a	$0.1\,\mu g\,m^{-3}$	20.0	9.9	14.7	31.8	30.0	+3	0.04
EX10m	χ_a	$10\,\mu g\,m^{-3}$	18.2	11.1	16.4	33.5	27.3	−7	0.0
EX11m	H_2O Depth	10 cm	16.0	7.7	20.7	37.9	24.1	−18	−0.18
EX12m	H_2O Depth	2 cm	23.1	13.4	8.2	27.1	34.6	+18	−0.31
EX13m	K_D	×0.5	20.7	11.6	9.4	33.8	31.0	+6	−0.12
EX14m	K_D	×2.0	17.8	8.5	22.9	30.4	26.8	−9	−0.09
EX15m	r_{max}	×0.5	20.7	11.0	16.7	27.0	31.1	+6	−0.12
EX16m	r_{max}	×2.0	17.5	9.0	13.0	40.5	26.3	−10	−0.10
EX17m	*manure comp*[12]		15.4	8.4	12.5	23.8	23.1	−21	

[1] Experiment name.
[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 ($Tg\,N\,yr^{-1}$).
[7] Nitrification ($Tg\,N\,yr^{-1}$).
[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] Change in manure composition to urine 41 %, available 21 %, unavailable 25 %, and resistant 13 %.

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Table 2. Fertilizer sensitivity tests.

Exper[1]	Parameter[2]	Value[3]	NH_3[4]	Run[5]	Soil[6]	Nitrif.[7]	Canopy[8]	ΔNH_3[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	−0.06
EX4f	k_{relax}	$10\,d^{-1}$	10.1	4.7	13.7	10.9	15.1	−7	−0.03
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	$f_{capture}$	0.4	16.3	5.3	12.3	9.8	10.9	+50	−1.2
EX8f	$f_{capture}$	0.8	5.4	5.3	12.3	9.8	21.7	−50	−2.1
EX9f	χ_a	$0.1\,\mu g\,m^{-3}$	10.9	5.2	12.3	9.8	16.3	+0	0.0
EX10f	χ_a	$10\,\mu g\,m^{-3}$	10.8	5.3	12.4	9.9	16.1	−1	0.0
EX11f	H_2O Depth	10 cm	9.0	4.0	15.2	12.9	13.4	−17	−0.17
EX12f	H_2O Depth	2 cm	12.9	6.8	8.3	7.2	19.3	+18	−0.31
EX13f	K_D	×0.5	11.8	6.1	7.6	11.3	17.7	+8	−0.17
EX14f	K_D	×2.0	9.6	4.2	18.3	7.9	14.4	−12	−0.12
EX15f	r_{max}	× 0.5	11.8	5.8	13.7	5.5	17.7	+8	−0.17
EX16f	r_{max}	× 2.0	9.4	4.4	10.3	16.3	14.2	−14	−0.14
EX18f	*Fert. Date*[12]		8.4	8.6	15.5	8.6	12.6	−23	
EX19f	*Fert. Rate*[13]		11.3	5.6	11.5	9.1	17.0	+4	
EX20f	*Fert Decomp*[14]		10.5	4.9	12.9	10.5	15.7	−4	

[1] Experiment name.
[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 ($Tg\,N\,yr^{-1}$).
[7] Nitrification ($Tg\,N\,yr^{-1}$).
[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] Change in fertilizer date to 20 March (NH) and 20 September (SH).
[13] Apply fertilizer over 20 days.
[14] Assume fast release ammonium nitrate decay of fertilizer.

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Table A1. 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	$N_{available}$	$g\,m^{-2}$	$dN_{available}/dt = f_a \times \alpha_{applied}(m) - K_a \cdot N_{available} - k_m \cdot N_{available}$	
Pool of nitrogen from applied manure that is resistant to forming TAN	$N_{resistant}$	$g\,m^{-2}$	$dN_{resistant}/dt = f_r \times \alpha_{applied}(m) - K_r \cdot N_{resistant} - k_m \cdot N_{resistant}$	
Pool of nitrogen from applied manure that does not form TAN	$N_{unavailable}$	$g\,m^{-2}$	$dN_{unavailable}/dt = f_{un} \times \alpha_{applied}(m) - k_m \cdot N_{unavailable}$	
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	$N_{TAN(m)}$	$g\,m^{-2}$	$N_{TAN}(m)/dt = f_u \times \alpha_{applied} + K_r \cdot N_{resistant} + K_a \cdot N_{available} - K_w \cdot N_{TAN}(m) - K_D^{NH_4} \cdot N_{TAN}(m) - F_{NH_3}(m) - F_{NO_3}(m)$	
Pool of nitrogen in TAN pool from fertilizer	$N_{TAN(f)}$	$g\,m^{-2}$	$N_{TAN}(f)/dt = k_f \cdot N_{fertilizer} - K_w \cdot N_{TAN}(f) - K_D^{NH_4} \cdot N_{TAN}(f) - F_{NH_3}(f) - F_{NO_3}(f)$	
Pool of surface NO_3^-	N_{NO_3}	$g\,m^{-2}$	$dN_{NO_3}/dt = F_{NO_3}(m/f) - K_D^{NO_3} \cdot N_{NO_3}$	
Pool of manure/fertilizer 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	$dN_{water}(f)/dt = S_w(f) \times \alpha_{applied}(f) - k_{relax} \times (N_{water}(f) - M_{water})$	

Table A1. Continued.

Description	Symbol	Unit	Value Used or Equation	Reference
Variables from CLM				
Ground Temperature	T_g	K	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 and Kissel (1995)
Resistant manure decomposition	K_r	s^{-1}	$K_r = k_{a2} T_R(T_g)$	Gilmour et al. (2003); Vigil and Kissel (1995)
Temperature dependence for K_a, K_r	T_R	NA	$T_R(T_g) = t_{r1} \exp(t_{r2}(T_g - 273.15))$	Vigil and 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	$K_D^{NH_4}$	s^{-1}	$K_D^{NH_4} = (1/l^2) \cdot (\Theta_w^{10/3}/\varphi^2)_{NH_4}^{aq}$	Génermont and Cellier (1997)
NO_3^- loss rate to soil pool	$K_D^{NO_3}$	s^{-1}	$K_D^{NO_3} = (1/l^2) \cdot (\Theta_w^{10/3}/\varphi^2)_{NO_3}^{aq}$	Génermont and Cellier (1997)
Base vertical diffusion for TAN pool	$\chi_{NH_4}^{aq}$	m^2 s^{-1}	$\chi_{NH_4}^{aq} = 9.810^{-10} \cdot 1.03^{(T_g - 273.15)}$	Génermont and Cellier (1997)
Base vertical diffusion for NO_3 pool	$\chi_{NO_3}^{aq}$	m^2 s^{-1}	$\chi_{NO_3}^{aq} = 1.310^{-8} \cdot 1.03^{(T_g - 273.15)}$	Génermont and Cellier (1997)
Water Content	Θ_w		$\Theta_{w=} N_{water}(m/f)/H$	

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Table A1. Continued.

Description	Symbol	Unit	Value Used or Equation	Reference
Flux of nitrogen lost as NH_3 for manure (m) or fertilizer (f)	$F_{NH_3}(m/f)$	$g\,m^{-2}\,s^{-1}$	$F_{NH_3}(m/f) = \frac{NH_3(g)(m/f)-\chi_a}{(R_a(z)+R_b)}$	Nemitz et al. (2000); Loubet et al. (2009); Sutton et al. (2013)
Flux of NH_3 to atmosphere	$F_{NH_{3atm}}(m/f)$	$g\,m^{-2}\,s^{-1}$	$F_{NH_{3atm}}(m/f) = (1 - f_{capture}) \times F_{NH_3}(m/f)$	e.g., Wilson et al. (2004)
$NH_3(g)$ in equilibrium with the TAN manure (m) or fertilizer (f) pool	$NH_3(g)\ (m/f)$	$g\,m^{-3}$	$NH_3(g)(m/f) = \frac{N_{TAN}(m/f)/N_{water}(m/f)}{1+K_H+K_H[H^+]/K_{NH_4}}$	Derived from Sutton et al. (1994)
Henry's Law Constant for NH_3	K_H		$K_H = 4.59\,(^{\circ}K^{-1}) \cdot T_g \cdot \exp^{4092\left(1/T_g-1/T_{ref}\right)}$	Sutton et al. (1994)
Dissociation Equilibrium Constant for $NH_3(aq)$	K_{NH_4}	$mol\,L^{-1}$	$K_{NH_4} = 5.67\,10^{-10}\exp^{-6286\left(1/T_g-1/T_{ref}\right)}$	Sutton et al. (1994)
Flux of nitrogen from TAN to NO_3^- pool	$F_{NO_3}(m/f)$	$g\,m^{-2}\,s^{-1}$	$F_{NO_3}(m/f) = \frac{2 \cdot r_{max} N_{TAN}(m/f) K_H [H^+]/K_{NH_4}}{\frac{1}{\Sigma(T_g)} + \frac{1}{\Pi(M)}}$	Stange and Neue (2009); Parton et al. (2001)
Soil temperature function	$\Sigma\,(T_g)$		$\Sigma\,(T_g) = \left(\frac{t_{max}-T_g}{t_{max}-t_{opt}}\right)^{a_\Sigma} \exp\left(a_\Sigma\left(\frac{T_g-t_{opt}}{t_{max}-t_{opt}}\right)\right)$	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	$S_w(f)$	$m^3\,g^{-1}$	$S_w(f) = \frac{1 \times 10^{-6}}{0.466 \times 0.66 \times e^{0.0239 \times (T_g-273)}}$	UNIDO and FIDC (1998)

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Table A1. Continued.

Description	Symbol	Unit	Value Used or Equation	Reference
Parameters				
Flux of manure nitrogen applied to the surface	$\alpha_{\text{applied}}(m)$	$\text{g m}^{-2}\,\text{s}^{-1}$	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	$\alpha_{\text{applied}}(f)$	$\text{g m}^{-2}\,\text{s}^{-1}$	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}	NA	$f_u = 0.5$, $f_a = 0.25$, $f_r = 0.225$, $f_{un} = 0.025$	Gusman and Marino (1999)
Mechanical incorporation of manure into soil	k_m	s^{-1}	$k_m = (365 \times 86\,400)^{-1}$	see Koven et al. (2013)
Fertilizer Decomp-osition	k_f	s^{-1}	$k_f = 4.83 \times 10^{-6}$	Agehara and Warncke (2005)
Water : N ratio in applied manure	$s_w(m)$	$\text{m}^3\,\text{g}^{-1}$	$s_w(m) = 5.67 \times 10^{-4}$	Sommer and Hutchings (2001)
Relaxation rate of TAN water pool to soil water pool	k_{relax}	s^{-1}	$k_{\text{relax}} = (3 \times 86\,400)^{-1}$	
Empirical factors for K_a, K_r	k_{a1} k_{a2}	s^{-1}	$k_{a1} = 8.94 \times 10^{-7}\,\text{s}^{-1}$, $k_{a2} = 6.38 \times 10^{-8}\,\text{s}^{-1}$	Gilmour et al. (2003)
Empirical factors for T_r	t_{r1}, t_{r2}	K^{-1}	$t_{r1} = 0.0106$, $t_{r2} = 0.12979\,\text{K}^{-1}$	Vigil and Kissel (1995)
Length Scale	l	m	$l = 10^{-2}\,\text{m}$	
Soil Porosity	ϕ		$\phi = 0.5$	
Depth of Soil Water Pool	H	m	$H = 5.0 \times 10^{-2}$	

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Table A1. Continued.

Description	Symbol	Unit	Value Used or Equation	Reference
Atmospheric NH_3 concentration	χ_a	$g\,m^{-3}$	$\chi_a = 0.3 \times 10^{-6}\,g\,m^{-3}$	Zbieranowski and Aherne (2012)
Fraction of ammonia emissions capture by canopy	$f_{capture}$		$f_{capture} = 0.6$	e.g., see Wilson et al. (2004)
Concentration of Hydrogen Ions	$[H^+]$	$mol\,L^{-1}$	$[H^+] = 10^{-7}$	
Reference Temperature	T_{ref}	K	$T_{ref} = 298.15$	Sutton et al. (1994)
Maximum rate of nitrification	r_{max}	s^{-1}	$r_{max} = 1.16 \times 10^{-6}$	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}	$kg\,m^{-3}$	$\rho_{soil} = 1050.$	

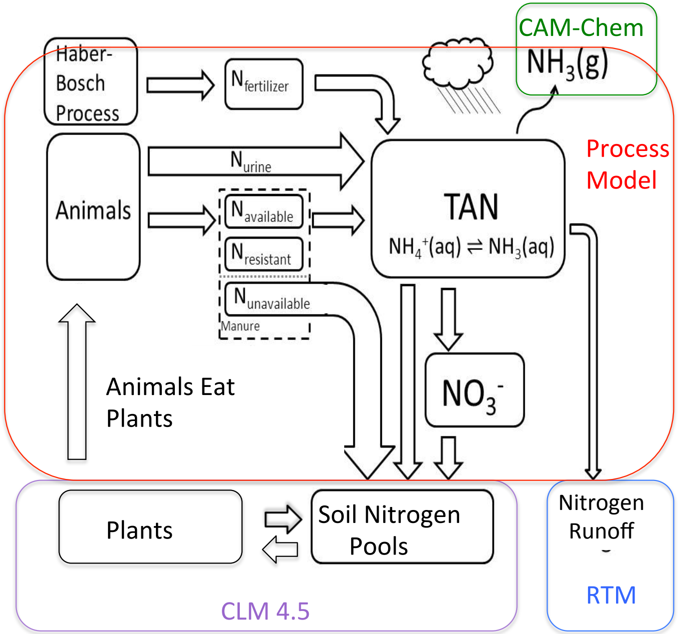

Figure 1. Schematic of the Process Model for the addition of manure and fertilizer to the CESM nitrogen cycle. Some minor pathways are not shown. Soil nitrogen pools and and plant nitrogen exist in CLM4.5. Urine nitrogen (N_{urine}) is directly input to the TAN pool while fecal matter is split into three 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.

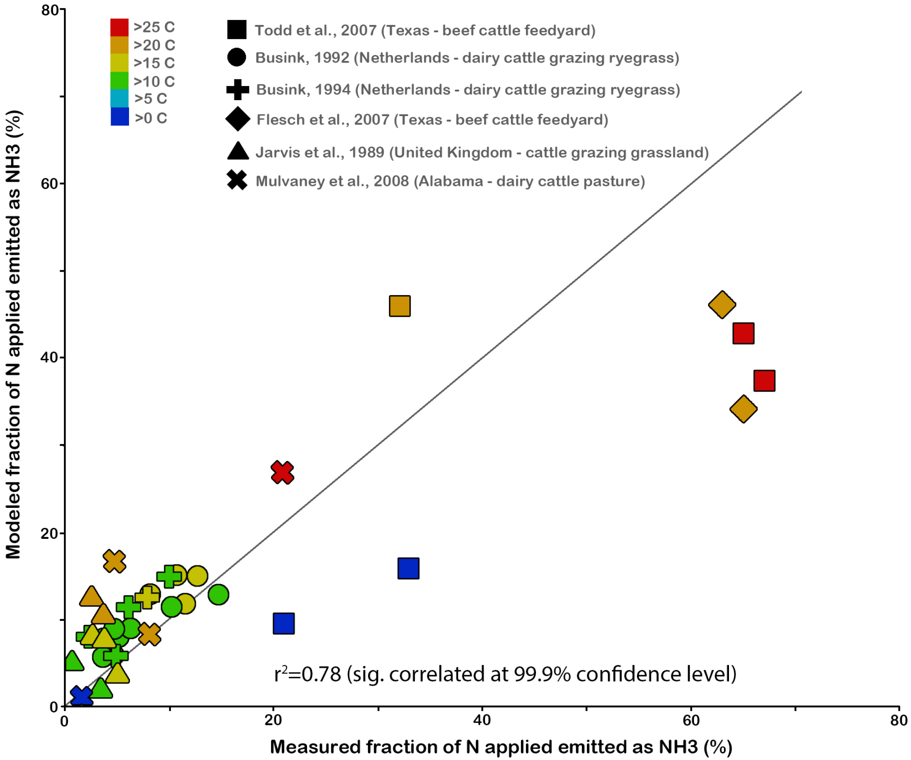

Figure 2. Comparison of model to measurements for percentage of nitrogen lost as NH_3 emissions from manure for a range of studies (see Supplement Table S1). Symbol color measures temperature at which emissions were made; shape gives the study.

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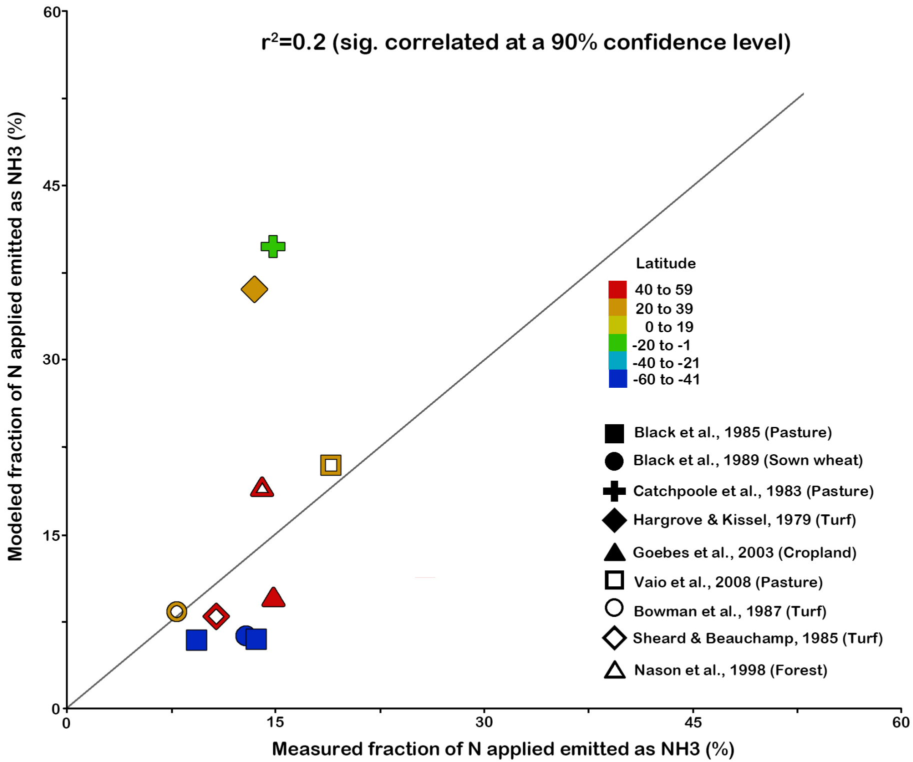

Figure 3. Comparison of model to measurements for percentage of nitrogen lost as NH_3 emissions from fertilizer (see Supplement Table 2). Symbol color gives the latitude at which the measurement was made; symbol shape gives the study and type of fertilizer application.

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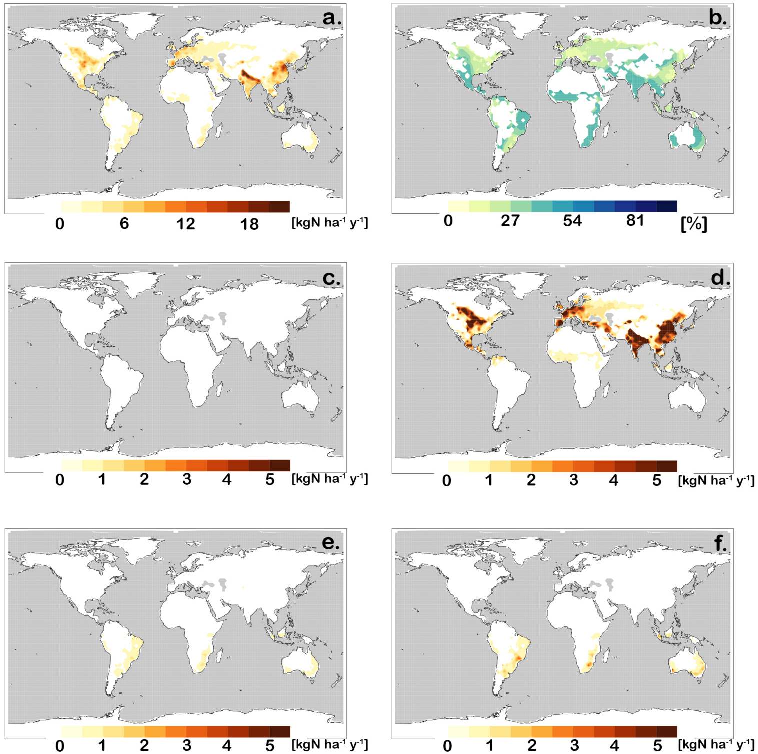

Figure 4. Simulated NH_3 emissions from fertilizer application from 1995–2004 for the present-day control simulation. Simulated emissions ($kg\,N\,ha^{-1}\,yr^{-1}$) as **(a)** an annual average, **(c)** January–February–March average, **(d)** April–May–June average, **(e)** July–August–September average, and **(f)** October–November–December average. Simulated emissions as a percent of annual fertilizer application, **(b)**.

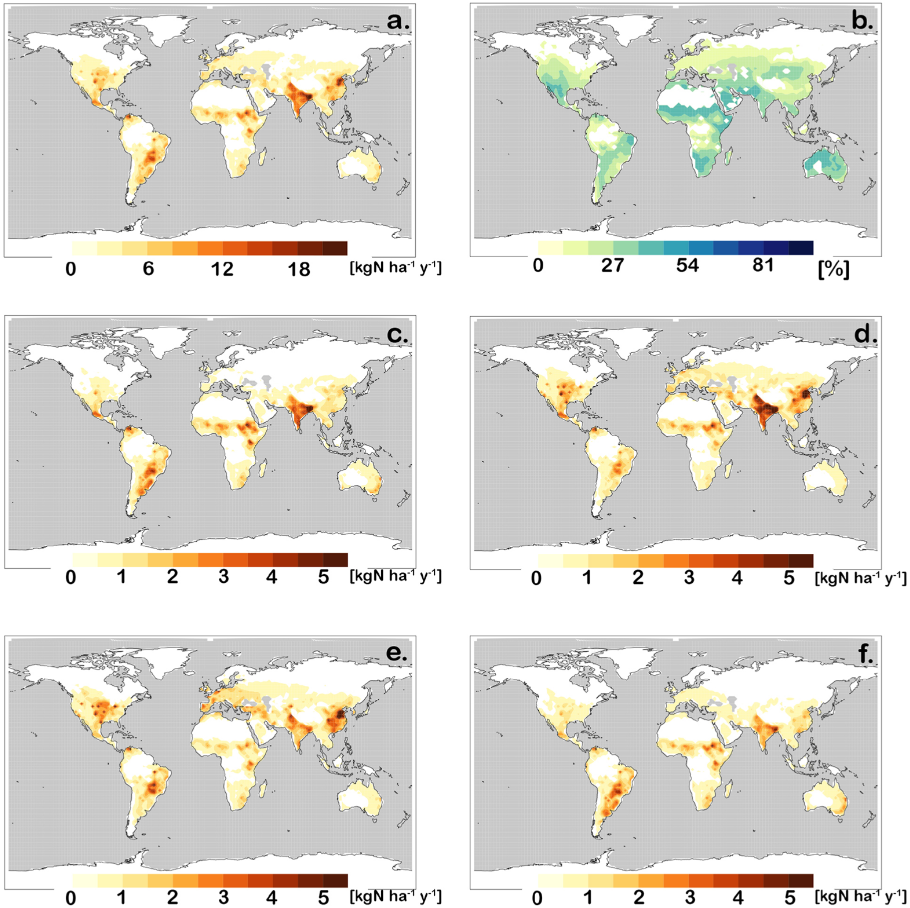

Figure 5. As in Fig. 4 but for manure application.

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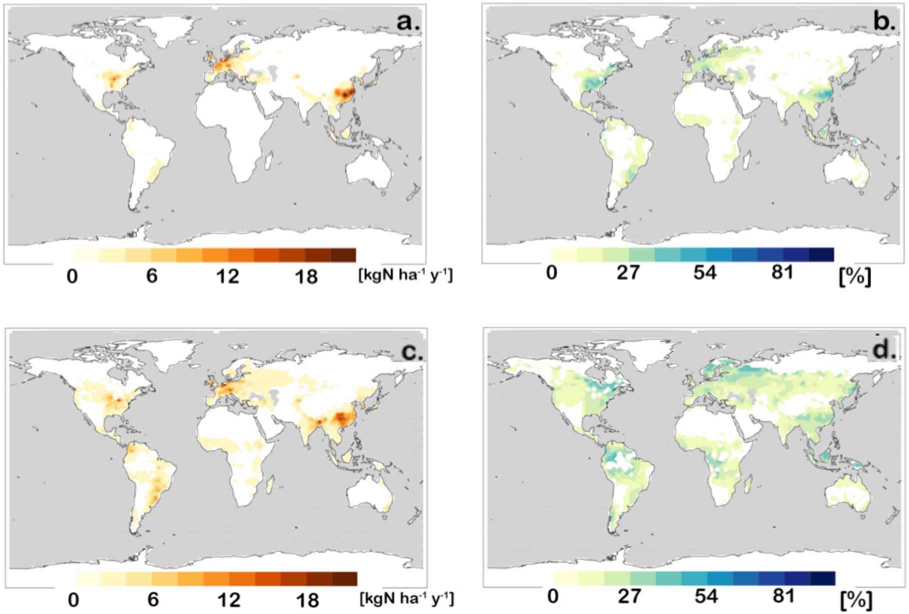

Figure 6. Simulated runoff from fertilizer and manure application from 1995–2004 for the present-day control simulation. Simulated runoff (kg N ha^{-1} yr^{-1}) as an annual average for **(a)** fertilizer, **(c)** manure. Simulated as **(b)** percent of annual fertilizer application, **(d)** percent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

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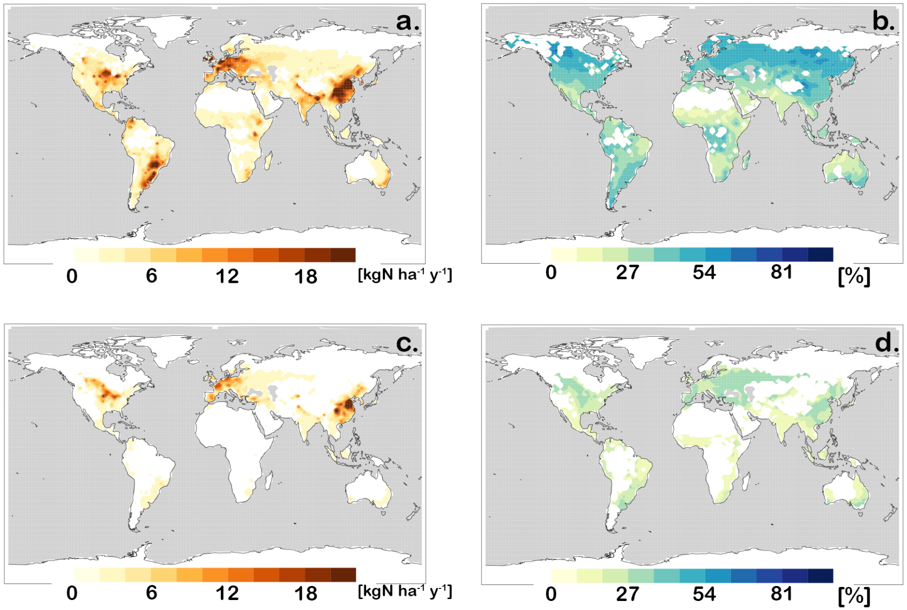

Figure 7. As in Fig. 6, but for simulated nitrification.

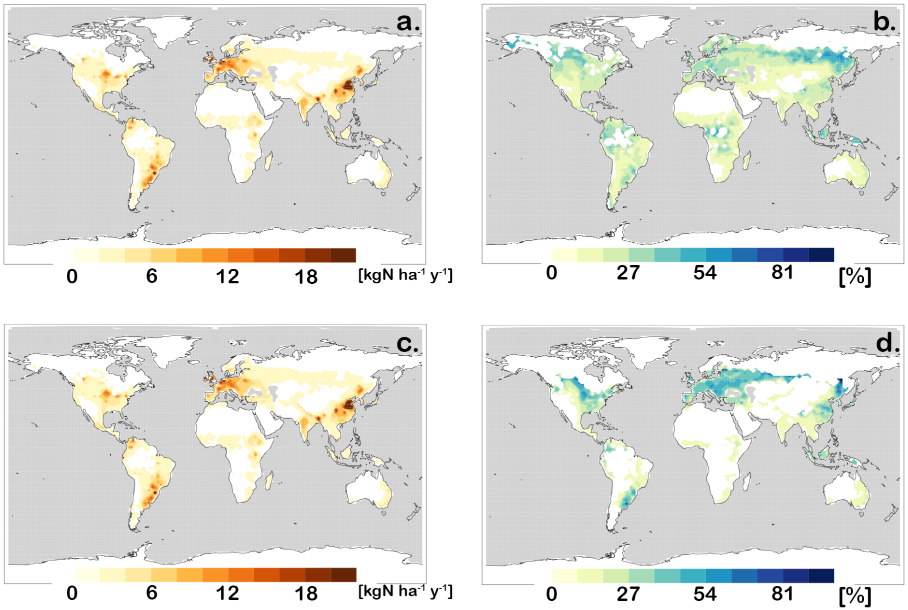

Figure 8. As in Fig. 6 but for flux of TAN nitrogen to the soil.

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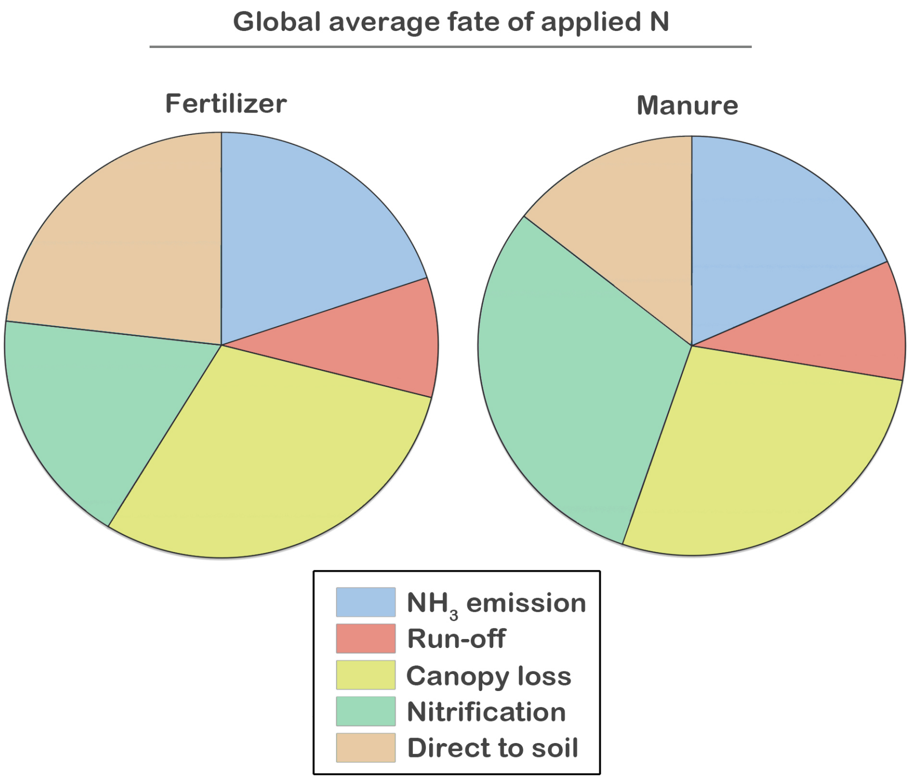

Figure 9. Global Fate of TAN N_r applied as fertilizer (left) or as manure (right). Emissions are split between those to the atmosphere and those captured by the canopy.

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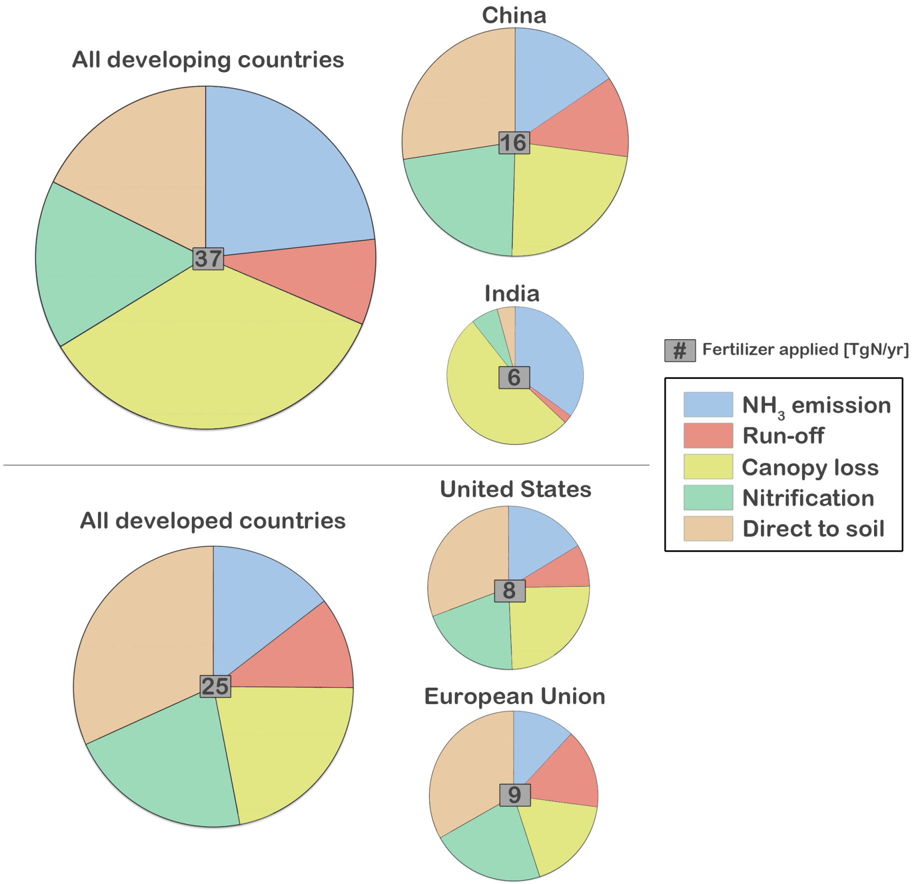

Figure 10. As in Fig. 9, but fate of TAN nitrogen by country and region. Countries are split between developed countries and developing countries.

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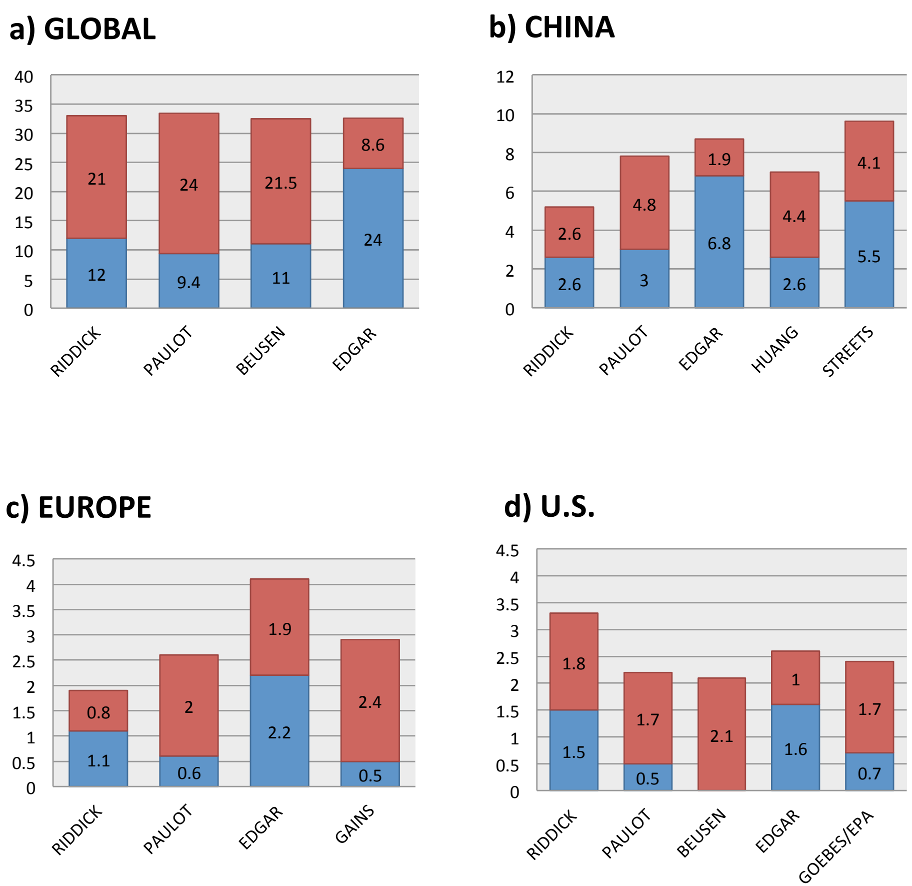

Figure 11. Comparison of manure (red) and fertilizer (blue) ammonia emissions ($\mathrm{Tg\,N\,ha^{-1}\,yr^{-1}}$) **(a)** globally, **(b)** China, **(c)** Europe and **(d)** US for this study (Riddick) and for other studies as collated by Paulot et al. (2014). Details on other studies in text.

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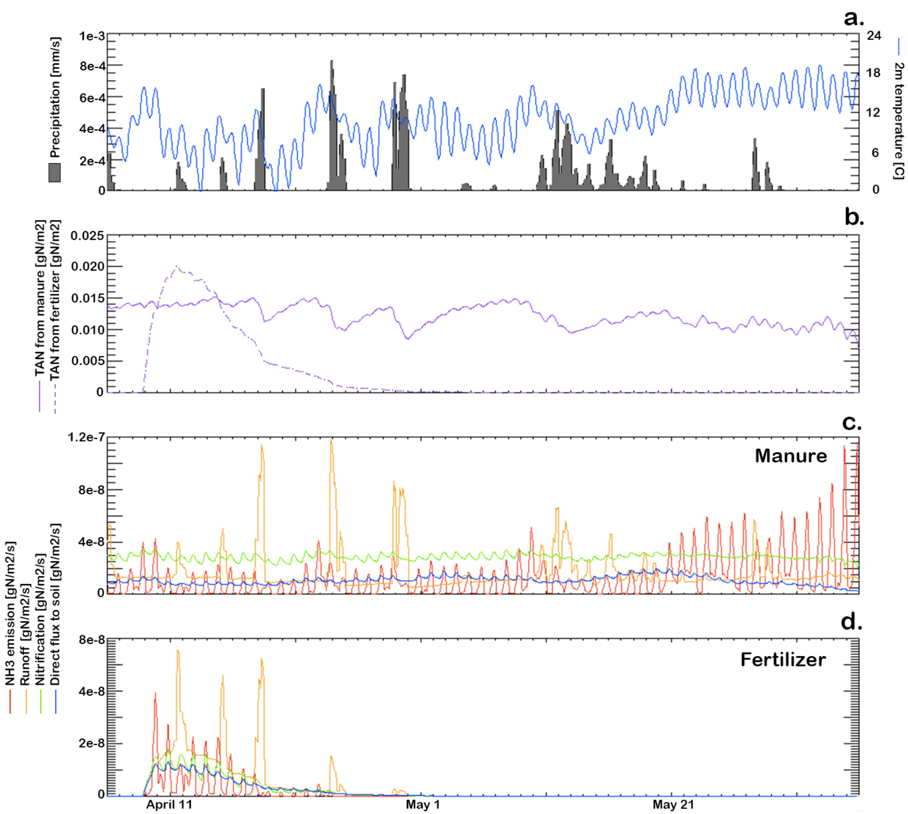

Figure 12. Site specific pathways for nitrogen budget at 35° N and 100° W, near the Texas panhandle. Panels show **(a)** the temperature (°C) and precipitation ($mm\,s^{-1}$) used to force the CLM, **(b)** the manure (solid) and fertilizer TAN pools (dashed) ($g\,N\,m^{-2}$), and the four major loss 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.

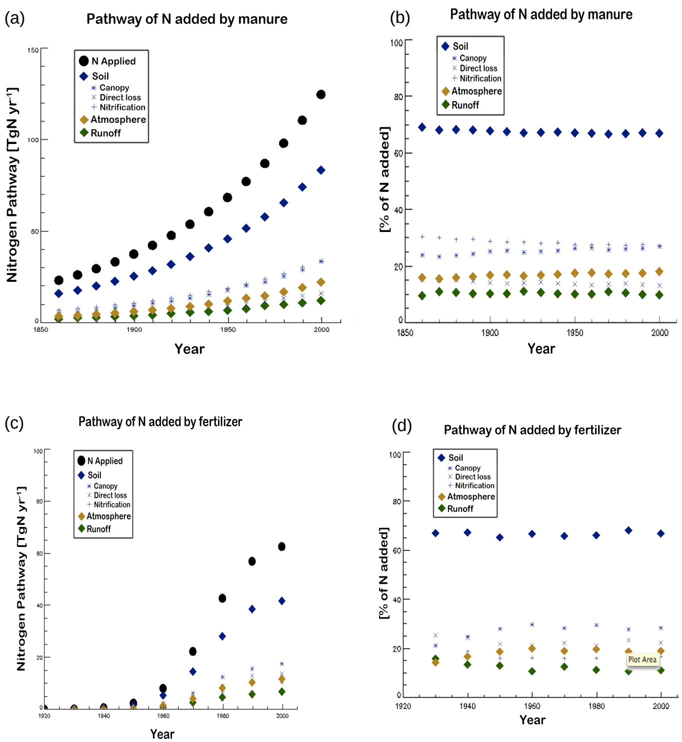

Figure 13. Applied nitrogen and nitrogen losses for the historical simulation in $\mathrm{Tg\,N\,yr^{-1}}$ for **(a)** manure and **(c)** fertilizer. Nitrogen losses from the TAN pool as a percentage of applied nitrogen for the historical simulation for **(b)** manure and **(d)** fertilizer. The losses 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 Sect. 3.2.3).

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