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Isotopic identification of global nitrogen hotspots across natural terrestrial ecosystems

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Abstract

Nitrogen (N) influences local biological processes, ecosystem productivity, the composition of the atmospheric-climate system, and the human endeavour as a whole. Here we use natural variations in N's isotopes, coupled with two models, to trace global pathways of N loss from the land to the water and atmosphere. We show that denitrification accounts for approximately 35 % of total N losses from natural soil, with NO, N_2O, and N_2 fluxes equal to 15.7 ± 4.7 Tg N yr^{-1}, 10.2 ± 3.0 Tg N yr^{-1}, and 21.0 ± 6.1 Tg N yr^{-1}, respectively. Our analysis points to tropical regions as the major "hotspot" of nitrogen export from the terrestrial biosphere, accounting for 71 % of global N losses from the natural land surface. The poorly studied Congo basin is further identified as one of the major natural sources of atmospheric N_2O. Extra-tropical areas, by contrast, lose a greater fraction of N via leaching pathways (~77 % of total N losses), than do tropical biomes, likely contributing to N limitations of CO_2 uptake at higher latitudes. Our results provide an independent constraint on global models of the N cycle among different regions of the unmanaged biosphere.

1 Introduction

Nitrogen (N) is essential to all life and affects many different aspects of the Earth system as a whole. At the molecular scale, for instance, N is a significant component of nucleic acids, protein and other biomolecules that regulate a suite of cell functions. At larger scales, N influences the climate system via its direct impact on climate forcing and indirectly via its role in constraining CO_2 uptake and storage on land and in the sea (Fig. 1). Consequently, biogeochemists, climatologists, and ecologists are fundamentally interested in understanding how N cycles among Earth's biomes and across a spectrum space-time scales – especially in terms of how much N enters and leaves the biosphere along dissolved vs. gaseous paths.

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However, two principal factors have greatly challenged this objective. First, N_2 – likely the dominant gaseous N product of soil bacteria – is difficult to measure accurately because of the large background concentration of N_2 in air (Scholefield et al., 1997; Swerts et al., 1995). This challenge has sparked controversies over the "missing N" in the global N budget (Galloway et al., 2004). Second, emissions of NO, N_2O or N_2 can vary significantly in space and time; hence, scaling up field measurements, using either empirical or computational models, imparts large, unexplained errors in estimates of gaseous N emissions (Matson et al., 1989; Galloway et al., 2004; Scheer et al., 2009; Butterbach-Bahl et al., 2002; McClain et al., 2003; Groffman et al., 2009). Consequently, modeling has become an essential tool for estimation of N gas emissions at regional to global scales.

Boyer et al. (2006) reviewed current approaches for modeling terrestrial N gas fluxes at regional scales. The two basic approaches involve either mass-balance (Howarth et al., 1996) or simulation models, particularly DAYCENT (Parton et al., 1998), DNDC (denitrification-decomposition) (Li et al., 1992), CASA (Carnegie-Ames-Stanford) (Potter et al., 1996), EPIC (erosion-productivity impact calculator) (Williams et al., 1984), and INCA (integrated nitrogen in catchment) (Whitehead et al., 1998). These latter models build on various rate-controlling properties of denitrification such as climatic, soil, nutrient, and land use characteristics. They are generated to varying degrees from empirical measurements that are extrapolated from lab and field studies to ecosystems, regions and the globe. However, due to the complexities in N transformations, these models are generally highly parameterized and poorly constrained by observations that integrate large scales of space and time. In addition, it is difficult to obtain good estimates of some spatially heterogeneous variables and some input data are not available at the global scale (Groffman et al., 2009).

Natural variations in N isotope abundance have provided insights into large-scale N dynamics of ecosystems on land and in the sea (Amundson and Baisden, 2000; Houlton et al., 2006; Handley et al., 1999; Brenner et al., 2001; Amundson et al., 2003; Houlton and Bai, 2009; Bai and Houlton, 2009; Altabet et al., 1995; Sigman et al.,

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2003; Devol et al., 2006). The stable isotopes of N, ^{15}N and ^{14}N, vary naturally in their abundance among biogenic materials owing to isotope fractionations, particularly kinetic ones, which are commonly associated with organisms' enzymatic preferences for isotopically light N (^{14}N) (Kendall, 1998). Within the terrestrial biosphere, coherent patterns in the N isotope composition of soils and ecosystems are observed across gradients in temperature, precipitation, and latitude (Handley et al., 1999; Amundson et al., 2003; Craine et al., 2009). Such $^{15}N/^{14}N$ patterns in total soil N pools reflect the dominant pathways by which N enters and leaves ecosystems (Amundson et al., 2003; Houlton et al., 2006; Bai and Houlton, 2009; Houlton and Bai, 2009). Houlton and Bai (2009) have developed an isotopic approach to partition the N losses between gaseous and leaching vectors for the natural land biosphere. However, their approach did not consider regional-scale variations in N loss fractions, fluxes or forms; rather it lumped the natural terrestrial environment into a single vector. Here we extend on Houlton and Bai (2009)'s approach by partitioning gaseous N losses into NO, N_2O and N_2 across different sectors of the unmanaged land biosphere, thereby identifying the major natural hot spots of leaching and denitrification (including NO, N_2O, and N_2) among regions. We then compare our estimates with other independent estimates of N gaseous emissions based on past analyses, including process-based modeling, statistical modeling, mass-balance calculations and satellite-based approaches.

Our approach involves three phases (Fig. 2). First, we use estimates of the N isotope composition of soils to constrain the proportion of N lost to denitrification vs. leaching pathways across different terrestrial ecosystems. Second, we use two separate models to provide spatially explicit estimates of N fixation (Wang and Houlton, 2009) and N deposition inputs (Lelieveld and Dentener, 2000) and thereby convert our N loss proportions to steady-state fluxes. Third, we use a simple model to further partitioning denitrification gases into the various N gas fates, including NO, N_2O and N_2 fates. In the case of NO, we compare the modeled results to satellite-based estimates of NO_2 emissions over the continent of Africa.

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2 Materials and methods

2.1 Nitrogen isotope model

N isotope ratios are presented in delta notation:

$$\delta = [(R_{\text{sample}} - R_{\text{STD}})/R_{\text{STD}}] \times 10^3 \quad (1)$$

where R_{sample} is the $^{15}N/^{14}N$ ratio of the sample and R_{STD} is the $^{15}N/^{14}N$ ratio of the atmospheric dinitrogen.

Our N isotope model is based on the conceptual model of controls on whole-ecosystem $^{15}N/^{14}N$ (Houlton et al., 2006). Under steady state conditions, internal N cycling processes (plant uptake and microbial uptake) do not influence bulk soil $^{15}N/^{14}N$ ratios because they are recycling N as opposed to affecting overall N balances (Bai and Houlton, 2009; Brenner et al., 2001; Houlton et al., 2006). This lack of internal N cycle control on $^{15}N/^{14}N$ has been proven mathematically (Brenner et al., 2001; Amundson et al., 2003; Houlton et al., 2006; Bai and Houlton, 2009) and is supported by empirical observations across a broad range of climatic and ecosystems conditions (Bai and Houlton, 2009; Houlton et al., 2006; Houlton and Bai, 2009). Although further inquiry into potential plant and microbial recycling effects on ecosystem $^{15}N/^{14}N$ would be useful in general (see discussion), we apply the steady-state assumption in our analysis of the N cycle here, consistent with other global biogeochemical modeling efforts (Potter et al., 1996; Bouwman et al., 2005a; Mayorga et al., 2010; Howarth et al., 1996). Thus we focus on N inputs that occur via deposition and fixation and losses from soil along gaseous (ammonia-volatilization/nitrification/denitrification) ($f_{\text{gas all}}$) and leaching pathways (f_{leaching}). Hence we derive the following set of equations:

$$\delta^{15}N_{\text{soil}} = \delta^{15}N_{\text{I}} + \varepsilon_{\text{gas\_all}} \times f_{\text{gas\_all}} + \varepsilon_{\text{L}} \times f_{\text{leaching}} \quad (2)$$

$$f_{\text{gas\_all}} + f_{\text{leaching}} = 1 \quad (3)$$

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where $\delta^{15}N_{soil}$ is the isotopic composition of bulk soil; $\delta^{15}N_I$ is that of atmospheric inputs; and ε_L and ε_{gas_all} is the enrichment factor for leaching and gaseous losses, respectively [ε (‰) = $(^{14}k/^{15}k - 1) \cdot 1000$].

Gaseous loss pathways include nitrification/denitrification processes and ammonia volatilization. In our model, denitrification includes both denitrification and nitrifier-denitrification, since these bacterial-groups fractionate N isotopes similarly (Sutka et al., 2006). From this point forward, "N gas" refers to collective denitrification; we account for the magnitude and isotopic impact of ammonia volatilization using results from previous models. We further partitioned $f_{gas\,all}$ to f_{gas} and f_{NH3}:

$$\varepsilon_{gas\_all} \times f_{gas\_all} = \varepsilon_G \times f_{gas} + \varepsilon_{NH3} \times f_{NH3} \quad (4)$$

$$f_{gas} + f_{NH3} = f_{gas\_all} \quad (5)$$

From Eqs. (2), (3), (4), and (5) one gets:

$$f_{gas} = \frac{\delta^{15}N_{soil} - \delta^{15}N_I - (\varepsilon_{NH3} - \varepsilon_L) \times f_{NH3} - \varepsilon_L}{\varepsilon_G - \varepsilon_L} \quad (6)$$

The N inputs to natural ecosystems via fixation and deposition have relatively low $^{15}N/^{14}N$ ratios that do not appear to vary substantially from system to system. N_2 fixation, for example, does not appear to fractionate N_2 in air; its $\delta^{15}N$ is close to 0‰ (Boddey et al., 2000; Yoneyama et al., 1986; Shearer and Kohl, 1986). In addition, the isotopic composition of deposited N is typically in the range of −3‰ to 3‰ (Buzek et al., 1998; Handley et al., 1999; Freyer et al., 1996; Houlton et al., 2006), with bulk nitrate deposition across various latitudes, altitudes, climates and biomes averaging $\delta^{15}N$ of −1.5‰ (Houlton and Bai, 2009). While ammonium and dissolved organic N compounds can also be deposited, their $^{15}N/^{14}N$ ratios either overlap with or are somewhat ^{15}N-depleted relative to that of nitrate in bulk precipitation (Cornell et al., 1995; Heaton et al., 1997; Houlton et al., 2006). Combining both fixation and deposition inputs, $\delta^{15}N_I$ is thus in the range of −1.5‰ to 0‰, in accord with previous syntheses (i.e., −2‰ to 1‰ (Handley et al., 1999)).

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Although N leaching pathways could remove low δ^{15}N compounds from soil (ε_L) in principle, empirical data suggest that the discrimination is small. Shi (1992) found the fractionation factor of losses by dissolved NH_4^+-N was 0‰ to 0.5‰. Feuerstein et al. (1997) reported that δ^{15}N of DON was 1–2‰ lower than coexisting particulate organic matter in surface water of the Great Lakes. Densmore et al. (2000) noted the difference between δ^{15}N of soil total N and δ^{15}N of leachable N was within 1‰ at Irwine and Bicycle basins in California. Houlton et al. (2006) found that the difference between the δ^{15}N stream total dissolved N and soil total N was no more than 1–2‰ across a suite of Hawaiian forests. Finally, Houlton and Bai (2009) found that the δ^{15}N of nitrate in small drainage streams was very close to that of soil particulate matter from arctic to tropical biomes, with an integrated ε_L equal to 0.85‰. This latter analysis pointed to uniformly small isotope effect expression of nitrification at the scale of entire ecosystems. Thus, we use a ^{15}N discrimination of 1‰ for ε_L in our model parameterization scheme, and 0‰–5‰ in our model uncertainty analysis (see below).

Gaseous N losses substantially discriminate against ^{15}N along three major paths – denitrification, nitrification, and ammonia volatilization. Isotope fractionation during ammonia volatilization is high (ε_{NH3}, 29‰ based on Hogberg, 1997), and has been shown to elevate the δ^{15}N of heavily grazed terrestrial ecosystems; however, ammonia volatilization from soils under natural vegetation accounts for a small fraction of N losses, less than 5% of total gaseous losses (Bouwman et al., 1997). Consequently, this process plays a minor role in elevating $\delta^{15}N_{soil}$ globally. By contrast, bacterial pathways of gaseous N removal lead to significant ^{15}N enrichments – and with a flux that is large enough to substantially elevate the δ^{15}N of soil above atmospheric N inputs. Indeed, the average isotope effect of denitrification on nitrate is substantial in both pure culture (~20‰) (Wellman et al., 1968) and in natural soil communities (~16‰) (Houlton and Bai, 2009). Consistent with empirical studies, we assume that nitrifier and denitrifier gases impart similar fractionations of N isotopes (Yoshida, 1988; Jinuntuya-Nortman et al., 2008), and we use a combined enrichment factor (ε_G) to represent the isotope effect of both processes on terrestrial $^{15}N/^{14}N$. We use an ε_G of 16‰ in our

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model parameterization, allowing it to vary between 16 ‰–20 ‰ in our model uncertainty analysis (see below).

Finally, geographic distributions of $\delta^{15}N_{soil}$ are relatively well known, with many compilations pointing to similar patterns across Earth's major ecosystems (Amundson et al., 2003; Handley et al., 1999; Martinelli et al., 1999). To estimate $\delta^{15}N$ at the scale of regions and biomes, we use the large-scale (i.e., regions, biomes) assessment in Amundson et al. (2003), which is based on empirical modelling. The range of $\delta^{15}N_{soil}$ globally is −2.1 ‰ to 10.4 ‰, generally higher than $\delta^{15}N_I$, indicating that $\delta^{15}N_{soil}$ is elevated compared to external N inputs. The standard variation of the estimate is 2.11 and the uncertainty is 40.7 %. Although this approach may introduce errors at small scales, it reasonably approximates shifts in $\delta^{15}N$ across temperate vs. tropical biomes to within ~1 or 2 ‰ of empirical observations (Houlton and Bai, 2009). Thus, we use this model to integrate soil $\delta^{15}N$ across ecosystems, realizing that it may slightly underestimate the actual magnitude of terrestrial ^{15}N enrichment, pointing to the conservative nature of our approach overall.

2.2 N deposition and N fixation

When the isotope model is coupled with N input models, f_{gas} can be converted to fluxes at steady state:

$$N_{gas} = (N_{fixation} + N_{deposition}) \times f_{gas} \quad (7)$$

Global symbiotic N_2 fixation (1 × 1 degree) is generated from the CASACNP model (Wang et al., 2007; Houlton et al., 2008; Wang and Houlton, 2009). Asymbiotic N_2 fixation is based on the biome average reported in Cleveland et al. (1999) and the global biome classification in CASACNP (Wang et al., 2007). Global N deposition (5 degree × 3.75 degree) is generated from a three-dimensional chemistry-transport model run in the early 1990s (Lelieveld and Dentener, 2000). Global ammonia volatilization fluxes for natural soils are based on the biome averages reported in Bouwman et al. (1997).

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2.3 N gas production submodel

We use an index of water filled pore space (WFPS, %) to represent the holes in the N flux pipe, simulating the effects of oxygen availability on gaseous N emissions. Nitrification and nitrifier-denitrification are the main process when WFPS is low and denitrification increases in importance when WPFS is more than 60 % (Bateman and Baggs, 2005). When WFPS exceeds 80 %, N_2 becomes the major gaseous N form (Davidson, 1991). Based on empirical findings (Bateman and Baggs, 2005) and previous modelling of the relationship between WFPS of soil and relative fluxes of N gases (Davidson, 1991; Potter et al., 1996), we use an index of WFPS to develop our "gas partition curve" (Fig. 3).

After Potter et al. (1996), the index of WFPS is unitless and is estimated by:

$$\mathrm{WFPS} = (E + \mathrm{FC})/\mathrm{PS} \quad E > 0 \tag{8a}$$

$$\mathrm{WFPS} = W/\mathrm{PS} \quad E = 0 \tag{8b}$$

Where FC is soil field capacity (m/m); PS is soil pore space capacity (m/m); W is monthly mean soil water content (m/m); and E is excess moisture input (i.e., monthly runoff) (m/m). When WFPS exceeds 100 %, 100 % is used in the modelling.

We compiled measured $N_2O/(NO + N_2O)$ and $N_2O/(N_2O + N_2)$ as a function of water filled pore space (WFPS) from various lab and field studies (Supplementary Table 1) and compared these observations to our N gas submodel (Fig. 4). Agreement between modelled and observed ratios is measured using Root Mean Squared Error (RMSE):

$$\mathrm{RMSE} = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(M_i - O_i)^2} \tag{9}$$

where M_i is modelled $N_2O/(NO + N_2O)$ or $N_2O/(N_2O + N_2)$ ratio, O_i is the corresponding observed ratio, and N is the total number of observations. RMSE is equal to 0.20 for $N_2O/(NO + N_2O)$ ratios ($n = 46$) and 0.42 for $N_2O/(N_2O + N_2)$ ratios ($n = 69$). When

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WFPS is low, NO is the major form of gaseous N loss. At higher WFPS, more N_2O is produced. When WFPS >70 %, due to increasing anaerobic conditions, N_2 production increases rapidly and becomes the dominate form of gaseous N (Fig. 4). We used the coefficient of variation of the global total denitrification flux to express the modelled range of each gas form (see above).

2.4 Seasonal variations of NO in Africa

Seasonal variations of NO in Africa was estimated using our model and compared to satellite observations (Jaegle et al., 2004). Mean annual total N gaseous fluxes were first apportioned equally to each month, and then partitioned to NO, N_2O and N_2 fluxes based on monthly mean WFPS (see above). Modelled NO in January, June, and August (Fig. 5a) reflects the recent fifty-year-mean (1948–2008) monthly variations in WFPS.

2.5 Data sets

After Amundson et al. (2003), we estimate soil $\delta^{15}N$ by applying multiple regression models to climate data:

$$\delta^{15}N_{soil} = 0.2048 \times MAT - 0.0012 \times MAP + 4.32 \quad (10)$$

The model is based on empirical relationships observed across various climnosequences, spanning different biomes and climatic conditions. Mean annual temperature (MAT) and precipitation (MAP) data (0.5×0.5 degree) are from Willmott and Matsuura (2000). The global unmanaged surface (0.1×0.1 degree) is based on the biome classification scheme of VUB and VITO, derived from a full year cycle (1998–1999) of 10-daily composites of SPOT-VEGETATION (http://www.geosuccess.net/). Areas classified as croplands, urban and built-up, and cropland and natural vegetation mosaic are considered as human-managed.

Soil moisture and runoff data are from Fan and van den Dool (2004), available on a $0.5^\circ \times 0.5^\circ$ monthly basis for the period from 1948 to the present, based on a one-layer

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"tipping-bucket" model (Mintz and Serafini, 1981; Huang et al., 1996) that uses the spatially explicit estimates of soil properties based on IGBP soil texture types. Global soil field capacity (FC) and soil texture data are from Webb et al. (2000) (1 × 1 degree). Soil pore space capacity (PS) is computed from IGBP soil texture (see Eq. 7 in Saxton et al., 1986).

2.6 Sensitivity and uncertainty analyses

Sensitivity analyses are conducted by evaluating the change in global denitrification owing to changes in model input parameters by ±10 %. Results of this analysis indicate a sensitivity range from 1.3 to 11.9 % (Fig. 6). Global denitrification is most sensitive to soil $\delta^{15}N$ ($\delta^{15}N_{soil}$) and the effective isotope effect of denitrification (ε_{den}): a +10 % increase in either $\delta^{15}N_{soil}$ or ε_{den} results in +11.9 % or −11.9 % variation in denitrification, respectively. A 10 % increase in the N input flux (N_{input}) corresponds to a 10 % increase in N outputs as implied by our steady state assumption. Therefore, better estimations of $\delta^{15}N_{soil}$ and ε_{den} would improve model accuracy.

We used Monte Carlo methodology to estimate uncertainties in our estimates of global denitrification. Assuming that the errors in $\delta^{15}N_{soil}$, $\delta^{15}N_i$, f_{NH3}, and N_{input} are normal distributed with a coefficient of variation of 50 %, and the errors of N isotope enrichment factors are uniformly distributed within the range of 25 ‰–35 ‰ for ε_{NH3}, 16 ‰–20 ‰ for ε_{den}, and 0 ‰–5 ‰ for ε_L, we randomly sampled 10 000 sets of these seven parameters from the prescribed probability distributions to estimate the mean and uncertainty of denitrification for each grid cell at $0.5^\circ \times 0.5^\circ$ resolution.

The mean global denitrification rate (μ_T) was calculated as the sum of the means of all grid cells. For the uncertainty, we considered spatial correlations of errors among adjacent grid cells. We first performed variogram analysis (Isaaks and Srivastava, 1989), which indicated that gaseous emissions were correlated within a range distance of 84 cells (ca. 4662 km). Based on this correlogram, we then estimated a correlation coefficient between two grid cells (cell (i, j) and cell (k, l)) ($\rho_{ij,kl}$):

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$$\rho_{ij,kl} = 1 - \frac{\gamma(h)}{\mathrm{VAR}} \quad (11)$$

where $\gamma(h)$ is the semi-variogram of the two grid cells with a distance of h, VAR is the total variance of all grid cells. We used an exponential model to describe the variation of $\gamma(h)$ with h. That is:

$$\gamma(h) = C_0 + C_s \times (1 - e^{-(3h/a)}) \quad (12)$$

where C_0 is the nugget (= 0.10 for our data), C_s is the partial sill (= 0.36 for our data), and a is the range (= 42 decimal degree for our data) of the variogram model.

The standard deviation of the mean global denitrification rate (i.e., σ_T) was calculated as:

$$\sigma_T^2 = \sum_{i=1}^{N}\sum_{j=1}^{M}\sum_{k=1}^{N}\sum_{l=1}^{M} \sigma_{ij} \times \sigma_{kl} \times \rho_{ij,kl} \quad (13)$$

where i, k and j, l refer to row and column numbers of the global grid cells; N and M refer to total latitudinal and longitudinal cells, respectively.

3 Results

The uncertainty of the global denitrification rate is expressed as the coefficient of variation (i.e., σ_T/μ_T) and the range is expressed at the 68 % confidence interval (i.e., $[\mu_T - \sigma_T, \mu_T - \sigma_T]$).

3.1 N loss pathways

At the global scale, our model indicates that 35 % of all N inputs to land biosphere each year is lost to denitrification in natural soils worldwide. This agrees with results from Houlton and Bai (2009), in which the N isotope composition of the entire biosphere

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suggested that about 1/3 of the N that enters the natural biosphere is emitted back to the atmosphere via denitrification pathways. It is also in agreement with Seitzinger et al. (2006) which was based on numerical simulation models and estimated 58 Tg N yr^{-1} global denitrification. Thus, our spatially-explicit analysis using N stable isotope constraints on the global N budget point to a substantial role for denitrification gases in removing N from land ecosystems, helping to close the overall global N budget.

Across the biosphere, f_{gas} varies substantially, however. Specifically, our analysis suggests that gaseous N losses vary from 0 % to 69 % of total N inputs across temperate vs. tropical latitudes (Fig. 7a). The highest gas loss fractions are associated with desert sites, where precipitation << potential evaportranspiration. Although the absolute fluxes in these areas may be low due to low N inputs, gaseous N efflux is estimated to be high relative to leaching, consistent with previous analyses (Galbally et al., 2008; Hartley and Schlesinger, 2000). In contrast, f_{gas} decreases at high latitudes, where limited quantities of nitrate, low NPP, and low temperatures (T) constrain denitrification for most of the year. In these environments, leaching ($f_{leaching}$) is the dominate vector of N loss. Globally, we estimate that 65 % of total N losses occurs via leaching, consistent with previous estimates (i.e., 72 %) for natural terrestrial ecosystems (Bouwman et al., 2005b).

Our results also point to marked spatial clustering in the magnitude of denitrification within the terrestrial biosphere, with a global denitrification flux of 46.9 ± 13.6 Tg N yr^{-1}, reasonably consistent with previous estimates (58 Tg N yr^{-1}) (Seitzinger et al., 2006). The highest fluxes are inferred for central Africa, South America, and Southeast Asia, where the combination of warm temperatures, moist soil conditions, and high N availability favors high rates of soil microbial activity (Fig. 7b). This agrees with previous work pointing to high potential for denitrification in moist tropical sites (Potter et al., 1996; Galloway et al., 2004). Monte Carlo analysis reveals a coefficient of variation (CV) of 29 % on our estimates for global denitrification fluxes.

In terms of dissolved pathways of N loss, we estimate that that 85.7 ± 24.8 Tg of dissolved N compounds leach through the plant rooting zone annually. Southern United

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States, northern South America, central Africa, and southern Asia display the largest leaching fluxes due to high N inputs and high precipitation amounts (Fig. 7c). Below the plant rooting zone (0–50 cm), leached N (especially nitrate) may be further denitrified as it enters ground water and streams (Seitzinger et al., 2006). While the fate of this N is beyond our study, our results provide an independent approach to dissolved N losses that can be incorporated into future studies of denitrification along the soil-river continuum. For example, our modelled spatial pattern of N leaching is similar to that of DIN yield predicted by NEWS-DIN (Dumont et al., 2005), indicating the source effect of leaching N on river export of DIN. In any case, leaching is important beyond its role as a vehicle of N removal from the land: it strongly influences the productivity of the coastal ecosystems and contributes to coastal hypoxia and anoxia.

3.2 Gaseous N forms

Our model integrates multiple datasets and several submodels, which is common for global-scale biogeochemical cycles due to the complex processes and the large spatial and temporal resolution of such inquiry (Charria et al., 2008; Schaldac and Pries, 2008; Thornton et al., 2009). Uncertainty in our model includes both model assumptions and input parameters. In particular, we assume ecosystem isotope balance, whereby internal N cycling processes – plant uptake, microbial uptake – do not influence bulk soil $^{15}N/^{14}N$ ratios (Amundson et al., 2003; Houlton et al., 2006; Bai and Houlton, 2009). This assumption seems to be valid at the scale of decades to centuries for most natural sites (Amundson et al., 2003); modern rates of N accumulation would have at most changed soil N pools <0.1 % over the past 100 years, implying negligible N accumulation effects on our isotopic calculations (Houlton and Bai, 2009). The steady-state assumption may be less valid in sites where relatively frequent and hot fires can lead to transient imbalances in N – especially on short time scales (Aranibar et al., 2003) (see below on importance of fire in N losses). Moreover, we use an empirically-derived model to estimate soil $\delta^{15}N$ across global ecosystems and this necessarily imparts errors in our assessment of $\delta^{15}N$, especially at sub-grid scales. This is an important

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area for future work – more data on the d15N of soil across ecosystems. Nevertheless, we note that the approach we used to estimate soil $\delta^{15}N$ is able to capture shifts across temperate to tropical biomes, typically within about 1 ‰ of actual measurements (Houlton and Bai, 2009).

We estimate that, on average, 0.152 ± 0.044 g N m^{-2} yr^{-1} are lost via bacterial NO production in the natural terrestrial soil (Table 1, Fig. 8a). Globally, the geographic area that is free from agriculture and major land cover transformation is equal to 103.5×10^{12} m^2 (based on VUB and VITO). Applying this to our NO production rates, we calculate that 11.2–20.3 Tg N yr^{-1} are emitted as NO globally. This estimate is significantly higher than natural NO emissions (3–8 Tg N yr^{-1}) as summarized in the Inter-governmental Panel on Climate Change's (IPCC) fourth assessment report (AR4) (Denman et al., 2007). Combining our estimate of natural NO emissions with that of cropland and managed grassland (Stehfest and Bouwman, 2006) (i.e., 1.8 Tg N yr^{-1}), we calculate a total NO flux of 13.0–22.1 Tg N yr^{-1} for the entire terrestrial biosphere. This falls between those of most process- (Potter et al., 1996) (9.7 Tg N yr^{-1}) and empirically-based models (Davidson and Kingerlee, 1997) (21.1 Tg N yr^{-1}) (Table 1), but is higher than some estimates reported in the literature (5–8 Tg N yr^{-1}) (Yan et al., 2005; Yienger and Levy, 1995; Lee et al., 1997) (Table 1).

Among different terrestrial regions, highest NO emissions are simulated for tropical environments (Fig. 8a). Among continents Africa falls out as the largest natural source of NO in the natural terrestrial biosphere (0.213–0.657 g N m^{-2} yr^{-1}, Supplementary Table 2). Our model simulates high NO emissions in tropical savanna/woodland environments (0.267–0.711 g N m^{-2} yr^{-1}, Supplementary Table 2) while tundra falls at the low end of the worldwide spectrum (0–0.007 g N m^{-2} yr^{-1}, Supplementary Table 2). NO fluxes fall between 0.023–0.055 g N m^{-2} yr^{-1} for temperate forest, in agreement with empirical data (Supplementary Table 2). In global grasslands, we estimate 0.101–0.179 g N m^{-2} yr^{-1} of NO, near the upper bound of previously published data (Supplementary Table 2).

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Importantly, the soil surface NO flux is probably higher than the atmospheric one, owing to scavenging of N by canopy vegetation (Bakwin et al., 1990). NO is often quickly oxidized to NO_2 upon emission, and can be absorbed onto leaf surfaces, reducing the total amount of NO_x that escapes to the atmosphere (Davidson and Kingerlee, 1997). Using leaf absorption factors (Yienger and Levy, 1995), we suggest that net emission of NO from unmanaged terrestrial ecosystems may be reduced by up to 10 Tg N yr^{-1}. Comparing our modelled spatial and temporal variations of soil surface NO emissions to satellite mapping of space-based observation of NO_2 in Africa (Jaegle et al., 2004) (Fig. 5), we find that both soil microbial activities and fire activity are responsible for the high levels of atmospheric NO_2 between 0° to 10° N latitude in January. In contrast, the unexpectedly high level of NO_2 above the Sahel region during June (shown in the pink rectangular in Fig. 5) is not caused by fire or industrial emissions; rather, Jaegle et al. (2004) speculated that this represented microbial NO_x pulses following the onset of rainfall over vast areas of dry soil, a notion confirmed by our model simulations (Fig. 5a). Thus, our isotope-based approach appears to integrate broad-scale dynamism in microbial gaseous N production rates.

For N_2O, we estimate that 7.2–13.2 Tg N yr^{-1} of this potent greenhouse gas is produced via bacteria living in natural soils worldwide (Table 1, Fig. 8b). Bouwman et al. (1995) estimated 6.8 Tg N yr^{-1} global pre-agricultural N_2O emissions based on a simple empirical model, while the IPCC adopted value of 3.3–9.9 Tg N yr^{-1} N_2O emissions from soils under natural vegetations in their 2001 report (Ehhalt et al., 2001). When our results are combined with the N_2O efflux associated with fertilized cropland and managed grassland (4.1 Tg N yr^{-1}) (Stehfest and Bouwman, 2006), we estimate a global N_2O flux between 11.3—17.3 Tg N yr^{-1}. Diverse global estimates of N_2O are available via process-based, statistical, or inverse models; they (Huang et al., 2008; Nevison et al., 1996; Ehhalt et al., 2001; Bouwman et al., 1995; Xu et al., 2008; Dalal and Allen, 2008; Bowden, 1986; Potter et al., 1996; Liu, 1996; Hirsch et al., 2006) generally vary from 10.6 Tg N yr^{-1} to 15 Tg N yr^{-1} (Table 1). Our isotope-based model independently confirms this range of estimates of global N_2O fluxes.

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Across the terrestrial biosphere, our model targets moist tropical areas, such as the east Amazon basin, central Africa, and northern Australia as natural hotspots of bacterial N_2O production (Fig. 8b). Specifically, we estimate that the natural tropical rainforest and savannas account for 77 % of global N_2O emissions. Tropical rainforests have the highest potential for N_2O production (0.176–0.400 g N m^{-2} yr^{-1}, Supplementary Table 2), whereas, similar to NO, tundra has the lowest (0–0.007 g N m^{-2} yr^{-1}, Supplementary Table 2). Previous models have reported a mean range of 0.12–0.29 g N m^{-2} yr^{-1} for N_2O emissions from tropical forests (Matson and Vitousek, 1990; Bowden, 1986; Dalal and Allen, 2008; Potter et al., 1996) and a mean range of 0.022–0.068 g N m^{-2} yr^{-1} N_2O emissions from temperate forests (Dalal and Allen, 2008; Stehfest and Bouwman, 2006). Our results fall within this range – except for tropical savanna where we estimate higher N_2O fluxes (0.150–0.398 g N m^{-2} yr^{-1}) than empirical- (Dalal and Allen, 2008) and process-based (Potter et al., 1996) models. Our model may overestimate this flux because fire-caused N losses are not considered. For example, Olivier et al. (1998) estimated that 4.8 Tg N yr^{-1} is removed by savanna fires, or approximately 62 % of total fire-induced N gas emissions in the terrestrial biosphere. Globally, fire removes a modest amount of N (7.7 Tg N yr^{-1}), ~5.8 % of total N inputs (Olivier et al., 1998).

Finally, to our knowledge, we here provide the first-ever simulations of global spatial pattern of terrestrial N_2 emissions, widely believed to be the dominant biogenic form of gaseous N. We estimate that 14.9–27.1 Tg N yr^{-1} is denitrified to atmospheric N_2 production in the natural soil. According to our model, N_2 originates mainly from southeast North America, north South America, central Africa, and Southeast Asia (Fig. 8c); anaerobic environments caused by high precipitation and poor soil drainage in these areas favor N_2 production (Galloway et al., 2004). In contrast, dry and low N throughput environments have uniformly low N_2 production potentials (Fig. 8c).

Due to methodological limitations, very few studies have assessed soil N_2 fluxes in the field. Recently, Schlesinger (2009) compiled all of the available data on N_2O-N/(N_2O + N_2)-N reported for terrestrial ecosystems under natural vegetation, with a

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mean fraction of 0.51 for grassland ($n = 4$), 0.41 for forest ($n = 14$), and 1.0 for desert ($n = 1$). Our model simulates an N_2O-N/($N_2O + N_2$)-N ratio of 0.22 for tropical and temperate forest, 0.43 for tropical savanna/woodland, 0.57 for grassland, and 0.71 for desert biomes – all of which seem to fit with Schlesinger's compilation (Schlesinger, 2009). For moist tropical forest, owing to high water availability and periods of extended anaerobiosis, and high NPP and N cycling rates, such a low N_2O-N/($N_2O + N_2$)-N ratio makes logical sense. In temperate forests, N_2O-N/($N_2O + N_2$)-N ratios are generally low and extremely variable. For example, Wolf and Brumme (2003) reported N_2O-N/($N_2O + N_2$)-N ratios ranging between 0.19 to 0.85 in beech forest with different mineral soils; Merrill and Zak (1992) found a much higher values (0.63–0.98) in upland forest in Michigan and a N_2O-N/($N_2O + N_2$)-N ratio of 0.25 under swampy forest conditions. Dannenmann et al. (2008) observed a N_2O-N/($N_2O + N_2$)-N ratio of 0.23 when water holding capacity (WHC) was 48–55 %, while the ratio dropped to 0.03 when WHC was 62–84 %. In sum, observed N_2O-N/($N_2O + N_2$)-N ratios varied within a large range; however, these limited data available suggest that moist forest environment has the greatest potential to contribute to the global N_2 budget, consistent with our modelled fluxes.

4 Discussion

Our results target tropical ecosystems as the global N cycling hotspot within the natural land surface. At the earth system scale, this fits with the notion that tropical forests are rich in N (Vitousek, 1984; Hedin et al., 2009), and implies a hitherto unrecognized coupling between natural paths of fixation (Houlton et al., 2008) and denitrification within this biome, similar to couplings observed for the global open ocean (Deutsch et al., 2007). Future studies on N_2 fixation and denitrification (and their couplings) in tropical forests are critical for understanding the integrated Earth-climate system – and the magnitude and direction of carbon (C) exchanges between tropical biomes and the atmosphere.

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Accurate partitioning of N losses along denitrification vs. leaching vectors is fundamental to understanding C and N couplings in the terrestrial biosphere. The response of N-limited ecosystem to increasing [CO_2] depends on how the N loss will change under increasing [CO_2] in the future. Losses of DON compounds are largely substrate-independent (Hedin et al., 2003) and therefore less unlikely to change with increasing [CO_2] (Rastetter et al., 2005) than the N loss via denitrification that depends on available substrates, or N availability. Denitrification may therefore decrease in response to progressive N-limitations under elevated [CO_2]. Our study reveals that leaching is a greater fraction of N losses (~77 %) at high latitudes, in contrast to the tropics where denitrification (leaching = 58 %) contributes more to the N economy of ecosystems. These results agree with empirical studies pointing to substantial DON losses from both boreal and unpolluted temperate forests and high denitrification rates in tropical sites as well (Seitzinger et al., 2006; Neff et al., 2003). We thus postulate the following: progressive N limitations will persist longer at high latitudes than other sectors of the terrestrial biosphere, with C uptake by boreal forests and tundra unlikely to increase substantially in response to the higher [CO_2] in the future.

Finally, global biogeochemical models have been used to study the change of nutrient limitation under future climate and higher [CO_2] conditions (Sokolov et al., 2008; Thornton et al., 2009; Zaehle et al., 2010a), but the spatial pattern of nitrogen limitation and its response to warming and increasing [CO_2] as predicted by those models are significantly different. For example, N limitation of tropical NPP was predicted by one model (Thornton et al., 2009), but was much weaker than the ecosystems at temperate and high latitude regions in other model under future conditions (Zaehle et al., 2010b). Global models of C and N cycles are poorly constrained (Wang et al., 2010), and therefore the uncertainties in their prediction are expected to be high, but yet to be quantified. The spatially explicit estimates of N losses from this study can provide an important constraint for benchmarking the performance of global biogeochemical models under present conditions. Additional work on the N isotope composition of natural ecosystems, coupled with examination for transient effects where appropriate, would

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not only advance our approach further, but would also be useful for ground-truthing global models.

Our isotope-based approach considers interactions between soil microbial processes, climate and soil conditions over large spatial scales thereby providing a novel and independent constraint against which empirical- and process-based models, and inverse chemical transport analyses can be evaluated. Our estimates of various N losses provide independent regional- and global-scale constraints on the cycling of N, and identify hot spots of NO emissions in Africa and N_2 emission in South-east USA where very few measurements have been made. Incorporating spatial and temporal complexities (hotspots and hot moments) into the N cycle is considered the biggest challenge in denitrification research (Groffman et al., 2009). Previous studies have used models that were calibrated locally and extrapolated globally, introducing unquantifiable uncertainties into estimates of denitrification. Episodic emissions of NO and N_2O in the arid and semiarid region are known to account for a significant fraction of total loss (Hartley and Schlesinger, 2000), for example, and these losses are poorly simulated by most global models, whereas our model integrates all isotopic-fractionating emissions including episodic pulses of NO and N_2O over a long period (> decade). The similarities between our modelled results and satellite observations of NO_2 and newly identified hot spots of N emissions points to the power of our N isotope model at large scales.

Our modelled maps provide a reference for future studies on N gaseous losses. For example, our map (Fig. 8b) points to the Congo Basin in Africa is the hotspot of soil sourced N_2O – a potent greenhouse gas (Fig. 1) and dominant ozone-depleting agent (Ravishankara et al., 2009) – while there are almost no published data on N_2O fluxes from this region; most published data on N_2O fluxes in the tropics are from South and Central American forests, with a few data from Southeast Asia and Northwest Australia. Thus continued advancement on such issues as climate change and the ozone hole would seem to benefit from empirical investigations of the world tropics.

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The spatial patterns of N_2 emissions we describe are crucial for understanding N dynamics of the Earth system. Soil N_2 is considered the most important pathway by which N is returned from the soil to the atmosphere (Schlesinger, 2009; Galloway et al., 2004). However, the lack of quantitative knowledge of N_2 emissions has hitherto limited our understanding of this N sink and denitrification processes as a whole. Our results support the common belief that N_2 emissions account for a significant fraction of the "missing N" (Schlesinger, 2009) in the global N cycle and provide the first-ever quantitative predictions of global patterns of N_2 fluxes among terrestrial ecosystems.

Our predictions can be improved with additional information, observations and experiments. In particular, knowledge on isotope fractionations via gaseous N losses are clearly warranted, since they can vary across different ecosystems and conditions; our sensitivity analyses (Fig. 6) indicate that our N loss fractions are most sensitive to variation in $\delta^{15}N$ ($\delta^{15}N_{soil}$) and the isotope effect of denitrification (ε_{den}). This points to the importance of a deeper understanding of isotope effect expression and additional measurements of soil $\delta^{15}N$. In addition, more information on the influence of soil properties such as soil texture, soil water availability on N gas partitioning would increase the robustness of our model. Further, uncertainties in N_2 fixation models are difficult to assess and are probably high, although they are the best available models at present; additional constraints on N inputs and climate and soil databases could help to reduce uncertainties in the model.

Finally, our estimates of the fraction of N lost along leaching vs. gaseous paths imply specific predictions for the fate of N additions in these environments. N deposition is on the rise and will continue to rise into the future, spreading rapidly into tropical ecosystems globally. Our results suggest that N inputs into tropical environments and arid sites will disproportionately mobilize to atmospheric gases when compared to extratropical moist environments, particularly boreal and temperate forests. Thus, for example, human-induced N deposition in tropical ecosystems is likely to release more N_2O from soils to the atmosphere, warming the climate in a way that is fundamentally

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different than when the same amount of N is deposited on high latitude environments.

Supplementary material related to this article is available online at: http://www.biogeosciences-discuss.net/8/12113/2011/bgd-8-12113-2011-supplement.pdf.

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Table 1. Comparison of global estimations of N gas productions by N isotope model with previously published empirical and modelling studies (NO fluxes are soil-surface emissions without canopy effects).

Sources	Area (10^{12} m^2)	NO (Tg N yr^{-1})	N_2O (Tg N yr^{-1})	N_2 (Tg N yr^{-1})	Method	Reference
Natural	103.5	11.2–20.3	7.2–13.2	14.9–27.1	N isotope model	this study
	114.0	9.1–16.0			statistical modelling	Davidson and Kingerlee (1997)
	97.7	5.02			statistical modelling	Yan et al. (2005)
	NR	7.22			statistical modelling	Yienger and Levy (1995)
	99.2	5.44			statistical modelling	Lee et al. (1997)
	NR	3.0–8.0			IPCC assessment	Denman et al. (2007)
	NR		3.3–9.9		IPCC assessment	Ehhalt et al. (2001)
	118.2		6.0		statistical modelling	Bouwman et al. (1995)
	NR		5.73–12.90		statistical modelling	Xu et al. (2008)
	135.2		10.7		statistical modelling	Dalal and Allen (2008)
	NR	5.0–26.0	7.0–16.0		statistical modelling	Bowden (1986)
	122.2	7.69	5.02		process-based modelling	Potter et al. (1996)
	NR		6.2		process-based modelling	Nevison et al. (1996)
Agricultural	16.0	3.9–5.5			statistical modelling	Davidson and Kingerlee (1997)
	14.5	2.41			statistical modelling	Yan et al. (2005)
	NR	2.98			statistical modelling	Yienger and Levy (1995)
	17.6	5.55			statistical modelling	Lee et al. (1997)
	NR	0–4.0			IPCC summary	Denman et al. (2007)
	NR		1.9–4.2		IPCC summary	Ehhalt et al. (2001)
	14.4		0.4		statistical modelling	Bouwman et al. (1995)
	NR		2.46–5.53		statistical modelling	Xu et al. (2008)
	19.06	1.8	4.1		statistical modelling	Stehfest and Bouwman (2006)
	13.1	2.00	1.10		process-based modelling	Potter et al. (1996)
	NR		2.58		process-based modelling	Nevison et al. (1996)
All	NR		11.33		process-based modelling	Liu (1996)
	NR		8.3–15.0		inverse modelling	Hirsch et al. (2006)
	NR		11.0–14.4		inverse modelling	Huang et al. (2008)

NR: Not reported

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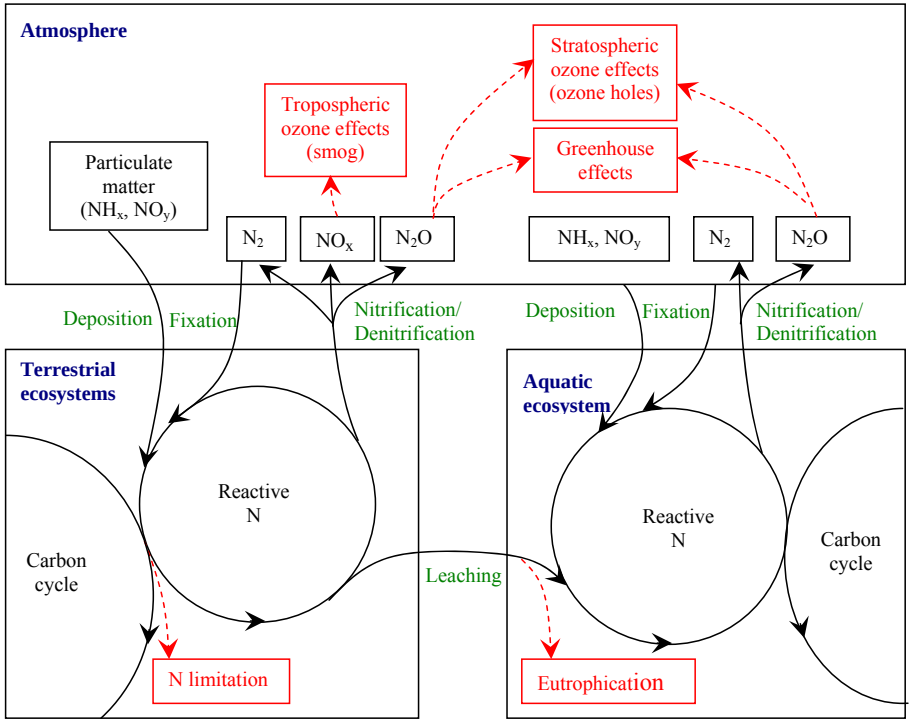

Fig. 1. Diagram of N cycling and its influences on global change.

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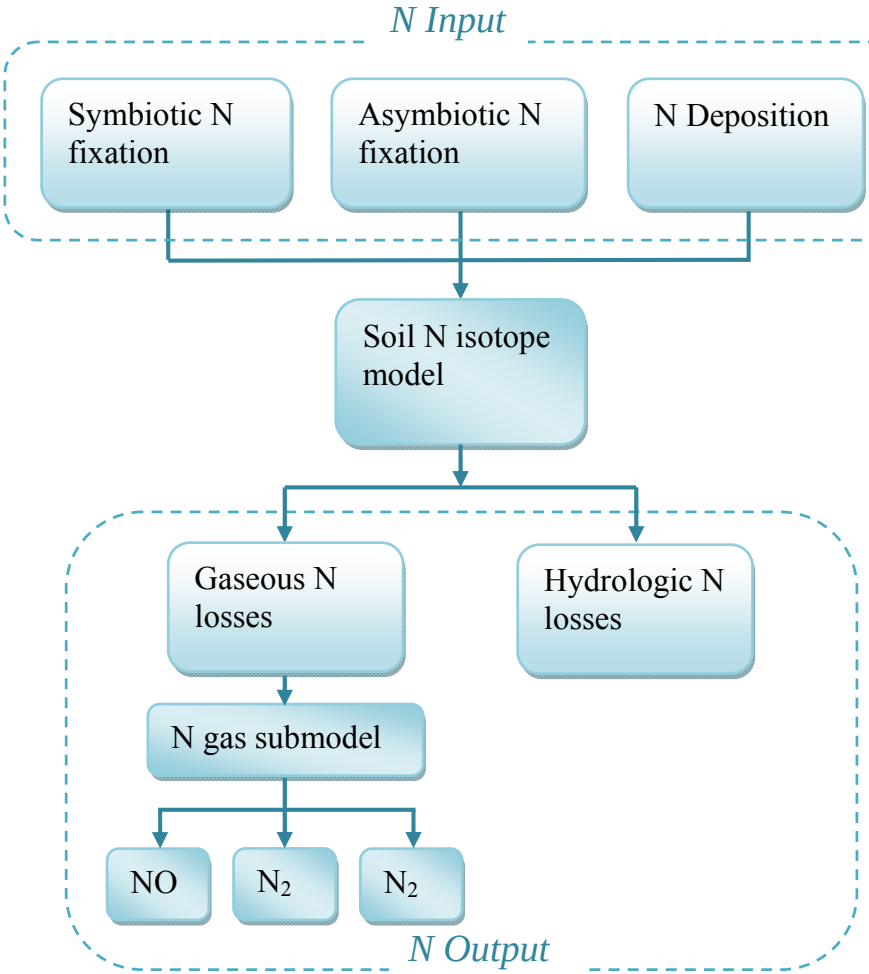

Fig. 2. Model structure.

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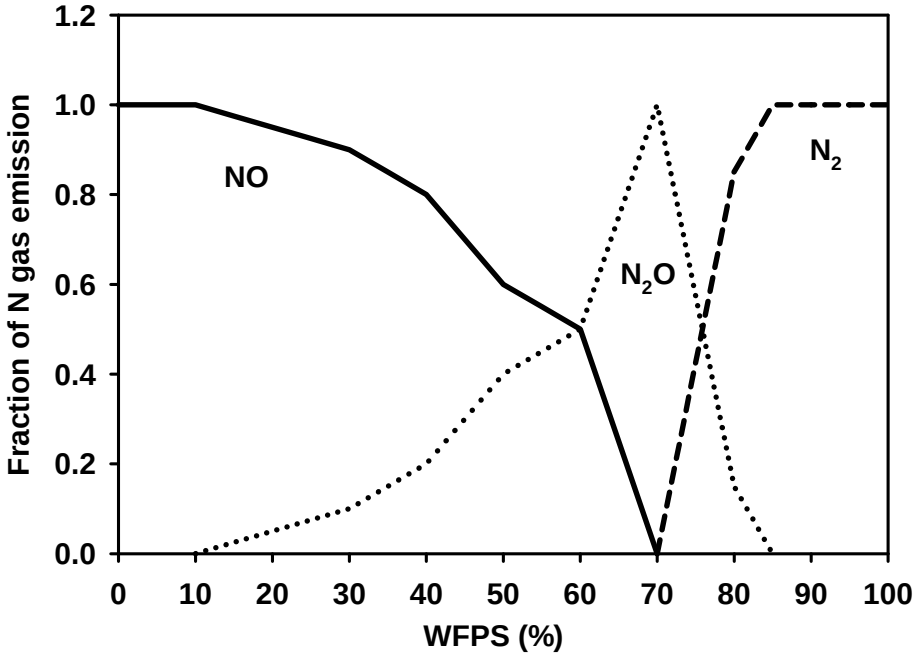

Fig. 3. Model of N gas production as a function of WFPS (water-filled pore space, %). The solid line represents NO; short dash line represents N_2O fraction; and long dash line represents N_2.

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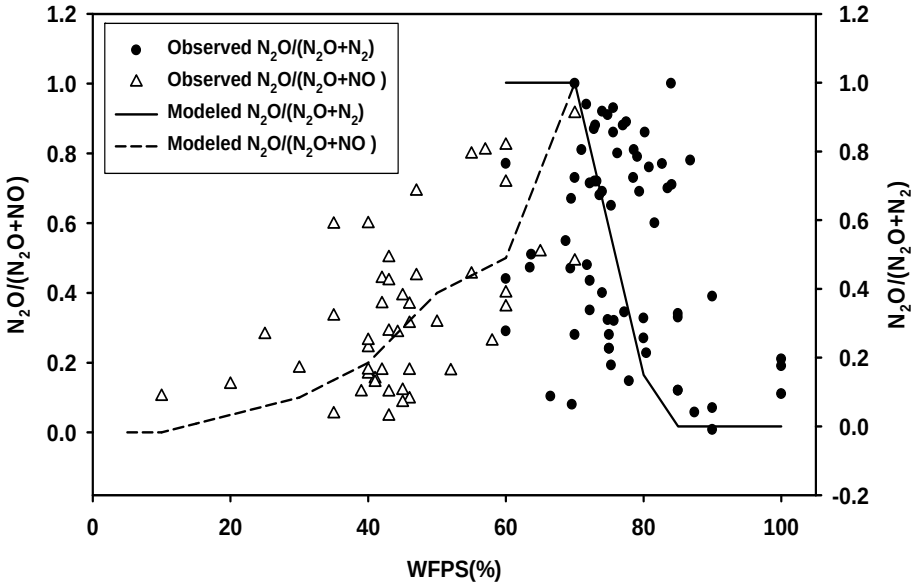

Fig. 4. Comparison of the ratios of N_2O-N/(N_2O-N + NO-N) and N_2O-N/(N_2O-N + N_2-N) from field measurements (points) with ratios predicted by the gas partitioning model (lines). Additional information on the field measurements is presented in Supplementary Table 1.

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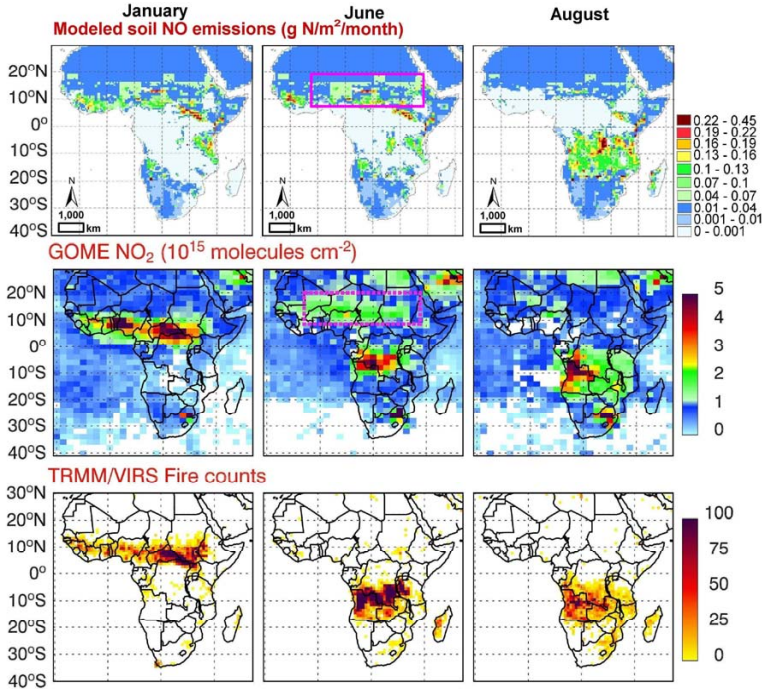

Fig. 5. Comparison of modelled soil NO emissions (g N m^{-2} $month^{-1}$) **(a)** with space-based observations of NO_2 column concentrations (10^{15} molecules cm^{-2}) as reported in Jaegle et al. (2004) and **(b)** fire counts as observed **(c)** by the visible and infrared scanner on board the TRMM satellite (Jaegle et al., 2004) over Africa for January, June and August 2000. The pink rectangular shows the area with unexpectedly high level of NO_2 **(b)** during June , which was not caused by fire or industrial emissions based on the fire count map **(c)**; rather, soil microbial NO_x pulses following the onset of rainfall over vast areas of dry soil, a notion confirmed by our model simulations **(a)**.

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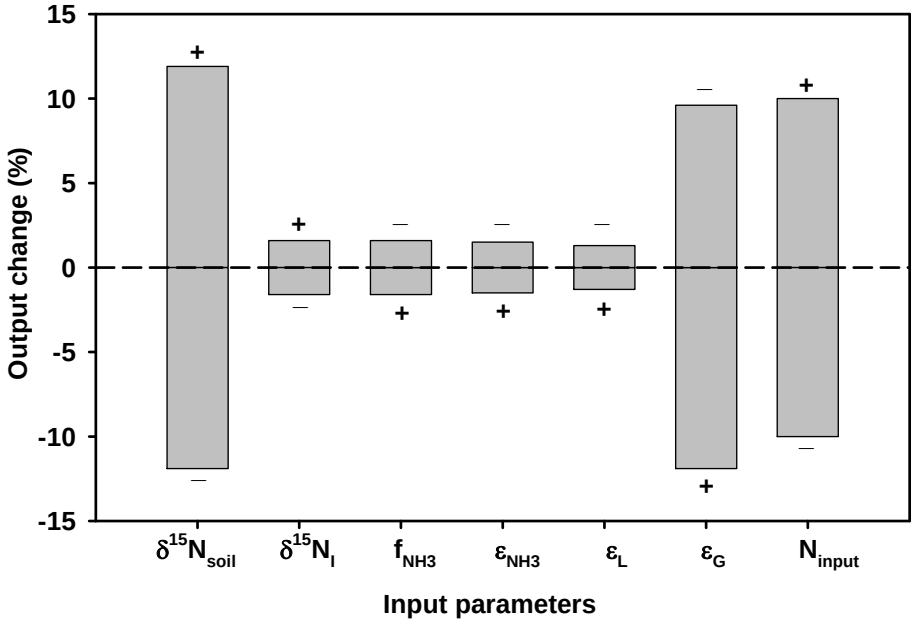

Fig. 6. Sensitivity of denitrification to different input parameters. "+" and "–" represent a 10 % increase and 10 % decrease in the input parameter, respectively.

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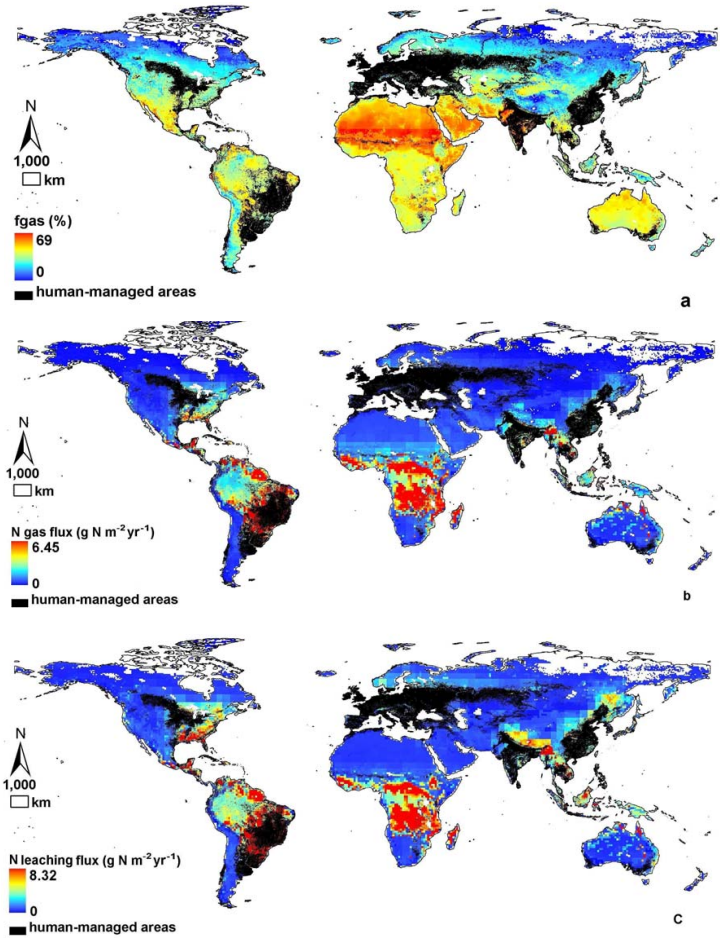

Fig. 7. Global patterns of fraction of gaseous N losses (f_{gas}) **(a)**, total gaseous N flux **(b)**, and total leaching N flux **(c)** from un-managed soils.

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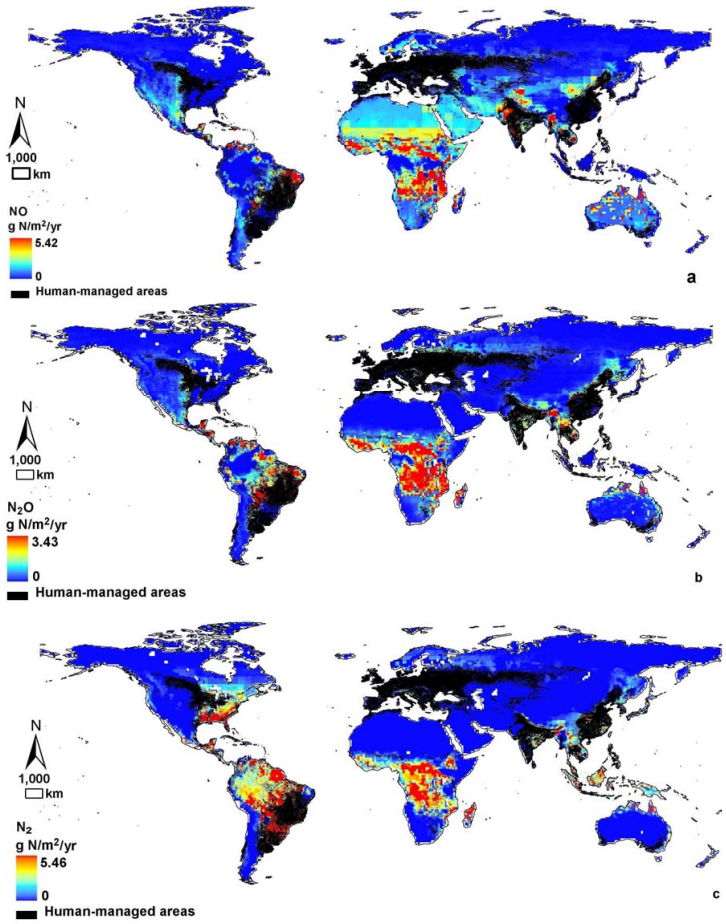

Fig. 8. Global patterns of NO **(a)**, N_2O **(b)**, and N_2 **(c)** from un-managed soils.

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