Warming and redistribution of N inputs drive long-term increase in terrestrial N₂O emission factor

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Warming and redistribution of N inputs drive long-term increase in terrestrial N₂O emission factor

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Key Points:

- Deposition N inputs dominated anthropogenic N₂O emissions from soils in 2020
- The long-term increase in N₂O emissions is driven by both fertilisation and deposition of N, however N fixation drives subdecadal variability
- The effective global emission factor for N₂O has significantly increased due to climate warming feedbacks and spatial redistribution of fertilisation N inputs
- Soil nitrogen isotopes can be used as an integrated proxy to facilitate estimation of emission factors and simple, fast global modelling of N loss pathways

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Abstract

Anthropogenic nitrogen inputs cause major negative environmental impacts, including emissions of the important greenhouse gas N_2O . Despite their importance, changes in terrestrial N loss pathways driven by global change and spatial redistribution of N inputs are highly uncertain. We present a novel coupled soil-atmosphere isotope model (IsoTONE) to quantify terrestrial N losses and N_2O emission factors from 1850-2020, initialised using a global dataset of natural soil $\delta^{15}\text{N}$, and optimized with a tropospheric timeseries of N_2O isotopic composition using a Bayesian framework.

N inputs from atmospheric deposition caused the majority (51%) of anthropogenic N_2O emissions from soils in 2020. Long-term growth in emissions was driven by fertilization and deposition, however biological fixation caused subdecadal variability in emissions. N_2O emission factors (EF) show large spatial variability due to climate and soil parameters. The mean effective global EF for N_2O (weighted by N inputs) was $4.3 \pm 0.3\%$ in 2020, much higher than the land surface area-weighted mean ($1.1 \pm 0.1\%$). Climate change and redistribution of fertilisation have driven an increase in global EF over the past century, which accounts for 18% of the anthropogenic soil flux in 2020. Predicted increases in fertilisation in emerging economies will accelerate N_2O -driven climate warming in coming decades, unless targeted mitigation measures focussing on fertiliser management and reduced N deposition are introduced.

1 Introduction

Nitrous oxide (N_2O) is a long-lived greenhouse gas and a key stratospheric ozone-depleting substance (Ravishankara, Daniel, & Portmann, 2009; Tian et al., 2020). The atmospheric N_2O mole fraction has increased from $\sim 270 \text{ nmol mol}^{-1}$ in the preindustrial era to $>332 \text{ nmol mol}^{-1}$ today (Tian et al., 2020; WMO, 2020). The primary global source of N_2O is production during N cycling by microbiota in soils, which also releases NO and N_2 . N cycling and thus N gas production are strongly enhanced by direct and indirect anthropogenic N inputs (Park et al., 2012; Tian et al., 2020, 2019; World Bank, 2019). Agricultural fertilisation accounts for around two thirds of anthropogenic N inputs (Hurt et al., 2020), with the remainder contributed by biological N_2 fixation and deposition of NO_x and NH_3 . Most anthropogenic N is not incorporated into crops or soils but lost to the environment (Sebilo, Mayer, Nicolardot, Pinay, & Mariotti, 2013), representing huge monetary losses for the agricultural sector and causing a cascade of environmental problems (Fowler et al., 2013; Galloway et al., 2008; Roy, Hammond Wagner, & Niles, 2021). In the coming decades, N inputs are expected to grow in line with increasing agricultural production, and to shift towards tropical regions and emerging economies as strict N pollution controls are introduced in many developed regions (Leitner et al., 2020; Lett & Michelsen, 2014; Peng et al., 2020; Verma & Sagar, 2020; W. Wang et al., 2019). Effective management of N fertiliser to achieve high N use efficiency is key to balancing food production with environmental protection and thus reducing N_2O emissions (Venterea et al., 2012; Wagner-Riddle, Baggs, Clough, Fuchs, & Petersen, 2020). However, mitigation is challenging, and N_2O emissions are currently exceeding the highest predicted scenarios (Tian et al., 2020).

N is lost from terrestrial ecosystems through several major pathways: Microbial and abiotic *N gas production* in soils; *leaching* of N species; and ammonia *volatilization*. Despite their importance, expected changes in N losses in the coming century are not well known (Galloway et al., 2008; Gruber & Galloway, 2008). Nitrification (aerobic) and denitrification (anaerobic) are the main processes emitting N gases (NO, N_2O and N_2) from soils. On the global scale, the impacts of climate change on N-gas production processes are poorly known: Warming is generally expected to enhance microbial activity, however interactions between factors such as N availability, plant growth, and precipitation changes are poorly constrained. Moreover, it is unknown if increased nitrification or denitrification rates would

in fact lead to increased N gas production (Hartmann, Barnard, Marhan, & Niklaus, 2013; Inatomi, Hajima, & Ito, 2019; Li et al., 2020). The proportion of N lost by leaching globally is not expected to change significantly over time in response to warming due to the contrasting effects of increased N mineralization and reduced moisture availability (He et al., 2018; Mas-Pla & Menció, 2019; Reichenau, Klar, & Schneider, 2016; Tian et al., 2020). However, leaching losses and predicted responses to warming vary widely between different regions depending on soil, hydrological and ecosystem parameters, and may also be strongly affected by precipitation regime changes (Frank et al., 2015; Stuart, Gooddy, Bloomfield, & Williams, 2011). Moreover, increasing atmospheric CO₂ generally enhances plant growth and N uptake, thus impacting the availability of N in soils for different loss pathways (Eisenhauer, Cesarz, Koller, Worm, & Reich, 2012; Mitchell, Mitchell, Driscoll, Franklin, & Lawlor, 1993). Process models have been used to simulate N loss pathways in a changing climate (e.g. Giltrap and Ausseil (2016); Xu-Ri and Prentice (2008); Xu-Ri, Prentice, Spahni, and Niu (2012)). These models used generally require large amounts of input data and parameterisations as well as high computing power, which makes it difficult to constrain model parameters with observations using inversion frameworks, and complicates investigations of global or long-term emissions. Top-down modelling efforts can give robust estimates of global emissions for recent decades (R. L. Thompson, Ishijima, et al., 2014; R. L. Thompson et al., 2019; R. L. Thompson, Patra, et al., 2014), however without the incorporation of isotopes, these approaches cannot provide mechanistic information.

The isotopic composition of soil N ($\delta^{15}\text{N}_{\text{soil}}$) has been proposed as an integrated indicator of N loss partitioning in natural systems (Bai, Houlton, & Wang, 2012; Craine, Brookshire, et al., 2015; Craine, Elmore, et al., 2015; Houlton & Bai, 2009). Leaching of soluble N species (eg. NO_3^-) involves very low isotopic fractionation, while losses through ammonia volatilization and N gas production strongly favour ^{14}N and thus cause ^{15}N enrichment in the remaining soil N pool (Bai et al., 2012). Observations have shown that mean global $\delta^{15}\text{N}_{\text{soil}}$ is elevated relative to N inputs, reflecting significant production of gaseous N species (Bai et al., 2012; Houlton & Bai, 2009), although the relationship may be unpredictable in some regions due to N immobilization (Craine, Elmore, et al., 2015). Previous studies have used $\delta^{15}\text{N}_{\text{soil}}$ models to constrain N losses at individual sites or globally for natural ecosystems (Bai et al., 2012; Houlton & Bai, 2009), however this approach has not been applied to estimate temporal changes in N loss pathways. Furthermore, the availability of complementary datasets to validate previous $\delta^{15}\text{N}_{\text{soil}}$ models has been limited to short-term measurements from individual sites. Recent advances in spectroscopic isotope instrumentation have delivered high precision long-term time series of background tropospheric N₂O mixing ratio and isotopic composition (Harris et al., 2017; L. Yu, Harris, Henne, et al., 2020), allowing an integrated view of N₂O sources and sinks. These results have been used to estimate total anthropogenic N₂O emissions based on two-box models of the atmosphere (Sowers, Rodebaugh, Yoshida, & Toyoda, 2002; Toyoda et al., 2013; L. Yu, Harris, Henne, et al., 2020), however this approach cannot give spatially resolved information on N₂O sources.

We aim to gain new insight into the N loss processes underlying global N₂O emissions and their spatiotemporal patterns, in order to understand how N losses are changing under the influence of anthropogenic activities and climate change. We use an artificial neural network to estimate a global isoscape of natural soil $\delta^{15}\text{N}$. This is used to initialise a soil module to simulate spatially resolved terrestrial N losses via leaching, volatilization and gas production pathways. N₂O emissions from the soil module are released to a two-box atmospheric module to simulate N₂O mixing ratio and isotopic composition from the preindustrial era to the present day. The novel coupled model framework, ‘IsoTONE’, is optimized within a Bayesian framework using a high precision time series of N₂O mixing ratio and isotopic composition from several background sites, as well as estimates of N₂O emission factors from the Global N₂O Database.

2 Results and discussion

2.1 Terrestrial N₂O emissions

12 key parameters in the IsoTONE model were optimized using a Markov Chain Monte Carlo (MCMC) approach with 120 000 iterations, described in detail in Section A.3 and Table A.1. Total terrestrial N₂O emissions from the optimised model (Table 1) agree well with previous results, providing confidence in the novel isotopic basis of the model. Total terrestrial N₂O emissions (Figure A.12) for 1860 and 2010 were 5.3 ± 0.4 and 12.6 ± 0.7 Tg N₂O-N a⁻¹ respectively, showing good agreement with 1860 and 2010 estimates of 6.3 ± 1.1 and 10 ± 2.2 Tg N₂O-N a⁻¹ from the N₂O Model Intercomparison Project (Tian et al., 2019). The range of 12.6 to 13.9 Tg N₂O-N a⁻¹ modelled for 2007-2016 additionally agrees with a recent global metaanalysis estimating total terrestrial emissions of 12.2-23.4 Tg N₂O-N a⁻¹ for the same period (Tian et al., 2020), and with the mean of 12.9 Tg N₂O-N a⁻¹ from a metaanalysis by Scheer, Fuchs, Pelster, and Butterbach-Bahl (2020). Total global soil NO emissions for 2010 were estimated to be 13.7 ± 3.9 Tg NO-N a⁻¹, agreeing well with the high end of estimates from a metaanalysis suggesting global soil NO emissions of 1.8-12.3 Tg NO-N a⁻¹ (Pilegaard, 2013).

The spatial distribution of emissions from fertilisation, deposition and fixation for natural and anthropogenic soils is shown in Figure A.12. Natural N₂O emissions are dominated by N inputs from fixation (4.7 ± 0.8 Tg N₂O-N a⁻¹, 90% of natural emissions). In contrast, anthropogenic soil emissions are dominated by N inputs from deposition (70% of 1940 and 51% of 2020 emissions), although fertilisation is becoming increasingly important (14% of 1940 and 22% of 2020 emissions) (Table 1). The spatial distribution of N₂O emissions agrees well with inversion estimates from the Copernicus Atmospheric Monitoring Service (CAMS; R. Thompson (2021)) using data from 123 ground-based sites (Figure 1), with significant differences only seen in small isolated regions. The IsoTONE framework assumes that land use changes have had a minor impact on N₂O emission factors compared to the pre-existing variability in emission factors driven by climate and soil parameters - this assumption is supported by the good agreement between inversion and IsoTONE emission estimates. The largest differences are seen in tropical South America, Africa and Australia, which may be due to the scarcity of atmospheric monitoring stations available to constrain inversion estimates in these regions (R. Thompson, 2021). Differences may also relate to extensive land use change and cultivation of N-fixing soybean crops in South America. Furthermore, fundamental differences in N cycling and immobilization in tropical and Arctic regions may affect the accuracy of the IsoTONE model in these regions, as most experimental and field studies were conducted in temperate soils (Craine, Brookshire, et al., 2015; Voigt et al., 2020). Total N₂O emissions agree very well between the two models, with 13.3 ± 0.1 Tg N₂O-N a⁻¹ and 13.9 ± 0.9 Tg N₂O-N a⁻¹ predicted for 2019 by the CAMS inversion and IsoTONE respectively.

Figure 1. Modelled total terrestrial N_2O fluxes from the IsoTONE model (a) and from CAMS (b) (R. Thompson (2021); regridded to 0.5° using linear interpolation) for the year 2019. Both panels use the same logarithmic colour scale. The difference between the IsoTONE and inversion estimates is shown in c; areas where the difference is significant compared to the uncertainty are highlighted with black outlines.

Table 1. Changing characteristics of the total and anthropogenic terrestrial N₂O flux at the beginning of the anthropocene (1850) and through the past century. The natural flux and the area-weighted EF do not vary temporally. Growth rate is the 10-year mean growth rate centred on the year of interest. The area-weighted EF is the mean global EF calculated using the areas of grid cells as weights; the N-input weighted EF is calculated using the total N inputs of grid cells as weights.

		1850	1940	1980	2020
Total soil flux	Tg N ₂ O-N a ⁻¹	5.3±0.4	6.3±0.5	8.7±0.6	12.4±0.8
Natural soil flux	Tg N ₂ O-N a ⁻¹		5.3±0.4		
Anthropogenic soil emissions	Tg N ₂ O-N a ⁻¹	0	1.0±0.7	3.4±0.7	7.1±0.9
Growth rate of emissions	Gg N ₂ O-N a ⁻²	19±10	23±0.1	60±5	134±6
Anth. soil emissions - fertilisation N	Tg N ₂ O-N a ⁻¹	0	0.1±0.1	0.9±0.2	1.7±0.4
Anth. soil emissions - deposition N	Tg N ₂ O-N a ⁻¹	0	0.7±0.1	1.8±0.2	3.6±0.3
Anth. soil emissions - fixation N	Tg N ₂ O-N a ⁻¹	0	0.2±0.6	0.7±0.7	1.8±0.6
Anth. emissions not from soils	Tg N ₂ O-N a ⁻¹	0	1.0±0.7	1.4±0.7	1.7±0.9
δ ¹⁵ N, natural soil emissions	‰		-22.4±2.7		
δ ¹⁵ N, anthrop. soil emissions	‰	NA	-15.3±1.1	-17.0±1.1	-18.7±1.1
SP, natural soil emissions	‰		6.7±0.6		
SP, anthrop. soil emissions	‰	NA	5.9±0.2	6.0±0.2	6.8±0.2
EF, area-weighted	%		1.1±0.1		
EF, N input-weighted	%	3.6±0.7	3.8±0.7	4.0±0.8	4.3±0.3

The incorporation of isotopic composition means that, unlike previous global models, the IsoTONE framework distinguishes between different N₂O production pathways (Section A.5). The model results furthermore suggest that on average, laboratory-measured fractionation factors for these pathways are only expressed at $\sim 55\%$ on average in soils ($\text{frac_ex} = 0.55 \pm 0.05$, Table A.1). This is a global average which we expect to vary widely between individual sites depending on soil structure, moisture, and the depth of N₂O production and consumption. For example, soils with small N cycling and gas diffusion rates would be expected to have higher isotopic fractionation during N loss processes compared to soils with high diffusivity. In 2020, 60% of N₂O emitted from soils ($7.5 \pm 0.4 \text{ Tg N}_2\text{O-N a}^{-1}$) was produced from denitrification and 39% ($4.7 \pm 0.8 \text{ Tg N}_2\text{O-N a}^{-1}$) from nitrification. The contribution of nitrification to soil N₂O emissions has decreased very slightly from 40% in 1850 to 39% in 2020 (Figure A.10). The spatial distribution of nitrification-N₂O from IsoTONE agrees very well with the global map produced by Pan, Lam, Wang, Mosier, and Chen (2021), with high nitrification in areas such as the Amazon basin, sub-Saharan Africa, Europe and coastal Australia. However the model of Pan et al. (2021), centers around total nitrification rate, which is not estimated in IsoTONE, so the results cannot be directly compared.

Globally, just 30% of fertiliser N appears to be available for N cycling (fert_EF_red , Table A.1) - the remaining fertiliser N is primarily incorporated into harvest, and may also be immobilised via increased soil storage, or lost through leaching pathways which are not explicitly modelled. This is consistent with previous metaanalyses, which show that 15-70% of fertiliser N is taken up by plants, a significant proportion could remain in soils, and 5-25% is unaccounted for in plant or soil pools and thus lost to the pathways modelled in this study (Corbeels, Hofman, & Van Cleemput, 1999; Gardner & Drinkwater, 2009; Jenkinson, Poulton, Johnston, & Powlson, 2004; Sebilo et al., 2013). Therefore, emission factors for fertiliser emissions can be significantly lower than for other N inputs, with implications for the applicability of EF measurements from agricultural sites. Mean global fertiliser N incorporation could be increasing as plant growth and thus N use is enhanced in response to increasing atmospheric CO₂, however water and nutrient limitations will also play a role in regulating plant growth (Tian et al., 2020) - this potential effect is not currently captured in IsoTONE and should be a focus of future model studies.

2.2 The anthropogenic N₂O budget: Inputs, losses and trends

The anthropogenic N₂O soil flux in 2020 was estimated to be $7.1 \pm 0.6 \text{ Tg N}_2\text{O-N a}^{-1}$, close to the highest projected emission scenario (RCP8.5) estimate for 2020 (IPCC, 2014; Tian et al., 2020) (Figures 2 and A.11). 1.7 ± 0.4 , 3.6 ± 0.3 and $1.8 \pm 0.6 \text{ Tg N}_2\text{O-N a}^{-1}$ of the anthropogenic flux were contributed by soil emissions from fertilisation, deposition and fixation N inputs respectively (Table 1), with an additional $1.7 \text{ Tg N}_2\text{O-N a}^{-1}$ from non-soil anthropogenic emission sources (emissions from EDGAR for categories 1A1, 1A3b, 2B and 6, Section 4.2.2). This agrees very well with a recent ensemble analysis, which estimated a total anthropogenic flux of 7.3 (4.2-11.4) $\text{Tg N}_2\text{O-N a}^{-1}$ (Tian et al., 2020). We find that deposition N accounts for $41 \pm 14\%$ of all anthropogenic emissions in 2020 compared to $19 \pm 12\%$ direct emissions from fertilisation, $21 \pm 15\%$ from enhanced fixation, and 19% from non-soil sources: Deposition N inputs clearly contribute the majority of anthropogenic emissions. This finding is in contrast to the results of Tian et al. (2020), who report that direct N₂O emissions from fertilisation are dominant. These contrasting results are due in part to the classification of all emissions above the 1850 baseline (eg. enhanced N₂O from natural sites due to warming, fixation and deposition) being classified as anthropogenic in this study, whereas in previous studies some or all of these processes are not considered in the calculation of the anthropogenic burden. Moreover, our results suggest that emission factors could be significantly underestimated from field measurements (see Sections 2.1 and 2.3) - particularly at agricultural sites where a significant proportion of N is removed through harvest or immobilization as described by fert_EF_red - which may lead to some underestimation of deposition emissions in different model frameworks.

Figure 2. Temporal evolution of N inputs and N₂O emissions, and growth rates of N₂O emissions and N₂O mixing ratio. The top panel shows annual inputs for fertilisation, deposition, fixation, and total N used in the model (see Section 4.1 for data sources). The second panel shows the anthropogenic flux broken down into N input categories of fertilisation, deposition and fixation, estimated by assuming that all increases in N₂O emissions for all input categories (fixation, fertilisation, deposition) after 1850 are due to anthropogenic influences. The shaded areas indicate the 1 σ uncertainty. The third panel shows the growth rate of N₂O emissions (Tg N₂O-N a⁻²) from each input category calculated over 3 (pale) and 10 (dark) year windows. The bottom panel shows the growth rate in modelled N₂O tropospheric mixing ratio (left axis; purple solid line) as well as the modelled change in mixing ratio growth rate (right axis; blue dotted line).

The 10-year mean growth of total anthropogenic N₂O emissions was between 0 and 0.04 Tg N₂O-N a⁻¹ a⁻¹ until ~1945 (Figure 2). Between 1945 and 1980 the 10-year mean growth rate in emissions increased to 0.12 ± 0.02 Tg N₂O-N a⁻¹ a⁻¹ due to rapid growth in fertiliser inputs, after which it stabilised at around 0.1 Tg N₂O-N a⁻¹ a⁻¹, corresponding to a steady rate of change of around 0.015 nmol mol⁻¹ a⁻¹ a⁻¹ in tropospheric background N₂O growth rate. The growth rate of anthropogenic emissions was particularly high between 2010 and 2015 (3-year growth rate up to 0.3 Tg N₂O-N a⁻¹ a⁻¹) compared to the average of the last 50 years (0.09 ± 0.06 Tg N₂O-N a⁻¹ a⁻¹), in agreement with two recent studies (R. L. Thompson et al., 2019; Tian et al., 2020). This caused the rate of change for the tropospheric N₂O burden to peak at 0.026 nmol mol⁻¹ a⁻² (Figure 2). After 2015, the growth rate of emissions strongly decreased, meaning the 10-year mean growth for 2010-2020 was 0.14 Tg N₂O-N a⁻¹ a⁻¹ and thus within then normal range for the last half-century (Figure 2). Fluctuations in the growth rate for tropospheric background N₂O mixing ratio reflected the growth rate

in emissions driven by different input categories. Variability in fixation N inputs dominates subdecadal interannual variability in total terrestrial N₂O emissions, such as the 2010-2015 peak, contributing >70% of variability within decadal bins (Figure 2). Fixation inputs are 2-10 times more variable than other input types at subdecadal timescales, thus accounting for their key role in driving variability in N₂O emissions. In contrast, changes in fertilisation inputs drive the changing growth rate of anthropogenic emissions at timescales larger than 1-2 decades. Increases in both fertilisation and deposition are responsible for the strong and constant increase in N₂O emissions and tropospheric background mixing ratio over the last century. These findings could be impacted by uncertainties in the input datasets, which should be investigated further using targeted isotopic and modelling approaches at the site and regional scale in regions with particularly high uncertainty.

The isotopic composition of the total anthropogenic source reflects changing emission processes (Figure A.11). $\delta^{15}\text{N}$ of the anthropogenic source is higher than the mean soil source (Table 1) and shows a strong decreasing trend, which may indicate an increasing dominance of agricultural emissions (Prokopiou et al., 2017). During the growth rate acceleration of 1945-1980, SP of the anthropogenic source was relatively constant, however after 1980 it strongly increased. These fluctuations were also observed by Prokopiou et al. (2017), who used a two-box model to interpret N₂O source isotopic composition from firn air data, and found similar but more uncertain values for anthropogenic source isotopic composition. Variability in SP and $\delta^{15}\text{N}$ are in opposite directions, and thus unlikely to be caused by changes in the extent of N₂O reduction to N₂, which would increase both the SP and $\delta^{15}\text{N}$ of remaining N₂O (L. Yu, Harris, Lewicka-Szczepak, & Mohn, 2020). An alternative explanation for changing SP and $\delta^{15}\text{N}$ could be a shift in the denitrification (low SP) to nitrification (high SP) ratio. Our results however suggest a 1% decrease in nitrification contribution to global N₂O emissions, which could not account for the observed increase of ~1‰ in SP of anthropogenic N₂O based on SP endmembers of 0 and 30‰ for N₂O from denitrification and nitrification.

Figure 3. Modelled N₂O emission factor: a) Global gridded N₂O emission factor (upper) and the 1 σ uncertainty (lower); b) Relationship between mean annual precipitation (MAP), mean annual temperature (MAT; point colour) and N₂O emission factor for each grid cell.

2.3 Drivers of spatiotemporal variability in N₂O emission factor

Soil moisture, N content, mean annual precipitation and soil bulk density (21, 9, 5, 4% of variability respectively) were the main parameters causing broad geoclimatic gradients in N gas production and N₂O EF between different regions (Figures 3 and A.13), consistent

with previous laboratory and field results (Cantarel et al., 2012; Smith, Thomson, Clayton, McTaggart, & Conen, 1998; Yao et al., 2010; Zhang et al., 2019). Mean annual temperature was important for total N gas production, but not for EF (5 vs. 0.2% of variability in f_{gas} and EF). Total gas production accounts for the largest proportion of N losses in warm, dry regions, whereas N_2O EFs are highest in non-desert tropical regions, in particular sub-Saharan Africa, southern India, China, and south east Asia, and low in drier and colder areas. This agrees well with results from Tian et al. (2020) and Q. Wang et al. (2020), as well as in situ measurement studies showing high N losses via both leaching and denitrification from ‘leaky’ N cycles in tropical regions (Brookshire, Gerber, Greene, Jones, & Thomas, 2017; Rütting et al., 2015). Geoclimate-driven variability in emission factors can be clearly seen in regions underrepresented in EF compilations, such as Australia, which shows a clear gradient from high total N gas production but low N_2O EF in the dry centre, to higher N_2O EF in coastal and northern regions. This pattern, whereby arid regions show relatively high N gas production dominated by NO, but low N_2O EF, can be seen across central North America, the Sahara, Australia, and central Asia. This suggests global applicability of the experimental results from Homyak et al. (2016), who used isotopic tracing to show high NO production from arid soils was due to reduced plant N uptake and low leaching.

The spatial distribution of N inputs plays a key role in determining the overall global EF for N_2O (Figure 4). The mean global EF for N_2O weighted by area was $1.1 \pm 0.1\%$, close to the IPCC default value of 1.4% for combined direct and indirect emissions (Davidson, Suddick, Rice, & Prokopy, 2015; IPCC, 2006). However, the mean global EF weighted by total N inputs per grid cell in 2020 was $4.3 \pm 0.3\%$, as a much greater proportion of total N inputs are in ‘high emission’ temperate and tropical non-arid latitudes compared to dry and cold areas (Figure 3). This builds upon the observation of Tian et al. (2020), who showed that the mean global EF for N_2O from agricultural soils is significantly higher than the IPCC default value. Measurements of mean annual EFs using chambers and similar methodologies are far more time intensive and expensive than measurements of soil $\delta^{15}\text{N}$, thus isotopic modelling of the N cycle can be used to understand regional variability in EFs to facilitate upscaling and extrapolation of data from traditional methods. Modelled EFs were compared to the compiled values for croplands used in the metaanalysis of Cui et al. (2021) by finding the mean and standard deviation of all EFs reported by Cui et al. (2021) in each gridcell. Field EF measurements are laborious and challenging, thus relatively few data points are available - of the 55 478 gridcells with a valid modelled EF, only 179 have one or more EF measurements. The agreement between modelled values and observations was relatively good, with a Spearman correlation coefficient of 0.4 ($p < 0.01$) indicating moderate agreement. However, the slope of 0.15 suggested that measurements may consistently underestimate EFs due to insufficient measurement frequency and duration and the importance of ‘hot spots’ and ‘hot moments’ for annual N_2O emission totals (Butterbach-Bahl, Baggs, Dannenmann, Kiese, & Zechmeister-Boltenstern, 2013; McDaniel, Kaye, & Kaye, 2014). The impact of climate change - in particular changing precipitation patterns - on N_2O emissions in rapidly developing regions like sub-Saharan Africa and India is not yet captured by observations, and should be a focus of future studies. Understanding the large-scale impact of moisture availability and other climate parameters on N loss processes through targeted measurements campaigns and model development will be key to predicting interactions between climate change-driven precipitation changes and N_2O emissions.

The proportion of N_2O lost to different pathways shows clear temporal changes, particularly for fertilisation N inputs, which show an increase in mean EF of N_2O from $<4\%$ prior to 1940 to $>5\%$ in 2020 (Figure A.14). This has two major causes: Changing spatial distribution of N inputs and climate warming feedback (Figure 4a). The shift in fertilisation from North America and other temperate regions ($\text{EF}_{\text{N}_2\text{O}}$ of 4-5%) towards emerging economies in warmer regions with higher EFs ($\text{EF}_{\text{N}_2\text{O}} > 7.5\%$), in particular China, has caused additional emissions of $0.5 \pm 0.3 \text{ Tg N}_2\text{O-N a}^{-1}$ since 1940 (Figure 4c). This effect is only seen for fertilisation N inputs: Deposition and fixation inputs show vary minor spatiotemporal

changes (Figure 4c). Deposition inputs are stabilising in China due to vigorous controls on N pollution (G. Yu et al., 2019), and changes in N₂O from deposition in coming decades are likely to be of minor importance compared to fertilisation- and climate-driven emissions. The impact of climate warming (Figure 4b) has led to an increase in total microbial gas production of around 3% between 1850 and 2020 (Figure A.14), resulting in additional emissions of 0.8 ± 0.4 Tg N₂O-N a⁻¹, and a consequent decrease in leaching losses. The parameterised ‘warming’ impact will be a combination of feedbacks driven by both changing precipitation and increased temperature, which cannot be separated in the current IsoTONE framework. The combined increase of 1.3 Tg N₂O-N a⁻¹ from spatial input changes and climate warming represents 18% of soil and 15% of total anthropogenic N₂O emissions in 2020. As climate warming continues, and fertiliser use increases in many tropical and subtropical regions, the mean EF of N₂O and thus the growth rate of tropospheric N₂O will accelerate, unless significant efforts are focussed on N₂O mitigation and increased fertiliser N use efficiency in emerging economies (Tian et al., 2020). Moreover, the impact of potential unknown climatic feedbacks, in particular non-linear responses associated with extreme events such as drought and flooding, should be a key focus for both measurement and model studies.

Figure 4. Impact of changing spatial distribution of fertilisation as well as climate warming on N₂O emissions from 1940 to 2020: *a)* The average change in annual N₂O emissions due to the shifting spatial distribution of fertiliser N inputs, calculated using the 1940 spatial distribution of fertilisation scaled to the 2020 total fertilisation quantity, and comparing this to the actual 2020 emissions. *b)* The average change in annual N₂O emissions due to climate warming and the temperature dependency of N₂O production, found by calculating 2020 emissions with and without the impact of warming on EF since 1940. *c)* The proportion of anthropogenic N inputs from fertilisation, deposition and fixation in 1940, 1980 and 2020 accounted for within bins defined according to the EF for N₂O. 20 bins were used; 19 were distributed evenly between the parameter minimum and the mean + 3 standard deviations; the highest bin was for all data >mean + 3 standard deviations.

3 Conclusion

N₂O emissions over the past decades have increased strongly, following the trajectory predicted by the highest emission scenario (RCP8.5) (Tian et al., 2020), which suggests an increase in the global emission factor for N₂O. We developed and applied a coupled soil-atmosphere nitrogen isotope model using soil $\delta^{15}\text{N}$ as an emission proxy to understand the processes underlying spatiotemporal dynamics of global N₂O emissions. The model results show that deposition N inputs drive the majority of N₂O emissions. Fertilisation N inputs are responsible for multidecadal variability in emissions, whereas subdecadal variability in N₂O emissions is driven by biological N fixation. We show that the effective (N-input weighted) EF in 2020 is $4.3 \pm 0.3\%$, much higher than the IPCC default value of 1.4%. N₂O EFs are highly spatially heterogeneous - highest in warm, wet ecosystems - and thus strongly underestimated by default values based on area-weighted means. N₂O EFs have increased over the past century, driven by climate warming as well as spatial redistribution of fertiliser N inputs. These two phenomena have led to additional emissions of 0.8 ± 0.4 and 0.5 ± 0.3 Tg N₂O-N a⁻¹ respectively between 1940 and 2020. Feedbacks between climate warming, spatial changes in agriculture, and N₂O emissions should be considered in the development of emission projections and mitigation policies. Monitoring of annual N₂O emissions as well as the soil $\delta^{15}\text{N}$ emission proxy in both understudied regions and regions with particularly high emission factors will be key to reduce uncertainty, focus mitigation efforts, and combat rising N₂O emissions.

4 Methods

4.1 Input data

4.1.1 Soil, climate and N input datasets

Mean annual surface temperature (MAT) and precipitation (MAP) at 10 minute spatial resolution were taken from the Climate Research Unit high resolution global climatology dataset (New, Lister, Hulme, & Makin, 2002). Global soil organic carbon estimates and topsoil (0-30 cm) bulk density were taken from the Harmonized World Soil Database with a spatial resolution of 30 arc seconds (FAO, IIASA, ISRIC, ISSCAS, & JRC, 2012; Hiederer & Köchy, 2012). Aridity index at a spatial resolution of 30 arc seconds was taken from the Global Aridity Index and Potential Evapotranspiration Climate Database (v2) (Trabucco & Zomer, 2019). Global soil pH at >60 000 sites worldwide was taken from the database compiled by Slessarev et al. (2016). The Worldwide Organic Soil Carbon and Nitrogen Dataset (Zinke, Stangenberger, Post, Emanuel, & Olson, 2004) was used to estimate soil organic nitrogen content with data from >4 000 sites rasterised using linear interpolation with `scipy`. Total fertiliser N inputs were taken from the Land Use Harmonization Database (LUH) with the historical dataset used for 1800-2015 (LUH2 v2h) and the future forcing dataset for 2015-2020 (LUH2 v2f) (Hurtt et al., 2020). The Community Atmosphere Biosphere Land Exchange (CABLE) Australian community land surface model (Kowalczyk, Wang, and Law (2006); Peng et al. (2020), <https://www.cawcr.gov.au/research/cable/>) was used to estimate global mean WFPS, fractional NH_3 losses (no temporal variability) and deposition and fixation N inputs (annual) (Houlton, Wang, Vitousek, & Field, 2008; Kowalczyk et al., 2006; Peng et al., 2020). All datasets were converted to the model grid with $0.5^\circ \times 0.5^\circ$ resolution for -180° to $+180^\circ$ longitude and -60° to $+85^\circ$ latitude (720×290 gridcells) using the Python function `scipy.interpolate.griddata` with linear interpolation.

4.1.2 Global dataset for $\delta^{15}\text{N}_{\text{soil}}$

Data for $\delta^{15}\text{N}_{\text{soil}}$ for >6 000 soil samples from natural (non-agricultural) sites was compiled by Craine, Elmore, et al. (2015). This database also includes ancillary data such as MAT, MAP, carbon and nitrogen concentration, C:N ratio, soil texture, density and pH, and site coordinates and elevation, although not all parameters are available for all samples. Geographical coverage was improved by adding a further 748 samples, including 112 samples from Australia (BASE database; Bissett et al. (2016)) and 392 from Africa - regions which were underrepresented in the Craine database. The majority of data was from near-surface soil (0-50 cm depth). Within this depth range, no significant effect of depth on $\delta^{15}\text{N}_{\text{soil}}$ was seen in the data. The sample-specific reported ancillary data was compared to the global gridded datasets (Section 4.1.1) at the same geographical locations to gapfill the ancillary data (Section A.1). Relationships between ancillary data and $\delta^{15}\text{N}_{\text{soil}}$ measurements were then used to predict $\delta^{15}\text{N}_{\text{soil}}$ using an artificial neural network (ANN) with the Python package Keras (Chollet (2015); details in Section A.1). Using the ANN, global $\delta^{15}\text{N}_{\text{soil}}$ on an $0.5^\circ \times 0.5^\circ$ grid was estimated in order to drive the soil isotope module (Section 4.2.1). A bootstrapping approach was used to estimate uncertainty in gridded $\delta^{15}\text{N}_{\text{soil}}$.

4.1.3 Atmospheric data

An tropospheric background time series of N_2O mixing ratio and isotopic composition since the preindustrial era formed the core set of observational data used to constrain simulation results in this study (Figure 5). The background mixing ratio, for the purposes of this study, is defined as the concentration of a given species when the impact of local or recent sources and sinks is absent - also known as the baseline concentration (IUPAC, 2019). The primary dataset comprised tropospheric background measurements of N_2O mixing ratio, $\delta^{15}\text{N}$ and N-isotope SP from the Jungfraujoch High Alpine research station

and the Cape Grim Air Archive (CGAA), as well as firn air sampled during the 2018 East Greenland Ice coring Project (EGRIP) campaign (L. Yu, Harris, Henne, et al., 2020; L. Yu et al., 2022) covering the period from 1982 to the present day, all measured at Empa, Switzerland. Additionally, mixing ratio, $\delta^{15}\text{N}$ and SP data from CGAA (1979-2005) and firn air (1939-1995) from Park et al. (2012) were used. These were corrected to the Empa dataset scale using the mean offset in the overlap period, with offsets of -1.1‰ and -1.0‰ found for firn and CGAA data for $\delta^{15}\text{N}$, and $+1.5\text{‰}$ and $+1.3\text{‰}$ for firn and CGAA data for SP. To extend the isotopic timeseries further back, ice core and interstitial snowpack air measurements from the Greenland Ice Sheet Project II (GISP II) (Sowers et al., 2002) were also used, covering the period from 1785-1990. This dataset showed no offset for $\delta^{15}\text{N}$ compared to the Empa dataset, and did not include SP measurements. Other available datasets (e.g. Toyoda et al. (2013), Prokopiou et al. (2017)) were not integrated, as they would not have improved the temporal range of the combined dataset, and would have introduced additional calibration scale uncertainty.

N_2O mixing ratio in the preindustrial era was constrained using two Antarctic ice core datasets - from Machida, Nakazawa, Fujii, Aoki, and Watanabe (1995) covering the period 1735-1964, and from Rubino et al. (2019) covering the period from 154-1986. Additionally, measurements of N_2O mixing ratio available at the World Data Centre for Greenhouse Gases (WDCGG, <https://gaw.kishour.go.jp>) supported by the Global Atmosphere Watch (GAW) Program at Jungfraujoch (2005-present) and the Cape Grim Baseline Atmospheric Pollution Station (1980-present; ALE/GAGE/AGAGE program) were used. Cape Grim data comprise measurements from three instruments covering different time periods, so overlapping periods were used to correct scale offsets, with the most recent dataset (1993-2018) used as an anchor. The dataset from 1981-1994 was $+0.03 \text{ nmol mol}^{-1}$ offset from the most recent dataset, and the dataset from 1978-1985 was $-0.07 \text{ nmol mol}^{-1}$ offset from the 1981-1994 dataset.

To allow comparison to simulated results and minimize the impact of any strong episodic local sources, average values for mixing ratio and isotopic composition were binned into 25-year intervals (1740-1940) and 2-year intervals (1940-2018) (Figure 5). Differences between northern and southern hemisphere sites were not significant given the measurement uncertainty, thus the troposphere was considered as a single well-mixed box to facilitate comparison with IsoTONE simulations. The average standard deviation within each time window for 1740-1940 data was $5.4 \text{ nmol mol}^{-1}$, 0.5‰ and 1.2‰ for mixing ratio, $\delta^{15}\text{N}$ and SP, compared to $0.8 \text{ nmol mol}^{-1}$, 0.2‰ and 0.6‰ for mixing ratio, $\delta^{15}\text{N}$ and SP for 2000-2020, reflecting both the strong improvement in measurement techniques for recent in situ data and the particular challenges of firn and ice core measurements. The trend in mixing ratio for averaged data over the last 40 years was $+0.8 \text{ nmol mol}^{-1} \text{ a}^{-1}$, with trends of -0.03 ‰ a^{-1} and -0.006 ‰ a^{-1} observed for $\delta^{15}\text{N}$ and SP respectively.

4.1.4 N_2O fluxes and emission factors

Data for N_2O fluxes and emission factors (EF) for >300 sites has been compiled in the ‘Global N_2O Database’ (Dorich et al., 2020). This database also includes ancillary data such as MAT, MAP, carbon and nitrogen concentration, C:N ratio, soil texture, density and pH, and site coordinates and elevation, although not all parameters are included for all samples. The sample-specific reported ancillary data was compared to the global gridded datasets (Section 4.1.1) at the same geographical locations (see Section A.1). The strongest relationships between ancillary data and emission factors were determined, and used to bin emission factor data into 16 different geographical regions to simplify comparison with modelled emission factors and minimise the impact of localised emission hotspots (see details in Section A.1.2).

Figure 5. Tropospheric background N_2O mixing ratio and isotopic composition ($\delta^{15}\text{N}$ and SP). Scale offsets between different datasets have been corrected using overlapping periods to match the Empa dataset as described in the text. Mean data at 25-year intervals (1740-1940) and 2-year intervals (1940-2018) are shown as orange points with black outline; the standard deviation of the data averaged for each point is shown as the orange shaded region.

4.2 Coupled soil-atmosphere model

The model used in this study is an extension of the simple soil isotope model presented by Bai et al. (2012), coupled to an extended version of the atmospheric box model described in L. Yu, Harris, Henne, et al. (2020) to simulate gridded N_2O fluxes as well as tropospheric mixing ratio and isotopic composition from 1800 to 2020. The full coupled model was written in **Python** and will be hereafter referred to as the **IsoTONE** model (**I**sotopic **T**racing **O**f **N**itrogen in the **E**nvironment). A schematic of the model is shown in Figure 6 and a detailed description is given in the following subsections.

Figure 6. A schematic view of the IsoTONE model and inversion structure, showing different input and output data types. Optimized variables (green) are defined in Table A.1. Sources of input and observation data are given in Section 4.1. Abbreviations: MAT = Mean Annual Temperature; WFPS = Water-Filled Pore Space; CABLE = Community Atmosphere Biosphere Land Exchange land surface model; MCMC = Markov Chain Monte Carlo; f_G , f_L , f_{NO} , $f_{\text{N}_2\text{O}}$, and f_{N_2} refer to the proportion of N lost through leaching and N gas production, discussed in Section 4.2.1.

4.2.1 Soil nitrogen module

The soil N module of IsoTONE estimates fractionational losses of N to different pathways based on $\delta^{15}\text{N}_{\text{soil}}$ (Section 4.1.2). The module is based on the equations used by Houlton and Bai (2009) and Bai et al. (2012), which state that the $\delta^{15}\text{N}_{\text{soil}}$ reflects the balance between N inputs (i), with a relatively constant rate and isotopic composition, and variable N losses. Loss pathways are divided into leaching (L), with low isotopic fractionation; NH_3 volatilization, with high isotopic fractionation but a low contribution to total losses (NH_3); and abiotic and microbial gas production (G), with high and variable isotopic fractionation. At steady state, inputs must equal outputs for both total amounts and isotopic composition:

$$f_L + f_{\text{NH}_3} + f_G = 1 \quad (1)$$

$$\delta^{15}\text{N}_{\text{soil}} = \delta^{15}\text{N}_i - \varepsilon_G \times f_G - \varepsilon_L \times f_L - \varepsilon_{\text{NH}_3} \times f_{\text{NH}_3} \quad (2)$$

where ε is the fractionation factor ($k^{15}\text{N}/k^{14}\text{N}$ expressed in permil, where k is the reaction rate) for the respective loss pathway and $\delta^{15}\text{N}_i$ was set as -1.5‰ (Bai et al., 2012). Assuming steady state, the fraction of N loss accounted for by leaching (f_L), NH_3 volatilization (f_{NH_3}) and gas production (f_G) can be calculated from $\delta^{15}\text{N}_{\text{soil}}$. The steady state assumption is only valid for natural ecosystems, thus only $\delta^{15}\text{N}_{\text{soil}}$ measurements from natural sites were used to initialise the model. Unlike Bai et al. (2012), ^{14}N and ^{15}N were traced separately in Eq. 2, whereby the rate of ^{15}N loss via a pathway is the rate of ^{14}N multiplied by the fractionation factor, for example, for leaching:

$$k_L^{15} = k_L^{14} \times \left(\frac{\varepsilon_L}{1000} + 1 \right) \quad (3)$$

The rate of ^{15}N addition was calculated analogously. Tracing isotopes separately facilitated calculation of the stepwise impact of N losses on the remaining N reservoir isotopic composition (‘Rayleigh fractionation’ (Mariotti et al., 1981)), and necessitated an iterative solution to Eq. 2. Rayleigh fractionation describes how the isotopic composition of reactant and product pools change as a reaction proceeds depending on the fractionation factor and the fraction of reactant consumed, assuming both reactant and product pools are well mixed (Mariotti et al., 1981).

We assumed that N loss processes are primarily linked with the inorganic N pools (i.e. NO_3^- and NH_4^+), and estimated fractionation factors related to the two species. Fractionation during N mineralization was assumed to be minor (Möbius, 2013). Soil organic N was not considered, given that the rates of turnover processes and their associated isotopic fractionation effects are very scarcely studied at the global scale. Fractionation during leaching (ε_L) was estimated to be 1‰ (Bai et al., 2012). Fractionation during NH_3 volatilization ($\varepsilon_{\text{NH}_3}$) was estimated to be -17.9‰ based on the equation in Stern, Baisden, and Amundson (1999). Fractionation during N gas production (ε_G) was estimated based on the relative contributions of the two dominant microbial processes:

- Fractionation for N_2O production during nitrification of NH_4^+ (ε_{nit}) was estimated as $-56.6 \pm 7.3\text{‰}$ with SP of $29.9 \pm 2.9\text{‰}$ (Denk et al., 2017).
- Fractionation for N_2O production during denitrification of NO_3^- ($\varepsilon_{\text{denit}}$) was estimated by adding the fractionation factor for reduction of NO_3^- to NO_2^- ($-31.3 \pm 6.1\text{‰}$) and for NO_2^- to N_2O ($-14.9 \pm 6.7\text{‰}$) (Denk et al., 2017), thus $\varepsilon_{\text{denit}} = -46.2\text{‰}$. SP for N_2O produced from denitrification was estimated as $-1.6 \pm 3.0\text{‰}$.
- Fractionation for N_2O reduction during denitrification (ε_{red}) was estimated as $-6.6 \pm 2.7\text{‰}$ with SP of $-5 \pm 3\text{‰}$ (Denk et al., 2017).

In contrast to bacterial and abiotic denitrification, fungal denitrification results in N_2O with a high and variable SP. The partitioning of N_2O production into fungal denitrification as compared to bacterial nitrification and denitrification (shown in Figure A.6) is currently not known and therefore cannot be parameterised within this model. Fungal denitrification is a minor source of N_2O , expected to contribute less than 10-15% globally (Rohe et al., 2020), and will be included in a future version of this model as data to drive parameterisations becomes available.

These fractionation factors refer to the immediate production or consumption of N substrates and N_2O , and thus do not account for the complexity of processes leading to the net isotopic composition of emitted N_2O in real environments. Several studies have recognised that soil gas is not a homogeneous, well-mixed environment - instead, gas production and consumption occurs in pores that are only partially connected relative to the rate of microbial processes (Bai & Houlton, 2009; Wen et al., 2016). This means that Rayleigh fractionation processes occur within all pores and microenvironments, and thus the effective net fractionation may be significantly lower than calculated from measured fractionation factors, often referred to as ‘underexpression’ (Bai & Houlton, 2009). We

therefore introduce a parameter called the fractionation expression factor (`frac_ex`) to the model such that net or effective fractionation = $\varepsilon \times \text{frac_ex}$ for all modelled processes. Thereby, `frac_ex` = 1 would reflect a well-mixed soil gas reservoir where effective fractionation is equal to expectations from laboratory measurements, and `frac_ex` = 0 would reflect a completely closed soil gas environment where all reactions go to completion within separate pores and thus no effective fractionation is observed. The initial value of `frac_ex` was set to 0.7 and it was optimized in the MCMC framework (Section 4.4) assuming a uniform error distribution between 0.3 and 1.0. In reality, different values for `frac_ex` may be expected for different processes and environments, in particular depending on soil texture and pore structure, however this cannot be determined within the available model-data framework.

The soil model was run on an $0.5^\circ \times 0.5^\circ$ grid from -60° to 80° latitude and -180° to 180° longitude. The $\delta^{15}\text{N}$ grid (Section 4.1.2; Figure A.2a) was first initialised in each model run by adding 5% of the uncertainty in $\delta^{15}\text{N}$ (Figure A.2b) multiplied by a normally distributed random number ($\mu = 0, \sigma = 1$). For each grid cell, the soil model was initialised with an available soil nitrogen pool of size 1 (unitless) with $\delta^{15}\text{N}$ of 0‰, and a soil N_2O pool of size 1 (unitless) with $\delta^{15}\text{N}$ and SP of 0‰. The ^{14}N input rate (k_i) was set at 1 (unitless) and the ^{15}N input rate ($k_{i,15}$) calculated using $\delta^{15}\text{N}_i$ of 0.5‰ (based on Bai et al. (2012); Beyn, Matthias, Aulinger, and Dähnke (2015); Unkovich (2013); Zhang, Liu, Fangmeier, Goulding, and Zhang (2008)). Changing the unitless pool sizes affects only the number of iterations until steady state is reached in the model, and not the final result of the model. Reducing $\delta^{15}\text{N}_i$ by 1‰ increased the calculated mean global f_G by $\sim 1\%$, while increasing $\delta^{15}\text{N}_i$ by 1‰ increased the calculated mean global f_G by $\sim 5\%$, with very little impact of spatial distribution of f_G .

To solve Eq. 2 for each grid cell, the soil module was run over four iterations ($n = 4$). For the first iteration, f_G was set at 0.1 for all gridcells. f_{NH_3} was estimated using the CABLE model (Kowalczyk et al., 2006; Peng et al., 2020). f_{NH_3} is nearly always < 0.05 , therefore the model results are not highly sensitive to the parameterisation of f_{NH_3} . f_L was then determined as $1 - f_G - f_{\text{NH}_3}$. Partitioning of total gas losses (f_G) into N_2O , N_2 and NO ($f_{\text{N}_2\text{O}}$, f_{NO} , f_{N_2}) was estimated with a sigmoid fit of WFPS to available experimental measurements (Section A.2, Figure A.5), with mean global WFPS from CABLE used to constrain partitioning for each grid cell in the model. Similarly, denitrification (f_{denit}) and nitrification (f_{nit}) contributions to N_2O production were estimated with a sigmoid fit to available experimental data (Section A.2, Figure A.6). Mean WFPS will not describe all variability in gas partitioning, given the highly variable and non-linear nature of N gas emissions, however it provides the best available estimate based on the current status of experimental and modelling research. An overall ε_G was estimated based on f_{denit} and f_{nit} and the fractionation factors for the individual processes multiplied by `frac_ex`, with a mean value of -30‰ . This is lower than in Bai et al. (2012) where a range of -16 to -20‰ was assumed for ε_G without explicit consideration of microbial pathways - measurements made since the publication of Bai et al. (2012) have shown that fractionation is much larger than previously estimated (Denk et al., 2017). To achieve steady state, 10 cycles of N addition and removal were conducted within each iteration. First, N inputs for ^{14}N and ^{15}N were added to the initial soil N pool. N was then removed via leaching, volatilization, and gas production for ^{14}N and ^{15}N . The steady state soil pool $\delta^{15}\text{N}$ value at the end of each iteration ($\delta^{15}\text{N}_{ss}$) was compared to the $\delta^{15}\text{N}$ value for the gridcell ($\delta^{15}\text{N}_{soil}$) to find an improved f_G for the next iteration according to:

$$f_{G,n+1} = f_{G,n} - \frac{\delta^{15}\text{N}_{soil} - \delta^{15}\text{N}_{ss}}{\varepsilon_G} \quad (4)$$

Following four iterations, $\delta^{15}\text{N}_{soil}$ and modelled $\delta^{15}\text{N}_{ss}$ agreed within 0.01‰ and final values of f_G and f_L were accepted.

In addition to the calculation of f_G and f_L , the soil module estimated N_2O production rate and isotopic composition for each grid cell. The production rates for ^{14}N - N_2O and ^{15}N - N_2O were calculated from the fractionation factors for each pathway multiplied by `frac_ex`;

both $^{15}\text{N}^\alpha$ and $^{15}\text{N}^\beta$ were traced separately to consider N_2O SP. For example, the ^{14}N reaction rate for nitrification N_2O production was estimated as $f_G \times f_{\text{N}_2\text{O}} \times f_{\text{nit}}$ and the corresponding reaction rate for ^{15}N as:

$$k_{^{15}\text{N},\text{nit}} = f_G \times f_{\text{N}_2\text{O}} \times f_{\text{nit}} \times \left(\frac{\varepsilon_{\text{nit}} \times \text{frac.ex}}{1000} + 1 \right) \quad (5)$$

Analogously, rates for each isotopic variant were also calculated for denitrification production and reduction. The production of N_2 was assumed to represent the consumption of N_2O via complete denitrification, as no other significant N_2 sources are known, thus the extent of N_2O reduction could be estimated and its isotopic effect calculated. N_2O production and consumption were estimated in each step of the steady state calculation to give a final N_2O flux and isotopic composition ($\delta^{15}\text{N}$ and SP) for each gridcell to pass on to the atmospheric module described in the following subsection.

4.2.2 Atmospheric N_2O module

The atmospheric module takes the fractional losses, estimated by the soil module described in the previous subsection, and uses a two-box model representing a well-mixed troposphere and stratosphere to reconstruct N_2O background mixing ratio and isotopic composition. Absolute N emissions into the tropospheric box were calculated using the fractional estimates of losses for each grid cell from the soil module, combined with annual N inputs to each grid cell for fixation, deposition and fertilisation for the period 1800-2020. Fertiliser N inputs were taken from the LUH database and covered the whole time period (see Section 4.1.1). Deposition N inputs for 1860-2050 were from Lamarque et al. (2013). Fixation (for 1901-2100) was estimated using the CABLE model with scenario A1 as described by Peng et al. (2020), where fixation is calculated using resource optimization with temperature dependence (Houlton et al., 2008). The 1901 fixation values were used to estimate fixation in earlier years and the 1860 values for deposition in earlier years, thus assuming negligible anthropogenic influence before 1850.

Deposition and fixation inputs were assumed to generally fulfil the steady state criteria required by the soil module, however harvest N exports mean that this assumption is not valid for fertiliser N inputs. Harvested N is often returned to the soil or atmosphere via manure or deposition at a different location (Schlesinger, 2009). Previous studies have shown that a large proportion of fertiliser N is incorporated into crops and therefore removed during harvest, as well as potentially stored in soils (Corbeels et al. (1999); Jenkinson et al. (2004); Schlesinger (2009); Sebilo et al. (2013) and references therein) - thus not available for ‘normal’ N loss partitioning. Therefore, we added a factor `fert_EF_red` to the model to account for N that is harvested or stored. Fertiliser N inputs are multiplied by `fert_EF_red` to account for the removal of harvested N or stored in soils before losses by other pathways are calculated; `fert_EF_red` of 0 would mean that all N is removed in harvest, and `fert_EF_red` of 1 would mean no N is removed. EF changes with fertilisation rate were not considered, as metaanalyses have shown that the dependence of EF on fertilisation rate is highly variable, and at the global scale EF is not strongly dependent on fertilisation rate (Kim, Hernandez-Ramirez, & Giltrap, 2013). Tian et al. (2020) also report that recent increases in EF for direct soil emissions are likely due to climate change feedbacks and interactions, rather than a direct increase in EF due to increasing fertiliser application. The majority of plant N uptake is not relevant in the IsoTONE model, as it is returned to the soil system at the same rate it is removed within the steady state assumption. This is not the case for harvested agricultural plant matter - the isotopic impact of harvest N exports cannot be accounted for within the scope of this study, as the required input data (in particular the proportion of N removed in harvest per grid cell annually) is not currently available. Harvest N will be explicitly incorporated into a future version of the IsoTONE framework.

Previous studies have shown that microbial N gas production is temperature sensitive (Hu, Chen, & He, 2015; Inatomi et al., 2019; Pilegaard, 2013) and likely increasing in a warming climate by between 0.5 and 1.0 Tg N_2O -N $\text{a}^{-1} \text{ } ^\circ\text{C}^{-1}$, with a best estimate of

0.6±0.2 Tg N₂O-N a⁻¹ °C⁻¹ (Tian et al., 2019; Xu-Ri et al., 2012; Zaehle, 2013). We assume that this increase in emissions relates to a general sensitivity of microbial activity to temperature, and is therefore likely to affect production of N₂ and NO as well as N₂O. We therefore incorporated a temperature sensitivity increase of 10% of microbial N emissions from the year 1800 per degree of warming (temp_sens = 1.1±0.04) for N₂O, N₂ and NO, which corresponds to 0.6 Tg N₂O-N a⁻¹ °C⁻¹ according to the best estimate of 6.3±1.1 Tg-N a⁻¹ for N₂O emissions in the preindustrial era (Tian et al., 2019). N losses through leaching were consequently reduced to maintain N mass balance.

Yearly soil emissions of N₂O, NO and N₂ were calculated for each input type for each grid cell incorporating both fert_EF_red and temperature sensitivity of emissions. In addition, EDGAR (Emission Database for Global Atmospheric Research, Crippa et al. (2020); Olivier and Berdowski (2001)) gridded emissions for the major non-soil anthropogenic N₂O emission categories (1A1 = power industry, 1A3b = road transport, 2B = chemical processes, and 6 = wastewater treatment) were added to estimate total terrestrial N₂O emissions. Isotopic composition was estimated as $\delta^{15}\text{N} = 3.9 \pm 2.9$ and SP = 17.6±0.5 for power industry, $\delta^{15}\text{N} = -7.2 \pm 1.2$ and SP = 10.0±4.3 for road transport, $\delta^{15}\text{N} = -8.3 \pm 10.6$ and SP = 3.3±5.5 for chemical processes, and $\delta^{15}\text{N} = -11.6 \pm 12.7$ and SP = 10.0±5.7 for wastewater treatment (Harris et al., 2017). Isotopic composition of natural soil N₂O emissions was given by the soil module for each grid cell, and weighted by the emissions per grid cell to calculate overall isotopic composition of soil N₂O emissions. The $\delta^{15}\text{N}$ isotopic composition of fertiliser N inputs is estimated to be 3‰ (Bateman & Kelly, 2007; Savard et al., 2010) compared to -1.5‰ for natural N inputs (Bai et al., 2012), thus increasing the $\delta^{15}\text{N}$ of emitted N₂O. Total global emissions were found by adding the oceanic emissions (F_{ocean}) to the global terrestrial emissions using the flux and isotopic compositions listed in Table A.1.

Total global N₂O was emitted into a two-box atmospheric model comprising a well-mixed troposphere and a well-mixed stratosphere, based on the model described in L. Yu, Harris, Henne, et al. (2020). Emissions were assumed to be immediately well-mixed through the atmosphere, as the time required for tropospheric mixing is estimated to be around one year (Bowman & Cohen, 1997), which is the time resolution of the model. Previous versions of this model explicitly calculate the required preindustrial terrestrial N₂O flux to achieve steady state in the preindustrial era accounting for best estimates of tropospheric N₂O mixing ratio, N₂O lifetime, and stratosphere-troposphere exchange. However, in the atmosphere module of IsoTONE, preindustrial terrestrial emissions (F_{terr}) are prescribed by the soil module. An iterative calculation (maximum of 20 iterations) is therefore used to optimize the preindustrial oceanic N₂O flux (F_{ocean}) and the troposphere-stratosphere exchange term (T_{to_S}) by shifting these two terms stepwise according to their prior uncertainty (Table A.1) using two equations until steady state is achieved. First, tropospheric N₂O inputs are balanced against losses to the stratosphere:

$$F_{\text{terr}} + F_{\text{ocean}} = T_{\text{to}_S} \times (MR_{\text{PI}} - MR_{\text{PI, strat}}) \quad (6)$$

where MR is the N₂O mixing ratio. The preindustrial stratospheric N₂O mixing ratio at steady state is then calculated based on stratosphere-troposphere exchange and stratospheric N₂O destruction (Toyoda et al., 2013; L. Yu, Harris, Lewicka-Szczepak, & Mohn, 2020):

$$MR_{\text{PI, strat}} = - \frac{MR_{\text{PI}} \times \text{moles}_{\text{trop}} \times MW_{\text{N}_2\text{O}-\text{N}} - T_{\text{to}_S} \times MR_{\text{PI}} \times MW_{\text{N}_2\text{O}-\text{N}} \times \tau_{\text{PI}}}{T_{\text{to}_S} \times MW_{\text{N}_2\text{O}-\text{N}} \times \tau_{\text{PI}} + \text{moles}_{\text{strat}} \times MW_{\text{N}_2\text{O}-\text{N}}} \quad (7)$$

where MW_{N₂O-N} is the molecular weight of N in N₂O (28 g mol⁻¹) and moles_{trop} and moles_{strat} are the moles of the troposphere and stratosphere (1.5 and 0.27×10²⁰ moles) respectively. This iteration meant that optimized values for both F_{ocean} and T_{to_S} were found for each solution of the model, although they were not explicitly targeted in the inversion described in the following subsection. F_{ocean} was not varied with time, as recent results suggest that the oceanic flux is relatively stable compared to the terrestrial flux (Tian et al., 2020). Smaller, dynamic aquatic and semiaquatic ecosystems, such as estuaries and

coastal wetlands, show highly dynamic and variably N cycling and N₂O emissions (Brase, Bange, Lendt, Sanders, & Dähnke, 2017; Moseman-Valtierra et al., 2011; Wells et al., 2018), but are too small to be resolved at the global scale of this study.

Once steady state was achieved for preindustrial N₂O fluxes and mixing ratio, model calculations proceeded as described by L. Yu, Harris, Henne, et al. (2020) and will therefore only be briefly presented here. First, net stratospheric fractionation and the isotopic composition of the preindustrial stratosphere were found for $\delta^{15}\text{N}$ and SP assuming steady state. The model was then run forwards with annual time steps using annual terrestrial emissions and isotopic composition provided by the soil module of IsoTONE. At each time step, N₂O inputs and destruction were considered to estimate the rate of change in N₂O mixing ratio and isotopic composition, and thus calculate a time series of mixing ratio, $\delta^{15}\text{N}$ and SP for a well-mixed troposphere (L. Yu, Harris, Henne, et al., 2020).

4.3 Optimization of model N cycle parameters

Twelve key model parameters were optimised using a Markov Chain Monte Carlo (MCMC) approach (Table A.1), with several datasets used to constrain the results. The geoclimatic gradients (spatial variability) were constrained using N₂O emission factors from the Global N₂O Database, binned for 16 climatic zones (Section 4.1.4). Temporal variability was constrained using a combined background tropospheric timeseries of N₂O mixing ratio and isotopic composition ($\delta^{15}\text{N}$ and SP) from several different sites, averaged for 25-year blocks from 1740 to 1940 and for 2 year blocks from 1940 to 2020 to give a total of 49 data points (Section 4.1.3 and Figure 5). Data was reduced to 16 climate zone EFs and 49 temporal data points to avoid strong overweighting of recent atmospheric results, which are much more frequent and less uncertain than older measurements (e.g. biweekly monitoring at Jungfraujoch station (L. Yu, Harris, Henne, et al., 2020)) but highly covariable. Observation uncertainty was defined as the standard deviation of measurements within each spatial or temporal block. Model uncertainty was set at 0.5 nmol mol⁻¹ for N₂O mixing ratio, 0.1‰ for $\delta^{15}\text{N}$ and SP, and 0.5 for climate zone EF. The incorporation of isotopic composition in the atmospheric model gave an implicit sensitivity to the spatial distribution of emissions, as the isotopic composition of emitted N₂O depends on the dominant emission processes in a particular gridcell, thus allowing the model to distinguish between changes in different regions and input types.

The MCMC was run with three different stepsizes: 0.75, 0.5 and 0.25. Within each iteration i of the MCMC, Gaussian parameters P_G (see Table A.1) were varied according to:

$$P_{i+1,G} = P_{i,G} + 1\sigma \text{ uncertainty} \times \text{stepsize} \times r_{\text{unif}} \quad (8)$$

where r_{unif} is a uniformly distributed random number between -1 and 1. Uniform parameters P_U were varied according to:

$$P_{i+1,U} = P_{i,U} + \frac{R_{\text{max}} - R_{\text{min}}}{4} \times \text{stepsize} \times r_{\text{unif}} \quad (9)$$

where R_{max} and R_{min} are the maximum and minimum of the parameter uncertainty range. Independent values of r_{unif} were determined for every parameter. Observation uncertainty follows a Gaussian distribution, thus observations were also varied within each iteration using Eq. 8, however r_{unif} was determined separately only for different groups of observations, e.g. N₂O mixing ratio, N₂O SP.

Once parameters were varied within an iteration i , the Metropolis rule was applied to determine if parameters and observations could be accepted (Rayner, 2020). If both were accepted, the model was run for the parameter set i , and the model-observation probability was calculated for i . The Metropolis rule was then applied to determine if model-observation i could be accepted compared to $i-1$. 5 000 iterations were run at each step size sequentially until a total of 120 000 iterations had been run (40 000 at each step size), which was sufficient

to achieve stable results with no significant difference between posterior parameters by step size, and no change in posterior parameters following more iterations. All tested and accepted parameter sets were saved; tested parameter sets were used to check coverage of the parameter uncertainty space (Figure A.7), and accepted parameter sets were used to find posterior results and uncertainties for the parameters (Table A.1). The parameters F_{ocean} and T_to_S (see Section 4.2.2) were not explicitly varied in the MCMC but were calculated to achieve steady state in the atmospheric module in each accepted iteration, thus posterior estimates for these parameters were also obtained.

4.4 Estimating uncertainty in posterior model results

The uncertainty in posterior parameters show in Table 1 was estimated as the standard deviation of all accepted results. To estimate uncertainty in the posterior model results, 100 iterations of the model were run using 100 randomly selected sets of accepted parameters. The standard deviation of results from all 100 iterations was used to estimate the uncertainty in the final model results. Standard error propagation was used to estimate uncertainty in all subsequently calculated values, eg. ratios and sums across time or space.

5 Data and code availability statement

Before publication of this manuscript, IsoTONE model code (written in Python) will be available open access on Github. Gridded datasets calculated in this study (eg. $\delta^{15}\text{N}_{\text{soil}}$, f_{gas} , N_2O emission factors, gridded $\delta^{15}\text{N}$ and SP of emissions) will be released together with the model code. $\delta^{15}\text{N}$ point data not present in the (Craine, Elmore, et al., 2015) dataset will be published as a compilation within 1-2 years, once associated research projects of the individual data owners are completed. Tropospheric background N_2O isotopic data collected at Empa and used for model optimization will be released open access in 2022 together with the associated manuscript (L. Yu et al., 2022).

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A Supplementary material

A.1 Geoclimatic gradients in $\delta^{15}\text{N}_{\text{soil}}$ and in N_2O emission factors

A.1.1 $\delta^{15}\text{N}_{\text{soil}}$

$\delta^{15}\text{N}_{\text{soil}}$ data from >7000 samples from natural (non-agricultural) sites was compiled as described in Section 4.1.2, however ancillary data for these measurements (e.g. MAT, MAP, pH) was incomplete. Ancillary data reported for the point measurements was therefore compared to the global gridded datasets (Section 4.1.1). Mean annual temperature ($R^2=0.96$, slope=0.98), precipitation ($R^2=0.87$, slope=0.67) and pH ($R^2=0.60$, slope=0.62) agreed well between the point and gridded datasets. Soil carbon showed moderate agreement ($R^2=0.3$, slope=0.35), while soil N and C:N ratio showed no correlation between the point and gridded datasets. The relatively poor for soil C and N can be attributed to the high spatial variability of these parameters; additionally, the gridded datasets refer to organic C and N while the point data does not always report whether organic or total C and N were measured. A complete ancillary dataset was compiled by gapfilling missing point values of MAP, MAT and pH with gridded dataset values. For C, N and C:N only gridded values were used, as point and gridded datasets were inconsistent and point values are likely less comparable between sites. Other relevant parameters, such as bulk density, which were not reported or very sparsely reported in the point measurements were taken from the gridded datasets.

An overview of the relationships between ancillary data and $\delta^{15}\text{N}_{\text{soil}}$ was gained using single linear correlation analyses and a multivariate principal components analysis (Figure A.1). The strongest positive linear correlations were found between $\delta^{15}\text{N}_{\text{soil}}$ and MAT, N and bulk density, and the strongest negative correlations between $\delta^{15}\text{N}_{\text{soil}}$ and C, C:N, elevation and aridity index. Only parameters with <1000 missing values were used for the principal components analysis, therefore elevation and soil texture were not included. PC1 was dominated by the broad geoclimatic gradient between wetter and drier areas (based on MAP), which did not relate strongly to $\delta^{15}\text{N}_{\text{soil}}$, in contrast to previous expectations (Amundson et al., 2003). PC2 (24.6% of variability) showed a relationship between MAT, N, C, C:N and $\delta^{15}\text{N}_{\text{soil}}$ evident from the single linear correlations, thus reflecting the impact of temperature on soil chemistry and N cycling. PC3 (12.4% of variability) showed a relationship between $\delta^{15}\text{N}_{\text{soil}}$, C, N, C:N and bulk density and aridity, and therefore a weaker relationship between water availability and soil chemistry. Similar to the results of Luo, Viscarra-Rossel, and Qian (2021) describing the spatial variability of soil organic carbon, climate was key in driving variability in $\delta^{15}\text{N}_{\text{soil}}$ of near-surface layers, and physicochemical properties were secondary but nonetheless important.

Figure A.1. Relationships between $\delta^{15}\text{N}_{\text{soil}}$ and ancillary data. *a*) Color map showing linear correlation coefficients (P = Pearson, S = Spearman) indicated with the color bar between $\delta^{15}\text{N}_{\text{soil}}$ and the specified parameter. *b*) Principal components analysis of the combined $\delta^{15}\text{N}_{\text{soil}}$ and ancillary data; soil parameters are shown in blue and climate parameters in orange.

The $\delta^{15}\text{N}_{\text{soil}}$ data is not globally representative and many large regions have very sparse data coverage, thus interpolation of the data to a global grid is not possible. An artificial neural network (ANN) was therefore used to predict $\delta^{15}\text{N}_{\text{soil}}$ based on geoclimate parameters and thus estimate a global grid of $\delta^{15}\text{N}_{\text{soil}}$ values using the ‘Keras’ package (Chollet, 2015) in Python. A sequential ANN was compiled with:

1. 9 input nodes;
2. A dense layer with 16 nodes using the rectified linear unit (ReLU) activation function;
3. A dense layer with 16 nodes using a hyperbolic tangent (tanh) activation function, and L2 regularization with a regularization parameter of 0.01;
4. Identical to layer 3. but using a linear activation function;
5. A batch normalization layer;
6. A dense output layer with one node using a ReLU activation function.

Weights were initialised with Xavier initialization using a uniform distribution (default initialization in Keras). The Adam optimizer was used with a learning rate of 0.0005 and root mean squared error (RMSE) as a loss function. During training, a validation split of 25% was used to minimise overfitting, and early stopping was implemented based on the minimum loss function for validation data with a patience level of 30 epochs. A model checkpoint was used to save the model that achieved the lowest RMSE for the validation data during the training period. Training was carried out over a maximum of 80 epochs with a batch size of 200, and data shuffling was activated. As samples were not distributed evenly across different regions, sample weighting to reduce the relative importance of samples from highly represented regions such as Europe was needed. Samples were grouped into 30 clusters according to latitude and longitude using the KMeans function from the ‘sklearn’ package. A sample weight vector was calculated as $\frac{1}{\sqrt{n}}$ where n is the number of members in a cluster. The sample weights were used to weight the loss function during the ANN training.

A bootstrapping approach was used to find the ANN model best able to predict the observation data and to estimate the uncertainty in predicted $\delta^{15}\text{N}_{\text{soil}}$. First, the relevant uncertainty in the $\delta^{15}\text{N}_{\text{soil}}$ measurements was determined; this relates primarily to the degree to which a single measurement is representative of soils in a grid cell, and is much higher than the measurement uncertainty (usually $<0.2\%$ for IRMS measurements). The representation uncertainty was estimated to be 1.2% , based on the mean of the standard deviation of all measurements placed within each grid cell for the 461 grid cells with more than 2 measurements. 250 bootstrap iterations were run, and within each iteration, data for $\delta^{15}\text{N}_{\text{soil}}$ was perturbed according to the representation uncertainty multiplied by normally distributed random numbers. $\delta^{15}\text{N}_{\text{soil}}$ and the chosen input parameters (latitude, absolute longitude, MAP, MAT, soil N, soil C, soil C:N, pH, bulk density, and aridity index) were randomly split into training ($\frac{2}{3}$ of data) and testing subsets. Data was normalised to a range of 0-1 for each parameter, and all rows containing NAs were removed. 6000 rows of data were used for training and 3000 for testing the ANN in each iteration. The trained ANN was used to predict the test dataset values of $\delta^{15}\text{N}_{\text{soil}}$. The predicted and observed test $\delta^{15}\text{N}_{\text{soil}}$ were compared using the weighted root mean square error (wRMSE) and the R^2 of a weighted linear fit within each bootstrap iteration, using $\frac{1}{\sqrt{n}}$ where n is the number of members in the k-means cluster size as the weight for each point. The ANN achieving the best fit (lowest wRMSE and highest R^2) on the test data was used for the final prediction of $\delta^{15}\text{N}_{\text{soil}}$, and the standard deviation of the predicted $\delta^{15}\text{N}_{\text{soil}}$ from all bootstrap iterations was used to estimate the uncertainty.

The final ANN was able to reproduce the observations with a slope of 1.04, R^2 of 0.41 and wRMSE of 2.6% , thus exhibiting significantly more explanatory power than a multiple linear regression, which was only able to reproduce data with R^2 of 0.27 and RMSE of 3.1% . The role of specific parameters in the ANN was examined using two methods: i) using the ANN to predict $\delta^{15}\text{N}_{\text{soil}}$ with all inputs set to their mean values, except for the parameter

of interest, to understand how much of the variability in $\delta^{15}\text{N}_{\text{soil}}$ is contributed by the parameter, and ii) shuffling all data for the parameter of interest before predicting $\delta^{15}\text{N}_{\text{soil}}$, to measure the reduction in goodness-of-fit. MAT was the most important parameter in the ANN, accounting for 30% of variability in $\delta^{15}\text{N}$ and an RMSE reduction of 0.8‰, followed by absolute longitude (14.5%, 0.3‰), latitude (9.5%, 0.2‰), pH (9.8%, 0.07‰) and bulk density (8.7%, 0.16‰). The importance of MAT as well as soil composition agrees with previous studies by Amundson et al. (2003) and Craine, Elmore, et al. (2015).

Figure A.2. *a)* Global gridded ($0.5^\circ \times 0.5^\circ$ grid) $\delta^{15}\text{N}_{\text{soil}}$ estimated using an artificial neural network. Note the colour scale is non-linear to better show the narrow range of most values. *b)* Estimated uncertainty in gridded $\delta^{15}\text{N}_{\text{soil}}$.

A.1.2 N_2O emission factors

2 793 measurements of N_2O fluxes and 3 629 EFs from 336 locations were taken from the ‘Global N_2O Database’ (Dorich et al., 2020), and used to examine variability in fluxes and EFs along geoclimatic gradients. Ancillary data was not provided for all measurement points, therefore as described in Section A.1 for $\delta^{15}\text{N}_{\text{soil}}$ data, incomplete ancillary data was filled in with the global gridded datasets for the same geographical locations. As described in the previous subsection, agreement was very good for well-defined parameters like MAT and MAP, and relatively poor for heterogeneous or variable parameters like soil N content. Linear correlations and PCA for the combined flux and EF dataset revealed the parameters linked most strongly to N_2O emissions - particularly aridity, pH, soil C, MAT and MAP (Figure A.3).

N_2O EFs are predicted to be highest at low pH, consistent with the observations in the from the ‘Global N_2O Database’ (Hu et al., 2015; Inatomi et al., 2019). Both water availability and bulk density impact O_2 availability, which is known to be key in determining nitrification and denitrification rates and thus N gas emissions (Hu et al., 2015; Pilegaard,

Figure A.3. Relationships between N₂O fluxes and emission factors (EF) and ancillary data. a) Color map showing linear correlation coefficients (P = Pearson, S = Spearman) for fluxes and EFs indicated with the color bar. b) Principal components analysis of the combined soil flux, EF and ancillary data; soil parameters are shown in blue, climate parameters in orange, and N-cycle parameters in red.

2013). The observations are inconclusive regarding the impact of soil N availability on EF. The correlation analysis shows a relationship between fertilisation and EF only for the Pearson correlation coefficient, which is potentially more affected by outliers, but no relationship between EF and soil N availability. Soil N and fertilisation do not plot strongly against PC1 or PC2; fertilisation shows a strong positive relationship and soil N availability shows a weak negative relationship to EF along PC3. This is consistent with previous studies, which show that although more N availability clearly leads to more N gas production, the relationship between N availability and N gas EFs is unclear (Butterbach-Bahl et al., 2013; Cui et al., 2021; Inatomi et al., 2019; R. L. Thompson et al., 2019). Tian et al. (2020) report increasing EF for direct soil emissions over recent decades that is attributed to climate change feedbacks and interactions as well as spatiotemporal variability of climate, rather than a direct increase in EF due to increasing fertiliser application.

Figure A.4. Mean emission factors for different climate zones based on measured EF data binned according to MAT and soil bulk density. a) Mean EFs for the different climate zones; MAT (mid-point of bin) is plotted on the x-axis and line colours refer to the bulk density bin. The standard deviation of values in each bin is shown with the shaded region and the number of values in each bin is annotated. b) Global map showing the spatial coverage of the 16 bins: MAT increases with bin number, and bulk density increases sequentially through bins 1-4, 5-8, 9-12 and 13-16.

In order to compare modelled EFs to the EF data, which came from a range of agricultural ecosystem types with varying management practices, measurement methods and

time periods, it was necessary to estimate mean EFs for different 'climate zones'. Although AI and soil C content correlated strongly with EF, there was strong non-linearity in these parameters, as well as limited variability within the dataset because the sites with EF data are strongly biased towards northern hemisphere temperate regions. Therefore, MAT and MAP were selected as the optimal parameters to define climate zones to bin EFs, based on both correlations with fluxes and EFs as well as good coverage ranges for available data within each bin. The quartile ranges for MAT and MAP were used to define 16 climate zones for which mean EFs could be calculated (Figure A.4). Standard deviation within each climate zone bin was high (Figure A.4), reflecting the high spatial and temporal variability of N₂O fluxes as well as the lack of robust annual flux monitoring in many locations. Due to the high uncertainty, no clear relationship between EFs and MAT or EFs and MAP was seen - except for sites with MAP >1074 mm a⁻¹, which had significantly higher EF at both low and high MAT. Hot spots and moments (Harris, Ladreiter-Knauss, Butterbach-Bahl, Wolf, & Bahn, 2018; Hoertnagl et al., 2018; Sihi, Davidson, Savage, & Liang, 2020; Wolf et al., 2010) mean that N₂O annual fluxes and EFs are challenging to measure and highly uncertain, often depending on methodological factors such as the number of replicates, spatial replication, and temporal frequency. The uncertain EF data will therefore place little constraint on the model, however the estimates of posterior EFs for the different climate zones will be useful to evaluate the accuracy of the measurement data and reduce uncertainty in estimates of EF in different regions.

A.2 Parameterisation of N gas production pathways

Production of N₂O, NO and N₂ as a proportion of total N gas production as well as the proportion of N₂O contributed by the nitrification and denitrification pathways were parameterised as a function of WFPS using experimental data. Experimental data was only available for N₂O/(N₂O + N₂) and N₂O/(N₂O + NO) and not for all three gases simultaneously, therefore each dataset was fit separately with a sigmoid curve using the `curve_fit` function from the `scipy` package (Figure A.5). Data covered a range of ecosystem types including forest, native and managed grassland, tropical forest, pasture and rice paddy (data used by Bai et al. (2012) and additional data from Harris et al. (2021); Ibraim et al. (2019); Verhoeven et al. (2019); Wolf et al. (2015); Xia et al. (2019)). The proportion of each gas of the total N gas production (N₂O + N₂ + NO) was found by combining the two sigmoid fits:

$$\frac{N_2O}{N_2O + NO} = a = \frac{1.2}{1 + e^{-0.04 \times (W - \mathbf{66.5})}} \quad (\text{A.1})$$

$$\frac{N_2O}{N_2O + N_2} = b = \frac{0.76}{1 + e^{0.07 \times (W - \mathbf{38.7})}} + 0.32 \quad (\text{A.2})$$

$$\frac{N_2O}{N_2O + N_2 + NO} = \frac{1}{\frac{1-a}{a} + \frac{1-b}{b} + 1} \quad (\text{A.3})$$

Two model parameters (fit_{N₂} and fit_{NO}) represented in the MCMC were used to optimize the parameterisation of N₂O, NO and N₂ as a fraction of total N gas emissions, by varying the most sensitive parameter in each sigmoid fit to cover the spread of the experimental data (parameter highlighted in red bold in the above equations; fits shown in Figure A.5). The optimized fit shows that NO dominates emissions at low WFPS and N₂ at high WFPS, while N₂O is emitted across the whole WFPS range. The contribution of N₂O steadily increases from ~1% at 0% WFPS to ~32% for WFPS >60%. Compared to the empirical fit made in Bai et al. (2012), N₂O remains higher and N₂ lower in very wet soils for both the prior and posterior. The posterior parameterisation is described by:

$$\frac{N_2O}{N_2O + NO} = a = \frac{1.2}{1 + e^{-0.04 \times (W - \mathbf{81.3})}} \quad (\text{A.4})$$

$$\frac{N_2O}{N_2O + N_2} = b = \frac{0.76}{1 + e^{0.07 \times (W - \mathbf{36.5})}} + 0.32 \quad (\text{A.5})$$

Figure A.5. Parameterisation of $\text{N}_2\text{O}/\text{NO}/\text{N}_2$ as a fraction of total N gas emissions based on water-filled pore space. The upper panels show experimental data (includes all data used by Bai et al. (2012) as well as additional data from Harris et al. (2021); Ibraim et al. (2019); Verhoeven et al. (2019); Wolf et al. (2015); Xia et al. (2019)). Prior estimates of the parameterisation using sigmoid fits to the data are shown as dotted lines, with the prior 1σ uncertainty range shown with pale shading. Posterior fits following the MCMC optimization are shown as solid lines with the posterior 1σ uncertainty range in darker shading. Eqs. A.1, A.2 and A.3 describe the prior and Eqs. A.3, A.5 and A.6 the final fits. The bottom panel shows the proportion of total N gas contributed by NO, N_2O and NO according to the parameterisation used by Bai et al. (2012) (dashed line), the prior fits (dotted line) and the posterior fits (solid line with uncertainty range shaded).

Experimental data to constrain the relative contributions of nitrification and denitrification to N_2O emissions is sparse; only 45 measurements were available, from grassland (Harris et al., 2021; Ibraim et al., 2019; Wolf et al., 2015) and rice paddy (Verhoeven et al., 2019) systems. Although the data was not representative of global ecosystem types, a wide range of WFPS was covered. A sigmoid curve fit the data well (Figure A.6):

$$\frac{\text{N}_2\text{O}_{\text{denit}}}{\text{N}_2\text{O}} = \frac{0.2}{1 + e^{-1.5 \times (W - 59.7)}} + 0.23 \quad (\text{A.6})$$

Unexpectedly, denitrification makes a slightly lower contribution to N_2O emissions at higher WFPS, because a significant amount of N_2O is reduced to N_2 before emission at high WFPS. However, the scarcity of data means that this parameterisation is highly uncertain, and further laboratory and field measurements of the partitioning between pathways are needed to better constrain the roles of nitrification and denitrification. Furthermore, the denitrification to nitrification ratio is likely also dependent on agricultural management and fertiliser application, estimation of which is currently beyond the scope of this model. Recent developments in spectroscopic isotope measurements offer a promising method for online, in situ quantification of nitrification and denitrification N_2O emissions (Harris et al., 2021; L. Yu, Harris, Lewicka-Szczepak, & Mohn, 2020), which offers the potential for improvements to the parameterisation as new data from a wider range of sites becomes available.

Figure A.6. Parameterisation of denitrification and nitrification contribution to N_2O emissions based on water-filled pore space. The upper panel shows experimental data for denitrification N_2O as a proportion of total N_2O emissions from Harris et al. (2021); Ibraim et al. (2019); Verhoeven et al. (2019); Wolf et al. (2015), with a sigmoid fit to the data. The lower panel shows N_2O (Eqs. A.3, A.5 and A.6), $\text{N}_2\text{O}_{\text{denit}}$ (dotted line) and $\text{N}_2\text{O}_{\text{nit}}$ (dashed line) as a proportion of total N gas emissions using the posterior fit described in Eqs. A.3, A.5 and A.6.

A.3 Model optimization

120 000 iterations of the MCMC framework were run and 1 667 solutions were found. 40 000 iterations were run for each step size 0.25, 0.5 and 0.75, with 1 760 (4.4%), 76 (0.2%) and 34 (0.1%) solutions accepted respectively (Figure A.7 and Table A.1). There were no significant differences in the means of accepted values for the different stepsizes, and no change in the final values if only a subset of the accepted values randomly sampled, showing that the posterior parameters were robust. The posterior parameters showed a strong reduction in uncertainty compared to the prior for most parameters (Figure A.7 and Table A.1), although $\tau_{\text{P1}}/\tau_{\text{PD}}$, τ_{PD} and temp_sens - which are all primarily constrained by N_2O mixing ratio increase - cannot be easily separated during model-data assimilation. F_{ocean} , τ_{PD} and $T_{\text{to.S}}$ showed the strongest correlations between accepted solutions and dominated PC1 in the PCA (Figure A.8), again reflecting their role in regulating N_2O mixing ratio increase in the atmosphere submodule. Addition of an independent tracer of $T_{\text{to.S}}$, or very high precision measurements from multiple sites in separate hemispheres, may help constrain these parameters in future model studies. PC2 reflected the role of temperature increase, while PC3 was dominated the chosen fractionation factors, which drive loss partitioning in the soil submodule through the parameter frac.ex . Both the correlation and PCA analysis show that most of the optimized parameters - particularly those related to isotopic composition - can be sufficiently discriminated by the model-data assimilation. Parameters only constrained by mixing ratio cannot be distinguished easily, reflecting the importance of isotopic data for constraining the global N cycle.

The MCMC approach led to a strong improvement in model-observation agreement (Section A.3), with RMSE decreasing from 14.1 to 1.7 nmol mol^{-1} for N_2O mixing ratio, 1.5 to 0.5‰ for $\delta^{15}\text{N}$, 1.5 to 1.1‰ for SP, and 5.4 to 1.8% for climate-zone emission factor (Figure A.9). The improvement in SP is lower than for $\delta^{15}\text{N}$ because measurements are more uncertain relative to the trend, and the timeseries is much shorter. Prior observation EFs were highly uncertain, and therefore EFs were the only observation parameter showing a significant difference between the prior and the posterior. Posterior observation EFs were higher than prior observations EFs, which is likely due to the extremely dynamic nature of

Table A.1. Prior and posterior values and uncertainty ranges for model input parameters optimized using the MCMC approach. ‘Abb.’ is the abbreviation for the parameter used throughout this paper. ‘Ref’ is the citation for the prior estimate. ‘PD’ is the probability distribution: G = Gaussian, U = uniform. References: 1. Sowers et al. (2002), 2. Röckmann et al. (2003), 3. Tian et al. (2019), 4. Prather et al. (2015), 5. Snider et al. (2015), 6. Toyoda et al. (2013), 7. Tian et al. (2020), 8. Schilt et al. (2014).

Abb.	Description	Unit	Prior	Ref.	Posterior	PD
MR _{PI}	N ₂ O mixing ratio for the preindustrial troposphere	nmol mol ⁻¹	265±7.5	1,2	276±2.2	G
frac_ex	Fractionation expression factor	Unitless	0.4 (0.3-1.0)	NA	0.55±0.05	U
fert_EF_red	EF reduction for fertiliser emissions	Unitless	0.4 (0-1.0)	NA	0.30±0.07	U
temp_sens	Temperature sensitivity of N ₂ O emissions (as a fraction of preindustrial emissions)	f_{PI} °C ⁻¹	1.1±0.04	3	1.10±0.03	G
τ_{PI}/τ_{PD}	Ratio of N ₂ O lifetime (τ) in the pre-industrial (PI) and the present day (PD)	Unitless	1.06±0.02	4	1.06±0.02	G
τ_{PD}	N ₂ O τ in the PD	years	116±9	4	131±6	G
$\delta^{15}N_{ocean}$	Mean $\delta^{15}N$ bulk for the ocean source	‰	5.1±1.9	5	5.3±1.6	G
$\delta^{15}N_{PI}$	Mean $\delta^{15}N$ bulk for the PI troposphere	‰	8.9±2.0	6	11.2±0.3	G
SP _{ocean}	Mean SP for the ocean source	‰	15.8±7.1	5	14.2±9.6	G
SP _{PI}	Mean SP for the PI troposphere	‰	19.1±2.0	6	19.8±0.3	G
fit _{N2}	Scaling factor for the parameterisation of N ₂ as a fraction of total N gas emissions	Unitless	1 (0.7-2)	NA	0.9±0.2	U
fit _{NO}	Scaling factor for the parameterisation of NO as a fraction of total N gas emissions	Unitless	1 (0.7-1.3)	NA	1.2±0.1	U
F _{ocean}	Total marine N ₂ O flux	Tg N ₂ O-N a ⁻¹	5.1±1.8	7	5.0±0.9	G
T_to_S	Exchange rate between the troposphere and stratosphere	×10 ¹⁷ kg a ⁻¹	5.4 (4.1-6.6)	8	4.1±1.1	U

Figure A.7. Tested and accepted model solutions from the MCMC optimization of a coupled soil-atmosphere model of N_2O emissions and isotopic composition. Parameter descriptions and references for prior estimates are given in Table A.1.

N_2O emissions, whereby emission peaks are not captured by most annual estimates which sample only weekly or biweekly (Butterbach-Bahl et al., 2013; Congreves, Wagner-Riddle, Si, & Clough, 2018; Wagner-Riddle et al., 2017). Model and observation posterior EFs agreed well for most climate zones, although in the wetter climate zones agreement was worse, with modelled EFs were higher than observations. Emissions are highly variable and dynamic in the wetland and tropical regions (Arias-Navarro et al., 2017; Kort et al., 2011; Rowlings, Grace, Scheer, & Liu, 2015), thus it is very challenging for observational studies to accurately capture annual emissions, which may account for this mismatch in these regions.

Figure A.8. Relationships between accepted solutions of parameters optimized with MCMC. *a)* Color map showing Pearson correlation coefficients between the specified parameters as indicated with the color bar. Only correlations significant at $p < 0.01$ are shown. *b)* Principal components analysis of all accepted solutions; soil and emissions module parameters are shown in orange, atmospheric parameters in blue, and isotopic parameters in red.

Figure A.9. Modelled N_2O mixing ratio, isotopic composition, and emission factors using prior and posterior estimates of the parameters shown in Table A.1. Left-hand panels shown model results and observations plotted against time or climate zone, and right-hand panels show a 1:1 comparison of model results and observations. The 1σ uncertainty in prior observations is shown as the blue shaded area for the upper three panels. The dotted grey line shows a 1:1 relationship. For EF (bottom panel) both the prior and posterior observations are shown with 1σ error bars, as the posterior observations are significantly different to the prior estimates.

A.4 Partitioning N₂O emissions between nitrification and denitrification

Total N losses to nitrification were estimated as the sum of NO emissions and nitrification N₂O emissions per grid cell, and denitrification total N losses were similarly estimated as the sum of N₂ emissions and denitrification N₂O emissions (Bai et al., 2012) (Figure A.10). Summing across all grid cells therefore allowed calculation of total nitrification and denitrification N losses over time, as well as estimation of the proportion of total N losses from each pathway, and the contribution of each pathway to N₂O emissions. The proportion of total N inputs lost to both pathways began decreasing around 1945, when fertilisation began to increase, as a significant amount of fertiliser N is removed and relocated via harvest. Since 1990, nitrification and denitrification loss fractions have slightly increased, as N inputs move from temperate to tropical regions which favour N gas production (Figure A.10).

Total N losses to nitrification were somewhat lower than to denitrification, totalling 25.2 ± 1.8 and 21.2 ± 1.7 Tg-N a⁻¹ in 2020 respectively. These are lower than suggested by a recent studies (Scheer et al., 2020; Schlesinger, 2009), which estimated total terrestrial denitrification N losses of 90-135 Tg-N a⁻¹. Our estimate of the mean terrestrial denitrification product ratio ($R_{N_2O} = \frac{N_2O_{denit}}{N_2O_{denit} + N_2}$) of $27 \pm 4\%$ in 2020 ($26 \pm 3\%$ in 1850) agrees very well with the estimate of 23% based on a metaanalysis of experimental studies by Schlesinger (2009). Wetland and estuarine soils are not represented in the $\delta^{15}N$ database used as the basis for modelling in this study, suggesting these regions may be hotspots for complete denitrification and N₂ production, accounting for the discrepancy in modelled total denitrification. Total denitrification N losses are highly uncertain due to the technical challenge of making accurate annual measurements of N₂ fluxes, thus model validation extremely difficult (e.g. Figure A.6). An improved quantitative understanding of the drivers of denitrification, as well as measurements of soil $\delta^{15}N$ in wetland and estuarine environments, will be key to achieving robust model estimates of total global denitrification.

Figure A.10. N losses to nitrification and denitrification. *a*) Global map of N losses in 2020 on a $0.5 \times 0.5^\circ$ degree grid. *b*) Total N losses to nitrification and denitrification per year from 1850 to 2020 (left axis) compared to total terrestrial N inputs (right axis). *c*) Percentage of total terrestrial N inputs lost to nitrification and denitrification from 1850 to 2020. *d*) Percentage of N₂O emissions contributed by nitrification and denitrification from 1850 to 2020. In all panels the shaded area indicates the 1σ uncertainty.

A.5 Estimation of anthropogenic N₂O flux and isotopic composition

The anthropogenic N₂O flux was calculated by assuming that all emission increases since 1850 are anthropogenic (Figure A.11). Most of the input datasets did not include data before 1850, so it was not possible to calculate a mean pre-anthropogenic baseline for either mixing ratio or isotopic composition over several decades prior to 1850, or to account for possible anthropogenic influences before 1850. Although natural emissions would show some variability due to natural climate fluctuations, natural emission variability is expected to be much lower than the key anthropogenic influences of climate change and agriculture (Tian et al., 2020). This method of estimating the total anthropogenic N₂O flux includes both direct and indirect emissions, as well as increased emissions from natural ecosystems due to anthropogenic climate change feedbacks, and is thus not directly comparable with many other studies that report only the flux directly accounted for by anthropogenic N inputs.

The isotopic composition of the anthropogenic source was found using:

$$\delta_{\text{total}} = f_a \times \delta_a + (1 - f_a) \times \delta_n \quad (\text{A.7})$$

where δ represents either $\delta^{15}\text{N}$ or SP of N₂O, ‘total’ designates the total source isotopic composition (directly modelled as the sum of fluxes across all gridcells), subscripts ‘a’ and ‘n’ refer to anthropogenic and natural sources respectively, and f_a is the fraction of N₂O from anthropogenic sources. Anthropogenic source isotopic composition was found for years where anthropogenic emissions contribute at least 10% of the total flux.

Figure A.11. Anthropogenic and natural N_2O emissions (top panel) and isotopic composition ($\delta^{15}\text{N}$ and SP) of natural and anthropogenic terrestrial N_2O emissions. The anthropogenic source was estimated by assuming that all increases in N_2O emissions for all input categories (fixation, fertilisation, deposition) as well as all changes in isotopic composition after 1850 are due to anthropogenic influences. The shaded areas indicate the 1σ uncertainty.

A.6 Supplementary figures

Figure A.12. Modelled terrestrial (natural + anthropogenic) N_2O soil emissions from different input types. The left panels show total emissions for inputs from biological N fixation, N deposition, and N fertilisation for the year 2020; all three subpanels have the same colour scale. The right panels show anthropogenic emissions for each input type in 2020, estimated by subtracting total emissions for the year 1800 from total 2020 emissions. All subpanels have the same colour scale.

Figure A.13. Modelled proportion of N lost through gas production: *a*) Global gridded f_{gas} (upper) and the 1σ uncertainty (lower); *b*) Relationship between mean annual precipitation, mean annual temperature (point colour) and f_{gas} for each grid cell.

Figure A.14. The simulated proportion of N from different input categories (fertilisation, deposition, fixation) that is lost via leaching, NH_3 volatilization, and gas production (N_2 , N_2O , NO) in soils from 1940-2020.

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