Isotopic constraints confirm the significant role of microbial nitrogen oxides emissions from the land and ocean environment

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ABSTRACT
Nitrogen oxides (NOx, the sum of nitric oxide (NO) and N dioxide (NO₂)) emissions and deposition have increased markedly over the past several decades, resulting in many adverse outcomes in both terrestrial and oceanic environments. However, because the microbial NOx emissions have been substantially underestimated on the land and unconstrained in the ocean, the global microbial NOx emissions and their importance relative to the known fossil-fuel NOx emissions remain unclear. Here we compiled data on stable N isotopes of nitrate in atmospheric particulates over the land and ocean to ground-truth estimates of NOx emissions worldwide. By considering the N isotope effect of NOx transformations to particulate nitrate combined with dominant NOx emissions in the land (coal combustion, oil combustion, biomass burning and microbial N cycle) and ocean (oil combustion, microbial N cycle), we demonstrated that microbial NOx emissions account for 24 ± 4%, 58 ± 3% and 31 ± 12% in the land, ocean and global environment, respectively. Corresponding amounts of microbial NOx emissions in the land (13.6 ± 4.7 Tg N yr⁻¹), ocean (8.8 ± 1.5 Tg N yr⁻¹) and globe (22.5 ± 4.7 Tg N yr⁻¹) are about 0.5, 1.4 and 0.6 times on average those of fossil-fuel NOx emissions in these sectors. Our findings provide empirical constraints on model predictions, revealing significant contributions of the microbial N cycle to regional NOx emissions into the atmospheric system, which is critical information for mitigating strategies, budgeting N deposition and evaluating the effects of atmospheric NOx loading on the world.

Keywords: nitrogen isotopes, nitrate, NOx emission, nitrogen deposition, microbial N cycle

INTRODUCTION
Atmospheric nitrogen oxides (NOx) loading influence human health (e.g. respiratory and cardiovascular diseases, acute bronchitis) [1], tropospheric chemistry (e.g. precipitation acidity, aerosol and ozone formation) [2–4], climate [4] and economic development [5]. In past decades, anthropogenic NOx emissions have significantly increased the fluxes of atmospheric NO₃⁻ deposition [6–8], altered N cycles in both terrestrial and marine ecosystems [9–12] and thus affected microbial NOx emissions to the atmosphere [13]. Hence, it is pivotal to accurately constrain land- and ocean-to-atmosphere NOx emissions due to uncertainties over microbial N cycles in both land and ocean.

In marine environments, the oil combustion of marine traffic transportation is a known source of NOx emissions [14–20]. According to the European Monitoring and Evaluation Programme Meteorological Synthesizing Centre West model, NOx emissions from oil combustion in the ocean averaged 6.4 ± 0.8 Tg N yr⁻¹ (5.0–7.8 Tg N yr⁻¹) [14–20]. However, the microbial N cycle occurring in the ocean is the other significant source of NOx emissions [21–24]. First, earlier studies based on molecular analysis and lab culture experiments have confirmed that multiple kinds of bacteria associated with several processes of microbial N cycles...
can produce NO, e.g. ammonium-oxidizing bacteria, nitrite-oxidizing bacteria, methanotrophic bacteria and denitrifying bacteria [25–29]. Second, nitrification in the oxic layer of the ocean is a significant source of NO [22] and NO can be produced in biofilms and marine sediments [30]. Third, Ulva prolifera (forming a belt on a vertical concrete wall in the upper intertidal zone at low tide) was the primary contributor to the high NO concentrations during the late-bloom period [31]. Meanwhile, the photolysis of NO$_2^-$ and NO$_3^-$ (in the surface water and on particles) or alkyl nitrates or dissolved organic matter may also be the sources of atmospheric NO in the ocean [32–35]. However, due to its high reactivity [36], NO would be involved quickly into the NOx cycle in the atmosphere [34]. Accordingly, it has long been difficult to accurately observe microbial NO emissions in the ocean [24]. Until now, microbial NO$_x$ emissions from the ocean and their fractional contribution to total NO$_x$ emissions from the ocean have not been quantified [21–24]. Hitherto, owing to the lack of microbial NO$_x$ emissions, the NO$_x$ from oil combustion has long been assumed as the total ocean NO$_x$ emissions in reports of the Intergovernmental Panel on Climate Change (IPCC) [20].

In the land environment, NO$_x$ emissions are mainly derived from coal combustion, oil combustion, biomass burning and microbial N cycles in substrates such as waters, soils and wastes [3,37–40]. Currently, emission amounts of NO$_x$ from coal combustion [10,41], oil combustion [42] and biomass burning [43,44] have been reported explicitly in national statistic yearbooks and emission inventories [45–47]. However, land NO$_x$ emissions from microbial N cycles have been observed chiefly for soils under natural vegetation and agriculture [40,43,48]. Therefore, estimates of NO$_x$ emissions from the land are based on limited empirical observations combined with process and statistical models and satellites used to scale up emissions [40,49,50]. Based on IPCC reports, microbial NO$_x$ emissions were budgeted at 5.6 Tg N yr$^{-1}$ before 2001, increasing to 11.0 Tg N yr$^{-1}$ when incorporating more observational data in the report of 2013 [40,49,50]. This doubling of emissions highlights a substantial underestimation of microbial NO$_x$ emissions in the land, which has shifted with additional measurements and better models. New methods are strongly needed to comprehensively constrain microbial NO$_x$ emissions from soils and many other unconsidered substrates (such as the surface water of rivers, lakes, swamps, etc.) and emission sources (such as wastewater, water treatment systems, solid wastes).

Here we provided a unique evaluation of the relative importance of the microbial NO$_x$ emissions in the land and ocean to the known fossil-fuel NO$_x$ emissions and then made a new budget for global microbial NO$_x$ emissions. First, we compiled stable N isotopes ($\delta^{15}$N values) of NO$_3^-$ in atmospheric particulates (denoted as $\delta^{15}$N$_{p-NO_3^−}$ hereafter) in the land and ocean, respectively (detailed in ‘Materials and methods’ section) (Fig. 1 and Supplementary Table S1). Second, based on concentrations and $\delta^{15}$N of NO$_x$, HNO$_3$ and p-NO$_3^-$ over the land, we estimated the $\delta^{15}$N of the initial NO$_x$ mixture from different emission sources in the atmosphere (denoted as $\delta^{15}$N$_{i-NO_x}$, Supplementary Fig. S1) and the
RESULTS AND DISCUSSION

Different $\delta^{15}$N signatures of atmospheric p-NO$_3^-$ between the land and ocean

Mean $\delta^{15}$N$_{p-NO_3^-}$ observed over terrestrial sites ($4.7 \pm 3.6‰; n = 91$) was significantly higher ($p < 0.05$) than that observed for ocean sites ($-3.5 \pm 3.9‰; n = 134$) (Fig. 2). This finding implied that human activities contributed relatively more $^{15}$N-enriched NO$_3^-$ to atmospheric NO$_3^-$ loading on the land than in the ocean.

First, the $\delta^{15}$N$_{p-NO_3^-}$ signal observed at land sites can represent land NO$_x$ emissions without a significant overprinting of marine sources. The net water vapor flux transported from the ocean to the land accounted for only 10% of the total water evaporation over the ocean [51,52]. According to the existing oceanic NO$_x$ emissions (6.4 ± 0.8 Tg N yr$^{-1}$ based on the known oil combustion) [14–20] and the land NO$_x$ emissions (53.3 ± 4.6 Tg N yr$^{-1}$) [43,53–58], the ocean-to-land atmospheric transport of NO$_x$ accounts for only 1.2% of land NO$_x$ emissions and thus is often assumed negligible [35]. Accordingly, the $\delta^{15}$N$_{p-NO_3^-}$ values observed at land sites can be directly used to differentiate dominant sources of NO$_x$ emissions (Equation 5 in the online Supplementary Data).

However, the $\delta^{15}$N$_{p-NO_3^-}$ signal observed at ocean sites cannot represent the NO$_3^-$ purely derived from ocean NO$_x$ emissions. Because the land has much higher NO$_x$ emissions and a smaller area, and thus a higher concentration than the ocean [57,59,60], the net transportation of atmospheric NO$_x$ occurs from the land to the ocean. The modeled NO$_x$ (the sum of NO$_x$ inorganic and organic nitrates in the atmosphere) transportation (11.0 Tg N yr$^{-1}$) [61] is about 1.7 times the oceanic and accounts for 21% of land NO$_x$ emissions. Accordingly, the $\delta^{15}$N signals of p-NO$_3^-$ derived from the land-to-ocean NO$_x$ transportation should be excluded (Equation 2 in the online Supplementary Data) to obtain the $\delta^{15}$N values of p-NO$_3^-$ derived only from the ocean NO$_x$ emissions (Supplementary Fig. S1) to differentiate the relative contributions between oil combustion and microbial NO$_x$ emissions (Equation 6 in the online Supplementary Data). Besides, the land-derived NO$_x$ and p-NO$_3^-$ are the dominant form of the land-to-ocean NO$_x$ transportation and between them, the p-NO$_3^-$ is the main type to be transported because the lifetime of NO$_3^-$ is much shorter [35,61,62]. So far, no substantial isotope effect was assumed for the physical processes of atmospheric transportation [63,64]. Thus, we thought that the ocean p-NO$_3^-$ produced by the land-derived NO$_3^-$ did not differ isotopically from the land p-NO$_3^-$ and used isotope mass-balance calculations to obtain the $\delta^{15}$N values of p-NO$_3^-$ derived only from the ocean NO$_x$ emissions (Equation 2 in the online Supplementary Data).

The calculated results revealed that the $\delta^{15}$N of p-NO$_3^-$ purely derived from ocean NO$_x$ emissions averaged $-12.5 \pm 8.2‰$ (Fig. 2), which was much lower than the $\delta^{15}$N$_{p-NO_3^-}$ observed for the land sites ($4.7 \pm 3.6‰$; Fig. 2). The increase in $^{15}$N/$^{14}$N of p-NO$_3^-$ over the land should be mainly influenced by $^{15}$N-enriched NO$_x$ sources to coal combustion, which was distinctly elevated in $\delta^{15}$N
Relative contributions of dominant NOx sources to p-NO3−

δ15Np-NO3− values are determined by the δ15N of sources and their relative contributions to total NOx emission and isotope effects of the NOx transformation to p-NO3− (15Δi-NOx→p-NO3− values) [65]. Accordingly, we compiled δ15N values of dominant sources of NOx emissions (Supplementary Table S2), constrained 15Δi-NOx→p-NO3− values (Supplementary Fig. S2) and thereby constructed isotope mass-balance models to further evaluate the contribution of dominant NOx sources to p-NO3− in the land and ocean, respectively (detailed in ‘Materials and methods’ section).

For source δ15N end-members, we considered coal combustion, oil combustion, biomass burning and the microbial N cycle as dominant NOx sources of p-NO3− over the land [65], while oil combustion and the microbial N cycle are dominant NOx sources to p-NO3− over the ocean [2,20]. The δ15N of such sources differ significantly from each other (p < 0.05, Supplementary Table S2), which is a prerequisite to differentiating their relative contributions isotopically. We assumed the same δ15N value of each NOx source for both land and ocean sites due to no δ15N observations on NOx from oil combustion and microbial N cycle in the ocean (detailed in ‘Materials and methods’ section). We did not consider lightning a dominant NOx source because the NOx produced by lightning in the land and ocean atmosphere is negligible. First, the global NOx production from lightning is 5.2 ± 1.0 Tg N yr−1 (Supplementary Text S1), which accounted for ~9.7% and ~7.2% of global NOx emissions by modeling methods (51.9–58.0 Tg N yr−1) and by isotopic methods in this study (Fig. 3). Moreover, the meridional distribution of global lightning in the atmosphere shows three main lightning centers of the Americas, Africa and the maritime continent in Southeast Asia. The minima represent the oceanic regions where little lightning is observed [66]. This baseline assumption of the dominant NOx sources is supported by emission inventory and deposition modeling [10,41,42,45–47].

Regarding isotope effects, we estimated 15Δi-NOx→p-NO3− values under two independent scenarios (detailed in ‘Materials and methods’ section) and found no significant differences between them (11.3 ± 2.1‰ and 13.1 ± 3.8‰, respectively) (Supplementary Fig. S2). Accordingly, we used the mean 15Δi-NOx→p-NO3− estimate (12.2 ± 2.2‰) in our subsequent isotope mass-balance calculations (Supplementary Fig. S2). The mean 15Δi-NOx→p-NO3− value in this study (12.2 ± 2.2‰) did not differ from the εNO→p-NO3− value estimated by Li et al. [67] (~15‰) and was also comparable with the global mean 15Δi-NOx→p-NO3− value (16.7 ± 2.3‰) [65]. The calculation of the global mean 15Δi-NOx→p-NO3− value by Song et al. [65] was based on the theoretical framework of computation established by Walters and Michalski [68,69], which combined natural 15N and 17O isotopes with environmental parameters relating to the NOx oxidation to p-NO3−. Relative contributions of dominant NOx sources
were calculated using the Stable Isotope Analysis model in R programming language (detailed in ‘Materials and methods’ section). Results showed that the NO\textsubscript{x} from coal combustion, oil combustion, biomass burning and microbial N cycle accounted for 23 ± 7%, 27 ± 11%, 26 ± 10% and 24 ± 4% on the land, respectively (Supplementary Fig. S3a). In contrast, the NO\textsubscript{x} from oil combustion and microbial N cycle accounted for 42 ± 3% and 58 ± 3% in the ocean, respectively (Supplementary Fig. S3a). Generally, high fractions of microbial NO\textsubscript{x} emissions revealed the vital contribution of this pathway to both land and ocean NO\textsubscript{x} emissions into the global atmosphere.

**Total and microbial NO\textsubscript{x} emissions on the land**

Based on statistical data on quantities and NO\textsubscript{x} emission factors of coal and oil combustions in the land system, previous studies have estimated global fossil-fuel NO\textsubscript{x} emissions with a relatively high degree of certainty [7,43,50,70,71]. Global fossil-fuel NO\textsubscript{x} emissions averaged 28.4 ± 1.8 Tg N yr\textsuperscript{-1}, showing a relatively low variation over past decades (25.6–30.0 Tg N yr\textsuperscript{-1}) [7,43,50,70,71]. By using the fraction and amount of fossil-fuel NO\textsubscript{x} emissions in the land (50 ± 14% and 28.4 ± 1.8 Tg N yr\textsuperscript{-1}, respectively, Supplementary Fig. S3a), we estimated that total land NO\textsubscript{x} emissions were 56.8 ± 18.6 Tg N yr\textsuperscript{-1} (Fig. 3 and Supplementary Fig. S3b). Our estimate falls in the range of the total land NO\textsubscript{x} emissions (50.0–61.4 Tg N yr\textsuperscript{-1}; averaging 55.6 ± 2.9 Tg N yr\textsuperscript{-1}) estimated by optimized modeling methods by considering more microbial sources of NO\textsubscript{x} emissions [54,57,58]. However, our estimate is higher than the total land NO\textsubscript{x} emissions (39.7–51.0 Tg N yr\textsuperscript{-1}; averaging 43.8 ± 5.0 Tg N yr\textsuperscript{-1}) estimated using the global NO\textsubscript{2} satellite column concentrations [43,55,56]. Due to no consideration of the influences of atmospheric NO\textsubscript{2} transformations, the estimates based on the satellite data were thought to underestimate global NO\textsubscript{x} emissions [72–74].

Based on the fraction and amount of total land NO\textsubscript{x} emissions (24 ± 4% and 56.8 ± 18.6 Tg N yr\textsuperscript{-1}, respectively, Fig. 3 and Supplementary Fig. S3), microbial NO\textsubscript{x} emissions on the land were calculated as 13.6 ± 4.7 Tg N yr\textsuperscript{-1} (Fig. 3 and Supplementary Fig. S3b). So far, observations on microbial NO\textsubscript{x} emissions on the land showed a relatively lower flux of 7.9 ± 1.5 Tg N yr\textsuperscript{-1} (5.0–11.0 Tg N yr\textsuperscript{-1}; data compiled from Refs [43,55,75–84]) than our estimate, because these observations have been conducted mainly on fertilized soils and merely on unfertilized soils and other land substrates. Besides, few modeling studies showed distinctly higher fluxes of land microbial NO\textsubscript{x} emissions ≤20.4 Tg N yr\textsuperscript{-1} [80] and 23.6 Tg N yr\textsuperscript{-1} [85] than the observation results and our estimate, due to overestimated N inputs in cropland and natural ecosystems and largely overlooked the influence of NO\textsubscript{x} sink uncertainties on the satellite-derived NO\textsubscript{2} fluxes. However, by considering more substrates of microbial N cycles on the land to optimize the modeling methods, some studies showed the land microbial NO\textsubscript{x} emissions as 11.5–13.6 Tg N yr\textsuperscript{-1} (12.4 ± 0.7 Tg N yr\textsuperscript{-1}) [53,71,86,87], which is very comparable with our estimate. The isotopic method in our study offers a comprehensive and accurate constraining on microbial NO\textsubscript{x} emissions.

**Total and microbial NO\textsubscript{x} emissions in the ocean**

Based on statistical data of quantities and NO\textsubscript{x} emission factors of oil combustions in the ocean system, ocean fossil-fuel NO\textsubscript{x} emissions have been estimated as 6.4 ± 0.8 Tg N yr\textsuperscript{-1} on average (5.0–7.8 Tg N yr\textsuperscript{-1}; compiled from [14–20]). Using the fraction of the ocean-fossil-fuel NO\textsubscript{x} emissions in our study (42 ± 3%, Supplementary Fig. S3a), we estimated the total ocean NO\textsubscript{x} emissions as 15.2 ± 2.3 Tg N yr\textsuperscript{-1} (Fig. 3 and Supplementary Fig. S3b). The ocean NO\textsubscript{y} deposition averaged 15.2 ± 2.3 Tg N yr\textsuperscript{-1} (15.0–23.0 Tg N yr\textsuperscript{-1}; from Refs [35,61,62,88–90]), which includes the land-to-ocean NO\textsubscript{y} transportation of 11.0 Tg N yr\textsuperscript{-1} [61]. Accordingly, the oceanic NO\textsubscript{y} deposition derived from oceanic NO\textsubscript{x} emissions was 10.3 ± 1.8 Tg N yr\textsuperscript{-1}, which is lower than our study’s total ocean NO\textsubscript{x} emissions. The generally higher NO\textsubscript{x} emissions than NO\textsubscript{y} deposition in the ocean might be attributed to other fates such as biological NO\textsubscript{x} uptake and atmosphere retention. Further, we calculated ocean microbial NO\textsubscript{x} emissions as 8.8 ± 1.5 Tg N yr\textsuperscript{-1} on average (Fig. 3 and Supplementary Fig. S3b). Our results updated the total and microbial NO\textsubscript{x} emissions in the marine environment.

**Total and microbial NO\textsubscript{x} emissions in the globe**

By integrating the land and ocean values together (detailed in ‘Materials and methods’ section), we calculated global total NO\textsubscript{x} emissions as 72.0 ± 18.1 Tg N yr\textsuperscript{-1} (Fig. 3 and Supplementary Fig. S3b). Before this work, the modeled total land
microbial NOx emissions in the land, ocean and globe, respectively (Fig. 3 and Supplementary Fig. S3b). By comparison, microbial NOx emissions in the land (13.6 ± 4.7 Tg N yr\(^{-1}\)), ocean (8.8 ± 1.5 Tg N yr\(^{-1}\)) and globe (22.5 ± 4.7 Tg N yr\(^{-1}\)) are ~0.5, 1.4 and 0.6 times fossil-fuel NOx emissions in the land, ocean and globe, respectively (Fig. 3 and Supplementary Fig. S3b). Our results highlight a vital role of the microbial NOx cycle in global NOx emissions. In addition to the direct impacts of fossil-fuel combustion on global NOx emissions, other human activities such as inefficient fertilizer use in cropping systems, wastes and sewage discharge and treatments, N deposition and water N enrichment all can accelerate microbial NOx emissions in the land, inland water bodies, estuaries and ocean [13, 91].

Our results offer an updated and isotopically grounded estimate of land- and ocean-to-atmosphere NOx emissions. Notably, our results revealed that previous reports have largely underestimated land-based microbial NOx emissions, constrained long-missing uncertainties over ocean microbial NOx emissions and therefore elevated the recognition of the substantial contribution of the microbial N cycle to global NOx emissions. Moreover, our findings highlight the unique significance of natural records of atmospheric N isotopes for understanding global N biogeochemical cycles. Currently, reducing NOx emissions to alleviate N pollution while sustaining economic development is a major challenge in the twenty-first century. Owing partly to unclear contributions of microbial processes to NOx emissions, many countries have been engaging in developing technologies and measures for reducing fossil-fuel NOx emissions to reduce airborne and water N pollution, with a focus on adjusting energy systems and increasing the chemical conversion of NOx to reduce emissions during fossil-fuel combustion. Our findings point to the need to consider the substantial contribution of the microbial N cycle to atmospheric NOx loadings while reducing fossil-fuel NOx emissions. Accordingly, the potential costs and impacts of reducing fossil-fuel NOx emissions need to be re-assessed when making more effective emission mitigation strategies—including the indirect effects of anthropogenic N on terrestrial and marine microbial processes. Moreover, the isotopically constrained microbial NOx emissions and updated total NOx emissions we provide are helpful for benchmarking atmospheric and earth system models that project the feedback between the biosphere, climate and global N cycle.

In summary, based on large-scale isotope observations of p-NO\(_3^-\) in the atmosphere, we established a simple but effective approach for estimating NOx sources in the atmosphere. Before, isotope mass-balance models have been constructed to successfully partition continental hydrologic fluxes and quantify the contributions of local evaporation and ocean-to-land water transport to the land moisture [92, 93]. Accordingly, the framework established in our study enriches the application of isotopic mass-balance approaches in quantifying processes and fluxes of global biogeochemical cycles. However, our method can only consider dominant sources of NOx emissions. Additional work on detailed measurements of \(\delta^{15}\)N values for all NOx emission sources could further refine our estimates. Isotope observations of p-NO\(_3^-\) in the atmosphere across more sampling areas will be critical to reducing uncertainties in our estimation and offering spatial tools to pinpoint source regions of great concern.

**MATERIALS AND METHODS**

Detailed materials and methods are given in the online supplementary materials.

**SUPPLEMENTARY DATA**

Supplementary data are available at NSR online.

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**AUTHOR CONTRIBUTIONS**

X.Y.L. designed the research. W.S. and X.Y.L. conducted the research (data collections and analyses). W.S. and X.Y.L. co-wrote the paper. B.Z.H. and C.Q.L. commented on the manuscript.

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REFERENCES

1. Davidson EA, David MB and Galloway JN et al. Excess nitrogen in the US environment: trends, risks, and solutions. *Issues Ecol* 2012; 15: 1–16.
2. Lerdau MT, Munger JW and Jacob DJ. The NO2 flux conundrum. *Science* 2000; 289: 2291–3.
3. Beirle S, Boersma KF and Platt U et al. Megacity emissions and lifetimes of nitrogen oxides probed from space. *Science* 2011; 333: 1737–9.
4. Mushinski RM, Phillips RP and Payne ZC et al. Microbial mechanisms and ecosystem flux estimation for aerobic NOx emissions from deciduous forest soils. *Proc Natl Acad Sci USA* 2019; 116: 2138–45.
5. Keeler BL, Gourevitch JD and Polasky S et al. The social costs of nitrogen. *Sci Adv* 2016; 2 e1600219.
6. Galloway JN, Dentener FJ and Capone DG et al. Nitrogen cycles: past, present, and future. *Biogeochemistry* 2004; 70: 153–226.
7. Fowler D, Coyle M and Skiba U et al. The global nitrogen cycle in the twenty-first century. *Phil Trans R Soc B* 2013; 368: 20130164.
8. Liu XJ, Zhang Y and Han WX et al. Enhanced nitrogen deposition over China. *Nature* 2013; 494: 549–62.
9. Clark CM and Tilman D. Loss of plant species after chronic low-level nitrogen deposition to prairie grasslands. *Nature* 2008; 451: 712–5.
10. Sutton MA, Oenema O and Erisman JW et al. Too much of a good thing. *Nature* 2011; 472: 159–61.
11. Bautres M, Drake TW and Verbeeck H et al. High fire-derived nitrogen deposition on central African forests. *Proc Natl Acad Sci USA* 2018; 115: 549–54.
12. Chen J, Luo YQ and Groenigen KJV et al. A keystone microbial enzyme for nitrogen control of soil carbon storage. *Sci Adv* 2018; 4: eaau1689.
13. Hall SJ and Matson PA. Nitrogen oxide emissions after nitrogen additions in tropical forests. *Nature* 1999; 400: 152–5.
14. Corbett JJ and Koehler HW. Updated emissions from ocean shipping. *J Geophys Res* 2002; 108: 4650.
15. Eyring V, Köhler HW and Aardenne J et al. Emissions from international shipping. T. The last 50 years. *J Geophys Res* 2005; 110: D17305.
16. Eyring V, Isaksen ISA and Berntsen T et al. Transport impacts on atmosphere and climate: shipping. *Atmos Environ* 2010; 44: 4735–71.
17. Holmes CD, Prather M and Vinken GCM. The climate impact of ship NOx emissions: an improved estimate accounting for plume chemistry. *Atmos Chem Phys* 2014; 14: 6801–12.
18. Yan F, Winijkul E and Streets DG et al. Global emission projections for the transportation sector using dynamic technology modelling. *Atmos Chem Phys* 2014; 14: 5709–33.
19. Johansson L, Jalkanen JP and Kukkonen J. Global assessment of shipping emissions in 2015 on a high spatial and temporal resolution. *Atmos Environ* 2017; 167: 403–15.
20. Jonson JE, Gauss M and Schulz M et al. Effects of global ship emissions on European air pollution levels. *Atmos Chem Phys* 2020; 20: 11399–422.
21. Zafiriou OC, McFarland M and Bromund RH. Nitric oxide in seawater. *Science* 1980; 207: 837–9.
22. Ward BB and Zafiriou OC. Nitrification and nitric oxide in the oxygen minimum of the eastern tropical north pacific. *Deep Sea Res Part I* 1988; 35: 1127–42.
23. Liu CY, Zhao M and Ren CY et al. Direct measurement of nitric oxide in seawater medium by fluorometric method. *Chin J Anal Chem* 2009; 37: 1463–7.
24. Lutterbeck HE and Bagge HW. An improved method for the determination of dissolved nitric oxide (NO) in seawater samples. *Ocean Sci* 2015; 11: 937–46.
25. Firestone MK, Firestone RB and Tiedje JM. Nitric oxide as an intermediate in denitrification: evidence from nitrogen-13 isotope exchange. *Biochem Biophys Res Commun* 1979; 91: 10–6.
26. Lipschultz F, Zafiriou OC and Wofsy SC et al. Production of NO and N2O by soil nitrifying bacteria. *Nature* 1981; 294: 641–3.
27. Yoshinari T. Nitrite and nitrous oxide production by *Methylisosinus trichosphorum*. *Can J Microbiol* 1985; 31: 139–44.
28. Freitag A and Bock E. Energy conservation in Nitrobacter. *FEMS Microbiol Lett* 1990; 66: 157–62.
29. Thamdrup B. New pathways and processes in the global nitrogen cycle. *Annu Rev Ecol Evol Syst* 2012; 43: 407–28.
30. Schreiber F, Polerecky L and de Beer D. Nitric oxide microsensor for high spatial resolution measurements in biofilms and sediments. *Anal Chem* 2008; 80: 1152–8.
31. Wang KK, Tian Y and Li PF et al. Sources of nitric oxide during the outbreak of Ulva prolifera in coastal waters of the Yellow Sea off Qingdao. *Mar Environ Res* 2020; 162: 1–10.
32. Williams JE, Bras GL and Kukui A et al. The impact of the chemical production of methyl nitrate from the NO+CH3O2 reaction on the global distributions of alkyl nitrates, nitrogen oxides and tropospheric ozone: a global modelling study. *Atmos Chem Phys* 2014; 14: 2383–82.
33. Fisher JA, Atlas EL and Barletta B et al. Methyl, ethyl, and propyl nitrates: global distribution and impacts on reactive nitrogen in remote marine environments. *J Geophys Res Atmos* 2018; 123: 12429–51.
34. Alexander B, Sherwen T and Holmes CD et al. Global inorganic nitrate production mechanisms: comparison of a global model with nitrate isotope observations. *Atmos Chem Phys* 2020; 20: 3859–77.
35. Atliere KE, Fawceet SE and Hastings MG. Reactive nitrogen cycling in the atmosphere and ocean. *Annu Rev Earth Planet Sci* 2021; 49: 523–50.
36. Schreiber F, Wunderlin P and Udert KM et al. Nitric oxide and nitrous oxide turnover in natural and engineered microbial communities: biological pathways, chemical reactions, and novel technologies. *Front Microbio* 2012; 3: 372.
37. Richter A, Burrows JP and Nüß H et al. Increase in tropospheric nitrogen dioxide over China observed from space. *Nature* 2009; 457: 129–32.
38. Kampschreur MJ, Star WRL and Wielders HA et al. Dynamics of nitric oxide and nitrous oxide emission during full-scale waste water treatment. *Water Res* 2008; 42: 812–26.
39. Poquet M, Wu Z and Queinnec I et al. A two pathway model for N2O emissions by ammonium oxidizing bacteria supported by the NO/NO2 ratio variation. *Water Res* 2016; 88: 948–59.
40. Almaraz M, Bai E and Wang C et al. Agriculture is a major source of NOx pollution in California. *Sci Adv* 2018; 4: eaao3477.
41. Streets DG, Yarber KF and Woo JH et al. Biomass burning in Asia: annual and seasonal estimates and atmospheric emissions. *Glob Biogeochem Cycle* 2003; 17: 1099.
42. Oberschelp C, Pfister S and Raptis C et al. Global emission hotspots of coal power generation. *Nat Sustain* 2019; 2: 113–21.
43. Jaegle L, Steinberger L and Martin RV et al. Global partitioning of NOx sources using satellite observations: relative roles of fossil fuel combustion, biomass burning and soil emissions. *Farad Discuss* 2005; 130: 407–23.
44. Jain AK, Tao ZN and Yang XJ et al. Estimates of global biomass burning emissions for reactive greenhouse gases (CO, NMHCs, and NOx) and CO2. *J Geophys Res* 2006; 111: D06304.
45. European Environment Agency. National Emission Ceilings Directive emissions data viewer 1990–2017. https://www.eea.europa.eu/data-and-maps/dashboards/necd-directive-data-viewer-2 (5 July 2022, date last accessed).

46. Government of Canada. Air Pollutant and Black Carbon Emissions Inventories online search. https://pollution-waste.canada.ca/air-emission-inventory (5 July 2022, date last accessed).

47. United States Environmental Protection Agency. Air Pollutant Emissions Trends Data. https://www.epa.gov/air-emissions-inventories/air-pollutant-emissions-trends-data (5 July 2022, date last accessed).

48. Oikawa PY, Ge C and Wang J et al. Unusually high soil nitrogen oxide emissions influence air quality in a high-temperature agricultural region. Nat Commun 2015; 6: 8753.

49. IPCC: Climate Change 2001: Synthesis Report: Contribution of Working Groups I, II, and III to the Third Assessment Report of the Intergovernmental Panel on Climate Change, edited by Watson RT, ALbritton DL and Barker T et al. Cambridge: Cambridge University Press, 2001, 1–397.

50. IPCC: Climate Change 2013: Carbon and Other Biogeochemical Cycles: Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change, edited by Ciais P, Sabine C and Bala G et al. Cambridge: Cambridge University Press, 2013, 485–560.

51. Oki T and Kanae S. Global hydrological cycles and world water resources. Science 2006; 313: 1068–72.

52. Abbott BW, Bishop K and Zarnetske JP et al. Human domination of the global water cycle absent from depictions and perceptions. Nat Geosci 2019; 12: 533–40.

53. McElroy MB and Wang YX. Human and animal wastes: implications for atmospheric N2O and NOx. Glob Biogeochem Cycle 2005; 19: GB2008.

54. Steinkamp J, Ganzeveld LN and Wilcke W et al. Influence of modelled soil biogenic NO emissions on related trace gases and the atmospheric oxidizing efficiency. Atmos Chem Phys 2009; 9: 2663–77.

55. Miyazaki, Eskes H and Sudo K et al. Decadal changes in global surface NOx emissions from multi-constituent satellite data assimilation. Atmos Chem Phys 2017; 17: 807–37.

56. Huang TB, Zhu X and Zhong QR et al. Spatial and temporal trends in global emissions of nitrogen oxides from 1960 to 2014. Environ Sci Technol 2017; 51: 7992–8000.

57. Geddes JA and Martin RV. Global deposition of total reactive nitrogen oxides from 1996 to 2014 constrained with satellite observations of NO2 columns. Atmos Chem Phys 2017; 17: 10071–91.

58. Qu Z, Henze DK and Cooper OR et al. Impacts of global NOx inversions on NO2 and ozone simulations. Atmos Chem Phys 2020; 20: 13109–30.

59. Beirle S, Platt U and Wenig M et al. Highly resolved global distribution of tropospheric NO2 using GOME narrow swath mode data. Atmos Chem Phys 2004; 4: 1913–24.

60. Eloharbany YF, Crutzen PJ and Steil B et al. Global and regional impacts of HONO on the chemical composition of clouds and aerosols. Atmos Chem Phys 2014; 14: 1167–84.

61. Tan JN, Fu JS and Dentener F et al. Multi-modal study of HTAP II on sulfur and nitrogen deposition. Atmos Chem Phys 2018; 18: 6847–68.

62. Jickells TD, Buitenhuis E and Altieri K et al. A reevaluation of the magnitude and impacts of anthropogenic atmospheric nitrogen inputs on the ocean. Glob Biogeochem Cycle 2017; 31: 289–305.

63. Morin S, Savarino J and Frey MM et al. Tracing the origin and fate of NOx in the arctic atmosphere using stable isotopes in nitrate. Science 2008; 322: 730–2.

64. Altieri KE, Hastings MG and Peter AJ et al. Isotopic evidence for a marine ammonium source in rainwater at Bermuda. Glob Biogeochem Cycle 2014; 28: 1066–80.

65. Song W, Liu YX and Liu CQ. New constraints on isotopic effects and major sources of nitrate in atmospheric particulates by combining $\delta^{15}$N and $\Delta^{17}$O signatures. J Geophys Res-Atmos 2021; 126: e2020JD034168.

66. Price C, Penner J and Prather M. NOx from lightning, global distribution based on lightning physics. J Geophys Res 1997; 102: 5829–41.

67. Li ZJ, Hasting MG and Walters WW et al. Isotopic evidence that recent agriculture overprints climate variability in nitrogen deposition to the Tibetan Plateau. Environ Int 2020; 138: 105614.

68. Walters WW and Michalski G. Theoretical calculation of nitrogen isotope equilibrium exchange fractionation factors for various NOx molecules. Geochim Cosmochim Acta 2015; 164: 284–97.

69. Walters WW and Michalski G. Theoretical calculation of oxygen equilibrium isotope fractionation factors involving various NOx molecules, radical OH, and H2O and its implications for isotope variations in atmospheric nitrate. Geochim Cosmochim Acta 2016; 191: 89–101.

70. Dentener F, Stevenson D and Ellingsen K et al. The global atmospheric environment for the next generation. Environ Sci Technol 2006; 40: 3586–94.

71. Vuuren DPV, Bouwman LF and Smith SJ et al. Global projections for anthropogenic reactive nitrogen emissions to the atmosphere: an assessment of scenarios in the scientific literature. Curr Opin Environ Sustain 2011; 3: 359–69.

72. Lambsal LN, Martin RV and Padmanabhan A et al. Application of satellite observations for timely updates to global anthropogenic NOx emission inventories. Geophys Res Lett 2011; 38: L05810.

73. Gu D, Wang YH and Smeltzer C et al. Anthropogenic emissions of NOx over China: reconciling the difference of inverse modeling results using GDEME-2 and OMI measurements. J Geophys Res Atmos 2014; 119: 7732–40.

74. Marais EA, Jacob DJ and Choi S et al. Nitrogen oxides in the global upper troposphere: interpreting cloud-sliced NO2 observations from the OMI satellite instrument. Atmos Chem Phys 2018; 18: 17017–27.

75. Müller JF. Geographical distribution and seasonal variation of surface emissions and deposition velocities of atmospheric trace gases. J Geophys Res 1992; 97: 3787–804.

76. Yienger JJ and Levy HII. Empirical model of global soil-biogenic NO x emissions. Geophys Res Lett 1995; 100: 11447–64.

77. Ganzeveld LN, Lelieveld J and Dentener FJ et al. Global soil-biogenic NOx emissions and the role of canopy processes. J Geophys Res 2002; 107: 9–17.

78. Yan XY, Dhara T and Akimoto H. Statistical modeling of global soil NOx emissions. Glob Biogeochem Cycle 2005; 19: GB3019.

79. Stavrou operatives and Boersma KA et al. Assessing the distribution and growth rates of NOx emission sources by inverting a 10-year record of NO2 satellite columns. Geophys Res Lett 2008; 35: L10801.

80. Stavrou T, Müller JF and Boersma KA et al. Key chemical NOx sink uncertainties and how they influence top-down emissions of nitrogen oxides. Atmos Chem Phys 2013; 13: 9057–82.

81. Steinkamp J and Lawrence MG. Improvement and evaluation of simulated global biogenic soil NO emissions in an AC-GCM. Atmos Chem Phys 2011; 11: 6063–82.

82. Hudman RC, Moore NE and Mebust AK et al. Steps towards a mechanistic model of global soil nitric oxide emissions: implementation and space based constraints. Atmos Chem Phys 2012; 12: 7779–95.
84. Weng HJ, Lin JT and Martin R et al. Global high-resolution emissions of soil NOx, sea salt aerosols, and biogenic volatile organic compounds. Sci Data 2020; 7: 148.
85. Wang C, Houlton BZ and Dai WW et al. Growth in the global N2 sink attributed to N fertilizer inputs over 1860 to 2000. Sci Total Environ 2017; 574: 1044–53.
86. Müller JF and Stavrakou T. Inversion of CO and NOx emissions using the adjoint of the IMAGES model. Atmos Chem Phys 2005; 5: 1157–86.
87. Vinken GCM, Boersma KF and Maasakkers JD et al. Worldwide biogenic soil NOx emissions inferred from OMI NO2 observations. Atmos Chem Phys 2014; 14: 10363–81.
88. Dentener F, Drevet J and Lamarque JF et al. Nitrogen and sulfur deposition on regional and global scales: a multimodel evaluation. Glob Biogeochem Cycle 2006; 20: GB4003.
89. Duce RA, Laroche J and Altieri K et al. Impacts of atmospheric anthropogenic nitrogen on the open ocean. Science 2008; 320: 893–7.
90. Vet R, Artz RS and Carou S et al. A global assessment of precipitation chemistry and deposition of sulfur, nitrogen, sea salt, base cations, organic acids, acidity and pH, and phosphorus. Atmos Environ 2014; 93: 3–100.
91. Weber B, Wu DM and Alexandra T et al. Biological soil crusts accelerate the nitrogen cycle through large NO and HONO emissions in drylands. Proc Natl Acad Sci USA 2015; 112: 15384–9.
92. Worden J, Noone D and Bowman K et al. Importance of rain evaporation and continental convection in the tropical water cycle. Nature 2007; 455: 528–32.
93. Good SP, Noone D and Bowen G. Hydrologic connectivity constrains partitioning of global terrestrial water fluxes. Science 2015; 349: 175–7.