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Key Points:

- Soil emission rates of NO in common inventories may be between 10× and 20× too low over the Amazon basin
- Higher soil NO over the Amazon basin alters the oxidative capacity of the atmosphere and decreases global methane lifetime by 1.4%–2.6%
- Global methane lifetime is more sensitive to Amazon soil NO fluxes than to the loss of terpene fluxes from total deforestation of the Amazon

Correspondence to:

A. L. S. Swann,
aswann@uw.edu

Author Contributions:

Conceptualization: Ben H. Lee, James Y. S. Yoon, Alexander J. Turner, Joel A. Thornton, Abigail L. S. Swann
Data curation: Ben H. Lee, J. William Munger, Steven C. Wofsy
Formal analysis: Ben H. Lee
Funding acquisition: Abigail L. S. Swann
Investigation: Ben H. Lee
Methodology: Abigail L. S. Swann
Project administration: Abigail L. S. Swann
Resources: J. William Munger, Steven C. Wofsy, Luciana V. Rizzo
Supervision: Abigail L. S. Swann
Visualization: Ben H. Lee
Writing – original draft: Ben H. Lee

Sensitive Response of Atmospheric Oxidative Capacity to the Uncertainty in the Emissions of Nitric Oxide (NO) From Soils in Amazonia

Ben H. Lee[1], J. William Munger[2] , Steven C. Wofsy[2] , Luciana V. Rizzo[3] , James Y. S. Yoon[1], Alexander J. Turner[1], Joel A. Thornton[1] , and Abigail L. S. Swann[1]

[1]University of Washington, Seattle, WA, USA, [2]Harvard University, Cambridge, MA, USA, [3]University of São Paulo, São Paulo, Brazil

Abstract Soils are a major source of nitrogen oxides, which in the atmosphere help govern its oxidative capacity. Thus the response of soil nitric oxide (NO) emissions to forcings such as warming or forest loss has a meaningful impact on global atmospheric chemistry. We find that the soil emission rate of NO in Amazonia from a common inventory is biased low by at least an order of magnitude in comparison to tower-based observations. Accounting for this regional bias decreases the modeled global methane lifetime by 1.4%–2.6%. In comparison, a fully deforested Amazonia, representing a 37% decrease in global emissions of isoprene, decreases methane lifetime by at most 4.6%, highlighting the sensitive response of oxidation rates to changes in emissions of NO compared to those of terpenes. Our results demonstrate that improving our understanding of soil NO emissions will yield a more accurate representation of atmospheric oxidative capacity.

Plain Language Summary Soils emit a gas called nitric oxide (NO). The amount of NO emitted from soils in tropical forests is not well known, but has been assumed to be small. We simulated how different amounts of NO emissions from soils in the Amazon impacted atmospheric chemistry. By comparing our modeled results to observations we found that NO emissions from soils in the Amazon may be between 10 and 20 times larger than the current default assumption. This matters because NO has a strong influence on the rate at which methane and other gasses are removed from the atmosphere. Therefore soil NO emissions end up impacting how long methane can last in the atmosphere, and that would have additional climate impacts. Even though soil NO emissions are smaller than other sources of NO emissions globally, we find that the amount of NO emitted in the Amazon matters a lot for how long methane can last in the atmosphere. Our results demonstrate that improving estimates of soil NO emissions is going to be necessary for making accurate estimates of how long methane and other reactive species will stay in the atmosphere.

1. Introduction

Nitrogen oxide radicals ($NO_x = NO + NO_2$) play a critical role in regulating the atmosphere's oxidizing capacity through reactions that recycle hydrogen oxides ($HO_x = OH + HO_2$) during the oxidation of hydrocarbons. Accurate representation of this chemistry is crucial, particularly in remote forested regions characterized by relatively low NO_x burdens and high emission rates of biogenic terpenes that give rise to steeply non-linear effects on HO_x, which govern the lifetimes of virtually all hydrocarbons including isoprene and methane. Notably and most recently, Wells et al. (2020) attributed the high-bias in modeled isoprene levels over Amazonia compared to those observed by the Cross-track Infrared Sounder (CrIS) to a low bias in NO, likely from soils, causing a low bias in OH, thus, a runaway increase in modeled isoprene lifetime.

The atmosphere in and above forests has long been thought to be depressed of hydroxyl (OH) radicals (Jacob & Wofsy, 1988; Logan et al., 1981; Spivakovsky et al., 2000) due to the high concentrations of volatile organic compounds (VOC), which react with OH to form organic peroxy radicals (RO_2), and limited availability of NO_x. In the absence of NO_x, RO_2 will self-react and react with hydroperoxy radicals (HO_2) to net remove OH and thus depress oxidative capacity. The availability of NO enables the catalytic recycling of OH during the daytime via reactions with RO_2 and HO_2.

$$RO_2 + NO \rightarrow RO + NO_2$$
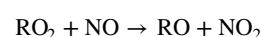
Writing – review & editing:
J. William Munger, Steven C. Wofsy,
Luciana V. Rizzo, James Y. S. Yoon,
Alexander J. Turner, Joel A. Thornton,
Abigail L. S. Swann

$$RO + O_2 \rightarrow HO_2 + R'O$$

$$HO_2 + NO \rightarrow OH + NO_2$$

$$NO_2 + hv\ (+O_2) \rightarrow NO + O_3$$
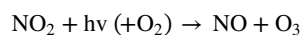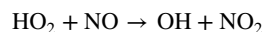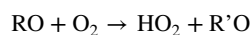
While there have been additional insights into OH recycling pathways from RO_2 chemistry which do not require NO_x, these recycling pathways are not sufficient to explain the Amazon regional observations of isoprene and formaldehyde from satellites (Wells et al., 2020). Tropical forests, and the associated large emissions of reactive VOC, are therefore significant influences on hemispheric if not global oxidizing capacity with consequences for the lifetimes of other trace gases such as methane. In-situ observations of OH and HO_2 in forested environments, however, often show that HO_x concentrations are in fact elevated above expectations (Lelieveld et al., 2008; Tan et al., 2001; Whalley et al., 2011). Implementation of updated chemical mechanisms focused on isoprene—globally the most abundantly emitted volatile organic compound (VOC) (Guenther et al., 2006; Messina et al., 2016)—have elevated modeled HO_x levels (Bates & Jacob, 2019; Squire et al., 2015; Taraborrelli et al., 2012). Recently, Jeong et al. (2022) report that measured OH during the GoAmazon campaign in the 2014 wet season near Manaus, Brazil agreed well with those calculated using multiple chemical models, suggesting that the $VOC-RO_2-HO_x-NO_x$ coupled chemistry is well understood. However, NO measurements during that experiment were unavailable, which is emblematic of the inherent challenges of deployments to such regions where testing of our understanding of emissions and chemistry is most lacking.

The sensitivity of the burden and lifetime of methane to global OH levels is well studied (Squire et al., 2015; Voulgarakis et al., 2013; Wild et al., 2020; Zhao et al., 2020). The role that anthropogenic NO_x plays in governing OH and therefore methane levels is also well documented (Laughner et al., 2021; Peng et al., 2022; Stevenson et al., 2022). Less emphasis has been placed on the role of NO_x from natural sources, though Song et al. (2021) report that approximately half of atmospheric NO_x is now derived from sources other than fossil fuel combustion. Soils produce NO through nitrification/denitrification with subsequent emission to the atmosphere moderated by a suite of environmental conditions including soil type, gas diffusivity, moisture, temperature, etc. (Pile-gaard, 2013). Alterations to forests, whether through conversion to pasture or logging, will consequently result in changes to soil emissions (Garcia-Montiel et al., 2001; Keller et al., 2005).

Numerous global chemical models—including the Community Earth System Model (CESM2) utilized here—refer to the work of Yienger and Levy (1995) to constrain soil NO emissions. More recent work by Hudman et al. (2012), on which Wells et al. (2020) rely, developed an updated parameterization including a more physical representation of soil processes derived from field observations that yielded greater soil NO emissions globally (10.7 Tg N yr^{-1}) compared to that of Yienger and Levy (7.4 Tg N yr^{-1}), though rates over Amazonia are significantly lower due likely to the inclusion of NO_x loss on canopy surfaces. Previously published inventories (Davidson, 1993; Ganzeveld et al., 2002; Jaeglé et al., 2005; Martin et al., 2003; Vinken et al., 2014; Yan et al., 2005) also show disagreement over the Amazon basin additionally highlighting the uncertainty in soil emission rates of NO, the tropospheric abundance of which is not reliably inferred from space.

We present the sensitivity of the oxidative capacity of the atmosphere, and specifically, the global lifetime of methane as a function of increasing soil NO emission rates over just the Amazon region as supported by in-situ observations at the Tapajos National Forest (54.580°W, 2.51°S, Pará, Brazil) from January to August of 2015. We compare this scenario to a set of simulations in which the region is fully deforested leading to a near ceasing of the emissions of biogenic terpenes, which are known to have implications on chemistry and climate (L. Ganzeveld et al., 2010; L. Ganzeveld & Lelieveld, 2004; Geddes et al., 2016; Heald & Spracklen, 2015; Keller et al., 2005; Lathière et al., 2006; Opacka et al., 2021; Unger, 2014; Wiedinmyer et al., 2006; Wu et al., 2012). Results presented here demonstrate the importance of capturing not only the magnitude of NO emissions but responses to evolving conditions given the sensitive response of the oxidative capacity, particularly in and above forests in tropical regions where methane oxidation is likely fastest and least certain (Turner et al., 2019).

2. Methods

We performed six sets of coupled biosphere-atmospheric chemistry simulations using the CESM2 model with CAM6-chem interactive chemistry (Danabasoglu et al., 2020; Emmons et al., 2020) and with active

biogeochemistry and fires ("FCfireHIST" compset in CESM2). The model is computed at a spatial resolution of ~1° and a time resolution of 30 min. We use the standard set of historical emissions provided with CESM2 which were derived for the Coupled Model Intercomparison Project version 6 (CMIP6; see full details in Emmons et al., 2020). We branched our forested baseline simulation in year 1970 from the standard transient historical simulation completed with CESM2 for CMIP6 using specified sea surface temperatures. We ran our forested baseline simulation from years 1970 to 2005 and all further model runs were branched from the forested baseline in the year 2001.

We completed three separate simulations with historical forest cover in Amazonia with a forested state from 1970. We completed an additional three simulations with a deforested Amazonia that was effectively devoid of trees by changing the plant functional type to a grassland over the region (from 16°S to 8°N and from 48°W to 78°W), as illustrated in Figure S1 in Supporting Information S1. Leaf area was calculated prognostically, as were other carbon fluxes and pools, however, atmospheric CO_2 concentrations were specified based on observed concentrations for each year. The removal of trees in the model changes physical fluxes of energy and water, as well as carbon and chemical species (e.g., isoprene). The model calculated total leaf area index for the Amazon basin is about 6.5 $m^2 m^{-2}$ in the forested scenarios and about 1.8 $m^2 m^{-2}$ in the deforested scenario, wherein the emission rates of isoprene and other larger biogenic terpenes are negligible. For each of the forested and deforested Amazonia scenarios we calculated three simulations representing different soil NO conditions: (a) baseline soil NO emission rate based on the work of Yienger and Levy (1995) as included in the POET inventory (Granier et al., 2005), and factors of (b) 10× that rate, and (c) 20× of that rate. The specified NO fluxes from Yienger and Levy (1995) are disconnected from the plant types specified in CESM, and thus the specified soil NO fluxes are identical between forested and deforested simulations for the same NO perturbation.

All simulation scenarios span from 2001 to 2005, except for the forested baseline soil NO scenario which spans from 1970 through 2014. All aspects of the model except for plant type and soil NO fluxes within the Amazon vary transiently across years based on observed quantities, including greenhouse gas concentrations, sea surface temperatures, and land cover change outside the Amazon basin as specified in CMIP6 historical simulations (Eyring et al., 2016).

We also utilized F0AM (Framework for 0-D Atmospheric Modeling; Wolfe et al., 2016), which leverages the more comprehensive Master Chemical Mechanism (MCM) version 3.3.1 (Jenkin et al., 1997, 2015; Saunders et al., 2003) to compare against the CESM2 results. We performed a series of simulations. Each was conducted with constant introduction rates of NO, O_3, and isoprene into the well-mixed volume with active photochemistry ($J_{NO2} = 2 \cdot 10^{-2} s^{-1}$), and allowed to evolve for 60 hr, much longer than the time needed for all species to reach steady state. The rate of NO introduction was varied widely to capture the response of oxidation chemistry to the steady state NO mixing ratios, while the rates of introduction of O_3 and isoprene were set such that the steady state resulting mixing ratios were comparable to the levels reported by CESM2 for the three soil NO emission rate scenarios. We compare in the section below the levels of OH and HO_2 calculated by CESM2 and F0AM.

Mixing ratios of NO, nitrogen dioxide (NO_2), and O_3 were measured at the Tapajos National Forest from January to August of 2015. The Tapajos National Forest site is located on a flat plateau and is considered a moist Tropical forest, falling in the 25th percentile for annual rainfall and 30th percentile for length of wet season (Saleska et al., 2003). Soils are primarily nutrient-poor clay oxisols with some sandy utisols (Rice et al., 2004). The site has not been recently disturbed and has minimal impact of anthropogenic air pollution (Rice et al., 2004). Ambient air in excess of instrument requirements was drawn in at 4–6 L per minute (lpm) through inlets located at eight heights off of the tall tower (0.91, 3.05, 10.42, 19.57, 28.71, 39.41, 53.04, 62.24 m above the ground). The NO chemiluminescence analyzer drew ~2 lpm and the O_3 analyzer drew ~1 lpm. To minimize sample residence time in the inlets and provide constant pressure to the analyzers, excess flow was pulled by a bypass pump to maintain constant pressure measured by a pressure controller. The inlets were sampled in sequence for 4 min each and the first 150 s after each level switch were discarded. NO and NO_2 were measured by an EcoPhysics CLD-780TR analyzer equipped with an external NO_2 photolysis cell using a Hamamatsu LED with peak wavelength at 365 nm (Pollack et al., 2010). The photolysis cell was toggled on and off at 60 s intervals to provide both NO and $NO + NO_2$ measurement at each sample height. All instruments were housed in an air conditioned shed near the base of the tower. The NO analyzer background signal was measured at the beginning of each profile sequence by adding O_3 generated by a Hg-vapor lamp to the sample stream to convert NO to NO_2 before the sample entered the detector. Instrument gain and NO_2 conversion efficiency were determined by routinely adding a small flow of NO
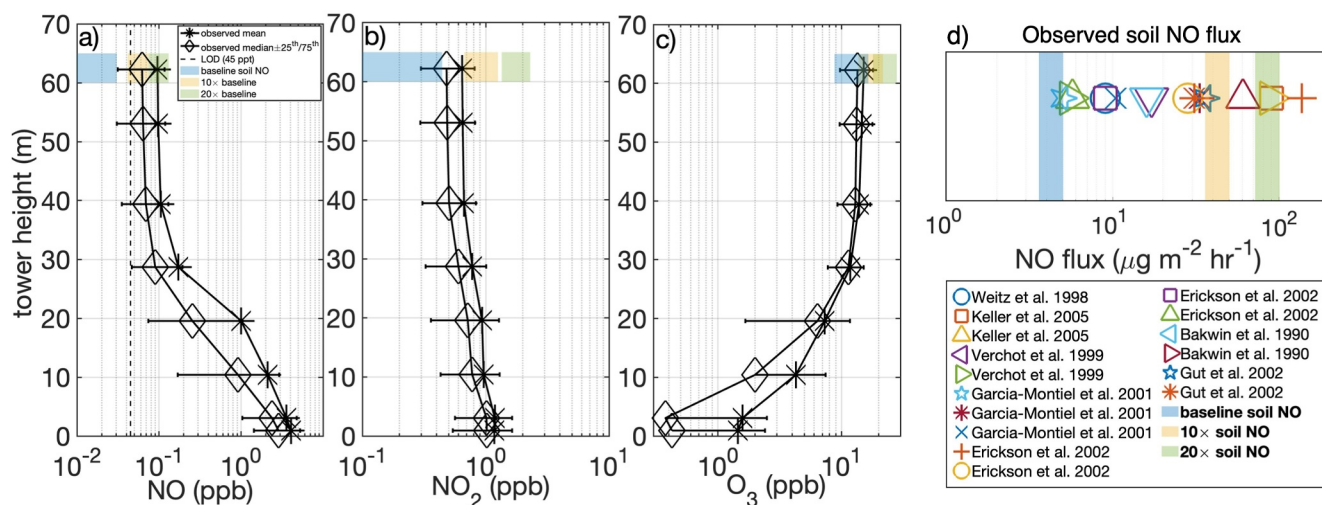
Figure 1. Mixing ratios of (a) NO, (b) NO_2, and (c) O_3 at the Tapajos National Forest as observed at eight heights on the tall tower from January to August of 2015, and as modeled for the lowest level of the atmosphere in CESM2 under three soil NO emission rate scenarios with baseline emissions in blue, 10× baseline in yellow and 20× baseline in green. The observational lower limit of detection for NO is plotted as the black dashed vertical line in panel (a). Panel (d) shows soil NO emission rates measured over tropical soils in unperturbed forests (Bakwin et al., 1990; Erickson et al., 2002; Garcia-Montiel et al., 2001; Gut et al., 2002; Keller et al., 2005; Verchot et al., 1999; Weitz et al., 1998). The measurements span different time periods and durations, seasons, soil type, etc. The shaded bars represent the modeled soil NO emission rate in CESM for the minimum and maximum rates over the course of a model year, with blue shading for the baseline soil NO emissions, yellow shading for 10× and green shading for 20×.

or NO_2 standard to the sample inlet. A minimum detection limit computed from twice the standard deviation of the signal during each zero check and the calibration factor measured nearest in time averaged 45 ppt over the course of the campaign. The average calibration factor uncertainty computed from standard deviations for the calibration and background signals was 10%, with most individual observations being closer to 5%. Observations of NO, NO_2, and O3 were measured every 4 min, and we averaged these high frequency values to monthly means before comparing with modeled values.

In addition to comparison with measured NO fluxes reported here we compare our CESM2 modeled quantities from observations reported previously in the literature. Observations of isoprene flux and mixing ratios were conducted at the Tapajos National Forest in June of 2016 and inferred from Sarkar et al. (2020). Observations of OH concentration were measured outside of Manaus, Brazil during GoAmazon in February–March of 2014 and inferred from Jeong et al. (2022).

3. Results and Discussion

In comparison to the measurements made above the forest canopy, CESM2 underestimates NO mixing ratio in the lower-most level of the atmosphere in the model-grid encompassing the Tapajos National Forest, when utilizing the baseline soil NO emission rate as prescribed by the work of Yienger and Levy (1995) (Figures 1a and 2a; Figure S2 in Supporting Information S1). Observed vertical profile from 0.9 to 62 m from the forest floor show that NO is most abundant near the forest floor, elevated to as high as a few parts per billion (ppb). Its mixing ratio decreases with height predominantly as it reacts with O_3 to form NO_2 (Bakwin et al., 1990), indicating that the dominant NO source at this site is likely from the soil underneath the forest canopy, and negligibly from an upwind source. The years 2015 and 2016 were characterized by El Niño conditions. The resulting drier-than-normal conditions in Amazonia could have contributed to higher than normal soil NO emissions, which exhibit a non-linear response to changing soil moisture levels (Davidson, 1993; Davidson & Kingerlee, 1997; Garcia-Montiel et al., 2001; Gut et al., 2002; Luo et al., 2012). However, El Niño became active at earliest in March of 2015, whereas the model underestimates observations throughout the year with no noticeable change in the model-observation discrepancy around that time. Biomass burning as well does not appear to have had a significant long-term impact on NO levels at the site given that the observations at the top of the tower do not exhibit periodic bursts or enhancements associated with influence from fresh or intense combustion sources (Figure S2 in Supporting Information S1).
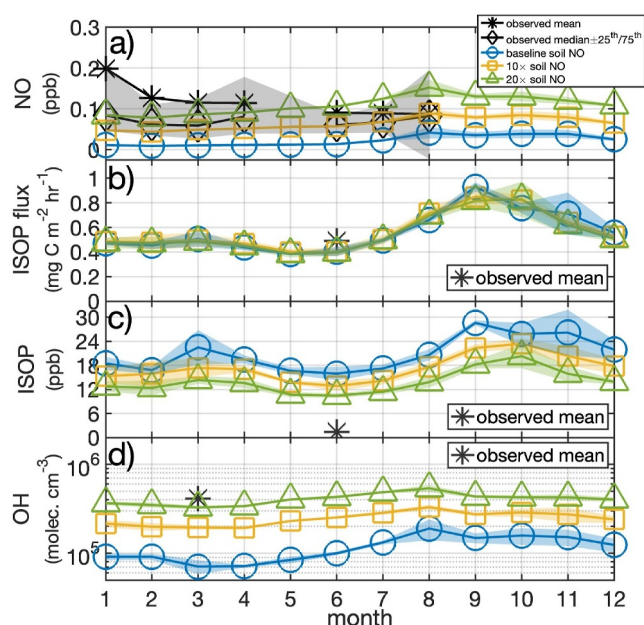
Figure 2. Monthly means of (a) NO mixing ratio, (b) isoprene flux, (c) isoprene mixing ratio, and (d) OH concentration in the lower-most level of the atmosphere above the Tapajos National Forest. Observations of isoprene flux and mixing ratios were conducted at the Tapajos National Forest in June of 2016 and inferred from Sarkar et al. (2020), while OH concentration was measured outside of Manaus, Brazil during GoAmazon in Feb-Mar of 2014 and inferred from Jeong et al. (2022). Observed isoprene and OH values represent respective campaign mean values.

Observed NO_2 and O_3 levels are, likewise, greater than those modeled above the canopy (the lowest level of the atmosphere) when implementing the baseline soil NO emission rate. One implication is that the modeled oxidative capacity of the atmosphere, namely OH and HO_2, is also likely biased low given NO cycles HO_2 to OH and that O_3 is the dominant primary HO_x source. As such, increasing the model soil NO emission rate enhances the levels of NO_x, HO_x, and O_3, as shown in Figure 1 (and Figure S3 in Supporting Information S1). Under the baseline soil scenario (blue range in Figure 1), the model underestimates above canopy NO_x much more (by ~factor 10) than it does O_3. As model NO emissions are increased, NO_x comes into closer agreement, while model O_3 overestimates observations by not more than factor of 2. The median level of NO measured above the forest canopy generally resides between that modeled with 10× and 20× soil emission rates. Similarly, modeled soil NO emission rates at 10× and 20× also show closer agreement with measured soil NO emission rates from unperturbed tropical forests (Figure 1d), indicating that the seemingly large increase in NO of 10× and 20× is easily within the range of observations. The mean ratios of the observed to modeled NO_x (NO + NO_2) resulting from utilizing the baseline, 10×, and 20× soil emission rates are lower at 2.7, 0.7, and 0.4, respectively, because NO_2 (and O_3) is overestimated by CESM2 with increasing soil NO fluxes for reasons detailed below. We note that the inventory from which CESM2 derives the default NO fluxes (Yienger & Levy, 1995) has substantially larger fluxes over the Amazon basin compared to a more recent inventory (Hudman et al., 2012). Thus our findings that the NO fluxes from Yienger and Levy (1995) appear too low by an order of 10× and 20× over the Amazon basin is not reconciled by the use of more recent inventories.

With the enhanced soil emission rates, OH—though never measured at the Tapajos National Forest—increases to levels that are well within an order of magnitude of that observed during the GoAmazon experiment (Jeong et al., 2022) (Figure 2d), with corresponding effects on the lifetime and burden of isoprene. However, the model overestimates isoprene mixing ratio compared to observations made at the Tapajos National Forest made in June of 2016 (Sarkar et al., 2020) by a factor between 8 and 12 (Figure 2c). This discrepancy is not necessarily due to inaccurate isoprene fluxes (Figure 2b), which Sarkar et al. (2020) finds agrees well at their site between what is measured by the eddy covariance approach and modeled using MEGAN (Model of Emissions of Gases and Aerosols from Nature) which also constrains biogenic terpene emissions for CESM2. However, Jo et al. (2021) evaluated the isoprene emissions in CESM2 and hypothesized that the emissions are too large, although they did not compare modeled quantities with direct observations from the Amazon basin.

In addition to a low bias in soil NO emission rate, mixing in the boundary layer within CESM2 may be too slow as evidenced by the overestimation of isoprene levels at the surface while model OH levels and model isoprene fluxes from the surface are reasonable. The vertical profile of modeled NO in the boundary layer exhibits a sharp enhancement in the lowest level of the atmosphere that interacts with the surface where emissions are continuously occurring (Figure S3 in Supporting Information S1) with O_3 showing a corresponding depletion comparable to what is observed from the tower beneath the forest canopy (Figure 1). Such erroneously slow vertical mixing leads to excessive accumulation of NO in the lower-most layer of the atmosphere and deprives the rest of the boundary layer of NO (and isoprene) that would otherwise lead to enhanced O_3 and HO_x levels, and therefore a shorter isoprene lifetime. For instance, while NO levels observed at Tapajos National Forest reside between those modeled with 10× and 20× soil NO flux (Figure 1a), observed NO_2 and O_3 levels are overestimated by the enhanced soil NO fluxes in CESM2 (Figures 1b and 1c). This is consistent with an over-abundance of modeled isoprene-derived peroxy radicals (RO_2) that react with NO to form NO_2, which with slow vertical mixing within the model would lead to an overproduction of O_3. Faster boundary layer mixing in the model would lead to dilution of NO in the surface layer and would in turn require an even stronger surface NO flux than what we have implemented here in order to match what was observed at the Tapajos National Forest. As such, the soil NO emission rate we infer here is likely a lower bound on the truth due to the slow mixing in CESM2. The rate of
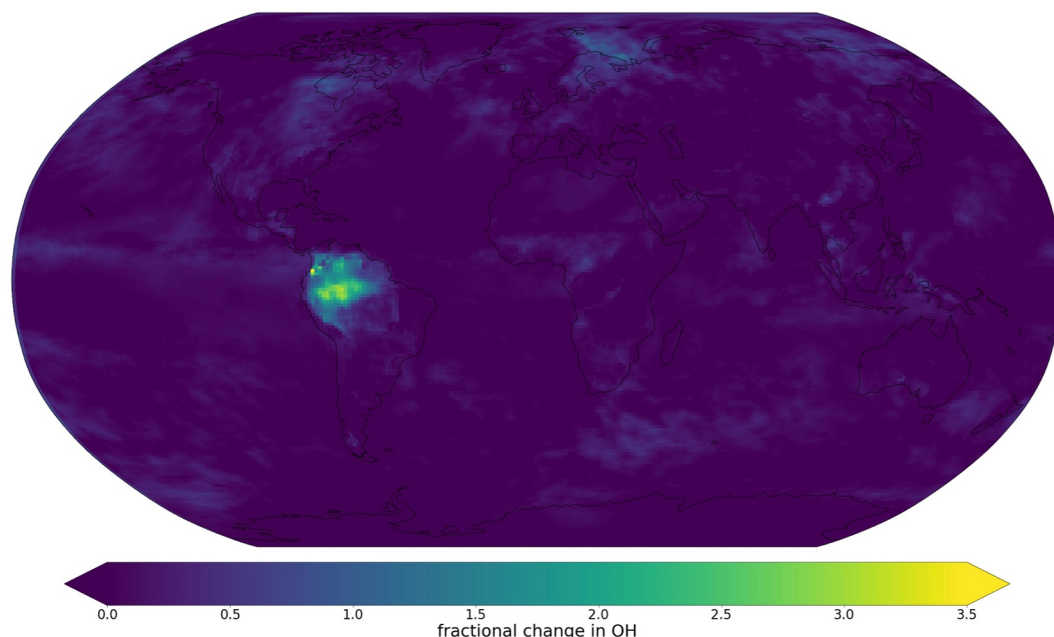
Figure 3. Fractional change in near-surface level (<800 hPa or <~2 km) OH due to increasing soil NO emissions from the Amazon by a factor of 20 relative to the baseline scenario in CESM2 for the month of September (wet season). Note the increase in OH due to increasing soil NO emissions is evident in all seasons (Figure 2d).

vertical mixing in CESM2 is not easily tuned. Additionally, given the lack of measured vertical profiles in the boundary layer of these compounds as well as the large variance of soil NO flux in time and space (Figure 1d), the focus of this work was not to quantify the soil NO flux at this one site, but rather to provide reasonable bounds and the subsequent impact on atmospheric oxidative capacity.

As soil NO emissions were increased in CESM2, so did the atmospheric levels of OH and HO_2. However, even with surface fluxes that appear within range of observations isoprene concentrations were still overestimated in CESM2. As such, to rule out underestimation of OH and HO_2 in CESM2, we employed F0AM to provide an additional check on the HOx budget.

There is good agreement between OH and HO_2 concentrations determined for the three forested simulations of varying soil NO emission rates and those of the F0AM simulations (Figure S4 in Supporting Information S1) indicating that all significant chemical mechanisms listed in the more comprehensive MCM v3.3.1 (Jenkin et al., 1997, 2015; Saunders et al., 2003) are represented by the chemistry module of CESM2 which is more condensed. Therefore, the high-bias in isoprene mixing ratios (Figure 2c) is likely not the result of deficient chemistry in CESM2.

We also note the variability in the observed NO values, as evidenced by the large difference in the observed mean and observed median NO mixing ratios (Figure 2). This is likely due to the dependence of nitrification and denitrification that generate NO on changes to conditions such as soil humidity and soil temperature. The modeled NO levels are much less variable—denoted by the shaded trace for a given month that represent the variability between the years 2001 and 2005—since its emissions are based on seasonally varying but annually repeating climatology. The minimum and maximum soil NO flux in the model region corresponding to the Tapajos National Forest are 3.6–10.1 µgNO m^{-2} hr^{-1}, respectively. As a result, the response of soil NO emissions to varying environmental conditions is not readily captured currently by CESM2.

The resulting increase in OH due to increasing the soil NO emission rate of Amazonia is significant enough to be globally relevant. We find that there is about a 3-fold increase in the fractional change in OH number concentration below 800 hPa in response to increasing the baseline soil emission rate by a factor of 20× (Figure 3). The factors of 10× and 20× increases in soil NO emission rates relative to baseline rates cause decreases in the global methane lifetime of 1.4% and 2.6%, respectively (Figure 4a), driven by the imposed 2.6% and 5.5% increases in
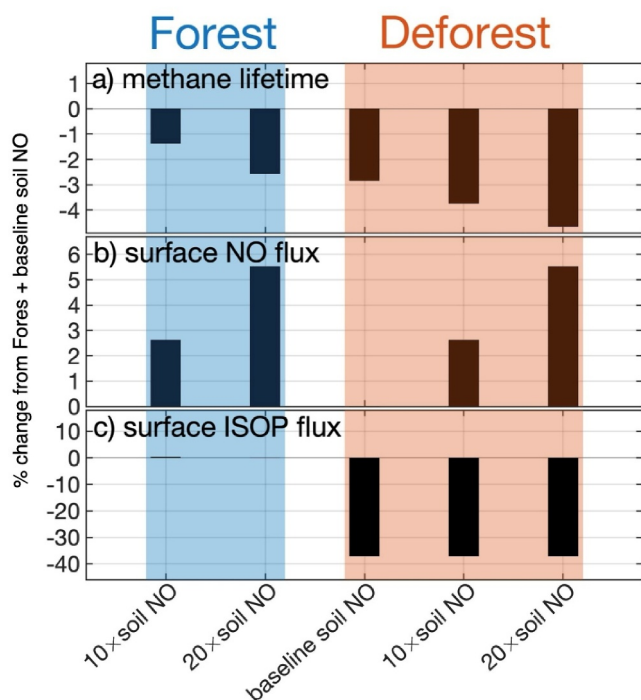
Figure 4. Impact on global (a) methane lifetime (b) soil NO emission rates and (c) biogenic isoprene emission rates due to changes in soil NO emission rate of Amazonia and/or deforestation of Amazonia, relative to the forested Amazonia scenario with baseline NO emission rate of CESM2.

the total (natural and anthropogenic) global surface NO_x emissions (Figure 4b). For context, this is approaching the amount needed to resolve the stabilization of methane observed between the years 2000 and 2007 (Dlugokencky et al., 2003; Lan et al., 2022), which can be explained by an approximately 4% increase in global OH levels as supported by remote-site measurements of methyl chloroform (Rigby et al., 2017; Turner et al., 2017), and which remains yet unresolved by models (Stevenson et al., 2020; Turner et al., 2019).

We compare the global methane lifetime's sensitivity to changes in Amazonian soil NO_x emissions and terpene emissions. Nearly ceasing Amazonia's emissions of biogenic terpenes including isoprene through simulated deforestation causes a 37% decrease in the global isoprene emission rate (Figure 4c) but a 2.8% decrease in the global methane lifetime. That a much larger change in regional isoprene emissions compared to regional NO emissions is required to induce a comparable change in global OH illustrates the much higher sensitivity of global OH levels and methane lifetime to the Amazonian emission rate of NO relative to that of terpenes.

Given the interactive nature of our CESM2 simulations which include chemistry, atmospheric processes, and land surface biogeochemistry there are additional feedbacks possible between deforestation, soil NO fluxes, and atmospheric chemistry. For example, water vapor is responsive to changes in temperature (less so to surface fluxes of evapotranspiration in the tropics), and secondary aerosol formation can impact cloud cover and cloud properties. We find that the totality of these feedbacks is small compared to the impact on methane lifetime of either soil NO fluxes or deforestation, resulting in an additional −0.39% to −0.67% change in methane lifetime on top of the effects of deforestation alone (−2.82%) and soil NO fluxes alone (−1.36% to −2.53%).

Lastly, simulating deforestation with a dynamic biosphere model shows its impact on soil characteristics such as moisture and soil temperature (Figure S5 in Supporting Information S1), both of which drive nitrification and denitrification processes that generate NO (Davidson et al., 2000; Garcia-Montiel et al., 2001; Luo et al., 2012), alongside a suite of other variables such as soil and tree types, extents of nitrogen input, and history of land-use (Bakwin et al., 1990; Erickson et al., 2002; Koehler et al., 2009; Pilegaard et al., 2006). These results call for the need for a dynamic soil model for NO emissions capable of incorporating the response of soil nitrogen processing to changes in environmental conditions (i.e., soil temperature, soil moisture), to adequately represent and forecast atmospheric oxidative chemistry which are currently being developed by several groups (Val Martin et al., 2023; Zaehle & Friend, 2010; Zhao et al., 2017).

4. Conclusions

Emission rates of NO from soils in CESM2 are underestimated by at least an order of magnitude compared to ground-based observations of NO_x fluxes, partitioning and vertical profiles. Factors that likely contribute to the low-bias in existing inventories include inadequate number of field measurements encompassing multiple seasons in numerous land types that provide model constraints, as well as implementation of overly aggressive NO_x loss on forest canopy surfaces. We show that correcting this low-bias in NO_x emissions enhances regional OH levels to such an extent as to be globally significant. The soil NO emission rate over Amazonia was increased by a factor of 10× to 20× relative to the rates prescribed by Yienger and Levy (Yienger & Levy, 1995) to achieve consistency with observations at the Tapajos National Forest, resulting in a global average methane lifetime decreases of 1.4% and 2.6%, respectively. The extent of NO flux underestimation may be even greater if the model utilized here suffers from slow vertical mixing of the boundary layer. The impact on the global oxidative capacity due to such increases in soil NO emissions over Amazonia is comparable to that due to the near complete ceasing of biogenic VOC emissions from the deforestation of Amazonia. Given the sensitivity of the global atmospheric oxidative capacity to relatively small changes in our current estimation of global NO_x emissions, understanding the

magnitude and sign of the response of soil NO emissions to past and future forcings including land use and land cover change are critical for assessing the lifetimes of all reactive species of the atmosphere.

Data Availability Statement

The observations made at the Tapajos National Forest as well as the model simulation output described in this paper are available at Lee et al. (2024).

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