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], 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, SP, Brazil

Corresponding author: Abigail L. S. Swann (aswann@uw.edu)

Key Points:

- Soil emission rates of NO in common inventories may be between 10x and 20x 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% to 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

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% to 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 is 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 reacts in the atmosphere with the gas that is the main gas that reacts with things like methane. 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 hydro-peroxy 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.

$$RO_2 + NO \rightarrow RO + NO_2$$

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

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

$$NO_2 + hv\ (+O_2) \rightarrow NO + O_3$$

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), though robust tests to confirm the validity of those updates remain elusive (Archibald et al., 2010). 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. 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 Atmosphere Model (CESM2-CAM-Chem) 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. Discrepancies amongst published inventories additionally highlight the uncertainty in soil emission rates of NO (Davidson, 1993; Ganzeveld et al., 2002; Jaeglé et al., 2005; Martin et al., 2003; Yan et al., 2005), 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-CAM-Chem global model (Danabasoglu et al., 2020; Emmons et al., 2010) with active biogeochemistry at ~1□spatial resolution. Three separate sets were initialized with forests in Amazonia in a state that is representative of the early 1980s. The other three were initialized with 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**. Leaf area is calculated prognostically, as are other carbon fluxes and pools, however, atmospheric CO_2 concentrations are 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 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 biogenic terpenes including isoprene and monoterpenes are negligible. For each of the forested and deforested Amazonia scenarios we calculated three sets of simulations representing different soil NO conditions: (i) baseline soil NO emission rate based on the work of *Yienger and Levy* (1995), and factors of (ii) 10× that rate, and (ii) 20× of that rate. All simulation scenarios span from 2001 to 2005, except for the forested baseline soil NO scenario which spans from 1980 to 2015. 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 ("FCfireHIST" compset in CESM2).

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., 2015; Jenkin et al., 1997; Saunders et al., 2003) to compare against the CESM2-CAM-Chem 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} = 2×10^{-2} s^{-1}), and allowed to evolve for 60 hours, 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-CAM-Chem for the three soil NO emission rate scenarios. We compare in the section below the levels OH and HO_2 calculated by CEMS2-CAM-Chem 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. Ambient air in excess of instrument requirements was drawn in at 4-6 liters 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. 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 minutes each. 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. Instrument background signal was measured by periodically 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 or NO_2 standard to the sample inlet.

3 Results and Discussion

In comparison to the measurements made above the forest canopy, CESM2-CAM-Chem 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 S2**). Observed vertical profile from 0.9 m 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**).

Observed NO_2 and O_3 levels are, likewise, greater than those modeled for 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 Figures S3, S4, and S5)**. 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 10x and 20x also show closer agreement with measured soil NO emission rates from unperturbed tropical forests (**Figure S7**). The mean ratios of the observed to modeled NO_x resulting from utilizing the baseline, 10×, and 20× soil emission rates are 2,7, 0.7, and 0.4, respectively.

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 modeled isoprene mixing ratio still overestimates observations 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 due to inaccurate isoprene fluxes (**Figure 2b**), which at the site agrees well 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-CAM-Chem.

In addition to a low bias in soil NO emission rate, mixing in the boundary layer within CESM2-CAM-Chem is likely too slow. 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**) with O_3 showing a corresponding depletion (**Figure S4**), 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. 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-CAM-Chem.

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 S8**) indicating that all significant chemical mechanisms listed in the more comprehensive MCM v3.3.1 (Jenkin et al., 2015; Jenkin et al., 1997; Saunders et al., 2003) are represented by the chemistry module of CESM2-CAM-Chem which is more condensed. Therefore, the high-bias in isoprene mixing ratios (**Figure 2c**) is likely not the result of deficient chemistry in CESM2-CAM-Chem.

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 2.0×10^9 and 2.8×10^9 molecules cm^{-2} s^{-1}, respectively. As a result, the response of soil NO emissions to varying environmental conditions is not readily captured currently by CESM2-CAM-Chem.

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 lead to 2.6% and 5.5% increases in the total (natural and anthropogenic) global surface NO_x emissions (**Figure 4b**), and cause decreases in the global methane lifetime of 1.4% and 2.6%, respectively (**Figure 4a**). 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 only a 4.6% decrease in the global methane lifetime. That a much larger change in isoprene emissions compared to NO emissions is required to induce a comparable change in OH illustrates the much higher sensitivity of global OH levels and methane lifetime to the emission rate of NO relative to that of terpenes. Lastly, simulating deforestation with a dynamic biosphere model shows its impact on soil characteristics such as moisture and soil temperature (**Figure S9**), 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, to adequately represent and forecast atmospheric oxidative chemistry.

4 Conclusions

Emission rates of NO from soils in CESM2-CAM-Chem 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 II, 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.

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Open Research

The observations made at the Tapajos National Forest as well as the model simulation output described in this paper are available through Dryad (available at this link during peer review: https://datadryad.org/stash/share/uWEs8q4jBPor-wijYBwdnmacFixCaNWV10yXIGxQzIo, final DOI to be provided after manuscript is accepted).

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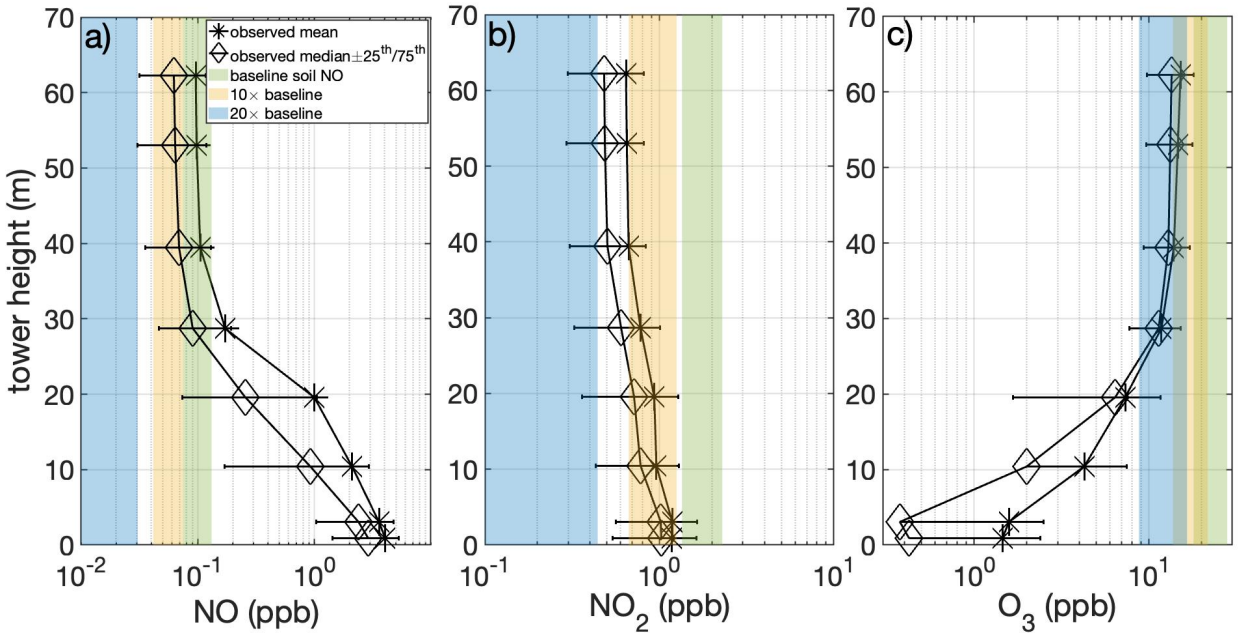


Figure 1. Mixing ratios of (a) NO, (b) NO_2, and (c) O_3 at the Tapajos National Forest as observed at eight heights on the tall tower from Jan to Aug of 2015, and as modeled for the lowest level of the atmosphere in CESM2-CAM-Chem under three soil NO emission rate scenarios. Model-observation comparison shows that soil NO emission rates in CESM2-CAM are biased low by at least an order of magnitude.

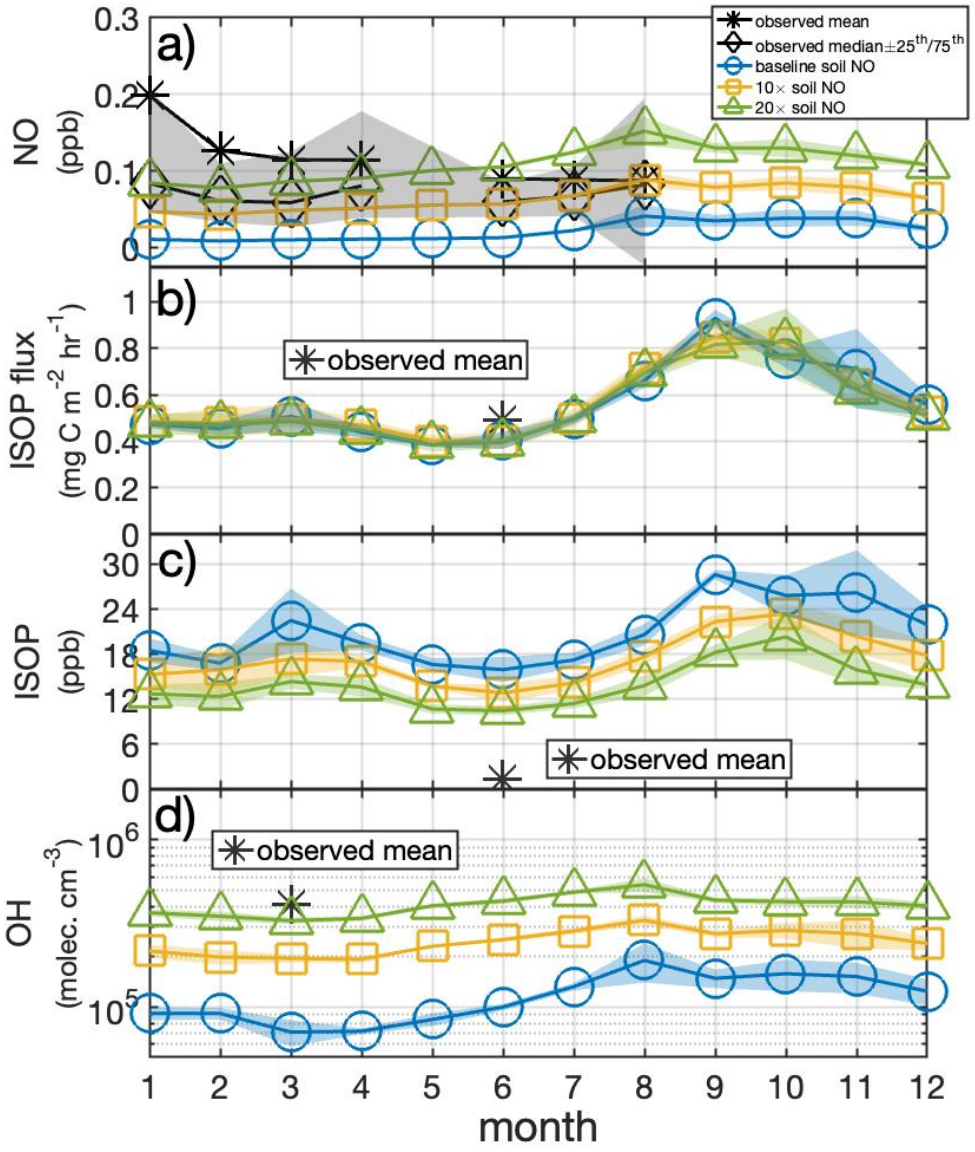


Figure 2. Monthly means of (a) NO mixing ratio, (b) isoprene flux, (c) isoprene mixing ratio, and (d) OH concentration in the lower-most level of the atmosphere above the Tapajos National Forest. Though there is general model-observation agreements in isoprene flux, NO mixing ratio and OH concentration by enhancing soil NO emission rate, there exists a large discrepancy in isoprene mixing ratio, indicating that accounting for the low-bias in soil NO emission rates does not fully resolve the high-bias in isoprene mixing ratio. Observations of isoprene flux and mixing ratios were conducted at the Tapajos National Forest in June of 2016 [Sarkar et al., 2020], while OH concentration was measured outside of Manaus, Brazil during GoAmazon in Feb-Mar of

2014 [Jeong et al., 2022]. Observed isoprene and OH values represent respective campaign mean values.

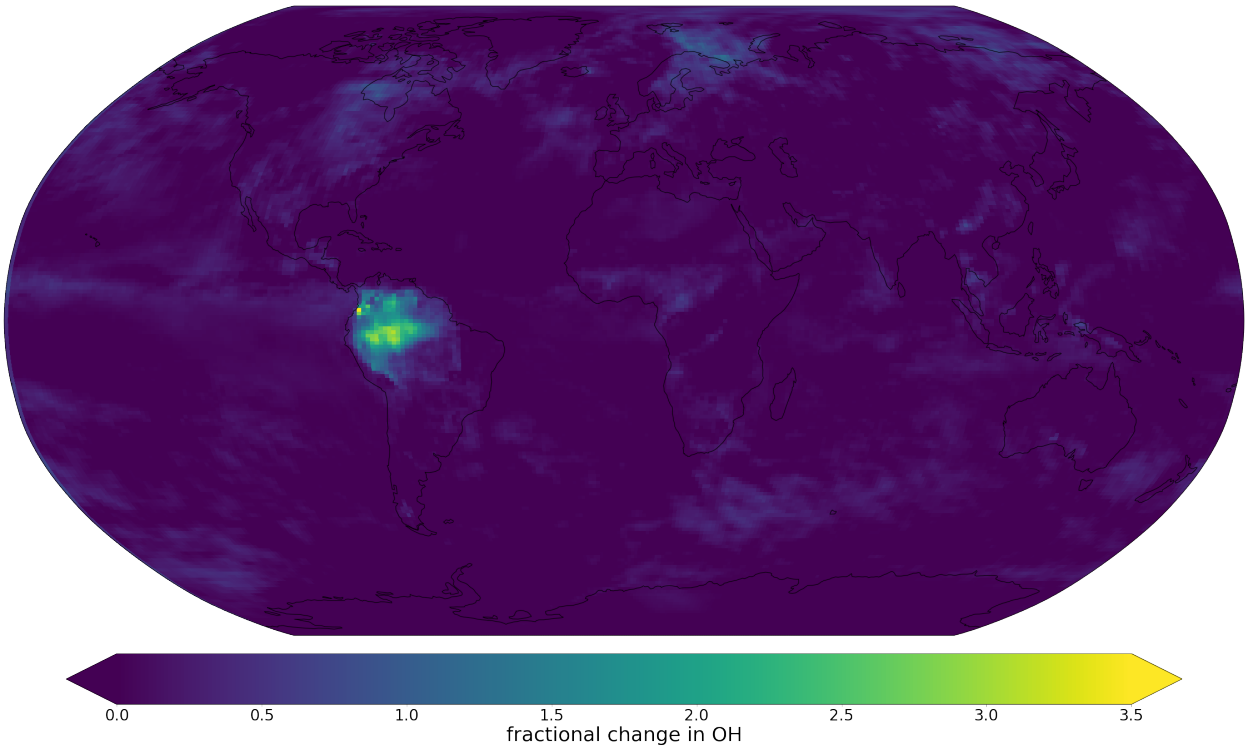
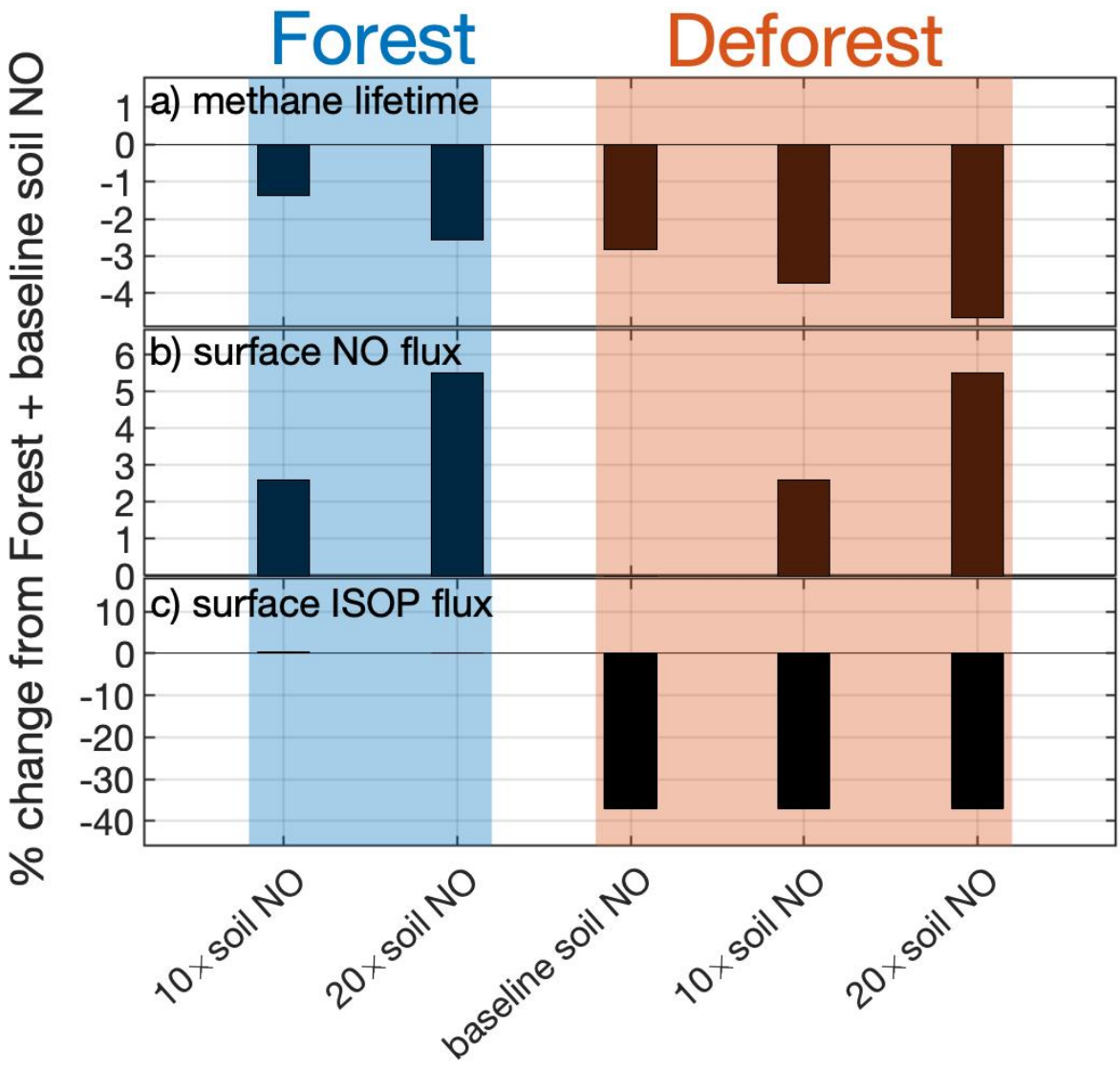


Figure 3. Fractional change in near-surface level (<800 hPa or <~2 km) OH due to increasing soil NO emissions from the Amazon by a factor of 20 relative to the baseline scenario in CESM2-CAM-Chem for the month of September (wet season). Note the increase in OH due to increasing soil NO emissions is evident in all seasons (**Figure 2d**).



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560 **Figure 4**. Impact on global (a) methane lifetime (b) soil NO emission rates and (c) biogenic
561 isoprene emission rates due to changes in soil NO emission rate of Amazonia and/or
562 deforestation of Amazonia, relative to the forested Amazonia scenario with baseline NO
563 emission rate of CESM2-CAM-Chem.

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