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RESEARCH ARTICLE
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Changes in the Relative Importance of Biogenic Isoprene and Soil NOx Emissions on Ozone Concentrations in Nonattainment Areas of the United States

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Key Points:

- Following anthropogenic nitrogen oxides (NOx) reductions, O_3 sensitivity to biogenic isoprene is decreasing in many US O_3-nonattainment areas
- Soil NOx dominates isoprene in interannual tendencies of O_3 in nonattainment areas of the Great Lakes, Ohio River Valley, and Northeast (NEA)
- Emerging importance of soil NOx emissions implies potentially unexpected variability in high O_3 where volatile organic compound-limitation previously dominated

Supporting Information:

Supporting Information may be found in the online version of this article.

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Abstract Reductions in anthropogenic emissions have drawn increasing attention to the role of the biosphere in O_3 production chemistry in U.S. cities. We report the results of chemical transport model sensitivity simulations exploring the relative impacts of biogenic isoprene and soil nitrogen oxides (NOx) emissions on O_3 and its temporal variability. We compare scenarios with high and low anthropogenic NOx emissions representing the reductions that have occurred in recent decades. As expected, summertime O_3 concentrations become less sensitive to perturbations in biogenic isoprene emissions as anthropogenic NOx emissions decline. However, we demonstrate for the first time that across policy relevant O_3 nonattainment areas of the United States, O_3 becomes more sensitive to perturbations in soil NOx emissions than to identical perturbations in isoprene emissions. We show that interannual variability in soil NOx emissions may now have larger impacts on interannual O_3 variability than isoprene emissions in many areas where the latter would have dominated in the recent past.

Plain Language Summary Ozone (O_3) is a criteria air pollutant that continues to pose a threat to more than one hundred million Americans each year, despite progress in regulating precursor emissions. In many O_3-polluted areas, the role of natural emissions of isoprene in the production of ground-level O_3 has been well recognized, but this chemistry depends strongly on local anthropogenic emissions which have been changing rapidly. We use an updated estimate of anthropogenic emissions to demonstrate that many areas that remain in nonattainment of the federally mandated O_3 standard are now much less sensitive to natural isoprene emissions, with biogenic nitrogen oxide emissions from soils becoming more and more important. The role of these soil emissions on O_3 in nonattainment areas has not been well characterized, but, as we show here, this will become increasingly necessary for good O_3 policy in nonattainment areas.

1. Introduction

Despite widespread improvements in air quality across the United States, more than 120 million Americans continue to live in regions that do not meet the current health-based ground-level ozone (O_3) standards (U.S. Environmental Protection Agency, 2019b). Known as "nonattainment areas," these areas have O_3 design values (defined as a 3-year average of the annual fourth-highest maximum 8 hr O_3 mixing ratio measured at an air quality monitoring site) that exceed 70 ppb (U.S. Environmental Protection Agency, 2019a). As anthropogenic precursor emissions have declined, we require increasing detail regarding the role of natural variability and background O_3 in local air quality management (Fiore et al., 2014; Guo et al., 2018; Jaffe et al., 2018; Lin et al., 2017; Parrish et al., 2017). This includes contributions from biogenic precursor emissions, such as volatile organic compounds (VOCs) from vegetation and nitrogen oxides (NOx) from soils. While some portion of these emissions may not be considered "natural" (e.g., NOx emissions from managed agricultural soils), their emission rates depend strongly on natural environmental variability.

Because O_3 chemistry in urban core areas has historically been largely VOC-limited (i.e., O_3 production is positively proportional to changes in organic compound emissions), past focus has been on quantifying the influence of biogenic isoprene emissions in particular (Bell & Ellis, 2004; Chameides et al., 1988; Hakami et al., 2006; Kleinman et al., 2005; Li et al., 2007; Tao et al., 2003; Zare et al., 2014). With wide reductions in NOx emissions across the United States (Duncan et al., 2016; Hidy & Blanchard, 2015; Parrish et al., 2011), satellite- and ground-based monitoring analyses demonstrate that O_3 production in urban areas of the country is transitioning from mostly VOC-limited to increasingly NOx-limited (Baidar et al., 2015; Blanchard & Hidy, 2018; He

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et al., 2019; Jin et al., 2017; Pusede & Cohen, 2012; Pusede et al., 2015). Recent observational evidence has subsequently supported the growing importance of soil NOx emissions on O_3 levels in some areas (Almaraz et al., 2018; Oikawa et al., 2015; Romer et al., 2018; Trousdell et al., 2019), but this work has been limited to short-term field campaigns in specific regions (e.g., California and the Southeast United States), without attention on the potential impacts across all U.S. nonattainment areas.

Biogenic emissions exhibit large temporal variability, so that their importance and relative contributions vary day-to-day and year-to-year. Both have underlying sensitivity to some overlapping environmental variables but could potentially drive changes in O_3 concentrations in different ways that would benefit from being understood fully under changing anthropogenic emissions. The influence of the biosphere on O_3 air quality during extreme climatological events or during the worst air quality days has been confirmed (Demetillo et al., 2019; Guo et al., 2018; Wang et al., 2017; Zhang & Wang, 2016). For example, the enhancement in O_3 from biogenic VOC emissions on the 10 highest O_3 days in the United States over 2004–2012 was estimated to be 1–7 ppb higher than their contribution to O_3 under more average conditions (Guo et al., 2018). Romer et al. (2018) estimate that soil NOx emissions are responsible for almost half of the 2.3 ppb $°C^{-1}$ increase in O_3 production rates with ambient temperatures in the southeast United States. This variability in biogenic emissions is often invoked as a mechanism behind well-documented correlations between O_3 concentrations and ambient temperature (Lu et al., 2019; Pusede et al., 2014, 2015; Rasmussen et al., 2012; Romer et al., 2018; Steiner et al., 2010). Increasing global temperatures and other effects of climate change could increase both the variability of these biogenic precursor emissions and/or their importance on O_3 concentrations in the United States (Demetillo et al., 2019; Gonzalez-Abraham et al., 2015; Lam et al., 2011; Lin et al., 2008, 2017; Steiner et al., 2006; Weaver et al., 2009).

The U.S.-wide reductions in anthropogenic NOx emissions should cause O_3 in nonattainment areas to become less sensitive to variability in isoprene, and potentially more sensitive to variability in soil NOx. The predominance of either biogenic isoprene or soil NOx in O_3 variability is relevant for understanding where management solutions can be focused. However, to our knowledge, this policy-relevant transition in the relative importance of biogenic O_3 precursors, especially in nonattainment areas specifically, has not yet been demonstrated across the contiguous U.S. with a chemical transport model and with up-to-date emissions. While a myriad of factors can determine ambient O_3 concentrations (e.g., natural and anthropogenic emissions, long-range transport, and local meteorology), chemical transport models allow us to perform experiments where the individual drivers can be isolated from each other. For example, the direct biogenic contributions to regional air quality are often examined in experiments where the natural (or anthropogenic) emissions for a single year are turned off individually and compared to a scenario where all emissions are combined (Curci et al., 2009; Sartelet et al., 2012; Tao et al., 2003; Zare et al., 2014). However, this experimental design overlooks how interannual variability and non-additive interactions might play a role in attaining air quality targets in any given year.

In contrast to previous work which removes or adds the biogenic components to a simulation, we explore the role of the biosphere by linearizing the response of O_3 to biogenic precursors around local chemical conditions, under multiple anthropogenic NOx emission scenarios. To do this, we test the sensitivity of simulated surface O_3 to $\pm$50% perturbations in isoprene and soil NOx emissions in hypothetical simulations with high and low anthropogenic NOx emissions that are representative of declines in anthropogenic NOx emissions in recent decades. We then combine these sensitivity experiments with predictions of biogenic emissions over a ~20-year timescale to estimate the interannual variability in summertime O_3 that is driven by these biogenic precursors in isolation from other sources of variability. We show how the importance of biogenic precursors is shifting over specific nonattainment regions across the country and discuss the relevance to policy and future development.

2. Methods

2.1. Chemical Transport Model Description

We use the GEOS-Chem v11-02 chemical transport model (http://geos-chem.org). GEOS-Chem simulates detailed NOx-hydrocarbon-O_3-halogen-aerosol tropospheric chemistry, including gas–particle interactions. Our simulations are driven by assimilated meteorological data for the year 2013 provided by the NASA Global Modeling and Assimilation Office Goddard Earth Observation System. We use the GEOS-FP product which provides a nested horizontal resolution of 0.25° × 0.315° over North America and run the model with 47 vertical layers. Boundary conditions are provided by a global simulation with a 2° × 2.5° horizontal resolution. This

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version of GEOS-Chem has been evaluated against observations of NOx, O_3, and isoprene using various satellite, aircraft, and surface measurements (Fisher et al., 2016; Travis et al., 2016). Travis et al. (2016) show that the model successfully reproduces spatial variability in boundary layer O_3 measured by aircraft observations from SEAC4RS after correcting an overestimate in anthropogenic NOx emissions, but a high bias in surface O_3 persists which is attributed to boundary layer mixing and O_3 production chemistry. Consistent with this, our baseline simulation for 2013 shows a nationwide bias in midday (12:00–04:00 p.m.) mean summertime surface O_3 concentrations compared to the CASTNET observations (NMB = 6.9 pb, $r = 0.625$). We argue that this bias does not preclude the use of GEOS-Chem in sensitivity experiments where the focus is on simulated differences in O_3 concentrations. We run our simulations from April to September. The first 2 months are used as spin-up, and we focus our results on summer months (June–July–August).

Anthropogenic emissions for the United States are provided by the National Emission Inventory (NEI-2011) for the United States as implemented by Travis et al. (2016) and by the Criteria Air Contaminants (CAC) inventory for Canada as implemented by van Donkelaar et al. (2008), respectively, with both scaled to 2013 based on economic data as described in van Donkelaar et al. (2008). Additional perturbations to the initial anthropogenic NOx emissions are discussed below. Biogenic VOC emissions are calculated online by the Model of Emissions of Gases and Aerosols from Nature (MEGAN) v2.1 inventory (Guenther et al., 2012) as implemented by Hu et al. (2015). The biogenic emission of a compound i (E_i) is governed by the following equation:

$$E_i = E_{i,o} \times \gamma_{\mathrm{PAR}} \times \gamma_T \times \gamma_{\mathrm{LAI}} \times \gamma_{\mathrm{Age}} \quad (1)$$

where $E_{i,o}$ is the base emission factor for some compound i (based on the fractional coverage of plant functional types within a grid box) under standard conditions, and deviations from these conditions are accounted for by activity factors for solar radiation (γ_{PAR}), temperature (γ_T), leaf area index (γ_{LAI}), and leaf age (γ_{Age}). Plant functional type distribution for VOC basal emission factors comes from the Community Land Model version 4 (Oleson et al., 2010), with monthly mean leaf area indices derived from Moderate Resolution Imaging Spectroradiometer (MODIS) observations (Myneni et al., 2007). Soil NOx emissions fluxes (S_{NOx}) are calculated online using the Hudman et al. (2012) parameterization, governed by the following equation:

$$S_{\mathrm{NOx}} = A'_{\mathrm{biome}}\left(N_{\mathrm{avail}}\right) \times f(T) \times g(\theta) \times P\left(l_{\mathrm{dry}}\right) \quad (2)$$

where A'_{biome} is a biome-specific coefficient (which itself is a function of available soil nitrogen, N_{avail}, that accounts for the standing pool of nitrogen, deposited nitrogen from the atmosphere, and fertilizer nitrogen applications, as described in Hudman et al., 2012). This coefficient is modified by functional dependencies on temperature, g(T) (where T is surface temperature), soil moisture, $g(\theta)$ (where θ is water-filled pore space), and precipitation pulsing, $P(l_{\mathrm{dry}})$ (where l_{dry} is the dry spell length). Maps of the isoprene and soil NOx emissions from our GEOS-Chem set-up are shown in Figure 1. Other emissions in the model include aircraft (Stettler et al., 2011), ships (Holmes et al., 2014; Vinken et al., 2011), biomass burning (GFED4.1), and lightning (Murray et al., 2012).

2.2. Sensitivity Simulations

To test the role of biogenic emissions on surface O_3, we perform two sets of sensitivity simulations: one at "high" anthropogenic NOx emissions, and at "low" anthropogenic NOx emissions (where anthropogenic NOx emissions are reduced by 50%).

Nationwide anthropogenic NOx emissions in the "high" emissions scenario are consistent with the Environmental Protection Agency's (EPA's) NEI estimate for the year 2013 (US EPA, 2021). However, many previous sources have proposed that the area and mobile anthropogenic NOx emissions in the NEI are an overestimate (Anderson et al., 2014; McDonald, McKeen, et al., 2018; Souri et al., 2016; Travis et al., 2016). We therefore compared our simulated NO_2 columns with observed tropospheric NO_2 columns from the Ozone Monitoring Instrument (OMI) satellite instrument over grid boxes where anthropogenic emission dominate (>75%), to estimate the time period for which these emissions are most representative. The OMI observations were accessed from https://disc.gsfc.nasa.gov/, filtered for pixels with a solar zenith angle smaller than 60, and cloud fractions less than 0.3. All June–July–August observations that pass these quality controls are gridded to the nested GEOS-Chem resolution

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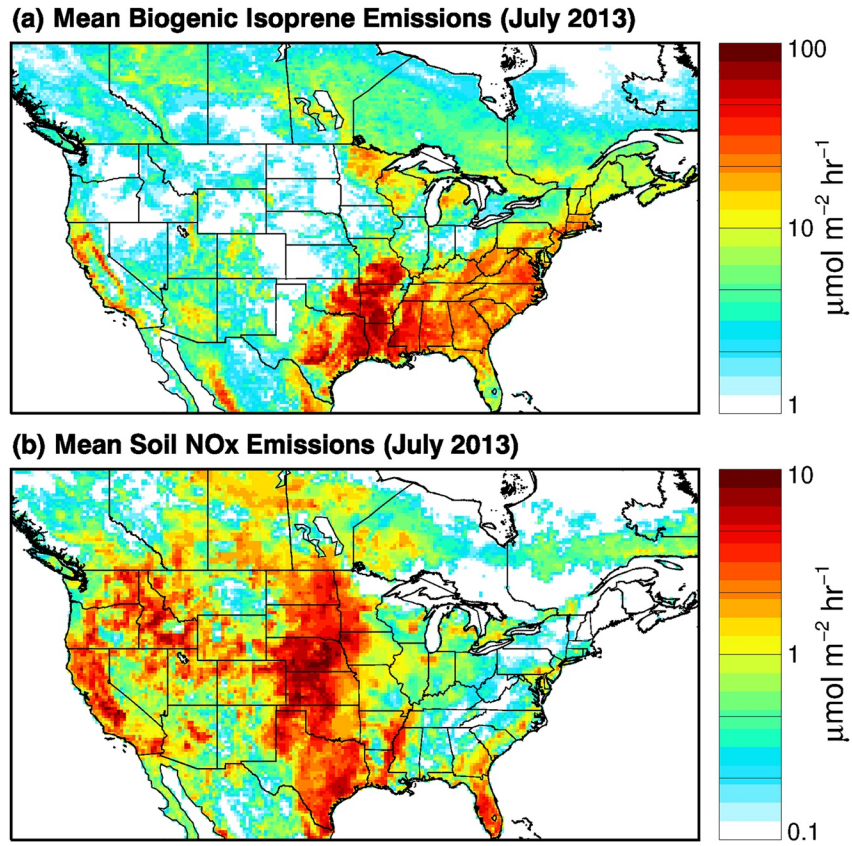

Figure 1. Mean biogenic isoprene emissions (a) and soil nitrogen oxides (NOx) emissions (b) from GEOS-Chem for July 2013.

using the physics-based oversampling approach documented in Sun et al. (2018). By only comparing pixels where anthropogenic emissions dominate, we minimize uncertainties in this comparison introduced by lightning and soil NOx variability, which would be affected by meteorology.

According to correlation coefficient and normalized mean bias when compared to 3 year running averages of OMI observations over urban areas, the NO_2 columns simulated by the "high anthropogenic NOx" scenario (NEI-2013) show the best agreement with OMI observations from 2005 to 2007, while the NO_2 columns simulated by the 50% reduction in anthropogenic emissions show the best agreement with OMI observations from 2016 to 2018. Figure 2 shows this comparison of the modeled and observed tropospheric NO_2 columns (Figure S1 in Supporting Information S1 shows the full comparison of modeled columns with all 3-year running averages from 2005 to 2019). Judging from this agreement, we infer that the first set of simulations represent anthropogenic NOx emissions most consistent with the years 2005–2007, while the second set of simulations represent anthropogenic NOx emissions most consistent with the years 2016–2018. The model simulated O_3 in the second scenario also compares favorably with CASTNET observations for 2018 with minimal bias and a high spatial correlation (NMB = 0.1 ppb, $r = 0.86$), but we include this comparison for reference only with the caveat that we have purposely used 2013 meteorology in our simulation for the reasons described below. Our NOx emission scenarios are therefore representative of reductions in anthropogenic NOx emissions over the last decade and a half. This 50% decline in emissions is consistent with changes reported in other analyses over urban areas of the United States for similar time periods (Duncan et al., 2016), and with emission trends reported by the EPA (https://www.epa.gov/air-emissions-inventories/air-pollutant-emissions-trends-data).

For each of the high- (~2005–2007) and low- (~2016–2018) anthropogenic NOx emission scenarios, we then perform sensitivity simulations where biogenic isoprene emissions are perturbed by +50% and −50%, respectively, and then where soil NOx emissions are perturbed by +50% and −50%, respectively. These perturbations are accomplished by allowing GEOS-Chem to calculate the emissions online, then applying a 0.5 or 1.5 scaling

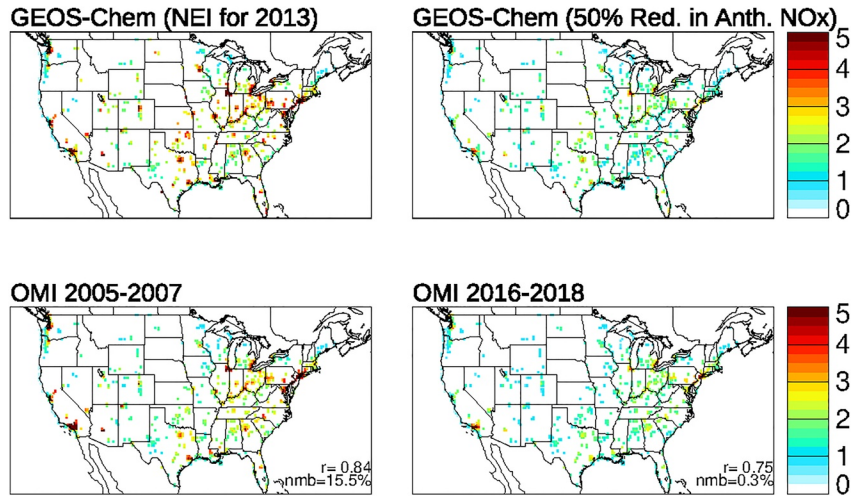

Figure 2. June–July–August mean NO_2 tropospheric column densities over model grid cells with >75% of nitrogen oxides (NOx) emissions from anthropogenic sources. Top panels: from the GEOS-Chem simulations using NEI-2011 anthropogenic NOx emissions scaled to 2013 ("high-NOx"), then a 50% reduction in anthropogenic emissions ("low-NOx"). Bottom panels: Ozone Monitoring Instrument (OMI) observations during the 3-year average period with the best model agreement. Pearson correlation (r) and normalized mean bias (nmb) in the model panels are shown in the bottom right corners.

factor to the calculated emissions before they are distributed into the lowest model grid box. MEGAN calculates emissions for many biogenic VOCs, and we only perturb isoprene emissions in our sensitivity experiments since our focus is on the gas-phase chemistry that impacts O_3 production (the rapid gas-phase chemistry with monoterpene and sesquiterpene emissions is not included in this model version, and this is discussed below). The ±50% perturbations represent reasonable and realistic regional-scale end-members given modeled long-term interannual variability in peak summertime emissions (shown below), even if the scale of interannual variability in nationwide biogenic emissions is not this large, for us to linearize the O_3 sensitivity to biogenic precursor variability around each anthropogenic emission scenario. These perturbations are also consistent with anticipated long-term changes in average emissions as a result of climate change (Gonzalez-Abraham et al., 2015).

We use the same meteorology in all our simulations to exclude minor variability in O_3 chemical sensitivity caused by meteorology, since the motivation of our study is to quantify changes in the chemical regimes resulting from emissions specifically. This provides a policy-relevant insight into the changing role of biogenic emissions, without other confounding factors. The choice of meteorological year (2013) is arbitrary. We show in Figure S2 of Supporting Information S1 that natural interannual variability alone has negligible impact on whether O_3 production is VOC- or NOx-sensitive, so that the choice of meteorological year would not impact the results of our study. Given the sensitivity of many relevant processes to ambient temperatures, we also demonstrate in Figure S3 of Supporting Information S1 that the 2013 meteorology used here is representative of long-term mean conditions over most of the regions highlighted in our study.

We also hold anthropogenic VOC emissions constant, which artificially isolates the role of anthropogenic NOx emissions over time. However, the NEI reports a national trend in anthropogenic VOC emissions over the United States of only −7% over the 2005–2018 period (17.753 million tons in 2005 to 16.435 million tons in 2018), so we argue this is a reasonable simplification (US EPA, 2021). It is also likely that the GEOS-Chem inventory does not accurately represent the current understanding of the importance of VOC emissions from consumer and industrial products (e.g., personal care and cleaning products) in urban areas (McDonald, De Gouw, et al., 2018; Qin et al., 2020; Coggona et al., 2021). This represents an important area of model development, but we argue that this potential omission makes our conclusions conservative since additional urban VOC emissions in our simulations could make present-day chemical conditions more NOx-limited than currently captured by the model.

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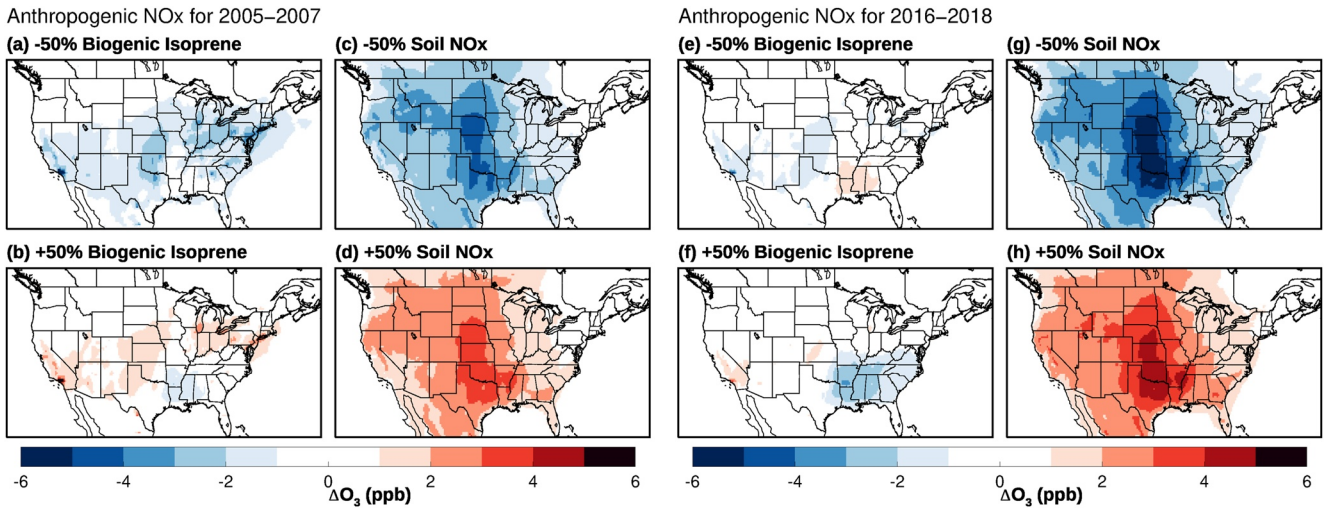

Figure 3. Sensitivity of midday (12–2 p.m. local time) mean June–July–August surface O_3 to perturbations in biogenic isoprene and soil nitrogen oxides (NOx) emissions under high anthropogenic NOx emissions (a–d) and low anthropogenic NOx emissions (e–h).

2.3. Interannual O_3 Tendencies

The impact of biogenic precursor emissions on ambient O_3 will not only depend on local-to-regional O_3 chemical sensitivity (which can be deduced from the sensitivity simulations described above), but also on the magnitude of the temporal variability in soil NOx emissions occurring year-to-year. We propose an approach where the local impact of either biogenic isoprene or soil NOx emissions on interannual variability in O_3 could be expressed as the following sum of partial derivatives:

$$\frac{\mathrm{dc_{O3}}}{\mathrm{dt}} = \frac{\partial \mathrm{c_{O3}}}{\partial E_{\mathrm{isop}}} \frac{\partial E_{\mathrm{isop}}}{\partial t} + \frac{\partial \mathrm{c_{O3}}}{\partial E_{\mathrm{soilNOx}}} \frac{\partial E_{\mathrm{soilNOx}}}{\partial t} + \ldots \quad (3)$$

where $\mathbf{dc_{O3}/dt}$ is the interannual deviation (from some reference year) in local O_3 concentrations, $\boldsymbol{\partial c_{O3}/\partial E}$ is the local O_3 sensitivity to either isoprene or soil NOx, and $\boldsymbol{\partial E/\partial t}$ is the interannual variability in their respective emission rates. Here, we call $\mathbf{dc_{O3}/dt}$ the hypothetical "interannual O_3 tendency," distinguishing it from the true interannual variability resulting from the combination of other non-linear, and often co-varying, factors, including meteorology, background O_3, and non-additive interactions between biogenic isoprene and soil NOx emissions.

This linearization around local chemical conditions is an improvement over simulations that simply turn emissions on or off entirely. By calculating the sensitivity under different anthropogenic NOx emission scenarios, this approach provides a useful framework to demonstrate how either process impacts O_3 in isolation and under varying anthropogenic NOx emission trends. We use the sensitivity of O_3 from our perturbation simulations to estimate the $\boldsymbol{\partial c_{O3}/\partial E_{isop}}$ and $\boldsymbol{\partial c_{O3}/\partial E_{soilNOx}}$ terms for every model grid box. We determine the $\boldsymbol{\partial E_{isop}/\partial t}$ and $\boldsymbol{\partial E_{soilNOx}/\partial t}$ terms using output from a long-term GEOS-Chem simulation driven by structurally identical biogenic emission parameterizations (Geddes & Martin, 2017). The interannual variability in isoprene and soil NOx emissions predicted by GEOS-Chem is consistent with previous model studies and with top-down estimates inferred from satellite observations (Bauwens et al., 2016; Hudman et al., 2010; Palmer et al., 2006; Tawfik et al., 2012). Together, the estimated O_3 sensitivity results ($\boldsymbol{\partial c_{O3}/\partial E_{isop}}$ and $\boldsymbol{\partial c_{O3}/\partial E_{soilNOx}}$) and the interannual variability in emissions ($\boldsymbol{\partial E_{isop}/\partial t}$ and $\boldsymbol{\partial E_{soilNOx}/\partial t}$) allow us to evaluate the interannual O_3 "tendency" ($\mathbf{dc_{O3}/dt}$) resulting from either process in isolation, under the high and low anthropogenic NOx emission scenarios, respectively.

3. Results and Discussion

3.1. O_3 Sensitivity in Nonattainment Areas

Figure 3 shows the sensitivity of simulated mean midday O_3 for June–July–August resulting from a ±50% increase/decrease in isoprene emissions, and a ±50% increase/decrease in soil NOx emissions, under each of the anthropogenic NOx emission scenarios tested. Examples of zoomed detail for the southwest and NEA are

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shown in Figures S4 and S5 of Supporting Information S1. In the high anthropogenic NOx emission scenario, the perturbation to biogenic isoprene emissions had the greatest impacts on mean midday O_3 in urban areas, with some influence on regional O_3 (Figures 3a and 3b; S4 in Supporting Information S1); the effects are largest in Los Angeles, California, where O_3 concentrations change by up to ±9–10 ppb. In most U.S. regions, we find the isoprene response in summertime midday O_3 is fairly linear (i.e., with the positive and negative perturbations having the same magnitude of impact on O_3), except in the southeast where the effects are more non-linear. In the scenario using low anthropogenic NOx emissions, the same ±50% perturbation in biogenic isoprene emissions yielded much smaller impacts as we would expect from increasingly NOx-limited chemistry that results from a reduction in anthropogenic NOx emissions, with O_3 unaffected in most of the urban areas (Figures 3e and 3f; S5 in Supporting Information S1). The largest response in O_3 was again observed in the Los Angeles region, but decreased to ±4–5 ppb, a ∼40%–60% reduction in sensitivity compared to the high anthropogenic emissions scenario. We note that the resolution of our chemistry simulation (0.25° × 0.3125°) could have led us to underestimate the true VOC-limitation within cities, but the observed decrease in isoprene sensitivity suggests at least a portion of urban VOC-limitation has been captured.

Soil NOx emission perturbations lead to changes in O_3 that are more regional. Whereas the isoprene chemical lifetime is as short as 1 hour during summer daytime (assuming OH of 0.1 ppt), the NOx chemical lifetime under the same conditions is typically at least a few hours. In addition, NOx can be temporarily stored in chemical reservoirs such as peroxy nitrates, such that the impacts of soil NOx emissions on O_3 production can occur in areas farther downwind. In the scenario using high anthropogenic NOx emissions (Figures 3c and 3d), the soil NOx perturbation had its greatest impact on mean midday O_3 in Texas, Oklahoma, and areas of the Midwest, where O_3 changes were as high as ±4–5 ppb. These simulations also show a reasonably linear response in summertime midday O_3. In the low anthropogenic NOx emission scenario (Figures 3g and 3h), the sensitivity to soil NOx emissions both amplified and spatially expanded. The largest response in mean midday O_3 still occurred in Texas, Oklahoma, and areas of the Midwest, but increased to ±5–6 ppb (a ∼20%–25% increase in sensitivity) compared to the high anthropogenic NOx emission scenario. We note that soil NOx emissions make up ∼25% of summertime NOx emissions in the US in the "low" anthropogenic NOx emission scenario, such that this 50% perturbation in soil NOx only results in a ∼12.5% change to total NOx emissions.

To visualize the policy-relevant effects of these perturbations, we evaluated their impacts using mean daily maximum 8 hr O_3 (MDM8 O_3) averaged within the 2019 U.S. EPA-designated nonattainment areas, based on the 8 hr O_3 2015 National Ambient Air Quality Standard of 70 ppb (shown in Figure 4a). Nonattainment areas are located predominantly in California on the west coast, the Washington-New York corridor of the NEA, and urban centers of the Great Lakes and Ohio River (GLO) valley, along with several other individual urban areas across the central, south, and southeast parts of the country. We group the nonattainment areas into regions with broadly similar biogenic precursor emissions profiles and climatic conditions: Southwest (SWE); Central (CEN); South and Southeast (SSE); GLO; and NEA.

In Figure 4, the solid lines represent the MDM8 O_3-sensitivity calculated from the high anthropogenic NOx emission scenario, while the dashed lines represent the sensitivity calculated based on the low anthropogenic NOx emissions. In the high anthropogenic NOx scenario, biogenic isoprene perturbations affected O_3 in all nonattainment areas, consistent with expectations that O_3-polluted areas have been strongly VOC-limited in the past. Calculated on a population-weighted scale nationwide, O_3 in nonattainment areas varied by [+2.2, −3.1 ppb] in response to ±50% perturbations in biogenic isoprene emissions, compared to [+1.1, −1.3 ppb] from the ±50% perturbations in soil NOx emissions. Nonattainment areas in the Southwest, GLO, and NEA regions, which together account for 78% of the U.S. population that is living in nonattainment, were the most isoprene sensitive. Therefore, despite the wider area impacts from the soil NOx perturbations, changes in biogenic isoprene had greater impacts on O_3 where most people live, under the anthropogenic NOx emissions consistent with ∼2005–2007 levels.

In contrast, MDM8 O_3 in all nonattainment areas became more sensitive to the soil NOx perturbations than the biogenic isoprene perturbations under the low anthropogenic NOx emission scenario (Figure 4, dashed lines). Calculated on a population-weighted scale nationwide, O_3 in nonattainment areas varied by [+1.7, −2.0 ppb] in response to ±50% perturbations in soil NOx emissions, compared to [+0.7, −1.5 ppb] from the ±50% perturbation in biogenic isoprene emissions. In the nonattainment areas of the NEA (Figure 4f) for example, *a* ±50% perturbation in biogenic isoprene affected MDM8 O_3 there by [+2.2, −3.3] ppb under high anthropogenic NOx

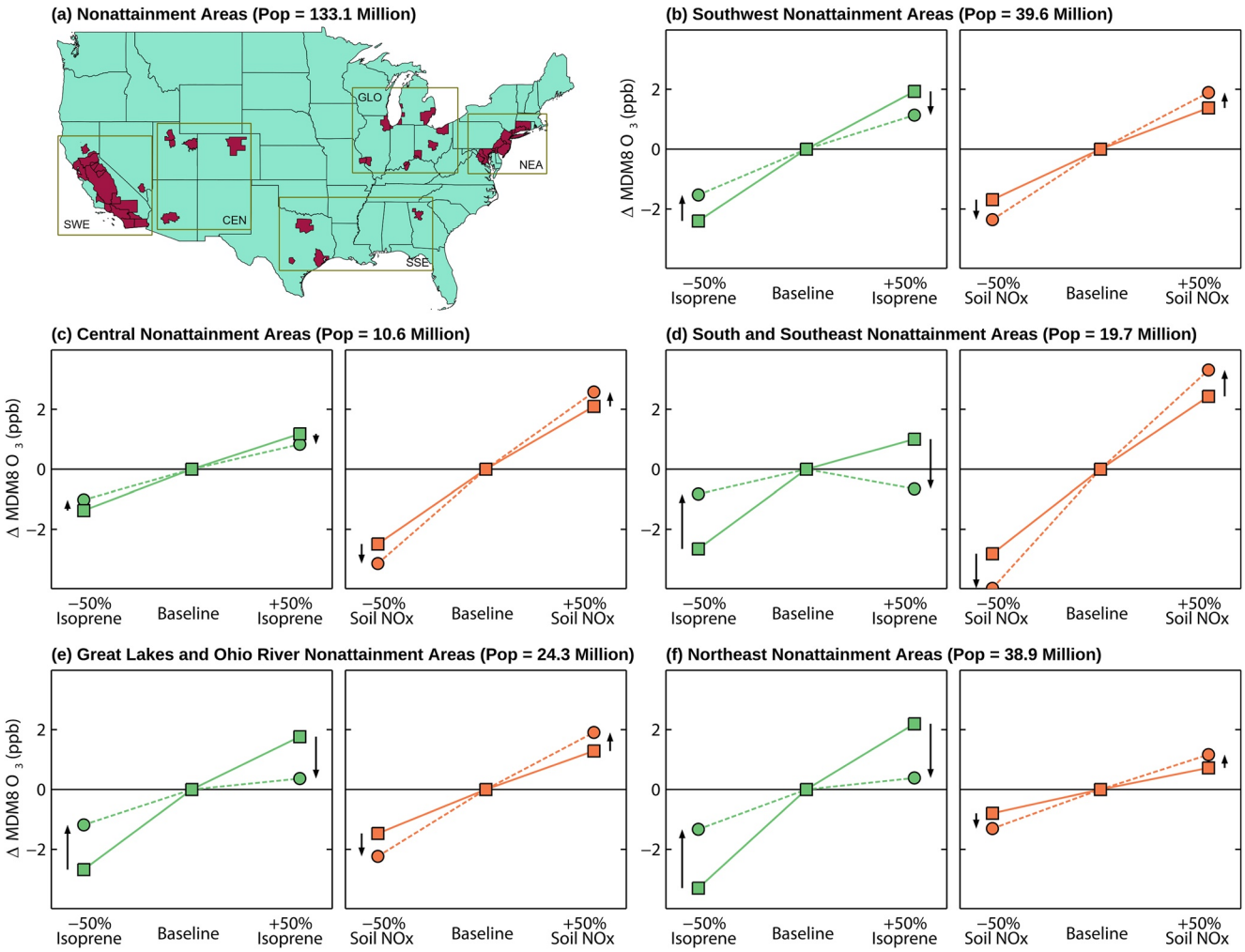

Figure 4. Sensitivity of area averaged MD8A O_3 in U.S. nonattainment areas. (a) Map of nonattainment areas (maroon) separated by regions (rectangles). (b–f) Sensitivity of MDM8 O_3 averaged over the nonattainment areas by region, under ±50% perturbations to biogenic isoprene or soil nitrogen oxides (NOx) emissions. Solid lines indicate sensitivity using an estimate of anthropogenic NOx emissions for 2005–2007, dashed lines indicate sensitivity using an estimate anthropogenic NOx emissions for 2016–2018 (a 50% reduction). Arrows guide the reader from the high to low NOx anthropogenic emission scenarios.

emissions, but that sensitivity decreased by 75% to [+0.4, −1.3] ppb at low anthropogenic NOx emissions. Meanwhile, O_3 sensitivity from the ±50% perturbation in soil NOx emissions in the nonattainment areas of this region increased from [+0.7, −0.8] to [+1.2, −1.3] under high and low anthropogenic NOx emissions, respectively.

In SSE nonattainment areas, the sensitivity of MDM8 O_3 to the ±50% biogenic isoprene perturbations switched signs between the two anthropogenic emission scenarios, varying from [+1.0, −2.7] ppb under high anthropogenic NOx emissions to [−0.7, −0.8] ppb at low anthropogenic NOx emissions. Meanwhile, O_3 sensitivity from the ±50% perturbation in soil NOx emissions in the nonattainment areas of this region increased from [+2.4, −2.8] to [+3.3, −4.0] under high and low anthropogenic NOx emissions, respectively. Therefore, despite the conventional expectation of VOC-limitation in urban areas, biogenic soil NOx has greater impacts on O_3 where most people live, under anthropogenic NOx emissions consistent with ~2018 levels.

We note that the 50% reduction in anthropogenic NOx emissions alone results in a 6 ppb decrease in population weighted mean MDM8 O_3 across the nonattainment areas nationwide in our simulations (compared to ~2 ppb decreases in population weighted mean MDM8 O_3 from the 50% reduction in soil NOx or biogenic isoprene), demonstrating the principal role that steady declines in anthropogenic NOx emissions has had overall on O_3 air quality in the United States.

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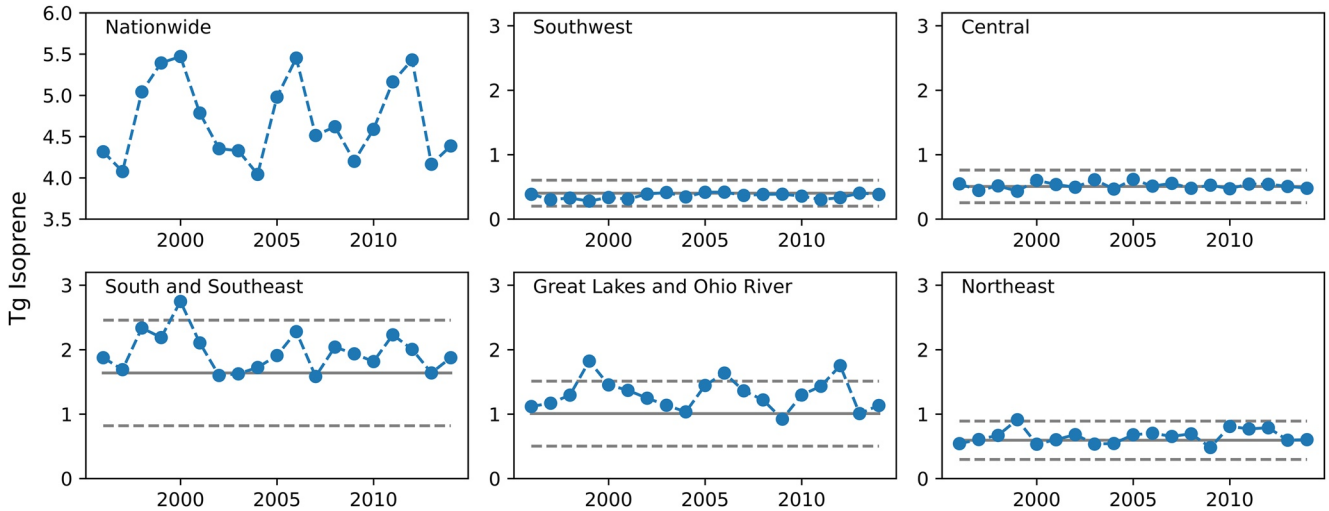

Figure 5. Interannual variability in July biogenic isoprene emissions nationwide, and for each of the individual regions highlighted in rectangles in Figure 4. The gray solid line denotes the year 2013 emissions (which are our baseline), and the dashed lines denote the ± 50% envelope used in the perturbation experiments.

3.2. Interannual Tendencies of O_3 in Nonattainment Areas

As described in the methods, the impact of biogenic precursor emissions on observed O_3 will not only depend on local-to-regional O_3 chemical sensitivity (which can be deduced from the experiments described above), but also on the magnitude of the temporal variability in soil NOx emissions occurring year-to-year. Here, we use the interannual variability in soil NOx and biogenic isoprene emissions calculated from a long-term GEOS-Chem simulation (Geddes & Martin, 2017) whose biogenic emissions are structurally identical to the nested model setup used here. July isoprene emissions over the United States in this model are on average 4.7 ± 0.5, ranging from as low as 4.0 Tg (in 2004) to as high as 5.5 Tg (in 2000), a difference of almost 40% relative to the minimum (or ± 15% relative to the long-term mean). The scale of interannual variability is consistent with the scale of interannual variability in previous MEGAN model studies (Tawfik et al., 2012) and inferred from top-down estimates based on satellite-observed formaldehyde (an atmospheric oxidation product of isoprene) (Bauwens et al., 2016; Palmer et al., 2006). July soil NOx emissions in this model are on average 0.15 Tg ± 0.02, and range from as low as 0.11 Tg (in 1997) to 0.20 Tg (in 2012), a difference of 82% relative to the minimum (or ± ~30% relative to the long-term national mean). These results are consistent with estimates of variability derived from satellite observations (Hudman et al., 2010).

Figures 5 and 6 show the timeseries of nationwide and regional biogenic isoprene and soil NOx emissions for the month of July as predicted by the model. We find that our choice of ±50% relative to our baseline 2013 conditions allows us to reasonably capture natural variability that does occur the regional scale. It is of course difficult to come up with a perturbation experiment that will be exactly representative of contemporary interannual variability in the emissions everywhere: in some cases, only the response in one direction (e.g., +50%, or −50%) is important; in other cases, this envelope can underestimate of the local variability (e.g., soil NOx variability in the SSE, and in the GLO regions). We are most interested in interpolating the response of O_3 between these two end members to estimate the O_3 response to natural interannual variability (Section 3.2), so the exact choice is less important that being able to fairly interpolate between the end members.

Using Equation 3 to linearize O_3 sensitivity around local chemical conditions, we calculate the interannual July mean O_3 tendencies driven by either soil NOx or biogenic isoprene emission variability from year to year under the "high" (2005–2007) and "low" (2016–2018) anthropogenic NOx emissions. To visualize the relative importance of biogenic isoprene and soil NOx emissions in the July mean interannual O_3 tendencies, we define a normalized difference index as:

$$\frac{\sigma_{\text{soil NOx}} - \sigma_{\text{isoprene}}}{\sigma_{\text{soil NOx}} + \sigma_{\text{isoprene}}}$$

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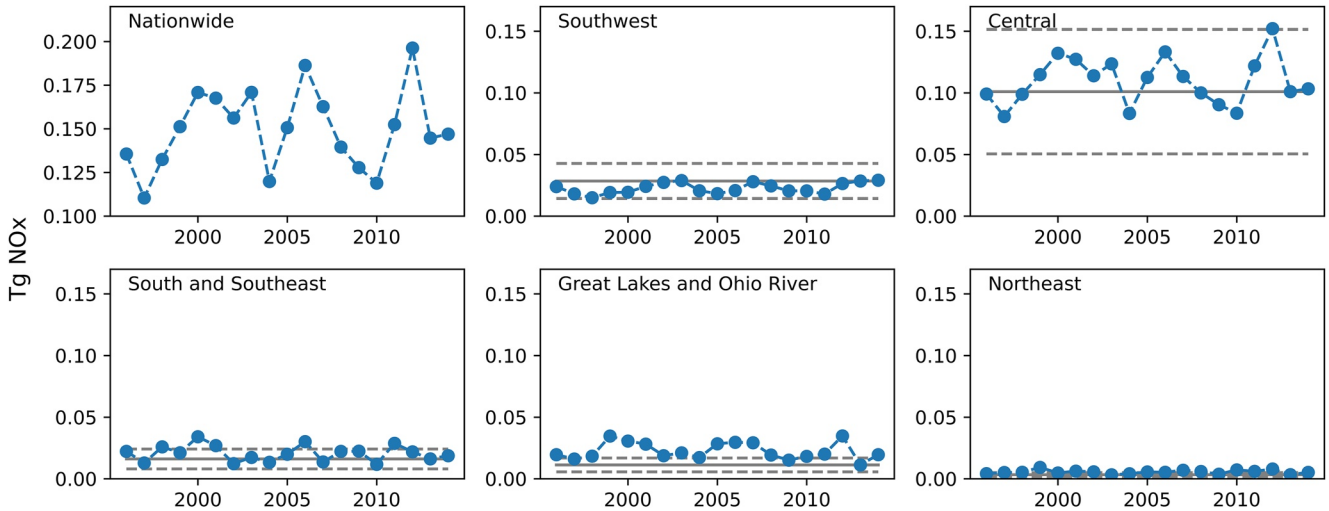

Figure 6. Interannual variability in July soil nitrogen oxides (NOx) emissions nationwide, and for each of the individual regions highlighted in rectangles in Figure 4. The gray solid line denotes the year 2013 emissions (which are our baseline), and the dashed lines denote the ± 50% envelope used in the perturbation experiments.

where $\boldsymbol{\sigma}_{\text{soil NOx}}$ is the standard deviation in the interannual tendencies of O_3 from soil NOx variability, and $\boldsymbol{\sigma}_{\text{isoprene}}$ is the standard deviation in the interannual tendencies of O_3 from soil NOx variability. Given this definition, a value of +1 indicates that soil NOx emissions dominate the standard deviation of the interannual tendencies while a value of −1 indicates that biogenic isoprene emissions dominate. Values closer to 0 mean that each are equally important in the interannual O_3 tendencies.

Figure 7 maps the normalized difference index under each hypothetical NOx emission scenario. We find that biogenic isoprene drives the interannual tendencies in several of the most populated nonattainment areas under the high anthropogenic NOx emission scenario, but that soil NOx drives the interannual tendencies in all nonattainment areas in the low anthropogenic NOx emission scenario, with some exceptions in California. In Figures 7c–7e, we present the distribution of interannual O_3 tendencies from three specific nonattainment locations: Los Angeles (Southwest), Dallas (Central), and Philadelphia (NEA). In all three examples, the role of biogenic isoprene emissions on July-mean interannual O_3 tendencies diminishes with the reduction in anthropogenic NOx emissions, while the contribution from soil NOx emissions increases. In Los Angeles, the dominance of variability in biogenic isoprene over soil NOx persists in both scenarios. In Dallas, which is representative of the nonattainment areas of the SSE region, soil NOx is more important than biogenic isoprene in the interannual O_3 tendencies under both scenarios. Finally, in Philadelphia, which is representative of nonattainment areas in the NEA region, the importance of biogenic isoprene versus soil NOx on interannual O_3 tendencies switches such that soil NOx now dominates low anthropogenic NOx scenario. This shift from isoprene-dominant interannual O_3 tendencies to soil-NOx dominated interannual O_3 tendencies throughout the nonattainment areas of the Great Lakes, Ohio River, and NEA regions (Figure 5a) is noteworthy. In these parts of the country where chemistry had traditionally been VOC limited and sensitive to interannual variability in biogenic isoprene, we expect interannual variability in soil NOx to become more important.

While idealized, these "O_3 tendencies" demonstrate how, given the observed reductions in anthropogenic NOx emissions, we can expect the importance of biogenic isoprene on O_3 interannual variability to decrease in many nonattainment regions across the country if anthropogenic NOx reductions continue. At the same time, the O_3 tendencies suggest O_3 interannual variability in nonattainment areas will be increasingly sensitive to soil NOx emissions variability. We note that the reduction in anthropogenic NOx in our simulations had a larger overall impact on O_3 than the interannual variability inferred from these biogenic precursors, demonstrating the more important role that steady declines in anthropogenic NOx have had on O_3 over the long term. But this analysis shows that these precursors are, and will continue to be, important to interannual variability in ways that are changing in response to the anthropogenic emission declines. In the model grid box over Philadelphia, for example, soil NOx emissions comprise ∼11% of the local NOx emissions in July (using anthropogenic NOx emissions consistent with 2016–2018). The variability in total NOx emissions here due to the interannual variability in soil

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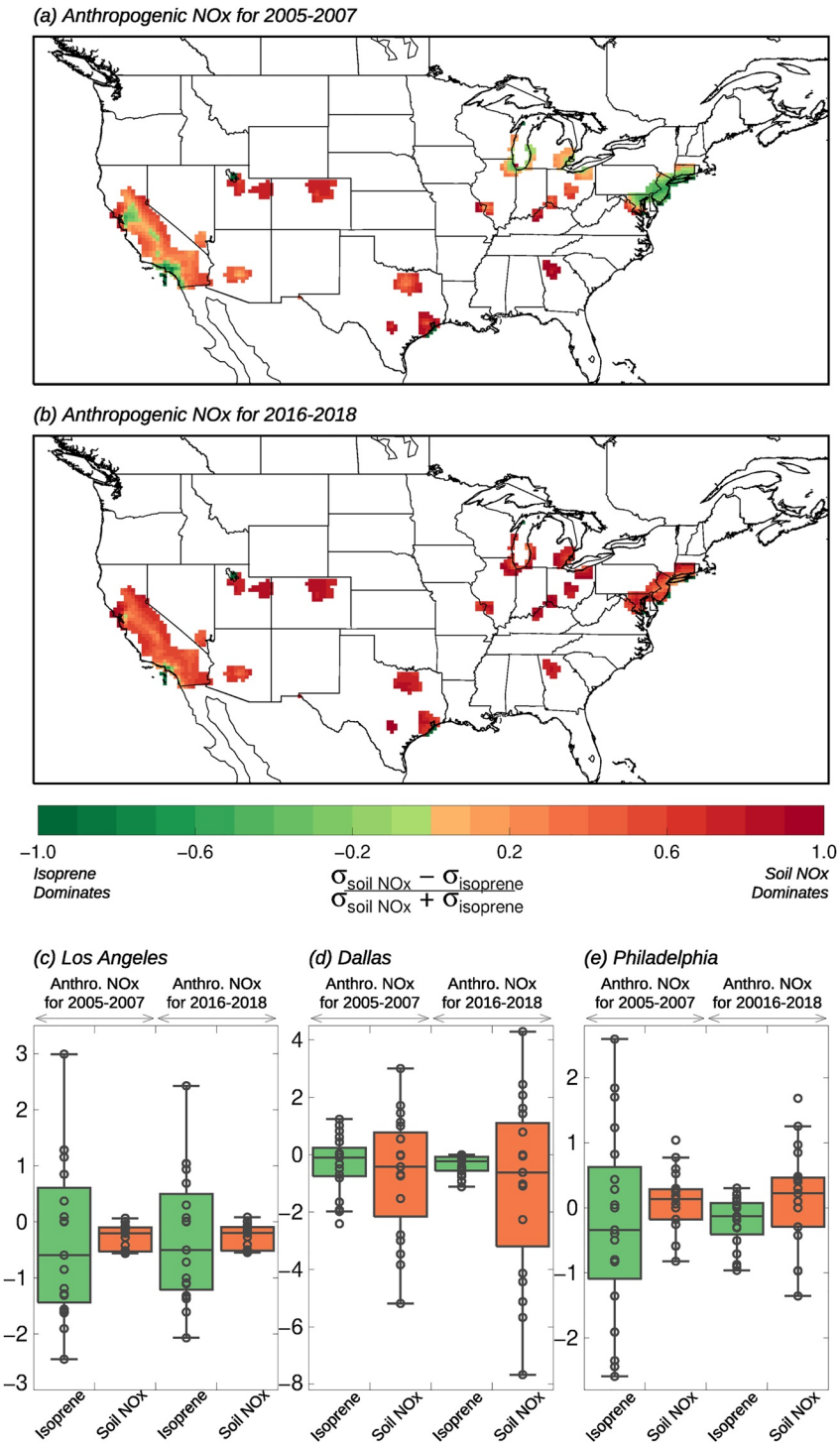

Figure 7. (a and b) Increasing importance of soil nitrogen oxides (NOx) processes on O_3 interannual tendencies across nonattainment areas of the United States using a normalized difference index (where σ is the standard deviation in interannual tendencies); and (c–e) the distribution of interannual July mean O_3 tendencies due to interannual variability in biogenic isoprene and soil NOx emissions for three specific nonattainment grid boxes, assuming O_3 sensitivity using high (~2005–2007) anthropogenic NOx emissions (green bars) versus O_3 sensitivity using low (~2016–2018) anthropogenic NOx emissions (orange bars).

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NOx emissions is therefore quite small locally, with interquartile range of [1%, 4%] relative to 2013; still, these perturbations cause a change in mean July O_3 relative to 2013 with an interquartile range of [0.29 ppb, 0.48 ppb], Figure 5f).

Our model experiments are also relevant to understanding an "O_3-climate penalty" (where the impact of emission controls on O_3 concentrations can be offset due to increasing environmental temperatures). The magnitude and mechanisms behind a climate penalty are sensitive to the local chemical environment, and thus to changes in anthropogenic emissions over time (Bloomer et al., 2009; Rasmussen et al., 2013). The results of our perturbation studies shed light on the specific role individual biogenic emissions can play in the O_3-climate penalty over non-attainment areas in the U.S., and how these roles evolve with changes in anthropogenic emissions. In the Philadelphia region for example, the interannual O_3 tendencies due to isoprene correlate strongly with temperature in both scenarios (from $r = 0.97$ to $r = 0.91$), but the interannual tendencies from soil NOx (which are also strongly correlated with temperature at that location, $r = 0.76$) dominate when anthropogenic NOx emissions are reduced, so that the absolute role of an isoprene-temperature correlation is less important.

Additional factors will contribute to the true O_3 variability depending on location, including meteorology, and chemistry; but we interpret these results to mean that soil NOx emissions will become an increasingly important control on high-O_3 days in many U.S. nonattainment areas. Environmental and land management factors play a role in the timing and magnitude of soil NOx emissions (Pilegaard, 2013; Stehfest & Bouwman, 2006; Steinkamp & Lawrence, 2011) in ways that differ from our understanding of the timing and magnitude of isoprene emissions. The dependence of soil NOx emissions on nitrogen availability (including fertilizer application), soil water content (including precipitation timing and the preceding dry spell length), and soil pH could introduce new sub-seasonal and/or episodic patterns in high O_3 that may not have historically been considered in nonattainment areas where chemistry has for a long time been VOC-limited. Agricultural land that is actively managed by humans contributes a disproportionate fraction of soil NOx emitted in the United States (Almaraz et al., 2018; Davidson et al., 1998). In our GEOS-Chem simulation, almost 40% of total soil NOx emissions in the United States occur over cropland or mixed cropland/natural vegetation mosaic, with 30% of total soil NOx emissions associated with fertilizer application. Almaraz et al. (2018) outline several approaches that could potentially be used to reduce soil NOx emissions from fertilized croplands (e.g., slow-release fertilizers, precision agriculture, and cover crops), and our results here provide further motivation to explore these strategies.

We note that our results also imply the importance of constraining our estimates of biogenic isoprene and soil NOx emissions. Several methods exist for predicting both biogenic isoprene and soil NOx emissions, and some aspects of our inferred O_3 sensitivity may be specific to the parameterizations used (Carlton & Baker, 2011; Hogrefe et al., 2011; Kim et al., 2017; Rasool et al., 2019). While uncertainties in biogenic isoprene emissions may be of decreasing importance as they relate to interannual O_3 nonattainment in the United States, it is becoming increasingly important to reduce uncertainties in soil NOx variability. Further constraints on the variability of soil NOx emissions, such as those informed by satellite-based observations (Hudman et al., 2010; Vinken et al., 2014), will be valuable. Sha et al. (2021) and Wang et al. (2021) recently showed that a revised version of the soil NOx parameterization scheme (mainly, an updated temperature response) tends to agree better with satellite observations of NO_2 over rural areas of the United States. More detail may be gathered from next-generation satellites that have improved spatial and temporal resolution.

Advancing our mechanistic understanding of NOx uptake by vegetation canopies (Delaria & Cohen, 2019) and within-canopy nitrogen chemistry (Min et al., 2014), improving our understanding of microbial controls over soil NOx emissions from natural landscapes including forests (Mushinski et al., 2019), and quantifying soil NOx emissions from baer or vegetated urban ground where atmospheric nitrogen inputs are particularly high (Decina et al., 2017; Rao et al., 2014) may be critical. Continued progress in representing isoprene chemistry (Bates & Jacob, 2019), as well as including other biogenic VOC gas-phase chemistry mechanisms (Fisher et al., 2016; Porter et al., 2017), is also important as O_3 sensitivity could be influenced by the choice of chemical mechanism (Dunker et al., 2016; Squier et al., 2014), though our results are spatially consistent with an earlier GEOS-Chem sensitivity experiment (Mao et al., 2013). Finally, this work highlights the importance of adopting accurate, up-to-date, and high resolution land cover maps in chemical transport simulations, with timely information about agricultural land management (Rasool et al., 2019). Despite the aspects of model development described above that would contribute to efficient O_3 policies going forward, our results provide a reasonable range of impact and highlight the emerging influence of soil NOx emissions on O_3 in U.S. nonattainment areas.

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4. Conclusions

U.S. urban areas are shifting to increasingly NOx-limited O_3 production, and we will therefore encounter greater O_3 sensitivity to interannual variability in soil NOx. In this study, we quantify this changing sensitivity by comparing the importance of biogenic precursors in a chemical transport model at high and low anthropogenic NOx emissions representative of declines observed in recent decades. Biogenic isoprene emissions are usually considered beyond regulatory control, so the finding that they are becoming less influential on surface O_3 variability in nonattainment areas is useful for air quality management. On the other hand, there is growing importance of soil NOx emissions on O_3 chemistry in nonattainment areas that is as large as isoprene effects 15 years ago, both by area-averaged and population-weighted metrics.

Understanding how soil NOx emissions will increasingly contribute to high O_3 episodes, in addition to season-long interannual variability, may be required in designing effective strategies for reducing the number of bad O_3 air quality days in the future. While our experiment focuses on the traditional summer O_3 season, O_3 soil NOx-sensitivity could have implications for the seasonal O_3 cycle and the timing of O_3 extremes within seasons, potentially varying with agricultural phenology, land management, and precipitation or soil wetness, which will be the subject of future work.

Data Availability Statement

The GEOS-Chem model output used in this study is freely accessible via the OpenBU Research Data repository (https://open.bu.edu/handle/2144/44806). This repository provides open access and long-term digital preservation of all data.

Acknowledgments
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References

Almaraz, M., Bai, E., Wang, C., Trousdell, J., Conley, S., Faloona, I., & Houlton, B. Z. (2018). Agriculture is a major source of NOx pollution in California. *Science Advances*, *4*(1), eaao3477. https://doi.org/10.1126/sciadv.aao3477

Anderson, D. C., Loughner, C. P., Diskin, G., Weinheimer, A., Canty, T. Y. P., Salawitch, R. J., et al. (2014). Measured and modeled CO and NOy in DISCOVER-AQ: An evaluation of emissions and chemistry over the eastern US. *Atmospheric Environment*, *96*, 78–87. https://doi.org/10.1016/j.atmosenv.2014.07.004

Baidar, S., Hardesty, R. M., Kim, S. W., Langford, A. O., Oetjen, H., Senff, C. J., et al. (2015). Weakening of the weekend ozone effect over California's South Coast air basin. *Geophysical Research Letters*, *42*(21), 9457–9464. https://doi.org/10.1002/2015GL066419

Bates, K. H., & Jacob, D. J. (2019). A new model mechanism for atmospheric oxidation of isoprene: Global effects on oxidants, nitrogen oxides, organic products, and secondary organic aerosol. *Atmospheric Chemistry and Physics*, *19*(14), 9613–9640. https://doi.org/10.5194/acp-19-9613-2019

Bauwens, M., Stavrakou, T., Müller, J.-F., De Smedt, I., Van Roozendael, M., van der Werf, G. R., et al. (2016). Nine years of global hydrocarbon emissions based on source inversion of OMI formaldehyde observations. *Atmospheric Chemistry and Physics*, *16*(15), 10133–10158. https://doi.org/10.5194/acp-16-10133-2016

Bell, M., & Ellis, H. (2004). Sensitivity analysis of tropospheric ozone to modified biogenic emissions for the Mid-Atlantic region. *Atmospheric Environment*, *38*(13), 1879–1889. https://doi.org/10.1016/j.atmosenv.2004.01.012

Blanchard, C. L., & Hidy, G. M. (2018). Ozone response to emission reductions in the southeastern United States. *Atmospheric Chemistry and Physics*, *18*(11), 8183–8202. https://doi.org/10.5194/acp-18-8183-2018

Bloomer, B. J., Stehr, J. W., Piety, C. A., Salawitch, R. J., & Dickerson, R. R. (2009). Observed relationships of ozone air pollution with temperature and emissions. *Geophysical Research Letters*, *36*(9), L09803. https://doi.org/10.1029/2009GL037308

Carlton, A. G., & Baker, K. R. (2011). Photochemical modeling of the Ozark isoprene volcano: MEGAN, BEIS, and their impacts on air quality predictions. *Environmental Science & Technology*, *45*(10), 4438–4445. https://doi.org/10.1021/es200050x

Chameides, W., Lindsay, R., Richardson, J., & Kiang, C. (1988). The role of biogenic hydrocarbons in urban photochemical smog: Atlanta as a case study. *Science*, *241*(4872), 1473–1475. https://doi.org/10.1126/science.3420404

Coggona, M. M., Gkatzelis, G. I., McDonald, B. C., Gilman, J. B., Schwantes, R. H., Abuhassan, N., et al. (2021). Volatile chemical product emissions enhance ozone and modulate urban chemistry. *Proceedings of the National Academy of Sciences of the United States of America*, *118*(32). https://doi.org/10.1073/pnas.2026653118

Curci, G., Beekmann, M., Vautard, R., Smiatek, G., Steinbrecher, R., Theloke, J., & Friedrich, R. (2009). Modelling study of the impact of isoprene and terpene biogenic emissions on European ozone levels. *Atmospheric Environment*, *43*(Issue 7), 1444–1455. https://doi.org/10.1016/j.atmosenv.2008.02.070

Davidson, E. A., Potter, C. S., Schlesinger, P., & Klooster, S. A. (1998). Model estimates of regional nitric oxide emissions from soils of the southeastern United States. *Ecological Applications*, *8*(3), 748–759. https://doi.org/10.1890/1051-0761(1998)008[0748:MEORNO]2.0.CO;2

Decina, S. M., Templer, P. H., Hutyra, L. R., Gately, C. K., & Rao, P. (2017). Variability, drivers, and effects of atmospheric nitrogen inputs across an urban area: Emerging patterns among human activities, the atmosphere, and soils. *The Science of the Total Environment*, *609*, 1524–1534. https://doi.org/10.1016/j.scitotenv.2017.07.166

Delaria, E. R., & Cohen, R. C. (2019). A model-based analysis of foliar NO_x deposition. *Atmospheric Chemistry and Physics Discussions*, 1–33. https://doi.org/10.5194/acp-2019-538

Demetillo, M. A. G., Anderson, J. F., Geddes, J. A., Yang, X., Najacht, E. Y., Herrera, S. A., et al. (2019). Observing severe drought influences on ozone air pollution in California. *Environmental Science and Technology*, *53*(9), 4695–4706. https://doi.org/10.1021/acs.est.8b04852

Duncan, B. N., Lamsal, L. N., Thompson, A. M., Yoshida, Y., Lu, Z., Streets, D. G., et al. (2016). A space-based, high-resolution view of notable changes in urban NOx pollution around the world (2005-2014). *Journal of Geophysical Research: Atmospheres*, *121*, 976–996. https://doi.org/10.1002/2015JD024121

Dunker, A. M., Koo, B., & Yarwood, G. (2016). Ozone sensitivity to isoprene chemistry and emissions and anthropogenic emissions in central California. *Atmospheric Environment*, *145*, 326–337. https://doi.org/10.1016/j.atmosenv.2016.09.048

Fiore, A. M., Oberman, J. T., Lin, M. Y., Zhang, L., Clifton, O. E., Jacob, D. J., et al. (2014). Estimating North American background ozone in U.S. surface air with two independent global models: Variability, uncertainties, and recommendations. *Atmospheric Environment*, *96*, 284–300. https://doi.org/10.1016/j.atmosenv.2014.07.045

Fisher, J. A., Jacob, D. J., Travis, K. R., Kim, P. S., Marais, E. A., Chan Miller, C., et al. (2016). Organic nitrate chemistry and its implications for nitrogen budgets in an isoprene- and monoterpene-rich atmosphere: Constraints from aircraft (SEAC4RS) and ground-based (SOAS) observations in the Southeast US. *Atmospheric Chemistry and Physics*, *16*(9), 5969–5991. https://doi.org/10.5194/acp-16-5969-2016

Geddes, J. A., & Martin, R. V. (2017). Global deposition of total reactive nitrogen oxides from 1996 to 2014 constrained with satellite observations of NO2 columns. *Atmospheric Chemistry and Physics*, *17*(16), 10071–10091. https://doi.org/10.5194/acp-17-10071-2017

Gonzalez-Abraham, R., Chung, S. H., Avise, J., Lamb, B., Salathé, E. P., Nolte, C. G., et al. (2015). The effects of global change upon United States air quality. *Atmospheric Chemistry and Physics*, *15*(21), 12645–12665. https://doi.org/10.5194/acp-15-12645-2015

Guenther, A. B., Jiang, X., Heald, C. L., Sakulyanontvittaya, T., Duhl, T., Emmons, L. K., & Wang, X. (2012). The model of emissions of gases and aerosols from nature version 2.1 (MEGAN2.1): An extended and updated framework for modeling biogenic emissions. *Geoscientific Model Development*, *5*(6), 1471–1492. https://doi.org/10.5194/gmd-5-1471-2012

Guo, J. J., Fiore, A. M., Murray, L. T., Jaffe, D. A., Schnell, J. L., Moore, C. T., & Milly, G. P. (2018). Average versus high surface ozone levels over the Continental USA: Model bias, background influences, and interannual variability. *Atmospheric Chemistry and Physics*, *18*(16), 12123–12140. https://doi.org/10.5194/acp-18-12123-2018

Hakami, A., Seinfeld, J. H., Chai, T., Tang, Y., Carmichael, G. R., & Sandu, A. (2006). Adjoint sensitivity analysis of ozone nonattainment over the Continental United States. *Environmental Science & Technology*, *40*(12), 3855–3864. https://doi.org/10.1021/es052135g

He, H., Liang, X.-Z., Sun, C., Tao, Z., & Tong, D. Q. (2019). The long-term trend and production sensitivity change of the U.S. ozone pollution from observations and model simulations. *Atmospheric Chemistry and Physics Discussions*, 1–37. https://doi.org/10.5194/acp-2019-601

Hidy, G. M., & Blanchard, C. L. (2015). Precursor reductions and ground-level ozone in the Continental United States. *Journal of the Air and Waste Management Association*, *65*(10), 1261–1282. https://doi.org/10.1080/10962247.2015.1079564

Hogrefe, C., Isukapalli, S. S., Tang, X., Georgopoulos, P. G., He, S., Zalewsky, E. E., et al. (2011). Impact of biogenic emission uncertainties on the simulated response of ozone and fine particulate matter to anthropogenic emission reductions. *Journal of the Air & Waste Management Association*, *61*(1), 92–108. https://doi.org/10.3155/1047-3289.61.1.92

Holmes, C. D., Prather, M. J., & Vinken, G. C. M. (2014). The climate impact of ship NOx emissions: An improved estimate accounting for plume chemistry. *Atmospheric Chemistry and Physics*, *14*(13), 6801–6812. https://doi.org/10.5194/acp-14-6801-2014

Hu, L., Millet, D. B., Baasandorj, M., Griffis, T. J., Turner, P., Helmig, D., et al. (2015). Isoprene emissions and impacts over an ecological transition region in the U.S. Upper Midwest inferred from tall tower measurements. *Journal of Geophysical Research: Atmospheres*, *120*, 3553–3571. https://doi.org/10.1002/2014JD022732

Hudman, R. C., Moore, N. E., Mebust, A. K., Martin, R. V., Russell, A. R., Valin, L. C., & Cohen, R. C. (2012). Steps towards a mechanistic model of global soil nitric oxide emissions: Implementation and space based-constraints. *Atmospheric Chemistry and Physics*, *12*(16), 7779–7795. https://doi.org/10.5194/acp-12-7779-2012

Hudman, R. C., Russell, A. R., Valin, L. C., & Cohen, R. C. (2010). Interannual variability in soil nitric oxide emissions over the United States as viewed from space. *Atmospheric Chemistry and Physics*, *10*(20), 9943–9952. https://doi.org/10.5194/acp-10-9943-2010

Jaffe, D. A., Cooper, O. R., Fiore, A. M., Henderson, B. H., Tonnesen, G. S., Russell, A. G., et al. (2018). *Scientific assessment of background ozone over the U.S.: Implications for air quality management*. Elementa. University of California Press. https://doi.org/10.1525/elementa.309

Jin, X., Fiore, A. M., Murray, L. T., Valin, L. C., Lamsal, L. N., Duncan, B., et al. (2017). Evaluating a space-based indicator of surface ozone-NOx-VOC sensitivity over midlatitude source regions and application to decadal trends. *Journal of Geophysical Research: Atmospheres*, *122*, 10439–10461. https://doi.org/10.1002/2017JD026720

Kim, E., Kim, B. U., Kim, H. C., & Kim, S. (2017). The variability of ozone sensitivity to anthropogenic emissions with biogenic emissions modeled by MEGAN and BEIS. *Atmosphere*, *8*(10), 187. https://doi.org/10.3390/atmos8100187

Kleinman, L. I., Daum, P. H., Lee, Y.-N., Nunnermacker, L. J., Springston, S. R., Weinstein-Lloyd, J., & Rudolph, J. (2005). A comparative study of ozone production in five U.S. metropolitan areas. *Journal of Geophysical Research*, *110*, D02301. https://doi.org/10.1029/2004JD005096

Lam, Y. F., Fu, J. S., Wu, S., & Mickley, L. J. (2011). Impacts of future climate change and effects of biogenic emissions on surface ozone and particulate matter concentrations in the United States. *Atmospheric Chemistry and Physics*, *11*(10), 4789–4806. https://doi.org/10.5194/acp-11-4789-2011

Li, G., Zhang, R., Fan, J., & Tie, X. (2007). Impacts of biogenic emissions on photochemical ozone production in Houston, Texas. *Journal of Geophysical Research*, *112*, D10309. https://doi.org/10.1029/2006JD007924

Lin, J. T., Patten, K. O., Hayhoe, K., Liang, X. Z., & Wuebbles, D. J. (2008). Effects of future climate and biogenic emissions changes on surface ozone over the United States and China. *Journal of Applied Meteorology and Climatology*, *47*(7), 1888–1909. https://doi.org/10.1175/2007JAMC1681.1

Lin, M., Horowitz, L. W., Payton, R., Fiore, A. M., & Tonnesen, G. (2017). US surface ozone trends and extremes from 1980 to 2014: Quantifying the roles of rising Asian emissions, domestic controls, wildfires, and climate. *Atmospheric Chemistry and Physics*, *17*(4), 2943–2970. https://doi.org/10.5194/acp-17-2943-2017

Lu, X., Zhang, L., & Shen, L. (2019). *Meteorology and climate influences on tropospheric ozone: A review of natural sources, chemistry, and transport patterns. Current pollution reports*. Springer. https://doi.org/10.1007/s40726-019-00118-3

Mao, J., Paulot, F., Jacob, D. J., Cohen, R. C., Crounse, J. D., Wennberg, P. O., et al. (2013). Ozone and organic nitrates over the eastern United States: Sensitivity to isoprene chemistry. *Journal of Geophysical Research: Atmospheres*, *118*, 11256–11268. https://doi.org/10.1002/jgrd.50817

McDonald, B. C., McKeen, S. A., Cui, Y. Y., Ahmadov, R., Kim, S.-W., Frost, G. J., et al. (2018). Modeling ozone in the eastern U.S. using a fuel-based mobile source emissions inventory. *Environmental Science & Technology*, *52*(13), 7360–7370. https://doi.org/10.1021/acs.est.8b00778

McDonald, B. C., De Gouw, J. A., Gilman, J. B., Jathar, S. H., Akherati, A., Cappa, C. D., et al. (2018). Volatile chemical products emerging as largest petrochemical source of urban organic emissions. *Science*, *359*(6377), 760–764.

21698996, 2022, 13, Downloaded from https://agupubs.onlinelibrary.wiley.com/doi/10.1029/2021JD036361, Wiley Online Library on [27/04/2023]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

Min, K.-E., Pusede, S. E., Browne, E. C., LaFranchi, B. W., & Cohen, R. C. (2014). Eddy covariance fluxes and vertical concentration gradient measurements of NO and NO2 over a ponderosa pine ecosystem: Observational evidence for within-canopy chemical removal of NOx. *Atmospheric Chemistry and Physics*, *14*(11), 5495–5512. https://doi.org/10.5194/acp-14-5495-2014

Murray, L. T., Jacob, D. J., Logan, J. A., Hudman, R. C., & Koshak, W. J. (2012). Optimized regional and interannual variability of lightning in a global chemical transport model constrained by LIS/OTD satellite data. *Journal of Geophysical Research*, *117*, D20307. https://doi.org/10.1029/2012jd017934

Mushinski, R. M., Phillips, R. P., Payne, Z. C., Abney, R. B., Jo, I., Fei, S., et al. (2019). Microbial mechanisms and ecosystem flux estimation for aerobic NO_y emissions from deciduous forest soils. *Proceedings of the National Academy of Sciences of the United States of America*, *116*(6), 2138–2145. https://doi.org/10.1073/pnas.1814632116

Myneni, R. B., Yang, W., Nemani, R. R., Huete, A. R., Dickinson, R. E., Knyazikhin, Y., et al. (2007). Large seasonal swings in leaf area of Amazon rainforests. *Proceedings of the National Academy of Sciences of the United States of America*, *104*(12), 4820–4823. https://doi.org/10.1073/pnas.0611338104

Oikawa, P. Y., Ge, C., Wang, J., Eberwein, J. R., Liang, L. L., Allsman, L. A., et al. (2015). Unusually high soil nitrogen oxide emissions influence air quality in a high-temperature agricultural region. *Nature Communications*, *6*(1), 8753. https://doi.org/10.1038/ncomms9753

Oleson, K. W., Lawrence, D. M., Bonan, G. B., Flanner, M. G., Kluzek, E., Lawrence, P. J., et al. (2010). Technical description of version 4.0 of the community land model (CLM). NCAR Tech. Note NCAR/TN-4781STR 257.

Palmer, P. I., Abbot, D. S., Fu, T.-M., Jacob, D. J., Chance, K., Kurosu, T. P., et al. (2006). Quantifying the seasonal and interannual variability of North American isoprene emissions using satellite observations of the formaldehyde column. *Journal of Geophysical Research*, *111*, D12315. https://doi.org/10.1029/2005JD006689

Parrish, D. D., Singh, H. B., Molina, L., & Madronich, S. (2011). Air quality progress in North American megacities: A review. *Atmospheric Environment*, *45*(39), 7015–7025. https://doi.org/10.1016/j.atmosenv.2011.09.039

Parrish, D. D., Young, L. M., Newman, M. H., Aikin, K. C., & Ryerson, T. B. (2017). Ozone design values in Southern California's air basins: Temporal evolution and U.S. Background Contribution. *Journal of Geophysical Research: Atmospheres*, *122*, 11166–11182. https://doi.org/10.1002/2016JD026329

Pilegaard, K. (2013). Processes regulating nitric oxide emissions from soils. In *Philosophical transactions of the royal society B: Biological sciences*. Royal Society of London. https://doi.org/10.1098/rstb.2013.0126

Porter, W. C., Safieddine, S. A., & Heald, C. L. (2017). Impact of aromatics and monoterpenes on simulated tropospheric ozone and total OH reactivity. *Atmospheric Environment*, *169*, 250–257. https://doi.org/10.1016/j.atmosenv.2017.08.048

Pusede, S. E., & Cohen, R. C. (2012). On the observed response of ozone to NOx and VOC reactivity reductions in San Joaquin Valley California 1995–present. *Atmospheric Chemistry and Physics*, *12*(18), 8323–8339. https://doi.org/10.5194/acp-12-8323-2012

Pusede, S. E., Gentner, D. R., Wooldridge, P. J., Browne, E. C., Rollins, A. W., Min, K.-E., et al. (2014). On the temperature dependence of organic reactivity, nitrogen oxides, ozone production, and the impact of emission controls in San Joaquin Valley, California. *Atmospheric Chemistry and Physics*, *14*(7), 3373–3395. https://doi.org/10.5194/acp-14-3373-2014

Pusede, S. E., Steiner, A. L., & Cohen, R. C. (2015). Temperature and recent trends in the chemistry of continental surface ozone. *Chemical Reviews*, *115*(10), 3898–3918. https://doi.org/10.1021/cr5006815

Qin, M., Murphy, B. N., Isaacs, K. K., McDonald, B. C., Lu, Q., McKeen, S. A., et al. (2020). Criteria pollutant impacts of volatile chemical products informed by near-field modelling. *Nature Sustainability*, *4*(2), 129–137. https://doi.org/10.1038/s41893-020-00614-1

Rao, P., Hutyra, L. R., Raciti, S. M., & Templer, P. H. (2014). Atmospheric nitrogen inputs and losses along an urbanization gradient from Boston to Harvard Forest, MA. *Biogeochemistry*, *121*(1), 229–245. https://doi.org/10.1007/s10533-013-9861-1

Rasmussen, D. J., Fiore, A. M., Naik, V., Horowitz, L. W., McGinnis, S. J., & Schultz, M. G. (2012). Surface ozone-temperature relationships in the eastern US: A monthly climatology for evaluating chemistry-climate models. *Atmospheric Environment*, *47*, 142–153. https://doi.org/10.1016/j.atmosenv.2011.11.021

Rasmussen, D. J., Hu, J., Mahmud, A., & Kleeman, M. J. (2013). The ozone-climate penalty: Past, present and future. *Environmental Science & Technology*, *47*(24), 14258–14266. https://doi.org/10.1021/es403446m

Rasool, Q. Z., Bash, J. O., & Cohan, D. S. (2019). Mechanistic representation of soil nitrogen emissions in the Community Multiscale Air Quality (CMAQ) model v 5.1. *Geoscientific Model Development*, *12*(2), 849–878. https://doi.org/10.5194/gmd-12-849-2019

Romer, P. S., Duffey, K. C., Wooldridge, P. J., Edgerton, E., Baumann, K., Feiner, P. A., et al. (2018). Effects of temperature-dependent NOx emissions on continental ozone production. *Atmospheric Chemistry and Physics*, *18*(4), 2601–2614. https://doi.org/10.5194/acp-18-2601-2018

Sartelet, K. N., Couvidat, F., Seigneur, C., & Roustan, Y. (2012). Impact of biogenic emissions on air quality over Europe and North America. *Atmospheric Environment*, *53*, 131–141. https://doi.org/10.1016/j.atmosenv.2011.10.046

Sha, T., Ma, X., Zhang, H., Janechek, N., Wang, Y., Wang, Y., et al. (2021). Impacts of Soil NOx Emission on O3 Air Quality in Rural California. *Environmental Science & Technology*, *55*(10), 7113–7122. https://doi.org/10.1021/acs.est.0c06834

Souri, A. H., Choi, Y., Jeon, W., Li, X., Pan, S., Diao, L., & Westenbarger, D. A. (2016). Constraining NOx emissions using satellite NO2 measurements during 2013 DISCOVER-AQ Texas campaign. *Atmospheric Environment*, *131*, 371–381. https://doi.org/10.1016/j.atmosenv.2016.02.020

Squire, O. J., Archibald, A. T., Abraham, N. L., Beerling, D. J., Hewitt, C. N., Lathière, J., et al. (2014). Influence of future climate and cropland expansion on isoprene emissions and tropospheric ozone. *Atmospheric Chemistry and Physics*, *14*(2), 1011–1024. https://doi.org/10.5194/acp-14-1011-2014

Stehfest, E., & Bouwman, L. (2006). N2O and NO emission from agricultural fields and soils under natural vegetation: Summarizing available measurement data and modeling of global annual emissions. *Nutrient Cycling in Agroecosystems*, *74*(3), 207–228. https://doi.org/10.1007/s10705-006-9000-7

Steiner, A. L., Davis, A. J., Sillman, S., Owen, R. C., Michalak, A. M., & Fiore, A. M. (2010). Observed suppression of ozone formation at extremely high temperatures due to chemical and biophysical feedbacks. *Proceedings of the National Academy of Sciences of the United States of America*, *107*(46), 19685–19690. https://doi.org/10.1073/pnas.1008336107

Steiner, A. L., Tonse, S., Cohen, R. C., Goldstein, A. H., & Harley, R. A. (2006). Influence of future climate and emissions on regional air quality in California. *Journal of Geophysical Research*, *111*, D18303. https://doi.org/10.1029/2005JD006935

Steinkamp, J., & Lawrence, M. G. (2011). Improvement and evaluation of simulated global biogenic soil NO emissions in an AC-GCM. *Atmospheric Chemistry and Physics*, *11*(12), 6063–6082. https://doi.org/10.5194/acp-11-6063-20

Stettler, M. E. J., Eastham, S., & Barrett, S. R. H. (2011). Air quality and public health impacts of UK airports. Part I: Emissions. *Atmospheric Environment*, *45*(31), 5415–5424. https://doi.org/10.1016/j.atmosenv.2011.07.012

21698996, 2022, 13, Downloaded from https://agupubs.onlinelibrary.wiley.com/doi/10.1029/2021JD036361, Wiley Online Library on [27/04/2023]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

Sun, K., Zhu, L., Cady-Pereira, K., Chan Miller, C., Chance, K., Clarisse, L., et al. (2018). A physics-based approach to oversample multi-satellite, multispecies observations to a common grid. *Atmospheric Measurement Techniques*, *11*(12), 6679–6701. https://doi.org/10.5194/amt-11-6679-2018

Tao, Z., Larson, S. M., Wuebbles, D. J., Williams, A., & Caughey, M. (2003). A summer simulation of biogenic contributions to ground-level ozone over the continental United States. *Journal of Geophysical Research*, *108*, 4404. https://doi.org/10.1029/2002JD002945

Tawfik, A. B., Stöckli, R., Goldstein, A., Pressley, S., & Steiner, A. L. (2012). Quantifying the contribution of environmental factors to isoprene flux interannual variability. *Atmospheric Environment*, *54*, 216–224. https://doi.org/10.1016/j.atmosenv.2012.02.018

Travis, K. R., Jacob, D. J., Fisher, J. A., Kim, P. S., Marais, E. A., Zhu, L., et al. (2016). Why do models overestimate surface ozone in the Southeast United States? *Atmospheric Chemistry and Physics*, *16*(21), 13561–13577. https://doi.org/10.5194/acp-16-13561-2016

Trousdell, J. F., Caputi, D., Smoot, J., Conley, S. A., & Faloona, I. C. (2019). Photochemical production of ozone and emissions of NO x and CH 4 in the San Joaquin Valley. *Atmospheric Chemistry and Physics*, *19*(16), 10697–10716. https://doi.org/10.5194/acp-19-10697-2019

U.S. Environmental Protection Agency. (2019a). Ozone designation and classification information. Retrieved from https://www.epa.gov/green-book/ozone-designation-and-classification-information 15 November 2019.

U.S. Environmental Protection Agency. (2019b). 8-Hour ozone (2015) designated area/state information. Retrieved November 15, 2019, from Retrieved from https://www3.epa.gov/airquality/greenbook/jbtc.html

US EPA. (2021). National Emissions Inventory (NEI). Retrieved from https://www.epa.gov/air-emissions-inventories/national-emissions-inventory-nei. last accessed 1 July 2022.

van Donkelaar, A., Martin, R. V., Leaitch, W. R., Macdonald, A. M., Walker, T. W., Streets, D. G., et al. (2008). Analysis of aircraft and satellite measurements from the Intercontinental Chemical Transport Experiment (INTEX-B) to quantify long-range transport of East Asian sulfur to Canada. *Atmospheric Chemistry and Physics*, *8*(11), 2999–3014. https://doi.org/10.5194/acp-8-2999-2008

Vinken, G. C. M., Boersma, K. F., Jacob, D. J., & Meijer, E. W. (2011). Accounting for non-linear chemistry of ship plumes in the GEOS-Chem global chemistry transport model. *Atmospheric Chemistry and Physics*, *11*(22), 11707–11722. https://doi.org/10.5194/acp-11-11707-2011

Vinken, G. C. M., Boersma, K. F., Maasakkers, J. D., Adon, M., & Martin, R. V. (2014). Worldwide biogenic soil NOx emissions inferred from OMI NO2 observations. *Atmospheric Chemistry and Physics Discussions*, *14*(10), 14683–14724. https://doi.org/10.5194/acpd-14-14683-2014

Wang, Y., Ge, C., Garcia, L. C., Jenerette, G. D., Oikawa, P. Y., & Wang, J. (2021). Improved modelling of soil NOx emissions in a high temperature agricultural region: Role of background emissions on NO2 trend over the US. *Environmental Research Letters*, *16*(8), 084061. https://doi.org/10.1088/1748-9326/ac16a3

Wang, Y., Xie, Y., Dong, W., Ming, Y., Wang, J., & Shen, L. (2017). Adverse effects of increasing drought on air quality via natural processes. *Atmospheric Chemistry and Physics*, *17*(20), 12827–12843. https://doi.org/10.5194/acp-17-12827-2017

Weaver, C. P., Liang, X. Z., Zhu, J., Adams, P. J., Amar, P., Avise, J., et al. (2009). A preliminary synthesis of modeled climate change impacts on U.S. regional ozone concentrations. *Bulletin of the American Meteorological Society*, *90*(12), 1843–1863. https://doi.org/10.1175/2009BAMS2568.1

Zare, A., Christensen, J. H., Gross, A., Irannejad, P., Glasius, M., & Brandt, J. (2014). Quantifying the contributions of natural emissions to ozone and total fine PM concentrations in the Northern Hemisphere. *Atmospheric Chemistry and Physics*, *14*(6), 2735–2756. https://doi.org/10.5194/acp-14-2735-2014

Zhang, Y., & Wang, Y. (2016). Climate-driven ground-level ozone extreme in the fall over the Southeast United States. *Proceedings of the National Academy of Sciences of the United States of America*, *113*(36), 10025–10030. https://doi.org/10.1073/pnas.1602563113

21698996, 2022, 13, Downloaded from https://agupubs.onlinelibrary.wiley.com/doi/10.1029/2021JD036361, Wiley Online Library on [27/04/2023]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License