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Modeling Ozone in the Eastern U.S. using a Fuel-Based Mobile Source Emissions Inventory

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Supporting Information

ABSTRACT: Recent studies suggest overestimates in current U.S. emission inventories of nitrogen oxides (NO_x = NO + NO_2). Here, we expand a previously developed fuel-based inventory of motor-vehicle emissions (FIVE) to the continental U.S. for the year 2013, and evaluate our estimates of mobile source emissions with the U.S. Environmental Protection Agency's National Emissions Inventory (NEI) interpolated to 2013. We find that mobile source emissions of NO_x and carbon monoxide (CO) in the NEI are higher than FIVE by 28% and 90%, respectively. Using a chemical transport model, we model mobile source emissions from FIVE, and find consistent levels of urban NO_x and CO as measured during the Southeast Nexus (SENEX) Study in 2013. Lastly, we assess the sensitivity of ozone (O_3) over the Eastern U.S. to uncertainties in mobile source NO_x emissions and biogenic volatile organic compound (VOC) emissions. The ground-level O_3 is sensitive to reductions in mobile source NO_x emissions, most notably in the Southeastern U.S. and during O_3 exceedance events, under the revised standard proposed in 2015 (>70 ppb, 8 h maximum). This suggests that decreasing mobile source NO_x emissions could help in meeting more stringent O_3 standards in the future.

INTRODUCTION

Tropospheric ozone (O_3) is of concern due to its impacts on human health, ecosystems, and climate.[1,2] Many U.S. urban regions violate the 8 h O_3 standard as regulated under the Clean Air Act.[3] In 2015, the U.S. Environmental Protection Agency (EPA) revised the 8 h standard from 75 to 70 ppb. If implemented, the new standard will result in more monitoring locations being in nonattainment for O_3 in the near-term.[4] However, over most of the U.S., the overall trend in the 8-h design value of O_3 has been decreasing.[5,6] Significant reductions in O_3 precursor emissions have been observed over several decades, including for nitrogen oxides (NO_x = NO+NO_2) emitted from transportation[7] and power plants,[8,9] as well as carbon monoxide (CO) and volatile organic compound (VOC) emissions from transportation.[10,11]

Given significant and rapid changes in anthropogenic NO_x, CO, and VOC emissions, it is challenging for emission inventories to stay up-to-date with the implementation of current and past efforts to manage air quality. Recent atmospheric modeling studies have suggested that there are possible overestimates of NO_x emissions in the National Emissions Inventory (NEI) 2011 reported by EPA. Anderson et al.[12] first reported high NO_x emissions in the NEI 2011 when evaluated against aircraft measurements collected during the DISCOVER-AQ 2011 campaign over the Baltimore-Washington region.

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Given the relative importance of transportation emissions in the urbanized region, the authors suggested that mobile source NO_x was potentially overestimated by 51−70%. In the Southeastern U.S., Travis et al.[13] also found NO_x emissions were high in the NEI 2011, and suggested decreasing mobile source and industrial NO_x emissions by 30−60% to be consistent with aircraft measurements from the Studies of Emissions and Atmospheric Composition, Clouds and Climate Coupling by Regional Surveys (SEAC^{4}RS) 2013 campaign. During the DISCOVER-AQ 2013 campaign, Souri et al.[14] reported high NO_x emissions in the NEI 2011 over urban areas of Texas, and suggested decreasing NO_x emissions from all sources by 30−60% to be consistent with satellite observations. This included emission reductions from area, mobile, and point sources. A consistent source of uncertainty across these studies are emissions from the mobile source sector.

Mobile sources are major emitters of NO_x and CO. Nationally, according to the NEI 2011[15] and 2014,[16] ∼ 55% of U.S. NO_x emissions are from mobile sources, ∼ 35% from point and area sources, and the rest mostly from natural sources. For CO, ∼ 50% of U.S. emissions are from mobile sources, ∼ 10% from point and area sources, and the rest mostly from natural sources. Similar sectoral allocations of emissions are found over the Eastern U.S. (EPA Regions 1−5) and Southeastern U.S. (EPA Region 4). In the past, models of motor vehicle emissions have been difficult to reconcile with atmospheric measurements of CO, NO_x, and VOCs.[17] Uncertainties arise from spatial and temporal patterns of activity, emission factors, and advancements made in improving emission control technologies over time.[7,11,17−20] An additional challenge is that vehicle emission models can change over time, such as with the transition to the current EPA Motor Vehicle Emission Simulator (MOVES) model from its predecessor MOBILE6.[21]

Here we explore the scalability of a fuel-based inventory as an alternative to map and model mobile source (on-road + off-road) emissions of air pollutants.[7,11,22−26] We have expanded the spatial coverage of the fuel-based inventory of motor-vehicle emissions (FIVE),[18] which has previously been used to model NO_x and CO mixing ratios in the Los Angeles basin,[27] and carbon dioxide (CO_2) emissions in the San Francisco Bay Area.[28] In Los Angeles, model simulations utilizing FIVE as the emissions input agreed well with ground- and aircraft-based measurements of NO_x and CO in the summer of 2010.[27] The emissions constructed in FIVE are year-specific and correspond to years when field measurements occurred. Here, we extend FIVE over the continental U.S., and perform chemical-transport model evaluations using FIVE and the NEI during the NOAA-led Southeast Nexus (SENEX) Study in 2013.[29] The research objectives of this study are to assess uncertainties in mobile source emissions of NO_x and CO, reconcile their emissions with atmospheric measurements, and then model their impacts on surface O_3.

MATERIALS AND METHODS

On-Road Emissions. We use a fuel-based approach to estimate NO_x and CO emissions, where activity is based on fuel use data, and emission factors are normalized to fuel use for the year of interest. On-road activity is quantified using state-level taxable fuel sales reports, with separate accounting of gasoline and diesel fuel.[30] In the U.S., gasoline is consumed mostly by light-duty passenger vehicles, and diesel by heavy-duty trucks. Additionally, we take into account nontaxable diesel fuel consumed by buses.[31]

On-road emission factors are quantified using in situ measurements over roadways. Here, we use NO_x and CO emission factors from Hassler et al.,[32] which updated previous emission factor analyses over a longer time frame.[7,11] The emission factors are derived from regression analyses of roadside infrared remote sensing and tunnel studies. For light-duty vehicles, the regression analysis of studies listed in Supporting Information (SI) Table S1 includes terms to control differences in mean vehicle fleet ages between states (SI Table S2). We also take into account overall aging of vehicle fleets due to the 2008 recession, which slowed reductions in tailpipe emission factors.[33] Lastly, we account for differences between California and non-California vehicle fleets. California is the only state allowed to implement emission standards separate from U.S. EPA,[34] and some differences are observed.[11] For diesel trucks, since the number of roadway studies reported in the literature is much fewer compared to passenger vehicles, we are only able to perform a simple linear regression.

We first estimate fuel-based emissions for on-road gasoline and diesel engines at a state-level. Emissions are then mapped onto a 12 × 12 km model grid, using the NEI 2011 spatial and temporal vehicle activity patterns available. The fuel-based calculation only takes into account running exhaust emissions, as roadway studies are typically in locations (e.g., highways) where the influence of cold-starting engines is expected to be minimized. For light-duty gasoline vehicles, we estimate cold start emissions by ratio to running exhaust emissions based on the EPA MOVES model,[35] accounting for 25% and 27% of NO_x and CO emissions in summertime, respectively. Beginning with 2010 model year engines, trucks are required to install selective catalytic reduction (SCR) systems. Currently MOVES does not estimate cold start emissions from heavy-duty trucks. By 2013, the year of the SENEX study and focus of our atmospheric modeling efforts, less than 20% of the heavy-duty truck fleet had SCR systems installed.[36] We do not account for cold start emissions from heavy-duty trucks in this study.

Off-Road Emissions. Similarly, we estimate off-road emissions for each state using a fuel-based approach. Sectors that were estimated include heavy-diesel equipment and small two- and four-stroke gasoline engines. Excluded were marine vessels and locomotives. For these larger diesel engines, we use emissions directly from the NEI. The state-level emissions are then projected on a 12 × 12 km grid using spatial- and temporal-activity patterns from the NEI 2011.

Off-road diesel fuel use is reported by the Energy Information Administration (EIA).[37] The NO_x emission factor for heavy diesel equipment is from the EPA NONROAD model,[38] with uncertainties reported by Dallmann et al.[22] previously. The CO emission factor is estimated by ratio to particulate matter (PM),[39] using PM emission factors from McDonald et al.[40]

For off-road gasoline engines, we use state-level statistics of nonhighway gasoline sales from the Federal Highway Administration (FHWA).[41] Because some gasoline consumed by nonhighway engines may be accounted for in sales intended for road transportation, we scale FHWA statistics of off-road gasoline fuel use to match output from the EPA NONROAD model.[38] We use scaling factors of 1.25 and 2 for small-watercraft and land-based equipment, respectively. We further subdivide fuel used for land-based equipment between two- and four-stroke engines based on the NONROAD model.[38] Uncertainties in off-road gasoline fuel use is taken as the difference between FHWA and EPA estimates. We use emission factors of NO_x and CO from in situ and laboratory

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studies of small watercraft[42] and two- and four-stroke engine lawn equipment.[43]

Other Emissions. In this study, we only modify anthropogenic emissions of NO_x and CO for mobile source engines, which is performed across the entire Continental U.S. model domain. For other pollutants (i.e., VOCs and sulfur oxides) and other anthropogenic sectors (i.e., power plants,[9] industry, shipping, and area sources) we use emissions from the NEI 2011 (version 1).[15] Since our focus is on modeling trace gases and ozone, we only model gas-phase chemistry and exclude aerosol species. Biogenic emissions are from the Biogenic Emissions Inventory System (BEIS) version 3.14.[44] We model emissions from agricultural fires, but do not include emissions from forest fires, which could bias our emissions low for CO.[45] We do include emissions of soil NO_x and direct emissions of CO from vegetation, which are accounted for in BEIS.

Chemical Transport Model. We use the Weather Research and Forecasting with Chemistry (WRF-Chem) model[46] (version 3.7) to model air quality during the SENEX Study, from June 1 to July 15, 2013. The model domain is shown in SI Figure S1, which covers the Continental U.S. at 12 × 12 km horizontal resolution. Our WRF-Chem configurations are listed in SI Table S3.

For chemistry, we use a modified version of the Regional Atmospheric Chemistry Mechanism (RACM).[47] The RACM_ESRL mechanism described by Kim et al.,[48] includes additional reactions and updated reaction rate coefficients. See SI for an additional modification made to account for recycling of hydroxyl (OH) radical due to the isomerization of isoprene oxidation products under low NO_x conditions, proposed by Paulot et al.[49]

For long-lived chemical species, including CO and O_3, we use static chemical boundary conditions based on observational data sets. We set a background concentration for CO of ~100 ppb on all boundaries, as estimated from 30 vertical profiles measured by research aircraft in and out of Nashville, TN, during SENEX. The ~100 ppb background in the free troposphere (>2 km above ground level) observed over the Southeast in 2013 is consistent with values observed off the coast of Los Angeles during the summer of 2010.[50] SI Figure S2 shows our chemical boundary conditions for O_3 based on ozonesondes,[51,52] whose locations are shown in SI Figure S1, as well as aircraft measurements made over the Gulf of Mexico during the SEAC^{4}S campaign.[13] We use a single median profile across nine ozonesondes for the western, northern, and eastern boundaries of our model domain, which were found to be similar (SI Figure S2). The southern boundary exhibited a distinct vertical profile, which was cleaner at the surface, and extended deeper into the troposphere. We use static boundaries in our WRF-Chem model because Parrish et al.[53] report that commonly used global chemistry-climate models tend to overestimate ozone by 5−17 ppb when compared with measurements made at global background monitors.

Ambient Data. To evaluate our air quality model, we compare with measurements made by the NOAA P-3 research aircraft and ground-based monitoring networks. Flight tracks are shown in SI Figure S1, and concentrated in the Southeastern U.S. The P-3 aircraft was equipped with instruments measuring: CO by vacuum ultraviolet resonance fluorescence (±5% uncertainty); total reactive nitrogen (NO_y) and O_3 by chemiluminescence (±10% uncertainty); isoprene, methacrolein (MACR), and methyl vinyl ketone (MVK) by proton-transfer-reaction mass spectrometry (PTR-MS, ± 20% uncertainty); and formaldehyde by laser-induced fluorescence (±10% uncertainty).[29] Uncertainties shown in parentheses are for 1-hz data.

Ground-based monitoring networks used in this study include the Southeast Aerosol Research and Characterization (SEARCH) network,[54] which was operational from 1999 to 2013. Data from the SEARCH network has been used in prior studies to assess long-term trends over the Southeastern U.S. in O_3, aerosols, and VOCs.[55,56] In 2013, the SEARCH network consisted of five locations across urban, suburban, and rural settings, and which overlap with the flight tracks of the NOAA P-3 aircraft. Model O_3 was also assessed with ambient monitoring network data from EPA's Air Quality System (AQS).

RESULTS AND DISCUSSION

Fuel-Based Mobile Source Emissions. Figure 1 illustrates comparisons of mobile source emissions of NO_x (panel a) and CO (panel b) as estimated by the fuel-based approach with emissions reported by current EPA inventories. We separate emissions by the four major mobile source categories: on-road gasoline, on-road diesel, off-road gasoline, and off-road diesel. We herein refer to fuel-based emissions from both on-road and off-road vehicles as FIVE 2013. The NEI reports emissions across all anthropogenic sectors periodically, including in 2011[15] and 2014.[16] The MOVES[35] and NONROAD[38] models estimate emissions for mobile source engines reported in the NEI. We interpolate mobile source emissions from the NEI 2011 (version 1) and NEI 2014 (version 1) to generate NEI emissions in 2013. The SENEX field campaign, the focus of this study, occurred during summer of 2013.

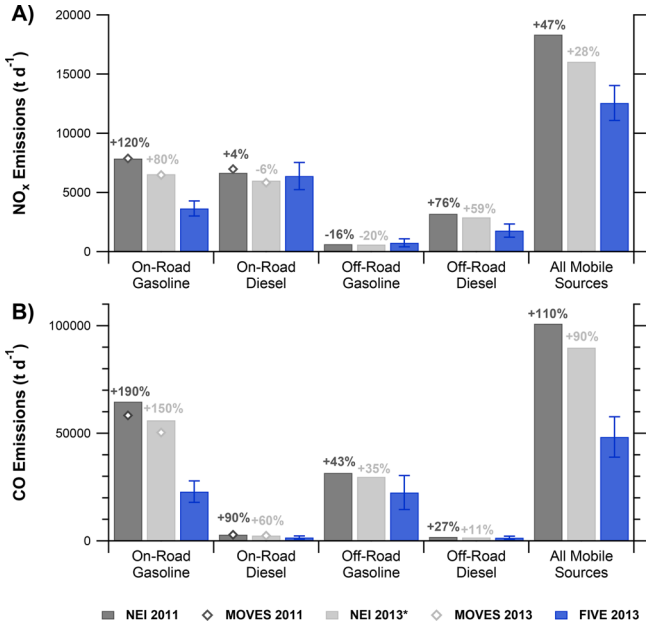

Figure 1. U.S. mobile source emissions summed across all 50 states of (A) NO_x and (B) CO by engine category. In each panel, the dark gray bars are emissions from the NEI reported in 2011. The light gray bars are emissions from the NEI for the year 2013, interpolated between the 2011 and 2014 versions. The open gray markers are emissions outputted from the MOVES model using national default settings. The blue bars are mobile source emissions estimated from a fuel-based approach (FIVE), and specific to the year 2013. Error bars on FIVE reflect uncertainties in fuel sales and emission factors.

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In Figure 1, FIVE 2013 shows that on-road diesel emissions of NO_x dominate over on-road gasoline engines, though in the U.S. only ~2.5 million heavy-duty trucks[57] are registered versus ~230 million light-duty passenger vehicles.[58] Relative to FIVE 2013, the interpolated NEI 2013 emissions of NO_x and CO from on-road gasoline engines are higher by 80% (Figure 1a) and 150% (Figure 1b), respectively. When all mobile source emissions are summed, the NEI 2013 NO_x and CO emissions are higher than FIVE by 28% (Figure 1a) and 90% (Figure 1b), respectively. Prior modeling studies have reported overestimates of mobile source NO_x emissions in the NEI 2011 by 30−70%.[12−14] Our fuel-based analysis is on the lower bound of this range.

We attribute most of the discrepancy between MOVES and FIVE to differences in emissions of on-road gasoline engines, which is the focus of the following discussion. We assess two possible reasons for the differences, related to (i) vehicle activity and (ii) emission factors. To perform this assessment, we compare FIVE with national defaults outputted from the MOVES model. For the NEI, MOVES is simulated using more detailed state-supplied input data and may differ slightly from national defaults, including inputs for vehicle mixes, driving conditions, and meteorological conditions. However, at a national-scale, default emissions from MOVES are similar to those reported in the NEI for NO_x (Figure 1a) and CO (Figure 1b).

With respect to vehicle activity, our estimate of on-road gasoline consumption is within ~10% of MOVES nationally (SI Figure S3). Therefore, we can rule out vehicle activity as the main source of difference between MOVES and FIVE in on-road gasoline NO_x (Figure 1a) and CO (Figure 1b) emissions. Next, we evaluate running exhaust emission factors (Figure 2). For the year 2013, on-road gasoline emission factors in MOVES are 2.0 times higher for NO_x (Figure 2a) and 2.5 times higher for CO (Figure 2b) when compared to regression analyses of near-roadway measurements used in this study.[32] We suggest that differences in emission factors are the most plausible explanation for why on-road gasoline emissions of NO_x (Figure 1a) and CO (Figure 1b) differ between MOVES and FIVE.

Representativeness of On-Road Emission Factors. Here we assess possible effects of driving conditions, high-emitting vehicles, and vehicle mixes on on-road gasoline emission factors using three recent remote sensing data sets compiled in 2013 (Los Angeles, Denver, and Tulsa).[59,60] These variables are not explicitly included in our regression analysis, but as discussed below, are unlikely to alter our findings.

Driving conditions can affect emission factors of NO_x and CO.[61,62] However, under urban driving, most fuel is consumed at engine loads between 0 and 20 kW/ton (~85% of the total), where fuel-based emission factors of NO_x (SI Figure S4a) and CO (SI Figure S4b) are less variable.[11,63] Passenger vehicles operating at higher engine loads (>20 kW/ton) are potentially under-represented by remote sensing, which are typically located near highway on-ramps. Following McDonald et al.,[11] we bin emission factors by vehicle specific power (VSP), and separate between the highest 10% of emitting vehicles and the other 90% of low-emitting vehicles. VSP is a metric that quantifies engine load by taking into account vehicle speed, acceleration, and road grade. For the low-emitting vehicle subgroup, emission factors are more sensitive to drive cycle, and remote sensing measurements potentially under-report NO_x and CO emissions by 11% and 9%, respectively, consistent with

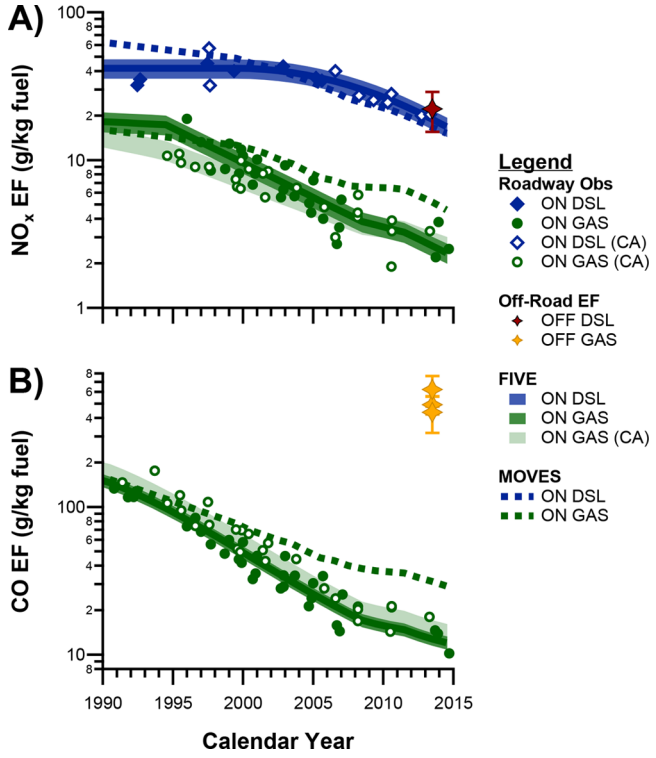

Figure 2. Trends in U.S. mobile source running exhaust emission factors for (A) NO_x and (B) CO. Emission factors for each point are listed in SI Table S1, with open markers representing roadway studies performed in California and filled markers outside California. The solid lines are emission factors used in FIVE for on-road gasoline (dark green) and on-road diesel (blue) vehicles, and represent U.S. averages. The bands show the 95% confidence interval of the regression. Light green bands represent emission factors of on-road gasoline vehicles in California. Dashed lines show default emission factors from the U.S. EPA MOVES2014 model and represent U.S. averages.

findings of Lee and Frey.[61] However, high-emitting vehicles now account for ~85% of the running exhaust emissions across all light-duty vehicles sampled by remote sensing in 2013, and their NO_x and CO emission factors are insensitive to drive cycle (SI Figure S4). Since emissions from high-emitting vehicles now dominate under hot stabilized exhaust conditions,[11,64] the effect of drive cycle on fleet-average emission factors should be small. Therefore, the mapping of NO_x and CO emissions should scale with fuel use or carbon dioxide (CO_2) emissions.

Given that fleet average emission factors are dominated by the highest 10% of emitting vehicles, we also assess the variability of NO_x (SI Figure S5a) and CO (SI Figure S5b) emission factors by high-emitters across the three remote sensing locations. For high-emitters, the variability of NO_x (−22% to +14%) and CO (−11% to +7%) emission factors are comparable to the uncertainty of our regression analyses shown in Figure 2. By contrast, the variability of emission factors for low-emitters is much larger for NO_x (−60% to +63%) and CO (−34% to +45%). The similarity in emission factors of high-emitting vehicles is surprising given that Tulsa lacks an emissions inspection and maintenance program,[59] while Los Angeles has one of the most stringent programs in the nation.

The fraction of light trucks (e.g., vans, sport-utility vehicles, pick-up trucks) in the passenger vehicle fleet have grown with time.[65] In SI Figure S6, we breakdown NO_x (panel a) and CO (panel b) emission factors between passenger cars and light

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Table 1. Summary Statistics for P-3 Aircraft and WRF-Chem Model Simulations during SENEX Study Limited to Planetary Boundary Layer (200−800 m) and Daytime Hours (10−18 CDT).[a−c]

	P-3[d] (obs.)	model I (NEI13)	model II (NEI13 + 2*ISO)	model III (FIVE13)	model IV (FIVE13 + 2*ISO)
NO_y (ppb)	2.1 ± 0.2	2.8 (+38%, 0.67)	2.8 (+37%, 0.67)	2.5 (+21%, 0.63)	2.3 (+13%, 0.58)
isoprene (ppb)	1.1 ± 0.2	0.56 (−48%, 0.65)	1.8 (+65%, 0.66)	0.61 (−43%, 0.65)	2.3 (+110%, 0.64)
MACR+MVK (ppb)	1.0 ± 0.2	1.3 (+28%, 0.79)	2.8 (+170%, 0.78)	1.4 (+35%, 0.79)	3.6 (+250%, 0.73)
HCHO (ppb)	4.3 ± 0.4	3.2 (−26%, 0.77)	4.1 (−3%, 0.73)	3.1 (−27%, 0.77)	4.4 (+2%, 0.77)
CO (ppb)	133 ± 7	142 (+7%, 0.89)	143 (+8%, 0.90)	130 (−2%, 0.88)	140 (+5%, 0.88)
O_3 (ppb)	47 ± 5	56 (+19%, 0.85)	56 (+19%, 0.84)	53 (+12%, 0.83)	50 (+6%, 0.75)
OH (ppt)		0.25	0.16	0.23	0.12

[a]Flight dates are as follows: 6/3, 6/10, 6/11, 6/12, 6/16, 6/22, 6/23, 6/25, 6/26, 6/29, 7/6, 7/8, and 7/10. [b]Power plant plumes excluded from model-observation comparisons. [c]Mean values shown. In parentheses below each model case is the relative difference in the model mean versus corresponding P-3 observations, and the Pearson correlation coefficient between the P-3 observations and each model case. [d]Error bars reflect aircraft measurement uncertainties (see Materials and Methods).

trucks, and by Tier 0−2 emission standards. We also show how emission factors from remote sensing data compare with MOVES. In the remote sensing data, the emission factors of NO_x (SI Figure S6a) and CO (SI Figure S6b) are similar between passenger cars and light trucks, whereas MOVES has higher emission factors for light trucks relative to passenger cars. Thus, the discrepancies in emission factors between remote sensing data and MOVES tend to be larger for light trucks than for passenger cars.

For heavy-duty diesel trucks, we show that NO_x emission factors are similar between MOVES and FIVE in 2013 (Figure 2a). However, recent testing of heavy-duty diesel trucks have found that SCR systems are significantly less effective at controlling NO_x under congested/local driving conditions.[66,67] Jiang et al.[68] observed using satellite data a slowdown in NO_x emission decreases, and suggested that trends in on-road diesel NO_x emissions (estimated using a fuel-based approach) could be contributing to the observed slowdown along with other factors. For this study, we utilize an earlier analysis of on-road diesel NO_x emission factors from Hassler et al.[32] (Figure 2a), whose emission factors are within ∼10% of Jiang et al.[68] for 2013, and within the uncertainty bands of the regression analysis. The main difference in diesel emission factors between Hassler et al.[32] and Jiang et al.[68] is in the trend, rather than in the absolute total.

Regional Burdens of O_3 Precursors. We test the sensitivity of O_3 to uncertainties in mobile source NO_x emissions, as well as in biogenic VOC emissions. Prior studies have suggested factor of 2 uncertainties in isoprene emissions, where BEIS is on the low end and another commonly used global model of biogenic emissions, MEGAN, is on the high end.[69,70] We perform the following model sensitivity cases:

(i) NEI 2013 + 1 * BEIS isoprene emissions;
(ii) NEI 2013 + 2 * BEIS isoprene emissions;
(iii) FIVE 2013 + 1 * BEIS isoprene emissions;
(iv) FIVE 2013 + 2 * BEIS isoprene emissions.

For each case, mobile source emissions are the same as those shown in Figure 1. Point and area source emissions are from the NEI 2011 (version 1) and kept the same across all modeling cases. Overall, we reduce the total U.S. budget of NO_x and CO emissions by 9% and 32%, respectively, when substituting FIVE 2013 mobile source emissions between cases i-ii and iii-iv. Since the biggest emission adjustments are for on-road gasoline vehicles, the grid cells most affected are in urban areas (SI Figure S7).

Table 1 summarizes each model case against NOAA P-3 aircraft data. In total, the measurements encompass 13 flight days, and comparisons are limited to the planetary boundary layer (PBL) during daytime hours (10−18 CDT). In the SI, we include model evaluations of meteorology in comparison to aircraft measurements of wind speed, wind direction, ambient temperature, and relative humidity (SI Figure S8). Over the campaign, the model captures the variance of these meteorological variables ($r \geq 0.77$) and mean biases are small. If there are disagreements between the model and observations for chemical species, then they most likely arise from uncertainties in emissions and chemistry. The focus of this study will be on emissions, with considerations made to reduce the influence of chemistry on model-observation comparisons.

To assess NO_x emissions, we evaluate the model using NO_y ($\sum$ = NO_x + PAN + HNO_3 + alkyl nitrates), which is a more conserved tracer of fresh NO_x emissions and their oxidation products in the ambient atmosphere. We also exclude power plant plumes, as the horizontal resolution of our model (12 × 12 km) is too coarse to resolve near-source chemistry and transport. Data are excluded to remove the influence of power plant plumes when the aircraft is within 12 km of a power plant, sulfur dioxide (SO_2) is greater than 6 ppb, or NO_y is greater than 6 ppb. Less than 0.1% of the measurements were excluded based on these thresholds. In the two NEI 2013 model cases (i) and (ii), model NO_y concentrations are high by 37−38% relative to aircraft observations (Table 1). The high biases in model NO_y are reduced in half when substituting mobile source emissions with FIVE 2013 (model cases iii and (iv). This finding is consistent with Travis et al.,[13] which suggested that to improve models of surface O_3 over the Southeastern U.S., NO_x reductions of 30−60% are needed in the NEI 2011 for both the mobile source and industrial sectors. Most industrial sources of NO_x are not continuously monitored, in contrast to stack monitors installed on nearly all power plants, and whose emissions are more uncertain. In this study, relative to the NEI 2011 we reduce only mobile source emissions by ∼30% (Figure 1a), and hence some overestimation in NO_y concentrations remains in the FIVE 2013 model cases (Table 1).

In the Eastern U.S., there are large emissions of biogenic VOCs,[71,72] with the most abundant being isoprene. While doubling isoprene emissions in our model significantly affects concentrations of isoprene and its oxidation products (i.e., MACR + MVK and formaldehyde), and halves OH levels, NO_y concentrations are insensitive to uncertainties in VOC emissions (Table 1). Though CO has significant primary emissions from fossil fuel combustion, another source is secondary formation from isoprene oxidation.[73,74] Because it is a relatively

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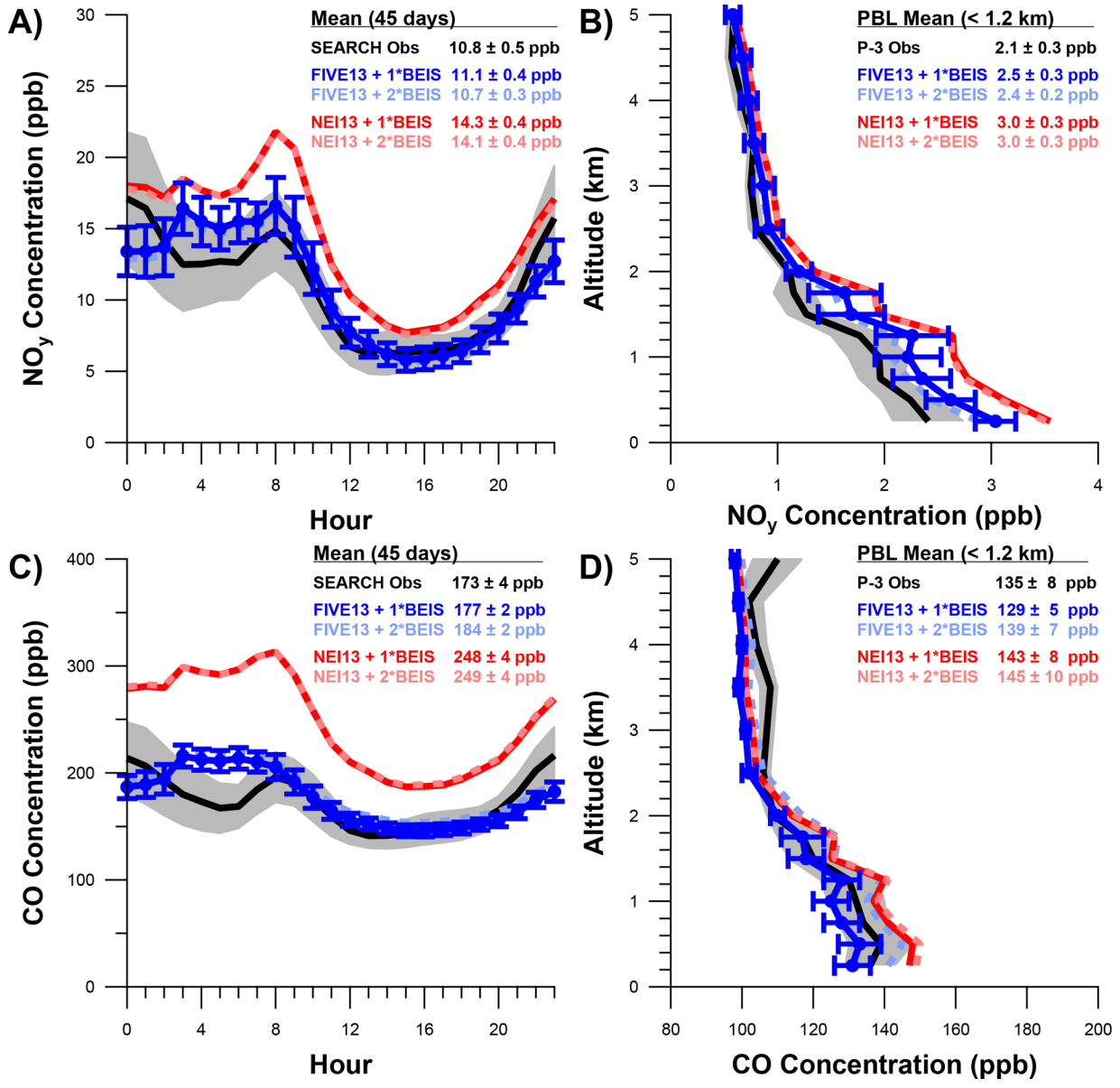

Figure 3. Evaluation of modeled NO_y with a (A) SEARCH network site in downtown Atlanta, and (B) vertical profiles from the NOAA P-3 aircraft near Nashville. WRF-Chem results simulating FIVE 2013 (blue lines) and the NEI 2013 (red lines) are shown against ambient observations (black lines) averaged over the SENEX period. The uncertainty bands and error bars reflect the 95% confidence interval of the mean. Panels (C) and (D) show the same model evaluations as panels (A) and (B), except for CO.

long-lived species, global background levels are significant. The two NEI 2013 model cases overpredict CO by 9−10 ppb. Reducing mobile source CO emissions by 50% lowers CO in the model by 12−13 ppb and improves agreement with the observations. Interestingly, doubling isoprene emissions between the two FIVE cases increases CO by 10 ppb. In other words, the effects on CO from uncertainties in anthropogenic and biogenic emissions are comparable in magnitude. Over forested regions (e.g., Eastern U.S.), it is becoming increasingly difficult to observe enhancements of CO in regional air masses resulting from fossil fuel combustion. Over many decades, motor vehicle emissions of CO have been reduced by over an order of magnitude through improved three-way catalytic converters.[11]

We also perform model evaluations across five SEARCH network ground sites operational in 2013 (SI Table S4). In general, the ground-based model evaluation yields similar findings to our analysis with aircraft data, though the correlation of the model with ground site data is lower. In contrast to ground sites, which can be strongly influenced by local emission sources, aircraft data are spatially averaged and likely more comparable to the 12 × 12 km resolution of our WRF-Chem model. When we decrease mobile source emissions (NEI 2013 to FIVE 2013), high NO_y biases are cut in half, and high CO biases of 25−26 ppb are eliminated.

We expect mobile sources to be a major source of NO_x and CO emissions in U.S. cities.[18] Therefore, urban plumes provide useful test cases for evaluating the fidelity of mobile source emissions. We focus on two Southeastern cities with repeated measurements. In Atlanta, we evaluate our model with a SEARCH network ground site located in a downtown location. In Nashville, we compare with NOAA P-3 aircraft data above nearby Smyrna, TN. In both Atlanta and Nashville, the NEI 2013 model cases overpredict NO_y concentrations by 30−40%

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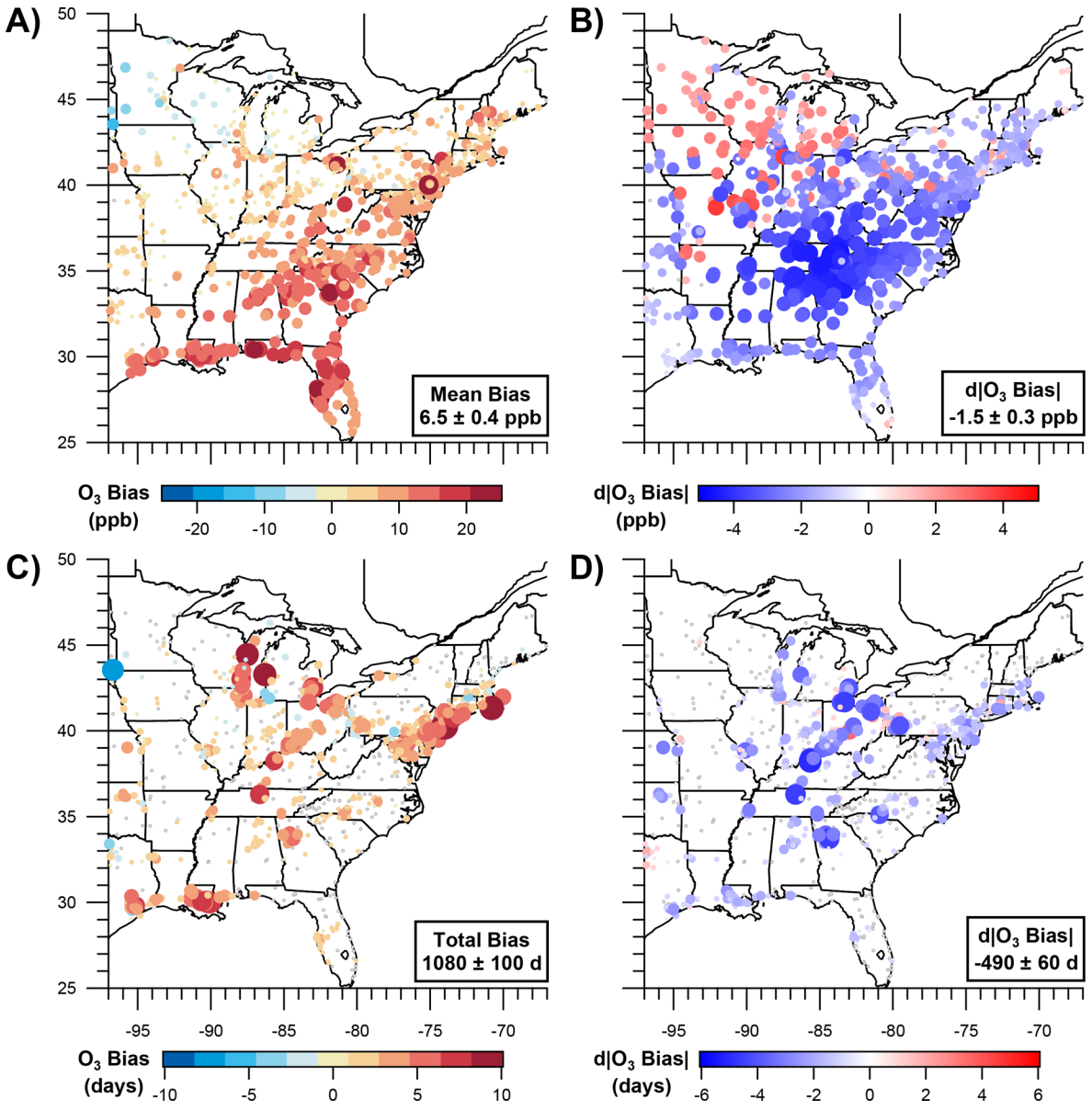

Figure 4. (A) Mean bias of the daily 8-h O_3 maximum simulating the NEI 2013 model cases in WRF-Chem, relative to ambient monitoring network observations (individual markers). Markers are sized by the magnitude of the bias. Error bars in the lower right-hand corner of each panel span the difference between the unadjusted and doubling of isoprene sensitivity runs. (B) Magnitude change in the mean bias when reducing mobile source NO_x emissions (Δbias = |model(FIVE 2013) − obs.| − |model(NEI 2013) − obs.|). Blue circles indicate locations where FIVE 2013 improved model predictions, and red circles where FIVE 2013 worsened model predictions, relative to the NEI 2013. Markers are sized by the magnitude of the change in bias. Panels (C) and (D) are the same as panels (A) and (B), respectively, except in terms of the number of ozone exceedance days (daily 8-h maximum >70 ppb).

(Figure 3a,b), and also overpredict CO (Figure 3c,d). When we utilize FIVE 2013 for mobile source emissions, model concentrations of NO_y and CO are now within the variability of observations, and result from reducing mobile source emissions for both species. At the two urban sites, model concentrations of NO_y are insensitive to doubling isoprene emissions. For CO, the downtown Atlanta site is insensitive to doubling isoprene emissions. At the Nashville location, there is a stronger influence of biogenic CO, as this site is capturing a regional mixture of anthropogenic and biogenic sources.

Sensitivity of O_3 to NO_x Emissions. Here we assess the sensitivity of ground-level O_3 to NO_x emissions between the NEI 2013 and FIVE 2013 model cases. The NO_x emission changes between the two sets of cases reflect ∼2 years of on-road gasoline emission reductions based on trends in fuel sales (SI Figure S3) and emission factors shown in Figure 2a. We do not adjust emissions from other anthropogenic sectors, and focus the following discussion on O_3 sensitivity to mobile source NO_x emissions.

Across ground-based monitors located in the Eastern U.S. (east of longitude 97° W), our model simulations using the NEI 2013 overestimate the mean 8-h maximum O_3 concentration by 6.5 ± 0.4 ppb at the surface (Figure 4a). Model predictions of O_3 are also high by 9 ppb when compared with aircraft data limited to the planetary boundary layer (Table 1). Reducing mobile source NO_x emissions decreases the overall O_3 bias by 1.5 ± 0.3 ppb (∼25% of the total, compare Figure 4a,b) at surface monitors, and by 4.5 ± 1.5 ppb in the

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planetary boundary layer as measured by the P-3 aircraft (Table 1). Biases in the model decreased the strongest in the Southeastern U.S. (up to 4.7 ppb, Figure 4b). Given the abundance of biogenic VOCs in the Southeastern U.S., we expect O_3 to be especially sensitive to changes in NO_x emissions in this region.[71,72]

A key finding is that reducing mobile source NO_x emissions does not improve model predictions of O_3 uniformly over the Eastern U.S., and likely reflects the importance of other chemical and physical processes on O_3. For example, one area of the country where O_3 model-observation agreement worsened when using FIVE 2013 is in the Upper Midwest (Figure 4b). This could suggest missing or under-accounted agricultural sources of NO_x, such as from soils.[14,75] Another possibility is the influence of variable boundary conditions. Here we use static boundary conditions for ozone, which could be missing long-range transport events of ozone from Asia.[4] Lastly, uncertainties in biogenic isoprene emissions and corresponding effects on OH, can impact ozone by 0−3 ppb (Table 1), comparable to ozone effects from uncertainties in anthropogenic NO_x emissions (Figure 4b).

We also assess NO_x sensitivities on high O_3 days. During the summer period of SENEX (N = 45 days) there were 502 exceedance days above the revised 70 ppb 8 h standard in the Eastern U.S. (east of longitude 97° W). The model simulations using the NEI 2013 overpredict the number of exceedances by 1080 ± 100 site-days (Figure 4c). Lowering mobile source NO_x emissions reduces the magnitude in the model bias in half, by 490 ± 60 site-days (Figure 4c to 4d). This indicates that mobile source NO_x emissions are more influential on high O_3 days than for summer-averaged concentrations, especially during air pollution episodes (SI Figure S9). Our results are consistent with recent modeling studies over the Eastern US indicating the effectiveness of NO_x control strategies as a means for reducing ground-level O_3.[76,77] If we scale our results to an entire O_3 season (May to September) over the Eastern U.S., we can attribute ∼2 years of vehicle emission reductions to a reduction of ∼1500 site-days above the revised 70 ppb standard. This suggests that future NO_x reductions, anticipated from SCR systems installed on a greater fraction of the heavy-duty truck fleet,[78] could result in significant improvements in O_3 for cities along the East Coast. Conversely, if NO_x emissions from diesel trucks are not declining as quickly as anticipated,[68,79] the number of high O_3 days will decline more slowly.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.8b00778.

Tables S1−S4 and Figures S1−S9 (PDF)

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Notes

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