AGU PUBLICATIONS

Geophysical Research Letters

RESEARCH LETTER
10.1002/2016GL069894

Key Points:
- Measured NO_x/CO enhancement ratio trends are compared to inventory emissions ratio trends in megacities
- Chemistry-climate modeling inventory fails to capture NO_x/CO emission ratio trends and regional differences
- Observations demonstrate divergent paths in motor vehicle emission control strategies in the U.S. versus Europe

Supporting Information:
- Supporting Information S1

Correspondence to:
B. Hassler,
birgit.hassler@noaa.gov

Citation:
Hassler, B., et al. (2016), Analysis of long-term observations of NO_x and CO in megacities and application to constraining emissions inventories, *Geophys. Res. Lett.*, *43*, 9920–9930, doi:10.1002/2016GL069894.

Received 8 JUN 2016
Accepted 29 AUG 2016
Published online 22 SEP 2016

Analysis of long-term observations of NO_x and CO in megacities and application to constraining emissions inventories

Birgit Hassler[1,2], Brian C. McDonald[1,2], Gregory J. Frost[2], Agnes Borbon[3], David C. Carslaw[4], Kevin Civerolo[5], Claire Granier[1,2,6], Paul S. Monks[7], Sarah Monks[1,2], David D. Parrish[1,2], Ilana B. Pollack[1,2,8], Karen H. Rosenlof[2], Thomas B. Ryerson[2], Erika von Schneidemesser[9], and Michael Trainer[2]

[1]Cooperative Institute for Research in Environmental Sciences, University of Colorado Boulder, Boulder, Colorado, USA, [2]Earth System Research Laboratory, National Oceanic and Atmospheric Administration, Boulder, Colorado, USA, [3]LaMP, OPGC, CNRS-UMR 6016, University of Blaise Pascal, Clermont-Ferrand, France, [4]Wolfson Atmospheric Chemistry Laboratories, Department of Chemistry, University of York, York, United Kingdom, [5]New York State Department of Environmental Conservation, Division of Air Resources, Albany, New York, USA, [6]LATMOS/CNRS, Paris and Laboratoire d'Aerologie/CNRS, Toulouse, France, [7]Department of Chemistry, University of Leicester, Leicester, United Kingdom, [8]Now at Department of Atmospheric Science, Colorado State University, Fort Collins, Colorado, USA, [9]Institute for Advanced Sustainability Studies e.V., Potsdam, Germany

Abstract Long-term atmospheric NO_x/CO enhancement ratios in megacities provide evaluations of emission inventories. A fuel-based emission inventory approach that diverges from conventional bottom-up inventory methods explains 1970–2015 trends in NO_x/CO enhancement ratios in Los Angeles. Combining this comparison with similar measurements in other U.S. cities demonstrates that motor vehicle emissions controls were largely responsible for U.S. urban NO_x/CO trends in the past half century. Differing NO_x/CO enhancement ratio trends in U.S. and European cities over the past 25 years highlights alternative strategies for mitigating transportation emissions, reflecting Europe's increased use of light-duty diesel vehicles and correspondingly slower decreases in NO_x emissions compared to the U.S. A global inventory widely used by global chemistry models fails to capture these long-term trends and regional differences in U.S. and Europe megacity NO_x/CO enhancement ratios, possibly contributing to these models' inability to accurately reproduce observed long-term changes in tropospheric ozone.

1. Introduction

Accurate knowledge of the sources and sinks of tropospheric ozone is important for understanding its effects on human health, air quality, and climate [*Monks et al.*, 2015]. Tropospheric ozone is produced through atmospheric photochemical oxidation of carbon monoxide (CO) and volatile organic compounds (VOCs) in the presence of nitrogen oxides ($NO_x = NO + NO_2$) and is also modulated by stratospheric influx. "Bottom-up" inventories of these ozone precursors provide spatially and temporally resolved emissions from all relevant source sectors and are critical input to atmospheric model simulations.

Global chemistry models (GCMs) are used in the Intergovernmental Panel on Climate Change Assessment Reports [*Intergovernmental Panel on Climate Change*, 2013] to understand the past atmospheric state and predict its future based on historical emissions trends and projected emissions scenarios, with the goal of providing guidance to policy makers. Multidecadal GCM simulations of tropospheric ozone have been used to assess model fidelity over historical time periods with measurement-based constraints. For example, over a dozen GCMs were run for the past several decades within the Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP, http://www.giss.nasa.gov/projects/accmip/) and the Chemistry-Climate Model Initiative (CCMI, http://www.igacproject.org/CCMI) [*Lamarque et al.*, 2010; *Eyring et al.*, 2013]. Comparisons with long-term ozone measurements show that these CCMs overestimate ozone mixing ratios and underestimate long-term ozone trends at Northern Hemisphere (NH) midlatitudes, where the effect of anthropogenic emissions on ozone is expected to be largest [*Logan et al.*, 2012; *Parrish et al.*, 2014]. The latitudinal distributions of NH ozone concentrations are also not well simulated by these models [*Young et al.*, 2013; *Cooper et al.*, 2014; *Parrish et al.*, 2014]. While the GCMs in these exercises had different representations

of transport and chemistry with their own uncertainties, all the models used the related inventories ACCMIP and MACCity [*Lamarque et al*., 2010; *Granier et al*., 2011] to prescribe the long-term evolution of emissions. Inaccuracies in these inventories thus represent a potential source of error common to long-term chemistry-climate simulations of tropospheric ozone and its impact on radiative forcing.

Methods for constructing bottom-up inventories are complex and continuously evolving, resulting in uncertainties that are difficult to quantify. Atmospheric observations can provide an objective evaluation of inventory emissions fluxes, spatial and temporal variability, and source sector partitioning. For example, observed atmospheric enhancement ratios of coemitted species above a local background can be directly compared to the corresponding emissions ratio in an inventory [*Parrish et al*., 2002; *Parrish*, 2006; *Pollack et al*., 2013]. Enhancement ratios are conserved at spatial and temporal scales appropriate to urban area sampling and are independent of atmospheric dilution into background air. Similarly, the fuel-based inventory approach [*Singer and Harley*, 1996] offers advantages over conventional bottom-up inventory methods by using roadway measurements of emissions factors of real-world vehicle fleets and fuel sales data to derive emissions for mobile sources. The fuel-based approach can improve emission estimates and, when used as input to chemical transport models, has been demonstrated to produce more realistic modeled ozone concentrations compared to conventional approaches [*Harley et al*., 1997; *Kim et al*., 2016].

In order to monitor progress toward air quality regulatory targets, long-term accurate measurements of NO, NO_2, and CO have been made for decades in several world megacities, including the Los Angeles (LA) Basin and New York City (NYC), USA; London, United Kingdom (UK); and Paris, France [*von Schneidemesser et al*., 2010; *Parrish et al*., 2011; *Pollack et al*., 2013]. Long-term accurate VOC measurements are sparser than those of NO_x and CO. However, CO and VOC concentrations are highly correlated in megacities where motor vehicle emissions dominate [*Parrish et al*., 2009; *Warneke et al*., 2012; *von Schneidemesser et al*., 2010; *Borbon et al*., 2013], allowing urban VOC levels to be estimated from their enhancement ratios relative to CO.

In this work, we compare ambient NO_x/CO enhancement ratios and NO_x/CO emission trends in U.S. and European cities. We find that a long-term fuel-based inventory can account for the drivers of multidecadal urban NO_x and CO emissions changes. We evaluate the MACCity global inventory against the long-term observations and the fuel-based inventory and explore causes for MACCity's inability to reproduce measured trends. Our study demonstrates that air quality monitoring can be used to assess the ability of global inventories to capture the long-term evolution and regional differences in emissions that impact ozone climate forcing.

2. Data and Methods

2.1. Ambient Measurements

The long-term evolution of the LA Basin's air pollution and emissions has been studied in detail [*McDonald et al*., 2012, 2013, 2015; *Warneke et al*., 2012; *Pollack et al*., 2013]. *Pollack et al*. [2013] (referred to as "POL13" hereafter) analyzed observations dating back to 1960 from ambient monitors maintained by the California Air Resources Board (CARB), intensive field research campaigns employing ground-based and aircraft sampling, and roadside remote sensing combined with vehicle identification. We adopted the same LA Basin spatial extent as POL13 (Table S1 in the supporting information) and used their reported 1965–2010 NO_x/CO enhancement ratios. We supplemented POL13's analysis with eight additional CARB stations (Figure S1 and Table S1) and extended the CARB data record through 2015. Most CARB monitors used here were chosen due to their location near busy roadways and thus their representativeness of motor vehicle emissions.

Following POL13, *Parrish et al*. [2002], and *Parrish* [2006], we derived NO_x/CO enhancement ratios from the slope of the correlation between observed NO_x and CO mixing ratios determined by a bivariate least squares linear regression (e.g., see Figure S2). Like POL13, we considered only CARB measurements taken during the weekday (Monday–Friday) morning rush hour (0500–0900 local time), to capture mostly fresh vehicle emissions and to minimize potential instrument artifacts from reactive nitrogen species other than NO or NO_2. For consistency with POL13, CARB data were filtered for the May–September peak ozone production season [*Parrish et al*., 2011]. For each CARB monitor, we included in our analysis only years when at least two thirds of the possible number of hourly data during weekday morning rush hours between May and September were available and for which $r^2 \geq 0.5$, where r is the correlation coefficient between hourly mixing ratios of NO_x and CO. Restricting our analysis to well-correlated enhancement ratio data helps to ensure that ambient NO_x and CO originates from the same emission source, i.e., mainly motor vehicles.

CO and NO_x mixing ratios from air quality monitoring and intensive field campaigns conducted in seven other U.S. cities were also considered in our analysis. Detailed explanation of observational data collection and processing in these cities is provided in the supporting information (Text S1).

Hourly measured mixing ratios of CO, NO, and NO_2 for 1989–2015 (Figure S4 and Table S1) were obtained from the UK National Air Quality Archive for 17 stations in London [*Dollard et al*., 2007; *von Schneidemesser et al*., 2010; *Derwent et al*., 2014]. Remote sensing NO_x and CO emission measurements of almost 70,000 vehicles are available from a system deployed at four locations in London in 2012 [*Carslaw and Rhys-Tyler*, 2013], identical to the system employed in the U.S. by *Bishop and Stedman* [2008]. Hourly measured mixing ratios for CO, NO, and NO_2 for 1995–2014 were obtained from Paris' AIRPARIF air quality network for five traffic sites (Table S1 and Figure S5) [*Parrish et al*., 2009]. Ambient enhancement ratios are calculated from the hourly London and Paris monitoring data following the same procedure as the LA Basin CARB data.

2.2. Emissions Inventories

The MACCity inventory [*Granier et al*., 2011] used in this work is based on the ACCMIP inventory [*Lamarque et al*., 2010] for the period 1960–2000 and after 2000 uses the Representative Concentration Pathways (RCP) 8.5 emissions. ACCMIP is input to the multicentury simulations performed within the Coupled Model Intercomparison Project (CMIP) Phase 5, while CCMI's hindcasts (REF-C1 simulations) use MACCity as input. ACCMIP's year 2000 emissions are based on several regional inventories, including from the U.S. Environmental Protection Agency (EPA) and the European Monitoring and Evaluation Programme, and elsewhere are based on the Emissions Database for Global Atmospheric Research (EDGAR) version-4 inventory. ACCMIP's 1960–2000 emission trends are a combination of EDGAR-History Database of the Global Environment [*van Aardenne et al*., 2001] and RETRO [*Schultz et al*., 2008]. All inventories contributing to MACCity and ACCMIP were constructed with conventional approaches using emission factors and source activity data specific to the economic sector and region of interest [*Lamarque et al*., 2010; *Granier et al*., 2011]. ACCMIP was built at the regional level and allocated to a global horizontal grid using population and other surrogates. A detailed description of ACCMIP's development can be found in *Lamarque et al*. [2010]. MACCity extends decadal ACCMIP and RCP 8.5 emissions to annual values with a seasonal cycle [*Granier et al*., 2011]. Details of MACCity data processing are given in the supporting information (Text S2).

We also produced our own 1970–2014 inventory for the LA Basin that incorporates emission estimates for mobile sources, including on-road and off-road engines, using a fuel-based approach for CO [*McDonald et al*., 2013, 2015] and NO_x [*McDonald et al*., 2012]. The data set reported here extends the fuel-based inventory reported in *McDonald et al*. [2013] for 1990–2010. Mobile source emissions were calculated using fuel sales reports as a measure of engine activity, and emission factors were calculated from a meta-analysis of roadside observations that are normalized to fuel use, most of which were collected by the University of Denver [*Bishop and Stedman*, 2008, 2014] at cities around the U.S., and at the Caldecott Tunnel in Oakland, California [*Kirchstetter et al*., 1996; *Kean et al*., 2002; *Ban-Weiss et al*., 2008; *Dallmann et al*., 2013]. The fuel-based mobile source emissions differ from conventional inventory approaches used by the U.S. EPA and CARB in that vehicle activity is quantified on the basis of the amount of fuel consumed and emission factors are expressed per unit of fuel burned, rather than as a function of vehicle distance traveled. The fuel-based approach is also novel because it relies on emission factor observations of vehicles under real-world driving conditions, in contrast to conventional approaches based on representative sampling of a few vehicles under idealized conditions (e.g., using dynamometers). CARB's official inventory quantifies emissions from other anthropogenic sectors, including stationary and area sources [*California Air Resources Board*, 2009, 2013b], which represent a minor fraction of the LA Basin's total NO_x and CO emissions during the period of interest. A detailed description of our long-term LA Basin inventory is provided in the supporting information (Text S3).

3. Results and Discussion

3.1. Los Angeles Basin and Other U.S. Cities

Figure 1a shows ambient NO_x/CO enhancement ratios derived from measurement platforms deployed in the LA Basin over the past 50 years. The variation in NO_x/CO enhancement ratios measured at different CARB stations across the basin in any given year reflects the precise mix of sources sampled at each site. For the

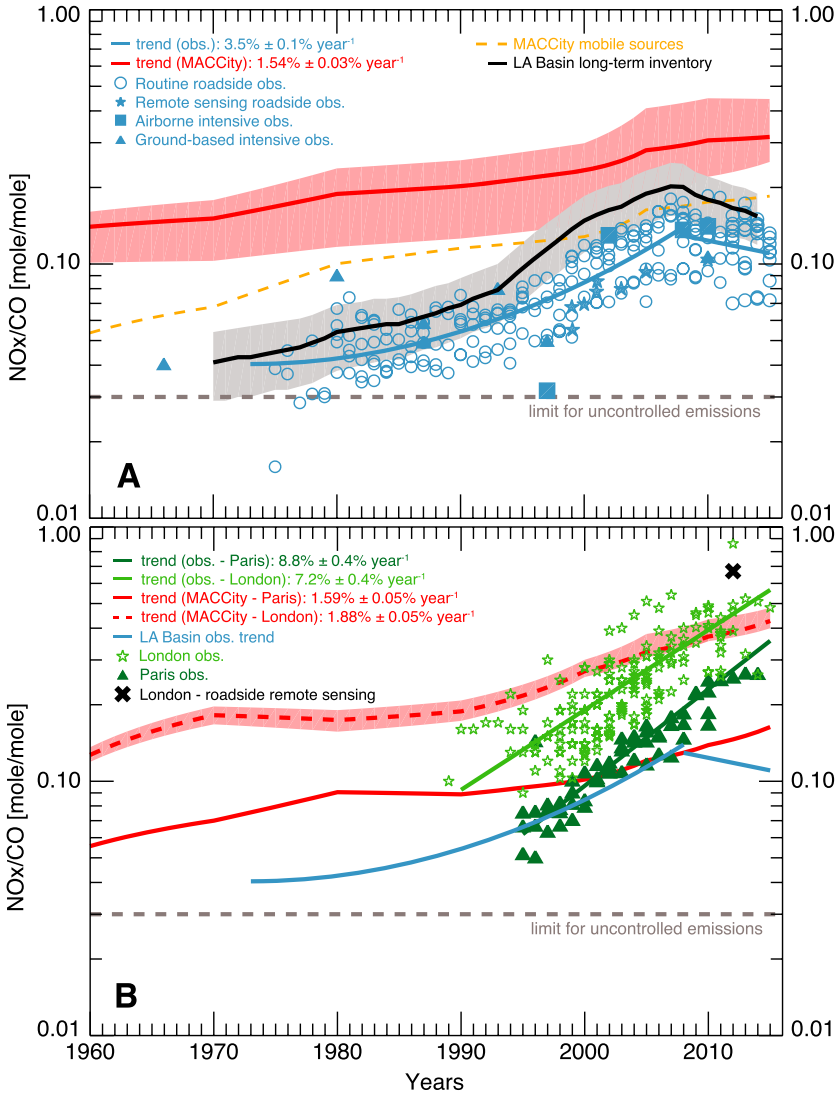

Figure 1. (a) Measured NO_x/CO enhancement ratios for the LA Basin from 10 CARB monitoring stations (blue circles), from remote sensing at West LA roadways (blue stars), and from airborne (blue squares) and ground-based (blue triangles) platforms during intensive field campaigns, along with a combination of a quadratic and linear fit to the logarithm of the observed ratios (blue line). Also shown are our LA Basin long-term inventory's NO_x/CO total emissions ratios (black line) with their 1σ uncertainties (gray shading), the MACCity average NO_x/CO total emissions ratios for the entire LA Basin (thick red line) and for each of the six grid cells in the LA Basin (red shading), and the average MACCity NO_x/CO mobile source emission ratio of the LA Basin (orange thick dashed line). The NO_x/CO ratio for uncontrolled gasoline vehicle emissions (= 0.03) is also shown (dotted gray line). (b) NO_x/CO enhancement ratios from hourly roadside monitor measurements at four Paris stations (dark green symbols) and 17 stations in London (light green stars), along with log-linear trends for the Paris (green dark line) and London (green light line) monitoring data. The trend for the LA Basin observations from Figure 1 a is shown for comparison (blue line). Also shown are MACCity NO_x/CO emissions ratios for Paris (solid red line) and averaged for all London grid cells (dashed red line) and the range for individual London grid cells (red shading). The fleet-weighted average NO_x/CO ratio from roadway remote sensing at four London sites in 2012 is denoted with a black cross.

same reason, ratios measured at these LA Basin stations differ somewhat from those observed by roadside remote sensing and from research intensive measurements collected at ground sites and across the entire basin using aircraft sampling (Figure 1a).

Taken together, NO_x/CO enhancement ratio observations from these different platforms present a consistent long-term trend (Figure 1a). The average 1965–2015 growth rate of the LA Basin ambient NO_x/CO ratio (i.e., the slope of a log-linear fit to the ratios as a function of year) is $3.5\% \pm 0.1\%\,yr^{-1}$ (all uncertainties are 1σ

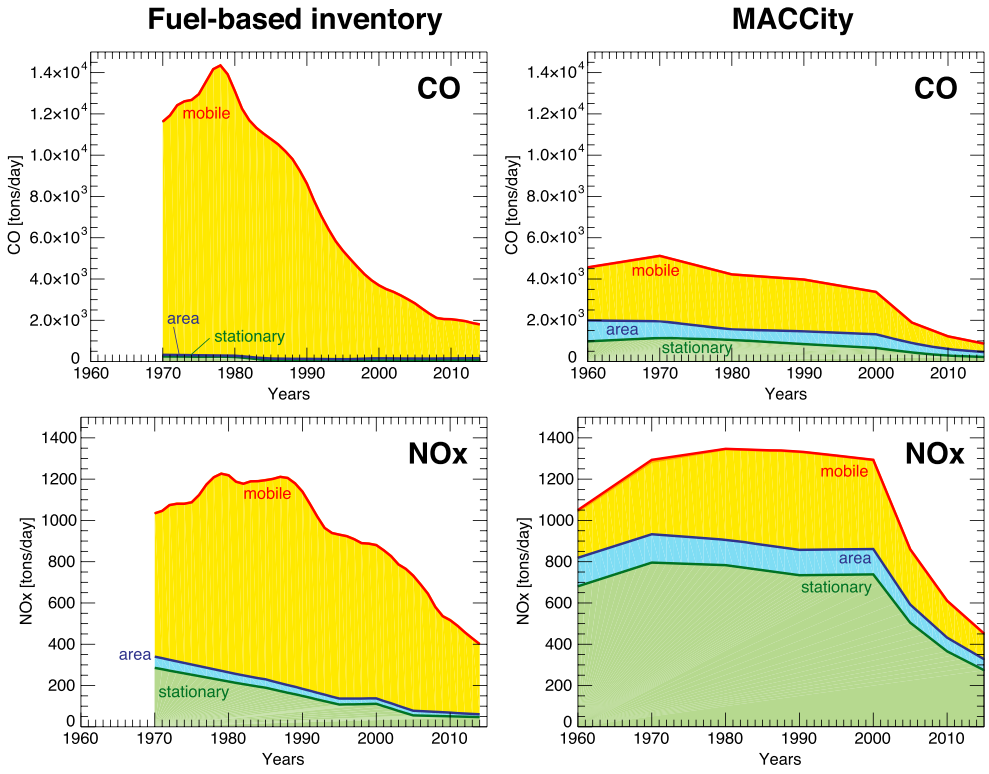

Figure 2. (top row) Total cumulative LA Basin annual CO emissions (given in t/d) from different sectors (left column) in our fuel-based inventory and (right column) in MACCity, with solid lines and colored areas representing the contributions from mobile (red/yellow), area (dark blue/light blue), and stationary sources (dark green/light green). (bottom row) Total cumulative LA Basin annual NO_x emissions (given in t/d) from our fuel-based inventory (Figure 2, left column) and MACCity (Figure 2, right column), with sectoral contributions indicated as in Figure 2 (top row).

uncertainties on the trend fit coefficient). This increase is smaller than the 1960–2010 average growth rate reported by POL13 ($4.9\% \pm 0.4\%\ yr^{-1}$; see Figure 6 in POL13). The 1965–2015 evolution of LA Basin ambient ln(NO_x/CO) is more closely fit with a combination of a quadratic and linear fit than a straight line (Figure 1a). The observed LA Basin NO_x/CO ratio increases slowly from 1970 to 1995, followed by a steeper increase until 2007 (described by a quadratic fit), and has begun to decrease since then (described by a linear fit). Differences from POL13 in the LA Basin NO_x/CO 1965–2015 trend result from using additional CARB monitoring sites and extending the data record to more recent years.

Our long-term fuel-based LA Basin NO_x/CO inventory emission ratios lie on the upper edge of the range of observed enhancement ratios (Figure 1a), and our inventory's 1970–2015 evolution is consistent with that of the observations. Our inventory captures the dominance of motor vehicles on the LA Basin's NO_x and CO emissions over this 45 year period (Figure 2). The first U.S. tailpipe emission standards were adopted in California in 1966. *Harley et al.* [1997] estimated that uncontrolled light-duty gasoline vehicles (LDGVs) have a molar NO_x/CO emissions ratio of 0.03. LDGV emissions of CO, VOCs, and NO_x decreased between 1970 and the mid-1990s due to the implementation of three-way catalytic converters, which simultaneously oxidize CO and VOCs and reduce NO_x, and due to modifications in vehicle fuels and engines [*Kirchstetter et al.*, 1996, 1999; *Sawyer et al.*, 2000]. NO_x/CO ratios have generally increased since 1970 because CO emissions from gasoline-powered vehicles decreased faster than those of NO_x [*Parrish et al.*, 2011], because the earliest two-way catalytic converters controlled CO and VOC emissions only. The steeper NO_x/CO trend in our inventory between the mid-1990s and mid-2000s results from faster decline in LDGV CO emissions relative to NO_x [*McDonald et al.*, 2013] and the increasing importance of higher NO_x-emitting heavy-duty diesel vehicles (HDDVs) [*Bishop and Stedman*, 2008; *McDonald et al.*, 2012, 2013]. Decreasing NO_x/CO after 2007 reflects the influence of the U.S. economic recession on freight traffic (which decreased NO_x emissions), the

beginning of the implementation of new HDDV NO_x emission control technologies, e.g., by selective catalytic reduction (SCR) systems [*Bishop et al*., 2015], and initial implementation of Tier two emission standards on U.S. light-duty vehicles where NO_x controls were emphasized in the regulations [*Bishop and Stedman*, 2015].

It is unclear why the NO_x/CO emissions ratio from this study is systematically higher than the ambient observations from weekday mornings. However, it is possible that congestion-related impacts, prevalent during the morning commute, could affect these differences. Severe congestion is estimated to increase the amount of fuel burned in the Los Angeles basin by 7–12% [*Barth and Boriboonsomsin*, 2008]. This would disproportionately impact gasoline vehicles, as diesel trucks avoid driving during morning and evening commuting periods [*McDonald et al*., 2014]. Because gasoline engines have lower NO_x/CO emissions than diesel engines, increasing gasoline emissions relative to diesel would bring our NO_x/CO emissions closer to the ambient observations. Under hard acceleration, gasoline engines can also become fuel-enriched, which significantly increases the emission factor of CO relative to NO_x (or lowers NO_x/CO emissions) [*Bishop and Stedman*, 2008; *Lee and Frey*, 2012]. The frequency of hard accelerations during congestion is unlikely to be fully captured by roadway studies used in this analysis. Lastly, it is also possible that the fleet of vehicles traveling during the morning commute period is newer than the typical fleet, which has more effective NO_x control technologies installed than older vehicles [*Bishop and Stedman*, 2015].

Our multidecadal LA Basin inventory (Figures 1a and 2) has already been independently evaluated. Using this inventory as input to a regional chemical transport model enabled accurate prediction of CO and NO_x concentrations in the LA Basin during the 2010 CalNex field campaign [*Kim et al*., 2016]. From CalNex data and observations from a 2002 aircraft campaign in California, *Brioude et al*. [2013] estimated 2002–2010 reductions in LA Basin CO and NO_x emissions of 41% and 37%, respectively, in good agreement with our inventory's predicted declines of 44% and 41%, respectively [*McDonald et al*., 2012, 2013]. Between 2005 and 2014, our inventory's NO_x emissions declined 45.3% ± 10.9%, in agreement with a reduction in satellite-derived NO_2 columns of 56.4% ± 5.6% over Los Angeles [*Duncan et al*., 2016].

Figure 1a also shows MACCity's NO_x/CO anthropogenic emissions ratio averaged for the LA Basin and the ratio's variation across the six grid cells encompassing the LA Basin. The 1960–2015 increase in MACCity's NO_x/CO emissions ratio is 1.54% ± 0.03% yr^{-1}, less than half of the observed NO_x/CO growth rate. MACCity's NO_x/CO emission ratio is also higher than observed enhancement ratios throughout the entire time period by a factor of 2–5, suggesting a significant overestimate of NO_x emissions and/or an underestimate of CO emissions. Compared to our inventory, MACCity's total CO emissions are much lower and total NO_x emissions are somewhat higher (Figure 2). Also, in contrast to our LA Basin inventory and the observed trends, MACCity's NO_x/CO emissions ratio increases monotonically and does not decline after 2007.

When considering mobile source emissions only (Figure 1a), the MACCity LA Basin NO_x/CO emissions ratios are still higher than the 1960–2000 observations and increase too slowly (2.2% ± 0.05% yr^{-1}). MACCity mobile source CO and NO_x emissions are much less, and CO emissions decreasing too slowly, compared to those derived from our fuel-based inventory (Figure 2). Since the mobile source emissions dominate LA Basin emissions in the fuel-based inventory, and the fuel-based emissions are closer to ambient observations during weekday mornings, we infer that MACCity does not accurately capture the city's motor vehicle emissions and their trends.

Additionally, MACCity's area and stationary source emissions of NO_x are much higher than the CARB estimates used in this study. The incorrect MACCity sector partitioning likely reflects errors arising from the use of a small number of generic spatial surrogates (e.g., population) to allocate national-level emissions to urban scales [*Lamarque et al*., 2010; *Granier et al*., 2011]. This spatial allocation scheme can also be problematic for large stationary sources, which may be located outside major urban areas.

The long-term trends in observed NO_x/CO enhancement ratios and their differences with MACCity emissions ratios seen in the LA Basin persist for seven other U.S. metropolitan areas with populations of 100,000–20,000,000 (see supporting information Text S1 and Figure S6). Measured NO_x/CO enhancement ratios from air quality monitoring and intensive field studies in a variety of U.S. cities show similar 1989–2013 trends as those measured in the LA Basin. Like in the LA Basin, average annual increases in the observed NO_x/CO in all U.S. cities considered here over the past 25 years (4.1% ± 0.2% yr^{-1}) are steeper than for MACCity emissions ratios (1.45% ± 0.06% yr^{-1}), which are also higher than the ambient ratios by factors of 2–5. We therefore

reach some general results for the U.S. cities considered here: the long-term trend in NO_x/CO enhancement ratios is driven by changes in motor vehicle emissions, and MACCity does not accurately capture changes in motor vehicle emissions over the past several decades and the urban-scale spatial distribution of the dominant emission sectors.

3.2. London and Paris

To understand how NO_x and CO emissions have changed over time in megacities outside the U.S., we consider NO_x/CO enhancement ratios recorded at monitoring stations in London (1989–2015) and Paris (1995–2014) and by roadside remote sensing in 2012 in London (Figure 1b). The combined data from different monitoring sites within London or Paris show a consistent interannual trend, with station-to-station variations in any given year in each city similar to those seen in Los Angeles. The growth rates in the observed NO_x/CO enhancement ratios for London and Paris are $7.2\% \pm 0.4\%\ yr^{-1}$ and $8.8\% \pm 0.4\%\ yr^{-1}$, respectively, about twice the average growth rate observed in U.S. cities. In London, observed NO_x/CO ratios are higher than those in the LA Basin, and the same is true of Paris for the past decade or so. The fleet-averaged emission ratio of NO_x/CO, based on the analysis from roadway remote sensing measurements at four London sites in 2012 [*Carslaw and Rhys-Tyler*, 2013], was 0.67 mol/mol, which compares well with London's monitoring data (Figure 1b).

Like the U.S., most heavy-duty vehicles in Europe use diesel fuel. However, in contrast to the predominance of gasoline fuel in U.S. light-duty vehicles, European nations have incentivized the use of light-duty diesel vehicles (LDDVs) to increase fuel economy and decrease CO_2 emissions. There are now similar numbers of LDGVs and LDDVs in the UK [*Carslaw et al*., 2011], where overall diesel currently accounts for the majority of transportation fuel burned [*Dunmore et al*., 2015]. France and other European countries have similarly high diesel usage in their vehicle fleets [*Weiss et al*., 2012; *Dunmore et al*., 2015]. European vehicle fleets have correspondingly higher NO_x emissions and lower CO emissions than in the U.S., as demonstrated by the London and Paris observations (Figure 1b). Higher NO_x/CO enhancement ratios in London compared to Paris also reflect measures to control congestion in central London, such as charging tolls on passenger vehicles, which encourage a higher fraction of diesel-powered buses and taxis in London compared to other European cities.

Interestingly, observed NO_x/CO enhancement ratios continue to climb in London and Paris in recent years despite more stringent controls implemented on motor vehicle NO_x emissions. Recent evidence [*Carslaw et al*., 2011; *Carslaw and Rhys-Tyler*, 2013] suggests that diesel vehicle emission controls have not been as effective as predicted, although the reasons for this observed behavior are unclear. Measurements of European Emission Standards 4 to 6 (Euro 4–6) LDDVs showed higher NO_x emissions on roadways compared to laboratory tests [*Chen and Borken-Kleefeld*, 2014]. While the newest Euro 6 SCR systems for LDDVs show promise in reducing on-road NO_x emissions compared to earlier Euro 4–5 technology, real-world tests of Euro 4–6 vehicles demonstrate that all can exceed European NO_x emissions standards [*Weiss et al*., 2012]. Meanwhile, NO_x concentrations near roadways in the UK have remained stable [*Carslaw et al*., 2011], and NO_x emissions from all diesel vehicle types in the UK have not declined much over the past two decades [*Carslaw and Rhys-Tyler*, 2013].

The observations presented in Figure 1b support the conclusions of these European studies, demonstrating that ambient air monitoring can detect trends in urban vehicle emissions. Agreement between the monitoring network and remote sensing observations in the LA Basin (Figure 1a) and in London (Figure 1b) further strengthens our conclusion that the long-term evolution of ambient NO_x/CO enhancement ratios in these cities are driven by motor vehicle emissions. Taken together, comparisons of observed NO_x/CO enhancement ratio trends in all cities considered here highlight the effect of different motor vehicle emissions control strategies pursued in the U.S. and Europe since the late 1990s. Before then, we might expect that the European emissions ratios would be similar to those in the LA Basin, because past European light-duty vehicle fleets had higher fractions of gasoline engines and relatively few diesels compared with recent years. However, Euro emissions standards began later than in the U.S., which may result in some differences between the U.S. and European trends prior to 1990.

MACCity captures the factor of 2–3 higher NO_x/CO emissions ratio in London compared to Paris seen in the ambient observations (Figure 1b). As in the U.S. cities studied here, increases in MACCity's NO_x/CO emissions ratio in London and Paris are smaller ($1.88\% \pm 0.05\%\ yr^{-1}$ and $1.59\% \pm 0.05\%\ yr^{-1}$, respectively) than the

observed trends in these cities ($7.2\% \pm 0.4\%\,yr^{-1}$ and $8.8\% \pm 0.4\%\,yr^{-1}$, respectively). London and Paris MACCity NO_x/CO emissions ratios are similar to observed enhancement ratios between 2000 and 2010. However, because of differing temporal trends, MACCity diverges from the observations in both cities before 2000 and after 2010. MACCity cannot be directly evaluated prior to 1990 in London or Paris due to the lack of available monitoring data for NO_x and CO. From 1970 to 1990, MACCity's NO_x/CO emissions ratio in both cities is higher than the curve fitted to the LA Basin observations (Figure 1b). Because we expect trends in London and Paris to be more similar to those in the LA Basin prior to 1990, we suggest that MACCity likely also overestimates NO_x/CO emissions ratios in European cities during this earlier time period.

4. Conclusions

We demonstrate that multidecadal observations of NO_x/CO enhancement ratios in source regions provide valuable information on emissions trends in U.S. and European megacities. In Los Angeles, agreement between a variety of measurement platforms and a long-term emissions inventory using a fuel-based approach for motor vehicles shows that the 1965–2015 evolution of ambient levels of NO_x and CO resulted from more stringent vehicle emission standards, the growing importance of heavy-duty diesel engines, and the influence of the 2008 economic recession. Similarities between Los Angeles NO_x/CO observations and those in seven other U.S. cities in the past 25 years indicate that the comparatively longer measurement record in Los Angeles can be used to understand the trends in U.S. motor vehicle emissions ratios over the past five decades. Comparisons of the past 25 years of NO_x/CO observations in London, Paris, and Los Angeles demonstrate the differences in these cities' vehicle fleets and highlight the atmospheric impacts of different emissions control strategies in Europe and the U.S. The long ambient monitoring record in London and Paris is consistent with recent observations showing higher-than-expected NO_x emissions from European diesel passenger vehicles.

Megacity observations provide a key constraint on global emissions inventories. Long-term trends in observed NO_x/CO enhancement ratios in Los Angeles, New York, London, and Paris are systematically higher than the trends in MACCity. In Los Angeles, comparisons of MACCity to our observationally validated fuel-based inventory show that MACCity underestimates motor vehicle CO emissions and incorrectly partitions emissions between mobile and nonmobile source sectors. The similarity of long-term MACCity NO_x/CO emissions trends in U.S. and European cities highlights a major challenge that must be addressed by global inventories: capturing important regional differences for key emission sectors around the world. Verification of transportation emissions is needed in other megacities, especially those with rapidly growing vehicle fleets. Fuel-based approaches employing roadway remote sensing of vehicles under real-world operating conditions, and using vehicle identification to correlate emissions with engine type, age, and control technology [*Bishop and Stedman*, 2008, 2015; *Carslaw and Rhys-Tyler*, 2013], could be replicated elsewhere.

Accurate long-term measurements of NO_x and CO are scarce or nonexistent in developing regions of the world, particularly in the rapidly changing cities of Asia, Latin America, and Africa. Accurate measurements from field campaigns outside the U.S. and Europe, e.g., in Tokyo and Mexico City [*Kondo et al*., 2010; *Parrish et al*., 2011; *Gallardo et al*., 2012], offer only brief snapshots when compared with the multidecadal measurement records discussed here. Recent findings [*Carslaw and Rhys-Tyler*, 2013; *Bishop and Stedman*, 2015] of higher-than-anticipated NO_x emissions from diesel passenger vehicles in Europe and the U.S. demonstrate that it is still difficult for developed nations to accurately assess their mobile fleet emissions by relying solely on laboratory testing of individual vehicles. The challenges are even greater for countries undergoing rapid economic changes that lack resources for systematic environmental monitoring and assessment.

Whether changes to MACCity indicated by our analysis will actually improve model simulations of tropospheric ozone is an open question. A critical issue is how well MACCity captures VOC emissions trends. Because CO and VOC emissions in the LA Basin are highly correlated [*Warneke et al*., 2012], we assume that MACCity's underestimation of CO emissions will translate to similar underestimates of VOC emissions, as was demonstrated for Beirut, Lebanon [*Salameh et al*., 2016]. Ozone predictions from different models in response to improved emissions estimates will also likely depend on model VOC emissions speciation and chemical mechanisms [*von Schneidemesser et al*., 2016]. Recent observations suggest that there are higher VOC

emissions from UK diesel vehicles than inventories report [*Dunmore et al*., 2015], further complicating efforts to accurately model ozone in global megacities.

MACCity is one example of a global emissions inventory used as input for global chemistry model simulations. The systematic differences with observations and inability to capture regional differences are likely not unique to MACCity, since global inventories rely on similar information about activity, emission factors, and spatial allocation. This study points to the utility of long-term urban atmospheric monitoring and analysis to critically evaluate emissions inventories and demonstrates the need for globally consistent bottom-up methods that incorporate regional knowledge about emissions sources. Constraining bottom-up emissions inventories against historical observations helps verify that the underlying emissions drivers are understood and gives confidence in using such methods to project future emissions, with attendant improvements in simulating future tropospheric composition, air quality, and climate impacts.

Acknowledgments
We thank ECCAD (Emissions of Atmospheric Compounds and Compilation of Ancillary Database, http://pole-ether.fr/eccad), which was used to download the MACCity emissions data. The contribution of AIRPARIF through access to their NOx and CO data is acknowledged. This study was supported in part by NOAA's Climate Program Office. The views expressed here do not necessarily reflect those of the participating agencies/organizations.

References

Ban-Weiss, G. A., J. P. McLaughlin, R. A. Harley, M. M. Lunden, T. W. Kirchstetter, A. J. Kean, A. W. Strawa, E. D. Stevenson, and G. R. Kendall (2008), Long-term changes in emissions of nitrogen oxides and particulate matter from on-road gasoline and diesel vehicles, *Atmos. Environ.*, *42*, 220–232, doi:10.1016/j.atmosenv.2007.09.049.

Barth, M., and K. Boriboonsomsin (2008), Real-world carbon dioxide impacts of traffic congestion, *Transport Res. Rec.*, *2058*, 163–171, doi:10.3141/2058-20.

Bishop, G. A., and D. H. Stedman (2008), A decade of on-road emissions measurements, *Environ. Sci. Technol.*, *42*(5), 1651–1656, doi:10.1021/es702413b.

Bishop, G. A., and D. H. Stedman (2014), The recession of 2008 and its impact on light-duty vehicle emissions in three western United States cities, *Environ. Sci. Technol.*, *48*, 14,822–14,827, doi:10.1021/es5043518.

Bishop, G. A., and D. H. Stedman (2015), Reactive nitrogen species emission trends in three light-/medium-duty United States fleets, *Environ. Sci. Technol.*, *49*(18), 11,234–11,240, doi:10.1021/acs.est.5b02392.

Bishop, G. A., B. G. Schuchmann, and D. H. Stedman (2013), Heavy-duty truck emissions in the South Coast air basin of California, *Environ. Sci. Technol.*, *47*, 9523–9529, doi:10.1021/es401487b.

Bishop, G. A., R. Hottor-Raguindin, D. H. Stedman, P. McClintock, E. Theobald, J. D. Johnson, D. W. Lee, J. Zietsman, and C. Misra (2015), On-road heavy-duty vehicle emissions monitoring system, *Environ. Sci. Technol.*, *49*, 1639–1645, doi:10.1021/es505534e.

Borbon, A., et al. (2013), Emission ratios of anthropogenic volatile organic compounds in northern mid-latitude megacities: Observations versus emission inventories in Los Angeles and Paris, *J. Geophys. Res. Atmos.*, *118*, 2041–2057, doi:10.1002/jgrd.50059.

Brioude, J., et al. (2011), Top-down estimate of anthropogenic emission inventories and their interannual variability in Houston using a mesoscale inverse modeling technique, *J. Geophys. Res.*, *116*, D20305, doi:10.1029/2011JD016215.

Brioude, J., et al. (2013), Top-down estimate of surface flux in the Los Angeles Basin using a mesoscale inverse modeling technique: Assessing anthropogenic emissions of CO, NO_x and CO_2 and their impacts, *Atmos. Chem. Phys.*, *13*, 3661–3677, doi:10.5194/acp-13-3661-2013.

Burgard, D. A., C. R. M. Bria, and J. A. Berenbeim (2011), Remote sensing of emissions from in-use small engine marine vessels, *Environ. Sci. Technol.*, *45*, 2894–2901, doi:10.1021/es1027162.

CARB (2007), *OFFROAD2007 Model*, California Air Resources Board, Sacramento, Calif. [Available at http://www.arb.ca.gov/msei/categories.html.]

California Air Resources Board (2009), *California Almanac of Emissions and Air Quality–2009 Edition*, California Air Resources Board, Sacramento, Calif. [Available at http://www.arb.ca.gov/aqd/almanac/almanac09/almanac09.htm.]

CARB (2013a), *California Motor Vehicle Emission Factor/Emission Inventory Model (EMFAC 2011)*, California Air Resources Board, Sacramento, Calif. [Available at http://www.arb.ca.gov/emfac/.]

California Air Resources Board (2013b), *CEPAM: 2013 Almanac—Standard Emissions Tool*, California Air Resources Board, Sacramento, Calif. [Available at http://www.arb.ca.gov/app/emsinv/fcemssumcat2013.php.]

Carslaw, D. C., and G. Rhys-Tyler (2013), New insights from comprehensive on-road measurements of NO_x, NO_2 and NH_3 from vehicle emission remote sensing in London, UK, *Atmos. Environ.*, *81*, 339–347, doi:10.1016/j.atmosenv.2013.09.026.

Carslaw, D. C., S. D. Beevers, J. E. Tate, E. J. Westmoreland, and M. L. Williams (2011), Recent evidence concerning higher NO_x emissions from passenger cars and light duty vehicles, *Atmos. Environ.*, *45*, 7053–7063, doi:10.1016/j.atmosenv.2011.09.063.

Chen, Y., and J. Borken-Kleefeld (2014), Real-driving emissions from cars and light commercial vehicles: Results from 13 years remote sensing at Zurich/CH, *Atmos. Environ.*, *88*, 157–164, doi:10.1016/j.atmosenv.2014.01.040.

Cooper, O. R., et al. (2014), Global distribution and trends of tropospheric ozone: An observation-based review, *Elementa*, *2*, 000029, doi:10.12952/journal.elementa.000029.

Dallmann, T. R., and R. A. Harley (2010), Evaluation of mobile source emission trends in the United States, *J. Geophys. Res.*, *115*, D14305, doi:10.1029/2010JD013862.

Dallmann, T. R., T. W. Kirchstetter, S. J. DeMartini, and R. A. Harley (2013), Quantifying on-road emissions from gasoline-powered motor vehicles: Accounting for the presence of medium- and heavy-duty diesel trucks, *Environ. Sci. Technol.*, *47*, 13,873–13,881, doi:10.1021/Es402875u.

Derwent, R. G., J. I. R. Dernie, G. J. Dollard, P. Dumitrean, R. F. Mitchell, T. P. Murrells, S. P. Telling, and R. A. Field (2014), Twenty years of continuous high time resolution volatile organic compound monitoring in the United Kingdom from 1993 to 2012, *Atmos. Environ.*, *99*(C), 239–247, doi:10.1016/j.atmosenv.2014.10.001.

Dollard, G. J., P. Dumitrean, S. Telling, J. Dixon, and R. G. Derwent (2007), Observed trends in ambient concentrations of C2–C8 hydrocarbons in the United Kingdom over the period from 1993 to 2004, *Atmos. Environ.*, *41*, 2559–2569, doi:10.1016/j.atmosenv.2006.11.020.

Duncan, B. N., L. N. Lamsal, A. M. Thompson, Y. Yoshida, Z. Lu, D. G. Streets, M. M. Hurwitz, and K. E. Pickering (2016), A space-based, high-resolution view of notable changes in urban NO_x pollution around the world (2005–2014), *J. Geophys. Res. Atmos.*, *121*, 976–996, doi:10.1002/2015JD024121.

Dunmore, R. E., J. R. Hopkins, R. T. Lidster, J. D. Lee, M. J. Evans, A. R. Rickard, A. C. Lewis, and J. F. Hamilton (2015), Diesel-related hydrocarbons can dominate gas phase reactive carbon in megacities, *Atmos. Chem. Phys.*, *15*, 9983–9996, doi:10.5194/acp-15-9983-2015.

EIA (2015), *California Adjusted Distillate Fuel Oil and Kerosene Sales by End Use, Energy Information Administration*, U.S. Dep. of Energy, Washington, D. C. [Available at http://www.eia.gov/dnav/pet/pet_cons_821usea_dcu_SCA_a.htm.]
Eyring, V., et al. (2013), Overview of IGAC/SPARC Chemistry-Climate Model Initiative (CCMI) community simulations in support of upcoming ozone and climate assessments, *SPARC Newsl.*, *40*, 48–66.
FHWA (2014a), *Highway Statistics: Motor-Fuel Volume Taxed by States (Table MF-2), Office of Highway Policy Information, Federal Highway Administration*, U.S. Dep. of Transportation, Washington, D. C. [Available at http://www.fhwa.dot.gov/policyinformation/statistics.cfm.]
FHWA (2014b), *Highway Statistics: Non-Highway Use of Gasoline (Table MF-24), Office of Highway Policy Information, Federal Highway Administration*, U.S. Dep. of Transportation, Washington, D. C. [Available at http://www.fhwa.dot.gov/policyinformation/statistics.cfm.]
Gallardo, L., J. Escribano, L. Dawidowski, N. Rojas, M. de Fátima Andrade, and M. Osses (2012), Evaluation of vehicle emission inventories for carbon monoxide and nitrogen oxides for Bogotá, Buenos Aires, Santiago, and São Paulo, *Atmos. Environ.*, *47*, 12–19, doi:10.1016/j.atmosenv.2011.11.051.
Gordon, T. D., et al. (2013), Primary gas- and particle-phase emissions and secondary organic aerosol production from gasoline and diesel off-road engines, *Environ. Sci. Technol.*, *47*, 14,137–14,146, doi:10.1021/Es403556e.
Granier, C., et al. (2011), Evolution of anthropogenic and biomass burning emissions of air pollutants at global and regional scales during the 1980–2010 period, *Clim. Change*, *109*(1–2), 163–190, doi:10.1007/s10584-011-0154-1.
Harley, R. A., R. F. Sawyer, and J. B. Milford (1997), Updated photochemical modeling for California's South Coast Air Basin: Comparison of chemical mechanisms and motor vehicle emission inventories, *Environ. Sci. Technol.*, *31*, 2829–2839, doi:10.1021/Es9700562.
Intergovernmental Panel on Climate Change (2013), *Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*, edited by T. F. Stocker, et al., 1535 pp., Cambridge Univ. Press, Cambridge, U. K., and New York, doi:10.1017/CBO9781107415324.
Kean, A. J., R. F. Sawyer, R. A. Harley, and G. R. Kendall (2002), Trends in exhaust emissions from in-use California light-duty vehicles, 1994-2001, SAE SP, 167-174.
Kim, S.-W., et al. (2016), Modeling the weekly cycle of NO_x and CO emissions and their impacts on O_3 in the Los Angeles-South Coast Air Basin during the CalNex 2010 field campaign, *J. Geophys. Res. Atmos.*, *120*, 1340–1360, doi:10.1002/2015JD024292.
Kirchstetter, T. W., B. C. Singer, R. A. Harley, G. R. Kendall, and W. Chan (1996), Impact of oxygenated gasoline use on California light-duty vehicle emissions, *Environ. Sci. Technol.*, *30*, 661–670, doi:10.1021/es950406p.
Kirchstetter, T. W., B. C. Singer, R. A. Harley, G. R. Kendall, and M. Traverse (1999), Impact of California reformulated gasoline on motor vehicle emissions. 1. Mass emission rates, *Environ. Sci. Technol.*, *33*, 318–328, doi:10.1021/es9803714.
Kondo, Y., et al. (2010), Formation and transport of aerosols in Tokyo in relation to their physical and chemical properties: A review, *J. Meteorol. Soc. Jpn.*, *88*, 597–624, doi:10.2151/jmsj.2010-401.
Lamarque, J.-F., et al. (2010), Historical (1850–2000) gridded anthropogenic and biomass burning emissions of reactive gases and aerosols: Methodology and application, *Atmos. Chem. Phys.*, *10*, 7017–7039, doi:10.5194/acp-10-7017-2010.
Lee, T., and H. C. Frey (2012), Evaluation of representativeness of site-specific fuel-based vehicle emission factors for route average emissions, *Environ. Sci. Technol.*, *46*, 6867–6873, doi:10.1021/Es204451z.
Logan, J. A., et al. (2012), Changes in ozone over Europe: Analysis of ozone measurements from sondes, regular aircraft (MOZAIC) and alpine surface sites, *J. Geophys. Res.*, *117*, D09301, doi:10.1029/2011JD016952.
McDonald, B. C., T. R. Dallmann, E. W. Martin, and R. A. Harley (2012), Long-term trends in nitrogen oxide emissions from motor vehicles at national, state, and air basin scales, *J. Geophys. Res.*, *117*, D00V18, doi:10.1029/2012JD018304.
McDonald, B. C., D. R. Gentner, A. H. Goldstein, and R. A. Harley (2013), Long-term trends in motor vehicle emissions in US urban areas, *Environ. Sci. Technol.*, *47*(17), 10,022–10,031, doi:10.1021/es401034z.
McDonald, B. C., Z. C. McBride, E. W. Martin, and R. A. Harley (2014), High-resolution mapping of motor vehicle carbon dioxide emissions, *J. Geophys. Res. Atmos.*, *119*, 5283–5298, doi:10.1002/2013JD021219.
McDonald, B. C., A. H. Goldstein, and R. A. Harley (2015), Long-term trends in California mobile source emissions and ambient concentrations of black carbon and organic aerosol, *Environ. Sci. Technol.*, *49*, 5178–5188, doi:10.1021/es505912b.
Monks, P. S., et al. (2015), Tropospheric ozone and its precursors from the urban to the global scale from air quality to short-lived climate forcer, *Atmos. Chem. Phys.*, *15*, 8889–8973, doi:10.5194/acp-15-8889-2015.
Nassar, R., L. Napier-Linton, K. R. Gurney, R. J. Andres, T. Oda, F. R. Vogel, and F. Deng (2013), Improving the temporal and spatial distribution of CO_2 emissions from global fossil fuel emission data sets, *J. Geophys. Res. Atmos.*, *118*, 917–933, doi:10.1029/2012JD018196.
Neuman, J. A., et al. (2006), Reactive nitrogen transport and photochemistry in urban plumes over the North Atlantic Ocean, *J. Geophys. Res.*, *111*, D23S54, doi:10.1029/2005JD007010.
Parrish, D. D. (2006), Critical evaluation of US on-road vehicle emission inventories, *Atmos. Environ.*, *40*, 2288–2300, doi:10.1016/j.atmosenv.2005.11.033.
Parrish, D. D., M. Trainer, D. Hereid, E. J. Williams, K. J. Olszyna, R. A. Harley, J. F. Meagher, and F. C. Fehsenfeld (2002), Decadal change in carbon monoxide to nitrogen oxide ratio in US vehicular emissions, *J. Geophys. Res.*, *107*(D12), 4140, doi:10.1029/2001JD000720.
Parrish, D. D., W. C. Kuster, M. Shao, Y. Yokouchi, Y. Kondo, P. D. Goldan, J. A. de Gouw, M. Koike, and T. Shirai (2009), Comparison of air pollutant emissions among mega-cities, *Atmos. Environ.*, *43*(40), 6435–6441, doi:10.1016/j.atmosenv.2009.06.024.
Parrish, D. D., H. B. Singh, L. Molina, and S. Madronich (2011), Air quality progress in North American megacities: A review, *Atmos. Environ.*, *45*, 7014–2025, doi:10.1016/j.atmosenv.2011.09.039.
Parrish, D. D., et al. (2014), Long-term changes in lower tropospheric baseline ozone concentrations: Comparing chemistry-climate models and observations at northern midlatitudes, *J. Geophys. Res. Atmos.*, *119*, 5719–5736, doi:10.1002/(ISSN)2169-8996.
Pollack, I. B., T. B. Ryerson, M. Trainer, J. A. Neuman, J. M. Roberts, and D. D. Parrish (2013), Trends in ozone, its precursors, and related secondary oxidation products in Los Angeles, California: A synthesis of measurements from 1960 to 2010, *J. Geophys. Res. Atmos.*, *118*, 5893–5911, doi:10.1002/jgrd.50472.
Salameh, T., S. Sauvage, C. Afif, A. Borbon, and N. Locoge (2016), Source apportionment vs. emission inventories of non-methane hydrocarbons (NMHC) in an urban area of the Middle East: Local and global perspectives, *Atmos. Chem. Phys.*, *16*, 3595–3607, doi:10.5194/acp-16-3595-2016.
Sawyer, R. F., R. A. Harley, S. H. Cadle, J. M. Norbeck, R. Slott, and H. A. Bravo (2000), Mobile sources critical review: 1998 NARSTO assessment, *Atmos. Environ.*, *34*, 2161–2181, doi:10.1016/S1352-2310(99)00463-X.
Schultz, M. G., et al. (2008), REanalysis of the TROpospheric chemical composition over the past 40 years: Emission data sets and methodologies for estimating emissions, Report on Work Package 1, Deliverable D1-6, EU-Contract No. EVK2-CT-2002-00170. [Available at http://retro-archive.iek.fz-juelich.de/data/documents/reports/D1-6_final.pdf.]

Singer, B. C., and R. A. Harley (1996), A fuel-based motor vehicle emission inventory, *J. Air Waste Manage. Assoc.*, *46*(6), 581–593.
Van Aardenne, J. A., F. J. Dentener, J. G. J. Olivier, C. G. M. Klein Goldewijk, and J. Lelieveld (2001), A 1 × 1 degree resolution dataset of historical anthropogenic trace gas emissions for the period 1890–1990, *Global Biogeochem. Cycles*, *15*(4), 909–928, doi:10.1029/2000GB001265.
Volckens, J., J. Braddock, R. F. Snow, and W. Crews (2007), Emissions profile from new and in-use handheld, 2-stroke engines, *Atmos. Environ.*, *41*, 640–649, doi:10.1016/j.atmosenv.2006.08.033.
von Schneidemesser, E., P. S. Monks, and C. Plass-Duelmer (2010), Global comparison of VOC and CO observations in urban areas, *Atmos. Environ.*, *44*(39), 5053–5064, doi:10.1016/j.atmosenv.2010.09.010.
von Schneidemesser, E., J. Coates, H. A. C. Denier van der Gon, A. J. H. Visschedijk, and T. M. Butler (2016), Variation of the NMVOC speciation in the solvent sector and the sensitivity of modelled tropospheric ozone, *Atmos. Environ.*, *135*, 59–27, doi:10.1016/j.atmosenv.2016.03.057.
Warneke, C., J. A. de Gouw, J. S. Holloway, J. Peischl, T. B. Ryerson, E. Atlas, D. Blake, M. Trainer, and D. D. Parrish (2012), Multiyear trends in volatile organic compounds in Los Angeles, California: Five decades of decreasing emissions, *J. Geophys. Res.*, *117*, D00V17, doi:10.1029/2012JD017899.
Weiss, M., et al. (2012), Will Euro 6 reduce the NO_x emissions of new diesel cars? Insights from on-road tests with Portable Emissions Measurement Systems (PEMS), *Atmos. Environ.*, *62*, 657–665, doi:10.1016/j.atmosenv.2012.08.056.
Yanowitz, J., R. L. McCormick, and M. S. Graboski (2000), In-use emissions from heavy-duty diesel vehicles, *Environ. Sci. Technol.*, *34*, 729–740, doi:10.1021/Es990903w.
Young, P. J., et al. (2013), Pre-industrial to end 21st century projections of tropospheric ozone from the Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP), *Atmos. Chem. Phys.*, *13*, 2063–2090, doi:10.5194/acp-13-2063-2013.