Lawrence Berkeley National Laboratory

Recent Work

Title

Spatial and Temporal Variations in Characteristic Ratios of Elemental Carbon to Carbon Monoxide and Nitrogen Oxides across the United States

Permalink

<https://escholarship.org/uc/item/8kg7h1hx>

Journal

Environmental Science and Technology, 51(12)

ISSN

0013-936X

Authors

Raman, A
Arellano, AF

Publication Date

2017-06-20

DOI

10.1021/acs.est.7b00161

Peer reviewed

Spatial and Temporal Variations in Characteristic Ratios of Elemental Carbon to Carbon Monoxide and Nitrogen Oxides across the United States

Aishwarya Raman^{id} and Avelino F. Arellano Jr.

Department of Hydrology and Atmospheric Sciences, University of Arizona, Tucson, Arizona 85721, United States

DOI: 10.1021/acs.est.7b00161

Publication Date (Web): May 26, 2017

*E-mail: aishwaryaraman@email.arizona.edu.

Abstract

A ratio-based method is used to characterize anthropogenic elemental carbon (EC_a) using in situ measurements and emissions of carbon monoxide (CO) and nitrogen oxides (NO_x). We use long-term records of ground-based measurements from the U.S. Environmental Protection Agency (EPA) Air Quality System and Interagency Monitoring of Protected Visual Environments to assess the patterns in anthropogenic combustion ratios ($\Delta EC_a/\Delta CO$ and $\Delta EC_a/\Delta NO_x$) across the U.S. Petroleum Administration for Defense Districts (PADD) regions for the years 2000–2015. We investigate the change in these ratios between the periods 2000–2007 and 2008–2015. Overall, $\Delta EC_a/\Delta CO$ ratios increase by 0.7–82% and $\Delta EC_a/\Delta NO_x$ by 6.8–104% across the East and West PADD regions. The urban West showed the largest increase relative to other regions. This is mainly attributed to a 13–

23% increase in ΔEC_a during the winter and fall seasons and significant reductions in urban ΔNO_x (except in winter). We also find that emission ratios derived from the EPA's National Emission Inventory (NEI) overestimate (underestimate) the increase in the observed enhancement ratios in the East (West). Analyses of changes in NEI emissions in the West reveal (a) smaller reductions in NEI emissions for NO_x from the off-road sector and (b) an increase in $PM_{2.5}$ (particulate matter 2.5 μm or less in diameter) emissions from commercial/residential combustion and smaller reductions in nonroad emissions.

Introduction

Aerosol black carbon (BC) is one of the dominant light-absorbing carbonaceous aerosols contributing to particulate matter (PM) pollution.⁽¹⁻⁴⁾ BC is emitted during incomplete combustion of fossil fuel, biofuel, and biomass.^(5, 6) It is considered as the second largest anthropogenic climate-forcing constituent next to CO_2 .^(7, 8) It has been suggested in recent studies that reducing BC emissions can shorten the rate of near-term climate change due to its shorter lifetime, which is on the order of days.⁽⁷⁻¹¹⁾ BC is also important to snow–ice albedo,⁽¹²⁾ atmospheric visibility, regional monsoonal circulation,⁽¹³⁾ and cardiovascular mortality.^(14, 15) BC contains other light-absorbing carbon components such as elemental carbon (EC).⁽¹⁶⁾ If the light-absorbing, nonvolatile, and refractory fraction is measured by thermal/optical methods,^(17, 18) it is called apparent elemental carbon (EC_a).⁽⁶⁾

In North America, key anthropogenic sources of BC include transportation/mobile (>50%) emissions followed by energy/power sources (~7%) and residential combustion (~4%).⁽¹⁹⁻²¹⁾ Major mobile sources of BC include on-road and off-road light-duty vehicles fueled by gasoline and heavy-duty trucks fueled by diesel.⁽²²⁻²⁴⁾ Heavy-duty diesel vehicles emit more fine particles per unit of mass of fuel burned compared to gasoline vehicles.⁽²⁵⁾ During the past couple decades, drastic improvements have been made to reduce emissions from gasoline engines through the use of catalytic converters and adjustments in the air-to-fuel ratio.^(26, 27) On the other hand, reductions in BC, $PM_{2.5}$ (PM 2.5 μm or less in diameter), and NO_x (nitrogen oxides) emissions from diesel engines have not been significant^(28, 29) despite recent control measures such as improvements in fuel injection strategies,⁽³⁰⁾ use of selective catalytic reduction systems,^(31, 32) and use of diesel particle filters⁽³³⁻³⁵⁾ (U.S. Environmental Protection Agency (EPA) Heavy Duty Highway (HDH) rule). This poses a major concern because, unlike light-duty vehicles, where several combustion

products (CO, NO_x, and hydrocarbons such as CH₂O) are observed from both in situ and remotely sensed measurement networks,[\(36-39\)](#) limited studies in the past have been performed to characterize BC (or PM) emissions from heavy-duty trucks. Another major contributor to BC, residential and industrial biofuel combustion, has also been given little attention, and long-term trends of BC emissions from this source are also not clear.[\(40\)](#) Furthermore, currently available ground-based measurements of ambient BC are very limited.

Long-term measurements of carbonaceous aerosols for the United States are provided by Interagency Monitoring of Visually Protected Environments (IMPROVE)[\(41\)](#) and the Chemical Speciation Network (CSN) in rural and urban/suburban regions, respectively. These networks measure EC_a using thermal optical methods. Although EC_a and BC are not directly equal in magnitude, prior studies in U.S. cities have found them to be strongly correlated,[\(42-45\)](#) and BC measured by aethalometers was 24% less than EC measured by thermal/optical methods.[\(46\)](#) We use EC_a instead of BC because we have relatively more measurements for EC_a rather than for direct BC and because BC emissions in inventories are based on EC from source emission samples of PM.[\(47\)](#) However, EC_a measurements are sparse and vary in design and measurement strategies between the monitoring networks. This makes identification and comparison of emission sources more challenging.[\(48, 49\)](#)

Recent studies have explored proxies of BC to provide constraints on its emissions and distribution. For example, more easily measured species that are correlated with BC, such as CO,[\(50-57\)](#) SO₂,[\(58\)](#) and NO_x,[\(59\)](#) have been shown to be useful constraints. Similarly, ratios of EC_a with coemitted or collocated species can be derived from either the statistics of observed enhancements or emission inventories. These ratios along with measurements of CO, SO₂, and NO_x, estimates of fuel usage, and technological changes in combustion-related sectors can be used to infer distributions of sparsely observed EC_a.[\(4\)](#) In regions with limited EC_a measurements, the ratios and trends in the covariation of coemitted species can provide useful diagnostics on the effectiveness of emission control strategies and/or regulation policies (see, e.g., refs [27](#) and [60](#)). As has been noted by Parrish et al.,[\(27\)](#) it is nontrivial to make inferences given the spatiotemporal variation of these ratios due to variations in their sources and sinks (lifetime), as well as their dependencies on economic activities, technology, emission controls, and combustion practices. The success of using these ratios for this purpose hinges upon careful data analysis and interpretation.

The main goal of this study is to extend these recent studies of using CO and NO_x to characterize anthropogenic EC_a in the United States on the basis of CSN and IMPROVE measurements. In particular, we investigate the covariations of EC_a, CO, and NO_x across different geopolitical regions

in the United States during the recent decade. This is another proof-of-concept on the utility of these proxies to provide constraints on EC_a by indirectly augmenting the current observation system for EC_a . Here, we attempt to address the issue of the dependency of these variations on the scale and/or processes by localizing our analysis to specific conditions that represent dominant combustion patterns. Analysis of the “local” variations of $\Delta EC_a/\Delta CO$ and $\Delta EC_a/\Delta NO_x$ ratios offers an opportunity to extract information on combustion characteristics for a given “local” condition. Here, we hypothesize that if to a certain extent we can account for these dependencies through localization and for variations in sinks through data filtering, the seasonal variations in ratios (along with their enhancements) will reflect inherent differences in fuel usage (activity) and combustion practices (efficiency). We also make use of the contrast in policy regulations and economic activity before and after 2008, which marks the beginning of the economic recession.[\(61\)](#) We investigate the contrast in air quality regulatory advances, fuel sales, and fleet characteristics between the 2000–2007 and 2008–2015 periods and relate these to our analysis of covariations in EC_a , CO , and NO_x , along with global and regional emission inventories of these species.

Data and Methods

Ground-Based Ambient Concentration Data

We use daily average measurements of CO and NO_x volume mixing ratios (ppbv) for the years 2000–2015 from the U.S. EPA ground station network.[\(62\)](#) The EPA makes CO measurements by extracting a gas sample from a stack and passing it through a gas analyzer. The CO concentration in the sample is then retrieved using the absorption and interference effects in the infrared wavelengths.[\(63\)](#) NO_x is obtained as a sum of the NO and NO_2 concentrations. NO_2 concentrations are measured using the chemiluminescence federal reference method technique.[\(64-66\)](#) These measurements are obtained by reducing NO_2 to NO on a heated molybdenum substrate, followed by reaction of NO with ozone through the chemiluminescence method. Previous studies have noted that EPA NO_x can be used as a surrogate for actual ambient NO_x for long-term analyses and if the NO_x concentrations used are consistent throughout the study.[\(67\)](#) Measurements of the EC_a mass density ($\mu g\ m^{-3}$) are derived from IMPROVE[\(41, 42, 68-70\)](#) and EPA’s CSN ambient aerosol monitoring networks. IMPROVE monitors the use of thermal optical reflectance (TOR). Prior to 2007, CSN used thermal optical transmittance (TOT) and the National Institute of Occupational Safety and Health (NIOSH) protocol. Several studies pointed to underestimation of EC_a at CSN stations. To be consistent with IMPROVE samplers, starting from 2007 to 2009, CSN transitioned from TOT to TOR

and started using URG-3000N for carbon sampling and analysis.[\(16, 71-74\)](#) Here, we use an adjusted version of CSN data released by the EPA (parameter code 88321) that is consistent with IMPROVE at collocated stations.[\(75\)](#)

Enhancement Ratios

To account for seasonal variations in meteorology, we converted the EC_a mass density ($\mu\text{g m}^{-3}$) from IMPROVE and CSN to EC_a mass mixing ratio (ppbm) by dividing the mass density by the air density (kg m^{-3}) derived from temperature and pressure measurements available from the EPA. For every station, the background concentrations of EC_a (ppbm), NO_x (ppbv), and CO (ppbv) are estimated for individual seasons (summer (JJA), winter (DJF), fall (SON), and spring (MAM)) and years using the fifth percentile of available data following Kondo et al.[\(76\)](#) and Matsui et al.[\(77\)](#) These background concentrations were subtracted from the associated daily average ambient concentrations to derive seasonal species enhancement (Δ). The analyses of the ratios are performed only at collocated stations where EC_a and CO (or NO_x) data pairs are available. The stations are collocated using the EPA site ID parameter. The results are discussed separately for rural (IMPROVE) and urban (CSN) stations, thereby eliminating any analytical artifacts associated with combining IMPROVE and CSN data, although we are using adjusted CSN data throughout this study. To localize our analysis for anthropogenic combustion signatures and to account for EC_a sinks, we removed stations for every year/every month that were severely affected by biomass burning (BB) and wet deposition. Further details on data filtering are given in the [Supporting Information](#) (supplementary text).

After careful screening of days and stations affected by fires and wet deposition, we regress EC_a enhancements (ΔEC_a , ppbm) at a given station against those of CO (or NO_x) (ΔCO or ΔNO_x , ppbv) for every season in a given year using the reduced major axis (RMA) regression method.[\(78, 79\)](#) $y + e_2 = \beta_0 + \beta_1 x + e_1$ (1) Here, y represents the enhancements of EC_a and x represents CO or NO_x enhancements. This is a model II regression that takes into account errors in the independent (e_1) and dependent (e_2) variables. Only positive enhancements were used for the analyses as this study primarily focuses on anthropogenic combustion sources of EC_a . Stations that successfully passed the above criteria were also tested for data density before regression. Stations with a number of data points for a given year (and season) greater than 20 and with a statistically significant positive Pearson correlation coefficient ($r > 0.5$) were selected. The slopes and correlation values were tested for significance using Student's t test at the 95% confidence level.

Finally, we group the stations in our analyses on the basis of stations located within predefined geopolitical regions classified under the Petroleum Administration for Defense Districts (PADD) regions[\(80\)](#) since we are considering the potential relationship between these ratios and fuel

consumption. The extent of these regions is shown in Figure S2 ([Supporting Information](#)). Hereafter, we will refer to the PADD regions using the following abbreviations: E, East; MW, Midwest; G, Gulf; RM, Rocky Mountain; W, West. The IMPROVE and CSN stations in these regions will represent rural and urban areas, respectively.

Emission Inventories

We use bottom-up emission estimates compiled under the auspices of the Global Emission Initiative (GEIA) and EPA's National Emission Inventory (NEI). EPA anthropogenic NEI emissions were downloaded for 2005 and 2011 ([81](#)) for point, mobile, and area sources. In addition to this, we also use sectoral emissions of $PM_{2.5}$, CO, and NO_x from the NEI trend database for elucidating changes in NEI emission ratios in the recent decade. ([82](#)) All gridded global emissions ($0.5^\circ \times 0.5^\circ$) were downloaded from the Emissions of Atmospheric Compounds and Compilation of Ancillary Data (ECCAD) database. ([83](#)) Global inventories, which span the period of the study (2000–2015) for all three species, include MACCity (Monitoring Atmosphere for Chemistry and Climate), ([21](#), [84](#)) Representative Concentration Pathway (RCP) scenarios 4.5 and 6 for 2005 and 2010, ([85](#)) and ECLIPSE-GAINS V4a (Evaluating the Climate and Air Quality Impacts of Short Lived Pollutants). ([86](#), [87](#)) We compare the enhancement ratios of $\Delta EC_a / \Delta CO$ and $\Delta EC_a / \Delta NO_x$ for each PADD region against the emission ratios.

Ancillary Data

State-based diesel and gasoline consumption, vehicle miles traveled, and population statistics were obtained from the Federal Highway Statistics public data archive. ([88](#)) We use these data to understand the changes in EC_a , CO, and NO_x in relation to diesel and gasoline fuel consumption and fleet activity.

Results and Discussion

Patterns of EC_a , CO, and NO_x

In this section, we compare and contrast the median mass concentration, enhancement, and interquartile range (IQR) of EC_a , CO, and NO_x concentrations between two periods, 2000–2007 and 2008–2015 (hereafter, P1 and P2), and across regions classified under PADD. While the spatial patterns and long-term trends of ground-level NO_x or CO have been analyzed in past studies, we present them here to illustrate their covariations with EC_a . We use the economic recession in 2008 as the divide between the study periods. December 2007 marks the beginning of the economic recession according to the National Bureau of Economic Research (NBER). ([61](#)) The peak of the financial crisis occurred during 2008 and 2009. During late 2006–2008, several air quality

regulations such as the EPA's HDH rule for diesel engines(35) and winter wood burning rule by the Bay Area Air Quality Management District(89) were introduced to reduce fine particulate emissions. Therefore, these contrasting periods offer an opportunity to find a relationship between the relative abundance of combustion products (EC_a in particular), environmental policies, fuel usage, and economic activity. For example, past studies have reported reductions in abundance during the recession.(90, 91) NO_2 column densities were reported to be reduced by $8\% \pm 5\%$ in U.S. megacities and across major energy producers during the peak of the recession.(90) These reductions in NO_2 during the recession are attributed to a decrease in diesel emissions resulting from lower economic activity.(88, 92-95) CO, on the other hand, has shown a significant decrease since 1990, and previous studies report a 7-fold decrease in CO emission factors over the United States.(94) The larger reductions in CO are mainly due to improvements in the performance of gasoline engines and implementation of catalytic converters.(38) Fewer studies have analyzed changes in EC_a during these periods. For example, BC annual average concentrations measured in Rochester, NY, during 2007–2010 showed 12% reductions from highway diesel engine emissions as a result of the EPA 2007 HDH rule.(96) On the U.S. West Coast, analysis of $PM_{2.5}$ measurements obtained at San Jose, CA, from 2002 to 2012 found a 40% reduction in the contribution of wood combustion to $PM_{2.5}$ between winter 2008 and winter 2009.(97) However, these studies are isolated, and long-term trends in EC_a in the context of coemitted species and source attributions are not available for PADD regions in United States for the past decade. Therefore, examining covariations in emissions and ambient concentrations of EC_a , CO, and NO_x highlights the significance of combustion activities driving the behavior of these species relative to each other.

We show in Figure S1 (Supporting Information) the median concentrations of EC_a , CO, and NO_x , together with their corresponding IQRs, at collocated stations for EC_a and CO (or NO_x) for P1 and P2. Reductions for CO and NO_x are greater than that for EC_a during P2. However, since conclusions drawn only from ambient concentrations do not directly represent local combustion activities, we also analyze the patterns using species enhancements. In P2, the median enhancements of CO and NO_x were reduced by 69–76% and 42–280%, respectively, in rural areas and by 27–68% and 35–48%, respectively, in urban areas across the E and W PADD regions. NO_x reductions reported here are comparable with those reported by Tong et al.(91) in urban areas, but the reductions are much higher in rural areas (especially in E). This is due to the inclusion of data for the years prior to 2005. Similarly, EC_a enhancements increased by 13% in urban E, and reductions in urban W were also 2.5–3 times smaller than NO_x or CO reductions (Table S1, Supporting Information). The poor reductions in EC_a in urban stations are also reflected in the IQR. We find an 8–12% increase in IQR

for E and W, whereas the IQR for CO and NO_x decreased by 30–60% ([Figure S1b](#)). We note that the results illustrated here do not involve stations potentially affected by fires, episodic events, and/or precipitation rates of >6 mm/day. Within these constraints, we see a few possibilities of why EC_a reductions (both median and IQR) are not as high as those of NO_x and CO. First of all, in terms of fossil fuel usage, reports on fuel sales, diesel truck activity data, roadway sensor measurements, and diesel truck age distribution consistently indicate a larger decrease in EC_a emissions during the peak of the economic recession (2008–2009) as a result of a countrywide decrease in diesel fuel sales and truck activity (e.g., [92](#)). As a potential consequence, vehicles that lasted longer (due to lower miles traveled) and subsequently with lesser emission controls joined the fleet after the recession. After 2010, the federal highway statistics data suggest that truck activity in California and New York improved by factors of ~1.03 and ~3.1, respectively. ([88](#)) This is also consistent with diesel fuel sales data that show an increase in diesel consumption and decrease in gasoline consumption in most states (except Texas) after 2010. ([88, 93](#)) While studies have pointed to reductions in BC and PM_{2.5} after 2006 (until 2010) in Rochester, NY, as a result of the EPA HDH rule, ([96, 98](#)) studies on total mobile emissions of EC_a or BC across the United States (especially after 2010) are unclear. ([29](#)) This is despite a clear trend in diesel fuel sales ([29](#)) in most states between 2000 and 2015. Even before 2010, 70% of the decrease in mobile source emissions of BC in the Los Angeles Basin ([95](#)) on the U.S. West Coast was attributed to off-road gasoline engines and only 30% to control of diesel truck PM emissions. In northern states, residential heating and biofuel combustion is also a major contributor to EC_a. ([40](#)) Smaller reductions in EC_a in E can possibly be explained by the combination of effects from diesel emissions from traffic, industrial activities, and residential combustion. Lastly, increased fleet traffic from commercial diesel trucks on the United States–Mexico border has also been considered a plausible reason for the increase in EC_a levels in monitoring stations in W close to the border. ([99](#))

While a quantitative source apportionment of EC_a is a separate study by itself, with the given data, we elucidate the utility of coemitted combustion products such as CO and NO_x in improving our understanding of the distribution and emissions of EC_a. We focus our discussions on PADD regions E and W due to the availability of the larger number of significant slopes in these regions for all seasons.

Joint Probability Distribution

Figures S3 and S4 ([Supporting Information](#)) show the joint probability histograms (JPHs) of EC_a with CO and NO_x concentrations for collocated stations in rural (panels a–d in [Figures S3 and S4](#)) and urban (panels e–h in [Figures S3 and S4](#)) areas. These JPHs are calculated using all the station data

points within the study period (2000–2015) for all seasons. Our goal is to quantify the general pattern of covariation between EC_a , CO, and NO_x without any localization. We find in [Figures S3 and S4](#), a strong non-Gaussian relationship of EC_a with CO and NO_x across the four PADD regions. The shape of the distribution exhibits asymmetric tails (toward higher EC_a , CO, and NO_x). In several cases, EC_a and CO (or NO_x) exhibit a clear bimodal pattern. For example, the JPHs for NO_x and EC_a show the highest probability (>40%) in the urban E and W regions, with two major modes occurring at NO_x levels of about 10 and 20 ppbv and EC_a levels of about ~15 ppbm. Rural E is different from urban E, and the highest probability occurs at relatively higher ambient levels (25 ppbm for EC_a and ~20 ppbv for NO_x). For EC_a and CO, the highest probability mode occurs at ~200–250 ppbv for CO and 5–15 ppbm for EC_a . The second mode is apparent in E for CO levels at about ~100 ppbv (panels a–e in [Figure S3](#)). In general, urban regions have a relatively higher probability of EC_a for given modes of NO_x or CO. While we find that these covariations exist, it is difficult to attribute these patterns to a particular driver (i.e., sources/sinks/emission control strategies adopted in these regions) at this resolution, given that these species have different lifetimes. As we highlighted earlier, these dependencies have to be localized to derive meaningful relationships.

$\Delta EC_a/\Delta CO$ and $\Delta EC_a/\Delta NO_x$

Here, we further investigate these covariations in terms of enhancement ratios between EC_a , CO, and NO_x . [Figure 1](#) shows RMA regression slopes of ΔEC_a against ΔCO ([Figure 1ab](#)) and ΔEC_a against ΔNO_x ([Figure 1cd](#)) for rural and urban areas in E and W (circles in [Figure 1](#) represent slopes per season, per station, per year). The slopes are color coded for P1, P2, rural, and urban areas (gray and green, rural and urban before 2008; black and orange, rural and urban after 2008). Corresponding statistics are also summarized in Table S2 ([Supporting Information](#)). We note here that the enhancement ratios shown in [Figure 1](#) are plotted along with median concentrations for comparisons with [Figure S1](#) ([Supporting Information](#)).

Figure 1. Enhancement ratios as a function of the EC_a , CO, and/or NO_x concentration. Panels a and b and panels c and d correspond to scatter plots of $\Delta EC_a/\Delta CO$ and $\Delta EC_a/\Delta NO_x$, respectively. The subplots for each panel correspond to the PADD regions: East (a, c) and West (b, d). The ratios (filled bubbles) are color-coded to represent two periods under study: 2000–2007 and 2008–2015. Rural (gray, 2000–2007; black, 2008–2015) and urban (green, 2000–2007; orange, 2008–2015) areas are also color-coded. Urban stations correspond to the Chemical Speciation Network (CSN), and rural stations correspond to the IMPROVE

network. Ratios represent values calculated per station, per season, per year by regressing seasonal ΔEC_a against ΔCO (or NO_x) using reduced major axis regression.

Overall, the highest median values of $\Delta EC_a/\Delta CO$ and $\Delta EC_a/\Delta NO_x$ ratios are found in E (~ 0.12 ppbm/ppbv). This occurs at stations where EC_a levels are higher and CO is lower or both EC_a and NO_x levels are moderate. The ratios also vary by rural and urban areas, which is apparent especially for $\Delta EC_a/\Delta NO_x$ as opposed to $\Delta EC_a/\Delta CO$. The highest median for $\Delta EC_a/\Delta NO_x$ ratios is found in urban E. However, the highest variability (1σ) for $\Delta EC_a/\Delta NO_x$ ratios is seen in rural E (1.69–2.18 ppbm/ppbv) and W (0.90–0.95 ppbm/ppbv). This can be attributed to stations with high EC_a and high NO_x levels (see panels e–h in [Figure 1](#) and Table S3, [Supporting Information](#)). The ratios are also associated with very different seasonalities depending on the location. Higher median ratios are common in summer and winter. The highest variations in seasonal concentrations of EC_a , CO, and NO_x (and ratios) are seen in W. Furthermore, $\Delta EC_a/\Delta NO_x$ ratios show stronger seasonality compared to $\Delta EC_a/\Delta CO$ ratios (Figure S5, [Supporting Information](#)). This can be attributed to NO_x from strong photochemistry and heterogeneous reactions that are uncommon for EC_a especially during the summer.[\(59\)](#) Comparisons of periods before and after 2008, in [Figure 1](#), also show that, in W, there is a distinct increase in $\Delta EC_a/\Delta NO_x$ ratios as a result of an increase in EC_a (from 20 to >40 ppbm) and NO_x (from 10 to >30 ppbv) levels. In E, urban areas show an increase in ratios (from 2.22 to 2.37) as a consequence of a proportionate decrease in both EC_a and NO_x , whereas rural areas show a decrease in ratios due to an increase in NO_x levels. These variations in ratios suggest that rural and urban areas in E and W are very different in terms of combustion sources and efficiency, which results in varying levels of emission reductions for coemitted species (especially for EC_a and NO_x). We discuss this in detail in the following sections. Note that we have excluded stations and days affected significantly by fires and rain.

These $\Delta EC_a/\Delta CO$ values are lower than those of previous studies. In particular, the values from this study (in the range of ~ 0.6 – 1.5 ng m $^{-3}$ ppbv $^{-1}$, converted to STP from the current units) are lower than shorter term $\Delta EC_a/\Delta CO$ ratios reported by Park et al.[\(100\)](#) over Baltimore in 2002 (1.7 – 4.6 ng m $^{-3}$ ppbv $^{-1}$) and Chen et al.[\(101\)](#) over Fort Meade, MD (2.7 – 6.7 ng m $^{-3}$ ppbv $^{-1}$), in 1999–2000. Median values of $\Delta EC_a/\Delta CO$ ratios in this study are lower than the values reported in Mexico City (2.89 ± 0.89 ng m $^{-3}$ ppbv $^{-1}$)[\(53\)](#) due to higher EC_a in Mexico City than the United States, but comparable to values downwind of Mexico City (~ 1.4 ng m $^{-3}$ ppbv $^{-1}$)[\(102\)](#) and in Europe (0.8 – 2.3 ng m $^{-3}$ ppbv $^{-1}$).[\(103\)](#) However, they are ~ 10 times smaller than those reported for the Indian Ocean (12 – 27 ng m $^{-3}$ ppbv $^{-1}$) and Maldives (21 ng m $^{-3}$ ppbv $^{-1}$)[\(50\)](#) and ~ 2 – 3 times smaller than those reported near urban centers of Tokyo (4.6 – 6.6 ng m $^{-3}$ ppbv $^{-1}$)[\(51\)](#) and Hedo, Japan (3.9 – 5.3 ng m $^{-3}$ ppbv $^{-1}$)[\(57\)](#) and

urban and industrial regions in Dallas and Houston, TX ($\sim 6.8 \text{ ng m}^{-3} \text{ ppbv}^{-1}$).⁽⁵²⁾ In general, the slopes derived in our study are smaller when compared to those of other studies for North America partially because most of these studies were performed during 1999–2002^(100, 101) when EC_a and CO levels were higher than those in 2000–2015, the time period of analysis was much shorter (a week to a few months), and the stations were closer to traffic and the values were measured only during rush hours,⁽¹⁰⁰⁾ resulting in very high EC_a .

Except the paper by Wang et al.,⁽⁵⁹⁾ we currently do not have much literature for EC_a and NO_x covariation. Further analyses require detailed comparisons of sources and sinks of EC_a , CO, and NO_x and meteorology across these regions using a chemical transport model or EPA's positive matrix factorization software (see, e.g., the paper by Wang et al.⁽⁹⁶⁾), which will be separate studies by themselves and are beyond the scope of the present work.

Change in Enhancements and Ratios between P1 and P2

CO levels drastically decrease in P2 to $<500 \text{ ppbv}$ at some stations. We present in [Figure 2](#) box plots of $\Delta\text{EC}_a/\Delta\text{CO}$ ([Figure 2a,b](#)) and $\Delta\text{EC}_a/\Delta\text{NO}_x$ ([Figure 2c,d](#)) during P1 and P2 for rural ([Figure 2a,c](#)) and urban ([Figure 2b,d](#)) areas, along with corresponding emission ratios derived from NEI emissions for 2005 and 2011 ([Figure 2e,f](#)). We also summarize the changes in ratios in Table 4 ([Supporting Information](#)). We interpret the change in ratios between these two periods to be dominated by the changes in emissions due to fossil fuel and biofuel combustion, given the constraints that days affected by fires and precipitation were removed prior to analyses. The changes between the two periods were tested using Student's *t* test for medians from two distributions (from P1 and P2) assuming unequal variances and a confidence level of 95%.

Figure 2. Box plots of regional enhancement and emission ratios for 2000–2007 and 2008–2015. The top panels (a, b) represent $\Delta\text{EC}_a/\Delta\text{CO}$ ratios for rural (left) and urban (right) areas, the middle panels (c, d) represent $\Delta\text{EC}_a/\Delta\text{NO}_x$ ratios, and the bottom panels (e, f) represent $E_{\text{BC}}/E_{\text{CO}}$ (left) and $E_{\text{BC}}/E_{\text{NO}_x}$ (right) emission ratios derived from the 2005 and 2011 U.S. EPA National Emission Inventory (NEI). Colors for each box plot represent the following PADD regions: East (gray), West (blue), Midwest (green), and Gulf (red). The box plot shows the median (center line), 25th and 75th percentiles (edge of the box), and minimum and maximum values (whiskers).

In general, the median values of $\Delta EC_a/\Delta CO$ and $\Delta EC_a/\Delta NO_x$ (using ratios estimated for individual seasons) increase across PADD regions in P2. One exception is rural E, where $\Delta EC_a/\Delta NO_x$ ratios decreased by 38% in P2 due to an increase in ΔNO_x by 280%. Overall, $\Delta EC_a/\Delta CO$ and $\Delta EC_a/\Delta NO_x$ increased by 0.7–82% and 6.8–104%, respectively. The largest increase is observed in urban W. (Figure 2b,d). We find that this pattern results from drastic reductions of ΔCO and ΔNO_x by 67% and 48% combined with an increase in ΔEC_a by 14–24% in winter and fall. ΔCO decreased at a faster rate among the three species. This is consistent with previous studies that attribute ΔCO reductions to more than 50% reduction in the light-duty emission factor and improvement in the emission standards for CO through the installation of catalytic converters in gasoline vehicles and improvements in the air-to-fuel ratio.(24, 94, 104) As mentioned earlier, reductions in EC_a in P2 are however slower in urban areas compared to rural areas. This is especially true for urban W where winter (23%) and fall (13%) seasons show an increase in ΔEC_a . Similar to ΔEC_a , urban ΔNO_x reductions are also lower in P2 during the winter. It is also interesting to see higher ΔEC_a and ΔNO_x reductions in rural W during the same period. This indicates that, in urban W, the increase in enhancements in P2 during winter can be attributed mostly to highway/off-road diesel engine emissions. However, during fall, higher ΔNO_x reductions and an increase in ΔEC_a point to combined effects of traffic emissions and residential/commercial oil combustion. In all seasons except winter, ΔNO_x reductions are comparable but less than that of ΔCO in most stations except in rural E, where ΔNO_x levels increased during summer (383%) and fall (222%), respectively. This is in contrast to patterns in CO and EC_a in rural E. An increase in point source NO_x emissions from electric utilities has been an issue in the northeastern United States. The switch from coal to natural gas combustion in electric generation units (EGUs) and state implementation plans reduced NO_x emissions by 40% from 1997.(105) However, a smaller increase in NO_2 column densities around rural areas from point sources in the central United States after 2009 has also been noted in previous studies.(90, 67) Previous studies also identified transport of NO_x emissions from the Midwest to downwind of the Northeast and seasonal effects of EGUs and other industrial sources as potential contributors to NO_x emissions in this region in addition to vehicular NO_x .(106) The largest increase in summer levels of ΔNO_x in P2 also suggests a contribution from biogenic soil NO_x and lightning.(106) Although we have not discussed G in detail due to a lack of significant slopes, it is important to note that rural G has also shown an increase in ΔEC_a (63% for all seasons) and ΔNO_x (224% for summer) in P2.

Comparison against Emission Inventories

The long-term changes in enhancement ratios can help constrain bottom-up emission inventories(60) for BC given existing observational constraints on CO and NO_x . We compare enhancement ratios against BC/CO and BC/ NO_x emission ratios derived using global emission

inventories such as MACCity, RCP, ECLIPSE, and the U.S. EPA's NEI. For clarification in terminologies, we emphasize that we use “EC_a” while discussing enhancement ratios and “BC” while discussing emission ratios. EC_a used in this study is obtained using thermal optical methods, and BC emissions are obtained from PM_{2.5} using EC-based source emission profiles.[\(47\)](#)

We derived NEI emission ratios for E_{BC}/E_{CO} and E_{BC}/E_{NO_x} for 2005 and 2011. Across the PADD regions, NEI 2011 shows an increase in E_{BC}/E_{CO} (52–86%) and E_{BC}/E_{NO_x} (6–29%) ratios relative to NEI 2005 ([Figure 2](#)). Regionwise comparisons show that NEI overestimates (underestimates) the increase in E (W) for E_{BC}/E_{CO} and E_{BC}/E_{NO_x} (Table S5, [Supporting Information](#)). Larger reductions for CO in NEI have previously been reported for E.[\(67\)](#) NEI changed the emissions models between NEI 2005 and 2011 from EPA's MOBILE6 to the Motor Vehicle Emission Simulator (MOVES), with the latter giving much higher NO_x emission rates. Tong et al.[\(107\)](#) noted that temporal changes from NEI during these periods are highly uncertain for this reason. Several studies have emphasized the need for efforts for improving carbonaceous aerosol emission inventories due to uncertainties in sectors to which activities are assigned (e.g., biomass burning added in miscellaneous) and assignment of fuel source such as diesel to all major source categories.[\(47\)](#) Further analysis of NEI trends in W reveals (a) smaller reductions in NEI emissions for NO_x from nonroad engines and on-road vehicles and (b) an increase in PM_{2.5} emissions from commercial/residential combustion and smaller reductions in nonroad emissions. We also see from NEI trends that the increase in ratios and enhancements in G corresponds well with the huge increase (~2-fold) in CO, BC, and NO_x emissions in petroleum and related sectors from NEI 2005 to NEI 2011.

In comparison against global emission inventories, we find that, from 2005 to 2010, the E_{BC}/E_{CO} and E_{BC}/E_{NO_x} ratios from global emission inventory MACCity decrease across all PADD regions (except MW for E_{BC}/E_{CO}) (Table S6, [Supporting Information](#)). The decrease in ratios is highest in W (10% for E_{BC}/E_{CO} and 19% for E_{BC}/E_{NO_x}). This is significantly different from enhancement ratios, which show an increase in ratios in P2. Although changes in emission ratios are reported here using emissions from 2005 and 2010 (2005 and 2011 for NEI), the ratios over the period 2000–2015 from global inventories also show a similar pattern of least increase in W. These differences in the trends of MACCity emission ratios are attributed to an exaggerated downward trend in MACCity emissions following the RCP8.5 scenario and missing combustion emissions for CO[\(108\)](#) and NO_x.[\(60\)](#) After 2000, MACCity emissions are based on emission reductions prescribed by the RCP8.5 emission scenario, which appears to be too optimistic. Reductions in BC emissions in particular are significantly larger relative to those from observed EC_a enhancements. These larger reductions in BC emissions drive the decrease in E_{BC}/E_{NO_x} . This is also because, in the case of W, the NO_x emission

reduction in MACCity matches the CARB emission reduction of 28% for 2005–2010, [\(92\)](#) which shows that most of the uncertainties in E_{BC}/E_{NO_x} arise from BC emissions rather than NO_x emissions for W. Furthermore, across all regions, the percentage change of E_{BC} is higher than that of E_{NO_x} but comparable to that of E_{CO} . This is not reasonable given the increase in diesel fuel consumption after 2010 and the higher gasoline emission reduction than that of diesel. In addition, MACCity emissions in the transportation sector have been reported to have a low bias. [\(108-110\)](#) Furthermore, MACCity has also been shown to underestimate residential combustion heating during the winter due to a lack of seasonal variation in emissions. [\(21, 60, 84\)](#)

Comparisons with other emission inventories reveal an issue similar to that of MACCity emission ratios. We show in Figures S7 and S8 ([Supporting Information](#)) the change in E_{BC}/E_{NO_x} and E_{BC}/E_{CO} from other RCP scenarios and ECLIPSE-GAINS for each PADD region (also see Table S6, [Supporting Information](#)) and key sectors after recession. We consider 2005 as the year before the recession and 2010 as the year after the recession. RCP4.5 shows a positive change but lacks the regional variation. RCP6 on the other hand shows almost no change between 2005 and 2010. The ratios from ECLIPSE-GAINS exhibit a more reasonable regional difference and positive changes (although still lower than the changes in enhancement ratios). BC emission reductions in ECLIPSE-GAINS are smaller than NO_x and CO reductions (Tables S9 and S8, [Supporting Information](#)). This helps ECLIPSE-GAINS to capture the increase in $\Delta EC_a/\Delta NO_x$ after the recession. We see major differences between MACCity and other emission inventories in residential and transportation sectors. For example, in the residential sector, MACCity's BC emission reductions are 4–25 times higher (Table S7, [Supporting Information](#)) and NO_x emission reductions are 1.5–3 times higher than those of other emission inventories. This results in the apparent lack of an increase of E_{BC}/E_{NO_x} ratios in MACCity. We also see slower reductions in NO_x and CO emissions in MACCity's transportation sector ([Tables S8 and S9](#)), which also contributes to a smaller increase in overall E_{BC}/E_{CO} and E_{BC}/E_{NO_x} ratios.

Implications and Limitations

The highest increase in $\Delta EC_a/\Delta CO$ and $\Delta EC_a/\Delta NO_x$ in urban areas owing to smaller EC_a reductions suggests that these regions are growing areas of concern for EC_a . This is also consistent with relatively slower reductions in off-road and on-road diesel emissions in W from the NEI trends database. These ratios can serve as potential indicators for monitoring the changes in covariations of species as a result of air quality regulations, fossil fuel emissions from diesel and gasoline engines, residential and commercial space heating, biofuel combustion in industries, and technological changes such as the switch to natural gas from coal for electricity generation in power plants. Comparisons with national and global emission inventories suggest large uncertainties in BC

and NO_x emissions compared to CO emissions. Changes in NEI estimates in 2011 do not represent the spatial variation in NO_x and BC emissions, especially in rural areas. The inability to capture the increase in E_{BC}/E_{NO_x} ratios by MACCity and RCP scenarios indicates an overestimation of BC emission reductions in these inventories, especially for the western United States. Previous studies recommend correcting for errors in redistributing countrywide emissions to urban scales.⁽⁶⁰⁾ It is unclear however if this alone can address the discrepancy. One of the limitations of this study is our less rigorous treatment of other confounding effects (e.g., transport, differences in sampling strategies, and representativeness of Air Quality System (AQS) stations). Refinements to our current approach require high-resolution modeling and a substantial increase in the number of collocated data. Our main goal for this work is to illustrate the utility of analyzing enhancement ratios in identifying potential inconsistencies in our understanding of EC_a abundance and emissions. Addressing uncertainties in BC emission inventories is challenging and requires continued effort in looking at synergistic information from existing and future observation systems as well as in improving forward and inverse modeling approaches. Our results call for immediate efforts to address BC emissions in urban areas given the rapidly increasing trend in population density and diesel fuel consumption, increase in the contribution of residential combustion to PM_{2.5} emissions (in W), uncertainties in natural gas prices,⁽¹¹¹⁾ and the potential skew toward the usage of high-emitting heavy-duty engines in the future.

Acknowledgment

This work was supported by NASA Atmospheric Chemistry Modeling and Analysis Program (ACMAP) Grant NNX13AK24G. The results and discussions presented here are solely from the authors and do not represent the opinions of the sponsors. We thank the EPA-AQS, ECCAD, and NASA GES-DISC Interactive Online Visualization and Analysis Infrastructure (GIOVANNI) data teams. We also thank Armin Sorooshian for helpful feedback.

- [Reference QuickView](#)
-

References

This article references 111 other publications.

1. [1.](#)

McConnell, J. R.; Edwards, R.; Kok, G. L.; Flanner, M. G.; Zender, C. S.; Saltzman, E. S.; Banta, J. R.; Pasteris, D. R.; Carter, M. M.; Kahl, J. D. 20th-century industrial black carbon emissions altered arctic climate forcing *Science* **2007**, 317 (5843) 1381– 1384 DOI: 10.1126/science.1144856

[\[Crossref\]](#), [\[PubMed\]](#), [\[CAS\]](#)

2. [2.](#)

Ramanathan, V.; Carmichael, G. Global and regional climate changes due to black carbon *Nat. Geosci.* **2008**, 1 (4) 221– 227 DOI: 10.1038/ngeo156

[\[Crossref\]](#), [\[CAS\]](#)

3. [3.](#)

U.S. EPA. *Report to Congress on Black Carbon*; EPA-450/R-12-001; U.S. Environmental Protection Agency: Washington, DC, **2012**.

4. [4.](#)

Bond, T. C.; Doherty, S. J.; Fahey, D. W.; Forster, P. M.; Berntsen, T.; DeAngelo, B. J.; Flanner, M. G.; Ghan, S.; Kärcher, B.; Koch, D. Bounding the role of black carbon in the climate system: A scientific assessment *J. Geophys. Res., [Atmos.]* **2013**, 118 (11) 5380– 5552 DOI: 10.1002/jgrd.50171

[\[Crossref\]](#), [\[CAS\]](#)

5. [5.](#)

Chow, J. C.; Watson, J. G.; Chen, L. W. A.; Arnott, W. P.; Moosmüller, H.; Fung, K. Equivalence of elemental carbon by thermal/optical reflectance and transmittance with different temperature protocols *Environ. Sci. Technol.* **2004**, 38 (16) 4414– 4422 DOI: 10.1021/es034936u

[\[ACS Full Text\]](#) , [\[CAS\]](#)

6. [6.](#)

Petzold, A.; Ogren, J. A.; Fiebig, M.; Laj, P.; Li, S.-M.; Baltensperger, U.; Holzer-Popp, T.; Kinne, S.; Pappalardo, G.; Sugimoto, N. Recommendations for reporting "black carbon" measurements *Atmos. Chem. Phys.* **2013**, 13 (16) 8365– 8379 DOI: 10.5194/acp-13-8365-2013

[\[Crossref\]](#), [\[CAS\]](#)

7. [7.](#)

Jacobson, M. Z.; Streets, D. G. Influence of future anthropogenic emissions on climate, natural emissions, and air quality *J. Geophys. Res., [Atmos.]* **2009**, 114 (D8) D08118 DOI: 10.1029/2008JD011476

[\[Crossref\]](#), [\[CAS\]](#)

8. [8.](#)

Hansen, J.; Sato, M.; Ruedy, R.; Lacis, A.; Oinas, V. Global warming in the twenty-first century: An alternative scenario *Proc. Natl. Acad. Sci. U. S. A.* **2000**, 97 (18) 9875– 9880 DOI: 10.1073/pnas.170278997

[\[Crossref\]](#), [\[PubMed\]](#), [\[CAS\]](#)

9. [9.](#)

Molina, M.; Zaelke, D.; Sarma, K. M.; Andersen, S. O.; Ramanathan, V.; Kaniaru, D. Reducing abrupt climate change risk using the Montreal Protocol and other regulatory actions to complement cuts in CO₂ emissions *Proc. Natl. Acad. Sci. U. S. A.* **2009**, 106 (49) 20616– 20621 DOI: 10.1073/pnas.0902568106

[\[Crossref\]](#), [\[PubMed\]](#), [\[CAS\]](#)

10. [10.](#)

Ramanathan, V.; Xu, Y. The Copenhagen Accord for limiting global warming: Criteria, constraints, and available avenues *Proc. Natl. Acad. Sci. U. S. A.* **2010**, 107 (18) 8055– 8062 DOI: 10.1073/pnas.1002293107

[\[Crossref\]](#), [\[PubMed\]](#), [\[CAS\]](#)

11. [11.](#)

Cape, J. N.; Coyle, M.; Dumitrean, P. The atmospheric lifetime of black carbon *Atmos. Environ.* **2012**, 59,256– 263 DOI: 10.1016/j.atmosenv.2012.05.030

[\[Crossref\]](#), [\[CAS\]](#)

12. [12.](#)

Flanner, M. G.; Zender, C. S.; Randerson, J. T.; Rasch, P. J. Present-day climate forcing and response from black carbon in snow *J. Geophys. Res., [Atmos.]* **2007**, 112 (D11) D11202 DOI: 10.1029/2006JD008003

[\[Crossref\]](#), [\[CAS\]](#)

13. [13.](#)

Meehl, G. A.; Arblaster, J. M.; Collins, W. D. Effects of black carbon aerosols on the Indian monsoon *J. Clim.* **2008**, 21 (12) 2869– 2882 DOI: 10.1175/2007JCLI1777.1

[\[Crossref\]](#)

14. [14.](#)

Janssen, N. A.; Hoek, G.; Simic-Lawson, M.; Fischer, P.; van Bree, L.; ten Brink, H.; Keuken, M.; Atkinson, R. W.; Anderson, H. R.; Brunekreef, B.; Cassee, F. R. Black

Carbon as an Additional Indicator of the Adverse Health Effects of Airborne Particles Compared with PM₁₀ and PM_{2.5} *Environ. Health Perspect.* **2011**, 119 (12) 1691– 1699 DOI: 10.1289/ehp.1003369

[[Crossref](#)], [[PubMed](#)], [[CAS](#)]

15. [15.](#)

Baumgartner, J.; Zhang, Y.; Schauer, J. J.; Huang, W.; Wang, Y.; Ezzati, M. Highway proximity and black carbon from cookstoves as a risk factor for higher blood pressure in rural China *Proc. Natl. Acad. Sci. U. S. A.* **2014**, 111 (36) 13229– 13234 DOI: 10.1073/pnas.1317176111

[[Crossref](#)], [[PubMed](#)], [[CAS](#)]

16. [16.](#)

Hand, J. L.; Schichtel, B. A.; Malm, W. C.; Frank, N. H. Spatial and temporal trends in PM_{2.5} organic and elemental carbon across the United States *Adv. Met.* **2013**, 2013, 1 DOI: 10.1155/2013/367674

[[Crossref](#)]

17. [17.](#)

Andreae, M. O.; Gelencsér, A. Black carbon or brown carbon? The nature of light-absorbing carbonaceous aerosols *Atmos. Chem. Phys.* **2006**, 6 (10) 3131– 3148 DOI: 10.5194/acp-6-3131-2006

[[Crossref](#)], [[CAS](#)]

18. [18.](#)

Chen, L. W.; Chow, J. C.; Watson, J. G.; Schichtel, B. A. Consistency of long-term elemental carbon trends from thermal and optical measurements in the IMPROVE network *Atmos. Meas. Tech.* **2012**, 5 (10) 2329 DOI: 10.5194/amt-5-2329-2012

[[Crossref](#)], [[CAS](#)]

19. [19.](#)

U.S. EPA. *Health Assessment Document for Diesel Engine Exhaust*; EPA/600/8-90/057F, Report by the National Center for Environmental Assessment, Office of Research and Development; U.S. Environmental Protection Agency: Washington, DC, **2002**. http://oaspub.epa.gov/eims/eimscomm.getfile?p_download_id=36319 (accessed April 11, 2017).

20. [20.](#)

U.S. EPA. National Emissions Inventory data and documentation, (2005. Clearinghouse for Inventories and Emissions Factors (CHIEF) Web site. <http://www.epa.gov/ttn/chief/net/2005inventory.html> (accessed April 11, 2017).

21. [21.](#)

Lamarque, J.-F.; Bond, T. C.; Eyring, V.; Granier, C.; Heil, A.; Klimont, Z.; Lee, D.; Lioussé, C.; Mieville, A.; Owen, B. Historical (1850–2000) gridded anthropogenic and biomass burning emissions of reactive gases and aerosols: methodology and application *Atmos. Chem. Phys.* **2010**, 10 (15) 7017– 7039 DOI: 10.5194/acp-10-7017-2010

[\[Crossref\]](#), [\[CAS\]](#)

22. [22.](#)

Watson, J. G.; Chow, J. C.; Lowenthal, D. H.; Pritchett, L. C.; Frazier, C. A.; Neuroth, G. R.; Robbins, R. Differences in the carbon composition of source profiles for diesel- and gasoline-powered vehicles *Atmos. Environ.* **1994**, 28 (15) 2493– 2505 DOI: 10.1016/1352-2310(94)90400-6

[\[Crossref\]](#), [\[CAS\]](#)

23. [23.](#)

Miguel, A. H.; Kirchstetter, T. W.; Harley, R. A.; Hering, S. V. On-road emissions of particulate polycyclic aromatic hydrocarbons and black carbon from gasoline and diesel vehicles *Environ. Sci. Technol.* **1998**, 32(4) 450– 455 DOI: 10.1021/es970566w

[\[ACS Full Text\]](#) , [\[CAS\]](#)

24. [24.](#)

Ban-Weiss, G. A.; McLaughlin, J. P.; Harley, R. A.; Lunden, M. M.; Kirchstetter, T. W.; Kean, A. J.; Strawa, A. W.; Stevenson, E. D.; Kendall, G. R. Long-term changes in emissions of nitrogen oxides and particulate matter from on-road gasoline and diesel vehicles *Atmos. Environ.* **2008**, 42 (2) 220– 232 DOI: 10.1016/j.atmosenv.2007.09.049

[\[Crossref\]](#), [\[CAS\]](#)

25. [25.](#)

Kirchstetter, T. W.; Harley, R. A.; Kreisberg, N. M.; Stolzenburg, M. R.; Hering, S. V. On-road measurement of fine particle and nitrogen oxide emissions from light- and heavy-duty motor vehicles *Atmos. Environ.* **1999**, 33 (18) 2955– 2968 DOI: 10.1016/S1352-2310(99)00089-8

[\[Crossref\]](#), [\[CAS\]](#)

26. [26.](#)

Sawyer, R. F.; Harley, R. A.; Cadle, S. H.; Norbeck, J. M.; Slott, R.; Bravo, H. A. Mobile sources critical review: 1998 NARSTO assessment *Atmos. Environ.* **2000**, 34 (12-14) 2161– 2181 DOI: 10.1016/S1352-2310(99)00463-X

[\[Crossref\]](#), [\[CAS\]](#)

27. [27.](#)

Parrish, D. D.; Trainer, M.; Hereid, D.; Williams, E. J.; Olszyna, K. J.; Harley, R. A.; Fehsenfeld, F. C. Decadal change in carbon monoxide to nitrogen oxide ratio in US vehicular emissions *J. Geophys. Res., [Atmos.]* **2002**, 107 (D12) ACH 5-1– ACH 5-9 DOI: 10.1029/2001JD000720

[\[Crossref\]](#)

28. [28.](#)

Harley, R. A.; Marr, L. C.; Lehner, J. K.; Giddings, S. N. Changes in motor vehicle emissions on diurnal to decadal time scales and effects on atmospheric composition *Environ. Sci. Technol.* **2005**, 39 (14) 5356–5362 DOI: 10.1021/es048172+

[\[ACS Full Text\]](#) , [\[CAS\]](#)

29. [29.](#)

Dallmann, T. R.; Harley, R. A. Evaluation of mobile source emission trends in the United States *J. Geophys. Res., [Atmos.]* **2010**, 115 (D14) D14305 DOI: 10.1029/2010JD013862

[\[Crossref\]](#), [\[CAS\]](#)

30. [30.](#)

Kook, S.; Park, S.; Bae, C. Influence of early fuel injection timings on premixing and combustion in a diesel engine *Energy Fuels* **2008**, 22 (1) 331– 337 DOI: 10.1021/ef700521b

[\[ACS Full Text\]](#) , [\[CAS\]](#)

31. [31.](#)

Johnson, T. V. Review of diesel emissions and control *Int. J. Engine Res.* **2009**, 10 (5) 275– 285 DOI: 10.1243/14680874JER04009

[\[Crossref\]](#), [\[CAS\]](#)

32. [32.](#)

Koebel, M.; Elsener, M.; Kleemann, M. Urea-SCR: a promising technique to reduce NO_x emissions from automotive diesel engines *Catal. Today* **2000**, 59 (3) 335– 345 DOI: 10.1016/S0920-5861(00)00299-6

[\[Crossref\]](#), [\[CAS\]](#)

33. [33.](#)

Yanowitz, J.; McCormick, R. L.; Graboski, M. S. In-use emissions from heavy-duty diesel vehicles *Environ. Sci. Technol.* **2000**, 34 (5) 729– 740 DOI: 10.1021/es990903w

[[ACS Full Text](#) , [[CAS](#)]

34. [34.](#)

Fino, D. Diesel emission control: Catalytic filters for particulate removal *Sci. Technol. Adv. Mater.* **2007**, 8 (1)93– 100 DOI: 10.1016/j.stam.2006.11.012

[[Crossref](#)], [[CAS](#)]

35. [35.](#)

U.S. EPA. Regulations for Emissions from Vehicles and Engines, (2007. <https://www.epa.gov/regulations-emissions-vehicles-and-engines/final-rule-control-air-pollution-new-motor-vehicles-heavy> (accessed April 11, 2017).

36. [36.](#)

Kirchstetter, T. W.; Harley, R. A.; Littlejohn, D. Measurement of nitrous acid in motor vehicle exhaust *Environ. Sci. Technol.* **1996**) 30 (9) 2843– 2849 DOI: 10.1021/es960135y

[[ACS Full Text](#) , [[CAS](#)]

37. [37.](#)

Marr, L. C.; Black, D. R.; Harley, R. A. Formation of photochemical air pollution in central California 1. Development of a revised motor vehicle emission inventory *J. Geophys. Res., [Atmos.]* **2002**, 107 (D6) ACH 5-1– ACH 5-9 DOI: 10.1029/2001JD000689

[[Crossref](#)]

38. [38.](#)

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

[[ACS Full Text](#) , [[CAS](#)]

39. [39.](#)

Bishop, G. A.; Schuchmann, B. G.; Stedman, D. H.; Lawson, D. R. Multispecies remote sensing measurements of vehicle emissions on Sherman Way in Van Nuys, California *J. Air Waste Manage. Assoc.* **2012**, 62 (10) 1127– 1133 DOI: 10.1080/10962247.2012.699015

[[Crossref](#)], [[PubMed](#)], [[CAS](#)]

40. [40.](#)

Park, R. J.; Jacob, D. J.; Logan, J. A. Fire and biofuel contributions to annual mean aerosol mass concentrations in the United States *Atmos. Environ.* **2007**, 41 (35) 7389– 7400 DOI: 10.1016/j.atmosenv.2007.05.061

[\[Crossref\]](#), [\[CAS\]](#)

41. [41.](#)

Malm, W. C.; Sisler, J. F.; Huffman, D.; Eldred, R. A.; Cahill, T. A. Spatial and seasonal trends in particle concentration and optical extinction in the United States *J. Geophys. Res., [Atmos.]* **1994**, 99 (D1) 1347–1370 DOI: 10.1029/93JD02916

[\[Crossref\]](#), [\[CAS\]](#)

42. [42.](#)

Schauer, J. J. Evaluation of elemental carbon as a marker for diesel particulate matter *J. Exposure Anal. Environ. Epidemiol.* **2003**, 13 (6) 443– 453 DOI: 10.1038/sj.jea.7500298

[\[Crossref\]](#), [\[PubMed\]](#), [\[CAS\]](#)

43. [43.](#)

Liousse, C.; Cachier, H.; Jennings, S. G. Optical and thermal measurements of black carbon aerosol content in different environments: Variation of the specific attenuation cross-section, sigma (σ) *Atmos. Environ., Part A* **1993**, 27 (8) 1203– 1211 DOI: 10.1016/0960-1686(93)90246-U

[\[Crossref\]](#), [\[CAS\]](#)

44. [44.](#)

Jeong, C. H.; Hopke, P. K.; Kim, E.; Lee, D. W. The comparison between thermal-optical transmittance elemental carbon and Aethalometer black carbon measured at multiple monitoring sites *Atmos. Environ.* **2004**, 38 (31) 5193– 5204 DOI: 10.1016/j.atmosenv.2004.02.065

[\[Crossref\]](#), [\[CAS\]](#)

45. [45.](#)

Allen, G. A.; Lawrence, J.; Koutrakis, P. Field validation of a semi-continuous method for aerosol black carbon (aethalometer) and temporal patterns of summertime hourly black carbon measurements in southwestern PA *Atmos. Environ.* **1999**, 33 (5) 817– 823 DOI: 10.1016/S1352-2310(98)00142-3

[\[Crossref\]](#), [\[CAS\]](#)

46. [46.](#)

Babich, P.; Davey, M.; Allen, G.; Koutrakis, P. Method comparisons for particulate nitrate, elemental carbon, and PM_{2.5} mass in seven US cities *J. Air Waste Manage. Assoc.* **2000**, 50 (7) 1095– 1105 DOI: 10.1080/10473289.2000.10464152

[\[Crossref\]](#), [\[PubMed\]](#), [\[CAS\]](#)

47. [47.](#)

Chow, J. C.; Watson, J. G.; Lowenthal, D. H.; Chen, L. W. A.; Motallebi, N. Black and organic carbon emission inventories: review and application to California *J. Air Waste Manage. Assoc.* **2010**, 60 (4) 497–507 DOI: 10.3155/1047-3289.60.4.497

[\[Crossref\]](#), [\[PubMed\]](#), [\[CAS\]](#)

48. [48.](#)

Koch, D.; Schulz, M.; Kinne, S.; McNaughton, C.; Spackman, J. R.; Balkanski, Y.; Bauer, S.; Berntsen, T.; Bond, T. C.; Boucher, O. Evaluation of black carbon estimations in global aerosol models *Atmos. Chem. Phys.* **2009**, 9 (22) 9001– 9026 DOI: 10.5194/acp-9-9001-2009

[\[Crossref\]](#), [\[CAS\]](#)

49. [49.](#)

Cohen, J. B.; Wang, C. Estimating global black carbon emissions using a top-down Kalman Filter approach *J. Geophys. Res., [Atmos.]* **2014**, 119 (1) 307– 323 DOI: 10.1002/2013JD019912

[\[Crossref\]](#), [\[CAS\]](#)

50. [50.](#)

Dickerson, R. R.; Andreae, M. O.; Campos, T.; Mayol-Bracero, O. L.; Neusuess, C.; Streets, D. G. Analysis of black carbon and carbon monoxide observed over the Indian Ocean: Implications for emissions and photochemistry *J. Geophys. Res., [Atmos.]* **2002**, 107 (D19) INX2 16-1– INX2 16-11 DOI: 10.1029/2001JD000501

[\[Crossref\]](#)

51. [51.](#)

Kondo, Y.; Komazaki, Y.; Miyazaki, Y.; Moteki, N.; Takegawa, N.; Kodama, D.; Deguchi, S.; Nogami, M.; Fukuda, M.; Miyakawa, T. Temporal variations of elemental carbon in Tokyo *J. Geophys. Res., [Atmos.]* **2006**, 111 (D12) D12205 DOI: 10.1029/2005JD006257

[\[Crossref\]](#), [\[CAS\]](#)

52. [52.](#)

Spackman, J. R.; Schwarz, J. P.; Gao, R. S.; Watts, L. A.; Thomson, D. S.; Fahey, D. W.; Holloway, J. S.; de Gouw, J. A.; Trainer, M.; Ryerson, T. B. Empirical correlations between black carbon aerosol and carbon monoxide in the lower and middle troposphere *Geophys. Res. Lett.* **2008**, 35 (19) L19816 DOI: 10.1029/2008GL035237

[\[Crossref\]](#), [\[CAS\]](#)

53. [53.](#)

Subramanian, R.; Kok, G. L.; Baumgardner, D.; Clarke, A.; Shinozuka, Y.; Campos, T. L.; Heizer, C. G.; Stephens, B. B.; de Foy, B.; Voss, P. B.; Zaveri, R. A. Black carbon over Mexico: the effect of atmospheric transport on mixing state, mass absorption cross-section, and BC/CO ratios *Atmos. Chem. Phys.* **2010**, 10(1) 219– 237 DOI: 10.5194/acp-10-219-2010

[\[Crossref\]](#), [\[CAS\]](#)

54. [54.](#)

Verma, R. L.; Sahu, L. K.; Kondo, Y.; Takegawa, N.; Han, S.; Jung, J. S.; Kim, Y. J.; Fan, S.; Sugimoto, N.; Shammaa, M. H. Temporal variations of black carbon in Guangzhou, China, in summer 2006 *Atmos. Chem. Phys.* **2010**, 10 (14) 6471– 6485 DOI: 10.5194/acp-10-6471-2010

[\[Crossref\]](#), [\[CAS\]](#)

55. [55.](#)

Arellano, A. F.; Hess, P. G.; Edwards, D. P.; Baumgardner, D. Constraints on black carbon aerosol distribution from Measurement of Pollution in the Troposphere (MOPITT) CO *Geophys. Res. Lett.* **2010**, 37(17) L17801 DOI: 10.1029/2010GL044416

[\[Crossref\]](#), [\[CAS\]](#)

56. [56.](#)

Pan, X. L.; Kanaya, Y.; Wang, Z. F.; Liu, Y.; Pochanart, P.; Akimoto, H.; Sun, Y. L.; Dong, H. B.; Li, J.; Irie, H.; Takigawa, M. Correlation of black carbon aerosol and carbon monoxide in the high-altitude environment of Mt. Huang in Eastern China *Atmos. Chem. Phys.* **2011**, 11 (18) 9735– 9747 DOI: 10.5194/acp-11-9735-2011

[\[Crossref\]](#), [\[CAS\]](#)

57. [57.](#)

Kondo, Y.; Oshima, N.; Kajino, M.; Mikami, R.; Moteki, N.; Takegawa, N.; Verma, R. L.; Kajii, Y.; Kato, S.; Takami, A. Emissions of black carbon in East Asia estimated from observations at a remote site in the East China Sea *J. Geophys. Res., [Atmos.]* **2011**, 116 (D16) D16201 DOI: 10.1029/2011JD015637

[\[Crossref\]](#), [\[CAS\]](#)

58. [58.](#)

Penner, J. E.; Eddleman, H.; Novakov, T. Towards the development of a global inventory for black carbon emissions *Atmos. Environ., Part A: Gen. Top.* **1993**, 27 (8) 1277– 1295 DOI: 10.1016/0960-1686(93)90255-W

[\[Crossref\]](#), [\[CAS\]](#)

59. [59.](#)

Wang, Y.; Wang, X.; Kondo, Y.; Kajino, M.; Munger, J. W.; Hao, J. Black carbon and its correlation with trace gases at a rural site in Beijing: Top-down constraints from ambient measurements on bottom-up emissions *J. Geophys. Res., [Atmos.]* **2011**, 116 (D24) D24304 DOI: 10.1029/2011JD016575

[[Crossref](#)], [[CAS](#)]

60. [60.](#)

Hassler, B.; McDonald, B. C.; Frost, G. J.; Borbon, A.; Carslaw, D.; Civerolo, K.; Granier, C.; Monks, P. S.; Monks, S.; Parrish, D. D.; Pollack, I. B.; Rosenlof, K. H.; Ryerson, T. B.; von Schneidemesser, E.; Trainer, M. Analysis of long-term observations of NO_x and CO in megacities and application to constraining emissions inventories *Geophys. Res. Lett.* **2016**, 43, 9920 DOI: 10.1002/2016GL069894

[[Crossref](#)], [[CAS](#)]

61. [61.](#)

The National Bureau of Economic Research. U.S. Business Cycle Expansions and Contractions. <http://www.nber.org/cycles.html> (accessed Oct 10, 2016).

62. [62.](#)

U.S. Environmental Protection Agency. Pre-Generated DataFiles. http://aqsdr1.epa.gov/aqsweb/aqstmp/airdata/download_files.html (accessed Jan 8, 2017).

63. [63.](#)

U.S. Environmental Protection Agency. Method 3—Gas Analysis for the Determination of Dry Molecular Weight. <https://www3.epa.gov/ttnemc01/promgate/m-03.pdf> (accessed Jan 8, 2017).

64. [64.](#)

U.S. Environmental Protection Agency. Quality Assurance Document 2.3, Reference Method for the Determination of Nitrogen Dioxide in the Atmosphere (Chemiluminescence). <https://www3.epa.gov/ttn/amtic/files/ambient/pm25/qa/no2.pdf> (accessed Jan 8, 2017).

65. [65.](#)

Winer, A. M.; Peters, J. W.; Smith, J. P.; Pitts, J. N., Jr. Response of commercial chemiluminescent nitric oxide-nitrogen dioxide analyzers to other nitrogen-containing compounds *Environ. Sci. Technol.* **1974**, 8 (13) 1118–1121 DOI: 10.1021/es60098a004

[[ACS Full Text](#) , [[CAS](#)]

66. [66.](#)

Lamsal, L. N.; Duncan, B. N.; Yoshida, Y.; Krotkov, N. A.; Pickering, K. E.; Streets, D. G.; Lu, Z. US NO₂ trends (2005–2013): EPA Air Quality System (AQS) data versus improved observations from the Ozone Monitoring Instrument (OMI) *Atmos. Environ.* **2015**, 110 (13) 130– 143 DOI: 10.1016/j.atmosenv.2015.03.055

[[Crossref](#)], [[CAS](#)]

67. [67.](#)

He, H.; Stehr, J. W.; Hains, J. C.; Krask, D. J.; Doddridge, B. G.; Vinnikov, K. Y.; Canty, T. P.; Hosley, K. M.; Salawitch, R. J.; Worden, H. M.; Dickerson, R. R. Trends in emissions and concentrations of air pollutants in the lower troposphere in the Baltimore/Washington airshed from 1997 to 2011 *Atmos. Chem. Phys.* **2013**, 13(15) 7859– 7874 DOI: 10.5194/acp-13-7859-2013

[[Crossref](#)], [[CAS](#)]

68. [68.](#)

Chow, J. C.; Watson, J. G.; Pritchett, L. C.; Pierson, W. R.; Frazier, C. A.; Purcell, R. G. The DRI thermal/optical reflectance carbon analysis system: description, evaluation and applications in US air quality studies *Atmos. Environ., Part A* **1993**, 27 (8) 1185– 1201 DOI: 10.1016/0960-1686(93)90245-T

[[Crossref](#)], [[CAS](#)]

69. [69.](#)

Chow, J. C.; Watson, J. G.; Crow, D.; Lowenthal, D. H.; Merrifield, T. Comparison of IMPROVE and NIOSH carbon measurements *Aerosol Sci. Technol.* **2001**, 34 (1) 23– 34 DOI: 10.1080/02786820119073

[[Crossref](#)], [[CAS](#)]

70. [70.](#)

Solomon, P. A.; Crumpler, D.; Flanagan, J. B.; Jayanty, R. K. M.; Rickman, E. E.; McDade, C. E. US National PM_{2.5} Chemical Speciation Monitoring Networks—CSN and IMPROVE: Description of networks *J. Air Waste Manage. Assoc.* **2014**, 64 (12) 1410– 1438 DOI: 10.1080/10962247.2014.956904

[[Crossref](#)], [[PubMed](#)], [[CAS](#)]

71. [71.](#)

Chow, J. C.; Watson, J. G.; Robles, J.; Wang, X.; Chen, L.-W. A.; Trimble, D. L.; Kohl, S. D.; Tropp, R. J.; Fung, K. K. Quality assurance and quality control for thermal/optical analysis of aerosol samples for organic and elemental carbon *Anal. Bioanal. Chem.* **2011**, 401 (10) 3141– 3152 DOI: 10.1007/s00216-011-5103-3

[[Crossref](#)], [[PubMed](#)], [[CAS](#)]

72. [72.](#)

Malm, W. C.; Schichtel, B. A.; Pitchford, M. L. Uncertainties in PM_{2.5} gravimetric and speciation measurements and what we can learn from them *J. Air Waste Manage. Assoc.* **2011**, 61 (11) 1131– 1149 DOI: 10.1080/10473289.2011.603998

[\[Crossref\]](#), [\[PubMed\]](#), [\[CAS\]](#)

73. [73.](#)

Watson, J. G.; Chow, J. C.; Chen, L. W. A.; Frank, N. H. Methods to assess carbonaceous aerosol sampling artifacts for IMPROVE and other long-term networks *J. Air Waste Manage. Assoc.* **2009**, 59 (8) 898– 911 DOI: 10.3155/1047-3289.59.8.898

[\[Crossref\]](#), [\[PubMed\]](#), [\[CAS\]](#)

74. [74.](#)

Watson, J. G.; Chow, J. C.; Chen, L. W. A. Summary of organic and elemental carbon/black carbon analysis methods and intercomparisons *Aerosol Air Qual. Res.* **2005**, 5 (1) 65– 102

[\[Crossref\]](#), [\[CAS\]](#)

75. [75.](#)

U.S. EPA. Parameter and Method Codes for Loading PM_{2.5} Chemical Speciation Network (CSN) URG 3000N Carbon Data in AQS, (2007. <https://www3.epa.gov/ttnamti1/files/ambient/pm25/spec/urg3000-method-codes.pdf> (accessed April 11, 2017).

76. [76.](#)

Kondo, Y.; Matsui, H.; Moteki, N.; Sahu, L.; Takegawa, N.; Kajino, M.; Zhao, Y.; Cubison, M. J.; Jimenez, J. L.; Vay, S. Emissions of black carbon, organic, and inorganic aerosols from biomass burning in North America and Asia in 2008 *J. Geophys. Res., [Atmos.]* **2011**, 116 (D8) D08204 DOI: 10.1029/2010JD015152

[\[Crossref\]](#), [\[CAS\]](#)

77. [77.](#)

Matsui, H.; Kondo, Y.; Moteki, N.; Takegawa, N.; Sahu, L. K.; Zhao, Y.; Fuelberg, H. E.; Sessions, W. R.; Diskin, G.; Blake, D. R. Seasonal variation of the transport of black carbon aerosol from the Asian continent to the Arctic during the ARCTAS aircraft campaign *J. Geophys. Res., [Atmos.]* **2011**, 116 (D5) D05202 DOI: 10.1029/2010JD015067

[\[Crossref\]](#)

78. [78.](#)

Ricker, W. E. Linear regressions in fishery research *J. Fish. Res. Board Can.* **1973**, 30 (3) 409– 434 DOI: 10.1139/f73-072

[Crossref]

79. [79.](#)

Park, R. J.; Jacob, D. J.; Kumar, N.; Yantosca, R. M. Regional visibility statistics in the United States: Natural and transboundary pollution influences, and implications for the Regional Haze Rule *Atmos. Environ.* **2006**, 40 (28) 5405– 5423 DOI: 10.1016/j.atmosenv.2006.04.059

[Crossref], [CAS]

80. [80.](#)

U.S. Energy Information Administration. PADD regions enable regional analysis of petroleum product supply and movements. <http://www.eia.gov/todayinenergy/> (accessed Oct 10, 2016).

81. [81.](#)

U.S. Environmental Protection Agency. Air Emission Inventories, National Emission Inventory (NEI). <https://www.epa.gov/air-emissions-inventories/national-emissions-inventory-nei> (accessed Oct 10, 2016).

82. [82.](#)

U.S. EPA. Air Pollution Emissions Trends Data. <https://www.epa.gov/air-emissions-inventories/air-pollutant-emissions-trends-data> (accessed April 11, 2017).

83. [83.](#)

Emissions of Atmospheric Compounds & Compilation of Ancillary Data, The GEIA Database. <http://ether.ipsl.jussieu.fr/eccad> (accessed Oct 10, 2016).

84. [84.](#)

Granier, C.; Bessagnet, B.; Bond, T.; D'Angiola, A.; van der Gon, H. D.; Frost, G. J.; Heil, A.; Kaiser, J. W.; Kinne, S.; Klimont, Z. Evolution of anthropogenic and biomass burning emissions of air pollutants at global and regional scales during the 1980–2010 period *Clim. Change* **2011**, 109 (1–2) 163– 190 DOI: 10.1007/s10584-011-0154-1

[Crossref], [CAS]

85. [85.](#)

van Vuuren, D. P.; Edmonds, J.; Kainuma, M.; Riahi, K.; Thomson, A.; Hibbard, K.; Hurtt, G. C.; Kram, T.; Krey, V.; Lamarque, J.-F. The representative concentration pathways: an overview *Clim. Change* **2011**, 109, 5– 31 DOI: 10.1007/s10584-011-0148-z

[Crossref]

86. [86.](#)

Amann, M.; Bertok, I.; Borken-Kleefeld, J.; Cofala, J.; Heyes, C.; Höglund-Isaksson, L.; Klimont, Z.; Nguyen, B.; Posch, M.; Rafaj, P. Cost-effective control of air quality and greenhouse gases

in Europe: Modeling and policy applications *Environ. Model. Software* **2011**, 26 (12) 1489– 1501 DOI: 10.1016/j.envsoft.2011.07.012

[Crossref]

87. [87.](#)

Klimont, Z.; Smith, S. J.; Cofala, J. The last decade of global anthropogenic sulfur dioxide: 2000–2011 emissions *Environ. Res. Lett.* **2013**, 8 (1) 014003 DOI: 10.1088/1748-9326/8/1/014003

[Crossref], [CAS]

88. [88.](#)

U.S. Department of Transportation Federal Highway Administration, Policy and Government Affairs, Office of Highway Policy Information. Highway Statistics Series. <https://www.fhwa.dot.gov/policyinformation/statistics.cfm> (accessed Oct 10, 2016).

89. [89.](#)

Spare the Air.Wood Burning Regulation. <http://www.sparetheair.org/stay-informed/particulate-matter/wood-smoke/regulation> (accessed April 11, 2017).

90. [90.](#)

Russell, A. R.; Valin, L. C.; Cohen, R. C. Trends in OMI NO₂ observations over the United States: effects of emission control technology and the economic recession *Atmos. Chem. Phys.* **2012**, 12 (24) 12197– 12209 DOI: 10.5194/acp-12-12197-2012

[Crossref], [CAS]

91. [91.](#)

Tong, D. Q.; Lamsal, L.; Pan, L.; Ding, C.; Kim, H.; Lee, P.; Chai, T.; Pickering, K. E.; Stajner, I. Long-term NO_x trends over large cities in the United States during the Great Recession: Comparison of satellite retrievals, ground observations, and emission inventories *Atmos. Environ.* **2015**, 107, 70– 84 DOI: 10.1016/j.atmosenv.2015.01.035

[Crossref], [CAS]

92. [92.](#)

California Air Resources Board. ARB Staff Assessment of the Impact of the Economy on California Trucking Activity and Emissions 2006–2014, December (2009. https://www.arb.ca.gov/msprog/onrdiesel/documents/truck_economic_documentation_v015.pdf (accessed Oct 10, 2016).

93. [93.](#)

Kim, S.-W.; Heckel, A.; Frost, G. J.; Richter, A.; Gleason, J.; Burrows, J. P.; McKeen, S.; Hsie, E.-Y.; Granier, C.; Trainer, M. NO₂ columns in the western United States

observed from space and simulated by a regional chemistry model and their implications for NO_x emissions *J. Geophys. Res., [Atmos.]* **2009** 114(D11) D11301 DOI: 10.1029/2008JD011343

[\[Crossref\]](#), [\[CAS\]](#)

94. [94.](#)

McDonald, B. C.; Gentner, D. R.; Goldstein, A. H.; Harley, R. A. Long-term trends in motor vehicle emissions in US urban areas *Environ. Sci. Technol.* **2013**, 47 (17) 10022– 10031 DOI: 10.1021/es401034z

[\[ACS Full Text\]](#) , [\[CAS\]](#)

95. [95.](#)

McDonald, B. C.; Goldstein, A. H.; Harley, R. A. Long-term trends in California mobile source emissions and ambient concentrations of black carbon and organic aerosol *Environ. Sci. Technol.* **2015**, 49 (8) 5178– 5188 DOI: 10.1021/es505912b

[\[ACS Full Text\]](#) , [\[CAS\]](#)

96. [96.](#)

Wang, Y.; Hopke, P. K.; Rattigan, O. V.; Chalupa, D. C.; Utell, M. J. Multiple-year black carbon measurements and source apportionment using Delta-C in Rochester, New York *J. Air Waste Manage. Assoc.* **2012**, 62 (8) 880– 887 DOI: 10.1080/10962247.2012.671792

[\[Crossref\]](#), [\[CAS\]](#)

97. [97.](#)

Wang, Y.; Hopke, P. K. A ten-year source apportionment study of ambient fine particulate matter in San Jose, California *Atmos. Pollut. Res.* **2013**, 4 (4) 398– 404 DOI: 10.5094/APR.2013.045

[\[Crossref\]](#), [\[CAS\]](#)

98. [98.](#)

Wang, Y.; Hopke, P. K.; Chalupa, D. C.; Utell, M. J. Long-term study of urban ultrafine particles and other pollutants *Atmos. Environ.* **2011**, 45 (40) 7672– 7680 DOI: 10.1016/j.atmosenv.2010.08.022

[\[Crossref\]](#), [\[CAS\]](#)

99. [99.](#)

Shores, C. A.; Klapmeyer, M. E.; Quadros, M. E.; Marr, L. C. Sources and transport of black carbon at the California–Mexico border *Atmos. Environ.* **2013**, 70, 490– 499 DOI: 10.1016/j.atmosenv.2012.04.031

[\[Crossref\]](#), [\[CAS\]](#)

100. [100.](#)

Park, R. J.; Jacob, D. J.; Palmer, P. I.; Clarke, A. D.; Weber, R. J.; Zondlo, M. A.; Bond, T. C. Export efficiency of black carbon aerosol in continental outflow: Global implications *J. Geophys. Res., [Atmos.]* **2005**, 110 (D11) D11205 DOI: 10.1029/2004JD005432

[\[Crossref\]](#), [\[CAS\]](#)

101. [101.](#)

Antony Chen, L. W.; Doddridge, B. G.; Dickerson, R. R.; Chow, J. C.; Mueller, P. K.; Quinn, J.; Butler, W. A. Seasonal variations in elemental carbon aerosol, carbon monoxide and sulfur dioxide: Implications for sources *Geophys. Res. Lett.* **2001**, 28 (9) 1711– 1714 DOI: 10.1029/2000GL012354

[\[Crossref\]](#)

102. [102.](#)

Baumgardner, D.; Kok, G. L.; Raga, G. B. On the diurnal variability of particle properties related to light absorbing carbon in Mexico City *Atmos. Chem. Phys.* **2007**, 7 (10) 2517– 2526 DOI: 10.5194/acp-7-2517-2007

[\[Crossref\]](#), [\[CAS\]](#)

103. [103.](#)

McMeeking, G. R.; Hamburger, T.; Liu, D.; Flynn, M.; Morgan, W. T.; Northway, M.; Highwood, E. J.; Krejci, R.; Allan, J. D.; Minikin, A.; Coe, H. Black carbon measurements in the boundary layer over western and northern Europe *Atmos. Chem. Phys.* **2010**, 10 (19) 9393– 9414 DOI: 10.5194/acp-10-9393-2010

[\[Crossref\]](#), [\[CAS\]](#)

104. [104.](#)

Twigg, M. V. Catalytic control of emissions from cars *Catal. Today* **2011**, 163 (1) 33– 41 DOI: 10.1016/j.cattod.2010.12.044

[\[Crossref\]](#), [\[CAS\]](#)

105. [105.](#)

De Gouw, J. A.; Parrish, D. D.; Frost, G. J.; Trainer, M. Reduced emissions of CO₂, NO_x, and SO₂ from US power plants owing to switch from coal to natural gas with combined cycle technology *Earth's Future* **2014**, 2 (2) 75– 82 DOI: 10.1002/2013EF000196

[\[Crossref\]](#), [\[CAS\]](#)

106. [106.](#)

Elliott, E. M.; Kendall, C.; Wankel, S. D.; Burns, D. A.; Boyer, E. W.; Harlin, K.; Bain, D. J.; Butler, T. J. Nitrogen isotopes as indicators of NO_x source contributions to atmospheric nitrate deposition across the midwestern and northeastern United States *Environ. Sci. Technol.* **2007**, 41 (22) 7661– 7667 DOI: 10.1021/es070898t

[[ACS Full Text](#) , [[CAS](#)]

107. [107.](#)

Tong, D.; Pan, L.; Chen, W.; Lamsal, L.; Lee, P.; Tang, Y.; Kim, H.; Kondragunta, S.; Stajner, I. Impact of the 2008 Global Recession on air quality over the United States: Implications for surface ozone levels from changes in NO_x emissions *Geophys. Res. Lett.* **2016**, 43 (17) 9280– 9288 DOI: 10.1002/2016GL069885

[[Crossref](#)], [[CAS](#)]

108. [108.](#)

Stein, O.; Schultz, M. G.; Bouarar, I.; Clark, H.; Huijnen, V.; Gaudel, A.; George, M.; Clerbaux, C. On the wintertime low bias of Northern Hemisphere carbon monoxide in global model studies *Atmos. Chem. Phys. Discuss.* **2014**, 14 (1) 245– 301 DOI: 10.5194/acpd-14-245-2014

[[Crossref](#)]

109. [109.](#)

Parrish, D. D. Critical evaluation of US on-road vehicle emission inventories *Atmos. Environ.* **2006**, 40 (13) 2288– 2300 DOI: 10.1016/j.atmosenv.2005.11.033

[[Crossref](#)], [[CAS](#)]

110. [110.](#)

Brown-Steiner, B.; Hess, P.; Chen, J.; Donaghy, K. Black carbon emissions from trucks and trains in the Midwestern and Northeastern United States from 1977 to 2007 *Atmos. Environ.* **2016**, 129, 155– 166 DOI: 10.1016/j.atmosenv.2015.12.065

[[Crossref](#)], [[CAS](#)]

111. [111.](#)

Brown, S. P.; Yücel, M. K. What drives natural gas prices? *Energy J.* **2008**, 29 (2) 45– 60 DOI: 10.5547/ISSN0195-6574-EJ-Vol29-No2-3

[[Crossref](#)]