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**Author**
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# High-Resolution Mapping and Long-Term Trends for Motor Vehicle Emissions

by

Brian Charles McDonald

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Professor Lee S. Friedman

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# Abstract

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Motor vehicles are a major source of greenhouse gas and other pollutant emissions that contribute to global climate change and urban and regional air pollution problems. Past efforts to develop motor vehicle emission inventories, needed for air quality planning, have been subject to significant uncertainties related to emission factors and spatial and temporal distributions of vehicle activity. The goal of this dissertation is to develop new inventories for vehicle emissions of greenhouse gases and co-emitted pollutants. A two-step approach was followed. First, motor vehicle emissions of carbon dioxide were mapped spatially and temporally using real-world traffic count data. The mapping was done separately for light- and heavy-duty vehicles so that emission factors specific to each vehicle type could be used to estimate associated air pollutant emissions. Second, long-term trends in emissions of nitrogen oxides, carbon monoxide, volatile organic compounds, and black carbon were analyzed. Emission trends were compared with long-term changes in the measured atmospheric concentrations of related pollutants, to assess the extent to which observed decreases in pollution can be attributed to motor vehicle emission control policies. The resulting motor vehicle emission inventories from this dissertation are more reliable than previous vehicle emission estimates, because spatial and temporal patterns of vehicle activity are explicitly accounted for using real-world traffic count data rather than transportation demand models, and emission factors are derived from real-world on-road studies rather than from laboratory testing.

A fuel-based inventory for vehicle emissions is presented for carbon dioxide ($CO_2$), and mapped at various spatial resolutions (10 km, 4 km, 1 km, and 500 m) using fuel sales and traffic count data. The mapping is done separately for gasoline-powered vehicles and heavy-duty diesel trucks. Emissions estimates from this study are compared with the Emissions Database for Global Atmospheric Research (EDGAR) and VULCAN. All three inventories agree at the national level within 5%. EDGAR uses road density as a surrogate to apportion vehicle emissions, which leads to 20-80% overestimates of on-road $CO_2$ emissions in the largest U.S. cities. High-resolution emission maps are presented for Los Angeles, New York City, San Francisco-San Jose, Houston, and Dallas-Fort Worth. Sharp emission gradients that exist near major highways are not apparent when emissions are mapped at 10 km resolution. High $CO_2$ emission fluxes over highways become apparent at grid resolutions of 1 km and finer. Temporal variations in vehicle emissions are characterized using extensive day- and time-specific traffic count data, and are described over diurnal, day of week, and seasonal time scales. Clear

differences are observed when comparing light- and heavy-duty vehicle traffic patterns and comparing urban and rural areas. Decadal emission trends were analyzed from 2000 to 2007 when traffic volumes were increasing, and a more recent period (2007-2010) when traffic volumes declined due to recession. We found large non-uniform changes in on-road $CO_2$ emissions over a period of ~5 years, highlighting the importance of timely updates to motor vehicle emission inventories.

A similar approach is used to estimate nitrogen oxide ($NO_x$ = NO + $NO_2$) emissions from gasoline- and diesel-powered motor vehicles. Estimates are made at the national level for the period 1990 to 2010. Vehicle emissions are also estimated at the state level for California, and for the South Coast (Los Angeles) and San Joaquin Valley air basins. Fuel-based emission estimates are compared with predictions from widely used emission inventory models. Changes in diesel $NO_x$ emissions vary over time: increasing between 1990 and 1997, stable between 1997 and 2007, and decreasing since 2007. In contrast, gasoline engine-related $NO_x$ emissions have decreased steadily, by ~65% overall between 1990 and 2010, except in the San Joaquin Valley where reductions were not as large due to faster population growth. In the San Joaquin Valley, diesel engines were the dominant on-road $NO_x$ source in all years considered (reaching ~70% in 2010). In the urbanized South Coast air basin, gasoline engine emissions dominated in the past, and have been comparable to on-road diesel sources since 2007 (down from ~75% in 1990). Other major anthropogenic sources of $NO_x$ are added to compare emission trends with trends in surface pollutant observations and satellite-derived data. When all major anthropogenic $NO_x$ sources are included, the overall emission trend is downward in all cases (–45% to –60%). Future reductions in motor vehicle $NO_x$ will depend on the effectiveness of new exhaust after-treatment controls on heavy-duty trucks, as well as further improvements to *durability* of emission control systems on light-duty vehicles.

Long-term trends in carbon monoxide (CO) emissions from motor vehicles were also assessed. Non-methane hydrocarbons (NMHC) are estimated based on my CO emission inventory, using ambient NMHC/CO ratios that were adjusted to exclude NMHC contributions from non-vehicular sources. Despite increases in fuel use of ~10-40%, CO running exhaust emissions from on-road vehicles decreased by ~80-90% in Los Angeles, Houston, and New York City, between 1990 and 2010. The ratio of NMHC/CO was found to remain constant at 0.24 ± 0.04 mol C/mol CO over time in Los Angeles, indicating that emissions of both NMHC and CO decreased at a similar rate and were affected by similar emission control policies, whereas on-road data from other cities suggest rates of reduction in NMHC versus CO emissions may differ somewhat. Emission ratios of CO/$NO_x$ (nitrogen oxides = NO + $NO_2$) and NMHC/$NO_x$ decreased by a factor of ~4 between 1990 and 2007 due to changes in the relative emission rates of passenger cars versus diesel trucks, and slight uptick thereafter, consistent across all urban areas considered here. These pollutant ratios are expected to increase in future years due to (1) slowing rates of decrease in CO and NMHC emissions from gasoline vehicles, and (2) significant advances in control of diesel $NO_x$ emissions.

New estimates of particulate matter (PM) and black carbon (BC) emissions from heavy-duty diesel trucks in the Los Angeles area were developed as part of this research. Emission trends are compared with trends in ambient concentrations of particulate black and organic carbon over a 35-year period starting in 1975. On-road heavy-duty diesel emission factors of PM and BC have

decreased by a factor of ~4 since 1975. After accounting for rapid growth in diesel fuel sales, on-road diesel BC emissions were found to have decreased by only ~20% between 1975 and 2010. In contrast, ambient measurements of BC concentrations in the Los Angeles basin show a clear downward trend, and have decreased steadily at an average rate of 4.2% per year since 1975. The slopes of best-fit lines in plots of measured OC versus BC concentrations have remained remarkably consistent over time. The stability of this ratio over time implies similar long-term trends in ambient black and organic carbon concentrations. We estimate that ambient OC levels in the Los Angeles basin have decreased by ~3.1% per year since 1975. Ongoing debate about the relative importance of gasoline versus diesel vehicle VOC emission contributions to secondary organic aerosol formation in urban areas is further informed by this research. Between 1995 and 2010, gasoline VOC emissions show a steeper downward trend, decreasing by 75 ± 7% compared to OC which decreased by only 45 ± 22%. The difference in slopes suggests that other sources of particulate organic carbon must also be contributing to the differing trends. When including other primary and secondary sources of organic aerosols from motor vehicles, the ambient and emission trends strongly agree. We conclude that long-term decreases in ambient OC likely resulted from efforts to control on-road gasoline emissions of VOCs. However, as a consequence of these efforts, other sources of organic aerosols have grown in relative importance including emissions from diesel trucks.

Recommendations for future research include development of urban $CO_2$ monitoring networks, modeling effects on air quality of long-term changes in motor vehicle emissions, and projecting future motor vehicle emissions and associated impacts on air quality.

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## Acknowledgments

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# Chapter 1: Introduction

## 1.1 Role of Motor Vehicle Emissions in Climate Change and Air Pollution Problems

The accumulation of $CO_2$ in the atmosphere, due mainly to fossil fuel combustion, is the largest positive radiative forcing that is leading to global climate change. Under likely future emission scenarios [*Moss et al.*, 2010], global average temperatures are expected to increase by more than 1.5 to 2˚C by 2100 relative to the 19th century, unless effective mitigation measures are implemented [*IPCC*, 2013]. A range of approaches have been suggested to reduce greenhouse gas emissions to levels that stabilize atmospheric $CO_2$ concentrations and help to minimize adverse impacts of climate change. The transportation sector plays a centrally important role as a source of $CO_2$ emissions and as a focus of climate change mitigation efforts. Policy measures include: (1) improving fuel efficiency of vehicles, (2) reducing travel demand, (3) increasing use of public transit, and (4) electrifying vehicles, coupled with efforts to decarbonize electricity generation [*Pacala and Socolow*, 2004; *J H Williams et al.*, 2012].

**Table 1.1.** Contribution from on-road motor vehicles to total U.S. anthropogenic emissions of various air pollutants.

| Pollutant | 1970 | 1990 | 2010 |
|---|---|---|---|
| Carbon Dioxide | -- | 23% | 26% |
| Carbon Monoxide | 83% | 77% | 46% |
| Volatile Organic Compounds | 50% | 41% | 18% |
| Nitrogen Oxides | 47% | 38% | 39% |
| Particulate Matter | | | |
| Coarse ($PM_{10}$) | 4% | 1% | 1% |
| Fine ($PM_{2.5}$) | -- | 4% | 3% |

Sources: National Emissions Inventory [*EPA*, 2013a]; Inventory of U.S. Greenhouse Gas Emissions and Sinks [*EPA*, 2013b].

In addition to $CO_2$, motor vehicles emit combustion byproducts that lead to air quality problems and exert short-lived effects on climate [*Fuglestvedt et al.*, 2008]. Relevant pollutants include carbon monoxide (CO), volatile organic compounds (VOCs), nitrogen oxides ($NO_x$), and particulate matter (PM). Table 1.1 shows the relative contributions of motor vehicle emissions to total U.S. emissions from anthropogenic sources. The contributions appear to be substantial in all cases except for particulate matter. The relavtive importance of vehicle emissions is even higher than shown in Table 1.1 for urban areas. Vehicle-related particles have an outsized effect on human health due to near-roadway exposures in cities especially [*Gauderman et al.*, 2007], and because diesel exhaust is a known human carcinogen [*Lloyd and Cackette*, 2001]. Some pollutants emitted from motor vehicles such as nitrogen oxides and volatile organic compounds

can react in the atmosphere to form other air pollutants such as ground-level ozone [*Sillman*, 1999] and secondary aerosols [*Kanakidou et al.*, 2005], which also pose human health concerns. Reducing emissions of volatile organic compounds and black carbon can simultaneously help to mitigate climate change and improve human health [*Smith et al.*, 2009]. At the global scale, increases in $NO_x$ emissions can lead to both cooling (due to shorter atmospheric lifetimes for other greenhouse gases) and warming (due to increased background levels of tropospheric ozone), and therefore there is a need to consider air quality management and climate change mitigation together in an integrated manner.

## 1.2 Current Challenges to Estimating Motor Vehicle Emissions

Emission inventories are needed for air quality planning, both to make emission control policy decisions and to support modeling of the effects of specific policies and regulations. Despite their importance, motor vehicle emission inventories still suffer from large uncertainties that undermine their usefulness as a sound basis for decision-making. For example, past EPA estimates of carbon monoxide emissions were found to be too high by a factor of two [*Parrish*, 2006]. Predicted $NO_2$ concentrations from air quality models were twice satellite observations of the same quantities over western US cities [*S W Kim et al.*, 2009]. Given their importance to urban air quality, accurate motor vehicle emission inventories are critical for modeling formation and control of photochemical air pollution [*Parrish*, 2006], quantifying exposure to vehicle exhaust [*Lipfert and Wyzga*, 2008], and developing emission control regulations that are not excessive in cost [*NRC*, 2000].

### *1.2.1 Spatial and Temporal Representation of Vehicle Activity*

Travel demand models are used to map traffic patterns based on population and employment data, resulting origins and destinations of vehicle trips, and spatial allocation of trips to the roadway network with a routing algorithm. Results from such models are commonly used in transportation planning and as a basis for describing the spatial distribution of mobile source emissions. In emission modeling, it is important to account for differences in spatial and temporal patterns of activity between light- and heavy-duty vehicles. In the U.S., light-duty vehicles are primarily powered by spark-ignition gasoline engines, whereas heavy-duty vehicles typically run on compression-ignition diesel engines. These engines differ greatly in the profile of pollutants emitted, and are regulated separately (see Section 1.3). However, transportation analysts and planners typically do not model heavy-duty truck traffic separately, due to resource constraints and lack of suitable modeling tools [*Spear et al.*, 2006]. Common practice in the past has been to assume a constant truck fraction, and to apply that fraction to total traffic volumes at all locations and hours to estimate truck traffic [*Harley et al.*, 2005]. This assumption will give incorrect results, as truck traffic patterns depend on other factors such as supply-chain logistics and locations of major freight handling facilities (e.g., ports and rail yards) [*Pendyala et al.*, 2000]. For air pollutants such as black carbon for which diesel engines are the dominant on-road source of emissions [*Bond et al.*, 2013; *Dallmann et al.*, 2013], large errors may arise in spatial and temporal distributions of emissions when modeled using traditional approaches.

### *1.2.2 Emission Factors*

Emission factors express the amount of pollution emitted per unit of activity by the source in question. In the case of motor vehicles, emission factors can be expressed per unit distance of vehicle, per unit of fuel consumed, or per unit of engine operating time. Emission factors are typically estimated using statistical models to extrapolate beyond limited samples of vehicles and ranges of operating conditions that have been observed in the laboratory [*Pokharel et al.*, 2002]. Emission models often give results that are inconsistent with on-road measurements of vehicle emissions [*Pierson et al.*, 1990], and with trends and/or ratios of ambient air pollutant concentrations [*Fujita et al.*, 1992; *Parrish*, 2006]. Reasons for disagreement include difficulties in recruiting and measuring emissions from high-emitting vehicles in laboratory-based testing, incorrect assumptions about the effectiveness and durability of emission control systems, and flawed representations of the effects of engine load on emissions [*NRC*, 2000; *Bishop and Stedman*, 2008]. A recent roadway study found that less than 1% of vehicles on the road were responsible for more than one third of total CO and VOC emissions from all vehicles [*Bishop et al.*, 2012b]. This presents a significant challenge when attempting to derive fleet-average emission factors based on laboratory testing. Large samples are needed for testing in order to capture contributions from a few high-emitting vehicles in the correct proportion. Such large samples are difficult to recruit, and time-consuming and costly to test in the laboratory. In contrast, on-road studies of vehicle emissions in highway tunnels [*Dallmann et al.*, 2013], on freeway ramps [*Bishop and Stedman*, 2008], and other on-road settings can measure emissions from many thousands of vehicles in a few days, and have a much better chance of capturing emission contributions from high-emitting vehicles.

Another challenge when mapping vehicle emissions is to account for variable emission rates due to effects of changes in engine load. Vehicle fuel consumption can increase by a factor of eight between idle and high-speed/heavy-acceleration operating conditions [*Lee and Frey*, 2012]. When normalized to fuel use rather than distance traveled, emission factors of co-emitted air pollutants have been shown to be less variable [*Yanowitz et al.*, 2000; *Bishop and Stedman*, 2008]. Unfortunately traditional emission modeling approaches are based on vehicle distance traveled or engine operating time, rather than fuel consumption, and therefore are challenged by wide variability in the underlying emission factors as a function of vehicle operating conditions. Additionally, emission factors are evolving over time as more stringent emission standards are implemented. Emission models incorporate assumptions about the effectiveness of various emission control policies. Those assumptions may be too optimistic and/or based on old data, and this can lead to emission model predictions that diverge from reality, to an increasingly large degree as conditions evolve over time.

## 1.3 Motor Vehicle Emission Regulations

Emissions from motor vehicles have long been regulated. California first began regulating motor vehicle emissions in 1957. The first federal regulations began in 1968 [*NRC*, 2006]. California is the only state allowed to develop its own emission standards separate from the federal government. In 1967, the automobile industry lobbied Congress to establish a single nationwide approach to setting vehicle emission standards. However, California was exempted because the state had the worst air quality in the nation, already had its own emission standards that pre-dated

federal standards, and would "act as a kind of laboratory for innovation" [*NRC*, 2006]. Since then, US EPA and California have assumed divergent roles in regulating motor vehicle emissions. Typically California leads on emission standards for light-duty vehicles, and US EPA leads for heavy-duty trucks. Since 1977, other states have been allowed to adopt California standards for light-duty vehicles, which are generally more stringent than the federal standards.

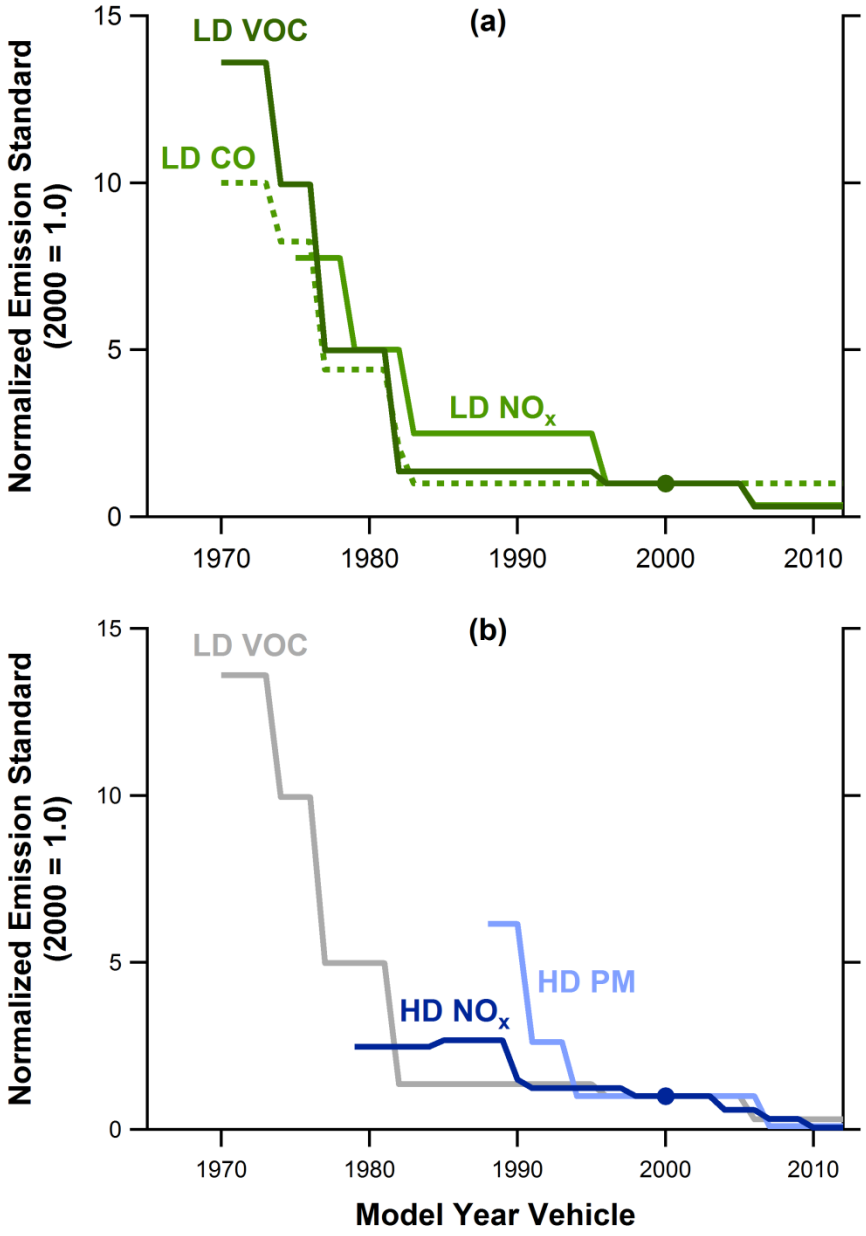


**Figure 1.1.** Federal emission standards for (a) light-duty (LD) [*NRC*, 2006] and (b) heavy-duty (HD) vehicles [*Yanowitz et al.*, 2000; *Ban-Weiss et al.*, 2008b] normalized to values that applied for new vehicles/engines as of model year 2000. Air pollutants shown above include carbon monoxide (CO), volatile organic compounds (VOCs), nitrogen oxides ($NO_x$), and exhaust particulate matter (PM).

Figure 1.1 shows how federal emission standards have evolved since the mid-1960s for both light- and heavy-duty vehicles. Prior to the year 2000, efforts were largely focused on control of light-duty vehicle emissions of carbon monoxide, volatile organic compounds, and nitrogen oxides. Emission standards for heavy-duty trucks came later and were not reduced as rapidly. After 2000, heavy-duty engines have been more aggressively targeted for control of particulate matter and nitrogen oxide emissions. Given that emission standards have been lowered significantly in recent years, especially on the diesel side, further changes in motor vehicle emissions should be expected. Future emission changes will also depend on growth in the vehicle population and the amount of driving per vehicle. Furthermore, as motor vehicle emissions are an important source of air pollution, changes in emissions should also lead to changes in observed air pollutant concentrations.

## 1.4 National Air Quality Trends

As mandated by the Clean Air Act of 1970, the U.S. Environmental Protection Agency (EPA) is responsible for establishing national ambient air quality standards (NAAQS) for pollutants that adversely affect human health and public welfare. Currently, there are six pollutants with air quality standards: carbon monoxide, nitrogen dioxide ($NO_2$), ozone ($O_3$), particulate matter (PM), sulfur dioxide ($SO_2$), and lead (Pb). To be able to track air quality progress and to identify regions that violate air quality standards, EPA and the states have established an extensive nationwide air monitoring network. Regions that consistently exceed the standards are designated as non-attainment, and are required to develop and implement plans that reduce pollutant emissions, leading to attainment of air quality standards in the future, on schedules that vary depending on the pollutant and severity of air pollution problems.

Figure 1.2 shows how air quality has improved since 1980 for four criteria air pollutants that will be evaluated further in this dissertation. The horizontal black lines on each plot show the current national air quality standards, some of which have been lowered from their original levels. For pollutants such as nitrogen dioxide (Figure 1.2a) and carbon monoxide (Figure 1.2b), large decreases in atmospheric concentrations have been observed. Currently, no region violates air quality standards for $NO_2$ or CO. For ozone and fine particulate matter ($PM_{2.5}$), many areas are currently in non-attainment, including many major metropolitan areas. This highlights the need for continued and well-targeted efforts to improve air quality.

Given the overall improving trends shown in Figure 1.2, some important questions are:

(1) Why are concentrations of air pollutants decreasing?
(2) Can the decreases be attributed to regulations on motor vehicle emissions?
(3) Will these trends continue in the future?

It is critical that policymakers have an accurate understanding of baseline conditions, so that cost-effective policies that mitigate both air pollution and climate change can be selected to reduce future emissions. Changes in climate are expected to make meeting air quality goals more difficult in the future [*Steiner et al.*, 2006].

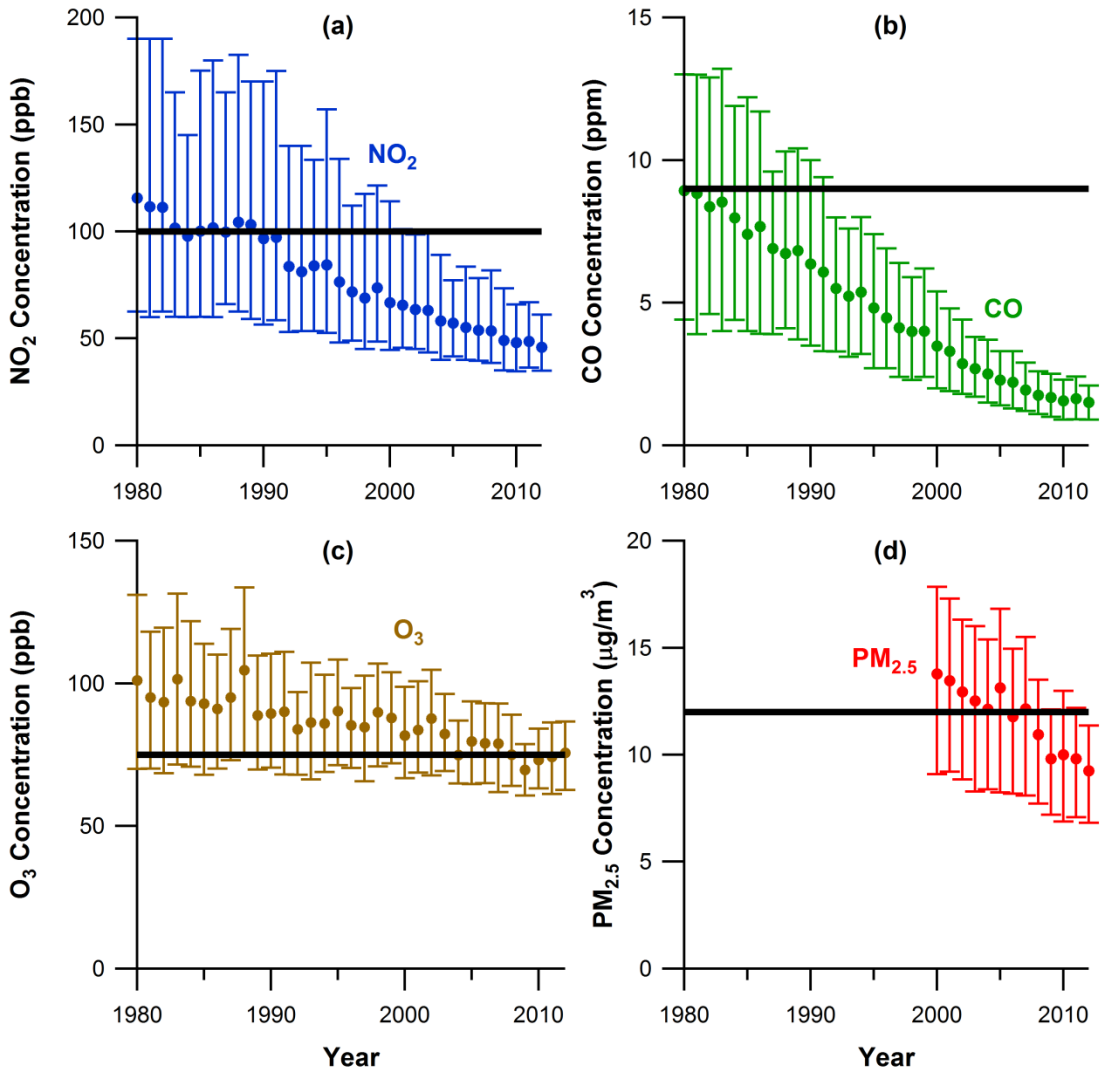


**Figure 1.2.** Trends in measured concentrations of criteria air pollutants for (a) nitrogen dioxide ($NO_2$), (b) carbon monoxide (CO), (c) ground-level ozone ($O_3$), and (d) fine particulate matter ($PM_{2.5}$) [*EPA*, 2011]. Current national air quality standards are shown using horizontal black lines. Error bars show the range from $10^{th}$ to $90^{th}$ percentile of measurements across all EPA monitoring sites.

### 1.5 Research Objectives

In my dissertation, a central goal is to develop new and more reliable inventories for motor vehicle emissions of:

(1) greenhouse gases that contribute to global climate change, and
(2) co-emitted pollutants that contribute to urban and regional air pollution problems.

Additionally, this dissertation assesses long-term changes in U.S. air quality, and the extent to which observed changes can be attributed to motor vehicle emission control policies. More detailed research objectives are as follows:

(1) Use traffic count and fuel sales data to allocate motor vehicle emissions of carbon dioxide in both space and time. Do this separately for light- and heavy-duty vehicles.

(2) Develop suitable fuel-based emission factors (in units of mass of pollutant emitted per mass of fuel burned), separately for gasoline and diesel engines, and apply those values to maps of vehicle $CO_2$ emissions to map other vehicle-related air pollutant emissions.

(3) Analyze how motor vehicle emissions have changed over time, separately for light- and heavy-duty vehicles.

(4) Compare long-term trends in motor vehicle emissions and ambient concentrations of air pollutants to assess effectiveness of emission control policies, the contribution of motor vehicles to total emissions, and to identify opportunities for making further air quality improvements.

### 1.6 Dissertation Outline

Chapter 2 maps motor vehicle emissions of carbon dioxide at various spatial resolutions (10 km, 4 km, 1 km, and 500 m) using fuel sales and traffic count data. High-resolution emission maps are presented for major urban areas including Los Angeles, New York City, San Francisco-San Jose, Houston, and Dallas-Fort Worth. The effect of mapping resolution on spatial gradients in $CO_2$ emissions is assessed, which in turn has implications for evaluating health effects of human exposure to motor vehicle emissions. Temporal variations in vehicle emissions are characterized using extensive day- and time-specific traffic count data, and are described over diurnal, day of week, and seasonal time scales. Decadal emission trends were also analyzed from 2000 to 2007 when traffic volumes were increasing, and a more recent period (2007-2010) when traffic volumes declined due to recession.

Chapter 3 describes long-term trends (1990-2010) in motor vehicle emissions of nitrogen oxides. Emissions are estimated at the national level, at the state level for California, and for the South Coast (Los Angeles) and San Joaquin Valley air basins. Emission trends are compared with trends in atmospheric concentrations derived from surface monitors and satellite data. This chapter concludes with an assessment of where future $NO_x$ emission reduction efforts should be targeted to continue progress in reducing emissions and improving air quality.

Chapter 4 investigates trends in motor vehicle emissions of carbon monoxide and hydrocarbons. Estimates are made for three large U.S. urban areas: Los Angeles, New York City, and Houston. Emissions of non-methane hydrocarbons (NMHC) are estimated using ambient ratios of NMHC/CO, after controlling for and removing contributions from non-vehicular sources. Trends in the emissions ratio of NMHC/$NO_x$ are assessed, including consideration of likely future changes. The NMHC/$NO_x$ ratio is an important determinant in the formation of ground-level

ozone, and reflects differing contributions from gasoline and diesel engines that depend on the pollutant.

Chapter 5 assesses trends in diesel engine emissions of particulate matter and black carbon from 1975 to the present day. Trends in ambient concentrations of particulate black and organic carbon are also assessed for the same time period using atmospheric observations from the Los Angeles air basin. Black carbon emissions and ambient trends are compared to evaluate the significance of regulations on emissions from heavy-duty diesel trucks in contributing to observed black carbon concentration trends. I also attempt to reconcile the large reductions in emissions of non-methane hydrocarbons documented in the previous chapter with smaller changes in ambient concentrations of particulate organic carbon observed in the Los Angeles area. This analysis is relevant to current debates about the relative importance of gasoline, diesel, and other sources of precursors that form secondary organic aerosol.

Chapter 6 summarizes major research findings and makes recommendations for future research.

# Chapter 2: High-Resolution Mapping of Motor Vehicle Carbon Dioxide Emissions

Reproduced in part from McDonald, B.C.; McBride, Z.C.; Martin E.W.; Harley, R.A. High-Resolution Mapping of Motor Vehicle Carbon Dioxide Emissions. *J. Geophys. Res.* **2014**, *119*, DOI: 10.1002/2013JD021219 with permission from John Wiley and Sons.

## 2.1 Introduction

Cities are estimated to account for ~70% of energy-related emissions of $CO_2$ globally, and will be foci of efforts to mitigate and adapt to climate change [*Rosenzweig et al.*, 2010]. To evaluate the effectiveness of these efforts, reliable emission inventories and ambient measurements of greenhouse gases are needed. Available emission inventories include the Emissions Database for Global Atmospheric Research (EDGAR, version 4.2) and the Vulcan Project (VULCAN). EDGAR maps emissions of $CO_2$ and other air pollutants globally at a spatial resolution of 0.1° × 0.1° (European Commission – Joint Research Center, 2011, http://edgar.jrc.ec.europa.eu, accessed July, 2013). VULCAN maps emissions of $CO_2$ in the U.S. at 10 km × 10 km resolution [*Gurney et al.*, 2009]. Both of these datasets are comprehensive in nature, and map anthropogenic emissions from all major sources including industrial, electricity generation, on-road, non-road, and residential/commercial sectors. Emission estimates for all sectors are needed in order to reconcile emissions with atmospheric observations. Inventories with higher spatial resolution are needed to guide local efforts to mitigate greenhouse gas emissions [*Parshall et al.*, 2010], and to assess human exposure to traffic-related air pollution. National and state-level emissions of motor vehicle $CO_2$ can be readily estimated in the U.S. using fuel sales data. However, additional uncertainties arise in downscaling annual emission totals to finer spatial and temporal scales [*Bellucci et al.*, 2012]. High-resolution $CO_2$ emission inventories are few in number; current examples include an inventory developed for Indianapolis at the building and street scale [*Gurney et al.*, 2012], and an inventory of motor vehicle emissions for all of Massachusetts on a 1 km × 1 km grid [*Gately et al.*, 2013].

Spatially and temporally-resolved emission maps will be useful in efforts to separate anthropogenic and biogenic contributions to observed $CO_2$ surface fluxes. The biosphere exerts major influences on the global carbon cycle, which vary by season and time of day [*Pataki et al.*, 2003; *Newman et al.*, 2013]. Constraining emission inventories with observations is important for improving reliability of inventory estimates. Measurement approaches to sampling atmospheric burdens of $CO_2$ include by satellite [*Morino et al.*, 2011; *Kort et al.*, 2012], aircraft [*Mays et al.*, 2009; *Brioude et al.*, 2012; *Brioude et al.*, 2013], and ground stations [*Wunch et al.*, 2009; *McKain et al.*, 2012]. Inversion methods have been developed that constrain bottom-up emission estimates and surface fluxes with top-down measurements using chemical transport models [*Streets et al.*, 2013]. Recent applications include aircraft observations to map $CO_2$ emissions on a 4 km x 4 km grid in Houston [*Brioude et al.*, 2012] and Los Angeles [*Brioude et al.*, 2013], and in determining minimum siting requirements for an urban $CO_2$ monitoring network [*Kort et al.*, 2013].

This study addresses the need for detailed, high-resolution maps of emissions from motor vehicles. We present a fuel-based inventory for vehicle emissions (FIVE), advancing an

approach that has typically been used to support air quality analyses at regional/air basin scales [*Singer and Harley*, 1996; *Pokharel et al.*, 2002; *Dallmann and Harley*, 2010; *McDonald et al.*, 2012; *McDonald et al.*, 2013], and report emissions at much higher spatial resolution (1 km and finer scales) than most prior studies. High-resolution emission maps (HI-FIVE) are shown for various highly-populated regions of the U.S. (California, Texas, and New York City metropolitan area in this study). We use publicly available data including fuel sales, road-level traffic counts, and time-resolved weigh-in-motion traffic count data, to demonstrate an emission mapping methodology that can be applied nationwide.

Another important feature of our approach is the separate mapping of on-road gasoline and diesel engine activity and emissions. This separation of emissions by engine type is essential to support inventory development for other air pollutants, for which the gasoline and diesel emission profiles are quite different. Furthermore, gasoline and diesel fuel consumption differ in their spatial and temporal patterns, and in their long-term growth rates over time. Future emission trajectories will also differ as emissions from the two engine types are regulated differently [*Dallmann et al.*, 2011]. High-resolution emission mapping will be useful for assessing human exposure to traffic-related air pollution, since current air quality monitoring networks and computer modeling efforts do not typically capture proximity-related differences in human exposure to traffic-related air pollution [*Kaur et al.*, 2007; *Apte et al.*, 2011].

The objectives of this study are to (1) develop and compare maps of on-road $CO_2$ emissions at resolutions of 10 km, 4 km, 1 km, and 500 m; (2) evaluate FIVE against published EDGAR and VULCAN inventories, and (3) provide diurnal, day-of-week, and seasonal time resolution, commensurate with high-resolution spatial mapping of vehicle emissions. On-road emissions and activity are described separately for gasoline and diesel-powered vehicles operating in urban and rural areas. We also assess the effects of spatial resolution on the magnitudes and variability in emission fluxes. The finest resolution (500 m) used in this study approaches length scales needed for characterizing near-roadway exposure to traffic-related air pollution [*Karner et al.*, 2010]. Our results are internally consistent, meaning that emissions are the same when aggregating from small to larger scales, and emissions are consistent with annually reported taxable fuel sales at the state and national levels. Finally, we assess changes in the magnitude and spatial patterns of vehicle emissions during the period 2000-2010, and consider the implications of these changes as they relate to needs for emission inventory updates.

## 2.2 Methods

### *2.2.1 State-Level Fuel Data*

The standard approach to estimating motor vehicle emissions is to use estimates of vehicle travel subdivided by different vehicle categories, and to multiply with $CO_2$ emission factors normalized to distance traveled that are specific to road and vehicle type [*Gurney et al.*, 2009; *Gately et al.*, 2013]. Other air pollutants are estimated in a similar manner using emission factors derived from laboratory emission tests, with adjustment factors to account for variations in vehicle speed, engine load, ambient temperature, fuel properties, etc. In this way, a bottom-up emission estimate can be calculated, with uncertainties that depend on the reliability of both vehicle travel data and emission factors [*Mendoza et al.*, 2013]. In this study, we use an alternative approach

that starts with taxable fuel sales reports for each state (Table MF-2) [*FHWA*, 2011b]. Fuel use can be allocated to finer spatial scales using relative rather than absolute estimates of vehicle travel. This fuel-based approach has been used previously to estimate vehicle emissions at air basin, state, and national scales [*Singer and Harley*, 1996; *Pokharel et al.*, 2002; *McDonald et al.*, 2012; *McDonald et al.*, 2013].

Sales of gasoline and diesel fuel intended for use in on-road engines are subject to highway fuel taxes. Dallmann et al. [2010] estimate uncertainties in reported on-road fuel use at ±3-5% at the national level. The uncertainties are due to issues that arise in excluding tax-free fuel consumed by off-road engines, and due to adjustments needed to reconcile aggregate fuel sales with amounts of fuel produced by refineries. In the U.S., gasoline is consumed mostly by on-road light-duty vehicles and diesel mostly by medium and heavy-duty trucks. The U.S. light-duty vehicle fleet differs from that in Europe, where diesel engines are more widely used in passenger vehicles. In this study, on-road use of gasoline is apportioned to fine spatial scales for three regions of the U.S. (California, Texas, and New York City and surrounding areas), with an emphasis on mapping passenger vehicle emissions in urban centers. Trucks drive to a greater extent than passenger vehicles on highways outside of cities. Additional $CO_2$ emissions from on-road diesel engines are mapped for California and Texas including both urban and rural areas.

A source of uncertainty in using state-level fuel sales data relates to whether the point of sale coincides with where fuel is consumed. In large states such as California and Texas, the contributions to total traffic from vehicles that cross state lines is expected to account for a relatively small fraction. If unaccounted for, long-haul trucking can result in a significant portion of diesel fuel that is sold in one state being consumed in other neighboring states [*Lutsey*, 2009]. However, state-level diesel sales reports are adjusted to reflect where fuel was used rather than where it was purchased, using reports filed by long-haul truck operators (International Fuel Tax Association, Inc., 2013, http://www.iftach.org, accessed January, 2014). The adjustments are made based on truck distances traveled in each state. Fuel taxes paid by interstate truckers are thereby proportionally redistributed from states where fuel was purchased to states where truck travel took place.

Following McDonald et al. [2013], uncertainties in gasoline fuel sales reports are estimated by comparing each state's share of national gasoline sales (Table MF-2) and total vehicle travel (Table VM-2) [*FHWA*, 2011b]. Uncertainty is calculated by subtracting the state share of national gasoline sales from shares of total vehicle travel, and then normalizing by the state's share of gasoline sales. Some of the difference results from the variable composition of light-duty vehicle fleets, i.e. light trucks versus automobiles that exist across states, and the rest from interstate traffic. Mendoza et al. [2013] suggest that vehicle fleet composition is not a significant source of uncertainty when estimating on-road $CO_2$ emissions in VULCAN. A positive difference suggests that the average fuel economy of a state's vehicle fleet is higher than the national average (i.e., more travel for a given amount of fuel burned), and/or there is a net import of fuel due to out-of-state fuel purchases being consumed within state borders. A negative difference suggests the opposite, and lower than average fuel economy and/or net export of fuel purchases. Using this approach, uncertainties in gasoline fuel sales and $CO_2$ emissions are estimated as follows: ±5% for California, ±13% for Texas, and ±6% for New York/New Jersey/Connecticut. Uncertainties in diesel fuel volumes are computed similarly by comparing

state shares of diesel fuel sales with truck travel (Tables VM-2 and VM-4) [*FHWA*, 2011b]. Similar uncertainties of ±10% result for both California and Texas, and may be due to incomplete accounting of interstate truck travel.

### *2.2.2 Road-Specific Traffic Count Data*

In the U.S., traffic count data collected from the Highway Performance Monitoring System (HPMS) are available at the roadway-level for highways and other principal arterial roads. Each state is responsible for collecting its own traffic data and reporting to the Federal Highway Administration. For example in California, highways are sampled comprehensively using portable detectors that are moved periodically. Partial day and 24-hour counts are typically used to characterize traffic on high-volume, urban highways, whereas 7-day counts are done on rural, low-volume roadways (California Department of Transportation, http://traffic-counts.dot.ca.gov/, accessed November, 2013). Random sampling methods are used to quantify vehicle travel on smaller roadways. The precision of these estimates is strongly influenced by site selection and sample size. The Federal Highway Administration provides guidelines to transportation agencies on how to meet required precision levels in traffic sampling [*FHWA*, 2013]. The precision requirements are more stringent for heavily trafficked roadways (principal arterial roads and larger) than for lower-volume roadways. Statewide traffic estimates are required to be within ±10% for major roads and freeways in large urban areas. The precision requirements are even higher for rural interstates at ±5%. In this study, we use traffic count data collected by the California Department of Transportation to map emissions in California. Counts are reported for an annual averaged day with totals for all vehicles, totals for all trucks, and trucks by axle category (2-axle/6-tire, and three or more axles). For other states, HPMS traffic counts for all vehicles and for trucks specifically are available from the Freight Analysis Framework (Federal Highway Administration, http://www.ops.fhwa.dot.gov/freight/freight_analysis/faf/, accessed November, 2012).

### *2.2.3 Fuel Apportionment*

Prior work has shown that emissions from on-road vehicles are correlated with population density, road density, and traffic counts [*Saide et al.*, 2009; *Shu and Lam*, 2011; *Brondfield et al.*, 2012; *Gately et al.*, 2013]. Traffic counts and road density were used in this study to apportion emissions spatially. We estimated the fraction of statewide fuel that is consumed on highways and major urban arterial roadways, for which traffic count data are available. This was done separately for passenger vehicles and for trucks using data tables that report vehicle travel on different road types (Table VM-2) and by vehicle class (Table VM-4) at the state level [*FHWA*, 2011b]. Not all vehicle travel can be accounted for considering only those roads for which traffic counts are explicitly available (i.e., traffic count x roadway length), and the difference is made up by travel on urban and rural arterial roads. Vehicle travel is then used as a proxy for fuel use, where total vehicle travel and travel by trucks with three or more axles are used as the proxies for on-road gasoline and diesel fuel use, respectively. We estimate that for both California and Texas ~70% of gasoline and ~80% of diesel fuel usage can be accounted for based on driving on roads where traffic has been counted explicitly.

We choose counts of trucks with three or more axles to map diesel fuel use rather than counts for all trucks, because more than half of the 2-axle/6-tire trucks are gasoline-powered, and these trucks tend to drive more within cities. Most diesel fuel is consumed by larger trucks, which have a significant fraction of their travel between cities and in rural areas. In California, route-specific truck counts are reported by axle category (California Department of Transportation, http://traffic-counts.dot.ca.gov/, accessed November, 2012). In other states, the proportion of medium and heavy-duty trucks is reported at the state level by road class (Table VM-4) [*FHWA*, 2011b]; these fractions are applied to total truck counts on individual roadways. Using counts of trucks with three or more axles (rather than totals for all trucks) as the proxy for diesel fuel use results in ~10-15% more diesel fuel use being assigned to rural areas with a similar reduction for urban areas.

The dominant fractions of on-road fuel consumed on roadways with explicit traffic count data (i.e., ~70% of gasoline and ~80% of diesel) are allocated from a state-level to specific grid cells, using vehicle travel from traffic count data as a spatial surrogate (i.e., traffic count x roadway length). Again, separate counts for total vehicles and for trucks with three or more axles are used as proxies for gasoline and diesel fuel use, respectively. The differences between statewide fuel sales and fuel quantities accounted for as outlined above (accounting for ~20-30% of fuel use), are assigned to remaining portions of the roadway network (i.e., those roads without traffic count data), using road length as a proxy. This is done separately for urban and rural grid cells to ensure that rural emissions are not overestimated, as travel on rural roads is expected to be lower [*Brondfield et al.*, 2012]. For example, in California ~30% of total vehicle travel occurs on roads without traffic counts, and of this subset ~90% is urban and ~10% is rural. However the length of all roadways in rural areas of California is ~2 times larger than in urban areas. Separate urban road length and rural road length are therefore used as spatial surrogates for apportioning emissions. The roadway network has been mapped nationally, and urban boundaries used throughout this analysis are as defined by the U.S. Census Bureau (http://www.census.gov/geo/maps-data/data/tiger-line.html, accessed July, 2013). In this analysis, only urbanized areas of 50 000 or more people are classified as urban. All other areas are considered rural, including urban clusters with greater than 2 500 people but less than 50 000 people.

For individual urban areas, vehicle travel is also reported by road class (Table HM-71) [*FHWA*, 2011b]. For selected urban areas with populations of 500 000 or more, fuel use by gasoline engines was constrained by comparing total reported vehicle travel within that urban area relative to the corresponding state total. We are unable to constrain diesel fuel consumption within individual urban areas in the same manner, since separate urban tables are not available for truck travel. However, diesel emissions are still constrained by statewide taxable fuel sales (Table MF-2), and between urban and rural areas using state-level reports of truck travel by road class (Table VM-4) [*FHWA*, 2011b]. The same emissions mapping approach outlined above was repeated at grid resolutions of 10 km, 4 km, 1 km, and 500 m. Fine-scale mapping of emissions (i.e., at 1 km and 500 m resolution) was only done for urban areas.

The density and carbon weight fractions of gasoline and diesel fuel reported by Kirchstetter et al. [1999b] were used to convert fuel sales volumes to equivalent mass rates of $CO_2$ emissions. Byproducts of incomplete combustion such as CO and unburned hydrocarbons that are co-

emitted with $CO_2$ were ignored because they account for minor fractions of total fuel use. McDonald et al. [2013] report that fleet-average light-duty vehicle emission factors for CO were 30-40 g/kg fuel burned in 2002, and had decreased to ~20 g/kg by 2010. The emissions of non-methane hydrocarbons were in turn an order of magnitude lower than for CO. The fraction of total fuel carbon emitted as CO in diesel exhaust is also minor [*Dallmann et al.*, 2012].

### *2.2.4 Weigh-in-Motion Data*

Traffic count data from weigh-in-motion (WIM) detectors are used to specify variations in $CO_2$ emissions over time. Binary data was obtained from the California Department of Transportation, and converted to a readable format using commercially available software (http://www.dot.ca.gov/hq/traffops/trucks/datawim/, accessed January, 2014). WIM stations exist to enforce size and weight limits on trucks, and stations count traffic and also weigh vehicles while they are in motion. Traffic counts are collected continuously on a year-round basis, with each vehicle classified based on the number of axles. Raw data are archived at high temporal resolution. Using WIM data, separate temporal activity profiles were developed for passenger vehicles and heavy-duty diesel trucks on multiple time scales: decadal, seasonal, day-of-week, and diurnal. We acquired and analyzed the complete WIM dataset for the state of California, including about 70 counting locations, for each year from 2000 to 2010. Prior studies have also made use of WIM data, typically for one specific year using data from a subset of the available sites [*Marr and Harley*, 2002; *Gurney et al.*, 2009].

Representative temporal profiles were developed to describe variations in vehicle traffic for urban and rural areas on finer time scales. Only the most complete WIM traffic count data from 2010 were used for this analysis. To classify WIM stations as urban or rural, we looked for a peak in passenger vehicle activity on weekday mornings. Morning traffic peaks associated with commuting are found in and near cities, but not in rural areas. Separate diurnal traffic profiles were developed for Monday-Thursday, Friday, Saturday, and Sunday following Marr et al. [2002], with separate profiles resulting based on urban and rural WIM station data. Day-of-week variations in daily traffic totals are reported for passenger vehicles and for trucks. Seasonal variations in traffic are described using factors calculated for each month and averaged across sites with at least nine complete months of data.

The WIM dataset is well-suited for analysis of changes in emissions over time, since the locations of counting stations have remained fixed for long periods. In earlier years, data are intermittent and available ~60 days per year. By 2010, data availability is close to 100% of days on a year-round basis at most sites. Traffic counts for each year were normalized to corresponding counts for 2007. This year was chosen as a reference point because traffic and fuel use in California reached a peak then and subsequently declined. Data were included for each site and year if at least 60 days of complete measurements were available. Stations were classified based on observed growth rates between 2000 and 2007 as either high (top 10%), average (10-90th percentile), or low. This analysis was done separately for passenger vehicles and heavy-duty trucks.

## 2.3 Results & Discussion

### *2.3.1 On-Road $CO_2$ Emissions and Comparisons with VULCAN and EDGAR*

Vehicle emissions (on-road gasoline + diesel) within major urban centers show up prominently on the maps for both California and Texas (see Figure 2.1). Overall, emissions from motor vehicles in urban areas are higher than in more sparsely populated areas, by about an order of magnitude. Emissions are greatest near urban cores (>1 000 tC $km^{-2}$ $y^{-1}$) and decrease as one moves to the periphery (300 tC $km^{-2}$ $y^{-1}$). In both California and Texas, on-road emissions of $CO_2$ are concentrated in a few metropolitan areas. Los Angeles and San Francisco-San Jose account for ~50% of on-road $CO_2$ emissions in California, and Dallas-Fort Worth and Houston account for ~30% of on-road emissions in Texas. Emissions due to vehicle travel on highways outside of the major urban areas are also apparent in Figure 2.1, with larger relative contributions to emissions on rural highways coming from diesel trucks.

Gasoline $CO_2$ emissions dominate over diesel especially in urban areas, accounting for 80-90% of the total (Table 2.1). In rural areas, diesel is relatively more important (30-40% of total emissions). Inventories that assume diesel trucks account for a constant fraction of total vehicular traffic at all locations will erroneously over-assign $CO_2$ emissions to urban areas. Larger errors will likely result in the spatial assignment of other pollutants such as $NO_x$ and black carbon (BC), for which the diesel contribution to total emissions is greater than for $CO_2$ [*Ban-Weiss et al.*, 2008b; *McDonald et al.*, 2012]. This is particularly true in Texas, where ~60% of diesel truck $CO_2$ emissions occur outside of urban areas, in contrast to passenger vehicles for which ~60% of emissions are within urban areas (Table 2.1).

Comparisons of on-road emissions estimates from FIVE (this study), VULCAN, and EDGAR are shown in Table 2.1 and Figure 2.1. We focus on three spatial scales: national, state, and urban. Note that in addition to including on-road motor vehicle emissions, VULCAN and EDGAR map many other sources of emissions that are not considered in this study, including industrial, electricity generation, non-road, and residential/commercial sectors. Also, results are not shown for the New York City metropolitan area because diesel emissions were not mapped in this study. Differences among emission estimates increase as the domain of interest becomes smaller. Nationally for the U.S., all three inventories of on-road $CO_2$ emissions agree to within 5% (Table 2.1). At the state level for California and Texas, VULCAN estimates are ~10% lower than this study. On-road $CO_2$ emissions in EDGAR are 30% higher for California, and 20% lower in Texas compared to the present study. The differences in emission estimates between EDGAR and FIVE increase when one focuses in on specific urban areas. EDGAR indicates on-road $CO_2$ emissions in California cities that are higher than this study by 40-80%, and also over-estimates emissions in Texas cities by as much as 20-30%. VULCAN estimates are in closer agreement with FIVE for all of the cities that we evaluated; differences are within the uncertainty of our estimates.

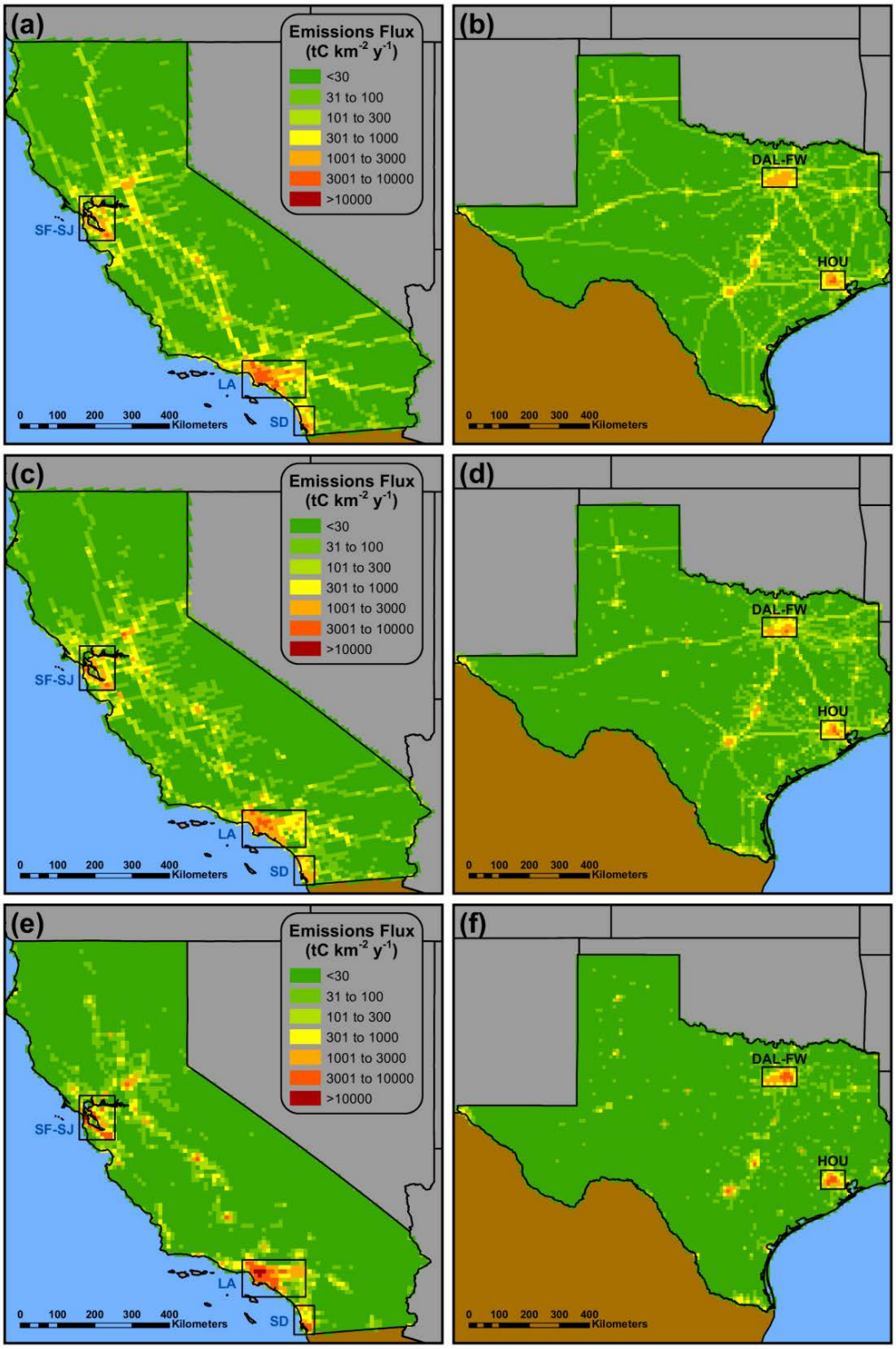


**Figure 2.1.** On-road emissions of $CO_2$ for California (left) and Texas (right) for FIVE (top row, a-b), VULCAN (middle row, c-d), and EDGAR (bottom row, e-f). All maps are on a 10 km grid for the year 2002, except for panels e-f which are mapped at 0.1 degree resolution. The same color scale applies to all panels. See Table 1 for details on marked urban areas.

**Table 2.1.** Comparison of annual on-road $CO_2$ emission estimates from FIVE (this study), VULCAN, and EDGAR for 2002.[a]

| Domain | Gasoline Engines ($10^6$ tC) | Diesel Engines ($10^6$ tC) | On-Road Total[b] ($10^6$ tC) | On-Road VULCAN[c] ($10^6$ tC) | On-Road EDGAR[d] ($10^6$ tC) |
|---|---|---|---|---|---|
| *U.S.*[e] | 321 ± 11 | 95 ± 5 | 416 ± 12 | 398 | 406 |
| *California* | 36.6 ± 1.8 | 8.0 ± 0.8 | 44.6 ± 2.0 | 40.1 | 56.1 |
| *Urban*[f,g] | 28.7 ± 3.2 | 4.5 ± 0.6 | 33.2 ± 3.3 | 30.4 | 50.4 |
| Los Angeles (LA) | 13.5 ± 1.5 | 2.0 ± 0.3 | 15.4 ± 1.5 | 13.8 | 27.8 |
| San Francisco/San Jose (SF-SJ) | 5.9 ± 0.7 | 0.7 ± 0.1 | 6.6 ± 0.7 | 6.4 | 10.7 |
| San Diego (SD) | 2.83 ± 0.32 | 0.29 ± 0.04 | 3.12 ± 0.32 | 3.1 | 4.2 |
| *Texas* | 27.0 ± 3.5 | 8.6 ± 0.9 | 35.6 ± 3.6 | 31.8 | 28.4 |
| *Urban*[f,g] | 17.4 ± 2.8 | 3.4 ± 0.5 | 20.7 ± 2.9 | 19.2 | 20.9 |
| Dallas/Fort Worth (DAL-FW) | 5.2 ± 0.9 | 1.1 ± 0.2 | 6.3 ± 0.9 | 6.0 | 7.9 |
| Houston (HOU) | 4.0 ± 0.7 | 0.7 ± 0.1 | 4.7 ± 0.7 | 4.5 | 5.7 |

a. Uncertainty bounds give 95% confidence intervals.
b. On-road Total = Gasoline + Diesel. Presented values are rounded and so may not sum exactly.
c. The VULCAN inventory, version 2.2, can be found at: http://vulcan.project.asu.edu.
d. The EDGAR inventory, version 4.2, can be found at: http://edgar.jrc.ec.europa.eu.
e. $CO_2$ emissions calculated from national taxable gasoline and diesel fuel sales.
f. Uncertainty at the urban-level is calculated as the propagation of errors in state-level fuel sales reports and spatial apportionment using traffic count data (see text).
g. A map of urban and rural grid cells for the VULCAN and EDGAR inventories can be found in auxiliary material. Grid cells were classified as urban if their centroids were within urban boundaries as defined by the U.S. Census Bureau. Individual metropolitan areas listed above are shown as boxes in Figure 2.1.

As the national inventories are closely aligned, differences in the ways that motor vehicle emissions are disaggregated from national totals down to state and urban scales must account for most of the discrepancies. EDGAR is a global inventory that disaggregates national data, and uses road density as a spatial proxy, which may cause overestimation of emissions in population centers. VULCAN is for the U.S. only and first estimates vehicle emissions at a county-level, projects the emissions onto a road atlas, and then aggregates to 10 km grid cells. VULCAN estimates are expected to agree more closely with the present study since similar traffic datasets are used. Similar findings have been reported by Gately et al. [2013], who compared their vehicle estimates of $CO_2$ emissions for Massachusetts with those from other inventories, and found that VULCAN agreed to within 5%, whereas EDGAR overestimated by 23% on average. EDGAR also assigns most of the on-road vehicle emissions to be within cities, and shows only minimal amounts in outlying areas (see bottom row of Figure 2.1). VULCAN has an urban to rural emission distribution that is similar to FIVE, but differences can be seen in specific cities. For example, in Dallas and Fort Worth, VULCAN shows two hotspots, while FIVE has emissions that are more evenly distributed over the broader region. For the Los Angeles area, our approach predicts higher emissions from traffic in inland communities than VULCAN.

### *2.3.2 Mapping Emissions at Higher Resolutions*

To illustrate how maps of on-road emissions of $CO_2$ are affected by spatial resolution, we evaluate emissions at resolutions of 10 km, 4 km, 1 km, and 500 m for the Los Angeles area (Figures 2.2 and 2.3). The traffic count data and roadway network, used to spatially apportion fuel usage in this study, are available at a roadway segment level. Therefore the spatial resolution of the underlying traffic data is still much less than the highest resolution emission maps (500 m) shown in this study. We chose to model vehicle emissions at these spatial resolutions because they represent a range of length scales commonly used in regional and local air quality models [*Kleinman et al.*, 2004; *S W Kim et al.*, 2009; *Brioude et al.*, 2011; *Brioude et al.*, 2013; *Joe et al.*, 2013], satellite retrievals of tropospheric air pollutants [*Russell et al.*, 2010; *Brauer et al.*, 2012; *Kort et al.*, 2012], and assessment of near-roadway air pollution [*Karner et al.*, 2010].

Increased spatial resolution is expected to result in sharper gradients, since emissions on heavily traveled highways are more accurately mapped and concentrated in smaller areas. For reference, the 10 km resolution emission map (Figure 2.2a) uses the same grid system as VULCAN. There are clear differences between the coarse and finer-resolution emission maps (see Figure 2.2). The highway network is readily apparent based on the much higher on-road $CO_2$ emission fluxes compared to surrounding areas, but only in the higher-resolution maps. The highway network is clearly distinguishable at 1 km, and emissions are brought into even sharper focus at 500 m resolution. With the 10 and 4 km grids, highway emissions are more widely distributed, and as a result strong horizontal emission gradients tend to disappear. Traffic on major arterial roadways is also visible in the 500 m resolution emission map. Finer details are especially apparent for the Los Angeles area because traffic count data are available for many of the major surface streets.

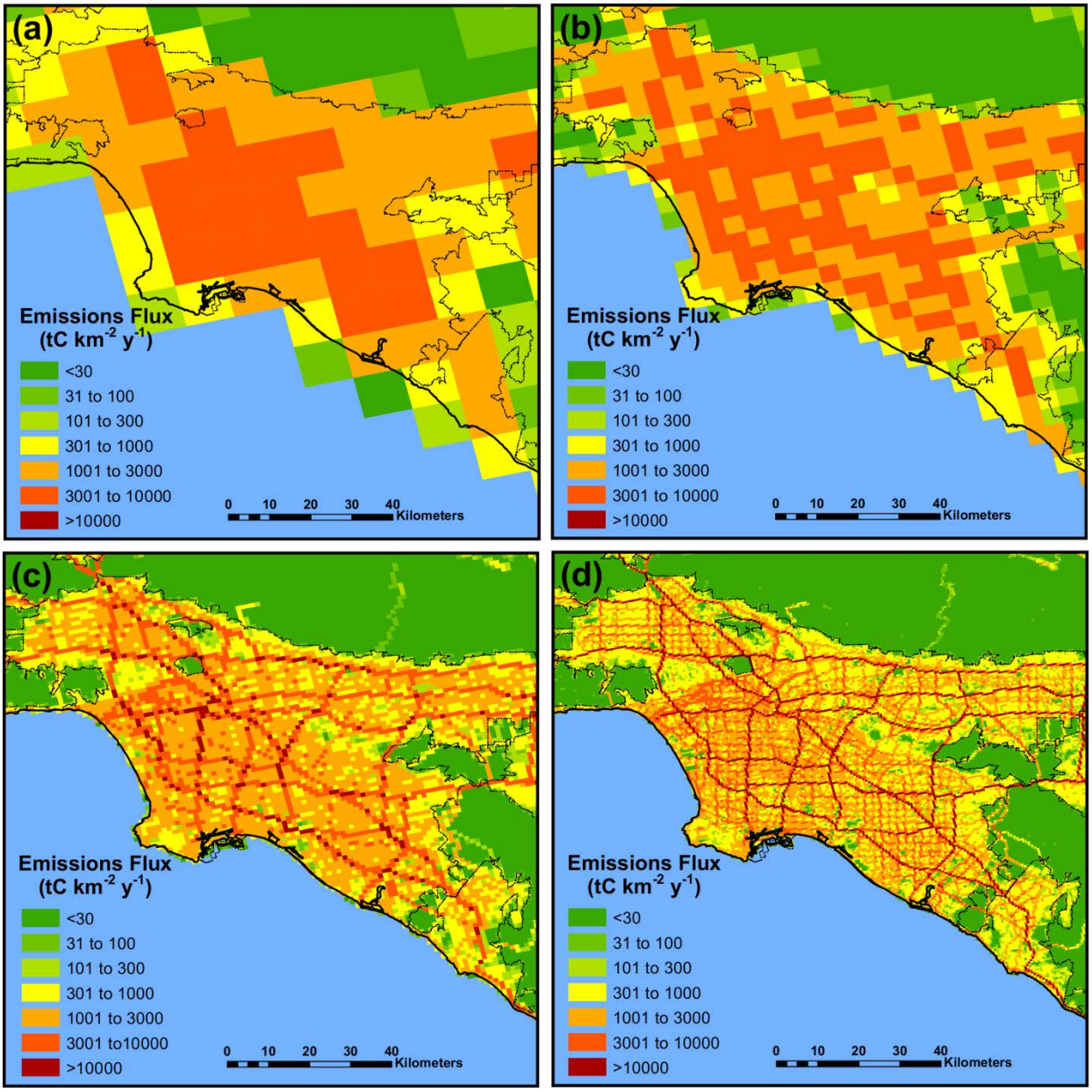


**Figure 2.2.** Effect of spatial resolution on on-road emission fluxes of $CO_2$ in Los Angeles at (a) 10 km, (b) 4 km, (c) 1 km, and (d) 500 m. Emissions are shown for the year 2010.

Generally, traffic count data on local roads are difficult to obtain, and are not sampled or archived in a comprehensive manner as compared to the highway network. Yet non-highway vehicle activity constitutes a large fraction (about half) nationwide [*FHWA*, 2011b]. To improve characterization of traffic patterns on local roads especially within cities, the integration of new data sources would be useful. Such sources include mobile phones which can record, store, and report data from global positioning systems while operating in vehicles that are in motion [*Herrera et al.*, 2010]. Such data are currently used by major internet and vehicle navigation service providers to show real-time traffic information. Traffic sensing on arterial roads is also increasing due to the proliferation of well-instrumented city streets and intersections. These sensors include traditional in-road traffic sensors as well as other technologies such as radio frequency identification readers used for automated collection of tolls [*Landt,* 2005]. The trend towards increasing vehicle activity information and open data platforms is clear, and new data sources are likely to increase empirical support for high-resolution emissions mapping.

The question of spatial resolution is relevant when integrating satellite observations of air pollutants with the development of bottom-up emission inventories, especially pollutants for which motor vehicles are a dominant source of emissions, such as in certain urban areas for $NO_x$ [*McDonald et al.*, 2012] and $CO_2$. Satellite columns of $NO_2$ have been retrieved with global coverage at spatial resolutions of ~13 km x 24 km using the Ozone Monitoring Instrument (OMI) [*Levelt et al.*, 2006]. The spatial resolution shown in Figure 2.2a aligns approximately with current capabilities of low Earth orbiting satellites to map $NO_x$ emissions from space. Spatial averaging techniques have been utilized to resolve $NO_x$ even more finely down to 5-10 km [*Russell et al.*, 2010]. In general, current satellite observations cannot resolve sharp pollutant emission gradients near roadways (Figures 2.2c and 2.2d), but may be appropriate for constraining emissions at urban and larger scales. For satellite retrievals of $CO_2$, the Greenhouse Gases Observing Satellite (GOSAT) is capable of resolutions of ~10 km at nadir [*Kort et al.*, 2012]. The Orbiting Carbon Observatory (OCO-2), a geostationary satellite to be launched in 2014, will have a footprint of ~3 $km^2$ at nadir [*Boesch et al.*, 2011], and also capable of achieving high temporal resolution (i.e., hourly data) at individual locations [*Streets et al.*, 2013].

To address further the question of what can be gained from increasing spatial resolution of emission maps within urban areas, the distribution of $CO_2$ emission fluxes (tC $km^{-2}$) in the Los Angeles area are ordered from lowest to highest for various spatial resolutions (Figure 2.3). There is a dividing line at emission levels of ~7 000 tC $km^{-2}$ $y^{-1}$ that separates freeways from other smaller roadway types. Figure 2.3 shows that on-road $CO_2$ emission fluxes over the most heavily traveled grid cells that include major highway segments, increase by a factor of 3 when spatial resolution increases from 10 km to 1 km. When the resolution is further increased from 1 km to 500 m, an additional increase of ~60% is seen. Interestingly, little increase is seen in emission fluxes when increasing the resolution from 10 km to 4 km. Highly-resolved emission maps are important for understanding transportation microenvironments. Karner et al. [2010] reviewed near-roadway air quality studies and found that pollutant concentrations typically fall to background levels at downwind distances of 115-570 m. A recent air quality modeling study in and around the Port of Oakland found twofold increases in predicted concentrations of elemental carbon in locations closest to diesel truck emissions, when spatial resolution in the model was changed from 1 km to 250 m [*Joe et al.*, 2013].

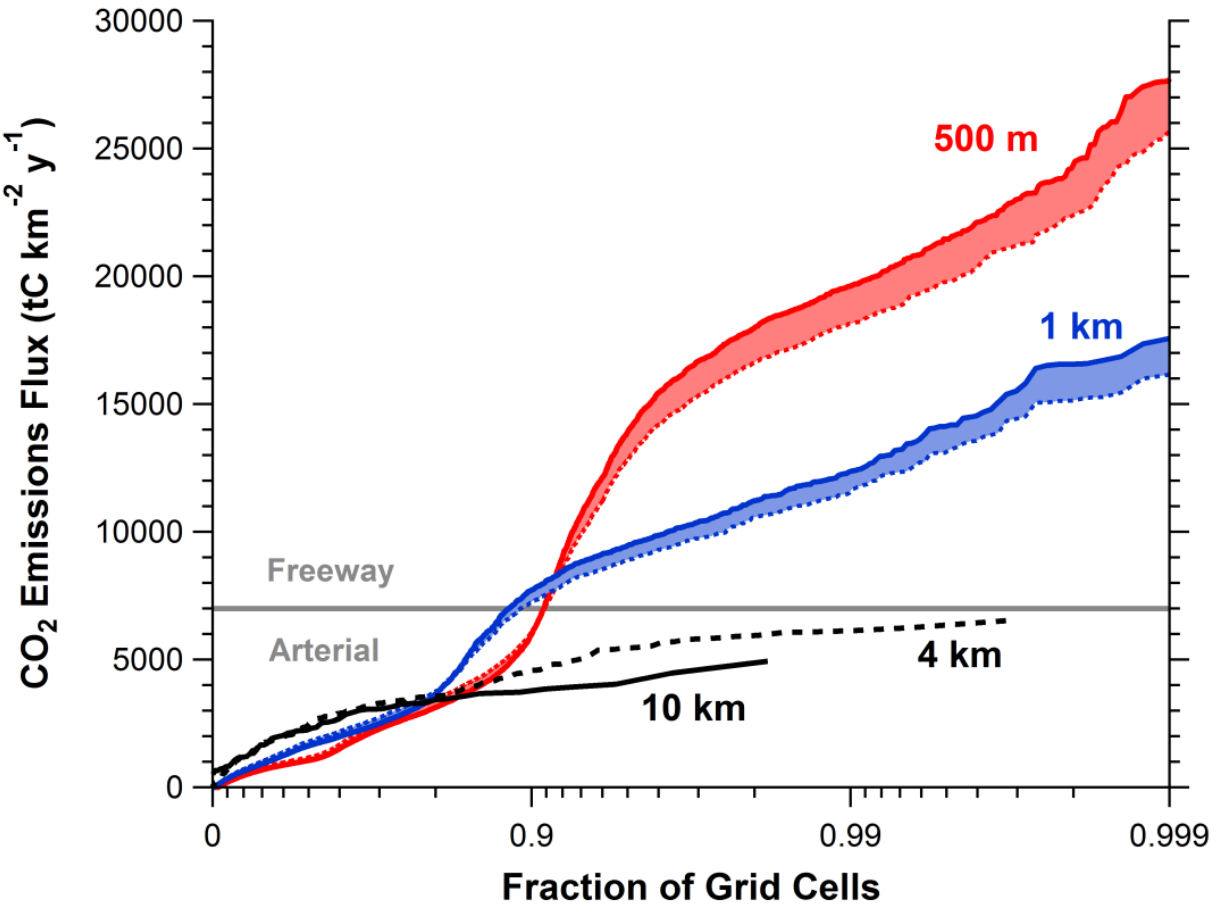


**Figure 2.3.** Distribution of emissions from lowest to highest for urbanized portions of Los Angeles (see Figure 2.2). For example, emission fluxes exceed ~7 000 tC $km^{-2}$ $y^{-1}$ for ~10% of the urbanized land area in Los Angeles. Above this dividing line, grid cells contain major highway segments. The dashed lines at 1 km and 500 m resolutions show results of an emission factor sensitivity analysis (see text). Emissions are shown for the year 2010.

A substantial fraction (about half) of vehicle activity occurs nationwide on roads characterized by high driving speeds (interstates/freeways + rural principal roads). It is well-known that most conventional internal combustion engines have lower rates of fuel consumption when driving on highways compared to stop-and-go city driving. To understand potential effects of fuel economy differences on $CO_2$ emission maps, we performed a sensitivity analysis allowing $CO_2$ emission factors to vary by road type. The shape of the curve relating $CO_2$ emissions (grams emitted per unit distance traveled) and vehicle speed is parabolic, with a minimum emission rate at vehicle speeds of 70-80 km $h^{-1}$ [*Barth and Boriboonsomsin*, 2008]. Emission factors for $CO_2$ increase by a factor of two when average vehicle speeds drop from 50 to 25 km $h^{-1}$, but vary relatively little at higher speeds. Therefore the largest changes in $CO_2$ emission factors are anticipated on congested urban arterial roadways where average vehicle speeds are commonly below 50 km $h^{-1}$ especially at peak traffic times. Fuel economy penalties associated with stop-and-go driving and traffic congestion may result in redistribution of $CO_2$ emissions away from highways relative to estimates in the present study. This can be seen in Figure 2.3, which shows the results of the sensitivity analysis when emission factors include speed adjustments for different road types. Emissions are first re-estimated at a state-level by road type, taking into account a higher $CO_2$ emission factor (g $CO_2$ $km^{-1}$) for urban arterial roads. State-level emissions are then gridded using the same spatial surrogates outlined in Section 2.2.3. These two approaches to $CO_2$ emission apportionment give similar results. Note that hybrid vehicles are expected to flatten the vehicle speed-$CO_2$ emissions relationship at lower speeds (i.e., similar fuel economy under stop-and-go driving conditions) [*Fontaras et al.*, 2008], making the results potentially even more similar if there is a high penetration of hybrid vehicles in the urban fleet.

Figure 2.4 presents examples of high-resolution $CO_2$ emission maps (HI-FIVE) for other urban areas, and demonstrates the extensibility of the general approach used here. The New York City example (Figure 4a) illustrates an application of the emissions mapping approach across a densely populated multi-state region. New York City also provides a point of contrast to Los Angeles in terms of population density. The highway network in New York is not as extensive, and on-highway emissions only become clearly visible in suburban areas on Long Island, and in neighboring states of New Jersey and Connecticut. The San Francisco Bay area (Figure 4b) features contrasts between a dense urban center (San Francisco) and other nearby lower-density cities (e.g., San Jose). In San Jose, a network of highways akin to Los Angeles exists. Emission maps for Houston and Dallas-Fort Worth are also shown in Figure 4, to provide examples of even lower-density sprawling cities, with resulting emission fluxes that tend to be lower on average than other cities considered here. Consistent mapping of vehicle emissions at high spatial resolution could facilitate more detailed study of relationships between urban form and transportation emissions, by allowing for sub-regional and cross-city comparisons [*Marshall*, 2008; *Gately et al.*, 2013].

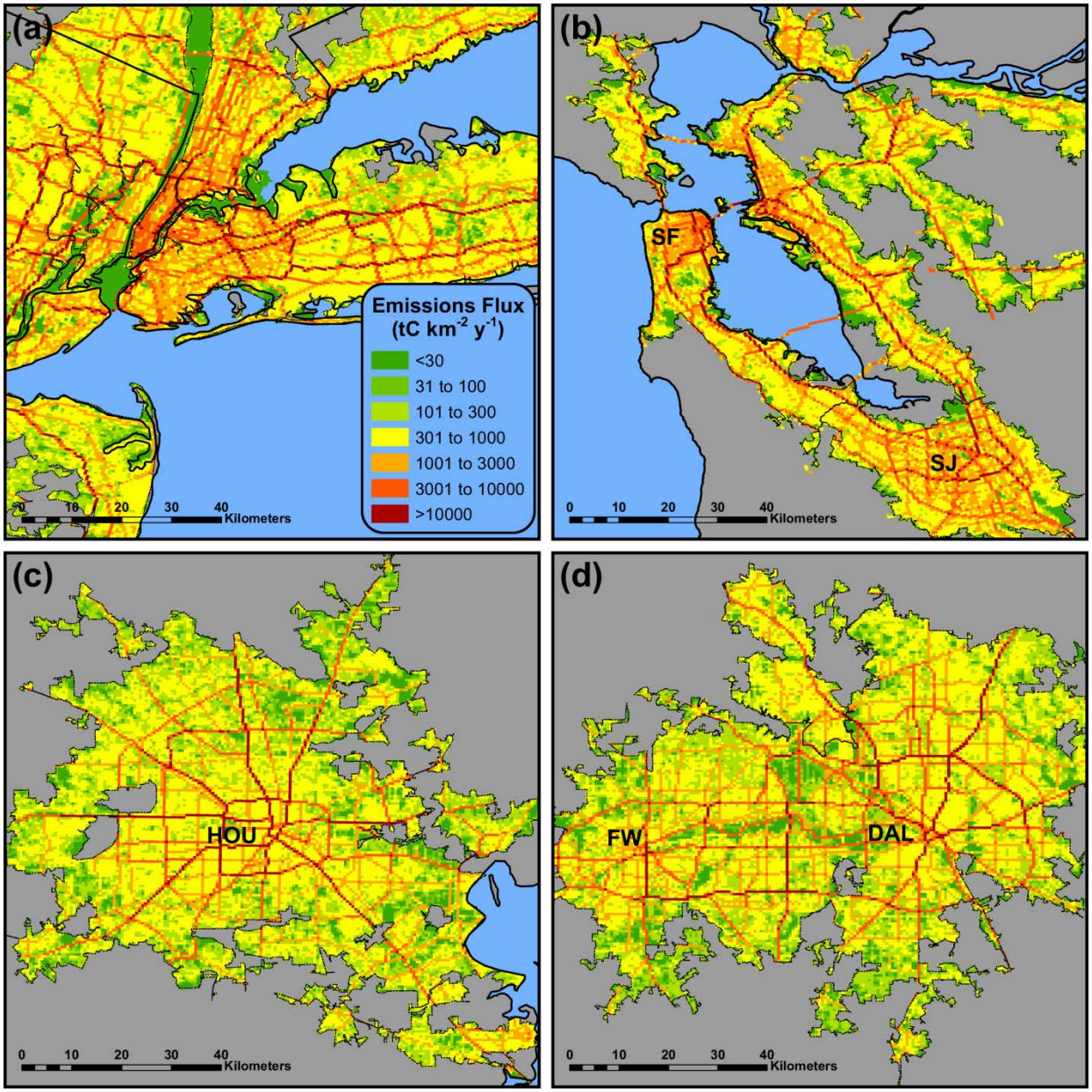


**Figure 2.4.** High resolution maps of $CO_2$ emissions (HI-FIVE) from gasoline-powered vehicles for (a) New York City, (b) San Francisco-San Jose, (c) Houston, and (d) Dallas-Fort Worth. Only emissions in urbanized areas are shown; maps are for the year 2010. Horizontal resolution is 500 m in all cases. Note also that the 0-40 km distance scale is the same for all four areas.

### *2.3.3 Variability in Emissions on Short Time Scales*

Both spatial and temporal resolution is needed when emissions estimates are used as input to atmospheric models, and in turn for comparison with atmospheric observations. In this study, weigh-in-motion traffic count data were analyzed to characterize variations in vehicular $CO_2$ emissions on various time scales: diurnal, day-of-week, and seasonal. Different temporal profiles are developed for light- and heavy-duty vehicle traffic, as shown in Figure 2.5. The diurnal activity patterns on weekdays clearly differ between the two vehicle types. Weekday passenger vehicle traffic exhibits two distinct (morning and evening) commuter-related peaks. In contrast, truck traffic shows a single midday peak. These findings are consistent with prior work [*Marr and Harley*, 2002]. Because passenger vehicles dominate on-road $CO_2$ emissions in urban areas (Table 2.1), the diurnal pattern of urban on-road emissions is similar to that for light-duty vehicles (Figure 2.6). For other pollutants where heavy-duty diesel emission factors are significantly higher than for gasoline vehicles, like for BC [*Dallmann et al.*, 2013], the diurnal profile of emissions is expected to follow more closely the activity pattern for heavy-duty trucks. This highlights the need to apply separate temporal profiles to characterize traffic and associated $CO_2$ emissions for light- and heavy-duty vehicles.

While large decreases in weekend truck traffic and their emissions are well documented [*Marr and Harley*, 2002; *Harley et al.*, 2005], day-of-week variations for passenger vehicle traffic are also of interest (Figure 2.5). Urban emissions of $CO_2$ are found to increase by ~10% through the workweek between Monday and Friday, due to changes in passenger vehicle activity, and then decrease by ~20% and ~30% relative to Friday peak levels on Saturdays and Sundays, respectively (Figure 2.6). Day-of-week variations in traffic can lead to noticeable changes in on-road $CO_2$ emissions, given that vehicle emissions are the largest anthropogenic source of $CO_2$ in many California and Texas cities (see Appendix A, Figure A1). Given a design goal of urban $CO_2$ monitoring networks to detect changes in emission fluxes that differ by 10% or more from the average [*Kort et al.*, 2013], then comparing $CO_2$ emissions on Fridays to other (especially weekend) days could serve as a repeatable real-world test case for detection capabilities of emerging $CO_2$ monitoring networks, at least in urban areas where motor vehicle emissions tend to dominate.

There are also clear contrasts between urban and rural vehicle activity patterns. The differences are most apparent for passenger vehicles (Figure 2.5); heavy-duty truck traffic shows similar activity patterns throughout the urban and rural areas considered here. Passenger vehicle traffic in rural areas follows a similar diurnal profile to heavy-duty trucks, and does not have commuter peaks as seen in urban areas on weekdays. As a result, when emissions are aggregated to the statewide level, emissions are highest on weekdays in the late afternoon/early evening hours rather than in the mornings (Figure 2.6), which is consistent with VULCAN for the contiguous U.S. [*Nassar et al.*, 2013].

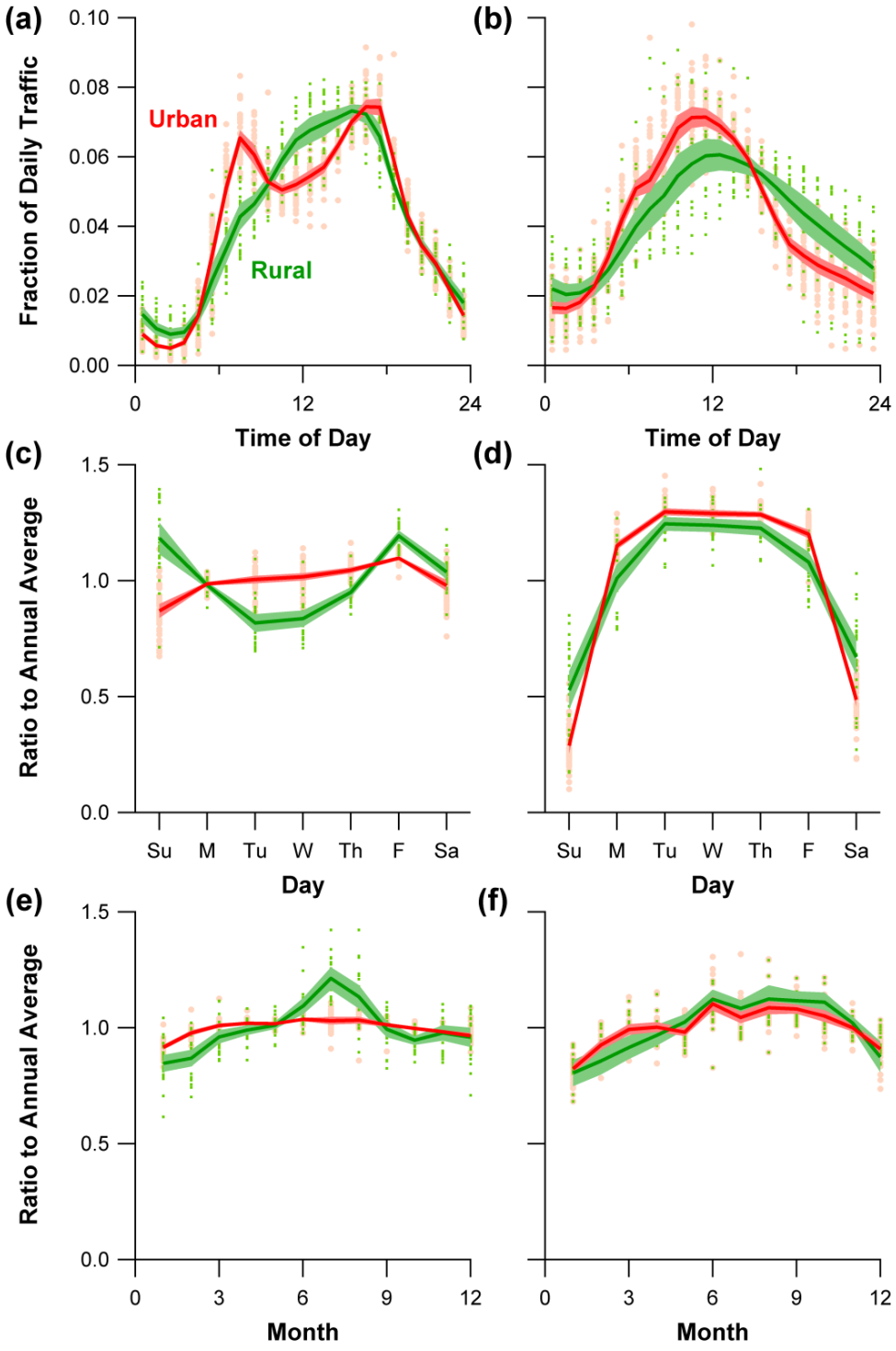


**Figure 2.5.** Diurnal (a-b), day of week (c-d), and seasonal variations (e-f) in counts of passenger vehicles (left column) and heavy-duty diesel trucks (right column). Diurnal profiles are for weekdays (Monday-Thursday); for profiles on other days, see auxiliary material. Each marker represents observations at an individual weigh-in-motion traffic count location. Colored bands represent 95% confidence intervals for the means across all urban (red) and rural (green) sites.

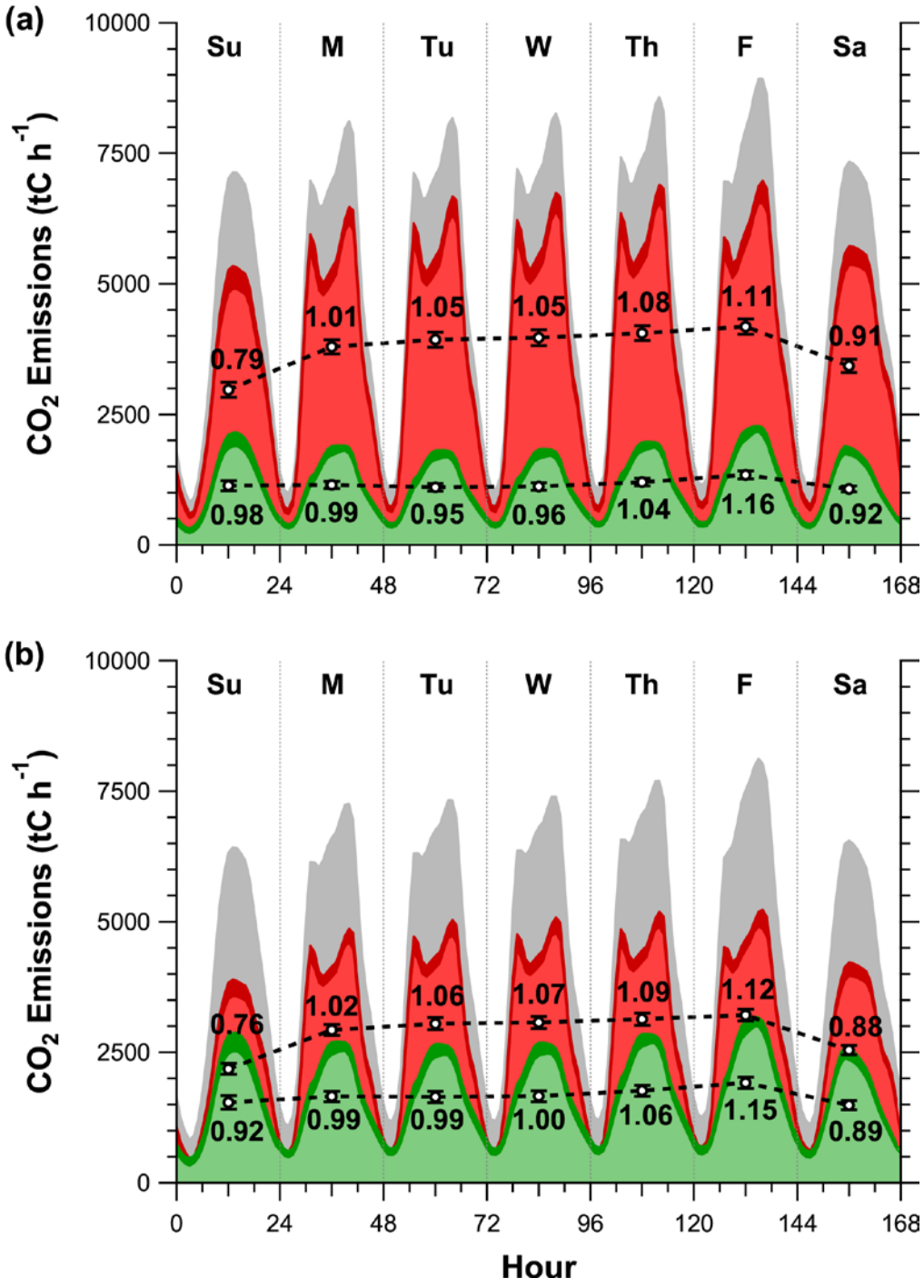


**Figure 2.6.** Diurnal (shaded) and day of week (dashed lines with labels) patterns of on-road $CO_2$ emissions for (a) California, and (b) Texas in 2010. Red and green shading denote emissions in urban and rural areas, respectively. Total (urban + rural) emissions are shown in gray. Ratios of day-specific emissions to the weekly average are labeled for each day. Uncertainty estimates indicate 95% confidence levels for diurnal (dark bands) and day of week (error bars) emissions. Confidence intervals are calculated using uncertainties in weigh-in-motion traffic count data shown in Figure 2.5.

Diurnal and day-of-week traffic profiles from this study are similar to results reported by Marr et al. [2002] using weigh-in-motion traffic count data from the mid-1990s for California. This suggests that diurnal and weekly patterns in vehicle activity have not changed much over longer time scales. We find smaller weekend decreases in heavy-duty truck traffic compared to Marr et al. [2002], who reported that weekend truck traffic decreases by ~80% and ~60% compared to weekday averages in urban and rural areas, respectively. Analysis of a larger and more complete WIM dataset in this study show decreases in weekend truck traffic of ~70% in urban and ~50% in rural areas. The seasonal activity patterns shown in Figures 2.5e and 2.5f are new, and all of the temporal profiles reported here are based on analysis of a more extensive database of traffic counts. Seasonal emission cycles are important to resolve, as they can be used to assign contributions to atmospheric observations from different emission sources [*van der A et al.*, 2008]. $CO_2$ fluxes due to biosphere-atmosphere exchange and natural gas combustion also exhibit seasonality [*Pataki et al.*, 2003]. Noteworthy increases of 35-40% are observed in heavy-duty truck traffic between January and August. The peak in August, especially in rural areas, may be linked in part to harvesting of crops. Passenger vehicle traffic in rural areas also exhibits strong seasonality, with year-round variation of ~40%. The peak occurs during summertime, presumably due to increased recreational and vacation-related driving. In contrast, seasonal variations in passenger vehicle traffic are limited to ~10% of mean levels in urban areas.

### *2.3.4 Decadal Emission Trends*

Due to the high data and time demands required to update bottom-up emission inventories, a common practice in air quality planning is to scale baseline emission inventories to represent conditions in other years. The scaling of emissions attempts to reflect effects of both increasing population and vehicle activity, as well as the effects of advances in vehicle and emission control technologies. An underlying implicit assumption often made when scaling baseline inventories is that the spatial distribution of emissions remains the same over time, and that any increases in traffic, for example, occur uniformly at all locations throughout the domain of interest. The EDGAR on-road inventory provides an example of this approach (Figure 2.7). The spatial distribution of on-road emissions remains constant over a 5-year period (from 2002 to 2007). We use weigh-in-motion traffic count data to consider whether non-uniform changes in vehicle activity have occurred since 2000. If population growth leads to new housing being built in suburban areas rather than as urban in-fill, evolution in spatial maps of emissions should be expected. Two time periods considered in this analysis are 2000 to 2007, and a later period from 2007 to 2010 that was affected by a major economic downturn. We choose to evaluate these two time periods because the recession provides a useful test case for detecting changes using weigh-in-motion traffic count data.

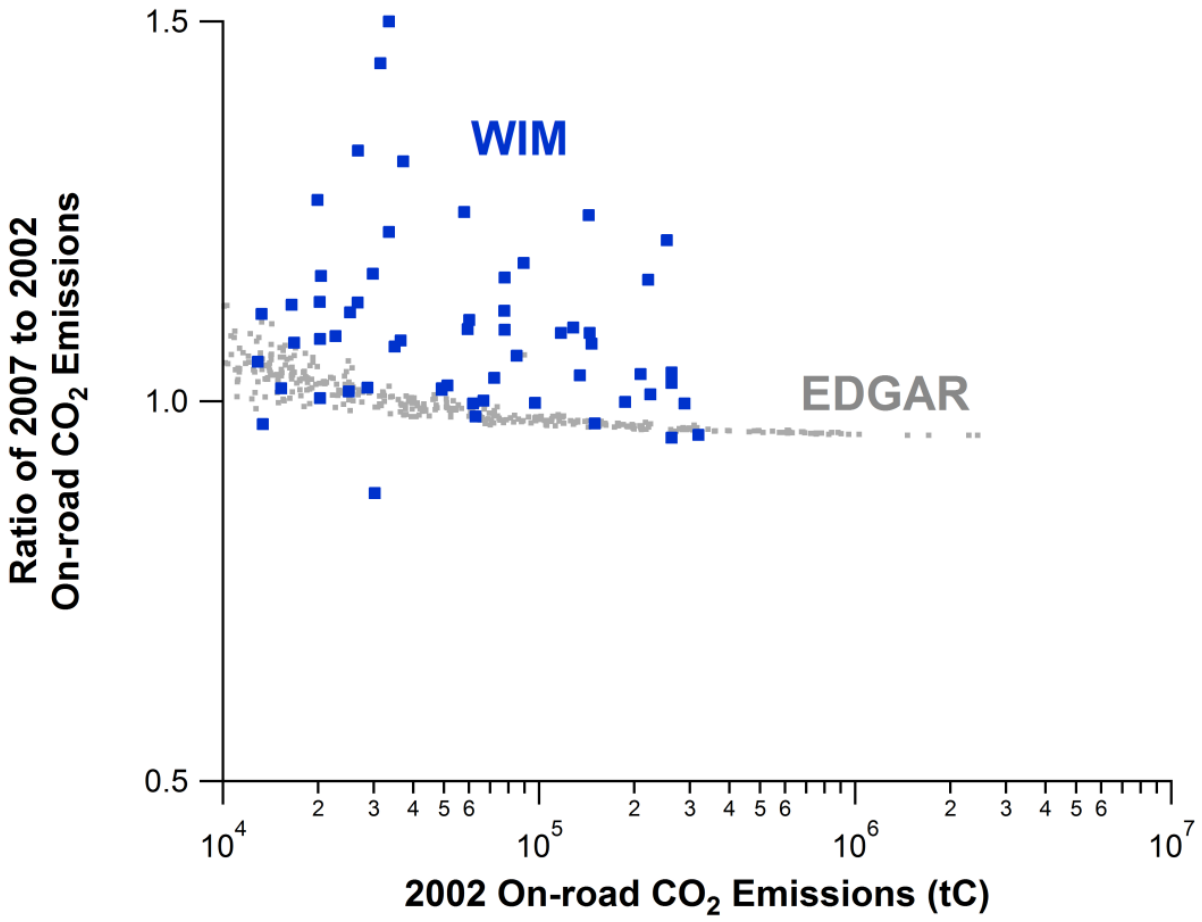


**Figure 2.7.** Change in on-road $CO_2$ emissions in EDGAR (version 4.2) between 2002 and 2007 for individual 0.1 x 0.1 degree grid cells over California. Changes in grid cells with weigh-in-motion detectors are calculated using the year 2002 inventory from this study, rather than from EDGAR. Grid cells with greater than $10^4$ tC emitted account for ~90% of the emissions in California.

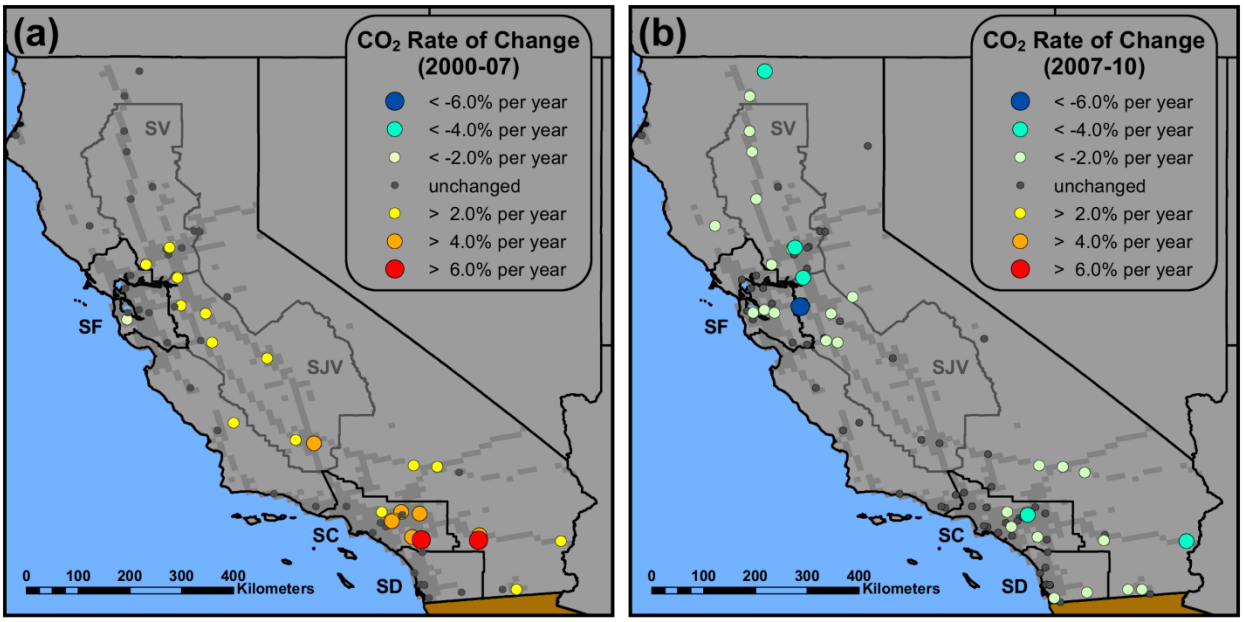


**Figure 2.8.** Annual growth rates in on-road $CO_2$ emissions in California for (a) 2000-07, and (b) 2007-10. Boundaries are shown for the five largest air basins in California: South Coast (SC), San Francisco Bay Area (SF), San Diego (SD), San Joaquin Valley (SJV), and Sacramento Valley (SV). Gray pixels are 10 km x 10 km grid cells with emission fluxes of >100 tC $km^{-2}$ $y^{-1}$.

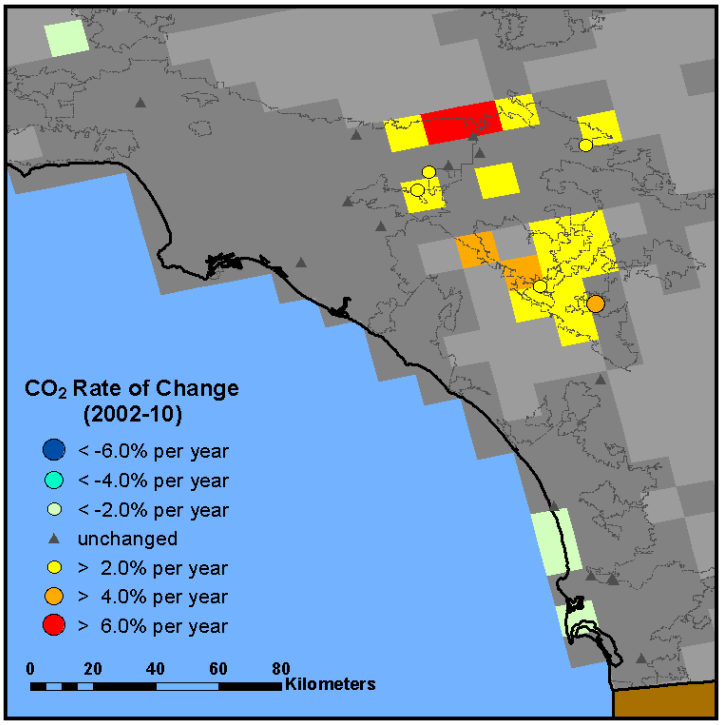


**Figure 2.9.** Comparison of changes in the on-road $CO_2$ emissions inventory (between 2002 and 2010) from this study with trends derived from weigh-in-motion traffic count data for Southern California. Each marker represents an individual weigh-in-motion detector.

In maps showing the rate of change in on-road $CO_2$ emission by location (Figure 2.8), differences among sites are evident during the period from 2000 to 2007 as described above. See Appendix B (Figure B1) for trends in weigh-in-motion traffic count data used in Figure 2.8. Since 2007, effects of the recession on traffic emissions were unevenly distributed. Prior to the recession (Figure 2.8a), high growth areas (>4% $y^{-1}$) are observed in inland areas of San Bernardino and Riverside counties, located east of Los Angeles. California's Central Valley also saw higher than average growth in on-road emissions (>2% $y^{-1}$). Little change in traffic was observed near the coast in Los Angeles, the San Francisco Bay area, or San Diego. A 2% $y^{-1}$ detection limit applies to this analysis, because when compounded over the period from 2000 to 2007, this matches the uncertainty in traffic counts from weigh-in-motion detectors. Using results from Li et al. [2010], we estimate ~15% uncertainty when traffic counts from WIM are compared with those obtained from video counting. After 2007 (Figure 2.8b), many locations saw decreases in emissions in excess of 2.0% $y^{-1}$. In general, locations with a high diesel truck traffic fraction exhibited the largest decreases in on-road $CO_2$ emissions after 2007, and these locations tended to be outside of major metropolitan areas.

As mentioned above, the EDGAR inventory shows little change in the spatial pattern of on-road emissions over a 5-year time period from 2002 to 2007. However, changes in on-road emissions of $CO_2$ at the ~70 weigh-in-motion stations show increases by as high as 50%, with many locations increasing by more than 25% (Figure 2.7). In Figure 2.9, we show that our approach to mapping emissions using year-specific taxable fuel sales and traffic count data, identify areas with higher than average growth in on-road emissions. Annual changes in emissions are not spatially homogenous, and this highlights the importance of periodically updating emission inventories as new information becomes available.

## 2.4 Conclusions

In this study, fuel sales reports and traffic count data were used to create a fuel-based inventory for vehicle emissions (FIVE) of $CO_2$ at various spatial resolutions, for major urban centers in the U.S. Passenger vehicles account for 80-90% of on-road $CO_2$ emissions in cities, whereas heavy-duty diesel trucks are relatively more important in rural areas and account for 30-40% of the on-road total. Results from FIVE were compared with other emission inventories, VULCAN and EDGAR. All three inventories agree within 5% at the U.S. national level. EDGAR appears to overestimate on-road $CO_2$ emissions in the largest cities in California and Texas by as much as 20-80%, while VULCAN estimates are in agreement with FIVE. We also show that spatial resolution has important effects on the mapping of motor vehicle emissions. At grid resolutions of 10 and 4 km, strong emission gradients that are known to exist near highways are not apparent. The highway network becomes clearly distinguishable at grid resolutions of 1 km. Increasing the resolution from 1 km to 500 m leads to further increases in $CO_2$ emission fluxes by ~60% for grid cells that contain segments of heavily trafficked highways.

Over shorter time scales (diurnal, day-of-week, and seasonal cycles), there are large contrasts in on-road vehicle emission patterns in urban and rural areas, and between light- and heavy-duty vehicles. In urban settings, daily on-road emissions of $CO_2$ are found to increase by 10% through the workweek, with a maximum on Fridays, followed by decreases from the Friday peak of 20-30% on weekends. This weekly cycle in traffic-related $CO_2$ emissions could serve as a useful test

case for evaluating the ability of urban $CO_2$ monitoring networks to detect future emission changes. We also find significant seasonal variability in both passenger vehicle and heavy-duty truck traffic in rural areas. Year-to-year changes in vehicle activity were found to be non-uniform across California between 2000 and 2007. High-growth areas where on-road emissions increased by >4% $y^{-1}$ were concentrated in fast growing suburbs to the east of Los Angeles. Between 2007 and 2010, decreases in vehicle emissions were seen over many parts of California. Changes of up to 50% in on-road emissions were found over a period of ~5 years, highlighting the need for timely updates to motor vehicle emission inventories.

# Chapter 3: Long-Term Trends in Nitrogen Oxide Emissions from Motor Vehicles at National, State, and Air Basin Scales

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## 3.1 Introduction

Nitrogen oxides ($NO_x$ = NO + $NO_2$) are trace gases that strongly influence atmospheric chemistry and air pollution. $NO_x$ is a critical precursor in the formation of tropospheric ozone. $NO_x$ is oxidized in the atmosphere to form nitric acid and aerosol nitrates, contributing to fine particulate matter concentrations, acid deposition, and visibility degradation. $NO_x$ emissions are predominantly anthropogenic, with natural sources such as soil and lightning estimated to account for ~20% of the global budget [*IPCC,* 2007]. Two of the most important anthropogenic emission sources are on-road motor vehicles and power plants. The relative importance of heavy-duty diesel engines as a source of $NO_x$ emissions has grown in the US in recent years, as light-duty vehicle and power plant sources have been controlled [*Frost et al.*, 2006; *S W Kim et al.*, 2006; *Bishop and Stedman*, 2008; *Dallmann and Harley*, 2010].

Continuous monitoring of $NO_x$ emissions from large power plant sources has been required in the US since the 1990s. In contrast, there is a much larger number of motor vehicles in operation, and emissions measurements for mobile sources are sparse. The distribution of motor vehicle emissions has become increasingly skewed over time, with a small number of vehicles being responsible for an increasingly large fraction of total emissions [*Bishop and Stedman,* 2008]. This skewed emission distribution makes it difficult and costly to acquire and test a representative sample of vehicles via laboratory measurements. Difficulties in measuring emissions and activity have led to large associated uncertainties in motor vehicle emission inventories, both in predicting emission trends over time, and in estimating absolute emissions of $NO_x$ [*Parrish*, 2006; *S W Kim et al.*, 2009; *Dallmann and Harley*, 2010]. Top-down techniques have been developed to constrain $NO_x$ inventories using satellite retrievals of tropospheric $NO_2$ columns [*Martin et al.*, 2003]. However, development of bottom-up inventories remains an important research priority [*NRC*, 2000], and is needed to understand the contributions of different sources to total emissions.

Mobile sources of air pollution are especially important in California, where fossil fuel-burning power plants mostly run on natural gas rather than coal, and a generally high degree of $NO_x$ emission control has been achieved. This study includes analysis of state-level $NO_x$ emission trends in California, as well as evaluations of emissions in the South Coast and San Joaquin Valley air basins. The South Coast air basin (~17 000 $km^2$) encompasses the Los Angeles area and is mostly urban with a population of 17 million people. The San Joaquin Valley (~61 000 $km^2$) is located in central California and is more rural with a population of ~4 million people (see auxiliary material for map and information on vehicle fleet demographics). Both air basins experience some of the highest concentrations of ozone ($O_3$) and fine particulate matter ($PM_{2.5}$) observed in the US. During the summer of 2010, a large-scale field measurement campaign

called CalNex (Research at the Nexus of Air Quality and Climate Change) took place in California, jointly sponsored by the California Air Resources Board, National Oceanic and Atmospheric Administration, and California Energy Commission. The present study addresses a key CalNex research question: whether there are important differences in precursor emissions or ozone formation chemistry in the San Joaquin Valley and South Coast air basins.

The primary objective of this study is to quantify trends in $NO_x$ emissions from on-road gasoline and diesel-powered vehicles. Compared to previous work [*Dallmann and Harley*, 2010], this study covers a longer time period (1990-2010), and includes air basin and state-level emission estimates as well as further evaluation of national trends. We use a fuel-based approach to estimate emissions, where fuel sales are used to measure pollution-causing activity by motor vehicles, and emission factors are normalized to fuel consumption. Fuel-based inventory estimates are then compared with predictions from the most current versions of the emission models EMFAC and MOVES, respectively developed by the California Air Resources Board and the US Environmental Protection Agency. Further comparisons at the national level are made with road transport emission estimates from the EDGAR database. $NO_x$ emission trends are also evaluated through comparisons with pollutant data derived from satellite and surface observations.

## 3.2 Methods and Data

### *3.2.1 Fuel Sales Data*

In the U.S., light-duty passenger vehicles are almost all gasoline-powered, whereas most of the on-road diesel fuel use is by medium and heavy-duty trucks. We use taxable fuel sales reports published annually to measure motor vehicle activity at the national level [*FHWA*, 2011b]. In California a state agency reports taxable fuel sales intended for on-road use in gasoline and diesel-powered vehicles [*California State Board of Equalization*, 2011b, a]. The diesel estimates for California have been adjusted to account for inter-state trucking, which often involves mismatches between where diesel fuel is purchased and where it is used. Estimates of diesel fuel consumed by transit and school buses were added separately; these relatively small on-road diesel fuel use categories are tax-exempt in California.

Fuel sales reported at the state level for California were apportioned to air basins using geocoded traffic count data available from the California Department of Transportation (http://traffic-counts.dot.ca.gov, accessed March, 2012); this was done separately for light and heavy-duty vehicles. Traffic counts for trucks with 3 or more axles were used as a proxy for the spatial distribution of diesel fuel, since these trucks are responsible for 92% of taxable on-road diesel fuel consumption in California [*California Department of Transportation*, 2009]. Most heavy-duty truck travel and fuel consumption occurs on the highway system [*Lindhjem et al.*, 2012]. We compared the spatial distribution of geocoded truck travel with the spatial distribution of diesel fuel in California's mobile source emissions model (California Air Resources Board, EMFAC 2011, http://www.arb.ca.gov/msei/modeling.htm, accessed April, 2012) (here-in referred to as EMFAC online data, 2012), and took the average of the two in allocating statewide diesel fuel sales to individual air basins.

In contrast to heavy-duty trucks, light-duty vehicles travel extensively on arterials and other surface streets. To apportion gasoline use from the state to air basin level, we used traffic data available from the Highway Performance Monitoring System (http://www.bts.gov/publications/national_transportation_atlas_database/2011/, accessed March, 2012) that include travel not just on highways but also on principal arterials. This left unmapped about a quarter of the total light-duty traffic, which was driving on collectors and smaller streets. The unmapped traffic and associated use of gasoline were apportioned to air basins based on the number of light-duty vehicles registered in each county. Gasoline use was apportioned separately for cars and light-duty trucks (i.e. sport-utility vehicles, pick-up trucks, small vans, etc.) following methods described by *Pokharel et al.* [2002]. Vehicle registration data were used to determine the fraction of total travel by each vehicle subgroup within each air basin. The light-duty truck fraction tended to be higher in rural areas. In apportioning statewide gasoline sales to individual air basins, we again used an average of the spatial distributions derived from geocoded traffic data and the EMFAC model. The resulting distribution agrees with reports [*California Department of Transportation*, 2009] on vehicle travel at the county level.

### *3.2.2 $NO_x$ Emission Factors for On-Road Vehicles*

Fleet-average $NO_x$ emission factors for heavy-duty diesel trucks were estimated using results from on-road measurements, including remote sensing and tunnel studies. Most of the relevant studies have been reviewed by *Dallmann and Harley* [2010] and are used again here. We added results from more recent measurements of truck emissions at the Peralta (Anaheim, CA) weigh station for 2009 and 2010 [*Bishop et al.*, 2012a] and at the Caldecott tunnel (Oakland, CA) for 2010 [*Dallmann et al.*, 2012]. A high $NO_x$ data point for 1997 from *Ban-Weiss et al.* [2008b] was excluded. Ordinary least squares regression was used to describe the trend in heavy-duty diesel $NO_x$ emission factors over the period from 1997 to 2010. Prior to 1997, we assumed that the heavy-duty diesel $NO_x$ emission factor remained constant, and matched the regression-derived value for 1997. This assumption is consistent with emission test results summarized by *Yanowitz et al.* [2000]. It has been reported that up until the mid-1990s, heavy-duty engines were certified in the laboratory to meet applicable $NO_x$ standards, but then operated differently on the road to minimize fuel consumption rather than $NO_x$ emissions [*Yanowitz et al.*, 2000]. Remote sensing measurements of truck emissions at the Peralta weigh station also show a plateau in $NO_x$ emission factors for 1997 and earlier model years [*Schuchmann et al.*, 2010]. Results from the 1992 Tuscarora, PA, tunnel study indicate a $NO_x$ emission factor for heavy-duty trucks that is consistent with our pre-1997 value [*Pierson et al.*, 1996]. $NO_x$ results from the Fort McHenry (Baltimore, MD) tunnel for heavy-duty trucks reported in the same study were somewhat lower, possibly due to a higher proportion of gasoline-powered trucks in a more urban setting.

Similarly, on-road measurements provide the basis for estimating $NO_x$ emission factors from light-duty vehicles in this study. The main on-road studies used here are a decade-long series of remote sensing measurements made in four US cities [*Bishop and Stedman*, 2008], and measurements of $NO_x$ emissions at the Caldecott tunnel in lanes where heavy-duty trucks are not allowed, for calendar years 1994-97, 1999, 2001, 2006, and 2010 [*Ban-Weiss et al.*, 2008b; *Harley et al.*, 2010]. We also included tunnel-derived emission factors for light-duty vehicles from Baltimore, MD in 1992 [*Pierson et al.*, 1996], and remote sensing measurements from San Jose, CA in 1999 and 2008 [*Bishop et al.*, 2010]. Wherever engine data were available from

vehicle registration records, we used only results for gasoline-powered vehicles in calculating fleet-average emissions.

A multiple regression analysis of the fleet-average emission factor over the period from 1990-2010 was performed, using calendar year and average vehicle age (travel-weighted, to account for the fact that newer vehicles tend to be driven more) as predictive variables. The mean vehicle fleet age across all of the available on-road studies is 5.7 years, which is newer than the national average of 6.5 years (again weighted by amount of driving as a function of vehicle age), and also newer than the California average of 7.1 years in 2000 (Federal Highway Administration, National Household Travel Survey, 2001, http://nhts.ornl.gov/download.shtml, accessed April, 2012, and EMFAC online data, 2012). While there was little change in average age of the passenger fleet between 1990 and 2000, both national and California data sources show increases in average vehicle age between 2000 and 2010 of 0.7-0.8 years. Aging of the vehicle fleet progressed more rapidly starting around 2005. From 1990 to 2000, the light-duty vehicle fleet operating in the South Coast air basin is modeled to be slightly newer, and in the San Joaquin Valley slightly older, than the state average (EMFAC online data, 2012). By 2009, the difference in average vehicle age between the two air basins had widened to ~1 year. Emission factors are adjusted to account for changes in average age of the vehicle fleet over time, and for differences in vehicle age among the various spatial domains considered in this study.

Cold start emissions from gasoline-powered vehicles were estimated using ratios of start-related to total exhaust (start + running) emissions derived from MOVES at the national level. A similar approach was used for California, based on emission estimates from the EMFAC model. The fraction of $NO_x$ emissions from light-duty vehicles associated with engine starting is estimated to range from 5-24% in MOVES, and from 7-20% in EMFAC.

Differences in emission control programs (e.g., reformulated gasoline, standards for new light-duty vehicles) between California and other states may affect emission factors. Effects of reformulated gasoline could be a factor to consider for carbon monoxide and hydrocarbons, but fuel effects on $NO_x$ are small and may be negligible [*Kirchstetter et al.*, 1999a]. Stricter emission standards would be expected over time to result in lower average emissions, although California's new-vehicle emission standards have been adopted in some other states, which reduces the effect of vehicle fleet differences. Most of the emission data for light-duty vehicles used in this study were derived from five sites: West Los Angeles, Caldecott Tunnel (San Francisco Bay area), Denver, Phoenix, and Chicago. Effects of differences in new-vehicle emission standards among these five sites may be small or confounded by other factors, and it is therefore difficult to quantify absolute differences in on-road $NO_x$ emission factors between national and California vehicle fleets. A much clearer feature in all of the on-road measurements is the long-term downward trend over time in $NO_x$ emission factors for light-duty vehicles.

### *3.2.3 Other Anthropogenic Sources of $NO_x$ Emissions*

Emission estimates for other major anthropogenic sources of $NO_x$ are included in later stages of this work in order to place on-road vehicle emissions in context with emissions from other sources, and to enable evaluation of emission inventory trends by comparison with observed trends in surface-based pollutant measurements and satellite-derived data. Off-road diesel

emissions were estimated using a fuel-based approach as described by *Dallmann and Harley* [2010], but extended to cover a longer time period (1990-2010 instead of 1996-2006). $NO_x$ emission factors from off-road equipment were assumed to track those for on-road diesel engines, and locomotives and marine vessels were assumed to have constant emission factors. Surveys of distillate fuel sales intended for use in off-road engines are conducted and reported annually at the national and state levels [*EIA*, 2012]. The spatial distributions of off-road construction and farm equipment, locomotive, and marine vessel emissions as reported by the California Air Resources Board (CARB) were used to apportion fuel-based emission estimates from state to air basin level.

Stationary (point and area) sources of emissions were also added, using the latest estimates from the US. Environmental Protection Agency (EPA) (http://www.epa.gov/ttn/chief/trends/, accessed May, 2012) (here-in referred to as EPA Trends Table, 2011), including fuel combustion and industrial processes. For California, stationary source emission estimates at the state and air basin levels from CARB were used [*Cox et al.*, 2010]. When taken together with fuel-based estimates of on-road and off-road mobile source emissions of $NO_x$, the overwhelming majority of near-surface anthropogenic emissions are accounted for in all cases. $NO_x$ sources missing from this analysis include off-road gasoline engines and aircraft.

**Table 3.1.** Summary of Relative Uncertainties in Fuel Consumption and $NO_x$ Emission Factor Estimates.

| Source Category | Fuel Consumption | | | | $NO_x$ Emission Factor[b,c] | | |
|---|---|---|---|---|---|---|---|
| | US[a] | CA | SC[d] | SJV[d] | 1990 | 2000 | 2010 |
| On-road Gasoline | ±3% | ±5% | ±6% | ±13% | ±13% (1.8) | ±9% (0.8) | ±43% (1.5) |
| On-road Diesel | ±5% | ±10% | ±13% | ±11% | ±16% (6.8) | ±13% (5) | ±20% (5.7) |

a. [*Dallmann and Harley*, 2010].
b. Uncertainty denoted as 2σ.
c. Absolute uncertainty estimates shown in parentheses are expressed in units of g $NO_x$/kg fuel.
d. SC = South Coast, SJV = San Joaquin Valley.

### *3.2.4 Uncertainty*

Uncertainties in fuel consumption and $NO_x$ emission factors have been estimated for on-road sources (see Table 3.1). The relative uncertainty in vehicle activity grows as the spatial domain becomes smaller, due to difficulties in apportioning fuel use to finer scales. For example, a portion of diesel fuel consumed by long-haul interstate trucks is known to be purchased from out-of-state vendors, and may be misallocated despite efforts to track and report interstate truck travel and fuel use separately for each state [*Lutsey*, 2009]. To estimate fuel use uncertainties at the state level, we compared California's share of national gasoline sales with the share of light-duty vehicle miles traveled, and similarly compare diesel fuel sales with truck miles traveled [*FHWA*, 2011b]. At the air basin level, uncertainties associated with statewide fuel sales reports and spatial apportionment methods were propagated in emission inventory calculations. Uncertainties in $NO_x$ emission factors were derived from error analysis of the least squares regression results. As the light-duty fleet becomes cleaner, the relative uncertainty grows, even though the absolute uncertainty changes little. For cold start emissions, the uncertainty is estimated to be ±65%, based on comparing start-related emission estimates from MOVES with its predecessor model MOBILE6.

Estimates of uncertainty for other major anthropogenic sources are also available. Uncertainties associated with off-road diesel engine emissions are described by *Dallmann and Harley* [2010]. *Frost et al.* [2006] report that electric power plants with continuous emission monitoring systems have a $2\sigma$ uncertainty of ±24%, which we assume applies to all large electric generator and industrial sources.

## 3.3. Results and Discussion

### *3.3.1 Fuel Sales*

Trends in fuel consumption by on-road vehicles from 1990 to 2010 are shown in Figure 1. At air basin, state, and national scales, consumption of diesel fuel grew more rapidly than gasoline up to 2007, which was the peak year for diesel fuel sales in all cases. Between 1990 and 2007, national sales of gasoline and diesel fuel for use by on-road vehicles increased by about 20% and 90%, respectively. Increases at the state level in California were not quite as large (see Figure 3.1). At the air basin level within California, increases in fuel use were more rapid in the San Joaquin Valley. Note that Figure 3.1 shows only relative changes in fuel use over time, and does not reflect differences in absolute amounts of fuel consumed across the various spatial domains. Another noteworthy feature of the data shown in Figure 3.1 is a marked reduction in diesel fuel sales due to the recent recession. Between 2007 and 2009, diesel fuel sales fell by 13-17% for the domains shown in Figure 3.1. In contrast, gasoline sales decreased by only 2-6% over the same time period. Sales of both fuels ceased to decline after 2009.

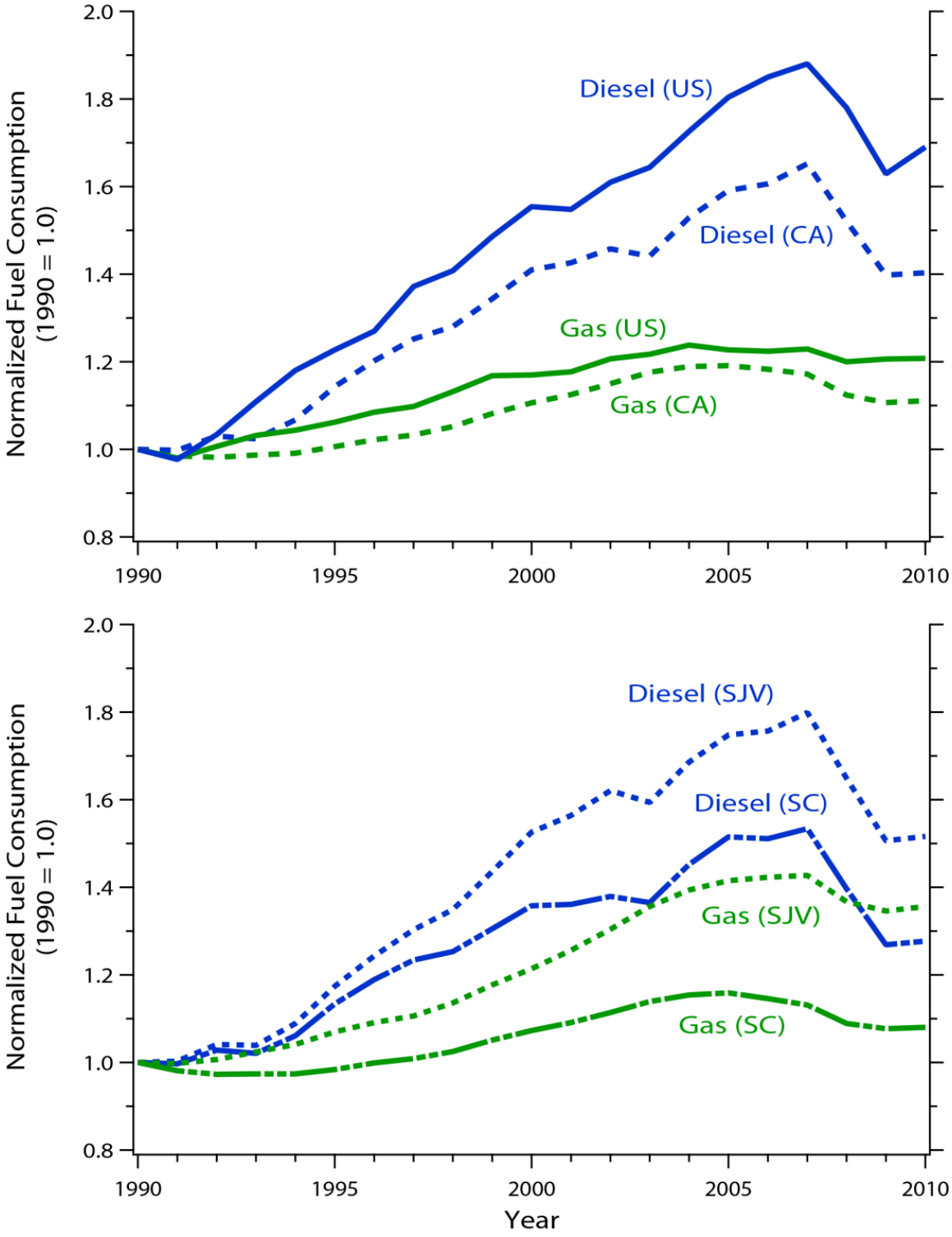


**Figure 3.1.** Normalized trends in on-road vehicle fuel consumption, 1990-2010. The top panel shows national (US) and California (CA) trends. The lower panel shows trends for the South Coast (SC) and San Joaquin Valley (SJV) air basins within California. Fuel consumption values for each year have been normalized by ratio to corresponding reference values for 1990.

### *3.3.2 Emission Factor Trends*

A summary of the available on-road measurements of vehicle $NO_x$ emission factors along with best-fit lines resulting from regression analyses are plotted in Figure 3.2. Further results for emission factors, reflecting light-duty vehicle fleet age distributions as appropriate for each region, are included as auxiliary material. As of 1990, the diesel $NO_x$ emission factor was ~3 times the emission factor for light-duty gasoline engines. Twenty years later, as of 2010, the corresponding ratio was ~8. This growing disparity in emission factors has been driven by nearly universal deployment of catalytic converters on gasoline engines, and multiple advances over time in the effectiveness and durability of related technology. Similar advanced technologies to reduce diesel $NO_x$ are just beginning to be deployed. Note the results shown in Figure 3.2 allow for a fairer comparison between light-duty gasoline and heavy-duty diesel engines by normalizing emissions to fuel consumption rather than distance traveled (this controls for the expected higher per-mile emissions from larger vehicles).

The trends in emission factors from this study for light and heavy-duty vehicles are similar to Dallmann and Harley [2010], though there are small differences in an absolute sense. Our heavy-duty emission factors are 6-9% lower because we treated a high-$NO_x$ data point from 1997 at the Caldecott tunnel as an outlier and excluded it (see Figure 3.2). Our light-duty emission factors are 4-16% higher than Dallmann and Harley because we adjusted for age differences between the national vehicle fleet and vehicles observed in remote sensing/tunnel studies. The most important change for gasoline engines is new estimates of cold start emissions (derived from MOVES rather than MOBILE in the present study).

Although emission factors for $NO_x$ are known to vary less when expressed per unit of fuel burned rather than per unit distance traveled, effects of unmodeled variations in emission factors should still be considered. Both Bishop and Stedman [2008] and Lee and Frey [2012] report nearly constant values for $NO_x$ emission factors over ranges of positive engine load ranging from 5 to 30 kW/t in the former case, and 1 to 23 kW/t in the latter study. The normalized measure of load used here is engine power output (in kW) divided by vehicle mass (in metric tons), also known as vehicle specific power.

For light-duty vehicles, $NO_x$ emission rates (g/kg basis) decrease by factors of about 2 for downhill driving [*Kean et al.*, 2003] and at idle [*Lee and Frey*, 2012], relative to other driving modes with positive values of vehicle specific power. $NO_x$ emissions from idling engines are not included in the tunnel and remote sensing measurements shown in Figure 2. Similar concerns may apply to $NO_x$ emissions from heavy-duty diesel engines. However, idling engines are responsible for a minor (<10%) fraction of overall fuel consumption. Reductions in $NO_x$ due to idling engines are likely to be offset by increases in emission factors at high load. The effect of high engine load on $NO_x$ is small compared to CO [*Kean et al.*, 2003; *Bishop and Stedman*, 2008; *Lee and Frey*, 2012]. We did not adjust our emission estimates to account for high-load driving.

For heavy-duty diesel trucks, previous work [*Yanowitz et al.*, 2000; *Gajendran and Clark*, 2003] similarly indicates that driving cycle and truck weight effects on $NO_x$ are minimal when emissions are expressed per unit of fuel burned rather than per distance traveled.

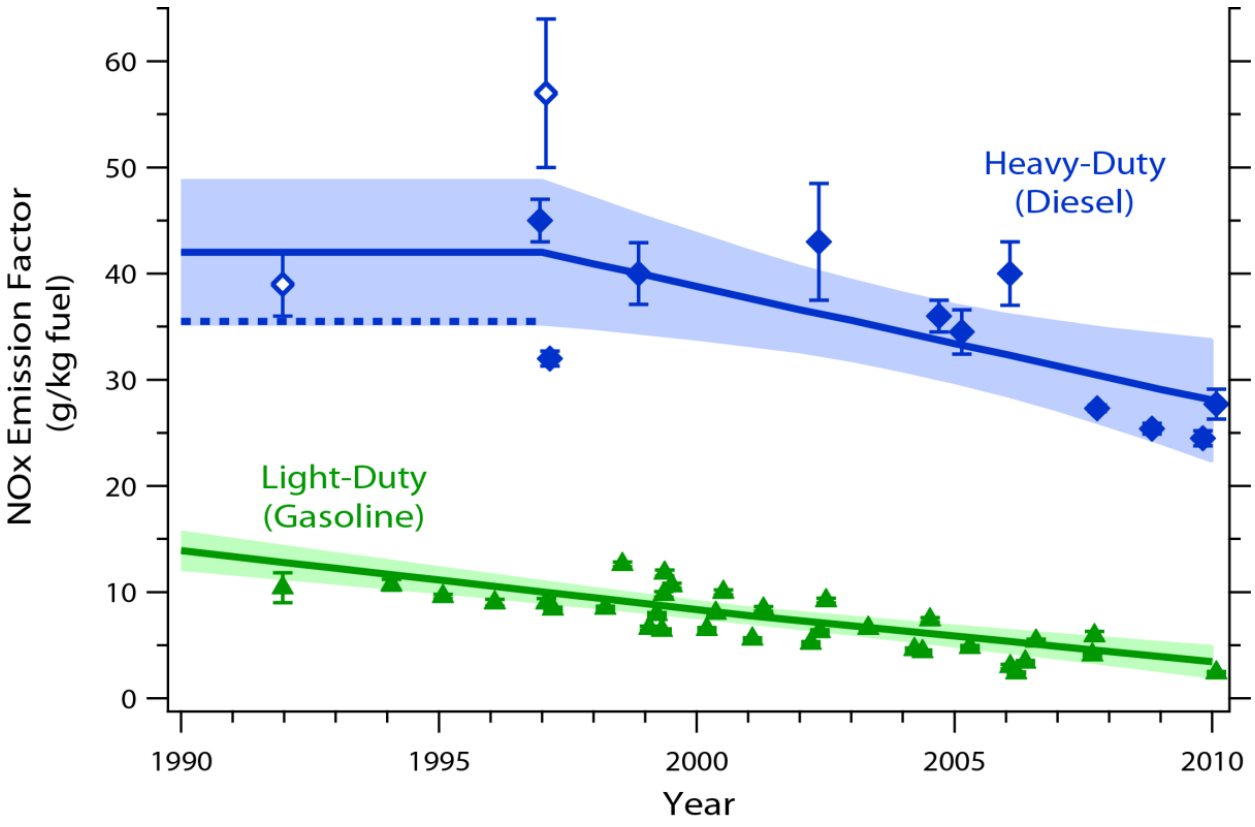


**Figure 3.2.** Trends in measured gasoline and diesel vehicle $NO_x$ emission factors from on-road studies. Also shown are linear fits to the observed data (solid lines) along with associated 95% confidence intervals (shaded areas). Two open blue diamond markers denote on-road data that were not used in the regression analysis (see text). The dashed blue line represents results from chassis dynamometer testing of heavy-duty diesel vehicles [*Yanowitz et al.*, 2000].

### *3.3.3 Motor Vehicle Emission Inventory Trends*

Trends in on-road vehicle $NO_x$ emissions are shown in Figures 3.3 and 3.4 (which present, respectively, national and California state/air basin emission trends, with separate results for gasoline and diesel-powered vehicles). Across all spatial domains considered in this study, gasoline vehicle emissions decreased by ~65% between 1990 and 2010, except in the San Joaquin Valley where reductions were not as large (~50%), due to faster growth in population and vehicle activity. Trends in diesel $NO_x$ emissions over the same time period are not the same as for gasoline-powered vehicles. Changes in diesel emissions vary in both sign and magnitude, and can be characterized as follows for three different time periods: (1) increasing between 1990 and 1997, (2) stable between 1997 and 2007, and (3) decreasing since 2007. Increasing emissions during the early years were driven by increases in diesel fuel sales, with little if any change in $NO_x$ emission factors. $NO_x$ emission factors decreased between 1997 and 2007, but the emission factor decreases were offset by increased diesel fuel sales, resulting in stable $NO_x$ emissions for this time period. Diesel $NO_x$ emissions have decreased since 2007, mainly due to reduced freight shipments and lower diesel fuel sales, reinforced by emission factor reductions that have occurred since 2007. National trends in total (gasoline + diesel) on-road vehicle $NO_x$ emissions increased during most of the 1990s, reached a plateau during the late 1990s, then began decreasing in 2000, with more rapid decreases since 2007 due to the recession.

As of 1990, gasoline-powered vehicles were the dominant on-road source of $NO_x$ emissions for all cases shown in Figures 3.3 and 3.4, except for the San Joaquin Valley. Since that time, however, diesel trucks have become of comparable or greater importance as on-road sources of $NO_x$. At the national scale, the cross-over point where the diesel contribution to on-road $NO_x$ emissions matched the gasoline contribution occurred in the mid to late 1990s. This transition occurred later in California, around 2005, though since then the recession has caused diesel emissions to decrease such that $NO_x$ contributions from both vehicle categories are similar. For air basins within California, diesel contributions to on-road $NO_x$ emissions vary dramatically. The diesel source is clearly dominant in the San Joaquin Valley over the entire twenty-year period considered in this study (reaching ~70% in 2010). As a consequence, the total on-road $NO_x$ emissions curve closely tracks the trend in diesel emissions. In the heavily urbanized South Coast air basin, on-road gasoline remains dominant (or at least of comparable importance in the last ~3 years) throughout the period 1990-2010 (down from ~75% in 1990). As expected, the trend in total on-road vehicle $NO_x$ emissions in southern California closely resembles the trend in light-duty vehicle emissions, with the exception of the more rapid decrease since 2007 driven by reductions in diesel emissions.

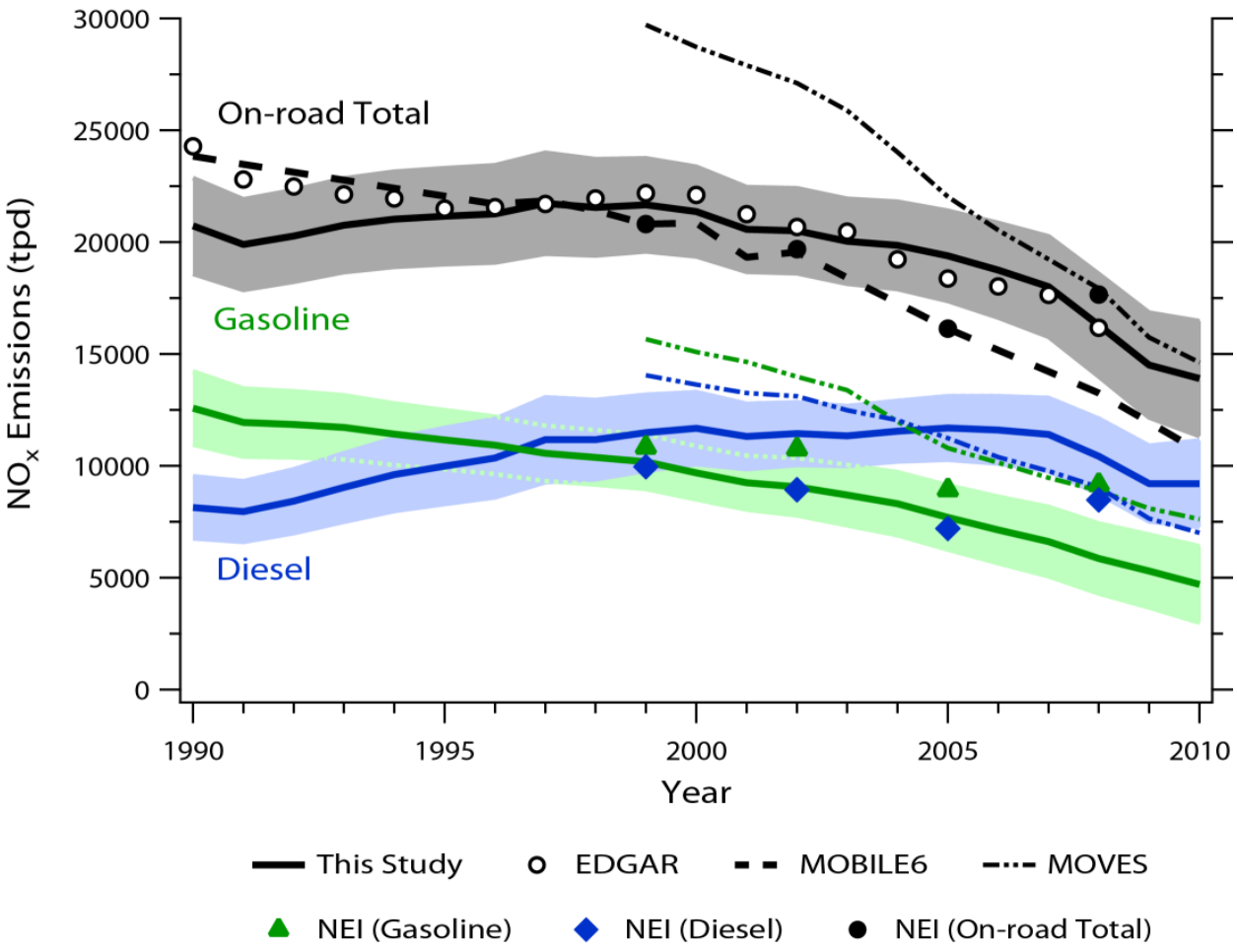


**Figure 3.3.** National trends in $NO_x$ emissions from on-road vehicles, 1990-2010. Units are metric tons per day, and $NO_x$ mass is reported in $NO_2$ equivalents. Shaded areas represent effects of emission factor and fuel sales uncertainties on fuel-based inventory estimates. Cold start emissions are included with on-road gasoline.

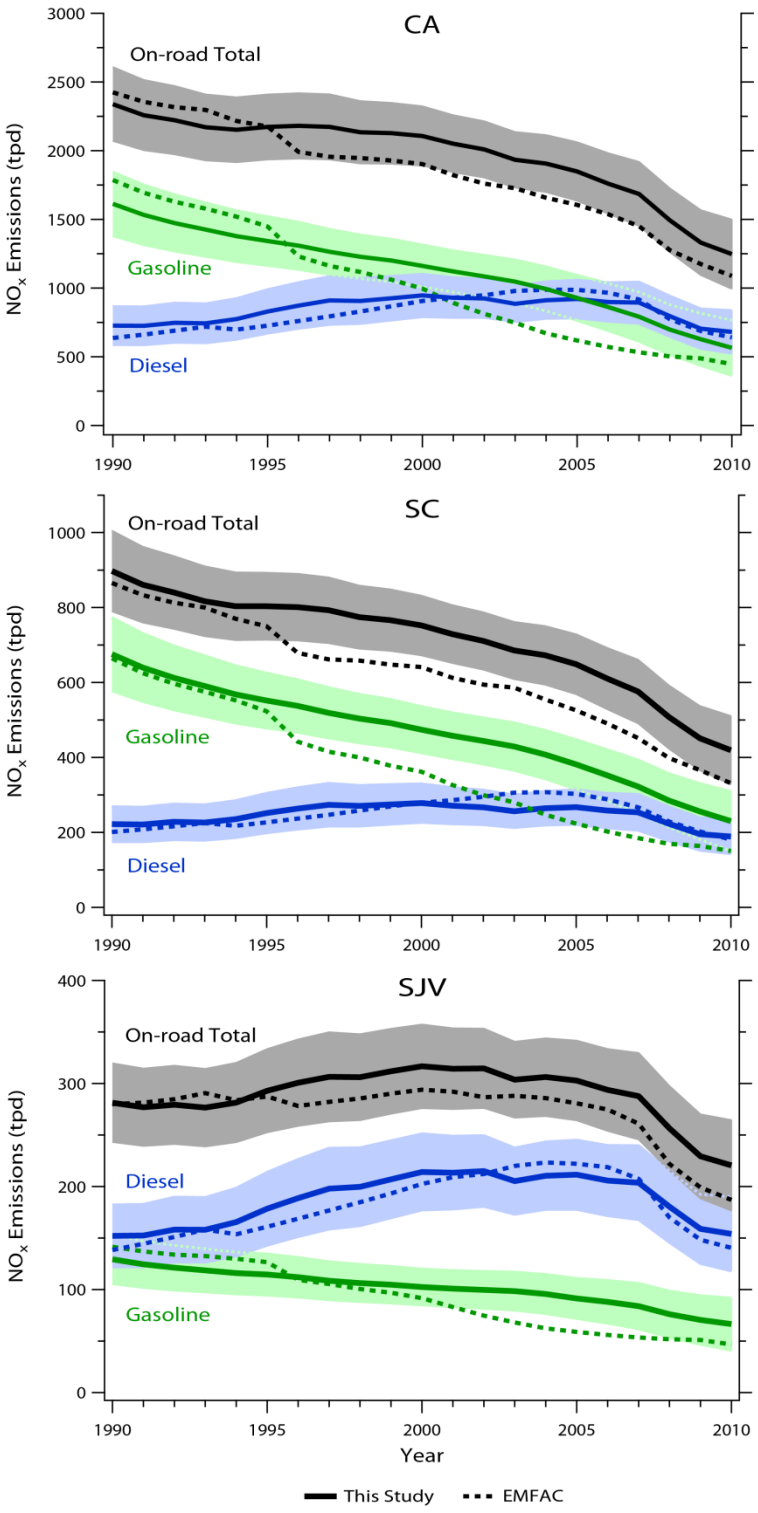


**Figure 3.4.** Trends in $NO_x$ emissions from on-road vehicles in California, 1990-2010. Spatial domains shown include statewide level (CA), South Coast air basin (SC) that includes the Los Angeles area, and San Joaquin Valley air basin (SJV). Shaded areas represent effects of emission factor, fuel sales, and spatial apportionment uncertainties on fuel-based inventory estimates. Cold start emissions (and associated uncertainties) are included with on-road gasoline.

The fuel-based emission inventory developed in this study shows varying levels of agreement with other established and widely used inventories. At the national level, there is close agreement between fuel-based emission estimates and the Emissions Database for Global Atmospheric Research (EDGAR version 4.2), for total $NO_x$ emissions from the road transport sector (European Commission – Joint Research Center, 2011, http://edgar.jrc.ec.europa.eu, accessed April, 2012). Comparisons with the National Emissions Inventory (NEI) estimates developed by EPA shown in Figure 3.3 indicate that in 3 out of the 4 most recent inventory years (1999, 2002, and 2008 version 2), estimates of total $NO_x$ emissions from on-road vehicles agree in an absolute sense (EPA, 2012, http://www.epa.gov/ttnchie1/net/2008inventory.html, accessed June, 2012). In the 2005 NEI, the on-road diesel $NO_x$ source appears to be underestimated by ~40% as noted previously [*Dallmann and Harley*, 2010]. Emission estimation methods and data used by EPA to develop the NEI are not necessarily consistent from one year to another, which makes it difficult to quantify emission trends over time using NEI data. EPA also publishes national emission trends tables (EPA Trends Table, 2011), using a consistent methodology to estimate vehicle emissions over multiple years. The long-term trend in on-road vehicle $NO_x$ emissions is shown using a dashed line in Figure 3.3 (labeled as MOBILE6). The trends table estimates match the three earlier NEI estimates, but differ in 2008. A change in methodology explains the difference: the 2008 NEI was the first to use MOVES in place of the older MOBILE model to estimate on-road vehicle emissions. Lindhjem et al. [2012] reported that $NO_x$ emissions increased by >50% for both light-duty gasoline and heavy-duty diesel vehicles when using emission factors from MOVES relative to MOBILE6.

Figure 3.3 also includes more detailed comparisons between the MOVES model and fuel-based emission estimates for the time period 1999-2010. The MOVES model is a modal emissions model that can estimate emissions for a wide range of different driving conditions. In Figure 3.3, default cycles were used in MOVES in making comparisons (J. Koupal, personal communication, May 16, 2012). In an absolute sense, total $NO_x$ emissions agree for the most recent years, however, the estimates of total emissions diverge when moving back in time. On-road diesel $NO_x$ emissions in MOVES decrease steadily and track the gasoline $NO_x$ estimate closely, whereas the fuel-based estimates show relatively stable diesel emissions up to 2007, followed by a sharp decrease. Figure 3.3 shows that trends in on-road gasoline engine emissions have the same slope, though MOVES estimates are 40-60% higher than the fuel-based estimates. MOVES is sensitive to differences in assumptions about driving conditions [*Lindhjem et al.*, 2012], especially for gasoline engines, which may affect comparisons in an absolute sense. We note that in a relative sense, the default cycle in MOVES places equal importance between on-road diesel and gasoline, in contrast to this study which found diesel to be the dominant source nationally after the mid to late 1990s. Emission trends over time are less affected by modeling/estimation uncertainties, and thus should be the focus in making comparisons among emission inventories. Underlying vehicle activity data are similar between MOVES and the fuel-based approach, with fuel consumption estimates within 5% of one another. This implies that differences in $NO_x$ emission estimates are driven by differences in emission factors.

Figure 3.4 shows comparisons of motor vehicle emission trends in California, including predictions from the latest version of the California motor vehicle emission model, EMFAC 2011 (EMFAC online data, 2012). In general, EMFAC-derived estimates of $NO_x$ emissions are within associated uncertainties of the fuel-based approach. Differences in the shape of the light-duty vehicle emission trends deserve a brief discussion. EMFAC shows a ~10% step decrease in gasoline-powered vehicle $NO_x$ emissions between 1995 and 1996. This is attributed to the use of phase 2 reformulated gasoline, which involved numerous changes to gasoline properties that were made to reduce vehicle emissions. Measurements of California light-duty vehicle emissions at the Caldecott Tunnel [*Kirchstetter et al.*, 1999a] showed significant (18 ± 4%) decreases in $NO_x$ emission factors between 1994 and 1997, but the authors could not discern a fuel effect on emissions separate from fleet turnover effects. The EMFAC model shows a slowing in $NO_x$ emission reductions from light-duty vehicles in more recent years (especially since 2005). In contrast, the fuel-based estimates show continued declines in emissions during this time period. The pace of reductions in California light-duty $NO_x$ emissions will likely slow down at some point in the near future if this has not already occurred, since emissions cannot decrease to negative values.

Parrish inferred trends in national-level $NO_x$ emissions from on-road vehicles based on analysis of ambient carbon monoxide (CO) concentrations and ambient CO to $NO_x$ ratios [*Parrish*, 2006]. Our results support his conclusion that vehicular $NO_x$ emissions increased during the 1990s, and we explain this finding to be a result of growth in $NO_x$ emissions from heavy-duty diesel trucks. A comparison of our emission estimates with those of Parrish is included in Figure 3.5.

### *3.3.4 Overall $NO_x$ Emission Trends*

Other anthropogenic sources of $NO_x$ emissions include stationary (point + area) and off-road mobile sources (diesel equipment + rail + ship). Estimates of these emissions, along with on-road motor vehicle emission estimates described above, are shown in Figure 3.5. These source categories are summed to estimate all anthropogenic emissions. Note the on-road vehicle source has been comparable to stationary source emissions since about 2000, due in part to reductions in power plant emissions that took place starting in the late 1990s.

We compare national emission trends against emission estimates derived using GOME/ SCIAMACHY satellite data by *Stavrakou et al*. [2008]. We choose to compare to Stavrakou et al. because they focus on anthropogenic sources of $NO_x$, report results for the continental U.S., provide a long-term time series of results from 1997 to 2006, and adjust for chemical feedbacks between $NO_x$ and hydroxyl radical due to changes in emissions. A downward trend in anthropogenic $NO_x$ emissions with a decrease of ~45% between 1997 and 2010 (see Figure 3.5) is consistent up to 2006 with the satellite-derived inventory (we show a plateau in emissions prior to 1997). The downward trend in emissions is driven by reductions from stationary and on-road gasoline vehicle sources. Despite decreases in emissions from gasoline-powered vehicles, the overall importance of on-road vehicle emissions have grown due to the slower rate of progress in controlling diesel $NO_x$ emissions.

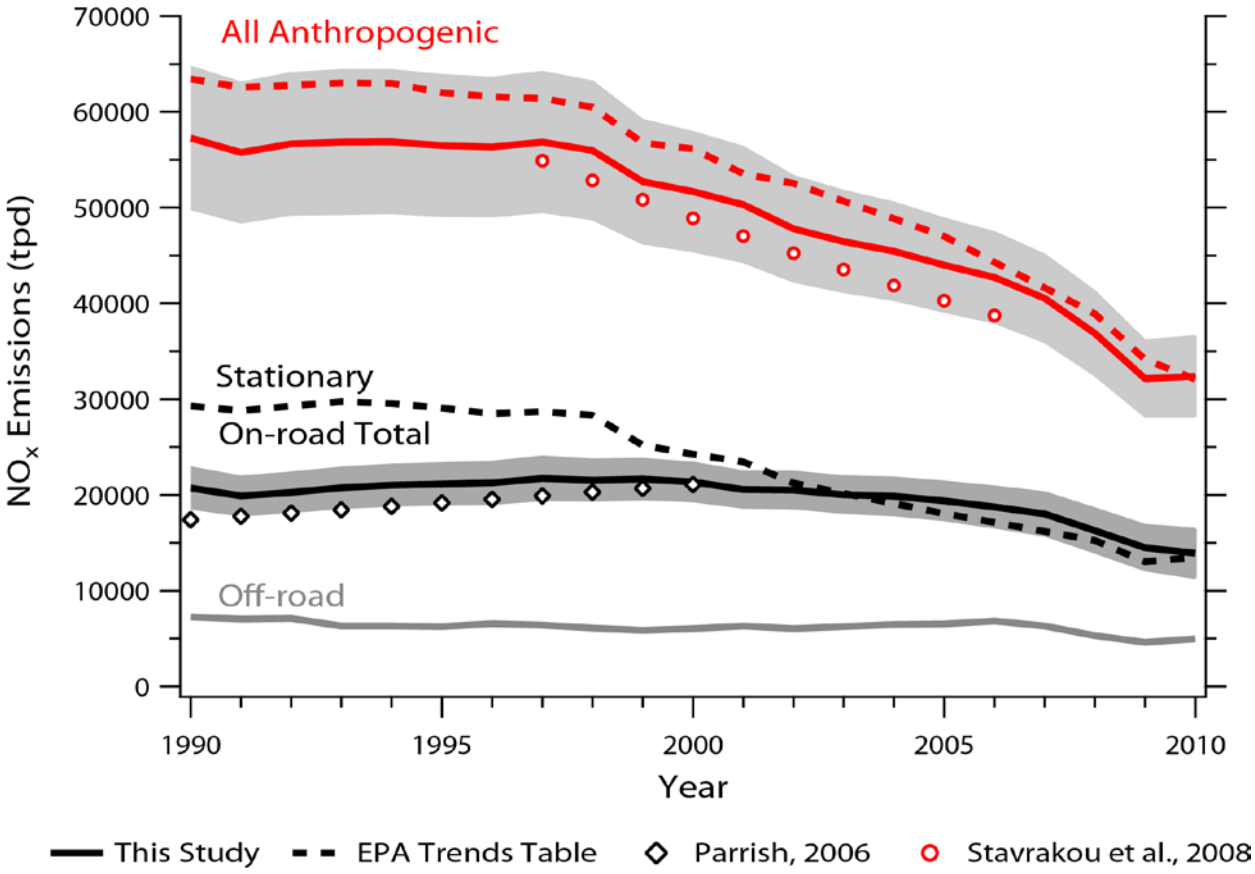


**Figure 3.5.** National $NO_x$ emission trends from 1990-2010, with comparisons to inventories inferred from ground-level and satellite measurements of pollutants. Emissions from off-road (e.g., farm and construction equipment, locomotives, ships), on-road (gasoline + diesel), and stationary (point + area) sources summed to give all anthropogenic. Shaded areas denote 2σ uncertainties.

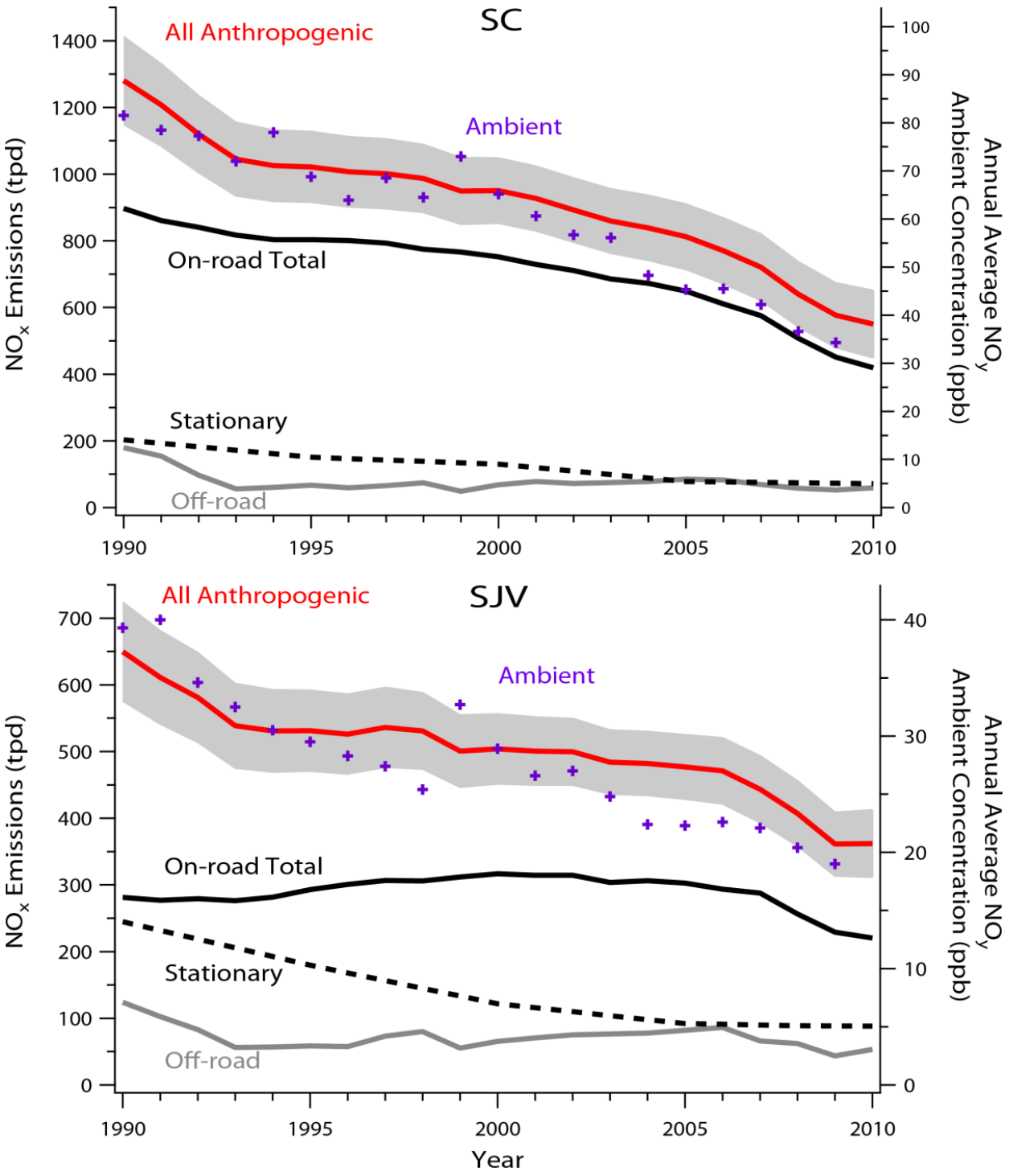


**Figure 3.6.** Anthropogenic $NO_x$ emissions trends from 1990-2010 with comparisons to annual average ambient $NO_y$ concentrations for the South Coast air basin (SC) and the San Joaquin Valley (SJV). Shaded areas denote 2σ uncertainties.

$NO_x$ emission trends for California air basins are compared in Figure 3.6 against trends in measured ambient $NO_y$ concentrations from surface air monitoring sites. Figure 3.6 shows annual average $NO_y$ for all monitors and days in a given air basin, for each year from 1990 to 2010. The number of monitoring sites reporting reasonably complete $NO_y$ data ranged from 7-18 in the San Joaquin Valley (the range reflects year-to-year variations), and from 16-22 in the Los Angeles area (see auxiliary material for map). The record of $NO_y$ observations is sparse in the San Joaquin Valley prior to 1995. The placement of the ambient monitors is biased towards urban areas, and may therefore under-sample $NO_x$ emissions from rural/remote areas. Ambient concentrations are plotted using a secondary y-axis that is aligned with emissions data for the year 2000 to facilitate comparison of trends in Figure 3.6. The absolute level of $NO_x$ emissions in the San Joaquin Valley is roughly half that of the South Coast air basin, with similar differences observed in ambient $NO_y$ concentrations. Not shown in Figure 3.6 are results of several recent studies that included analysis of satellite data for California [*van der A et al.*, 2008; *S W Kim et al.*, 2009; *Russell et al.*, 2010]. While there are differences in the magnitudes of estimated emission changes, the sign of the change appears to be negative in all cases. Our results agree with the assessment of Russell et al. that $NO_x$ emissions are decreasing in California, and at a slower pace in the San Joaquin Valley than in southern California.

The relative importance of major source categories differs between air basins. On-road vehicles account for ~80% of $NO_x$ emissions in the Los Angeles area. In contrast, in the San Joaquin Valley stationary and off-road mobile sources, taken together, are of similar importance to on-road vehicle sources. Nevertheless, there is a general downward trend in emissions for both air basins. Between 1990 and 1993, reductions in $NO_x$ were ~6% per year in both areas. The large declines in off-road diesel emissions shown in Figure 6 between 1990 and 1993 is a result of decreases in reported fuel sales for California. The effect is most evident in the San Joaquin Valley where off-road sources are more important. Between 2007 and 2009, both air basins saw a ~10% decrease per year in $NO_x$. This was largely driven by recession-related effects, especially in the freight sector. Some off-road mobile source activities (e.g., construction) also decreased since 2007. Subtle differences in emission trends between air basins are observed between 1993 and 2007, which we attribute to the relative importance of heavy-duty diesel $NO_x$ in the San Joaquin Valley. Overall, we find that the anthropogenic emission trend was downward in California (-45% to -60%), with decreases in the San Joaquin Valley at the lower end, South Coast at the upper end, and the state-average in the middle.

### *3.3.5 Future On-Road Vehicle Emissions and Control Strategies*

Figure 3.7 shows the distribution of on-road vehicle emissions by source category: diesel-running, gasoline-running, gasoline-start, and gasoline-high emitters. The first three categories sum to give total on-road vehicle emissions. The last category, gasoline-high emitters, represents a contribution to gasoline-running emissions from the highest-emitting 10% of vehicles. These vehicles contribute disproportionately to total emissions. Lipfert and Wyzga [2008] show that skewness of light-duty vehicle $NO_x$ emission distributions has increased over time. For the present study, we estimate from an analysis of remote sensing datasets [*Bishop and Stedman*, 2008] that high-emitters accounted for 26 ± 10%, 50 ± 8%, and 75 ± 9% of total $NO_x$ emissions from gasoline vehicles in 1990, 2000, and 2010, respectively. The main implication of Figure 7

is that strategies to reduce future $NO_x$ emissions from on-road vehicles should focus on control of gasoline-high emitters and diesel vehicles.

Policies have already been implemented to control the diesel $NO_x$ source, in particular national emission standards for 2010 and newer heavy-duty engines. Meeting these standards for the largest on-road engines commonly involves the use of selective catalytic reduction (SCR) to treat the exhaust [*NRC*, 2010]. Recent emission tests in Europe of heavy-duty trucks equipped with SCR showed that in-use $NO_x$ emissions were higher than anticipated [*Velders et al.*, 2011]. This is a reminder that robustness and durability of exhaust after-treatment systems will affect the future trajectory of diesel $NO_x$ emissions. Instead of deploying SCR, trucks may be switched to spark-ignition engines using either gasoline or natural gas as fuel, and equipped with catalytic converters to reduce $NO_x$.

To address the long service life and slow turnover rate for heavy-duty vehicles, the California Air Resources Board has implemented a policy [*California Code of Regulations*, 2008] requiring retrofits (for diesel particulate filters) and truck replacement (to control $NO_x$). By 2023, all heavy-duty engines used in on-road vehicles must meet current $NO_x$ emission standards that apply to 2010 and newer engines. A consequence of California's approach is that some older trucks (and their emissions) will be exported to other regions [*Bishop et al.*, 2012a]. Further analysis is needed to understand the tradeoffs involved, and to consider whether other regions should also pursue accelerated truck retrofit and replacement programs.

Additional steps to promote the durability of emission control systems and reduce life-cycle emissions from light-duty vehicles should be considered. Such measures could be more productive than requiring further reductions in cold start-related emissions. To continue progress in control of high-emitting vehicles, policies and assumptions should be re-examined. Given improvements in the durability of vehicle emission control systems that have occurred in recent years [*Bishop and Stedman*, 2008], the high-emitting sub-population of vehicles is disproportionately older models (see Figure 3.8). A key challenge for vehicle inspection and maintenance (I&M) programs is to focus more on repairing or retiring high-emitting vehicles [*NRC*, 2001]. Adjustments to I&M programs in California and elsewhere should be considered, such as increasing exemptions for new and middle-aged vehicles, and reducing or eliminating exemptions for the oldest vehicles.

The reduction of greenhouse gas emissions from motor vehicles is likely to have effects on air quality as well. *Williams et al. [2012]* have suggested that for California to meet its long-term greenhouse gas emission reduction target (i.e., 80% below 1990 levels by 2050), much of the on-road vehicle fleet will need to be electrified, and the carbon intensity of electricity generation must be reduced dramatically. To this end, California has adopted regulations that aim to increase the sales of fully electric and plug-in hybrid electric models by 2025 [*California Code of Regulations*, 2012]. Effects of such policies should be investigated further to understand the implications for air quality. The success of heavy-duty diesel engine $NO_x$ control programs may prove to be even more critical for improving future air quality.

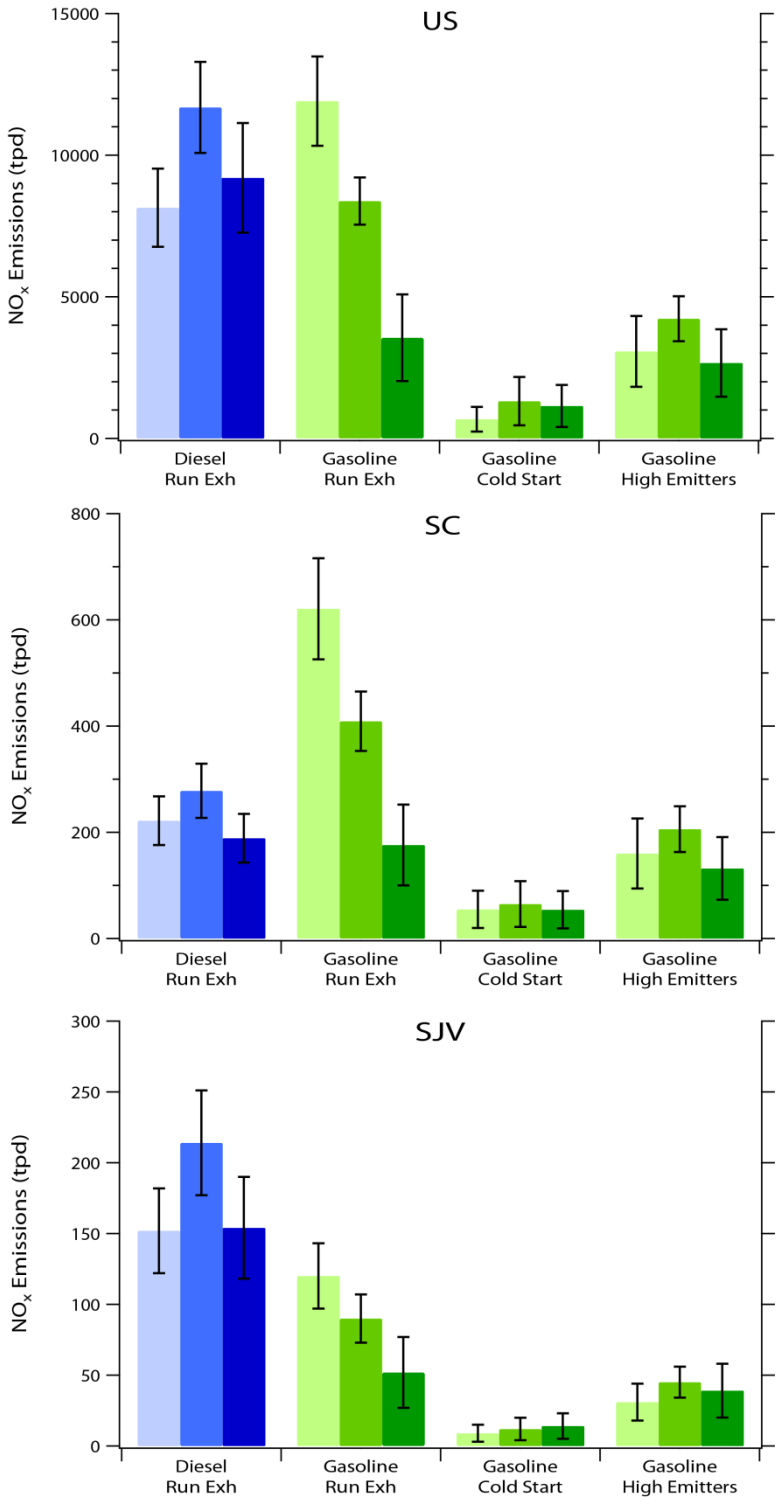


**Figure 3.7.** Contributions to on-road vehicle $NO_x$ emissions in 1990 (light bars), 2000 (medium-color bars), and 2010 (dark bars) for U.S., South Coast air basin (SC), and San Joaquin Valley (SJV). Error bars denote 2σ uncertainties. Contributions from high-emitting vehicles shown separately at right are also included in running exhaust estimates for gasoline engines.

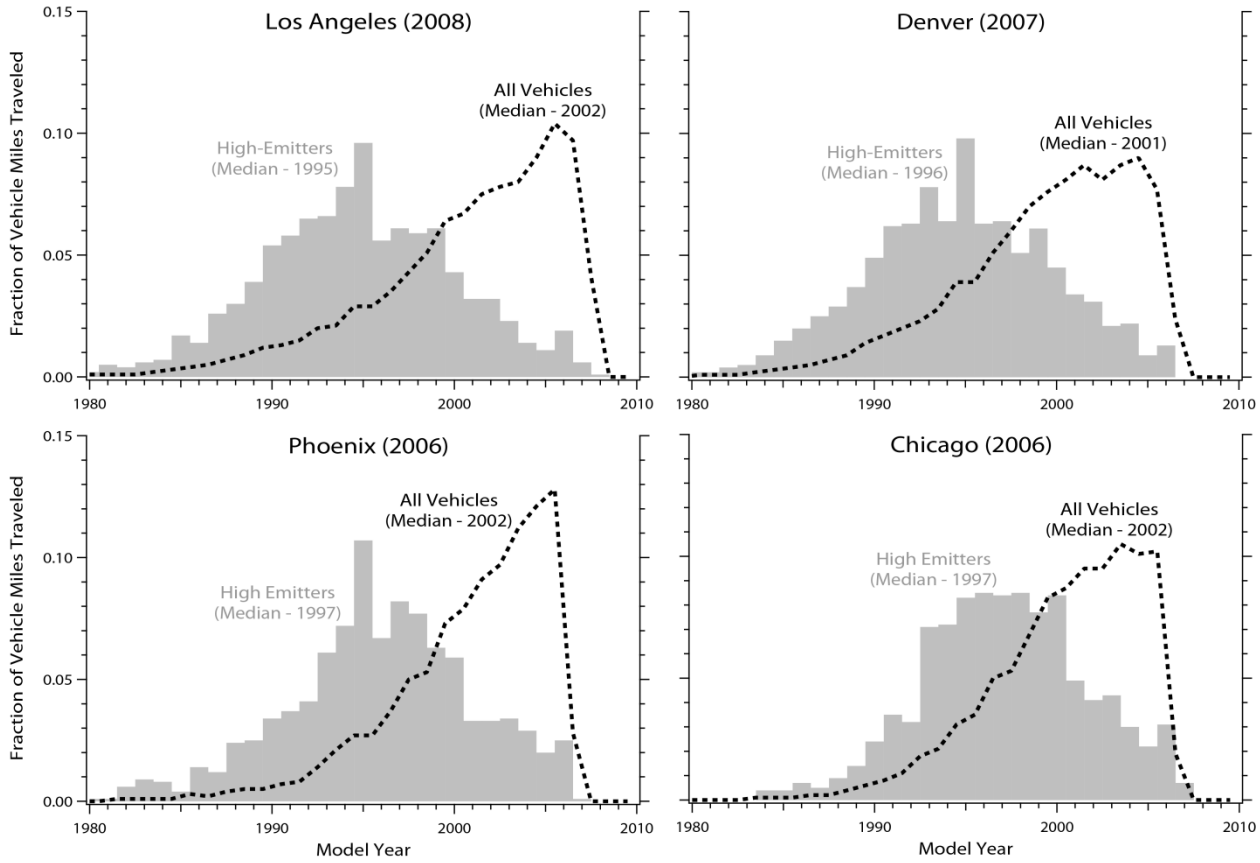


**Figure 3.8.** Age distribution of the highest emitting 10% of passenger vehicles for (top-left) Los Angeles in 2008, (top-right) Denver in 2007, (bottom-left) Phoenix in 2006, and (bottom-right) Chicago in 2006. Diesel-powered vehicles are excluded where possible (for Denver and Phoenix).

## 3.4 Conclusions

A fuel-based approach was used to estimate $NO_x$ emissions from gasoline and diesel-powered on-road vehicles, for the time period from 1990 to 2010. This analysis was performed at national, state (California), and air basin levels, and results were compared with other emission inventories including MOVES, EMFAC, and EDGAR. On-road emission estimates were combined with estimates for other major anthropogenic sources, and were compared with satellite and ground-based observations.

Growth in on-road diesel fuel consumption outpaced gasoline from 1990 to 2007, across all spatial domains considered here. Between 2007 and 2009, diesel fuel sales fell by 13-17% while gasoline activity decreased by only 2-6%. The ratio of $NO_x$ emission factors for heavy-duty diesel versus light-duty gasoline engines grew from ~3 in 1990 to ~8 in 2010. This growing disparity is attributed to the near-universal deployment and improved effectiveness of catalytic converters on gasoline engines. In contrast, $NO_x$ emission factors for heavy-duty diesel trucks showed little change during the 1990s, and have decreased only gradually since then. Combining trends in activity and emission factors, we found that gasoline engine emissions of $NO_x$ decreased steadily, by ~65% between 1990 and 2010, except in the San Joaquin Valley where reductions were not as large (~50%). In contrast, on-road diesel engine emissions increased between 1990 and 1997, remained stable between 1997 and 2007, and decreased after 2007. As a result, the relative importance of diesel $NO_x$ emissions has increased. In the San Joaquin Valley, diesel sources were already the dominant on-road $NO_x$ source in 1990, and have since grown to account for ~70% of on-road emissions. In the South Coast air basin, on-road gasoline remains dominant and of comparable importance to diesel in the last few years (but down from ~75% in 1990).

After adding in other major sources of anthropogenic emissions, our results agree well with trends in satellite-derived $NO_2$ columns and ground-based observations of $NO_y$. The overall emission trend is downward in all cases (–45% to –60%). At the air basin level, our results support the finding that $NO_x$ emissions are decreasing at a slower pace in the San Joaquin Valley than in the South Coast air basin. On-road vehicles are clearly the dominant source in the Los Angeles area, accounting for ~80% of anthropogenic $NO_x$. Stationary and off-road mobile source emissions are of similar importance when compared to on-road sources in the San Joaquin Valley.

# Chapter 4: Long-Term Trends in Motor Vehicle Emissions in U.S. Urban Areas

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## 4.1 Introduction

Non-methane hydrocarbons (NMHC), nitrogen oxides ($NO_x$ = NO + $NO_2$), and carbon monoxide (CO) are co-emitted with carbon dioxide ($CO_2$) during combustion. These pollutants are important to tropospheric ozone ($O_3$) and secondary organic aerosol (SOA) formation [*Seinfeld and Pandis*, 1998; *Volkamer et al.*, 2006], which have impacts on health [*Bell et al.*, 2004; *Curtis et al.*, 2006; *Mauderly and Chow*, 2008] and climate [*IPCC*, 2007]. In urban settings, motor vehicles are among the most important sources of emissions for NMHC, $NO_x$, and CO. In the U.S., motor vehicles can be divided between light-duty passenger vehicles which are mostly gasoline powered, and heavy-duty trucks and buses which are mostly diesel powered. Emission reduction measures in the U.S. have been implemented over a period stretching back to the 1960s. Control efforts on gasoline engines include adjustments to air/fuel ratios, changes in the way fuel is metered into engines, changes to fuel properties, and use of catalytic converters that oxidize CO and NMHC and reduce $NO_x$ [*Sawyer et al.*, 2000]. For diesel engines, installation of exhaust gas recirculation (EGR) and more recently the use of selective catalytic reduction (SCR) systems have lowered $NO_x$. Tailpipe CO and hydrocarbon emissions can be reduced with diesel oxidation catalysts and particle filters along with particulate matter [*Sandhu and Frey*, 2012]. Initial control efforts emphasized achieving reductions in NMHC and CO emissions, before shifting to $NO_x$ [*Parrish et al.*, 2011]. Additionally, emissions from light-duty vehicles were controlled earlier than heavy-duty diesel trucks. This has had important consequences for $NO_x$, as heavy-duty truck emissions have become an increasing share of emissions in the U.S. [*Dallmann and Harley*, 2010; *McDonald et al.*, 2012].

Emission inventories are central to air quality planning and atmospheric modeling studies, but inventories are subject to large uncertainties [*Fujita et al.*, 1992; *Parrish*, 2006]. In estimating motor vehicle emissions, challenges arise in accurately representing traffic volumes and driving conditions as a function of location and time, and in specifying appropriate emission factors [*Borge et al.*, 2012]. As fleet-average emissions decrease over time, it is becoming increasingly important to account for skewness in emission factor distributions, and in particular to include the contributions to overall emissions from high-emitting vehicles [*Bishop et al.*, 2012b]. As emission factor distributions become more tail-heavy, larger and larger vehicle sample sizes are required in emission studies to maintain the same level of accuracy in estimates of population mean values. Fleet-average emission factors that reflect emissions from thousands of in-use vehicles are available from roadside remote sensing [*Bishop and Stedman*, 2008], roadway tunnel studies [*Kirchstetter et al.*, 1996; *Fraser and Cass*, 1998], and inspection and maintenance program data [*EPA*, 2013c]. Similarly large and unbiased vehicle samples are very difficult to obtain and costly to test in laboratory settings.

A related challenge is controlling for effects of driving mode (e.g., vehicle speed, acceleration, and roadway grade) on emission factors, which can vary by pollutant [*Kean et al.*, 2003; *Bishop and Stedman*, 2008; *Lee and Frey*, 2012]. Measurements taken at any single location are unlikely to represent the full range of emission factors and driving conditions observed on the road. Also excess emissions associated with cold engine starting are not usually captured in on-road emission studies. In laboratory testing, the cold start phase that includes the first few minutes of vehicle operation can be the dominant source of pollutant emissions for many vehicles, this is especially true for exhaust emissions of NMHC [*Weilenmann et al.*, 2009]. Evaporative NMHC emissions from vehicles are also difficult to describe, in part because these emissions vary with changes in ambient temperature, and because some of the emissions occur while vehicles are parked.

The main goal of this study is to evaluate long-term trends (1990-2010) in motor vehicle emissions for major urban areas in the U.S. New estimates for CO and NMHC emissions are developed in this study, and these values are compared with available estimates for $NO_x$ [*McDonald et al.*, 2012]. An important feature of this work is the use of both source-oriented (bottom-up) and ambient air (top-down) measurements to constrain NMHC emission factors. Previous evaluations of emission inventories indicate that bottom-up and top-down studies of vehicle emissions have not converged [*Fujita et al.*, 1992; *Parrish*, 2006]. Only a few of the top-down evaluations have considered changes in emissions over a long time period. Ambient air measurement studies reporting selected individual hydrocarbon species in urban air have highlighted the importance of motor vehicle contributions [*Warneke et al.*, 2007; *Baker et al.*, 2008; *Warneke et al.*, 2012], but total mass emissions are not estimated, and many hydrocarbons known to be present in liquid fuels are missing (i.e., unmeasured or not reported) from ambient air studies. This paper focuses on three major U.S. metropolitan areas: Los Angeles, New York City, and Houston. These metropolitan areas have large populations (6-22 million), violate ambient air quality standards, and have been focal points for field studies and air pollution control efforts.

## 4.2 Methods

### *4.2.1 Activity Data*

A fuel-based approach is used in this study to estimate motor vehicle emissions, where on-road vehicle activity is measured by fuel consumed rather than distance traveled, and emission factors are expressed per unit of fuel burned. In the U.S., gasoline is consumed primarily by light-duty passenger vehicles, whereas diesel is consumed mostly by heavy trucks and buses. Fuel sales are reported at national and state levels, and are allocated in this study to finer spatial scales using traffic count data.

The spatial domain for Los Angeles was the South Coast air basin. New York City and Houston were represented as urban areas as defined by the U.S. Census Bureau. For the South Coast air basin, McDonald et al. [2012] have estimated gasoline and diesel fuel use, and these estimates are used here. For New York City and Houston, only gasoline fuel use is estimated. Annual reports of fuel sales and traffic data are available from the Federal Highway Administration [*FHWA*, 2011b]. Vehicle travel is reported for individual urban areas as well as by state, and is

used as a spatial surrogate for gasoline use. The amount of vehicle travel in each urban area as a fraction of state totals is calculated for each year and multiplied by statewide gasoline sales to arrive at estimates of fuel consumption in each metropolitan area of interest.

Because ambient measurements were selected only for weekdays (see below), inventory estimates were adjusted to reflect weekday emissions for comparison. Heavy-duty truck fuel use is known to decrease by 70-80% on weekends, and day-of-week specific truck count data reported by Marr et al. [2002] were used to derive weekday-specific estimates of diesel emissions.

### *4.2.2 Bottom-up CO Emission Factors*

We use CO running exhaust emission factors measured in tunnel and remote sensing studies, expressed in grams of CO emitted per kilogram of fuel burned. Remote sensing measurements of light-duty vehicle emissions in the Los Angeles area span a period of 20 years, and have been made at multiple locations [*Lawson et al.*, 1990; *Beaton et al.*, 1995; *Singer and Harley*, 1996, 2000; *Pokharel et al.*, 2003; *Bishop and Stedman*, 2008; *Bishop et al.*, 2010; *Bishop et al.*, 2012b]. Vehicle emissions have also been measured at a tunnel in Van Nuys, CA, spanning a similar time period [*Fraser and Cass*, 1998; *Bishop et al.*, 2012b; *Fujita et al.*, 2012]. Multi-year studies of vehicle emissions in other U.S. and California cities are available for comparison, including remote sensing studies in Chicago [*Y Zhang et al.*, 1996; *Bishop and Stedman*, 2008], Denver [*Y Zhang et al.*, 1996; *Stedman et al.*, 1997; *Stedman et al.*, 1998; *Bishop et al.*, 2000; *Bishop and Stedman*, 2008], Phoenix [*Bishop and Stedman*, 2008], and San Jose [*Bishop et al.*, 2010], and tunnel measurements in Oakland [*Kirchstetter et al.*, 1996; *Kean et al.*, 2002; *Ban-Weiss et al.*, 2008a; *Dallmann et al.*, 2013] (Table 4.1). We focus on studies with sample sizes larger than 10 000 vehicles, to capture contributions from high-emitting vehicles (in the earliest years of field sampling in Denver, vehicle sample sizes were smaller, on the order of several thousand vehicles). Since both emission factors and fuel economy vary with vehicle age, emission factors for each vehicle model year were weighted by corresponding estimates of fuel economy [*EPA*, 2012], following an approach described by Singer et al. [*Singer and Harley*, 1996]. Further fuel economy differences between cars and light-duty trucks were also taken into account. This places greater weight on emissions from vehicles with lower fuel economies in calculating fleet-average emissions. Fuel economy-related adjustments are less influential after 2000, as new vehicle fuel economy standards did not change significantly between the mid-1980s and 2010. Typical uncertainties of the remote sensor for CO are ±5% [*Bishop and Stedman*, 2008]. The uncertainty of the regression analysis in this study reflects differences in fleet characteristics between remote sensing locations, such as vehicle fleet age and driving mode.

Emission values can be affected by seasonal differences in fuel formulation, especially in earlier years when CO emission rates were higher and oxygenates were added to gasoline during winter months only [*Bishop and Stedman*, 1990; *Kirchstetter et al.*, 1996]. In most cases, field sampling of vehicle emissions took place during the summer or fall and therefore exclude wintertime oxygenate effects on emissions. For Denver, both summer and wintertime measurements were taken. To ensure consistency in comparison of trends across cities, only summer emissions results were included in the analysis in earlier years.

**Table 4.1.** Summary of On-road Studies for Gasoline CO Run Exhaust Emission Factors.

| Location | Type | Date | CO EF [g/kg fuel] | Mean Age [y][a] | Reference |
|---|---|---|---|---|---|
| Chicago, IL (Central Ave) | Remote Sensing | Aug/89 | 154.5 | 6.1 | [*Y Zhang et al.*, 1996] |
| | | Oct/90 | 133.3 | 5.5 | |
| | | Jun/92 | 127.8 | 6.4 | |
| Chicago, IL (Arlington Heights) | Remote Sensing | Sep/97 | 55.8 | 5.0 | [*Bishop and Stedman*, 2008] |
| | | Sep/98 | 48.3 | 5.1 | |
| | | Sep/99 | 44.2 | 5.1 | |
| | | Sep/00 | 32.5 | 5.2 | |
| | | Sep/02 | 28.1 | 5.3 | |
| | | Sep/04 | 21.3 | 5.5 | |
| | | Sep/06 | 15.8 | 5.7 | |
| Phoenix, AZ | Remote Sensing | Nov/99 | 41.9 | 5.9 | [*Bishop and Stedman*, 2008] |
| | | Nov/00 | 35.5 | 5.7 | |
| | | Nov/02 | 28.8 | 5.5 | |
| | | Nov/04 | 24.1 | 5.5 | |
| | | Nov/06 | 14.4 | 5.6 | |
| Denver, CO (Speer Blvd) | Remote Sensing | May/89 | 170.3 | 6.6 | [*Bishop and Stedman*, 1990] |
| | | Oct/91 | 116.1 | 6.3 | [*Bishop et al.*, 2000] |
| | | Apr/92 | 116.5 | 6.4 | |
| | | Jul-Aug/96 | 84.4 | 7.0 | |
| | | Dec/02[b] | 34.4 | 6.5 | |

| Location | Type | Date | CO EF [g/kg fuel] | Mean Age [y][a] | Reference |
|---|---|---|---|---|---|
| Denver, CO (6th Ave) | Remote Sensing | Dec/95-Jan/96 | 73.8 | 6.8 | [*Stedman et al.*, 1997] |
| | | Dec/96-Jan/97 | 67.9 | 6.7 | [*Stedman et al.*, 1998] |
| | | Jan/99 | 59.7 | 6.6 | [*Bishop and Stedman*, 2008] |
| | | Jan/00 | 57.7 | 6.6 | |
| | | Jan/01 | 46.6 | 6.4 | |
| | | Jan/03 | 46.5 | 6.6 | |
| | | Jan/05 | 30.4 | 6.9 | |
| | | Jan-Feb/07 | 25.5 | 7.2 | |
| Oakland, CA (Caldecott) | Tunnel | Aug/94 | 105.7 | 6.4[c] | [*Kirchstetter et al.*, 1996] |
| | | Jul-Aug/95 | 94.6 | 6.3 | [*Kean et al.*, 2002] |
| | | Jul-Aug/96 | 74.3 | 6.5 | |
| | | Jul-Aug/97 | 75.7 | 6.7 | |
| | | Jul-Aug/99 | 52.0 | 6.4[c] | [*Ban-Weiss et al.*, 2008a] |
| | | Jul-Aug/01 | 43.0 | 6.2 | |
| | | Jul-Aug/06 | 24.0 | 6.3 | |
| | | Jul/10 | 14.3 | 6.4[c] | [*Dallmann et al.*, 2013] |
| San Jose, CA | Remote Sensing | Oct/99 | 49.6 | 6.9 | [*Bishop et al.*, 2010] |
| | | Mar/08 | 16.9 | 7.6 | |
| Los Angeles, CA | Remote Sensing | Dec/89 | 202.1 | 7.7 | [*Lawson et al.*, 1990] |
| | | May-Jun/91 | 146.4 | 6.5 | [*Singer and Harley*, 1996] |
| | | May-Oct/97 | 108.1 | 6.6 | [*Singer and Harley*, 2000] |

| Location | Type | Date | CO EF [g/kg fuel] | Mean Age [y][a] | Reference |
|---|---|---|---|---|---|
| W Los Angeles, CA | Remote Sensing | Nov/99 | 69.6 | 7.2 | [*Bishop and Stedman*, 2008] |
| | | Oct/01 | 56.9 | 7.3 | |
| | | Oct/03 | 44.3 | 7.2 | |
| | | Oct/05 | 28.1 | 6.9 | |
| | | Mar/08 | 21.1 | 7.0 | [*Bishop et al.*, 2010] |
| Van Nuys, CA | Remote Sensing | Aug/10 | 20.9 | 9.1 | [*Bishop et al.*, 2012b] |
| | Tunnel | Sep/93 | 175.7 | 7.3 | [*Fraser and Cass*, 1998] |
| | | 1995 | 120.0 | 11.2 | [*Gertler et al.*, 1997] |
| | | Aug/10 | 21.3 | 9.1 | [*Fujita et al.*, 2012] |
| Riverside, CA | Remote Sensing | Jun-Jul/99 | 70.3 | 7.1 | [*Pokharel et al.*, 2003] |
| | | May-Jun/00 | 65.6 | 7.3 | |
| | | Jun/01 | 50.9 | 7.0 | |

a. Age [y] = CY – mean vehicle fleet MY, where CY = Calendar Year and MY = Model Year.
b. This dataset can be found at: http://www.feat.biochem.du.edu/light_duty_vehicles.html.
c. The mean model year was not reported for these studies. Age was calculated as the average of study years where fleet age information was available.

A multivariate regression of CO running exhaust emission factors with time is performed on the aforementioned studies using a second order polynomial fit (Table 4.2). Differences in vehicle fleet age across on-road studies are controlled for, and included as an additional independent variable to account for (1) California having an older vehicle fleet than the national average, and (2) aging of the vehicle fleet in recent years due to recession-related effects on new vehicle sales. The mean vehicle age is estimated from the National Household Travel Survey (NHTS) [*FHWA*, 1991, 2004, 2011a]. These values are then inputted into the regression model for each urban domain. Age distributions at remote sensing locations are similar to the U.S. and California vehicle fleets. Because California vehicles were certified to meet *less* stringent CO emission standards during the 1980s and early 1990s [*Calvert et al.*, 1993], we include a dummy variable to account for differences between California vehicles and those from other states. This effect diminishes over time: since 1993, CO emission standards for new California vehicles have been the same as or more restrictive than national standards. Cold engine starting emissions are estimated for California only. The ratio of start to running emissions is taken from the EMFAC model (California Air Resources Board, EMFAC 2011, http://www.arb.ca.gov/msei/modeling.htm) and multiplied with running exhaust emissions from this study.

For heavy-duty diesel trucks, we use linear regression to describe CO emission factor trends (Table 4.3). Data points include remote sensing measurements of truck exhaust plumes in Anaheim, CA [*Bishop et al.*, 2012b], and San Marcos, TX [*Bishop et al.*, 2001]. We exclude port locations where truck fleets may not be representative, and also exclude high-elevation sites that show increases in CO emissions, but that are not relevant for the cities that are the focus of this study. Tunnel measurements of CO emissions from Tuscarora, PA in 1992 [*Pierson et al.*, 1996] and Oakland, CA in 2010 [*Dallmann et al.*, 2012] are included in the regression. To augment CO emissions data for the 1990s to support the regression analysis, we calculated fleet-average emission factors for calendar years 1992-98, based on heavy-duty vehicle chassis dynamometer emission tests summarized by Yanowitz et al. [2000].

**Table 4.2.** Summary of On-road Gasoline CO Run Exhaust Emission Factor Regression.[a,b]

| | Coef. | s.e. | t value[c] |
|---|---|---|---|
| $\beta_0$ | 118.7 | 11.5 | 10.3 |
| $\beta_1$ | 0.395 | 0.046 | 8.5 |
| $\beta_2$ | -14.26 | 0.85 | -16.7 |
| $\beta_3$ | 5.10 | 1.65 | 3.1 |
| $\beta_4$ | -2.28 | 0.58 | -3.9 |
| $\beta_5$ | 33.7 | 6.6 | 5.1 |

a. Model: $Y_{CO,EF}$ (g/kg fuel) = $\beta_0 + \beta_1*(CY - 1990)^2 + \beta_2*(CY-1990) + \beta_3*Age + \beta_4*CA + \beta_5*CA*(CY-1990)$, where Age [y] = CY – mean vehicle fleet MY, CA = (0: US, 1: CA).
b. $R^2 = 0.95$.
c. All coefficients are statistically significant to the 99% confidence level.

**Table 4.3.** Summary of On-road Diesel CO and NMHC Run Exhaust Emission Factor Regressions.

| | Coef. | s.e. | t value |
|---|---|---|---|
| CO EF[a]: | | | |
| $\beta_0$ | 19.25 | 1.58 | 12.2[c] |
| $\beta_1$ | -0.470 | 0.123 | -3.8[c] |
| NMHC EF[b]: | | | |
| $\beta_0$ | 2.083 | 0.488 | 4.3[c] |
| $\beta_1$ | 0.000423 | 0.035 | 0.01[d] |

a. CO Model: $Y_{CO,EF}$ (g/kg fuel) = $\beta_0 + \beta_1*(CY - 1990)$; $R^2 = 0.62$.
b. HC Model: $Y_{HC,EF}$ (g/kg fuel) = $\beta_0 + \beta_1*(CY - 1990)$; $R^2 < 0.01$.
c. Coefficients are statistically significant to the 99% confidence level.
d. Coefficient is not statistically significant.

### *4.2.3 Top-Down Gasoline NMHC/CO*

Light-duty NMHC emission factors are estimated using a top-down approach by determining ratios of gasoline-related NMHC to CO in ambient air using a combination of literature values and monitoring data (Table 4.4). Gasoline-related NMHC are emitted as evaporated fuel and tailpipe exhaust from vehicles in use or at rest, or from storage tanks [*Gentner et al.*, 2009]. To isolate gasoline-related emissions, we either use an over-constrained chemical mass balance (CMB) method, or scale the sum of unburned fuel species predominantly emitted by motor vehicles by their mass fraction in liquid fuel samples. Ambient NMHC/CO reported here include evaporative and fugitive emissions in addition to tailpipe exhaust, because tracer species are emitted via each of these pathways [*Gentner et al.*, 2009].

CMB was applied to hourly ambient air measurements (N=57; morning rush hour samples only) from the 1987 Southern California Air Quality Study [*Harley et al.*, 1997], and PAMS monitoring network data from downtown Los Angeles between 1994 and 2001 (N=357). A detailed description of CMB analysis can be found in Gentner et al. [2012]. PAMS samples were collected every third day from July to August at 5 AM, and also at noon from 1994 to 1999. Tracer compounds whose emissions are mainly due to motor vehicles were selected and scaled up to reflect other unmeasured fuel-derived species, based on the content of the measured ambient species in liquid gasoline samples collected over the same time period [*Harley et al.*, 1992; *Gentner et al.*, 2012]. Compounds used included isopentane, 3-methylpentane, 3-methylhexane, methylcyclohexane, and isooctane (as well as n-butane in 1987). Based on results of Kirchstetter et al. [1996], we estimate that 24 ± 2% of exhaust NMHC emissions by mass are products of incomplete combustion (e.g. ethane, ethene, acetylene, propene), which are not captured by the CMB analysis. This value is used to adjust upward results for the gasoline source contribution in ambient air. The motor vehicular contribution to ambient NMHC is then regressed with concentrations of CO to derive the ambient ratio of NMHC/CO.

For field measurements where ambient results are reported as study averages [*Warneke et al.*, 2007; *Baker et al.*, 2008; *Warneke et al.*, 2012], we scaled up each tracer species individually based on corresponding mass fractions in unburned fuel, and used averages of the ensemble of the results. This resulting value was adjusted to include products of incomplete combustion as described above. NMHC emission factors were obtained by multiplying bottom-up CO running exhaust emission factors for each calendar year by the average ambient NMHC/CO ratio resulting from the analyses described above.

**Table 4.4.** Summary of Gasoline NMHC/CO Ratios from Summertime Ambient Studies.

| Year | Data | NMHC/CO Ratio [g/g][a,b] | Comments |
|---|---|---|---|
| 1987 | SCAQS network N. Main site | 0.126 ± 0.024 (95% CI) (N=57, r=0.82) | Over-constrained CMB[c,d] |
| 1994-2001 (summer data) | PAMS network N. Main Site | 0.093 ± 0.007 (95% CI) (N=357, r=0.83) | Over-constrained CMB[c,d], No trend observed |
| 2002 | [*Warneke et al.*, 2007] | 0.125 ± 0.054 | Ensemble average of scaled up compound ratios[d-f] |
| 2005 | [*Baker et al.*, 2008] | 0.144 ± 0.044 | Ensemble average of scaled up compound ratios[d-f] |
| 2005 | [*Gentner et al.*, 2009] | 0.104 ± 0.008 (95% CI) | Basic CMB[d] |
| 2010 | [*Warneke et al.*, 2012] | 0.119 ± 0.059 | Ensemble average of scaled up compound ratios[d-f] |

a. The NMHC/CO ratios presented here include unburnt fuel, products of incomplete combustion in tailpipe exhaust, and fugitive (e.g. evaporative) emissions from vehicles and storage tanks.
b. Ratios are shown with standard deviations unless indicated otherwise.
c. Over-constrained CMB methods are described in detail in Gentner et al. [*Gentner et al.*, 2012] and used fuel data from the periods of interest. Tracer compounds used in this analysis were isopentane, 3-methylpentane, 3-methylhexane, methylcyclohexane, and isooctane (& n-butane in 1987).
d. Ambient ratios are scaled up assuming 24% of NMHC emissions are products of incomplete combustion [*Kirchstetter et al.*, 1996].
e. Ambient ratios are scaled up assuming 24% of total gasoline-related emissions are non-tailpipe, which was derived from Gentner et al. [2009] for 2005 and from CMB analysis in this study for 1987 and PAMS 1994-2001.
Each gasoline tracer is scaled to total NMHC by their presence in liquid fuel samples taken over this time period [*Harley et al.*, 1992; *Gentner et al.*, 2012]. These analyses are more uncertain and likely an upper limit due to the contribution of other sources of hydrocarbon emissions.

### *4.2.4 Bottom-up Diesel NMHC*

For heavy-duty diesel trucks, a regression analysis of remote sensing [*Bishop et al.*, 2001; *Bishop et al.*, 2012b], tunnel [*Gentner et al.*, 2012], and chassis dynamometer [*Yanowitz et al.*, 2000] measurements was used to estimate bottom-up fleet-averaged NMHC emission factors (Table 4.3). Infrared (IR) remote sensors calibrated using propane are known to underestimate NMHC emissions from gasoline engines by a factor of ~2 when compared to flame ionization detectors (FID) [*Singer et al.*, 1998]. Because the mix of hydrocarbons present in exhaust emissions differs between gasoline and diesel engines, a separate NMHC scaling factor was derived based on comprehensive diesel fuel speciation profiles published by Gentner et al. [2012], and generalized IR/FID response factors reported by Singer et al. [1998]. The IR/FID response for alkanes and cycloalkanes is approximately equal to 1. For single-ring aromatics we estimate the response to be (n – 6)/n, where n is the number of carbon atoms in the molecule (i.e., the aromatic ring and associated C-H bonds are invisible at the IR wavelengths used for remote sensing). For polycyclic aromatics we assumed zero response. We included diesel emissions of ethene reported by Dallmann et al. [2012], which Singer et al. report to have IR/FID response of ~0. Overall, a scaling factor of ~1.2 applies for diesel exhaust, in contrast to the higher value of ~2 for gasoline engine NMHC emissions. The differences in IR/FID response between fuels are driven by the higher alkane/cycloalkane and lower aromatic fractions in diesel fuel compared to gasoline, and the presence of longer alkyl constituents on aromatics present in diesel fuel. Oxygenated products of incomplete combustion are not included in these calculations, such as formaldehyde which is an important species in diesel exhaust [*Dallmann et al.*, 2012]. If included, the scaling factor would increase to reflect non-methane organic carbon (NMOC) rather than NMHC mass.

### *4.2.5 Ambient Air Monitoring Data*

We compare bottom-up CO emission trends derived in this study with top-down trends in surface observations of CO and $CO/NO_x$ ratios derived from ambient air monitoring networks. To isolate motor vehicle emissions, comparisons are made during the morning commuter peak period, on weekdays from 0500 to 0800 hours local standard time over the entire year [*Fujita et al.*, 1992; *Parrish*, 2006]. Cold start effects are included in ambient data. To reduce effects of year-to-year meteorological variations in extreme values of the distribution, we calculated the annual mean of the daily 3-hour morning average of weekday CO levels, rather than using absolute maxima for each year. For Southern California, we used long-term records (1990-2011) of measured CO concentrations at 9 urban sites located in Los Angeles and Orange Counties where CO mixing ratios are highest. In New York City, data from 7-14 monitoring sites were available in each year, and for Houston 3-4. For $CO/NO_x$, we limit the analysis to Los Angeles and include four additional monitoring sites located further inland. Ambient $CO/NO_x$ molar ratios were computed by regression analysis of daily 0500-0800 average concentrations for each year.

## 4.3 Results and Discussion

### *4.3.1 CO Emission and Ambient Trends*

Significant progress has been made in controlling motor vehicle CO running exhaust emissions over the last twenty years (Figure 4.1a). For gasoline-powered vehicles since 1990, there were 10-fold and 7-fold reductions in CO emission factors of running exhaust measured in California and the US, respectively. During the early 1990s, California vehicles consistently emitted CO at higher amounts, due to emission control tradeoffs that were made to enable more effective control of $NO_x$ [*Calvert et al.*, 1993]. In terms of CO emission factors, California vehicles appear to have converged with the US fleet by around 2005. The large decreases in CO running exhaust emission factors observed both in California and at the national scale can be attributed to improved performance and durability of catalytic converters [*Bishop and Stedman*, 2008], and associated improvements in control of air-fuel ratios in gasoline engines.

As a result of the notable success in CO emission control, the distribution of running exhaust emission factors is becoming increasingly skewed, such that a smaller and smaller proportion of vehicles on the road are accounting for the majority of overall emissions (Figure 4.1b). The distribution is based on the assumption that remote sensing captures a representative sample of vehicles for the region on a distance traveled basis. In 1989, the highest-emitting 10% of vehicles in Los Angeles accounted for ~50% of running CO emissions [*Lawson et al.*, 1990], whereas by 2010, the top 10% of vehicles were responsible for ~85% of the emissions [*Bishop et al.*, 2012b]. Similarly, ~80% of vehicles contributed negligible amounts of CO in 2010. This suggests that further reductions in light-duty CO emissions should target high-emitters rather than the vehicle fleet as a whole, which are ~5-7 years older than the rest of the fleet (Figure 4.2). Emission factor distributions are also skewed for other pollutants (Figure 4.3). The skewness for light-duty NMHC, CO, and $NO_x$ emissions is -4.9, -3.9, and -2.9, respectively. The distribution of $NO_x$ emission factors for heavy-duty trucks is currently much less skewed (skewness = -0.6 to -0.7) [*Bishop et al.*, 2012b; *Dallmann et al.*, 2012] than for gasoline-powered vehicles (skewness = -2.9), and results because most trucks at present are not equipped with advanced systems for $NO_x$ control (Figure 4.3).

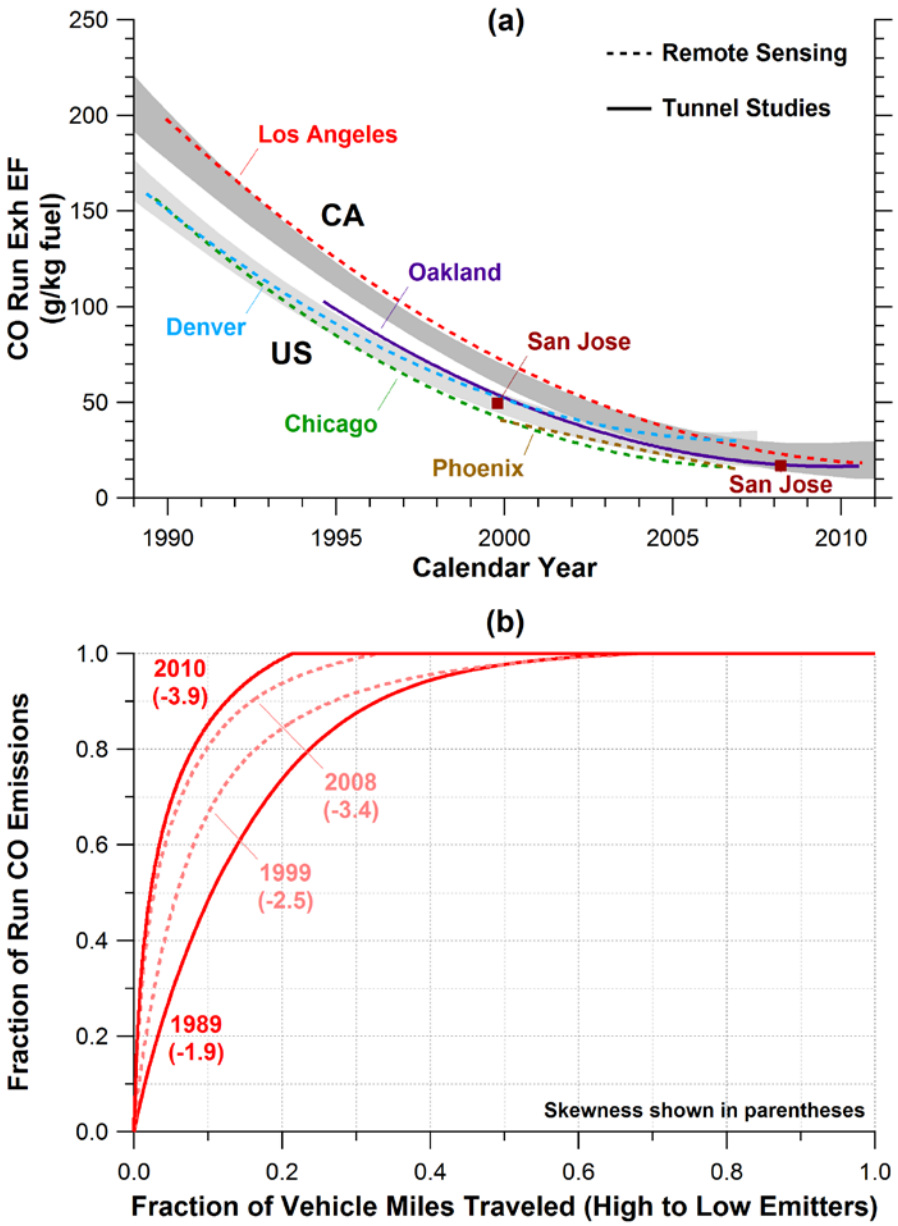


**Figure 4.1.** (a) Carbon monoxide stabilized (running) emission factor trends for light-duty gasoline-powered vehicles. All trends shown here are derived from remote sensing data, except for California tunnel measurements made in Oakland, and are reflective of long-term changes in summertime emissions (see text). Gray bands show 95% confidence intervals of the regression for California (upper band) and US (lower band). Individual emission factors for a given calendar year reflect local vehicle mixes across model years. (b) Cumulative distributions of stabilized CO emissions from gasoline-powered vehicles in Los Angeles, based on remote sensing measurements of many individual vehicle exhaust plumes. The fraction of total CO emissions coming from the highest-emitting 10% of vehicles on the road increased from ~50 to ~90% between 1989 and 2010. The skew of emissions shown in panel b were not incorporated in the emission factor regression shown in panel a. Also, the distribution curves reflect fuel economy weighting by vehicle model years.

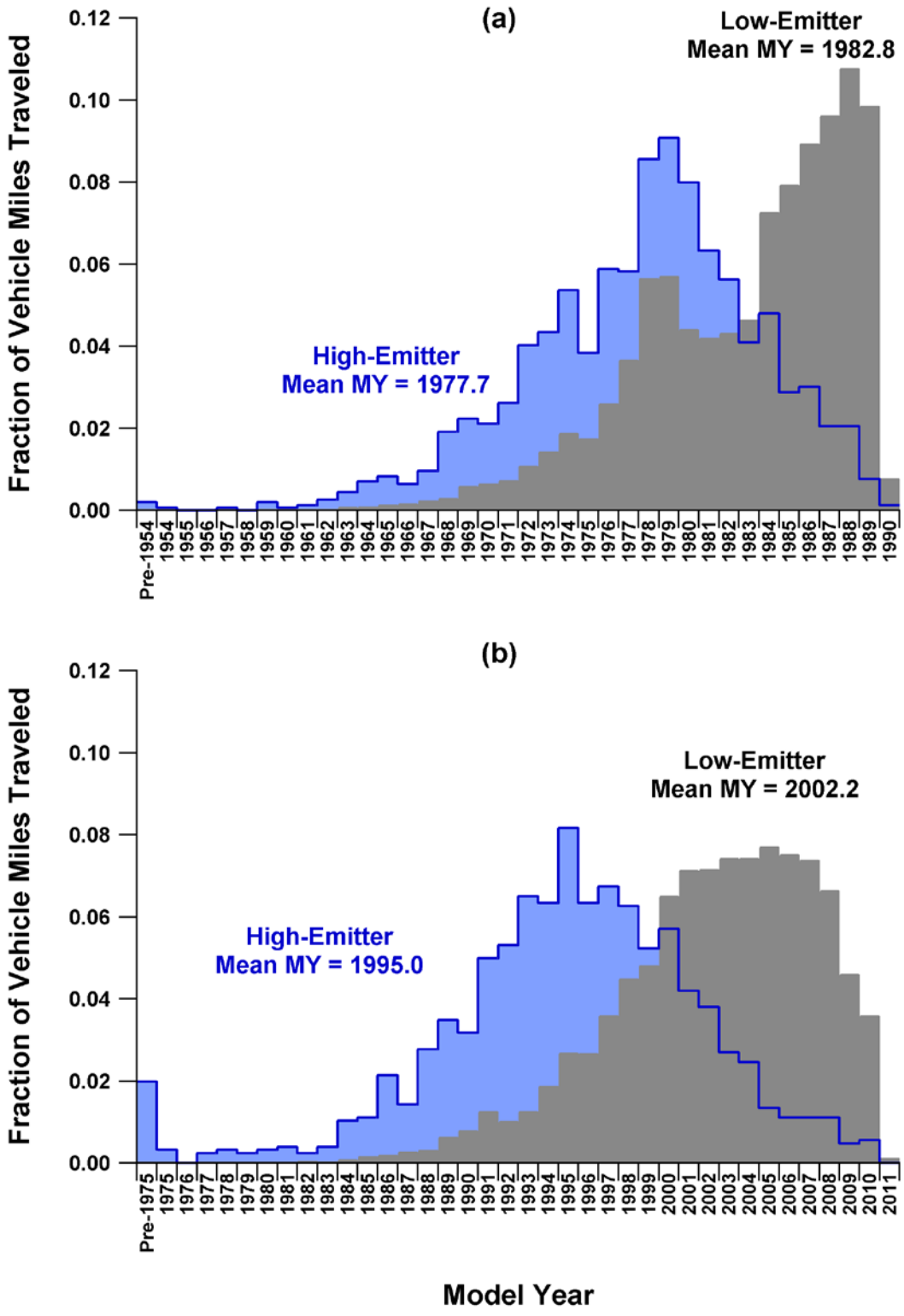


**Figure 4.2.** Vehicle age distributions of high and low emitting vehicles for running exhaust emissions of CO from remote sensing in Los Angeles for (a) 1989 and (b) 2010. High emitting vehicles are defined as the top 10% and low emitting as the bottom 90%.

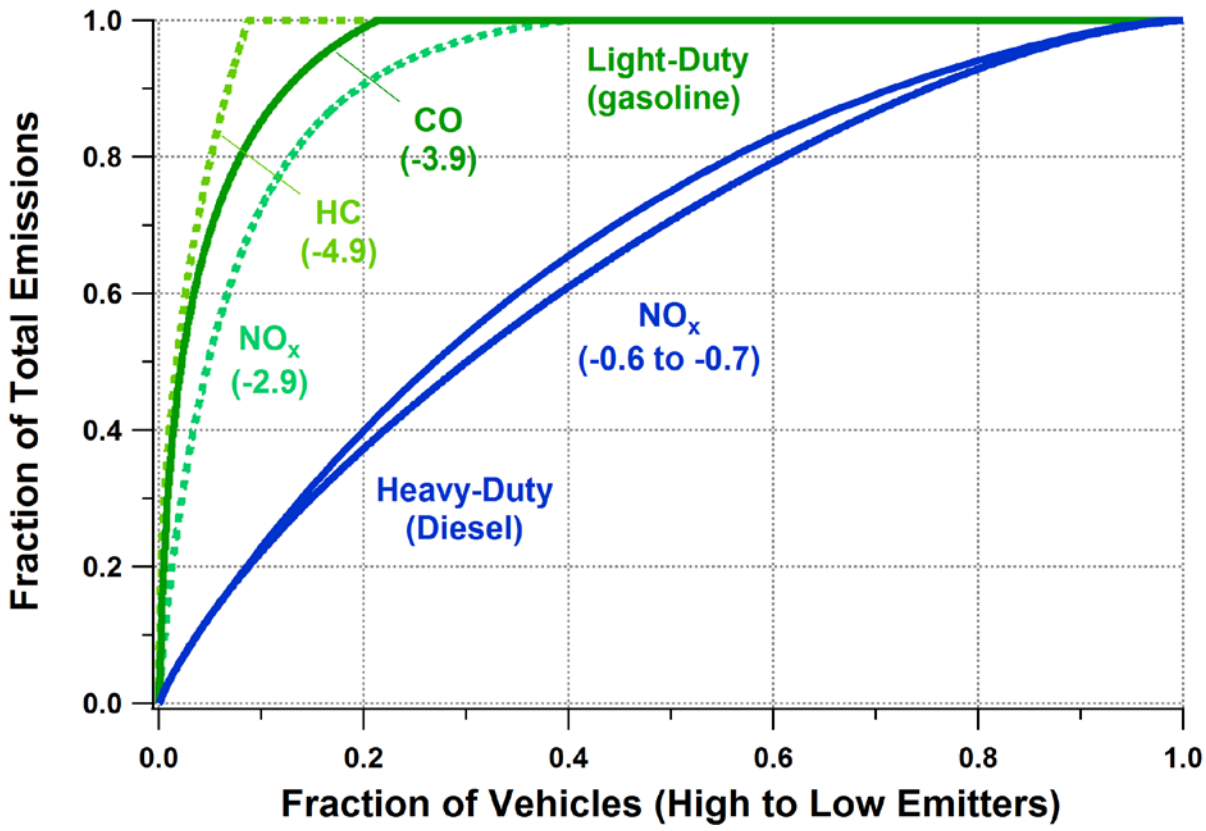


**Figure 4.3.** Distribution of running exhaust emissions for NMHC, CO, and $NO_x$ in 2010. Light-duty measurements are for the same location in Los Angeles. Similar results for heavy-duty diesel NOx are shown based on remote sensing at Peralta weigh station in Anaheim (lower blue line) and tunnel measurements in Oakland (upper blue line).

Bottom-up running exhaust emissions and ambient concentrations of CO are compared in Figure 4.4 for the three metropolitan areas. The long-term trends in emissions are reflective of changes during summertime. Because gasoline vehicles heavily dominate the on-road inventory of CO emissions in Los Angeles, only gasoline is shown. The large reductions in CO running exhaust emission factors are more than enough to offset 10-40% increases in gasoline sales from 1990 to 2010. Los Angeles and New York City saw growth in gasoline use near the lower end of this range, while Houston saw a larger increase in gasoline use. Running CO emissions from on-road vehicles decreased by 80-90%, despite increases in the number of vehicles on the road and the amount of fuel burned. The results of this study are consistent with trends in ambient CO concentrations measured in all three cities. Comparisons of fuel-based emission estimates for the Los Angeles area with estimates from the most recent version of the EMFAC model are also in reasonable agreement, though our rate of CO reduction may be slightly steeper than EMFAC.

The fuel-based trend of decreasing CO running emissions appears to be slowing and may have stopped completely in recent years. This emissions-related finding is consistent with ambient observations that show little change in CO concentrations in the most recent years, which is true in all three cities (Figure 2). Federal tailpipe emission standards for CO have not been lowered since Tier 0 standards were first implemented on 1981 model year vehicles (Figure 4.5) [*Parrish*, 2006]. The slowdown in the ambient trend is also due to aging of the vehicle fleet, and the growing importance of cold start emissions. In California, start emissions have accounted for an increasing fraction of CO emissions: from 15% in 1990 to 27% in 2010. The influence of deterioration on ambient trends may depend on the extent to which model year vehicles 1991-2000 remain in the fleet. A decade analysis of remote sensing data found deterioration rates were near zero for model year vehicles 1990 and earlier, and 2001 and later [*Bishop and Stedman*, 2008].

Running emission factors for CO are known to vary depending on engine load [*Kean et al.*, 2003; *Bishop and Stedman*, 2008; *Lee and Frey*, 2012]. When expressed per unit of fuel burned, the CO emission factor increases both at idle, and especially when accelerating while driving at high speed. Engine load can be described using a normalized measure known as vehicle specific power (VSP = engine power output divided by vehicle mass, in W $kg^{-1}$ or kW $t^{-1}$) which is a function of vehicle speed, acceleration, and roadway grade [*Jimenez et al.*, 1999]. For the West Los Angeles remote sensing site [*Bishop and Stedman*, 2008], we calculated VSP for each vehicle and compared the resulting distribution of engine load with the corresponding fuel use distribution derived from the Unified LA92 drive cycle [*Austin et al.*, 1992], which is used to represent the full range of in-use driving conditions observed on-road in California. Driving conditions at the West Los Angeles site encompass most of the range of the Unified cycle, but idle and high engine load operating conditions are under-represented (Figure 4.6). For VSP values between 0 and 25 kW $t^{-1}$, which accounts for ~95% of the fuel use in the Unified cycle, the CO emission factor is relatively stable. For comparison, driving conditions are similar at the Denver site, while engine loads are lower in Chicago but predominantly between 0 and 25 kW $t^{-1}$ [*Bishop and Stedman*, 2008]. This suggests that effects of engine load on CO emission rates do not introduce substantial bias in the fleet-average results reported here, though some high load driving may be missing in this analysis.

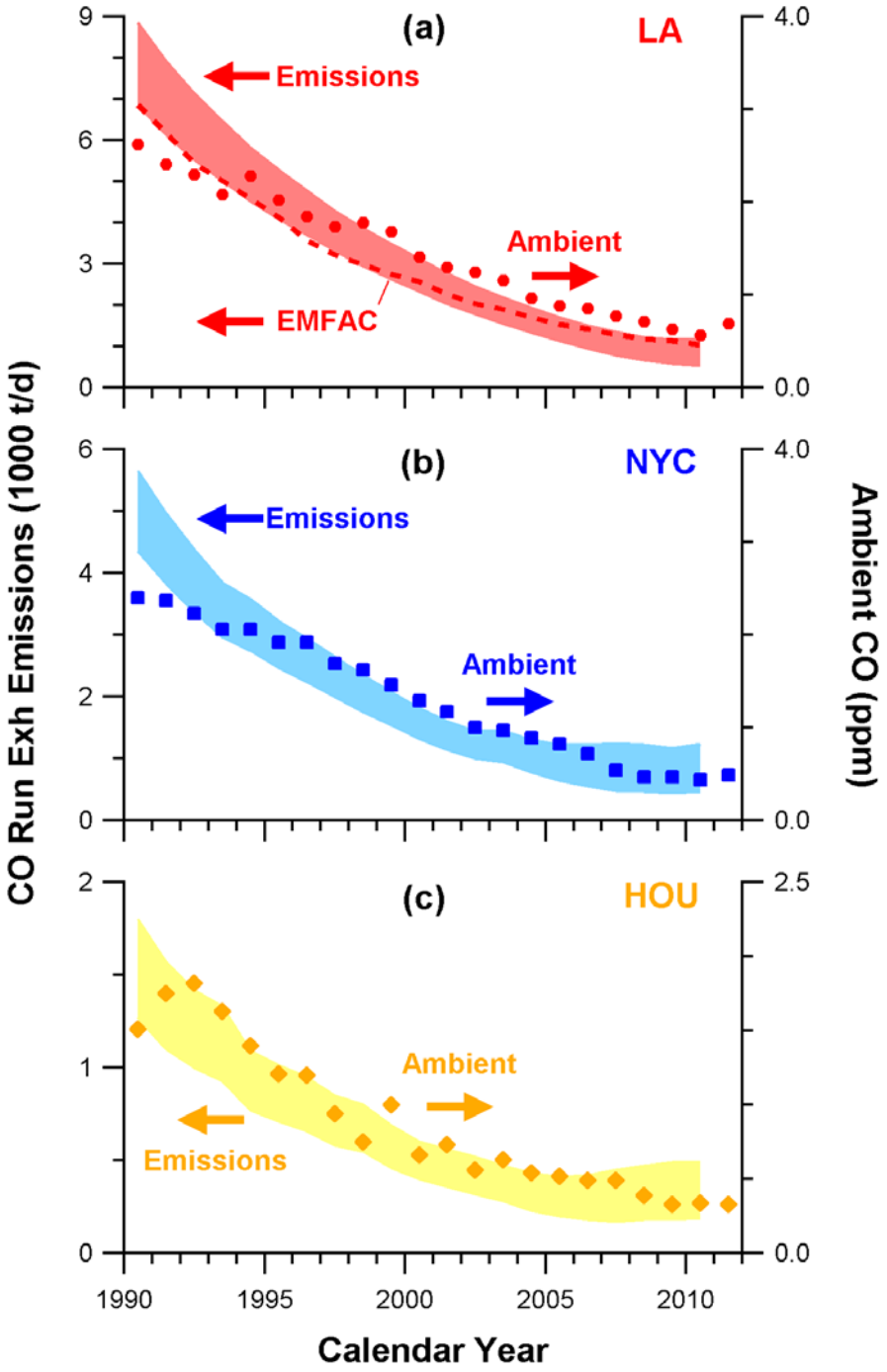


**Figure 4.4.** Ambient concentration and on-road gasoline vehicle trends for stabilized (running) CO emissions in (a) Los Angeles, (b) New York City, and (c) Houston metropolitan areas. Emission estimates shown as bands give 95% confidence intervals, and the long-term emission changes are reflective of summertime. EMFAC model predictions (dashed line) are shown for Los Angeles. Ambient CO data reflect morning rush hour conditions on weekdays when CO levels are high and vehicle emissions dominate, and are shown as the annual average (see text). Start emissions are not shown, but have accounted for an increasing share of on-road gasoline emissions in California from 15% to 27% between 1990 and 2010.

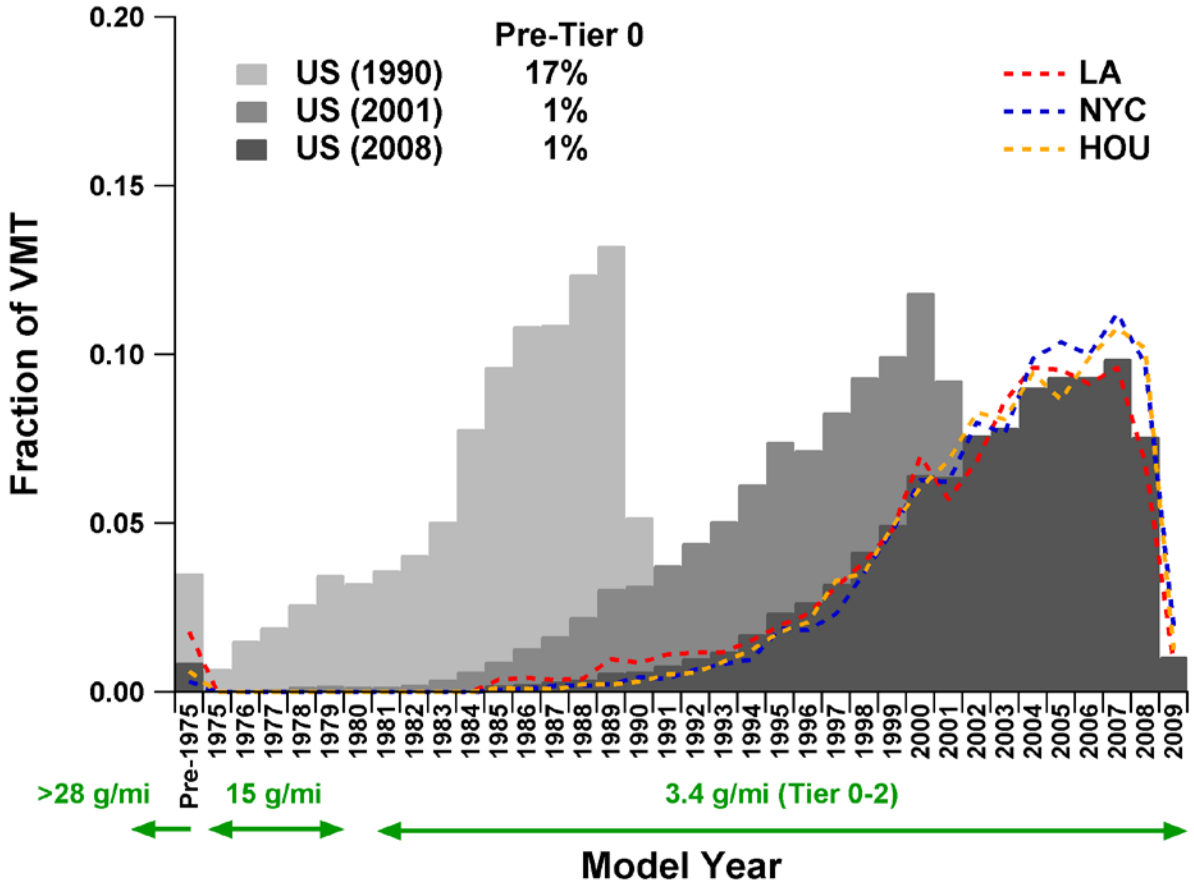


**Figure 4.5.** Vehicle age distribution of U.S., Los Angeles, New York City, and Houston vehicle fleets over time [*FHWA*, 1991, 2004, 2011a]. Successive federal CO emission standards are shown for light-duty vehicles at bottom [*Parrish*, 2006]. Large changes in emission standards occurred prior to Tier 0 standards, which started with model year 1981.

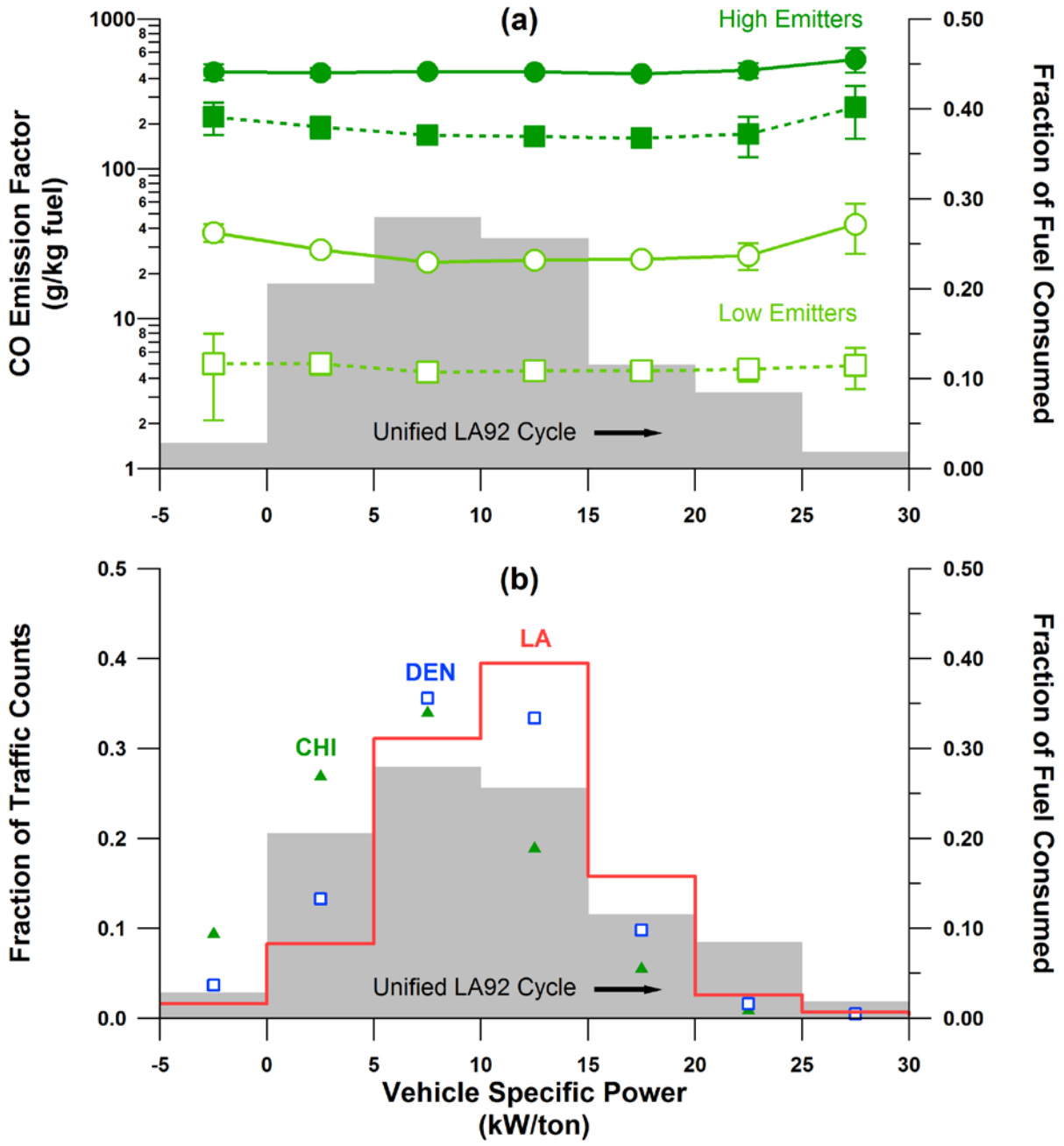


**Figure 4.6.** (a) Variability of CO emission factors with engine load at remote sensing from West Los Angeles. High-emitters are defined as the top 10% of vehicles. Vehicle specific power is calculated as VSP = 4.39*sin(slope)*v + 0.22*v*a + 0.0954*v + 0.0000272*$v^3$, where slope is in degrees, v = velocity in mph, and a = acceleration mph/s [*Jimenez et al.*, 1999]. The remaining vehicles are labeled as low emitters. Emission factors for each subgroup are shown for the years 1999 (solid lines) and 2008 (dashed lines). (b) Distribution of engine loads for remote sensing in West Los Angeles, Denver, and Chicago as compared to the California Unified LA92 drive cycle.

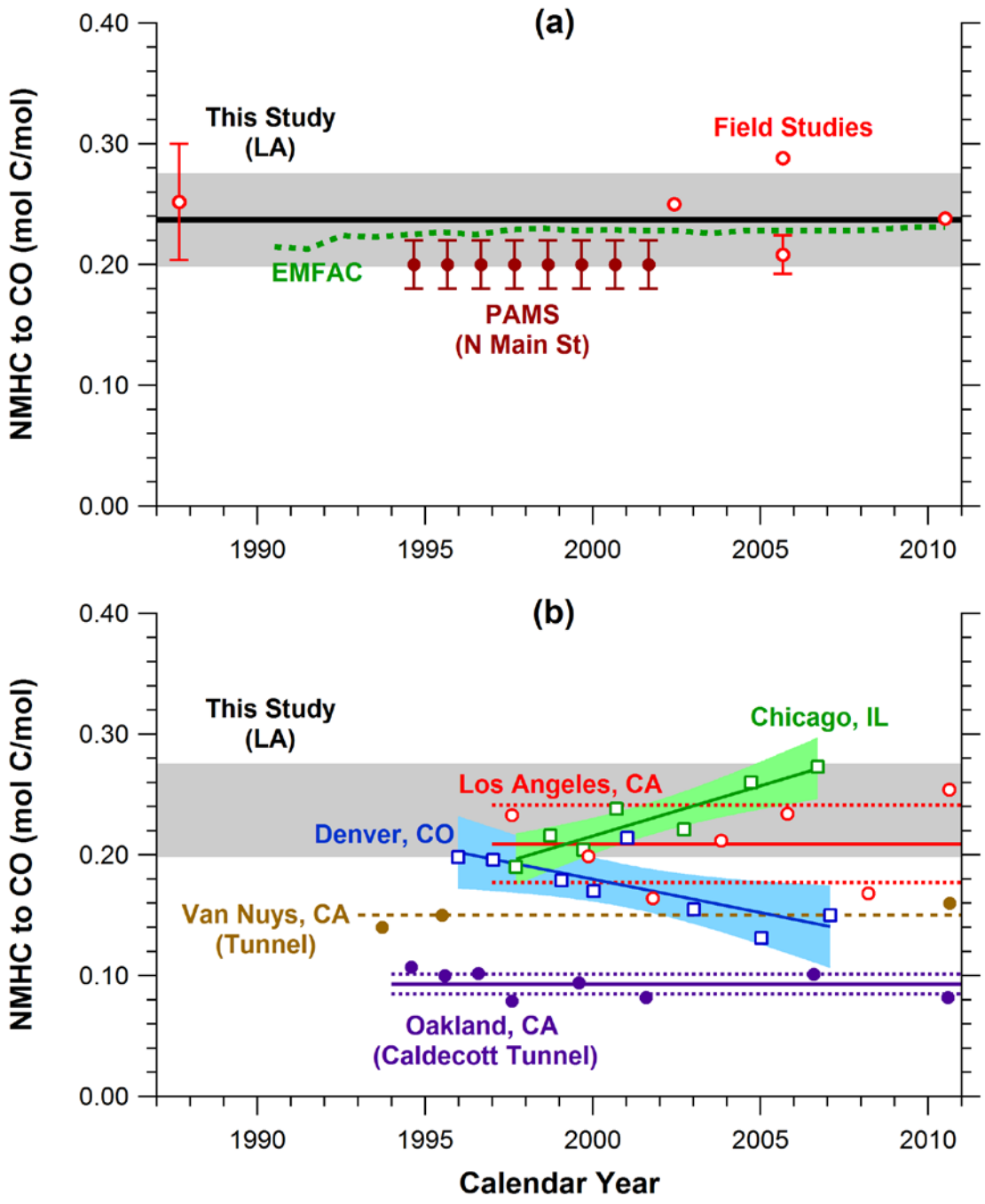


**Figure 4.7.** (a) Trends of ambient NMHC/CO in Los Angeles derived from special field studies and Photochemical Assessment Monitoring Stations (PAMS) data during summertime. NMHC data have been adjusted to exclude non-vehicular emissions (see text). Comparisons to ratios from EMFAC are also shown. (b) Measured NMHC/CO emission ratios derived from remote sensing (open symbols) and tunnels (solid symbols). Uncertainty bands reflect 95% confidence intervals in both panels. Note that "This Study (LA)" is the same in both panels.

### *4.3.2 NMHC Emission and Ambient Trends*

Figure 4.7 shows a stable top-down ambient NMHC/CO ratio of 0.24 ± 0.04 mol C/mol CO in Los Angeles. Units are shown as molar ratios to be consistent with prior studies reporting ambient species relative to CO [*Baker et al.*, 2008; *Warneke et al.*, 2012]. Given reductions in CO described above, this result suggests that vehicular emissions of NMHC and CO have been decreasing at a similar rate, and that gasoline powered vehicles dominate the emissions of NMHCs used in this study. This is consistent with pollutant concentration trends observed in the Los Angeles area over a 50-year period [*Warneke et al.*, 2012]. Note that the ambient-derived trend includes evaporated fuel in addition to tailpipe emissions. The EMFAC model also shows similar reductions in CO and NMHC emissions over time, and a roughly constant emission ratio that is similar to our estimate.

When compared to on-road diesel engines, hydrocarbon emission factors for gasoline engines have historically been much higher when expressed per unit of fuel burned. Diesel engines operate with excess oxygen, and these fuel-lean conditions are conducive to oxidation of CO and NMHC. While near-stoichiometric combustion conditions typical in gasoline engines lead to higher engine-out CO and NMHC emissions, widespread use of the three-way catalytic converter has proved very effective at reducing these emissions from gasoline engines. Diesel CO and NMHC emissions have also declined over time, but the reductions have not been as great, such that for NMHC especially the gap between gasoline and diesel emission factors has narrowed considerably. Gasoline engines still dominate in terms of overall NMHC mass emissions, because of larger volumes of gasoline sold and used compared to diesel fuel. Looking ahead, trucks will increasingly be equipped with diesel particulate filters and associated upstream oxidation catalysts used for regeneration of the filter, and this is expected to reduce diesel NMHC emissions significantly [*Herner et al.*, 2009].

Bottom-up NMHC/CO emission ratios from remote sensing studies and tunnel measurements in Oakland (Caldecott) and Los Angeles (Van Nuys) are shown for comparison in Figure 4.7b. A key result is that the on-road studies in California also show NMHC/CO emission ratios that are stable over time, consistent with trends in top-down pollutant ratios derived from ambient air studies discussed above. However, the absolute ratios in on-road studies differ by a factor of 2, with the Caldecott tunnel measurements on the lower end, remote sensing on the upper end, and Van Nuys tunnel study results in the middle. A potential explanation is systematic differences in driving conditions and engine load among study sites. Vehicles inside the Caldecott tunnel are driving uphill on a 4% grade at speeds of 60-100 km $h^{-1}$ [*Kean et al.*, 2003]. Vehicles traveling through the Van Nuys tunnel move at a uniform speed of ~65 km $h^{-1}$ with a small net downhill grade of ~0.1% in the eastbound direction [*Fraser and Cass*, 1998; *Fujita et al.*, 2012]. It has been suggested that higher NMHC/CO ratios measured by remote sensing, when compared to tunnel measurements at Van Nuys, could be due to differences in driving conditions between two nearby sampling locations [*Bishop et al.*, 2012b]. Differences in NMHC/CO ratios appear to arise primarily due to engine load effects on NMHC as opposed to CO emissions. A methodological difference between approaches shown in Figure 4.7b is that remote sensing captures tailpipe emissions only, tunnel studies include evaporative running loss emissions [*Kirchstetter et al.*, 1996; *Bishop et al.*, 2012b], and ambient ratios include the full range of evaporative and exhaust emissions. The lowest NMHC/CO ratio should be from remote sensing,

but the magnitude is comparable to the ambient-derived ratio, highlighting the need for checking bottom-up estimates of NMHC with top-down measurements.

We did not estimate NMHC in New York City and Houston in this analysis, and we recommend caution in applying the ambient NMHC/CO ratios discussed above outside of California. Local conditions including temperature, humidity, altitude, and characteristics of vehicle fleets can all influence emissions. NMHC/CO ratios derived from remote sensing are increasing over time in Chicago, and decreasing in Denver, although in an absolute sense the emission ratios from other cities are in rough agreement with Los Angeles (Figure 4.7b).

### *4.3.3 $CO/NO_x$ and $NMHC/NO_x$ Trends*

Bottom-up CO and top-down derived NMHC emission results reported here are compared with $NO_x$ emission results reported by McDonald et al. [2012] for the South Coast air basin (Figure 4.8). In this section of the analysis, cold start emissions are included with running exhaust. Results are reported with $NO_x$ in the denominator to be consistent with prior work [*Fujita et al.*, 1992; *Parrish et al.*, 2002]. Between 1990 and 2007, the bottom-up $CO/NO_x$ emissions ratio from on-road vehicles decreased by ~4, with slight increases after 2007. The same result is true for emissions of NMHC to $NO_x$, since the ambient NMHC/CO remained unchanged. The large decreases in on-road emissions of $CO/NO_x$ and $NMHC/NO_x$ ratios are a result of two factors: (1) larger decreases in gasoline CO and NMHC emissions relative to gasoline $NO_x$, and (2) increases in diesel $NO_x$ emissions during the 1990s. The flattening of the $CO/NO_x$ emissions ratio after 2002, and the uptick after 2007 appear to be a result of diminishing returns on efforts to control CO and NMHC emissions from light-duty vehicles, as well as decreases in diesel $NO_x$ emissions since 2007 due to recession-related reductions in goods movement. We expect that $CO/NO_x$ and $NMHC/NO_x$ emission ratios for on-road motor vehicles will continue to increase. Advanced systems for $NO_x$ emission control are now required on new heavy-duty diesel trucks nationwide, and a California rule will further require replacement of all pre-2010 heavy-duty truck engines over the next ten years. Significant further reductions in $NO_x$ emissions are therefore expected. In contrast, decreases in gasoline CO and NMHC emissions are not expected to be as large over the coming decade, so ratios to $NO_x$ should increase.

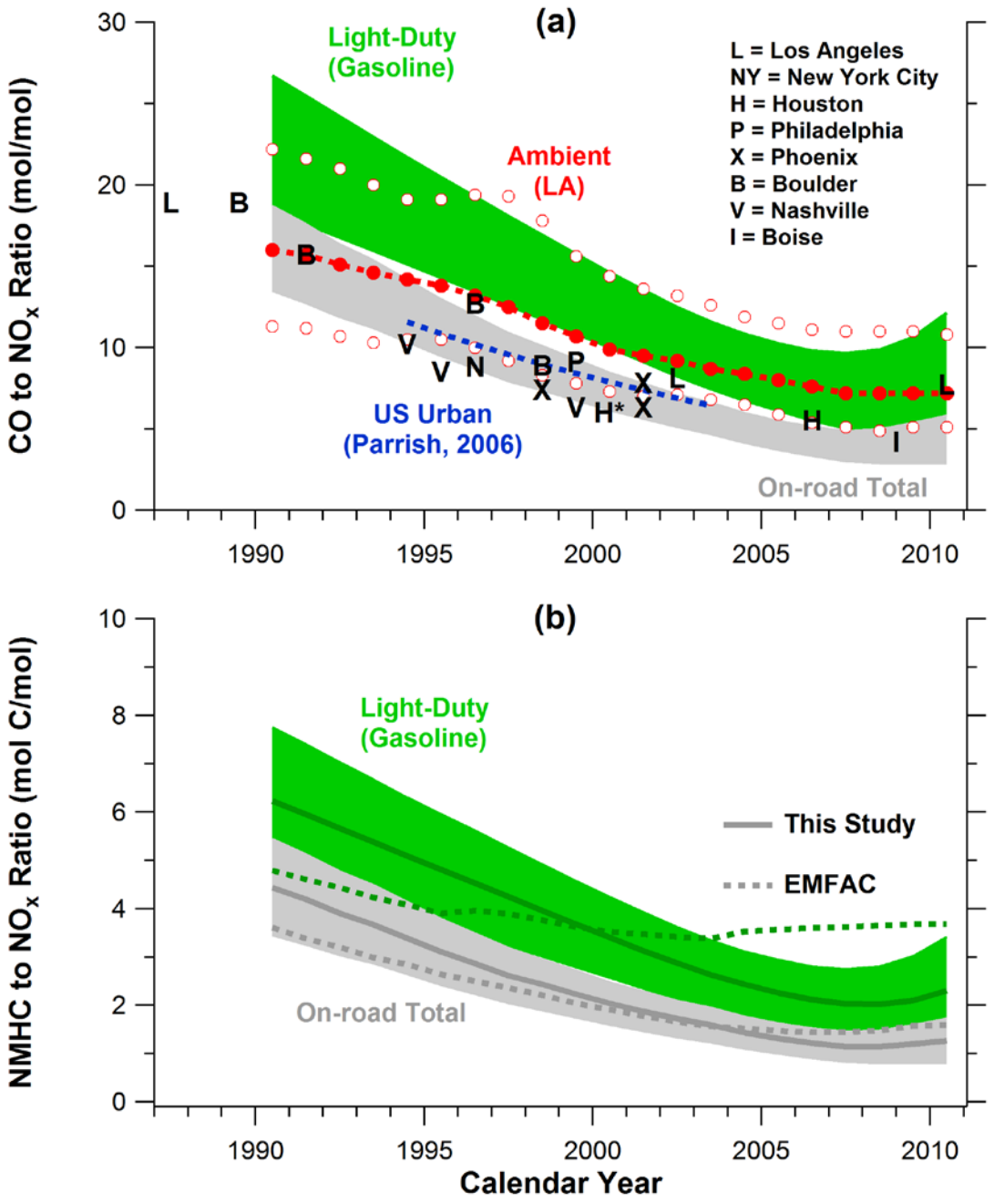


**Figure 4.8.** (a) Trends in $CO/NO_x$ emission ratios. Ratios for Los Angeles shown as bands reflect emissions from light-duty vehicles only (including running + start; upper band in green), and total emissions from all on-road vehicles (including diesel; lower band in gray). The mean, maximum, and minimum values from the ambient monitoring data are shown as a 3-year moving average for the morning commute period (0500 to 0800 PST). City abbreviations are shown for ambient literature values. (b) Trends in $NMHC/NO_x$ emission ratios. Results from this study are compared with EMFAC (including running + start). Uncertainty bands reflect 95% confidence intervals in both panels, see supporting information for details. $NO_x$ emissions taken from McDonald et al. [2012].

Mean ambient $CO/NO_x$ are also shown from the monitoring network in the South Coast air basin in Figure 4.8a. The monitoring ratio is ~25% higher than bottom-up emissions of CO to $NO_x$, which represent the California on-road vehicle fleet (gasoline + diesel), though the trend appears consistent. This suggests underestimation of CO and/or overestimation of $NO_x$ emissions using a fuel-based approach. The comparison could also be complicated by the influence of start emissions as ambient monitoring ratios are for the morning commute. Additionally, spatial heterogeneity of the vehicle mix (gasoline vs. diesel) could affect the comparison. In supporting information, we show that the ambient ratio of $CO/NO_x$ varies by a factor of 2 across 13 urban sites in southern California, due to spatial differences in the local mix of gasoline versus diesel vehicles. Areas with lower $CO/NO_x$ ratios are more diesel-dominated on average, since even a small amount of diesel traffic can add significantly to $NO_x$ emissions. Comparisons between basin-wide emission inventory ratios and ambient $CO/NO_x$ or $NMHC/NO_x$ ratios derived from sites within the air basin are increasingly subject to uncertainties due to spatial and temporal variations in diesel $NO_x$ sources. This emphasizes the need for motor vehicle emission inventories that provide high spatial and temporal resolution.

Figure 4.8a compares our bottom-up emission results with ambient $CO/NO_x$ ratios reported in the literature based on measurements made by either ground-based ambient monitors or by aircraft in Los Angeles [*Harley et al.*, 1997; *Pollack et al.*, 2012; *Brioude et al.*, 2013], New York City [*Kleinman et al.*, 2000], Houston [*Ryerson et al.*, 2003; *Brioude et al.*, 2011], Atlanta [*Parrish*, 2006], Philadelphia [*Kleinman et al.*, 2004], Phoenix [*Nunnermacker et al.*, 2004], Boulder [*Parrish et al.*, 2002], Nashville [*Parrish et al.*, 2002], and Boise [*Wallace et al.*, 2012]. Most of the literature values for ambient $CO/NO_x$ are for weekdays during the morning commute period. Also shown in Figure 4.8a is an ambient $CO/NO_x$ trend derived by Parrish [*Parrish*, 2006], representing a US urban average from 300 monitoring sites. A key finding is that both in absolute terms and in trend over time, measurements in other US cities appear to show consistent $CO/NO_x$ ambient ratios and trends that are consistent with results for Los Angeles. This suggests general similarity in motor vehicle emission trends across US urban areas.

The EMFAC model (running + start) provides a different explanation for trends in $CO/NO_x$ and $NMHC/NO_x$ for Los Angeles (Figure 4.8b). The trend in overall emissions (gasoline + diesel vehicles) agrees with fuel-based emission estimates of the present study, but there is a difference for light-duty vehicles. EMFAC indicates that the $CO/NO_x$ and $NMHC/NO_x$ emission ratios for light-duty vehicles have remained constant over the period 1990-2010, while this study suggests that the corresponding emission ratios decreased through the 1990s especially, and have leveled off since then. Because there was good agreement between this study and EMFAC in bottom-up CO emissions and top-down NMHC/CO ratios, the discrepancy is mainly due to $NO_x$ emissions [*McDonald et al.*, 2012]. The ambient data also suggests a decreasing trend in $CO/NO_x$ emission ratios from passenger vehicles, as represented by the maximum value of ambient $CO/NO_x$ from the monitoring network shown in Figure 4a. The maximum value represents a location with a predominantly gasoline vehicle mix. As an offsetting effect in the estimation of total emissions from on-road vehicles, the EMFAC model predicts larger increases in diesel $NO_x$ emissions as compared to a fuel-based estimate [*McDonald et al.*, 2012], and hence why $NMHC/NO_x$ from total on-road is in better agreement with this study.

### *4.3.4 Policy Implications*

In the greater Los Angeles area, peak ozone concentrations decreased by a factor of 2 between 1980 and 2000, but ozone reductions appear to have slowed greatly since 2000 [*Parrish et al.*, 2011]. Slow decreases in peak ozone have also been observed in Houston and New York City since 2000. The hydrocarbon to $NO_x$ emissions ratio is one of several important factors that determine $NO_x$ and hydrocarbon-sensitivity regimes that govern urban and regional ozone formation [*Sillman*, 1999]. Given that motor vehicles are a major source of ozone precursors in urban environments, changes in the effects of emission control strategies during the 1990s ($\Delta$% NMHC > $\Delta$% $NO_x$) versus since 2000 ($\Delta$% NMHC ≈ $\Delta$% $NO_x$) are likely to have affected atmospheric chemistry and ozone formation regimes, although other sources (e.g. industry, solvents, biogenics) of $O_3$ precursors may also be important. In the period 2010-2020, another shift is predicted in decadal emission changes: $\Delta$% NMHC < $\Delta$% $NO_x$, due mainly to installation of SCR systems on heavy-duty trucks.

In this study, running CO and evaporative and tailpipe NMHC emissions from gasoline-powered vehicles are shown to have decreased by almost an order of magnitude over the last twenty years using a fuel-based approach. However, decreases in emissions of these pollutants appear to be slowing down and may have leveled off. As shown, the success in control of emission from gasoline vehicles has led to greater skew in emission factor distributions, such that the highest-emitting 10% of vehicles are now responsible for the overwhelming majority of running CO (skewness = -3.9), NMHC (skewness = -4.9), and $NO_x$ (skewness = -2.9) (Figure 4.3). If progress in reducing emissions is to continue, vigorous efforts will be needed to identify and repair or replace high-emitting vehicles. Fuel economy improvements are an alternative approach being pursued over the coming decade that could help to reduce overall emissions of CO and NMHC, even if fleet-averaged emission factors (in g/kg fuel) do not change. High-emitting engines can also be expected to increasingly dominate emissions from the heavy-duty truck fleet in the future, especially as the use of diesel particle filters and selective catalytic reduction (SCR) systems becomes more widespread [*Sandhu and Frey*, 2012] (Figure 4.3).

# Chapter 5: Long-Term Trends in Motor Vehicle Emissions and Ambient Concentrations of Particulate Black and Organic Carbon

## 5.1 Introduction

Two major constituents of airborne fine particulate matter are black carbon (BC) and organic carbon (OC). Bond et al. [2013] estimate that black carbon is the second largest contributor to anthropogenic climate forcing behind only carbon dioxide. In North America, the two largest sources of black carbon are on-road and off-road diesel engines, which together account for about half of total BC emissions [*Bond et al.*, 2013]. Because black carbon is abundant in diesel particulate matter emissions [*Watson et al.*, 1994], black carbon is sometimes used as a tracer for diesel sources [*Lloyd and Cackette*, 2001]. Black carbon present in exhaust emissions provides solid particle surface area upon which other compounds, including volatile, semi-volatile, and low-volatility organics that are present in diesel exhaust [*Ristovski et al.*, 2012], may condense or adsorb. Diesel exhaust has been classified as a known human carcinogen by the International Agency for Research on Cancer. Short-term exposure to diesel exhaust has been associated with impaired vascular function [*Mills et al.*, 2007; *Smith et al.*, 2009; *Barath et al.*, 2010].

Organic aerosols (OA) have been found to comprise a major fraction of submicron airborne particle mass at urban and rural/remote measurement sites around the world [*Q Zhang et al.*, 2007; *Jimenez et al.*, 2009]. Organic aerosols are light scattering and have a negative forcing on global climate [*IPCC*, 2013]. Unlike black carbon, all of which is emitted directly from sources into the atmosphere, organic aerosols arise due to both primary emission and secondary in situ atmospheric formation pathways. Primary organic aerosol (POA) refers to organics that are directly emitted to the atmosphere in the particle phase. Secondary organic aerosol (SOA) refers to organic aerosol that is generated in situ from volatile or semi-volatile organic gas precursors. Many of these organics can be oxidized in the atmosphere to form condensable low-volatility products [*Goldstein and Galbally*, 2007; *Jimenez et al.*, 2009]. A complicating factor is that partitioning of POA emissions between gas and particle phases varies depending on OA mass loadings and the extent to which exhaust emissions have been diluted in ambient air [*Robinson et al.*, 2007].

There have been several debates surrounding organic aerosols. An early debate was on the relative importance of POA versus SOA. During air pollution episodes, studies in the Los Angeles basin reported high formation of SOA relative to POA as early as 1987 [*Turpin and Huntzicker*, 1991, 1995; *Schauer et al.*, 2002]. Other studies found POA to dominate SOA during non-air pollution episodes [*Turpin and Huntzicker*, 1995; *Schauer et al.*, 1996]. Recent work in Los Angeles [*Docherty et al.*, 2008; *B J Williams et al.*, 2010; *Hayes et al.*, 2013] and from around the world [*Q Zhang et al.*, 2007; *Jimenez et al.*, 2009] have concluded that SOA is the dominant source of OA, contributing ~2/3 of the urban submicron mass globally. Downwind of major urban areas, the contribution of SOA relative to POA is even higher. It is generally believed that SOA is now more important to the total OA budget than POA.

Another debate relates to the relative importance of gasoline versus diesel vehicles in the emissions of POA. Schauer et al. [1996] found diesel exhaust accounted for a majority to dominant fraction of POA from gasoline and diesel engines in Los Angeles. Watson et al. [1998]

concluded the opposite in Denver, and found gasoline emissions dominated POA. A more recent analysis found that in parts of Los Angeles diesel emissions dominated total carbonaceous aerosol (TC = BC + OC), but were comparable to on-road gasoline contributions in other areas [*Fujita et al.*, 2007]. A current debate relates to the importance of on-road gasoline [*Bahreini et al.*, 2012] versus diesel [*Gentner et al.*, 2012] emissions in the formation of anthropogenic SOA. There is a lack of long-term data on the full range of organic compounds emitted in motor vehicle exhaust, especially from diesel engines, which form SOA in the atmosphere. Precursor emissions of volatile organic compounds (VOCs) are much higher from gasoline than from diesel vehicles [*McDonald et al.*, 2013]. However, the composition of VOCs emitted from each type of vehicle is also important. Gentner et al. [2012] estimate that the fraction of VOC emissions that is converted to SOA from diesel engines is 6.7 ± 2.9 times greater than from gasoline engines, due to a higher abundance of intermediate volatility products, which more easily form SOA than lighter and more volatile compounds found in gasoline exhaust. Questions remain as to whether SOA yields of compounds emitted in motor vehicle exhaust are underestimated from smog chamber studies as compared to real world observations of the atmosphere [*Ensberg et al.*, 2014].

The objectives of this study are to describe long-term trends in (1) on-road diesel engine emissions of black carbon, and (2) ambient particulate black and organic carbon concentrations in urban settings. The emissions and ambient trends are then compared to reconcile observed concentration changes with efforts to control motor vehicle emissions. Previous studies have assessed long-term trends in emission factors and emissions from gasoline and diesel vehicles for particulate matter, carbon monoxide, volatile organic compounds, and nitrogen oxides [*Yanowitz et al.*, 2000; *Gertler et al.*, 2002; *Parrish*, 2006; *Ban-Weiss et al.*, 2008b; *Bishop and Stedman*, 2008; *Kirchstetter et al.*, 2008; *Dallmann and Harley*, 2010; *McDonald et al.*, 2012; *McDonald et al.*, 2013; *Xing et al.*, 2013]. However, previous motor vehicle emission studies have not estimated long-term trends in the emissions of carbonaceous aerosols (black and organic carbon) that combine changes in both vehicle activity and emission factors. In this study, we also examine how the relative contribution of POA versus SOA precursor emissions from motor vehicles has evolved with time, which has not been well documented previously.

Other studies have estimated long-term trends in concentrations of carbonaceous aerosols [*Cass et al.*, 1984; *Christoforou et al.*, 2000; *Kirchstetter et al.*, 2008; *Bahadur et al.*, 2011b; *Ahmed et al.*, 2014]. However, a longer historical archive was needed from the mid-1970s to the present day, in order to test hypotheses on the importance of motor vehicle emissions to particulate black and organic carbon in urban aerosols. The present study synthesizes a historical data record of both field studies and routine monitoring that span many decades in the South Coast air basin, and which encompasses the greater Los Angeles area. The U.S. national ambient air quality standard for $PM_{2.5}$ was not established until 1997, and the available data record is still relatively short (~15 years). Other measurement networks existed prior to this date, but are not easily merged with measurements at urban sites that have been made since 1997. The IMPROVE network has measured $PM_{2.5}$, BC, and OC at many sites across the U.S. since 1990, but monitoring sites are typically in parklands located in rural areas. From 1980 to 2002, fine ($PM_{2.5}$) and coarse ($PM_{10} - PM_{2.5}$) particulate matter concentrations were measured in California using dichotomous samplers [*Blanchard et al.*, 2011]. However, only Teflon filter samples were collected, and these were not intended for analysis of BC or OC concentrations. Coefficient of

haze (COH) data has been used to estimate long-term trends and concentrations of black carbon for the San Francisco Bay Area [*Kirchstetter et al.*, 2008]. However, sadly a similar historical archive for the Los Angeles region spanning many decades does not exist.

## 5.2 Methods

### *5.2.1 Diesel Activity Data*

We use taxable sales volumes of diesel fuel as a measure of on-road diesel truck activity. These data are available at the state and national levels on an annual basis. At the state level, diesel fuel sales have been adjusted to account for long-haul interstate truckers, for whom fuel purchases versus amounts of driving in each state may differ. In the U.S., on-road consumption of diesel fuel occurs primarily in the engines of medium and heavy-duty trucks rather than in passenger vehicles. For the period from 1990 to 2010, we use estimates of on-road diesel fuel use for California and the South Coast air basin reported by McDonald et al. [2012]. Uncertainties in fuel use are ±10% at the state level, and ±13% for the Los Angeles basin. To extend diesel engine activity and emission trends further back in time, (Figure 5.1), ratios of fuel sales in earlier years relative to 1990 were estimated from federal fuel sales reports (Table MF-2) [*FHWA*, 2011b]. These ratios were then applied to the 1990 state- and air basin-level diesel fuel sales estimated by McDonald et al. [2012].

We also estimated activity by off-road diesel engines (Figure 5.1). These engines include locomotives, marine vessels, construction and farm equipment, and other mobile commercial and industrial engines. Diesel fuel intended for off-road use is exempt from excise taxes that help pay for highway construction and maintenance. To account for the additional diesel engine activity not reflected by taxable fuel sales data, we rely on annual surveys of wholesalers of distillate fuel conducted by the U.S. Energy Information Administration (EIA). These surveys resolve distillate fuel by end use sector [*EIA*, 2012]. Based on previous work by Kean et al. [2000] we exclude sector-specific fractions of reported distillate fuel sales, to account for use in residential and commercial furnaces, boilers, and for electric power generation. Figure 5.1 shows a three-year moving average of off-road diesel fuel use. This was done to reduce year-to-year fluctuations in off-road fuel sales survey data; this has no effect on our assessment of long-term trends.

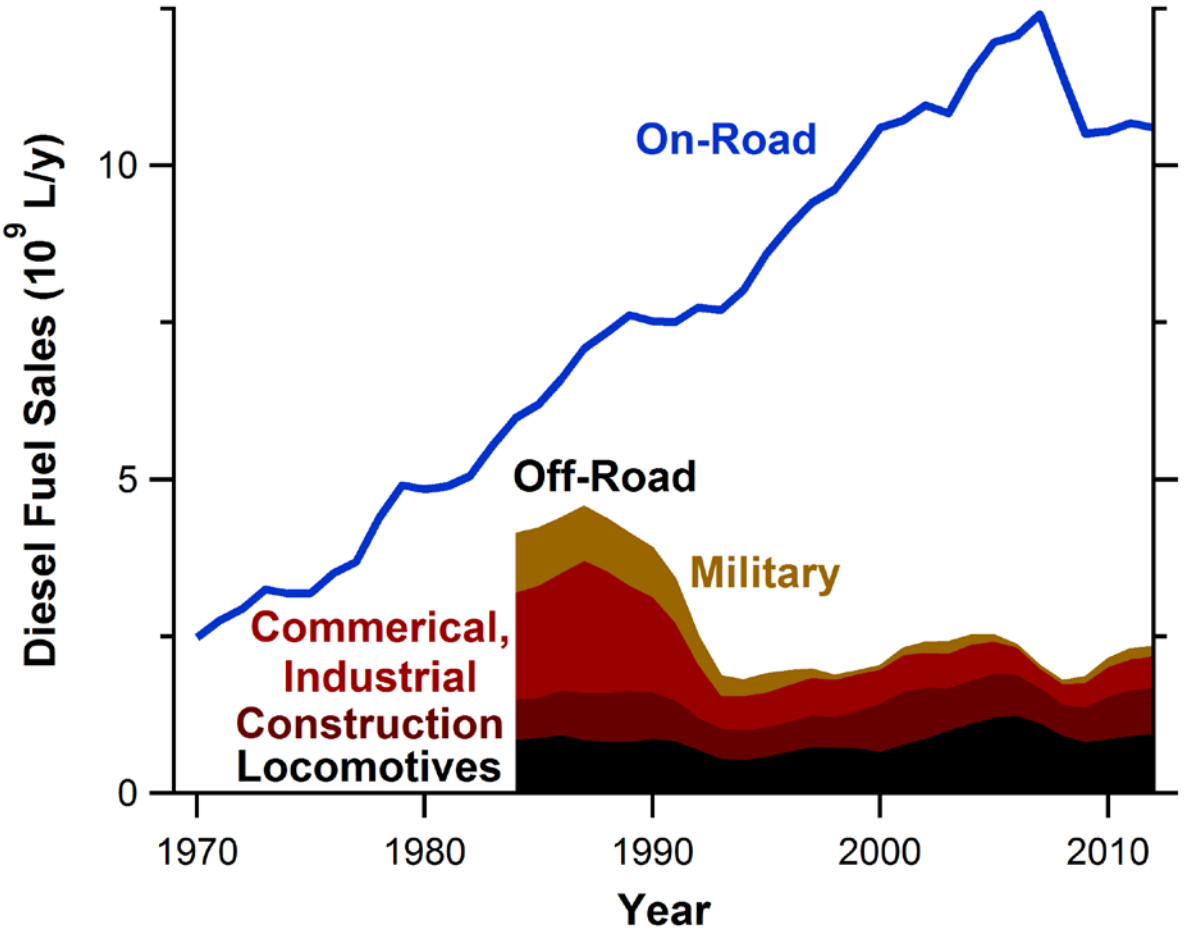


**Figure 5.1.** Trends in California on-road and off-road diesel fuel sales volumes, 1970 to 2011.

### *5.2.2 Heavy-Duty Diesel Truck PM and BC Emission Factors*

Emission factors for exhaust particulate matter (PM) and black carbon (BC), expressed in units of grams of pollutant emitted per kilogram of diesel fuel burned, are derived from an analysis of emission measurements made in various highway tunnels. Table 5.1 summarizes the data used for this analysis, which includes multi-year measurements at the Tuscarora and Allegheny Mountain Tunnels in Pennsylvania [*Pierson and Brachaczek*, 1983; *Gertler et al.*, 2002], and the Caldecott Tunnel in the San Francisco Bay area [*Hering et al.*, 1984; *Miguel et al.*, 1998; *Kirchstetter et al.*, 1999b; *Allen et al.*, 2001; *Geller et al.*, 2005; *Ban-Weiss et al.*, 2008b; *Dallmann et al.*, 2012]. Additional emission measurements have been made at the Fort McHenry Tunnel in Baltimore [*Gertler et al.*, 2002], the Washburn Tunnel in Houston [*Fraser et al.*, 2003], and the Squirrel Hill Tunnel in Pittsburgh [*Grieshop et al.*, 2006]. In about half of these studies, emission factors for both PM and BC are reported. In the remaining studies, emission factors are reported for only one of PM or BC but not both. In Figure 5.2, we show that BC and PM emission factors are well correlated for the studies where both species are reported. We use a mass ratio of BC/PM = 0.52 ± 0.09 to estimate missing diesel BC or PM emission factors in cases where direct measurements are not available for both. A regression analysis of emission factors for the studies listed in Table 5.1 was used to characterize changes in fleet-average emission factors for on-road diesel trucks, over a 35-year time period between 1975 and 2010 (Figure 5.3).

**Table 5.1.** On-road measurements of exhaust PM and BC emission factors for heavy-duty diesel trucks.

| Tunnel | Year | PM (g/kg fuel)[a] | BC (g/kg fuel)[a] | Reference |
|---|---|---|---|---|
| Allegheny (PA) | 1975 | 5.2 ± 1.5 | 2.7 ± 0.9[b] | [*Pierson and Brachaczek*, 1983][c,h] |
| | 1976 | 4.3 ± 0.8 | 2.2 ± 0.6[b] | |
| | 1977 | 3.7 ± 0.5 | 1.9 ± 0.4[b] | |
| | 1979 | 3.8 ± 0.3 | 2.0 ± 0.4[b] | |
| Tuscarora (PA) | 1976 | 3.0 ± 0.8 | 1.6 ± 0.5 | [*Pierson and Brachaczek*, 1983][c,i] |
| | 1977 | 3.1 ± 1.1 | 1.7 ± 0.6 | |
| | 1999 | 0.5 ± 0.1 | 0.3 ± 0.1 | [*Gertler et al.*, 2002][d,i] |
| Caldecott (CA) | 1996 | 2.8 ± 0.6[b] | 1.4 ± 0.2 | [*Miguel et al.*, 1998][e] |
| | 1997 | 2.7 ± 0.3 | 1.4 ± 0.6 | [*Kirchstetter et al.*, 1999b][d] |
| | 1997 | 1.1 ± 0.2 | 0.7 ± 0.3 | [*Allen et al.*, 2001][f,j] |
| | 2004 | 1.0 ± 0.2 | 0.7 ± 0.1 | [*Geller et al.*, 2005][d] |
| | 2006 | 1.4 ± 0.3 | 0.9 ± 0.1 | [*Ban-Weiss et al.*, 2008b][d] |
| | 2010 | 1.1 ± 0.3[b] | 0.6 ± 0.1 | [*Dallmann et al.*, 2012][d] |
| Ft. McHenry (MD) | 1993 | 1.6 ± 0.6 | 0.8 ± 0.4[b] | [*Gertler et al.*, 2002][g,k] |
| Washburn (TX) | 2000 | 1.6 ± 0.6 | 0.8 ± 0.4 | [*Fraser et al.*, 2003][d,j] |
| Squirrel Hill (PA) | 2002 | 1.1 ± 0.2 | 0.4 ± 0.2 | [*Grieshop et al.*, 2006][d] |

a. Emission factors expressed per unit mass of diesel fuel burned. Uncertainty reported as 2σ.
b. Estimated using ratio of BC to PM from Figure 5.2 (see text).
c. Measured as total suspended particulate matter (TSP).
d. Measured as $PM_{2.5}$.
e. Measured as $PM_{1.3}$.
f. Measured as $PM_{1.9}$.
g. Measured as $PM_{10}$.
h. Emission factors reported as g/km and converted to g/kg fuel assuming truck fuel economy of 4 km/L [*Pierson and Brachaczek*, 1983] and diesel fuel density of 0.84 kg/L [*Kirchstetter et al.*, 1999b].
i. Emission factors reported as g/km and converted to g/kg fuel assuming fuel economy of 3.0 km/L [*Pierson and Brachaczek*, 1983; *Gertler et al.*, 2002], and diesel fuel density of 0.84 kg/L [*Kirchstetter et al.*, 1999b].
j. Emission factor reported as g/kg C and converted to g/kg fuel using diesel carbon fraction of 0.87 kg C/kg fuel [*Kirchstetter et al.*, 1999b].
k. Emission factors reported as g/km and converted to g/kg fuel assuming fuel economy of 3.2 km/L [*Pierson et al.*, 1996] and diesel fuel density of 0.84 kg/L [*Kirchstetter et al.*, 1999b].

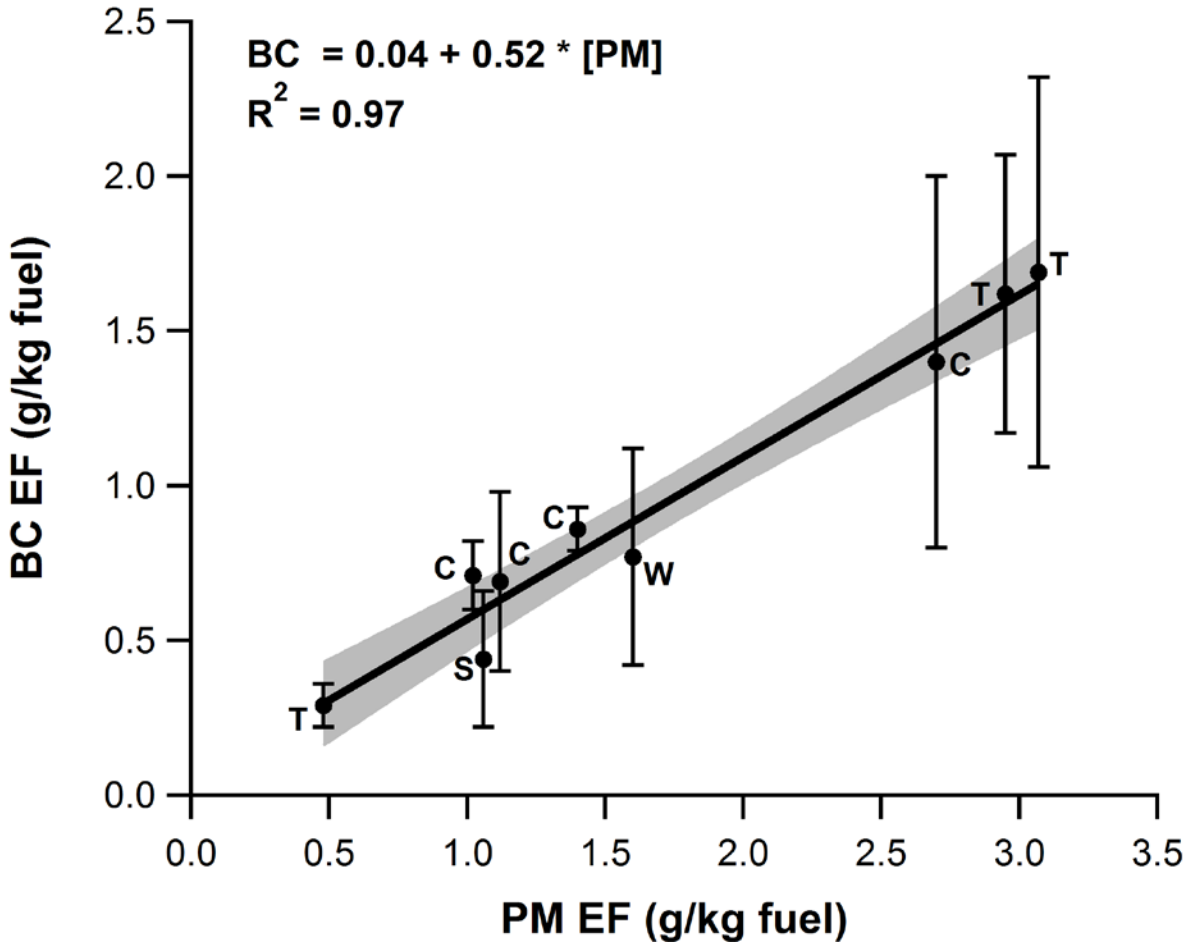


**Figure 5.2.** Correlation of heavy-duty diesel truck emission factors of black carbon (BC) and particulate matter (PM) from tunnel studies in Table 1. Tunnel abbreviations are as follow: T = Tuscarora, C = Caldecott, W = Washburn, and S = Squirrel Hill.

### *5.2.3 Ambient BC Data*

Table 5.2 summarizes studies that were used in this analysis to derive long-term trends in ambient concentrations of fine particulate matter (cutpoints vary; $D_{PC}$ = 2.1 or 2.5 μm depending on the study), black carbon, and organic carbon in the South Coast air basin. Data sources include a series of yearlong studies led by Glen Cass [*Gray et al.*, 1984, 1986; *Christoforou et al.*, 2000], special studies led by the South Coast Air Quality Management District [*B M Kim et al.*, 2000; *SCAQMD*, 2008], and $PM_{2.5}$ monitoring data from the Speciation Trends Network (STN). All but one of the above studies includes a year of measurements of PM, BC, and OC using filters. Sampling frequencies vary from once every sixth day to daily sampling. Filter samples are collected in the field over 24 hours, and then analyzed in the lab. Thermal optical analysis techniques were used to differentiate and quantify black and organic carbon contributions to total carbon mass on each filter. There can be significant differences in the amount of carbon that is attributed to BC relative to OC depending on the carbon analysis technique. For each of the studies listed in Table 5.2, a similar thermal optical reflectance (TOR) protocol was used [*Johnson et al.*, 1981; *Huntzicker et al.*, 1982; *Chow et al.*, 1993; *Chow et al.*, 2007]. We include only measurements made after 2007 from the Speciation Trends Network routine monitoring sites. This timeframe coincides with a switch in the analytical protocol for STN sites to match the protocol used in the IMPROVE network. The reason for excluding the older STN data was to increase consistency and comparability across data sources shown in Table 5.2. Prior to 2007, particulate carbon was analyzed using a total optical transmittance (TOT) NIOSH 5040 carbon method. When compared to the TOR method used in IMPROVE, black carbon measured by the NIOSH method was found to be roughly half that of the IMPROVE method [*Chow et al.*, 2001].

The black and organic carbon concentrations shown in Table 5.2 are basin-wide averages with the number of sites varying from 4 to 10 depending on the study. Measurements from the routine monitoring network (2008-11) are the average of data from two locations: central Los Angeles and another site further inland at Rubidoux. The average black carbon concentration shown for 1978 is derived from coefficient of haze (COH) measurements at 23 locations across the South Coast air basin. It has been shown that COH is well-correlated with BC [*Kirchstetter et al.*, 2008].

**Table 5.2.** Ambient measurements of particulate organic (OC) and black carbon (BC) in Los Angeles basin.

| Study Year | Data Source | OC ($\mu g/m^3$) | BC ($\mu g/m^3$) | Sampling Frequency | Flow Rate (L/min) | Back-up Filter |
|---|---|---|---|---|---|---|
| 1975 | NASN[a] | 9.7 ± 1.9 | 5.1 ± 1.2 | every 12th day | unknown | unknown |
| 1978 | COH[b] | n/a | 4.4 ± 1.0 | daily | n/a | n/a |
| 1982 | Cass Group[c] | 6.3 ± 1.1 | 3.9 ± 0.7 | every 6th day | 10 | QBQ[g] |
| 1986 | Cass Group[c] | 4.6 ± 1.8[f] | 2.7 ± 0.9 | every 6th day | 4.9 | none |
| 1993 | Cass Group[c] | 3.6 ± 1.5[f] | 1.8 ± 0.6 | every 6th day | 10 | none |
| 1995 | SCAQMD[d] | 5.2 ± 0.8 | 3.2 ± 0.6 | 1-6 days | 20 | QBT[g] |
| 1999 | SCAQMD[d] | 4.6 ± 0.9 | 2.2 ± 0.7 | 1-6 days | 20 | QBT[g] |
| 2005 | SCAQMD[d] | 3.7 ± 1.1[f] | 1.9 ± 0.4 | every 3rd day | 6.7 | none |
| 2008 | STN[e] | 3.6 | 1.4 | every 3rd day | 22.8 | none |
| 2009 | STN[e] | 3.0 | 1.2 | every 3rd day | 22.8 | none |
| 2010 | STN[e] | 2.6 | 1.1 | every 3rd day | 22.8 | none |
| 2011 | STN[e] | 2.7 | 1.1 | every 3rd day | 22.8 | none |

a. National Air Surveillance Network.
b. Coefficient of haze.
c. Gray et al. [1986] and Christoforou et al. [2000]. Measured as $PM_{2.1}$.
d. Special field studies led by South Coast Air Quality Management District for PTEP (1995) [*B M Kim et al.*, 2000], TEP (1999), and MATES III (2005) [*SCAQMD*, 2008]. Measured as $PM_{2.5}$.
e. Routine monitoring from urban Speciation Trends Network (STN) sites; only years when quartz filter samples were analyzed using IMPROVE protocol are listed here, for consistency with other studies.
f. Derived from BC using ratio of ambient OC to BC shown in Figure 5.2 (see text).
g. QBQ = quartz-behind-quartz; QBT = quartz-behind-Teflon.

## 5.3 Results and Discussion

### *5.3.1 BC Trends*

Over a 35-year period between 1975 and 2010, heavy-duty diesel truck emission factors of PM (Figure 5.3a) and BC (Figure 5.3b) both decreased by factors of ~4. Our trend agrees well with three fleet-average estimates of emission factors reported for the mid-1990s based on chassis dynamometer emission testing (Figure 5.3a). Also shown is an emission factor trendline from Yanowitz et al. [2000] based on engine model year (in contrast, other data plotted in Figure 5.3 are plotted relative to specific calendar years and include a mix of engines of various ages). In the 1970s, early model year trucks have emission factors similar to our fleet-averaged emission factor (Figure 5.3a). The first organized emission inspections for heavy-duty trucks started in 1970 and were targeted at reducing visible smoke under steady state operation [*Lloyd and Cackette*, 2001]. The first diesel engine exhaust PM emission standards were implemented much later -- in 1988 [*Yanowitz et al.*, 2000; *Ban-Weiss et al.*, 2008b]. A possible explanation for the similarity between emission factors of the average on-road truck fleet and emission factors for new (at the time) 1975 engines is that early emission standards were not stringent, and were set to match fleet-average values that prevailed at the time. Decreases in PM emission factors for new trucks based on engine model year are expected to be more rapid than what is observed on-road in terms of fleet-average values. This is because of long in-service lifetimes for heavy-duty diesel engines, and a resulting significant time lag (two decades or more) in replacing older engines with new equipment (Figure 5.3a). Some flattening of the fleet-average PM emission factor trend might be expected, since for 12 years between 1994 and 2006, diesel exhaust PM emission standards remained unchanged. Initial efforts to lower diesel PM emissions involved changes to engine design to reduce lubricating oil emissions and to improve air-fuel mixing (thereby lowering BC emissions), rather than installing after-treatment control technologies [*Lloyd and Cackette*, 2001]. Starting with the 2007 engine model year, heavy-duty diesel exhaust PM emission standards were reduced by an order of magnitude. Diesel particle filters are now included as standard equipment on new heavy-duty diesel engines, and large decreases in BC emission factors have been observed in on-road settings as a result [*Dallmann et al.*, 2011]. The effect of large numbers of 2007 and newer engines entering service is not accounted for in this analysis, so the emission factor trends shown in Figure 5.3 should not be extrapolated forward in time beyond ~2010. A more rapid rate of decrease in diesel exhaust PM and BC emission factors should be expected going forward.

Because of site-to-site variability in engine loads and truck ages, we compare our emission factor trend with a trend derived at a single location, the Caldecott tunnel, where emissions have been sampled repeatedly over many years [*Hering et al.*, 1984; *Venkataraman et al.*, 1994; *Miguel et al.*, 1998; *Kirchstetter et al.*, 1999b; *Allen et al.*, 2001; *Geller et al.*, 2005; *Ban-Weiss et al.*, 2008b; *Dallmann et al.*, 2012]. The evolution of measured pollutant concentrations within the Caldecott Tunnel (Table 5.3) are plotted on the secondary axis of Figure 5.3, and this trend is a proxy for changes in diesel truck emission factors shown on the same plot. Tunnel concentrations are shown because a key early study by Hering et al. [1984] measured tunnel PM mass and composition, but not carbon dioxide which is needed in order to calculate emission factors. Venkataraman et al. [1994] measured tunnel BC concentrations, but did not estimate emission factors.

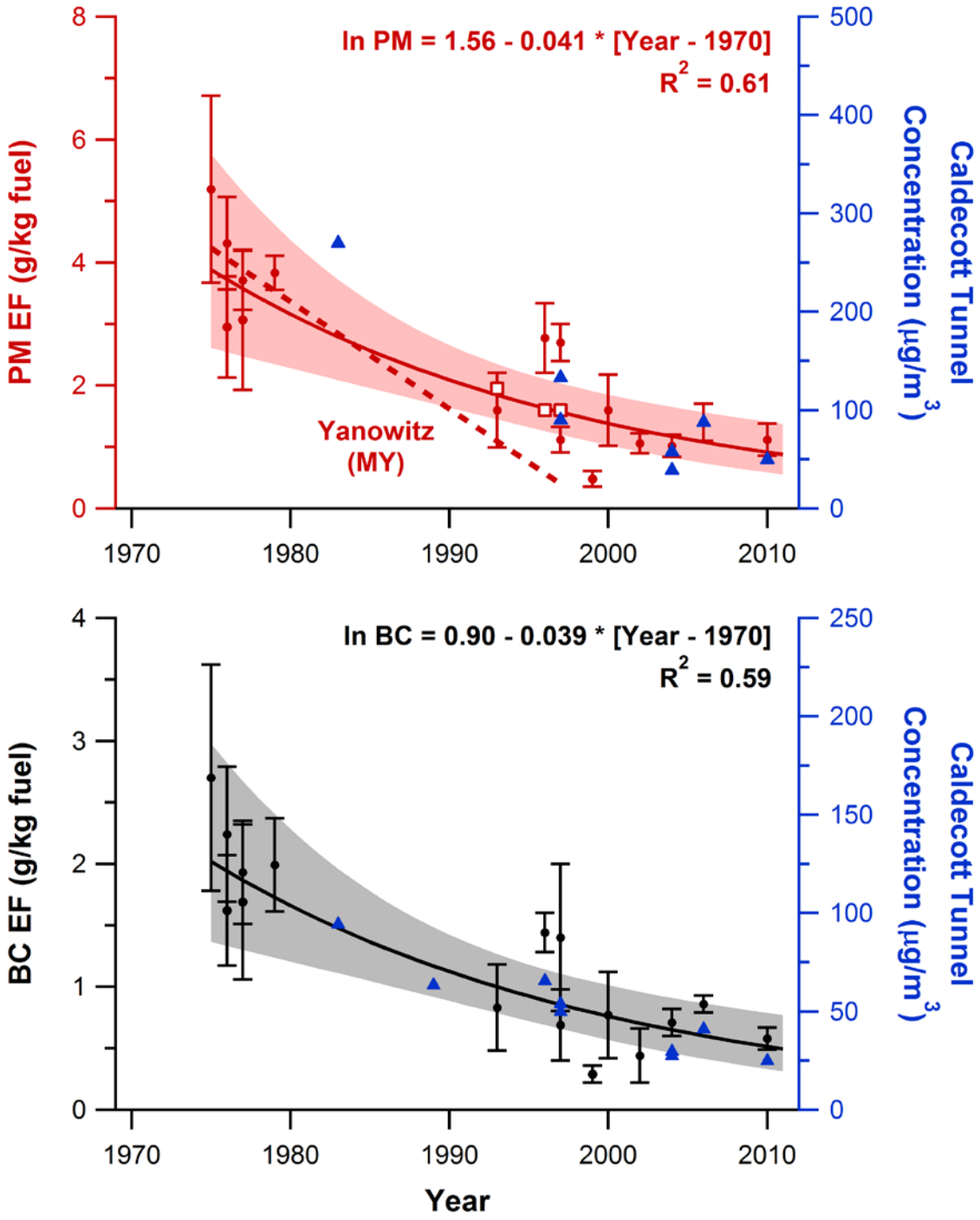


**Figure 5.3.** Heavy-duty diesel truck emission factors for (a) PM and (b) BC derived from a regression analysis of tunnel studies shown in Table 5.1. Results for PM are compared with results of chassis dynamometer emission testing reviewed by Yanowitz et al. [2000], who report fleet-average emission factors for selected calendar years (open squares) and by truck engine model year (dashed line). Error bars show 2σ uncertainty for individual studies. Error bands show the 95% confidence intervals for the regression. Emission factor trends are also compared with measured PM and BC concentrations inside the Caldecott Tunnel (blue triangles; see text).

**Table 5.3.** Caldecott Tunnel concentrations of fine particulate matter (PM) and black carbon (BC) on weekdays.

| Year | PM ($\mu g/m^3$) | BC ($\mu g/m^3$) | Hour | HD Truck Flow (veh/h) | Reference |
|---|---|---|---|---|---|
| 1983 | 270 | 95 | | | [*Hering et al.*, 1984][a] |
| 1989 | | 64 | | | [*Venkataraman et al.*, 1994][b] |
| 1996 | | 66 | 13:00-15:00 | 100 | [*Miguel et al.*, 1998][a] |
| 1997 | 133 | 58 | 12:30-15:30 | 98 | [*Kirchstetter et al.*, 1999b][c] |
| 1997 | 90 | 50 | 12:00-15:00 | 130 | [*Allen et al.*, 2001][d] |
| 2004 | 39 | 28 | 12:00-20:00 | 110 | [*Geller et al.*, 2005][c] |
| 2006 | 88 | 41 | 12:00-14:00 | 104 | [*Ban-Weiss et al.*, 2008b][c] |
| 2010 | 50 | 25 | 12:00-14:00<br>16:00-18:00 | | [*Dallmann et al.*, 2012][c] |

a. Measured as $PM_{1.3}$.
b. Measured as $PM_{4.0}$.
c. Measured as $PM_{2.5}$.
d. Measured as $PM_{1.9}$.

Factoring in changes in fuel sales as well as emission factors over time, the resulting trend in BC emission inventory for on-road diesel engines is shown in Figure 5.4. Given the ratio of BC to PM in diesel exhaust has remained relatively stable over time (Figure 5.2), emission trends for BC and PM from diesel engines are similar. A key result is that between 1975 and 2010, after accounting for growth in diesel fuel sales, on-road diesel BC emissions decreased by only ~20% (Figure 5.4), a value which lies within the uncertainty range of our estimates. BC emissions increased by ~30% between 1975 and 1990, before emission standards came into force for new engines, and then decreased by ~40% over the ensuing two decades. Despite large decreases in exhaust PM and BC emission factors from diesel engines since 1990, the offsetting effect of growth in diesel fuel sales (Figure 1) has been substantial. As a further point of comparison, diesel engines are also a significant on-road source of nitrogen oxide ($NO_x$) emissions. Between 1990 and 2010, McDonald et al. [2012] found that diesel truck emissions of $NO_x$ decreased by only ~15% in the Los Angeles basin, compared to a ~40% decrease for PM and BC in this study. This is because efforts to reduce diesel $NO_x$ emission factors prior to 2010 were less successful than for PM.

Ambient measurements of fine particle BC concentrations in the Los Angeles basin show a clear downward trend that spans seven intensive monitoring study years and four recent years of routine monitoring data (Figure 5.4). The basin-averaged BC concentration decreased from 4.6 ± 0.6 μg $m^{-3}$ in 1975 to 1.0 ± 0.5 μg $m^{-3}$ as of 2011. The corresponding rate of decrease is 0.1 ± 0.02 μg $m^{-3}$ or 4.2% per year. This rate of decrease is similar to decreases seen over rural California [*Bahadur et al.*, 2011b]. Bahadur et al. [2011b] found annual BC concentrations decreased from 0.46 μg $m^{-3}$ in 1989 to 0.25 μg $m^{-3}$ in 2008, a decrease of ~50%. In this study, decreases of ~60% are found over the urban Los Angeles basin from 1989 to 2008. This is within the -40% to -60% range Bahadur et al. [2011a] found across all IMPROVE monitoring sites.

Figure 5.4 compares our estimates of on-road diesel emissions with ambient BC concentration trends between 1975 and 2011. We align the two independent vertical axes in this figure using routine monitoring network (STN) data collected between 2008 and 2011. The on-road diesel emissions estimates show a clear decrease in emissions associated mainly with reductions in diesel truck activity during the severe recession that started around 2008. The ambient data show a similar trend in ambient BC concentrations over the same time period. When anchoring the comparison of the two trends in the most recent years, it is clear that the long-term downward trend in ambient BC is significantly steeper than for on-road diesel emissions (Figure 5.4). From 1975 to 1990, the two trends diverge to an extent that goes well beyond the uncertainty of the fuel-based emission inventory for BC; the ambient trend is decreasing while the BC emissions trend is increasing. We conclude that decreases in ambient BC concentrations in the Los Angeles basin during the 1970-1990 timeframe did not result from emission control policies that applied to on-road diesel engines, but rather were driven by control efforts that focused on other air pollution sources. Winter season home heating using solid fuels (e.g., wood burning; coal was also used for this purpose in many eastern U.S. and European cities in the past) is another contributing source of BC, though use of coal for home heating has not been common in California. Increased use of natural gas in place of other fuels in the residential, commercial, and industrial sectors is likely to have contributed to reductions in ambient BC concentrations shown in Figure 5.4, especially in the pre-1990 timeframe.

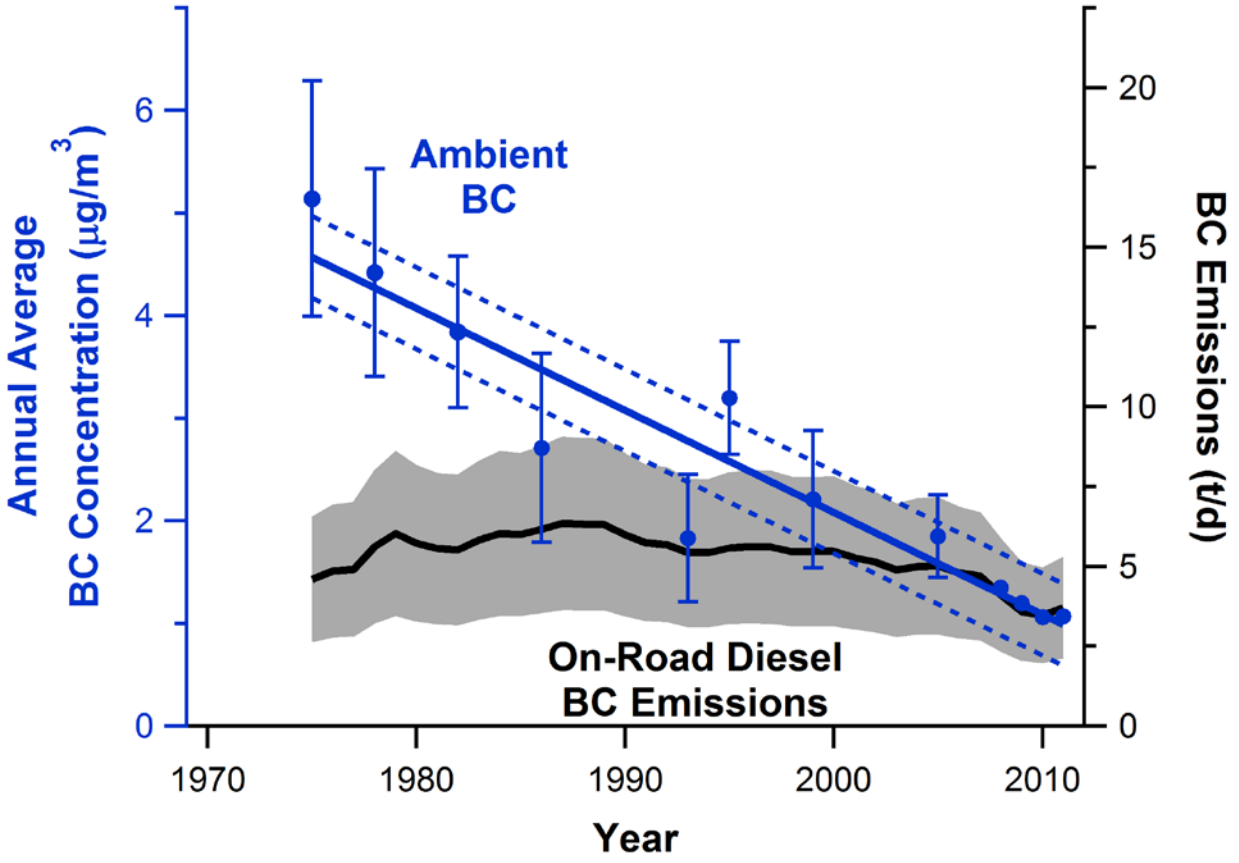


**Figure 5.4.** Trends in annual average ambient black carbon concentrations (left-hand axis) for the Los Angeles basin compared with trends in a fuel-based inventory of diesel BC emissions constructed using results from Figures 5.1 and 5.3. The ambient trend is derived from a linear regression of studies listed in Table 5.2. Error bars on the ambient data show the 95% confidence interval of the basin-average concentration, and represent spatial variability. Error bands for the fuel-based inventory represent a 95% confidence interval.

Figure 5.1 shows how off-road diesel fuel use for non-farm equipment has changed in California. From the mid-1990s to the present, off-road engine activity has remained fairly stable. However, in the late 1980s and early 1990s there was a steep decrease in off-road diesel fuel sales by a factor of about two. The decreases came largely from the commercial, industrial, and military sectors. Emission standards for off-road diesel engines were implemented later than for heavy-duty trucks, beginning in 1996 [*Lloyd and Cackette*, 2001], so changes in activity rather than emission factors are likely to the dominant effect for off-road diesel engines circa 1990. Relative to on-road diesel trucks, the emissions of BC from off-road engines was important in the past. In the mid-1980s, the amount of diesel fuel consumed by off-road engines was similar to the amount of diesel fuel purchased for use in on-road trucks. Additionally, Dallmann et al. [2010] summarize data showing emission factors for $PM_{2.5}$ were 2-3 times higher for off-road diesel engines compared to on-road trucks. This explanation of the importance of off-road diesel engines could be consistent with a study performed on filter samples collected in 1982 attributing 88-96% of fine particle BC in the Los Angeles basin to diesel exhaust [*Schauer et al.*, 1996].

### *5.3.2 Ambient OC Concentration Trends*

An uncertainty in the analysis of ambient organic aerosol trends is the possibility of systematic long-term changes in the OA/OC mass ratio; the numerator (OA) includes mass of oxygen, hydrogen and other elements associated with organic molecules whereas the denominator (OC) includes only carbon. Note, however, that studies reporting high SOA contributions to ambient organic aerosol in the Los Angeles basin date back more than 25 years ago [*Turpin and Huntzicker*, 1991]. It appears to us unlikely that ambient organic aerosol in the Los Angeles basin has been transformed from heavily POA- to heavily SOA-dominated over the timeframe of interest for this study. Our analysis is based on OC measured using thermal-optical methods, and so we acknowledge unquantified and possibly variable contributions to OA mass due to other elements associated with OC.

Another challenge in quantifying long-term trends arises due to effects on OC readings due to differences in thermal-optical analysis protocols. Here we included only studies that used similar analytical methods – namely thermal/optical reflectance (TOR) based on methods of Huntzicker et al. [1982]. Yet another challenge in quantifying ambient concentrations of particulate OC is a potentially large sampling artifact due to adsorption of gas-phase organics onto quartz filters, which can lead to systematic biases of up to +50% [*Turpin et al.*, 2000; *B M Kim et al.*, 2001; *Chow et al.*, 2010]. A negative sampling artifact from the volatilization of particle-phase organics collected on the filter sample is also possible, and can occur when there is a large pressure drop over the filter [*Turpin et al.*, 2000]. Turpin et al. [1994] concluded that the dominant sampling artifact in the Los Angeles basin was due to adsorption of gas-phase organics. Similarly, Watson et al. [2009] found the positive artifact to be larger than the negative artifact when analyzing rural filter samples across the U.S. Adsorbed carbon is often estimated by difference between a front and back-up filter, either using a quartz-behind-quartz (QBQ) or a quartz-behind-Teflon (QBT) filter sampling configurations. However, measurements of OC are not always corrected to account for known sampling artifacts (see Table 5.2). For measurements that are not corrected, the filter face velocity (air flow rate divided by cross-sectional area of the filter) is known to influence the amount of OC collected. For higher face velocity, the extent of the OC adsorption artifact tends to be smaller [*Turpin et al.*, 1994].

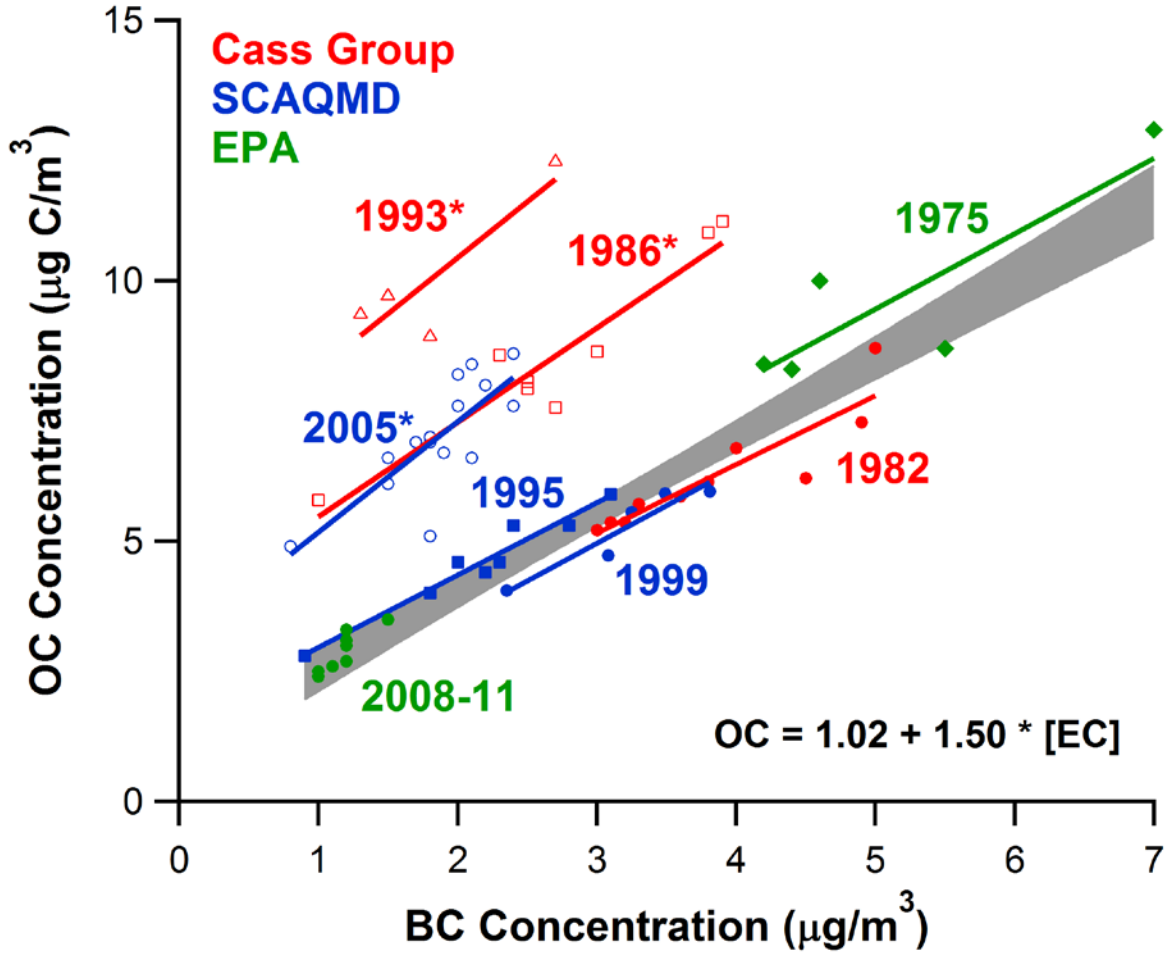


**Figure 5.5.** Correlation of ambient OC and BC concentrations for individual study years (see Table 5.2). Each data point represents measured annual average concentrations of OC plotted against corresponding concentrations of BC for individual measurement sites: 1975 (closed diamonds), 1982 (closed circles), 1986 (open squares), 1993 (open triangles), 1995 (closed squares), 1999 (closed circles), 2005 (open circles), and 2008-11 (closed circles). Study years shown with asterisks are expected to have large positive OC sampling artifacts (see text). The gray bar indicates average OC to BC ratio across all sites and study years with a 95% confidence interval, and excluding starred study years 1986, 1993, and 2005 for which OC/BC ratios were higher.

Given difficulties in measuring organic carbon directly, with results that can vary greatly depending on sampling and analytical protocols, we instead estimate OC concentrations by ratio to BC. In Figure 5.5, we show correlations of OC and BC at locations across the South Coast air basin. The slope of OC to BC is remarkably consistent over a multi-decadal time period. For three study years where organic carbon is not back-up filter corrected, and where sampling was done using low volumetric air flow rates (see Table 5.2), the OC to BC ratio is elevated compared to other studies shown in Figure 5.5. This is expected given the likelihood of large positive sampling artifacts in these studies. To infer OC concentrations for 1986, 1993, and 2005 quantified on a basis that is more consistent with other studies, we derive an ambient OC/BC ratio using data from the other studies shown in Figure 5.5. The equation is then applied to measured ambient BC concentrations to estimate OC. The stability of the OC to BC ratio over time (see Figure 5.5) implies similar long-term trends in ambient black and organic carbon concentrations (Figure 5.6). We estimate that ambient OC in the Los Angeles basin decreased from $7.9 \pm 1.2$ μg $m^{-3}$ in 1975 to $2.5 \pm 1.0$ μg $m^{-3}$ in 2011. The corresponding rate of decrease is $0.15 \pm 0.06$ μg $m^{-3}$ or 3.1% per year, slightly less than for BC.

McDonald et al. [2013] reported 80-90% decrease in emissions of carbon monoxide (CO) and volatile organic compound (VOC) emissions from on-road gasoline vehicles for the period between 1990 to 2010. The reductions in VOC emissions from gasoline engines are much larger than those shown in Figure 5.4 for BC emissions from on-road diesel engines. This is because growth in gasoline sales has been slower than for diesel fuel, and more importantly because of near-universal use of catalytic converters to treat gasoline engine exhaust. Catalytic converters on gasoline engines are a mature and well-developed emission control technology that has been through multiple rounds of system efficiency and durability improvement.

Here we consider the following hypothesis: if emissions of VOC from gasoline vehicles are the dominant contributor to particulate organic carbon via pathways that involve secondary organic aerosol formation, then decreases in the ambient concentrations of particulate organic carbon should be observed over time, commensurate with reductions in emissions of VOC from gasoline engines that are known to have occurred over the last several decades [*Bishop and Stedman*, 2008; *Warneke et al.*, 2012; *McDonald et al.*, 2013]. To test this hypothesis we compare our ambient trend in particulate organic carbon with concentrations of CO. It has been shown that the ratio of gasoline-related VOC to CO has remained constant over a multi-decadal time period [*Warneke et al.*, 2012; *McDonald et al.*, 2013]. Therefore, we use CO trends as a proxy for trends in gasoline engine VOC emissions, as CO is more routinely and consistently measured compared to VOC. Concentrations of CO shown in Figure 5.6a are from a nine-site average of monitors in Los Angeles and Orange counties, which were repeatedly measured beginning in 1981, and are the same sites used in an analysis by McDonald et al. [2013]. Measurements are restricted to the morning commute period (0500 to 0800 PST) on weekdays, because ambient concentrations of CO are highest then, and are dominated by emissions from motor vehicles. Background levels of ~120 ppb are subtracted [*Pollack et al.*, 2012]. Between 1990 and 2010, the decrease in ambient CO shown in Figure 5.6a is ~80%, similar to emission decreases of CO and VOC from on-road gasoline vehicles in McDonald et al. [2013].

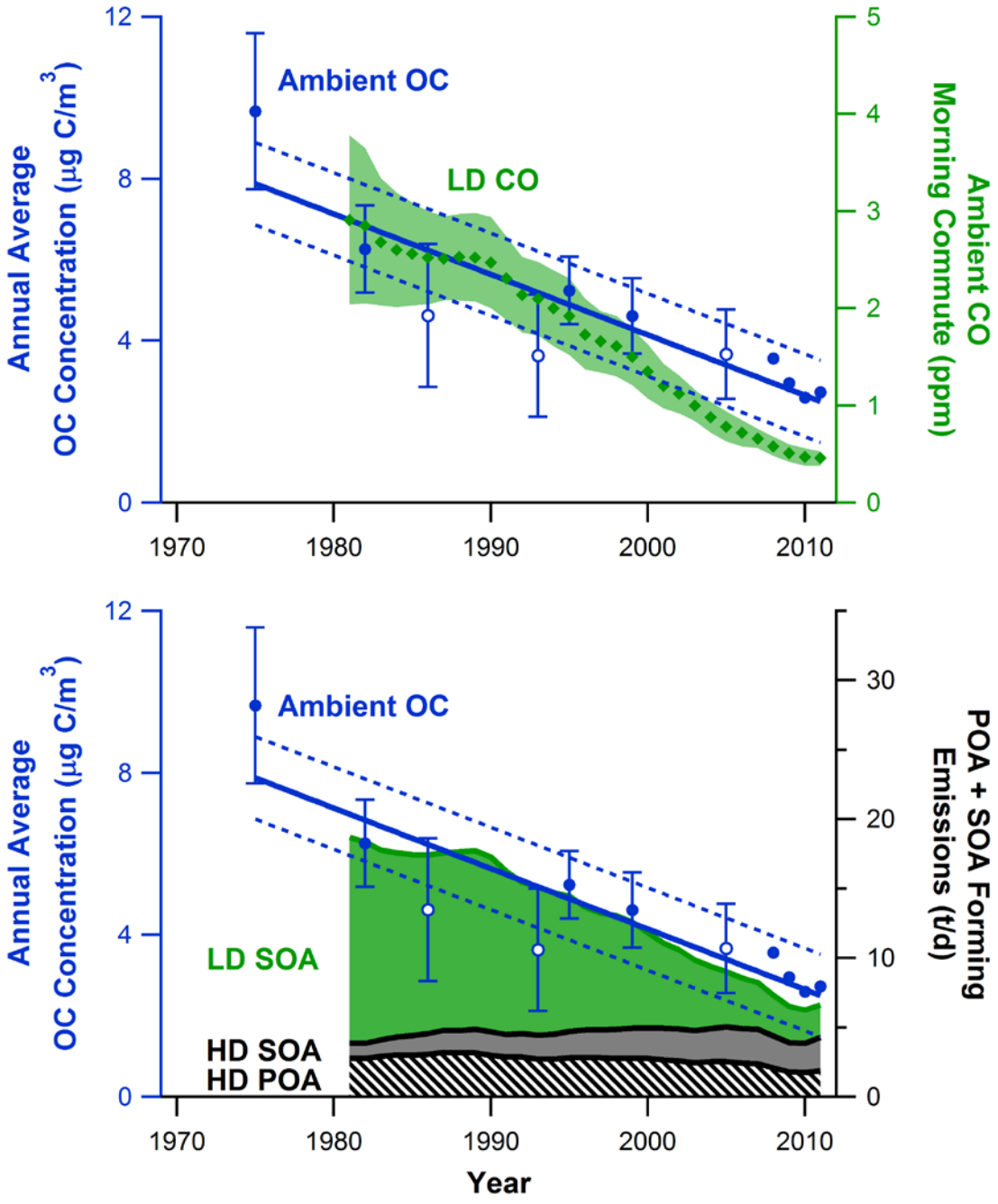


**Figure 5.6.** (a) Ambient particulate OC and gas-phase CO concentration trends, and (b) ambient OC and primary (hatched) and secondary emissions (filled) of OA from light- (LD) and heavy-duty (HD) vehicles in the Los Angeles area. Adjusted OC values are shown using open circles (see text). Error bars show the 95% confidence interval of the basin-average OC concentrations, and represent spatial variability. CO concentrations were measured at nine locations during the morning commute period (0500 to 0800 PST) on weekdays, and are background subtracted. CO trends are shown as a proxy for closely related changes in gasoline-related VOC emissions (see text). Error bands on CO trend reflect the 95% confidence interval for annual average concentrations. See text for methods used to estimate motor vehicle emissions of POA and SOA.

Between 1981 and 1995, the trend in CO matches that for OC (Figure 5.6a). Between 1995 and 2007, CO shows a steeper downward trend, decreasing by 75 ± 7% compared to OC which decreased by only 45 ± 22%. The difference in slopes suggests that other sources of particulate organic carbon must also be contributing to the differing trends in the Los Angeles basin, either via primary or secondary emissions. On-road gasoline vehicles are likely contributing to the overall downward trend in OC (Figure 5.6a), but as VOC emissions from these vehicles decrease, other sources of OA are expected to become relatively more important. If these other OA sources have not been controlled as quickly, then they could slow decreases in ambient OC in relation to changes expected from controlling gasoline VOC emissions. The hypothesis that VOC emissions from gasoline vehicles are the dominant contributor to particulate organic carbon via secondary organic aerosol formation holds for the period prior to 1995. However, after 1995 we reject this hypothesis, and next examine whether other on-road sources of primary and secondary organic aerosol can explain the observed trend in ambient OC over the entire period from 1981 to 2011.

We now consider a second hypothesis: if emissions from motor vehicles are the dominant contributor to particulate organic carbon via primary and secondary pathways, then decreases in ambient concentrations of particulate organic carbon should be observed over time, commensurate with reductions in the total emissions of POA and SOA precursors from motor vehicles. To test the hypothesis, we make a best estimate on SOA precursor emissions from both on-road gasoline and diesel vehicles, and POA emissions from on-road diesel only. Though POA emissions from gasoline vehicles are not estimated in this study, we note that source apportionment studies using chemical mass balance methods in the Los Angeles basin have found diesel exhaust to be the majority to dominant portion of POA relative to gasoline vehicles, this was true as early as 1982 as well as in 2001 [*Schauer et al.*, 1996; *Fujita et al.*, 2007].

To estimate SOA from gasoline vehicles, we first use CO emissions from McDonald et al. [2013] for the year 2010 estimated at the air basin level. To extend CO emissions further back in time, the trend in ambient CO (Figure 5.6a) was applied relative to 2010. Next, gasoline emissions of VOCs are estimated by ratio to CO [*McDonald et al.*, 2013] with non-tailpipe emissions excluded. Non-tailpipe emissions are excluded because they have negligible SOA formation potential due to their high volatility [*Gentner et al.*, 2012]. SOA is estimated using bulk yields reported by Gentner et al. [2012] applied to VOC emissions from gasoline exhaust.

To estimate SOA from diesel vehicles, first VOC emissions are estimated. Fuel-based VOC emission factors (g/kg fuel) from McDonald et al. [2013] are multiplied with air basin-level fuel data described in Section 5.2.1. The authors found that VOC emission factors from heavy-duty trucks did not change significantly between 1990 and 2010. This is not surprising given that VOC emission standards on heavy-duty trucks have not been lowered significantly since 1978 [*Yanowitz et al.*, 2000]. Again SOA is estimated using bulk yields reported by Gentner et al. [2012] applied to VOC emissions from diesel exhaust. To estimate POA emissions from heavy-duty trucks, BC emissions shown in Figure 5.4 are multiplied with an OC/BC mass ratio of 0.36 ± 0.15 (Figure 5.7), and an OA/OC conversion factor of 1.4 [*Gray et al.*, 1986]. The resulting SOA and POA emission trends from this analysis are shown in Figure 5.6b.

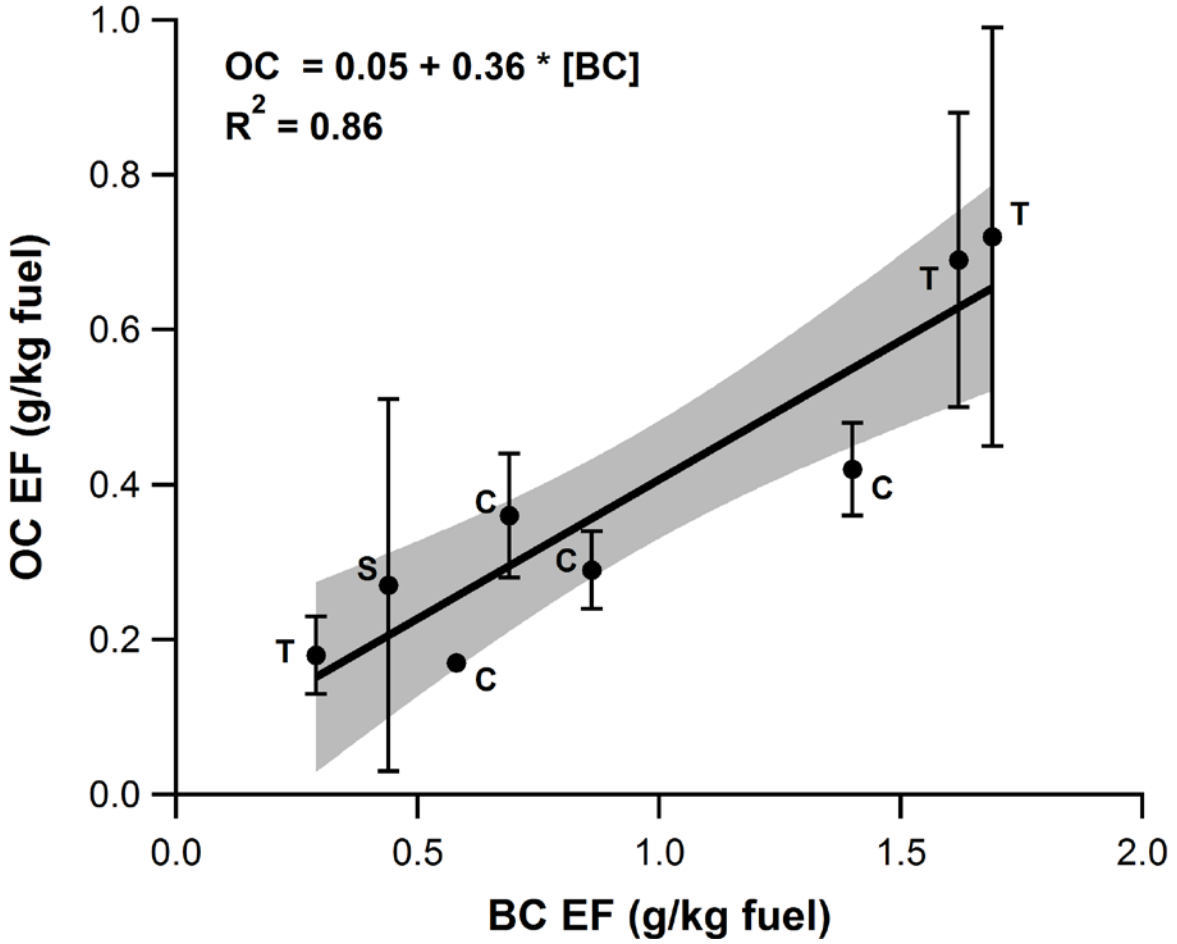


**Figure 5.7.** Correlation of heavy-duty diesel truck emission factors of organic carbon (OC) and black carbon (BC) from tunnel studies in Table 1. Tunnel abbreviations are as follow: T = Tuscarora, C = Caldecott, and S = Squirrel Hill.

The trend in on-road emissions of SOA and heavy-duty emissions of POA now agrees strongly with the ambient OC trend from 1981 to 2011 (Figure 5.6b). Of the three on-road sources shown, gasoline emissions that lead to the formation of SOA has historically been the most dominant, though its share of the on-road total has decreased dramatically from ~80% in 1981 to ~1/3 in 2011. Conversely, the share of OA (OA = POA + SOA) from heavy-duty vehicles has grown, while emissions have not changed significantly. Interestingly, the relative contribution between POA and SOA from diesel vehicles is now about the same. The similarity of the emissions and ambient trend (Figure 5.6b), suggests that motor vehicle emissions have been important to observed decreases in ambient OC. Furthermore, long-term decreases in on-road OA emissions were driven by controlling VOC emissions from gasoline engines. The slower decreases in ambient OC since 1995 relative to decreases in gasoline VOCs can partly be explained by the growing importance of diesel vehicles.

It is also possible that other non-vehicular sources could be important to the observed trends in ambient OC. If non-vehicle emissions are important, then their emissions must be unchanging. Other important identified sources of POA include from food cooking and wood smoke [*Hildemann et al.*, 1991; *Schauer et al.*, 1996]. Emission decreases from food cooking and wood smoke are expected to be flatter than VOC emission trends from gasoline engines, as they have not been as aggressively targeted by air pollution control efforts. Biogenic contributions of SOA are small in the Los Angeles basin [*B J Williams et al.*, 2010], so the influence on SOA is expected to be mostly from anthropogenic sources. A recent study by Ensberg et al. [2014] suggests that vehicle emissions may not dominate anthropogenic SOA in the Los Angeles basin, as one possible explanation for why expected concentrations of SOA from vehicle emissions do not equal observed concentrations. A second possibility raised by the authors is that mass yields derived from laboratory experiments substantially underestimate the amount of SOA generated in the atmosphere from vehicle emissions. The results of Figure 5.6b imply that regardless of the relative importance of motor vehicles to other anthropogenic sources of SOA, the trends in other non-vehicular sources of primary or secondary OA must be flat. We conclude that long-term trends seen in ambient OC for the Los Angeles basin are likely to have resulted from multi-decade efforts to control emissions of VOCs from gasoline engines. As a consequence of these efforts, other sources of OA have become more important to the urban OA budget at least by 2010, including emissions from diesel trucks.

### *5.3.3 Policy Implications*

In this study, we show that from 1975 to 2010, the heavy-duty diesel truck emission factor for PM and BC decreased by factors of ~4 (Figure 5.3). However, decreasing PM and BC emission factors were offset by large growth in on-road diesel activity. As a consequence, on-road diesel PM and BC emissions decreased by only ~20% over a 35 year time period (Figure 5.4). This suggests that exposure to diesel PM in near-roadway environments did not change substantially from efforts to control particle emissions from heavy-duty trucks. The installation of diesel particle filters (DPFs) as standard operating equipment on new heavy-duty diesel engines is expected to significantly reduce roadway concentrations of fine particles in the future. As an example, Dallmann et al. [2011] found that the average BC emission factor for drayage trucks traveling to and from the Port of Oakland, decreased by 54 ± 11% when trucks were retrofitted

with DPFs or replaced with new trucks. California has extended this accelerated retrofit and fleet turnover program statewide, beyond initial mandates at port facilities and rail yards only.

We show that efforts to control gasoline VOC emissions from improved catalytic converters have led to decreasing concentrations of OC over the Los Angeles basin. From 1975 to 2011, ambient OC decreased by ~70%. However, as catalytic converters have become more durable and effective at controlling gasoline emissions of VOCs, other anthropogenic sources that emit POA and SOA precursors have grown in relative importance, including from diesel exhaust. The strong similarity in the trend for ambient OC and motor vehicle emissions of POA and SOA-forming compounds (Figure 5.6b), suggests that gasoline and diesel vehicles remain important to the emissions and formation of anthropogenic organic aerosol in urban environments. An important vehicular source of OA that warrants more attention in urban air quality management is the control of SOA precursor emissions from high-emitting gasoline vehicles. As an example of how highly skewed the distribution of VOC emissions is towards a few high-emitting vehicles, a recent study found that out of 13 000 vehicles whose tailpipes were sampled ahead of a roadway tunnel in Los Angeles, ~4% of total VOC emissions at the study location could be accounted for by a single vehicle [*Bishop et al.*, 2012b]. Controlling SOA precursor emissions from high-emitting gasoline vehicles can complement current efforts underway to control diesel emissions of POA through widespread deployment of DPFs, and aid in reducing future concentrations of urban OA. Additionally, oxidation catalysts used to regenerate DPFs are expected to reduce VOC emissions from trucks significantly [*Herner et al.*, 2009], and reduce diesel emissions of SOA precursors.

# Chapter 6: Conclusions

## 6.1 Summary of Major Findings

The goal of this dissertation was to develop new inventories for motor vehicle emissions of greenhouse gases and co-emitted pollutants that contribute to urban and regional air pollution problems. The resulting motor vehicle emission inventories from this dissertation are more reliable than previous vehicle emission estimates, because spatial and temporal patterns of light- and heavy-duty vehicle activity are explicitly accounted for using real-world traffic count data rather than transportation demand models, and emission factors are derived from real-world on-road studies rather than from laboratory testing. Given that motor vehicle emissions are a significant source of urban air pollution, long-term changes in U.S. air quality were also assessed to see if observed changes could be attributed to changes in motor vehicle emissions.

In Chapter 2, a fuel-based inventory for vehicle emissions was developed for carbon dioxide ($CO_2$), and mapped at various spatial resolutions (10 km, 4km, 1 km, and 500 m) using fuel sales and traffic count data. Temporal variations in vehicle emissions were also characterized using extensive day- and time-specific traffic count data.

- When compared to two other commonly used emission inventories, the Emissions Database for Global Atmospheric Research (EDGAR) and VULCAN, differences between this study and EDGAR were apparent. EDGAR overestimates on-road $CO_2$ emissions in the largest U.S. cities by 20-80%, and the bias arises from using road density rather than traffic count data as a spatial surrogate for allocating vehicle emissions.

- High-resolution emission maps were generated for several major U.S. metropolitan areas. The high-resolution emission maps (1 km and finer) revealed sharp emission gradients that exist near major highways, and that were not apparent when emissions are mapped at coarser resolution (10 km). Highly-resolved emission maps are important for understanding near-roadway exposure to vehicle-related air pollution.

- Urban vehicular emissions of $CO_2$ were found to increase by ~10% through the workweek between Monday and Friday, and then decrease by ~20% and ~30% relative to Friday peak levels on Saturdays and Sundays, respectively. Comparing $CO_2$ emissions on Fridays to other (especially weekend) days could serve as a repeatable real-world test case for detection capabilities of emerging $CO_2$ monitoring networks, at least in urban areas where motor vehicle emissions tend to dominate.

- Clear differences were observed when comparing light- and heavy-duty vehicle traffic patterns and comparing urban and rural areas over diurnal, day-of-week, and seasonal time scales. Seasonal cycles in traffic, newly presented in this work, showed noteworthy increases of 35-40% in heavy-duty truck traffic between January and August. Passenger vehicle traffic in rural areas varied by ±20% of annual average values, with a peak during summertime. In contrast, seasonal variations in passenger vehicle traffic are limited to ~10% of mean levels in urban areas.

- Decadal trends in emissions were analyzed from 2000 to 2007 when traffic volumes were increasing, and for a more recent period (2007-2010) when traffic volumes declined due to recession. Large non-uniform changes in on-road $CO_2$ emissions were found over a period of ~5 years, highlighting the importance of timely updates to motor vehicle emission inventories.

In Chapter 3, a fuel-based approach was used to estimate long-term trends in nitrogen oxides ($NO_x$ = NO + $NO_2$) emissions from motor vehicles. Estimates are made at the national and state levels, and for the South Coast (Los Angeles) and San Joaquin Valley air basins.

- Long-term changes in $NO_x$ emissions have distinctly different patterns between light- and heavy-duty vehicles. Changes in diesel $NO_x$ emissions have varied over time: emissions were increasing between 1990 and 1997, stable between 1997 and 2007, and decreasing since 2007. In contrast, gasoline engine-related $NO_x$ emissions have decreased steadily, by ~65% overall between 1990 and 2010.

- The relative importance of on-road diesel versus gasoline emissions differs between urban and rural areas. In the rural San Joaquin Valley, diesel engines were the dominant on-road $NO_x$ source in all years considered (reaching a ~70% contribution in 2010). In the urbanized South Coast air basin, gasoline engine emissions dominated in the past, and have been comparable to on-road diesel sources since 2007 (gasoline engine contribution is down from ~75% in 1990).

- Contributions from other anthropogenic sources of $NO_x$ were added to permit comparison of emission trends with observed trends in ambient pollutant concentrations. When all major anthropogenic $NO_x$ sources are included, the overall emission trend is downward in all cases (45 to 60% decrease in emissions between 1990 and 2010).

- In the urban South Coast air basin, motor vehicles dominate total anthropogenic $NO_x$, accounting for ~80% of total emissions. Long-term decreases in $NO_x$ emissions have been driven by changes in motor vehicle emissions. Given that similar decreases in ambient concentrations were observed over the same time period, this suggests that air quality improvements were due to controlling emissions from motor vehicles.

- The two largest contributors to on-road $NO_x$ emissions are diesel exhaust and high-emitting gasoline vehicles. Emission control strategies should therefore focus on ensuring the effectiveness of new emission control systems on heavy-duty trucks, as well as making further improvements to *durability* of control systems installed on light-duty vehicles.

In Chapter 4, a fuel-based approach is used to estimate long-term trends in carbon monoxide (CO) emissions from motor vehicles. Non-methane hydrocarbons (NMHC) are estimated using ambient NMHC/CO ratios after controlling for non-vehicular sources.

- For gasoline-powered vehicles, there have been ten- and seven-fold reductions in CO emission factors measured in California and the US, respectively, since 1990. During the early 1990s, California vehicles were allowed to emit CO at higher levels due to permit

design tradeoffs that enabled more effective control of $NO_x$. Convergence of average CO emission rates between California and U.S. vehicle fleets occurred after CO emission standards for new vehicles were harmonized and enough old vehicles had been retired, which had happened by 2005. Decreases in CO can be attributed to improved catalytic converters on gasoline engines and better control of combustion air-fuel ratios. On-road diesel trucks are not a significant source of CO emissions.

- Despite increases in gasoline sales volumes of 10-40% between 1990 and 2010, running CO exhaust emissions from gasoline vehicles decreased by 80-90% in major urban centers including Los Angeles, Houston, and New York City over the same time period. Similar decreases were observed in ambient CO concentrations for these cities, as expected given the dominance of gasoline engines as a source of CO emissions in urban areas

- The ratio of NMHC/CO in ambient air was found to be 0.24 ± 0.04 mol C/mol CO in Los Angeles, and this ratio has remained stable over time. Give substantial decreases in CO reported above, this indicates that NMHC emissions have decreased at a similar rate. Ratios of NMHC/CO were also found to be stable over time in on-road emission studies, suggesting that emission control efforts had similar effects on both pollutants.

- Emission ratios of $CO/NO_x$ (nitrogen oxides = NO + $NO_2$) and $NMHC/NO_x$ decreased by a factor of ~4 between 1990 and 2007 due to changes in the relative importance of passenger cars versus diesel trucks as sources of $NO_x$. There was a slight uptick in CO and NMHC ratios to $NO_x$ thereafter, consistent across the urban areas considered here. These pollutant ratios are expected to increase in future years due to (1) slowing rates of decrease in CO and NMHC emissions from gasoline vehicles, and (2) significant advances in control of diesel $NO_x$ emissions. The $NMHC/NO_x$ emission ratio in urban areas, which has been falling in the past, is expected based on this research to increase again in the future. This emission ratio is an important factor that affects the efficiency of ground-level ozone formation.

In Chapter 5, a fuel-based approach is used to estimate changes since 1975 in particulate matter (PM) and black carbon (BC) emissions from heavy-duty diesel trucks for the Los Angeles area. Emission trends are compared with trends in ambient concentrations of particulate black and organic carbon over the same time period.

- On-road heavy-duty diesel emission factors of PM and BC decreased by a factor of ~4 since 1975. After accounting for rapid growth in diesel fuel sales, on-road diesel BC emissions were found to have decreased by only ~20% between 1975 and 2010. BC emissions increased by ~30% between 1975 and 1990, before more stringent emission standards started affecting the emission performance of new engines around 1990. Emissions of BC then decreased by ~40% over the ensuing two decades.

- Ambient measurements of BC concentrations in the Los Angeles basin show a clear downward trend. The basin-average BC concentration decreased from 4.6 ± 0.6 $\mu g\ m^{-3}$ in 1975 to 1.0 ± 0.5 $\mu g\ m^{-3}$ as of 2011. The corresponding rate of decrease is 4.2% per year.

In comparison, decreases in on-road diesel emissions of BC estimated in this research were minor. My conclusion is that, contrary to inferences made by other researchers, decreases in BC concentrations observed in the Los Angeles area between 1970 and 1990 did not result from emission control policies that applied to on-road diesel engines, but rather were driven by control efforts that focused on other air pollution sources. For example, commercial and industrial combustion processes appear to have switched to using natural gas in place of distillate fuels, and a number of California military bases were closed.

- The slopes of best-fit lines in plots of measured OC versus BC concentrations have remained remarkably consistent over time. The stability of this ratio over time implies similar long-term trends in ambient black and organic carbon concentrations, which is useful to know because compared to BC, OC observations are sparser and harder to interpret due to various sampling issues. We estimate that ambient OC in the Los Angeles basin decreased by $0.15 \pm 0.06$ μg $m^{-3}$ or 3.2% per year between 1975 and 2011.

- Between 1981 and 1995, the trend in CO matches that for OC (Figure 5.6a). Between 1995 and 2007, CO shows a steeper downward trend, decreasing by 75 ± 7% compared to OC which decreased by only 45 ± 22%. The difference in slopes suggests that sources of particulate organic carbon other than light duty gasoline vehicles must increasingly be contributing to the differing trends, with the other sources becoming more important at least by 2010.

- The trend in on-road emissions of SOA and heavy-duty emissions of POA agrees strongly with the ambient particulate organic carbon trend from 1981 to 2011. Given the similarity of the two trends, we conclude that emission trends in other anthropogenic sources of OA must be unchanging. It is also concluded that long-term decreases in ambient OC are likely to have resulted from efforts to control VOC emissions from gasoline engines. As a consequence of these efforts, other sources of OA are now more important, including emissions from diesel trucks.

## 6.2 Recommendations for Future Research

### *6.2.1 Developing Urban $CO_2$ Monitoring Networks*

Unlike traditional air pollutants that are routinely monitored (Figure 1.2), robust measurement networks for $CO_2$ in urban areas are lacking even though cities are estimated to account for ~70% of energy-related emissions of $CO_2$ globally [*Rosenzweig et al.*, 2010]. This is a critical gap that must be remedied. Efforts to track and verify progress in reducing $CO_2$ emissions are needed in conjunction with pursuit of a wide array of greenhouse gas mitigation options. This will provide needed accountability for existing and future climate change legislation. In the U.S., California has been a leader in regulating the emissions of greenhouse gases. In 2006, Assembly Bill 32, the California Global Warming Solutions Act, was enacted. Through a combination of regulatory and market-based mechanisms, AB32 will reduce statewide greenhouse gas emissions to 1990 levels by 2020. In 2008, California passed Senate Bill 375, the Sustainable Communities

and Climate Protection Act, which will reduce transportation emissions of greenhouse gases through better coordination of transportation and land use planning efforts.

In Chapter 2, a high-resolution motor vehicle emissions inventory for carbon dioxide was presented. Figure A1 shows that in the major metropolitan areas of California and Texas, motor vehicles are the dominant source of $CO_2$ emissions. The $CO_2$ maps presented in this dissertation, when combined with other major point and area sources of emissions, can aid in designing urban $CO_2$ monitoring networks. Additionally, the emission maps can serve as key points of comparison for satellite-derived data, especially in urban settings. New high-resolution space-based measurements of $CO_2$ should soon be available from the Orbiting Carbon Observatory (OCO-2). Comparing emissions models with satellite-based measurements is important in quantifying emissions and trends, especially in rapidly growing cities in the developing world where on-the-ground data are often lacking or of doubtful quality. Data on fuel use and air pollutant emissions in such locations are also lacking, so well-tested observation-based approaches will be needed to understand what is going on in rapidly-growing cities in the developing world.

### *6.2.2 Modeling Effects of Long-Term Changes in Motor Vehicle Emission*

In Chapters 3 to 5, long-term trends in motor vehicle emission were characterized for nitrogen oxides, carbon monoxide, volatile organic compounds, particulate matter, and black carbon. Emissions of these pollutants can be linked to the spatial and temporal maps of vehicular carbon dioxide emissions developed in Chapter 2. The resulting motor vehicle emission inventories, combined with emission estimates for other major point and area sources of pollution, can then be input into air quality models to evaluate how emission control policies (past, present, and future) affect air quality (Figure 1.2). Some possible areas of further inquiry are:

- To what extent do air quality problems persist? Why have improvements for ground-level ozone been slower than for other pollutants?
- What have been the public health benefits to date, both regionally and in near-roadway environments? What further benefits may accrue from future emission controls?
- Was the most cost-effective path pursued in efforts to control air pollution?

A multitude of observational datasets exist (e.g. satellite, aircraft and surface field studies, and routine monitoring), which can be used to constrain uncertainties in air quality and emission models needed for quantifying the effects of air pollution. The air quality impacts from motor vehicle emissions occur at both regional scales throughout urbanized air basins, and at highly localized scales near major roadways. The emission maps developed in Chapter 2 are useful for modeling air quality impacts of vehicle emissions at both scales. In addition to addressing public health concerns, an emerging topic of interest is control of short-lived climate forcings due to air pollution. As described in the introduction, reducing emissions of some pollutants can simultaneously mitigate climate change and improve human health [*Smith et al.*, 2009]. The comprehensive emission inventories developed here, for pollutants that also exert short-lived climate forcings ($NO_x$, CO, VOCs, and BC), can be used for calculating direct radiative forcings due to motor vehicle emissions.

### *6.2.3 Projecting Future Motor Vehicle Emissions and Air Quality Impacts*

It is also important to project emissions into the future, and to model expected air quality impacts. In the U.S., several new regulations are expected to further reduce motor vehicle emissions in the coming years:

- More stringent standards have taken effect recently for heavy-duty truck emissions of exhaust particulate matter and nitrogen oxides. Diesel particle filters to reduce PM and selective catalytic reduction systems to reduce $NO_x$ have become standard pieces of equipment on new heavy-duty diesel engines.
- New tailpipe and evaporative emission standards have been established for light-duty vehicles, including Low Emission Vehicle (LEV) III standards by California, and Tier 3 standards set by U.S. EPA.
- Fuel economy standards for passenger cars and light trucks will rise from 12.6 to 21.1 kilometers per liter on a fleet-average basis between 2012 and 2025. Improved fuel efficiency reduces co-emitted air pollutants and $CO_2$ emissions simultaneously.
- The first fuel economy standards for heavy-duty trucks are under development currently by US EPA.

Emission projections also need to take into account:

- Growth in population and economic activity.
- Changing travel behavior due to integrated land use and transportation planning [*NRC*, 2009].
- The prevalence of high-emitting vehicles, which could reduce expected benefits from more stringent vehicle emission standards.
- Upstream emissions associated with energy extraction and generation from switching to alternative fuels, e.g. vehicle electrification or increased reliance on natural gas as fuel.

Once vehicle emissions have been projected for future years, these estimates can be input into atmospheric models to assess future air quality and to design implementation plans for meeting ambient air quality standards. Air quality standards for ground-level ozone are still exceeded in many major U.S. metropolitan areas. However, given the non-linear relationship between ozone formation and the emissions of nitrogen oxides and volatile organic compounds [*Sillman*, 1999], it is not clear how reducing $NO_x$ and VOC emissions from motor vehicles will affect ozone concentrations a priori. Additionally, climate change is expected to exacerbate ground-level ozone problems [*Steiner et al.*, 2006]. Modeling of the effects on air quality of future changes in emissions is needed to assess whether additional air pollution control policies will be effective and are of sufficient magnitude to protect human health and public welfare.

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## Appendix A: Map of Dominant Urban Fossil Fuel $CO_2$ Emissions Source

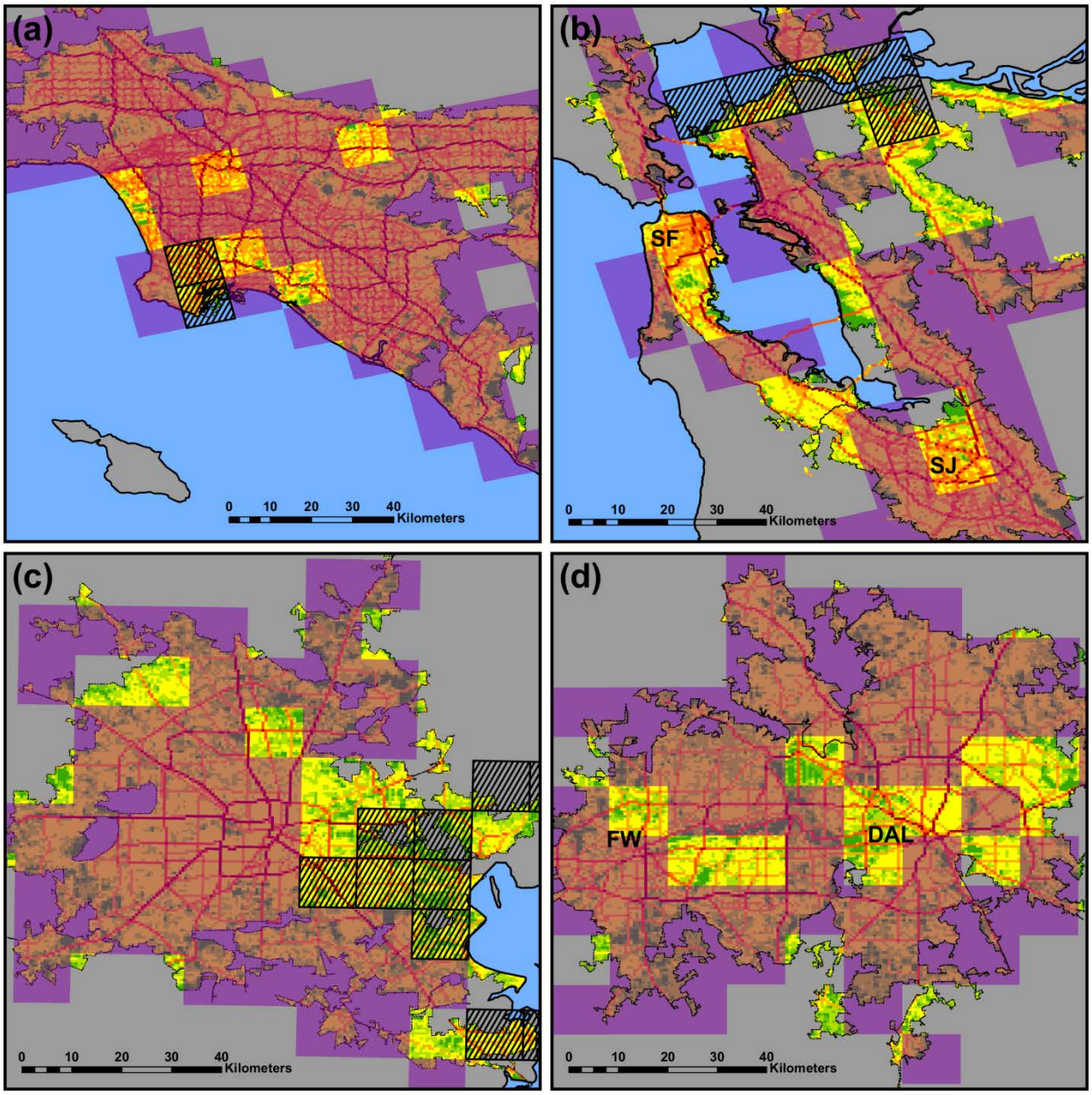


**Figure A1.** Map of dominant fossil fuel $CO_2$ emissions source in (a) Los Angeles, and (b) San Francisco/San Jose, (c) Houston, and (d) Dallas-Fort Worth. On-road emissions account for 50% or greater of the annual average where shading is purple. Industrial emissions account for 50% or greater in areas with black hashing. The relative proportion of anthropogenic emissions by source is calculated using on-road emissions from this study and VULCAN for all other emission categories in 2002.

## Appendix B: Analysis of Long-Term Weigh-in-Motion Data

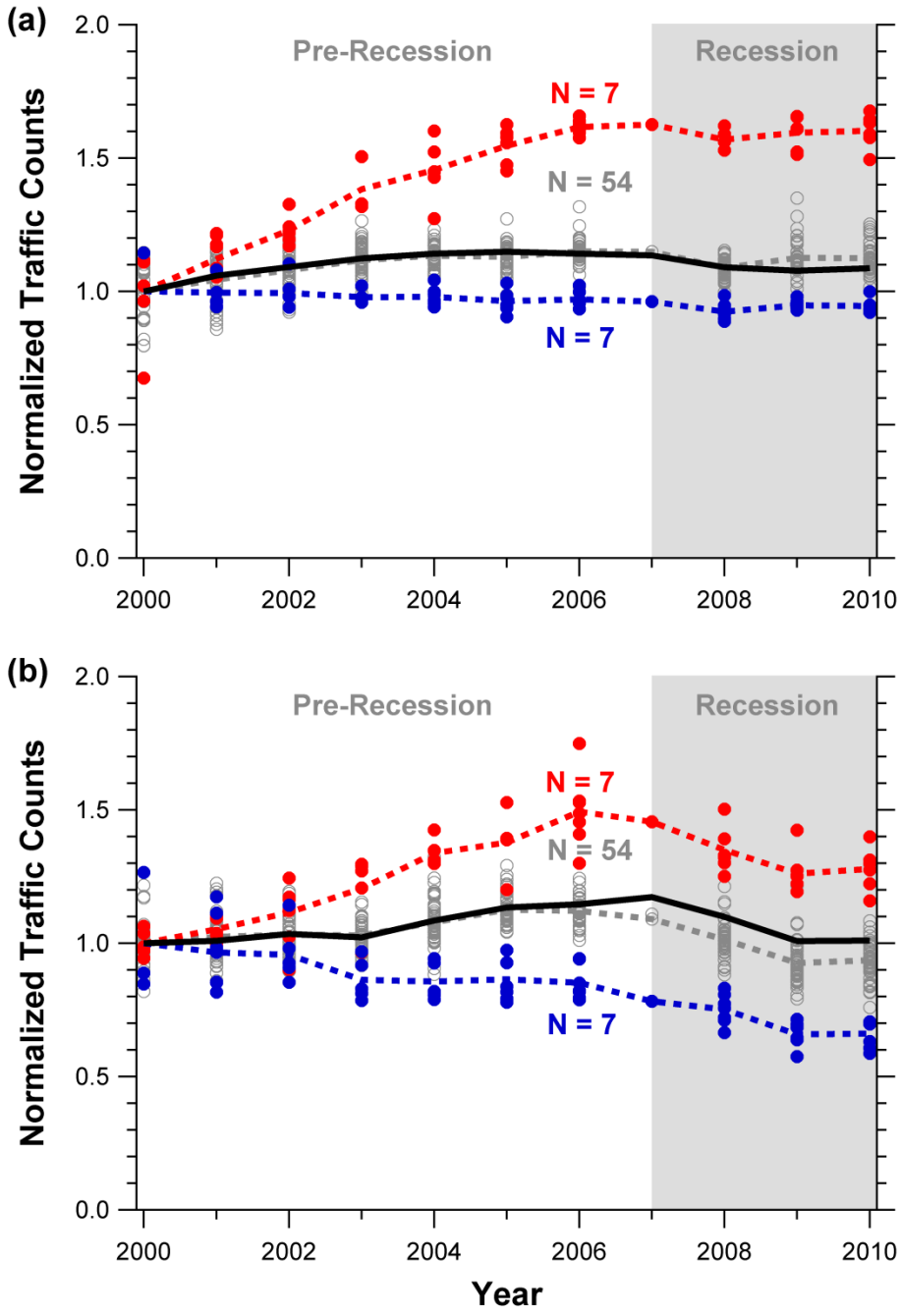


**Figure B1.** Decadal trends in (a) light and (b) heavy-duty vehicle traffic in California. Each marker represents a weigh-in-motion station. For each marker, weigh-in-motion stations are ranked by growth from highest to lowest and subdivided into top 10% (red), bottom 10% (blue), and middle 80% (gray). The number of stations is shown for each cohort (i.e., N=XX). The dashed lines show the mean in each year for each cohort. Trends in statewide fuel sales multiplied by changes in fuel economy are shown (black line) for comparison with the traffic count-derived data.