MASTER'S THESIS

New Method of Diesel Particulate Matter Estimation with NO_X to BC Correlation

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Abstract

Soot, measured as black carbon (BC) and elemental carbon (EC), is a potent climate-warming species associated with toxic health effects, emitted from both anthropogenic and natural sources, such as fossil fuel and biomass burning, respectively. In the past, heavy duty diesel trucks (HDDT) have been notorious emitters of anthropogenic soot, among other particulates and toxic gases (collectively known as diesel particulate matter, or DPM). In California, due to successful regulation in urban areas, anthropogenic BC levels have declined, but the health impacts of BC and its co-emitted DPM constituents are still significant; thus, the need to determine a new method for estimating DPM motivated the work for this thesis.

Existing methods of DPM estimation were reviewed. Two were combined to form the "Combined Alpha Method" and evaluated. With data currently available, it performed within 20% of two different methods, but further work, such as updated speciation and source testing profiles, can enhance the discussed method. To further assess the method, correlation between NO_X and BC were examined at three geographically different locations and determined that at sites in close proximity to diesel vehicles, NO_X is a good indicator of BC—making it valid to use NO_X (in combination with EC) in DPM estimations; and at rural locations, the two have low correlation.

Done in cooperation with the **South Coast Air Quality Management District**:
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List of Abbreviations

ANAH	Anaheim
AQMIS	Air Quality and Meteorological Information System
BC	Black carbon
Caltrans	California Department of Transportation
CARB	California Air Resources Board
CELA	Central Los Angeles
CMB	Chemical Mass Balance
CTMP	Comprehensive Truck Management Program
DPF	Diesel particulate filter
DPM	Diesel particulate matter
EC	Elemental carbon
EGR	Exhaust gas recirculation
EI	Emission inventories
FONT	Fontana
HDDV / HDDT	Heavy duty diesel vehicles / heavy duty diesel trucks
LEZ	Low Emissions Zone
LNT	Lean NO_X Trap
MATES	Multiple Air Toxics Exposure Studies
MY	Model year
NAAQS	National Ambient Air Quality Standards
NATTS	National Air Toxics Trends Station Network
NO, NO_2, NO_X	Nitrogen oxide, nitrogen dioxide, oxides of nitrogen
O_3	Ozone
PAH	Policyclic aromatic hydrocarbon
$PM_{2.5}$	Particulate matter (smaller than 2.5 microns in diameter)
PMF	Positive Matrix Factorization
POLA	Port of Los Angeles
POLB	Port of Long Beach
RIVR	Rubidoux
SA	Source apportionment (studies)
SCAQMD	South Coast Air Quality Management District
SCR	Selective catalytic reduction
SoCAB	South Coast Air Basin
SVOC	Semivolatile organic compound
TAC	Toxic air contaminant
U.S. EPA	U.S. Environmental Protection Agency
VMT	Vehicle miles traveled
α	$DPM_{2.5}/NO_X$ ratio

1 Background and Introduction

As of November 2016, California ranks as the sixth largest economy in the world.[1] While commonly known for its movie and entertainment industry, California's economy owes a large part of its economic success to its agriculture, trade, and transportation sectors, among others.[2] The large economy combined with California's title as most populous state in the U.S. results in at least 35 million registered vehicles in 2016,[3] including passenger vehicles, motorcycles, heavy duty trucks and trailers, and the like. Contributing to both the economy and the number of vehicles in operation are the three megaports of Los Angeles (POLA), Long Beach (POLB), and Oakland (Port of Oakland)—three of the four largest ports in the nation. Nearly half of the U.S.'s container cargo volume travel through these ports to be transported via truck and train the rest of the country.[4–6]

The bustle of activity fueled largely in part by ships, trains, and heavy duty diesel trucks (HDDT) that operate in and around ports, railyards, and highly traveled roadways gives rise to unhealthy emissions and, consequently, poor air quality, notably diesel particulate matter (DPM).[7] Diesel exhaust contributes to high levels of regional ozone as well as global air pollution, which affects the health of many. DPM is the solid portion of diesel exhaust, falling under the category of fine particulate matter, or $PM_{2.5}$ (particulate matter smaller than 2.5 microns in diameter). Originating from combustion of diesel fuels, DPM consists of carbon particles (black carbon (BC) or elemental carbon (EC), depending[a] on the measurement method, or colloquially, "soot") as well as organic compounds, many of which are carcinogenic. Additionally, because $PM_{2.5}$ as a whole is so small, it can easily be inhaled into and deposited onto the lungs, which can cause cardiovascular and respiratory problems, as well as premature death.[7]

However, since trade and transportation are so integrated into California's economy, these operations are imperative for the functionality of the State. Thus, on top of regulations already in place aiming to reduce greenhouse gas (GHG) levels such as the listed, regulations limiting DPM and implementing newer, cleaner diesel technologies were set to preserve the health of Californian residents as well as California's economy.

[a] See Appendix B: EC v. BC for more detail

- Clean Air Act of 1970 – Federal law that regulates emissions of hazardous air pollutants (HAP) from stationary and mobile sources, established National Ambient Air Quality Standards (NAAQS), required the development of state implementation plans (SIP), among others;
- AB 32 – California Global Warming Solutions Act of 2006, which requires GHG reductions to 1990 levels by 2020;
- SB 375 – Sustainable Communities Act of 2008, which aims to coordinate transportation and land use planning towards more sustainable communities in California;
- E0 B-30-15 – 2015 Executive Order under Governor Edmund G. (Jerry) Brown Jr. calling for reductions of GHG in California to 40% below 1990 levels by 2030);
- SB 1383 – Short-Lived Climate Pollutants Plan of 2016, which requires the implementation of strategies to reduce short-lived climate pollutant emissions to at least 40% below 2013 levels by 2030.

Starting in 1987, the U.S. Environmental Protection Agency (U.S. EPA) and the California Air Resources Board (CARB) required manufacturers to provide proof that their heavy-duty engines met emission standards before they were sold,[8] and later in 2006, the sulfur content of diesel fuel was capped at 15 parts per million by weight (ppmw).[9] In 1998, the State of California declared DPM a toxic air contaminant (TAC); subsequently, the Diesel Risk Reduction Plan was formed with the goal of 85% reduction in DPM by 2020. Proposition 1B was passed as the Highway Safety, Traffic Reduction, Air Quality, and Port Security Bond Act of 2006, which created a fund to aid in the reduction of emissions due to goods movement in California's trade corridors. In 2007, stricter standards for nitrogen dioxide (NO_2) were adopted, lowering the 1-hour average from 0.25 ppm to 0.18 ppm, and the annual average standard set at 0.30 ppm. In the same year, CARB approved of the Statewide Drayage Truck Regulation which essentially required Class 7 and 8 trucks[b] to reduce PM emissions by 85% immediately with diesel particulate filters (DPF) or engines with a newer model year.[11] In 2008, a similar rule targeted trucks and buses. The Truck and Bus Regulation aimed to reduce

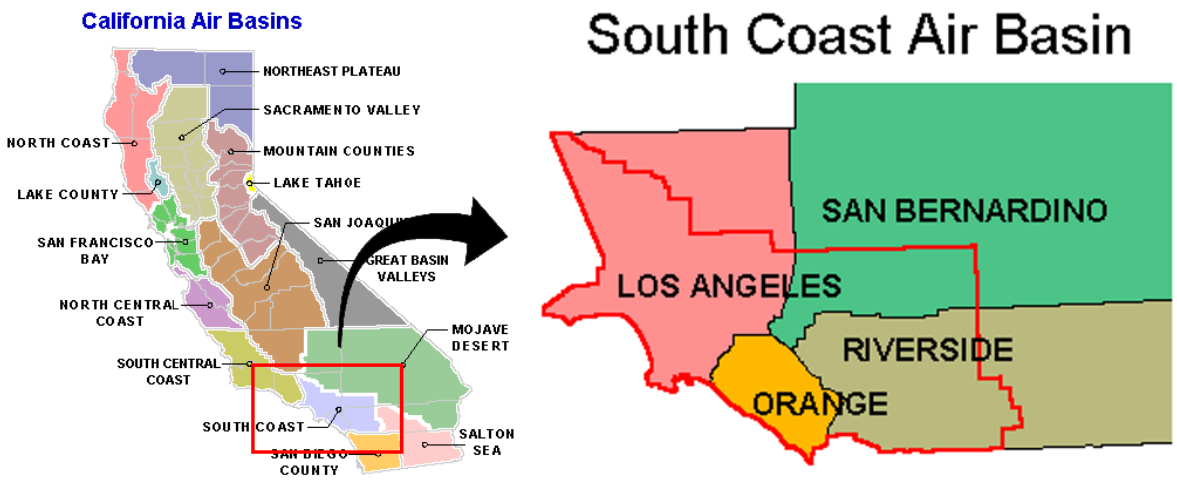
[b]Commercial trucks in the US are classified by gross vehicle weight rating (GVWR), on a scale of 1 through 8. Class 7 and 8 trucks are classified as heavy duty. Class 7 trucks weigh 26,001 – 33,000 lbs; Class 8 trucks are the largest with GVWR over 33,000 lbs.[10]

PM and oxides of nitrogen (NO_X) emissions on a phase-out basis based on engine model year (MY) with the goal of achieving 2010 MY engines on all vehicles by 2020.[12] See Appendix A: California Regulations for a comprehensive list of regulations related to diesel and air quality. On top of these regulations, each of the three megaports listed above have their own plan to contribute towards improved air quality, such as the Clean Air Action Plan for the combined ports of POLA and POLB, and the Comprehensive Truck Management Program (CTMP) for the Port of Oakland.[13,14]

1.1 Focus on South Coast Air Basin

The following thesis was completed in cooperation with the South Coast Air Quality Management District (SCAQMD), which is responsible for managing the air quality of the South Coast Air Basin (SoCAB), pictured in Figure 1. SoCAB encompasses all of Orange County and the urban areas of Los Angeles, Riverside, and San Bernardino Counties—the smoggiest regions of the US.[15] The California Department of Transportation (Caltrans) indicated the top three counties with the highest Average Annual Daily Truck Miles of Travel in 2009 were San Bernardino, Los Angeles, and Riverside Counties.[16] This is likely due to the transport of goods from the ports to the national and regional distribution center warehouses located in the Inland Empire.

Figure 1: (Left) The boxed area indicates where the South Coast Air Basin is relative to the rest of California. (Right) An enlargement of the boxed area. The red outline represents the jurisdiction area (all of Orange County and the urban areas of LA, San Bernardino, and Riverside Counties) of the South Coast Air Quality Management District. (Source: California ARB)



The SCAQMD has conducted Multiple Air Toxics Exposure Studies (MATES) for the past 30 years with the goal of quantifying the magnitude of population exposure risk from select air toxic contaminants.[17] One of the goals of both the latest and upcoming MATES (MATES IV from 2015 and MATES V in 2019, respectively) is determining the health risks associated with DPM. The Basin-wide cancer risk from DPM dropped 65% from MATES III, and accounted for 68% of the air toxics cancer risk in MATES IV. MATES IV highlights the importance of a continued focus in reducing DPM, despite uncertainties in ambient estimates, especially when goods movement is projected to increase.

1.2 Outline

This thesis will focus on the quantification of DPM, particularly in SoCAB, and then examine the correlation between NO_X and BC at different locations. Relevant background literature is provided in Section 2. Section 3 will overview what methods have previously or are currently being used to estimate DPM. Section 4 will briefly look in to what species were considered as a DPM surrogate. Section 5 explores a combination of two DPM estimation methods, and then discusses why interest in NO_X was piqued. Section 6 is a case study focusing on SoCAB, London, and Thüringen, Germany and how the NO_X/BC correlation differs at each geographically different location.

2 Literature Review of Declining Emissions

Recent literature has cited decreases in NOx, EC or BC, and other emissions from HDDT due to implementation of various measures. The effects of these regulations, such as the Drayage Rule, were almost immediate in some cases, as shown in Figure 2.

In 2010, Kuwayama et al.[18] collected samples at the Port of Oakland to observe the effects of implementing Phase 2 of the CTMP. They sampled from March to May, encompassing April, the month the implementation took effect. Analyzing their data with PMF, they were able to apportion source contributions to different elements and concluded[18] that the fraction of EC contributed by port truck traffic dropped approximately 66% after the CTMP was in place. Similarly, Dallmann et al.[19] sampled on select weekdays in November 2009 and again in June 2010 to measure the changes brought about by the CTMP. Analysis of plume capture from an overpass near the Port of Oakland revealed[19] a 54% reduction in BC emissions in that time period, during which 1994 MY and older trucks were banned and 1994 – 2003 MY trucks were retrofitted or replaced with newer equipment. Data from this study was later compared to data collected with the same method also near the Port of Oakland by Preble et al.[20] in November 2011 and March 2013. The comparison showed a 76% decrease in fleet-averaged BC emission factors from the 2009 fleet (MY 1970 – 2009 from Dallmann et al.[19]) to the 2013 fleet (MY 1994 – 2013 from Preble et al.[20]). Additionally, trucks with MY 2010 or newer engines and DPF and selective catalytic reduction (SCR) systems had the lowest BC emission factor.[20]

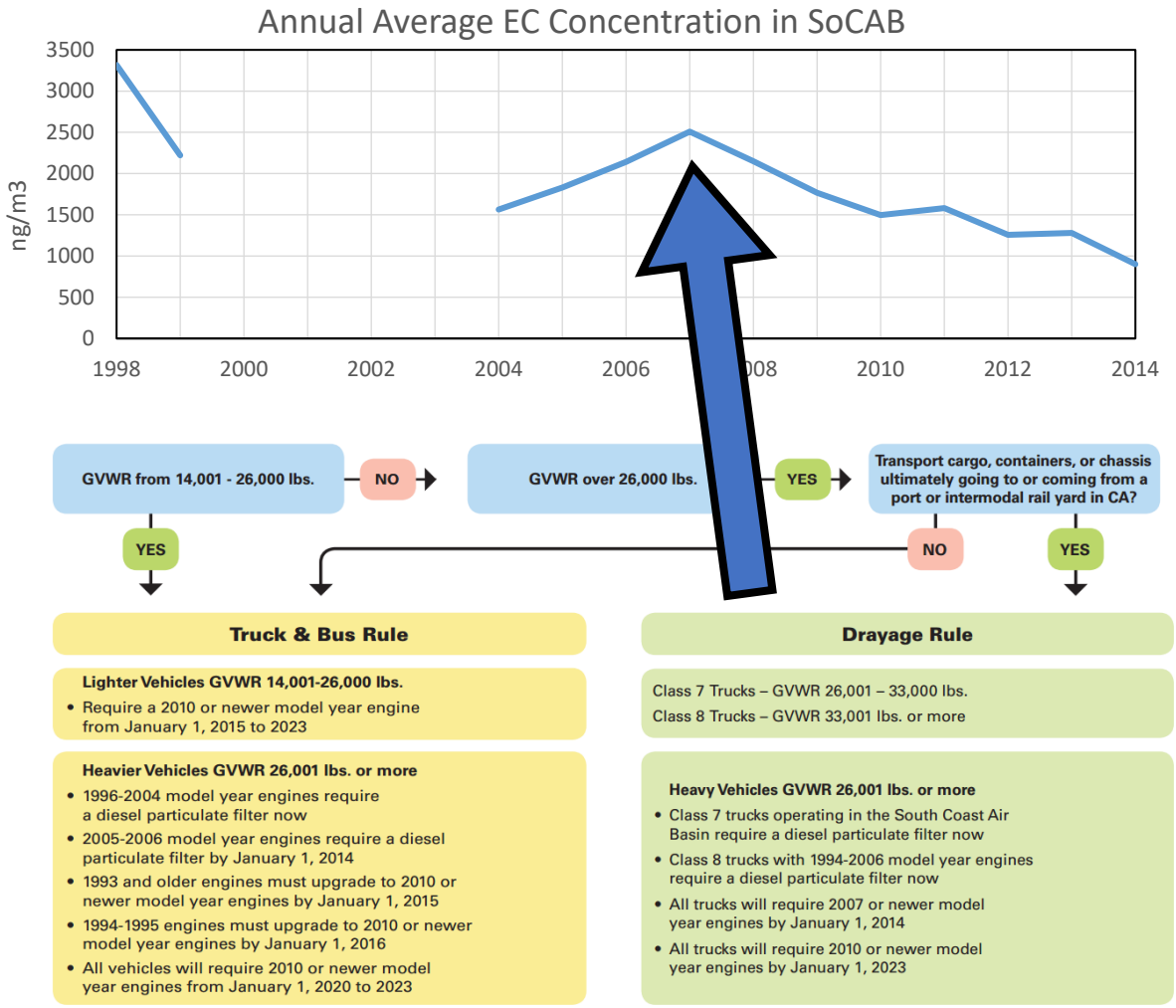
Likewise, Hasheminassab et al.[21] conducted sampling from 2002 – 2013 in Los Angeles and Rubidoux, which encompasses the timeframe of a few CARB- and port-mandated regulations. PMF results revealed[21] that contributions from vehicular emissions (diesel and gasoline) in 2013 were 70 and 52% lower than their peaks in 2007 and 2005 for LA and Rubidoux, respectively.

In 2013, Bishop et al.[22] set up on-road measurement stations at POLA and at the Cottonwood weigh station, just off I-5 in Northern California. In both locations, PM and BC emission factors (mean g/kg fuel) decreased with newer chassis model year, as expected; and at Cottonwood, emissions from the 2011 MY and newer engines were more than a factor of 30 lower than the pre-2008 MY ones.[22] The same study was repeated in 2015 by Haugen and Bishop.[23] At

POLA, the average age of the fleet increased, increasing PM and BC emission factors; conversely, at Cottonwood, the fleet age dropped, decreasing PM and BC emission factors by 66 and 65%, respectively.

Pakbin et al.[24] compares the two most recent MATES conducted by the SCAQMD, noting that ambient EC levels were lower in the MATES IV study, spanning July 2012 – July 2013, compared to the MATES III study, which spanned April 2004 – April 2006. Figure 2 (top) plots the annual average EC levels in SoCAB, which shows that emissions of EC, among others, have been declining. The decline is attributed to the success of many regulations and incentive programs, such as the Truck and Bus and Drayage Rules which are compared at the bottom of Figure 2.

Figure 2: (Top) Decline of EC levels over time. (Bottom) Flow chart comparing the Truck & Bus Rule (2008) to the Drayage Rule (2007), among other regulations, that played a part in lowering EC concentrations. (Source: California Air Resources Board)



3 Diesel Particulate Matter Estimation

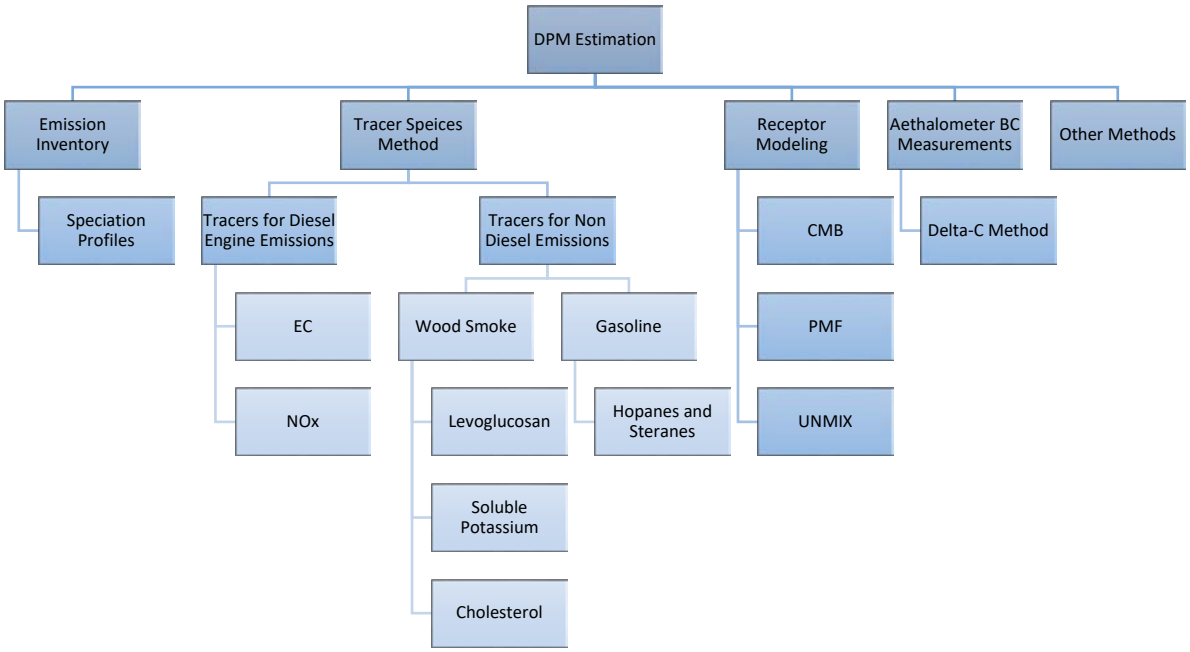
Since DPM was determined to be a TAC, there have been many attempts at quantifying it. This section briefly discusses the different categories of DPM estimation and highlights past studies that have put different methods of DPM estimation to test.

3.1 Classification of Methods

As summarized in Figure 3, there are at least four different categories of DPM estimation: Emission Inventory, Tracer Species Method, Receptor Modelling, and Aethalometer BC Measurements. The Emission Inventory essentially relies on speciation profiles to provide estimates on chemical emissions to distinguish diesel emissions from those of gasoline vehicles. The Tracer Species Method separates emissions contributed by biomass burning and fossil fuels by use of tracers: levoglucosan, water-soluble potassium, and cholesterol represent biomass burning emissions, while EC and/or BC[c], NO_X, and hopanes and steranes indicate fossil fuel emissions. Receptor Modelling methods attribute emissions to different source profiles and compositions. Methods include Chemical Mass Balance (CMB, as detailed in Section 3.2.3), Positive Matrix Factorization (PMF), and UNMIX, an EPA model. Emission Inventory and Receptor Modeling methods are oftentimes used together to improve the emission inventory. And lastly, Aethalometer BC Measurements use the difference between two wavelength channels to determine Delta-C, an indicator of wood smoke (as detailed in Section 3.2.6).

[c]EC and BC have been loosely interchanged in the literature; see Appendix B: EC v. BC for more detail.

Figure 3: Tree map of different categories of DPM estimation (Source: Pakbin[25])



3.2 Past Methods

3.2.1 PM_{10} Ratio

In 1998, CARB estimated[26] DPM_{10} by using a factor determined by CMB and emission inventory estimates to scale ambient PM_{10} measurements. Depending on if the DPM_{10}/PM_{10} ratio were larger or smaller than the base case ratio, the DPM_{10}/PM_{10} ratio was further scaled by another factor determined from the emission inventory. The report estimated average ambient outdoor concentrations of diesel exhaust PM_{10} in California and SoCAB to be 3 and 3.6 $\mu g/m^3$, respectively.

However, exhaust particles fall under the fine PM category, or $PM_{2.5}$, thus making this method, compared to the following methods, less accurate. In addition, it is heavily dependent on (1) measurements of ambient PM_{10} concentrations, which were not representative of diesel, as a large portion was crustal material with less than 7% contributed by diesel, (2) base cases determined by early source apportionment studies, many of which are not nearly as accurate as today's methods (such as organic marker species-based CMB methods), and (3) emission inventory estimates, which likely did not account for as many source emissions as more recent models.[26]

3.2.2 Emission Inventory Ratio

In 2000, SCAQMD's MATES II report[27] as well as CARB's Final Diesel Risk Reduction Plan[28] estimated DPM levels using the ratio of ambient EC measurements to Basin-wide EC emissions inventories[d] of a base year and setting it proportional to that of the year in question, as follows:

$$\frac{Statewide\ diesel\ PM\ concentration\ (base\ year)}{Diesel\ PM\ emissions\ inventory\ (base\ year)} = \frac{Estimated\ DPM\ levels\ (year\ X)}{Diesel\ PM\ emissions\ inventory\ (year\ X)}$$

To provide estimates of the statewide diesel PM concentration, MATES II relied on a 1980 study for emissions ratios of DPM and EC, while CARB relied on three studies for speciated PM_{10} data, ambient PM_{10} monitoring network data, and the 1990 PM_{10} emission inventory.

The ratio used in MATES II to estimate DPM was 1.04 times the concentration of PM_{10} EC, bringing estimated DPM levels in SoCAB to 3.4 µg/m^3. CARB estimated statewide population-weighted annual outdoor average DPM concentration to be 1.8 µg/m^3.

As shown, there is a large discrepancy in the basin- to state-wide ratio between this method (1.89) to the PM_{10} Ratio method (1.2). MATES III indicates[29] that the Emission Inventory Ratio method likely grossly underestimates DPM contribution compared to the methods used in MATES III, as detailed below.

3.2.3 Chemical Mass Balance

In 2008, MATES III looked at several methods to estimate DPM. In addition to the Emission Inventory Ratio method[e], Chemical Mass Balance (CMB) and a method using ambient $PM_{2.5}$ emissions ratios were used to apportion emissions.[30] Ultimately, the CMB source apportion model, a linear regression model based on select chemical species and source profiles, was chosen as the method of estimating DPM for MATES III because it accounts for geographic differences and major source categories.[29]

The method using ambient $PM_{2.5}$ emissions ratios is described in more detail in Section 3.2.5 and uses a 2005 emissions inventory to come up with a $DPM_{2.5}/EC_{PM2.5}$ ratio of 1.95. This

[d] Emissions inventories are continuously updated, encompassing emissions from stationary sources, area sources, mobile (on- and off-road) sources, and natural sources, among others.[28]

[e] In MATES III, using the Emission Inventory Ratio Method, DPM concentration was calculated to be 2.16 µg/m^3 whereas it was estimated to fall between 3.20 – 3.49 µg/m^3 using the CMB method as detailed in Section 3.2.3.

resulted in a DPM estimation of 3.5 µg/m^3; the CMB method estimated DPM concentration to be 3.20 – 3.49 µg/m^3. These two methods yield results within 5% of each other, compared to the estimate using the Emission Inventory Ratio method for the same time period, which results in a difference greater than 40%. Refer to Table 1 for more information.

The disadvantage to CMB, however, is that it may not identify all sources of BC and/or EC (due to co-linearity issues), requires rich datasets (which is limited for short term studies) with recent emission profiles (which vary significantly and are not always available from sources in the general area CMB is to be performed), and heavily relies on unverifiable assumptions.[31,32]

3.2.4 DPM to NO_X Ratio (NO_X Tracer Method)

In 2010, CARB's Truck and Bus Regulation[26] estimated DPM using the following equation,

$$S = \alpha C$$

where S is the annual average ambient concentration of $DPM_{2.5}$, α is a scaling factor, and C is the annual average ambient concentration of NO_X. This method uses scaled ambient NO_X concentrations due to the correlation between diesel-engine emitted NO_X to total ambient NO_X.[26] The scaling factor, α, is ideally location-independent and represents the ratio of $PM_{2.5}$ produced by diesel fueled engines to total ambient NO_X concentrations produced by all sources. Four site-specific source apportionment (SA) studies were compared to county-wide emission inventories (EI) to determine α.[26,32] The source apportionment studies are based off two year-long and a few short-term CMB studies—which, as stated above, are dependent on several important but typically unverifiable assumptions.

Uncertainties encountered in the aforementioned studies included difficulties in creating a single source profile due to significant variability across vehicles; oxidation of molecular markers, which does not follow the assumption that chemical species used in CMB mass balance equations must be conserved; assuming off-road diesel emissions were similar in composition to those of on-road diesel; as well as differences in source apportionment methodology and carbon measurement method (NIOSH v. IMPROVE).[26] In addition, the atmospheric lifetime of DPM is greater than a day whereas NO_X is less. This would bias the DPM/NO_X ratio towards higher values, but the residence time of an air parcel in SoCAB, typically a day, dominates the removal rate, allowing the assumption that the DPM and NO_X removal rates are equal.[26]

Due to these uncertainties and assumptions, values of α from SA studies differed by a factor of two, but the averages of the four SA studies and the 2000 EI county average compare well, giving an estimate of α = 0.023 for the State.[26]

3.2.4.1 EC Apportionment

Additionally, within one of the SA studies,[26] $DPM_{2.5}$ was estimated by scaling EC. Apportionment of total carbon ($TC_{2.5}$) and $EC_{2.5}$ were determined, and $EC_{2.5}$ from diesel ($DEC_{2.5}$) was scaled by 1.36 to determine $DPM_{2.5}$,

$$DPM_{2.5} = 1.36 \times DEC_{2.5}$$

which was then used in the $DPM_{2.5}/NO_X$ ratio (α).

3.2.5 DPM to EC Ratio

The most recent estimation method is from SCAQMD's MATES IV in 2015 which used the product of two ratios:

$$\frac{PM_{diesel}}{EC_{total}} = \frac{PM_{diesel}}{EC_{diesel}} \times \frac{EC_{diesel}}{EC_{total}}$$

The first term is determined by PM speciation profiles, which is based on recent dynamometer tests and source testing. Not only does the EC fraction of speciation profiles vary substantially depending on fleet type, engine technology, model year, emission control technologies, driving cycles, etc.,[25] but they are also dependent on a limited number of dynamometer tests to be extrapolated to represent the entire basin. Thus, the first term is only as accurate as the most recent speciation profiles. In MATES IV, this term was estimated to be 0.81.

The second term, determined by source testing profiles, is the amount of EC from diesel compared to total EC emissions in the basin, which include sources such as biomass burning, cooking, residential fuel combustion, petroleum production, and cleaning and coating processes, in addition to diesel EC. For MATES IV, it was measured[30] to be 1.17 µg/m^3. This term fluctuates with the sources of EC emissions, making the entire method location dependent.

Thus, this method estimates DPM to be 0.95 µg/m^3. It is interesting to note that using this method along with the updated speciation profiles (which affect EC levels) drops the MATES III DPM estimation from 3.5 to 1.24 µg/m^3.

3.2.6 BC Apportionment

Generally, BC is emitted from two major sources: biomass burning and fossil fuel combustion, where BC from biomass burning dominates BC in the low-to-mid troposphere, and BC from fossil fuel combustion contributes to ground level BC.[33] Delta-C, an indicator of wood smoke, can be determined by utilizing two channels of an aethalometer (370 and 880 nm). By identifying source contributions from biomass burning, an approximate estimate of the fossil fuel contribution should be able to be determined from the difference. A few campaigns[34–38] within the last decade used the aethalometer method along with levoglucosan as a tracer for wood smoke; however, the majority of them were performed either in locations with climates vastly different from that of Southern California, or where wintertime behaviors were different. In SoCAB, it is rare to have residential wood smoke, simply due to the mild climate experienced year-round. Campaigns performed in SoCAB and the vicinity were done so during the summer wildfire season.[35,38]

4 Species Considered as DPM Tracer

EC and/or BC have been common surrogates for DPM since at least 2000.[29,39] As noted in Section 1, BC and EC have been in decline; however, when the species used as a tracer for DPM is also decreasing in concentration, problems arise for future estimations. Thus, a new tracer or improvement upon an old method for estimating DPM must be determined. Preliminary research resulted in considerations of the following species as tracers. However, the next sub-sections summarize why further research into each of them was not pursued.

4.1 Ammonia

New regulations and retrofits introduced the use of selective catalytic reduction (SCR) technology in trucks to reduce NO_X levels[f]. When operating correctly, SCR systems have higher exhaust pipe temperatures, likely due to the conversion of urea, which can potentially lead to ammonia slip. However, in terms of feasibility and practicality, ammonia is a difficult (and expensive) pollutant to measure and likely not a reliable tracer for diesel, as most SCR systems now include a slip catalyst to prevent tailpipe emissions of ammonia. SCR systems are also purposefully deactivated when exhaust temperatures are too low for complete urea decomposition.[40]

4.2 Light Molecular Weight PAHs

A major source of polycyclic aromatic hydrocarbons (PAHs) are from vehicular emissions as well as biomass burning: while gasoline vehicles tend to have higher emission factors of high molecular weight PAHs, diesel vehicles are associated with low molecular weight PAHs such as naphthalene, phenanthrene, fluoranthene, or pyrene.[39,41,42] However, while PAHs displayed higher concentration levels during the colder months, warmer months showed low concentration or even levels below detection limit, likely due to reactions with ozone, nitrogen oxides, or hydrogen peroxide.[39]

4.3 Metals

Metal compounds are primarily emitted from brake wear or catalytic converters, some of which are unique enough to be used as tracers; however, Dwivedi et al.[43] found that the metal content of DPM peaked at the idling stage, which is generally not the state at which vehicles

[f] Section 6.2 provides further detail on SCR and other NO_X abatement technologies

are moving in SoCAB. On top of that, while Fe, Cu, Zn, and Pb are the most abundant metals in break lining[43,44]—where Fe can reach up to 60% by weight—Fe, in addition to Mg and Ca, is also one of the main components of crustal elements. Common tracers of brake wear are Cu and Sb; but, while HDV have emission factors of brake wear PM_{10} an order of magnitude higher than those of LDV, these elements are not unique to one class of vehicle or another.[43,44] The abundant and ubiquitous characteristics of metals make identifying one as a unique tracer difficult.

4.4 Hopanes and Steranes

Hopanes and steranes, mostly emitted from lubrication oil, are reliable tracers of vehicular emissions due to their stability in transport.[39] However, as semivolatile organic compounds (SVOCs), they are not good representations of PM or DPM.

4.5 NOx

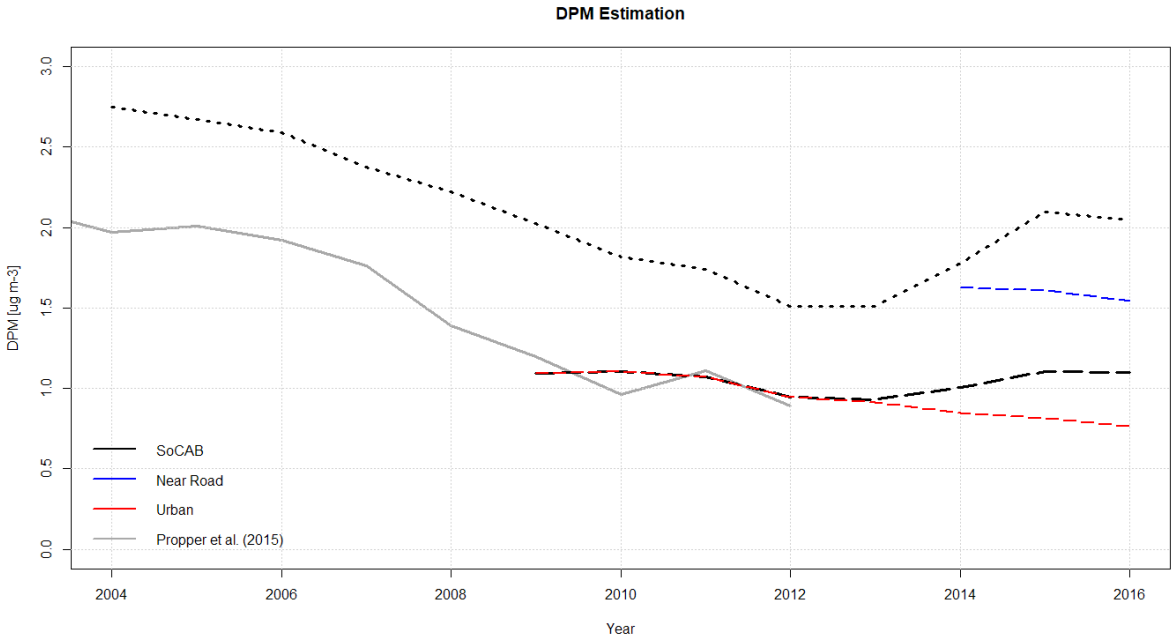
Approximately half of the global budget of nitrogen oxides (NO_X = NO + NO_2) comes from fossil fuel combustion,[45,46] and diesel engines emit more NO_X than do gasoline engines.[47] Dallmann et al.[47] demonstrate that a single average emitting HD truck can show disproportionate NO_X and BC emissions when driving in a sea of gasoline fueled vehicles. Studies from the Port of Oakland reveal that between 2009 and 2013, NO_X levels dropped 53% due to the implementation and use of exhaust gas recirculation (EGR) and SCR technology.[20,48,49] While SCR systems are very effective at lowering NO_X emissions, NO_X is still emitted from exhaust when the SCR is not fully functional, such as at low temperature exhausts (indicated by exhaust pipes operating below minimum temperatures), during cold starts, low load, low speeds, or low urea levels.[20,48,50] However, while NO_X can be used to identify between diesel and gasoline vehicles, CARB notes that NO_X alone is not a unique tracer for diesel PM.[26]

5 Combination of DPM Estimation Methods

While the species in Section 4 do not compare to how well BC represented DPM, NO_X is a potential species to look further in to.

The NO_X family has, on many occasions,[51,52] been represented by NO_2 as a surrogate; and NO_2, as well as BC concentrations, tend to drop sharply on scales of tens to hundreds of meters,[53] making it a good indicator of near-road diesel. A few[31] studies have stressed the benefit of using multiple DPM estimation methods to quantify DPM. With this in mind, CARB's DPM-to-NO_X Ratio method of estimating DPM combined with SCAQMD's DPM-to-EC Ratio may be a combination of methods to further explore. In-depth calculations are provided in Appendix C: DPM Estimation. Figure 4 plots DPM estimates using the combined methods (henceforth referred to as "Combined Alpha Method") at two different subsets of locations within SoCAB. The location subsets are described in detail in Section 6.3.1.

Figure 4: Combined Alpha estimates of DPM compared to reported values from Propper et al.[32] which estimates DPM using the DPM-to-NOx ratio



5.1 Data and Analysis

The figure above compares reported DPM values from Propper et al.[32] (solid gray line)—which estimated DPM using the NO_X-to-BC ratio—to DPM estimates using the Combined Alpha Method.

The dotted and dashed lines represent DPM calculated using different NO_X datasets: the dotted line represents DPM estimates derived from NO_X extracted from CARB's Air Quality and Meteorological Information System[54] (AQMIS)—a set of 27 monitoring locations; the dashed lines are DPM estimates derived from averaged NO_X data from select sites, as described in Section 6.3.1, chosen to potentially represent the Basin as a whole.

The set of Select sites (dashed black line) is subdivided into two smaller location subsets as listed in the figure: near road and urban. Refer to Figure 6 for a map of these locations. Near road locations (blue) are three of the seven select sites that are stationed next to (diesel) truck-traffic-heavy freeways. Monitoring for these sites did not begin[g] until late 2013. Urban locations (red) are the remaining four sites, chosen to represent each county under SCAQMD's jurisdiction.

Analysis of the figure can confirm that SoCAB is not accurately represented, indicated by the dashed black line being, on average, 0.5 $\mu g/m^3$ lower than the dotted black line. It is important to note that the AQMIS data (dotted black) is represented by the highest value of daily averages from the 27 sampling sites—which is oftentimes data from a near road site. Near road monitoring is not represented until 2014, as shown in the figure. Prior to that, the dotted and dashed black lines held a relatively constant difference from each other, but after near road monitoring begins, the difference between the dotted and dashed line approximately doubles, indicating that AQMIS data is more affected by the addition of near road concentrations. This concludes that AQMIS data, as a representation of SoCAB, is reporting higher NO_X values than SoCAB represented by the average of the seven (dashed black), consequently estimating higher DPM values.

Basin-wide NO_X concentrations may be better represented by the average of the seven Select sites (as will be used in Section 6.3.1 later). But, higher NO_X values, such as those from AQMIS, may describe DPM levels in the basin more accurately and will be explored in Section 6.4.

Because α values in the Combined Alpha Method are calculated using 2012 values, DPM estimation for earlier years (2004 to 2008) are likely underestimations due to aggressive

[g] Near road monitoring began in late 2013. Data from 2013 was removed from near road subset (blue dashed) because they do not represent a full year, but was kept in the "SoCAB" dataset (black dashed)

regulation[h] introduced between 2007 and 2009 that lowered DPM emissions leading into 2012. Thus, analysis would be more comprehensive with information from updated speciation or source testing profiles to update the α value. Ultimately, it is difficult to gauge whether this method of combining the DPM-to-EC and NO_X ratio is more accurate than others, especially as estimates from past methods are continuously being modified to report values all over the board, as shown for the MATES III period in Table 1.

Table 1: A comparison of DPM estimations for different methods during the MATES III period shows a wide range of numbers—there is a 95% difference between the largest and smallest estimations

Method	MATES II	MATES III	MATES IV
	4/1998 - 3/1999	4/2004 - 3/2006	7/2012 - 6/2013
EI	3.40	2.16	-
PM2.5	-	3.50	-
CMB	-	3.2 - 3.49	-
DPM/NOx	2.42 - 2.61	1.92 - 2.01	0.89
DPM/EC	-	1.24	0.95
Combined	-	2.58 - 2.75 (AQMIS)	1.5 (AQMIS) 0.94 (Select)

While the accuracy of the Combined Alpha Method is unknown, it is interesting to look further into the NO_X-to-BC correlation to, perhaps, further validate a DPM estimation method incorporating NO_X. This correlation is explored in the following section.

[h] See Appendix A: California Regulations for a detailed timeline

6 Case Study: CA – DE – UK

This section presents a case study comparing SoCAB to the London area to sites in the state of Thüringen, Germany. Southern California and London are notoriously known for their poor air quality, and Germany is home to the recent Volkswagen emissions scandal. It will be interesting to see how to such different cities in vehicular terms compare in emissions and diesel PM. First, an examination of the fleet makeup must be considered, followed by an analysis of the different regulations set upon both regions (US and EU). Finally, the correlation between NO_X and BC in the three areas will be examined and compared.

6.1 Fleet Makeup

To start, the fuel choice for the US and the European Union (EU) are very different. In the EU, diesel vehicles accounted for approximately half of the new passenger car sales in 2015. Likewise, in the 28 EU member states for the same year, 20,000 ktoe (thousand tonnes of oil equivalent) of diesel and 8,000 ktoe of gasoline were consumed, representing approximately 66 and 20% of fuels consumed for transportation purposes, respectively.[55]

Conversely, in California, assuming 90% of light duty cars and 75% of light duty trucks run on gasoline engines, and all medium and heavy-duty vehicles are diesel, 80% of all on-road vehicles consume gasoline, whereas only 20% consume diesel.[56] Consequently, California's gasoline consumption in 2016 was around 7,500,000 barrels and diesel at 2,000,000, equivalent to approximately 1,000 ktoe of gasoline and 270 ktoe of diesel.

While California's consumption of diesel is a mere 27% of its gasoline consumption, the EU's diesel consumption is 2.5 times its consumption of gasoline. Additionally, one should note that with regards to passenger vehicles in California, diesel vehicles account for less than 1% of new cars sold, many of which are German car brands (e.g. VW, Audi, BMW, Mercedes).[57]

6.1.1 Combustion Dynamics (and why NOx is produced)

As noted in Section 4.5, half of the global budget of NO_X originates from fossil fuel combustion. High compression rates, such as in the compression chamber of both gasoline and diesel powered vehicles, are favorable in the formation of NO_X.

Gasoline engines are spark ignition engines, where a mixture of fuel and air is compressed and, as the name suggests, ignited with a spark plug. On the other hand, diesel engines, or

compression-ignition engines, compress air as opposed to fuel. They run fuel-lean, meaning the air-to-fuel ratio is higher—allowing for higher efficiency. Compared to gasoline engines, the compression ratio of a diesel engine is higher, therefore eliminating the need for a spark plug. While diesel engines have higher compression ratios and thus a higher temperature in the combustion chamber, the high efficiency lowers the exhaust temperature. High exhaust temperatures decrease soot (BC) emissions, but higher nitric oxide (NO) emissions are formed, as is the case with gasoline engines.

NO_X abatement technologies, which are described in the next section, are installed to mitigate such emissions, but their effectiveness varies by engine type. For example, exhaust gas recirculation (EGR) systems effectively reduce NO_X emissions from gasoline engines; however, because diesel powered vehicles produce more soot due to lower exhaust temperatures, the recirculated gas is mixed with soot, which clogs the EGR valve.[58] Thus, diesel vehicles emit more BC and NO_X than typical gasoline engines.

The emitted NO rapidly oxidizes to NO_2, which collectively make up NO_X.[59] The emission of NO_X can be adjusted with the timing of the fuel injection at the cost of fuel efficiency[57]—the premise of which the 2015 Volkswagen emissions scandal[i] is based.

6.2 Comparison of Regulations

The Volkswagen scandal, which is described in detail in Appendix D: Emissions Scandal, occurred mainly due to more stringent NO_X regulations in the US, and in particular, California, compared to the EU. NO_X, though not a criteria pollutant, is a precursor for tropospheric ozone (O_3) and PM, exposure to both of which can cause respiratory or cardiovascular-related illnesses. California was affected immensely by the emissions scandal, largely because SoCAB is already heavily burdened by, and over the federal standard 8-hour average for O_3 levels. There were 27,000 affected vehicles in LA and San Bernardino counties combined, which created up to 3,000 additional tons of NO_X, contributing up to an estimated six premature deaths due to the additional emissions.[60]

US and California regulations on passenger vehicles are fuel neutral, whereas the European regulations differ for gasoline and diesel.[57] Furthermore, while US regulations refer to fleet

[i] Also known as Dieselgate or Emissionsgate, the 2015 civil enforcement case against Volkswagen (VW) for cheating in emissions testing. See Appendix D: Emissions Scandal for more information.

averages, EU regulations are based off maximum limits, which is cited[61] to not motivate incentive to introduce cleaner models. Not only that, but the two use different test cycles: the EU tests on the New European Driving Cycle (NEDC)[j], while the US uses the Federal Test Procedure (FTP). The NEDC is a better test for gasoline vehicles as it runs cold starts; however, it is a weaker test for diesel vehicles as it does not test under high load conditions—a mode of driving that emits high NO_X concentrations. The EU also sets higher fuel economy standards, at around 10 mpg more than the US. Table 2 compares US and EU regulations for both HDDV and passenger cars.

Table 2: Comparison of US, CA, and EU regulations for (a) HDDV and (b) passenger cars. Emissions are in (a) g/kWh and (b) g/km. For passenger cars (b), Euro standards are different for gasoline (petrol) and diesel vehicles, indicated by (gasoline) / (diesel) values

(a)	Year	CO	NOx	HC	PM	
Regulation		g/kWh			General	Urban Bus
US & California	1990	20.79	8.05	1.74	0.80	-
	1991	20.79	6.71	1.61	0.34	0.13
	1993	20.79	6.71	1.61	0.34	0.13
	1994	20.79	6.71	1.61	0.13	0.09
	1996	20.79	5.36	1.61	0.13	0.07
	1998	20.79	5.36	1.61	0.13	0.07
	2004	20.79	-	-	0.13	0.07
	2007	20.79	0.27	0.19	0.01	-
	2015	20.79	0.03	0.19	0.01	-
Euro I, ≤ 85 kW	1992	4.5	8	1.1	0.612	-
Euro I, > 85 kW		4.5	8	1.1	0.36	-
Euro II	1996	4	7	1.1	0.25	-
	1998	4	7	1.1	0.15	-
Euro III	2000	2.1	5	0.66	0.1	-
Euro IV	2005	1.5	3.5	0.46	0.02	-
Euro V	2008	1.5	2	0.46	0.02	-
Euro VI	2013	1.5	0.4	0.13	0.01	-
Regulation	Year	g/kWh			General	Urban Bus
		CO	NOx	HC	PM	

[j] The EU will soon switch to the World Light Duty Test Cycle (WLTC) which is more similar to FTP

(b) Stage	Date	NMOG	CO	NOx	PM	HCHO	HC+NOx
		g/km					
LEV I	1990	0.056	2.610	0.186	0.050	0.011	-
Tier 1	1991	0.193	2.610	0.373	-	-	-
LEV II	1998	0.056	2.610	0.044	0.006	0.011	-
LEV III	2012	0.056	2.610	0.044	0.006	0.002	-
Euro 1	1992	-	2.72 / 2.72	-	- / 0.14	-	0.97 / 0.97
Euro 2	1996	-	2.2 / 1	-	- / 0.08	-	0.5 / 0.7
Euro 3	2000	-	2.3 / 0.64	0.15 / 0.5	- / 0.05	-	- / 0.56
Euro 4	2005	-	1 / 0.5	0.08 / 0.25	- / 0.025	-	- / 0.3
Euro 5	2009	-	1 / 0.5	0.16 / 0.18	0.005 / 0.005	-	- / 0.23
Euro 6	2014	-	1 / 0.5	0.16 / 0.18	0.005 / 0.005	-	- / 0.17
Stage	Date	g/km					
		NMOG	CO	NOx	PM	HCHO	HC+NOx

As Table 2 shows, the largest differences are in CO and NO_X, which come from the two nation's historically different approach to regulating emissions:[62] the EU initially prioritized fuel economy before GHG emissions—thus favoring diesel engines which is reflected in their lower CO and higher NO_X standards—and the US vice versa. In both passenger and HDDV cases, regulations on NO_X are growing increasingly stringent, requiring more sophisticated technology to limit emissions. Interestingly, the use of NO_X abatement technologies also exhibit a different pattern between the US and the EU, as shown in Figure 5. Stricter regulation and more widespread implementation has called for application of more effective, or even a combination of NO_X abatement technologies in the US.

6.2.1 SCR

As mentioned in previous sections, SCR systems operate at high temperatures (generally above 190 °C)[57] and can have NO_X reduction rates of up to 90%. The drawback, however, is they are not functional if the engine is not warm enough—such as during cold starts, low loads, short trips, and frequent stops. A solution[k] of 32.5% urea and 67.5% deionized water is

[k] Known as Diesel Exhaust Fluid (DEF) in the US, AdBlue® in Europe, or AUS32 (Aqueous Urea Solution 32.5%)

required for the operation of SCR systems and essentially converts NO_X into N_2 and water, based on the following three equations:[63]

$$8NH_3 + 6NO_2 = 7N_2 + 12H_2O$$

$$4NH_3 + 4NO + O_2 = 4N_2 + 6H_2O$$

$$2NH_3 + NO_2 + NO = 2N_2 + 3H_2O$$

6.2.2 Lean NO_X Trap

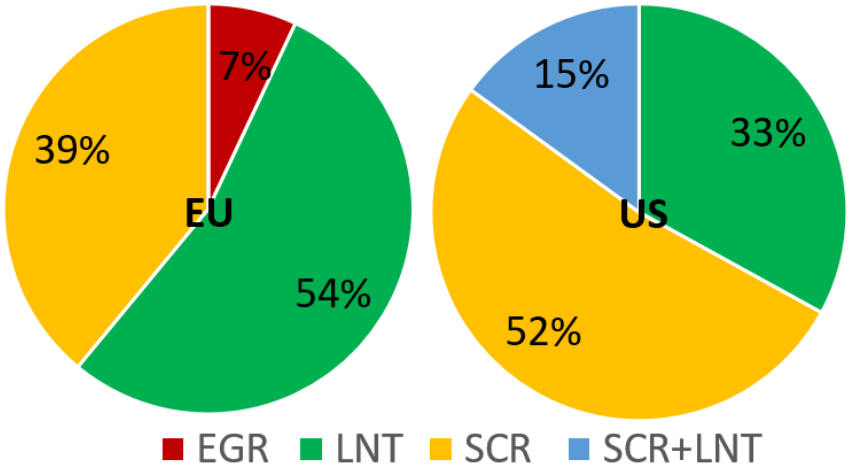
Lean NO_X Traps (LNT), or NO_X absorbers, function—as one might expect—as an absorber of NO_X emissions. The two classifications of LNTs, active and passive, both operate based on the same concept: NO_X is stored on the catalyst washcoat during lean exhaust conditions, and at high temperatures or rich operation, released.[64]

For active LNTs, NO_X is released at a constant frequency under rich air-to-fuel conditions and catalytically converted to nitrogen. However, their performance decreases under high exhaust temperatures, a situation not ideal for HDDV.[64] Passive LNTs absorb NO_X during cold starts and release it under higher temperature conditions. The released NO_X is converted downstream, likely with an SCR system, as indicated by the blue 15% wedge in Figure 5.

6.2.3 Exhaust Gas Recirculation

Exhaust gas recirculation (EGR) systems reduce NO_X emissions by reintroducing (relatively) low temperature and oxygen concentration exhaust gas into combustion chambers. While they operate sufficiently in gasoline powered vehicles, EGRs operating alone in diesel vehicles are problematic, as previously mentioned.

Figure 5: A comparison of EU and US choice of NOx abatement technologies. Data from Nesbit et al.[57]

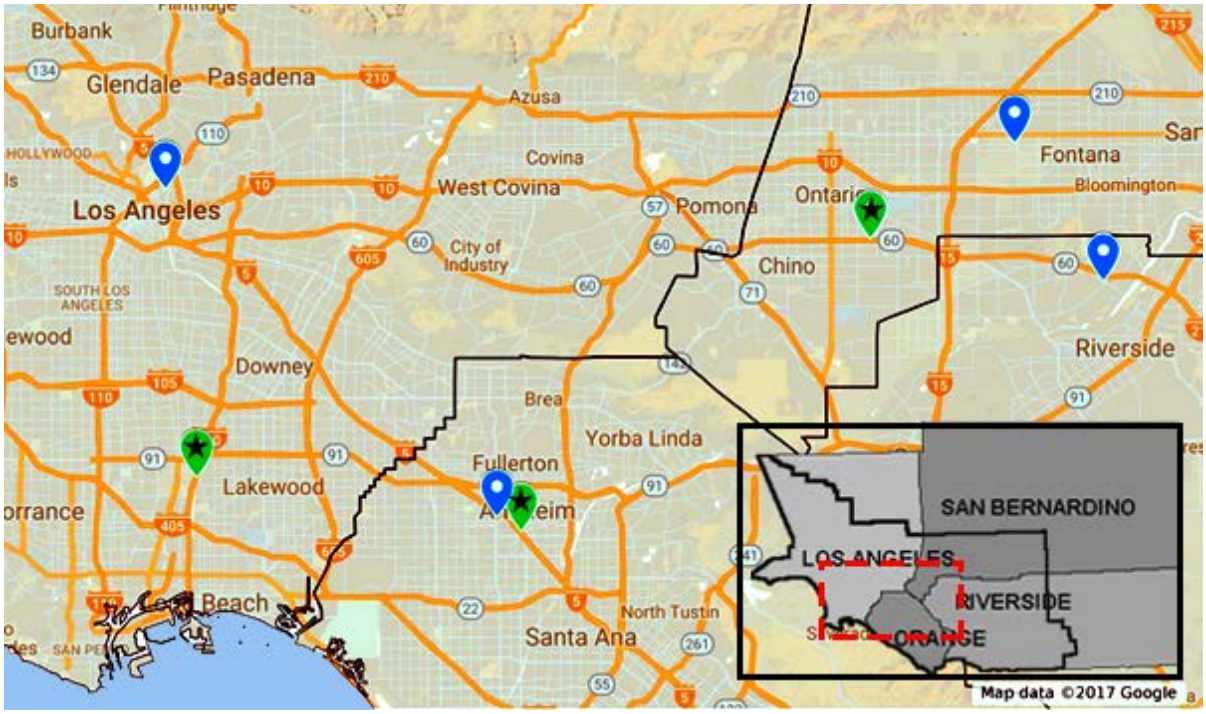


6.3 Monitoring Locations

6.3.1 SoCAB

There are seven monitoring sites within SoCAB of interest to this thesis, as mapped in Figure 6, each of which measure NO_X and BC, among other species.

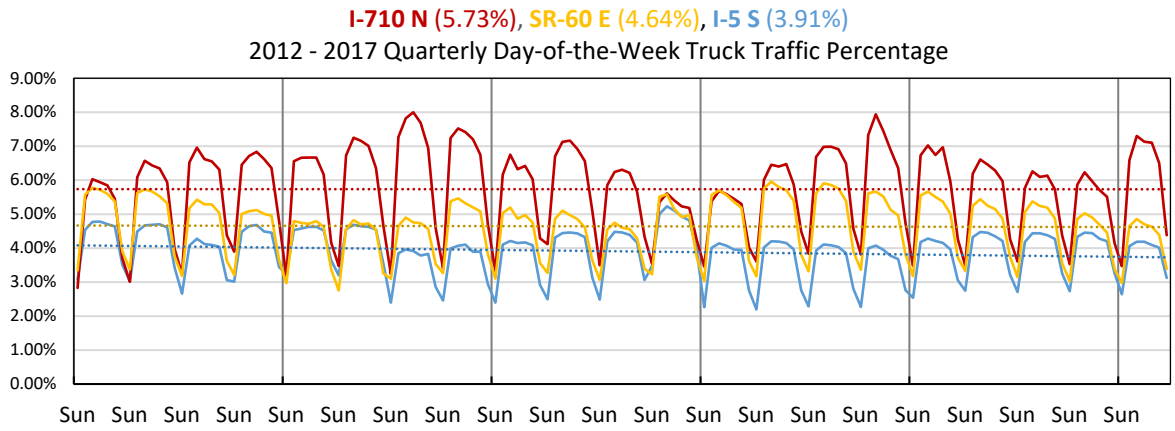
Figure 6: Map of monitoring stations referenced in this paper. Starred green markers indicate near road monitoring stations at freeways with heavy truck traffic: (left to right) I-710, I-5, SR-60. Blue markers indicating urban background sites are stationed in each county: (clockwise from top left) Central Los Angeles (CELA), Fontana (FONT), Rubidoux (RIVR), and Anaheim (ANAH). The dotted box in the inset indicates the map in relation to the rest of SoCAB.



The three near road monitoring stations, indicated by starred green markers, are located next to freeways that experience heavy truck traffic. The leftmost near-road marker located in Long Beach is next to Interstate 710 (I-710), Long Beach Freeway. I-710 runs north-to-south, terminating at POLB, and transports most of the trucks going to and from the Port. Interstate 5 (I-5) (represented by the near-road marker in the middle of Figure 6 in Anaheim) also runs north-to-south, through the entirety of California. The segment of interest to this paper is called the Santa Ana Freeway, beginning at the I-405 junction in southern Orange County and heads northwest to the Orange-Los Angeles County line (post-mile range 95.94 – 116.57). The near-road marker on the right of the map represents the monitoring station for State Route 60 (SR-60), which runs east-to-west, intersecting both I-5 and I-710 in the west and servicing the Inland Empire (i.e. the metropolitan areas of Riverside and San Bernardino Counties) to the east. According to Caltrans,[65] SR-60 is a major truck route, as trucks use I-710 to SR-60 as

a trade corridor to move goods east towards the national and regional distribution centers located in the Inland Empire. Figure 7 compares the average quarterly day-of-the-week vehicle miles traveled (VMT) percentage of the three near road locations showing I-710 has the highest percentage of truck traffic at 5.7%, followed by SR-60 with 4.6%, and I-5 with 3.9%.

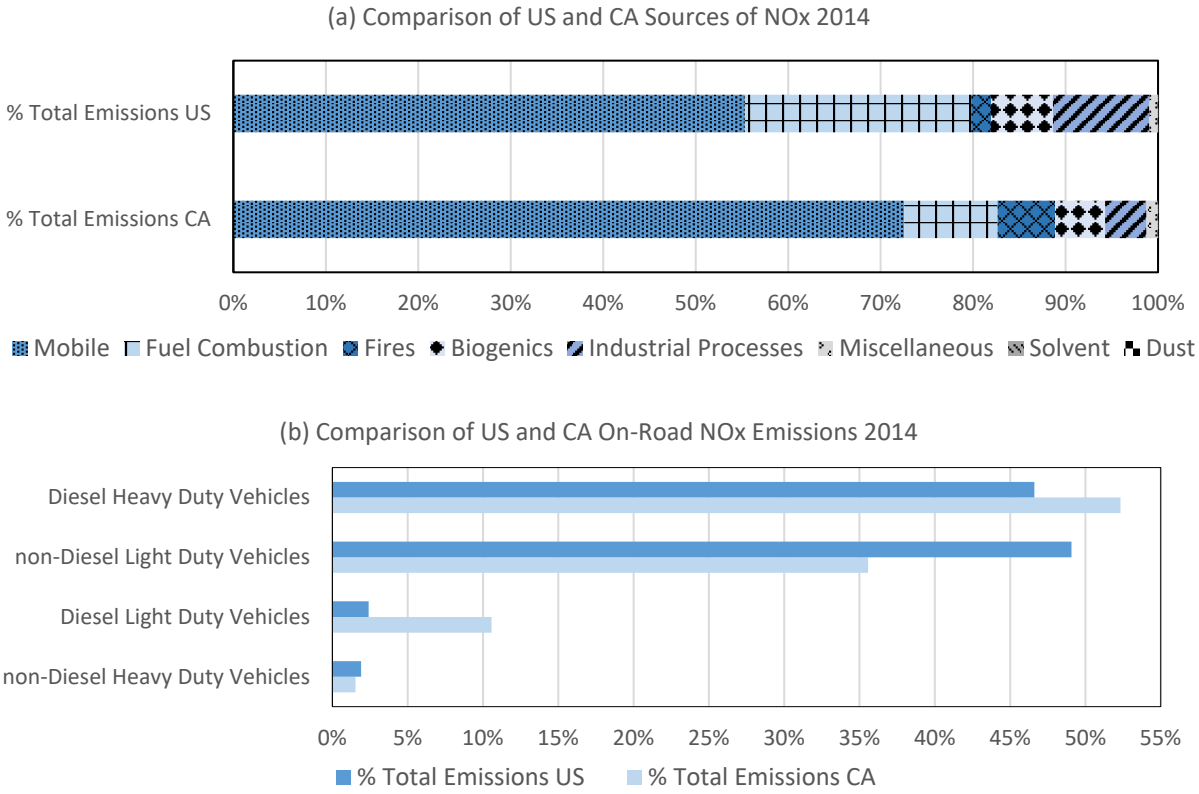
Figure 7: A comparison of the truck traffic percentage (Truck VMT/VMT) from the three near road sites, showing I-710 has the highest percentage, followed by SR-60, then I-5. Data represents day-of-the-week (Sunday – Saturday) averages over every quarter from 2012 Q1 to 2017 Q1. Dotted lines are a linear fit, roughly showing the averages of each site. Vertical gridlines represent a new year. (Data: Caltrans Performance Measurement System (PeMS))



There are four urban stations indicated by blue markers in Figure 6. Central Los Angeles (CELA), on the far left, and Rubidoux (RIVR), on the far right, are part of the NATTS (National Air Toxics Trends Station) Network. The CELA site represents urban mobile source emissions, while RIVR is an inland, downwind site that takes the brunt of LA and urban pollution. The remaining two monitoring stations are Anaheim (ANAH) and Fontana (FONT), in Orange and San Bernardino Counties, represented by the bottom-most and top right blue markers, respectively.

NO_X emission patterns in California are significantly different from those of the rest of the US in that a significantly larger portion of it is from on-road diesel, as shown in Figure 8. This, along with the tendency of NO_2 concentrations declining within a relatively short distance, largely indicates that NO_X measured at near-road locations in California are likely representative of on-road diesel.

Figure 8: Comparison of US and CA NOx emissions patterns. (a) Emissions from mobile sources dominate a larger percentage in California than the rest of the US. (b) HDDV emit more NOx than other on-road vehicles in California. Data from US EPA Air Emissions Sources



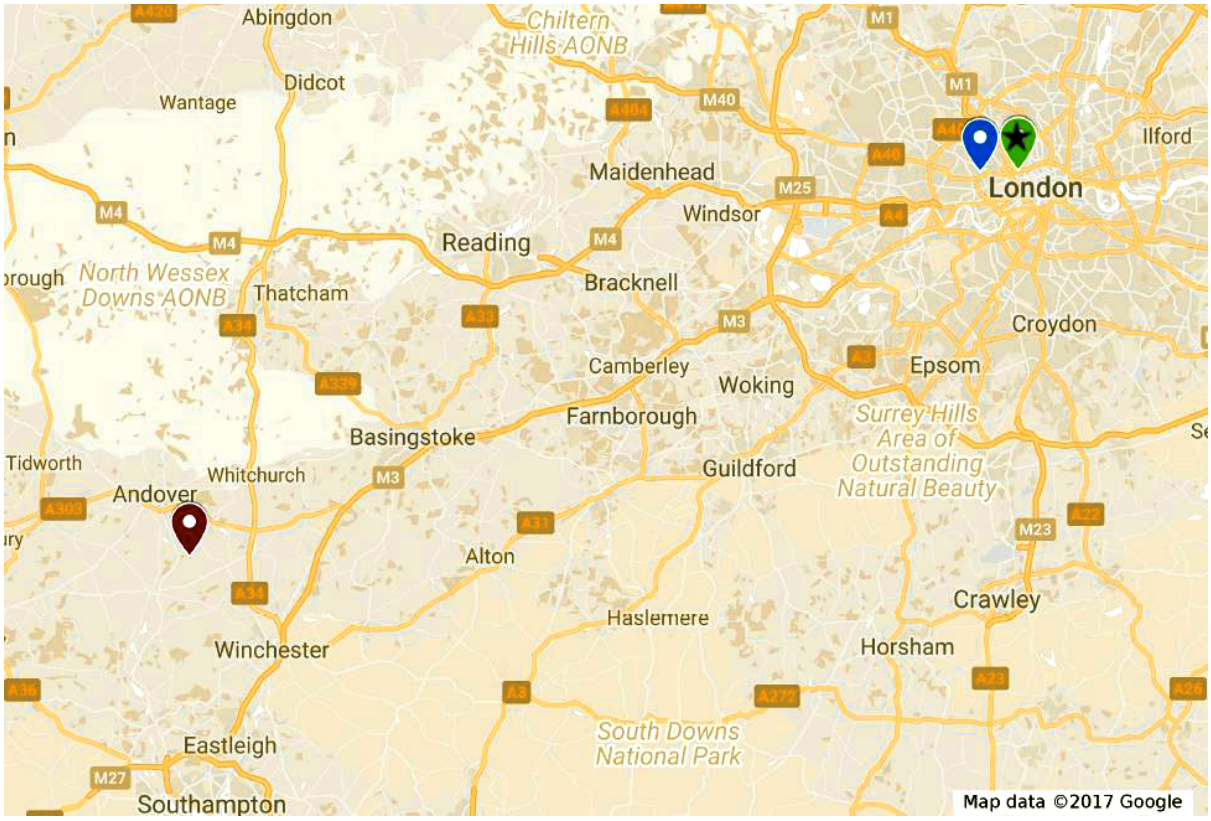
Generally, analysis related to SoCAB will refer to the locations as a group: "NR CA" for near-road locations, and "Urban CA" for the four urban sites.

6.3.2 England, UK

London is famously known for the Great Smog of 1952, when a shroud of smog—soot from coal factories, fireplaces, and diesel-fueled automobiles mixed with fog—covered London for five deadly days.[66] Conditions have gotten better since then, but an increase of automobiles are considerably raising the concentration of NO_2 and small particles.[67] Data obtained for the subsequent analysis is courtesy of UK-AIR (United Kingdom Air Information Resource).

The Marylebone Road monitoring station, set up in 1997, is located in the City of Westminster, opposite from Madame Tussauds. It is one meter away from a frequently congested 6-lane road (A501) that leads to the A40, which accesses the M40 motorway, and the A5 to the M1 motorway, and transports much of the traffic leaving central London to the North.[68] This site represents the near road monitoring station ("UK NR"), as indicated by the starred green marker in Figure 9.

Figure 9: Map of monitoring stations in the UK. Green starred pin represents Marylebone Rd, a near road site; blue marker is for the urban North Kensington site; and Chilbolton Observatory, the rural background site, is located at the maroon marker.



NO_X emissions in London, like in California, are from a number of different sources, such as agriculture, wastewater management, power stations, and motor vehicles. However, in 2011, the City of London[69] estimated 65% of NO_X in the city was from major roads, and 26% from commercial gas, with the remaining 9% split between domestic gas, minor roads, and other sources. With Marylebone Road being a central site next to a major roadway, it is highly likely that the measured NO_X is from vehicular sources.

The London North Kensington station, located on the campus of Sion Manning School, is the site of the "UK Urban" data. The monitoring station is about 5 meters (approximately 20 feet) from St. Charles Square, the nearest road in the residential neighborhood. In Figure 9, it is marked by the blue urban marker.

The Chilbolton Observatory in Hampshire, England was used to represent rural background measurements ("UK Rural"). This rural background station, marked by a maroon pin, is situated in arable farmland, about 200 meters (less than a quarter mile) southeast of Chilbolton Village, 30 km (about 20 mi) north of Southampton.[68] It is likely that many of the NO_X measurements at this location originate from agriculture.

6.3.3 Thüringen, Germany

Germany is home to Volkswagen, among many automakers, whose recent emissions scandal has heightened awareness of NO_X levels in urban areas across the EU. The state of Thüringen, located in an area of dense forest, does not house any automobile manufacturers, but its central location makes it an important hub for transit traffic. The Autobahns A4 and A71 cross just southeast of its capital, Erfurt, each carrying traffic to and from Frankfurt-Dresden to the East and West, and Schweinfurt-Sangerhausen to the North and South, respectively.

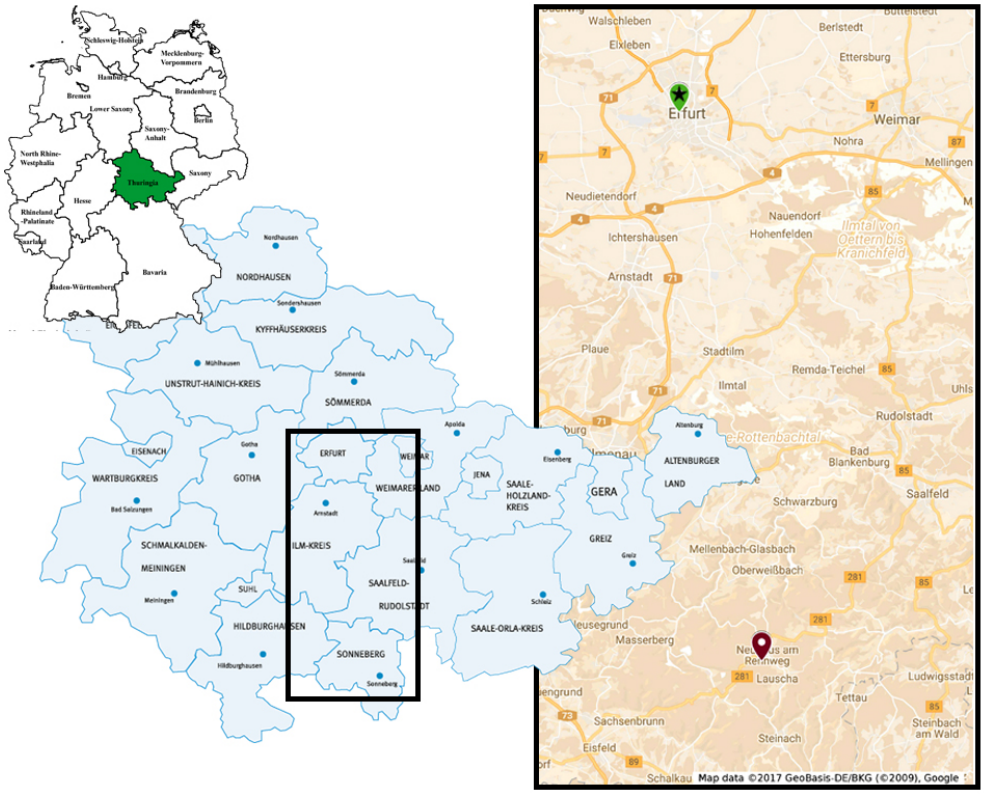
Data from the two monitoring sites related to Germany (denoted by "DE") in this paper are from Thüringer Landesanstalt für Umwelt und Geologie and Umwelt Bundesamt, the German Federal Environmental Agency, and mapped in Figure 10 with the same marker conventions.

The urban traffic monitoring site ("NR DE") is located in the state's capital of Erfurt, on Bergstraße, just west of its intersection with Nordhäuserstraße—a major road that connects Erfurt Altstadt (Old Town) in the south, to the districts of Andreasvorstadt (where the hospital and Universität Erfurt are located), Berliner Platz, Moskauerplatz (where a shopping mall is located), and Gispersleben, leading to the A71 in the north.

NO_X emissions in Germany, as of 2015, were 34% road transport, 25% energy production and distribution, and 11% agriculture.[70] The city of Erfurt has a tradition in farming and horticulture, which is interlinked with its foodstuffs industry of noodle and oil production, as well as a dairy and meat processing factory.[71] Thus, the sources of NO_X at this sampling location may not all be from vehicular traffic—although, with the site's proximity to the road and city center, it is likely that most are.

The rural background monitoring station ("Rural DE") is situated on the outskirts of the town of Neuhaus am Rennweg, 80 km (about 50 mi) south of Erfurt. While the site is relatively remote, located in a 13,000 m^2 clearing surrounded by dense trees, it is also 750 m (about 0.5 mi) from the central bus station, and 3 km (about 1.5 mi) northwest of Glaswerk Ernstthal, a glass container factory that melts up to 600 tons of glass daily.[72] The glass industry, which produces a significant amount of NO_X in the melting process,[73] is a large part of the economy of Neuhaus am Rennweg. Thus, sources of NO_X at this sampling location may not all be rural background—but emissions from the industry are highly regulated, so most likely are.

Figure 10: Map of Germany and Thüringen (left), with monitoring locations in the boxed area marked in green, starred, for near road Bergstr., Erfurt, and in maroon for rural Neuhaus am Rennweg. (Source: thueringen-hilft.de and Google Maps)



6.4 NO_X-to-BC Correlation: Data and Analysis

As mentioned, NO_2 (as a surrogate for NO_X) and BC concentrations tend to sharply decline within tens to hundreds of meters. Thus, those from the same source should show some sort of correlation. The following plots (Figure 11, Figure 12, and Figure 13) show daily averages of near road (NR), urban, and rural BC and NO_X correlations, respectively, for the different locations over a varied range of years. Their corresponding values are listed in Table 3, Table 5, and Table 6.

Assuming constant air density throughout the day and no variations in atmospheric conditions between locations, the correlation between NO_X and BC is clear for the near road locations, as the R^2 values are, on average, well above 0.75. While Erfurt (DE NR) has a similar year-to-year NOx/BC ratio, represented by the slope, the NOx/BC ratio for SoCAB and Marylebone Road vary, with SoCAB's decreasing and Marylebone Road's distinctly increasing every year. The varying slope can be explained by changing BC levels, as shown in Figure 14, which plots monthly averages of NO_X and BC for all sites. With limited data available for SoCAB, it is difficult to definitively state this is the reason, but for Marylebone Road, there is

a stark drop in BC from 2012 to 2017 which can explain the increasing NO_X/BC ratio as NO_X levels do not seem to have a trend.

Figure 11: Comparison of NOx and BC correlation for near road locations. Inset shows a higher resolution view of NR CA.

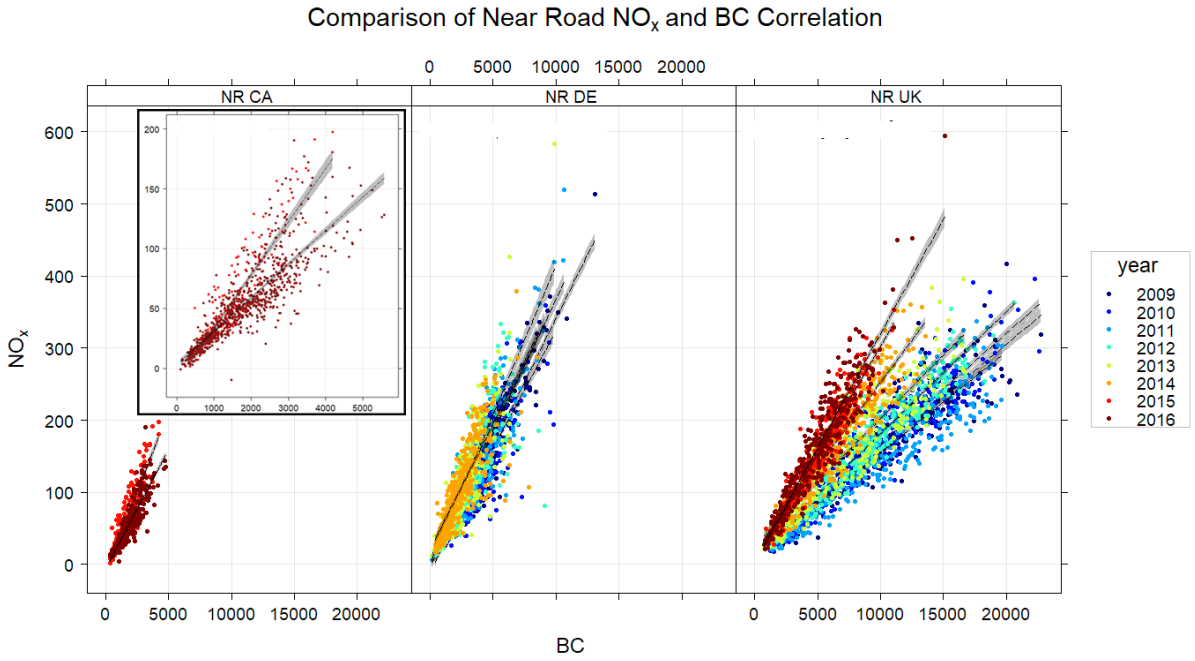


Table 3: Values corresponding to Figure 11 (CA: combination of I-710, SR-60 and I-5; DE: Bergstr in Erfurt, Thüringen; UK: Marylebone Rd in London, England)

Near Road									
Year	CA			DE			UK		
	m	b	R^2	m	b	R^2	m	b	R^2
2009	-	-	-	0.035	-11	0.91	0.015	13	0.85
2010	-	-	-	0.033	-2.1	0.78	0.015	12	0.91
2011	-	-	-	0.037	-3.6	0.83	0.014	15	0.82
2012	-	-	-	0.036	7	0.71	0.017	12	0.92
2013	-	-	-	0.041	1.5	0.74	0.018	26	0.83
2014	-	-	-	0.035	20	0.68	0.023	18	0.87
2015	0.044	-11	0.83	-	-	-	0.03	3.6	0.9
2016	0.028	3	0.71	-	-	-	0.032	2.4	0.88
2017	-	-	-	-	-	-	-	-	-
Year	m	b	R^2	m	b	R^2	m	b	R^2
[NOx] = m [BC] + b									

To compare further, the three near road locations in California were plotted by day of week, separating Sunday from the rest of the week, as Sundays tend to have less truck traffic. Table 4 lists the correlation data for the three near road locations combined ("CA"), I-710, and SR-60 (I-5 had too few data points to be informative). It shows that on days with less HDDT traffic, the correlation between NO_X and BC is significantly weaker.

Table 4: Day of week comparison of California near road locations' NOx to BC correlation. "CA" columns are a combination of I-710, SR-60, and I-5; I-5 is not shown individually because it has too few data points to be informative. Correlation on Sundays is significantly weaker

Near Road									
Weekday	**CA**			**I-710**			**SR-60**		
	m	**b**	**R^2**	**m**	**b**	**R^2**	**m**	**b**	**R^2**
Mon - Sat	0.036	-6.9	0.73	0.043	-10	0.84	0.024	5.7	0.78
Sun	0.023	3.4	0.69	0.028	2	0.79	0.015	9.6	0.56
Weekday	**m**	**b**	**R^2**	**m**	**b**	**R^2**	**m**	**b**	**R^2**
[NOx] = m [BC] + b									

Correlation between NO_X and BC for the two urban sites, below, is also strong. In California, emissions at urban locations are dominated by passenger vehicles, which are gasoline powered as opposed to diesel. As expected, they show a relatively weaker correlation (lower R^2 value) compared to what data is available for the near road sites, which are in much closer proximity to HDDV. In terms of consistency, the NO_X/BC ratio for urban CA has the least amount of variation among all locations.

In London, Marylebone Road (NR) and N. Kensington (urban) both have clear increases in slope, and both have the same average R^2 value (0.87). The NO_X/BC ratios at N. Kensington are significantly higher than those at Marylebone Road, likely due to the difference in BC levels at the two sites as shown in Figure 14, with relatively similar NO_X levels. The rapid decrease of BC at Marylebone Road (and slight decrease at N. Kensington) starting in 2012 is likely due to the Low Emissions Zone (LEZ) regulation—introduced in 2008 and completely phased in in 2012—to discourage heavily polluting diesel vehicles from driving into greater London. Because Marylebone Road sees a higher volume and a larger variety of vehicular traffic than does N. Kensington, a residential area, any decrease in emissions will have a more pronounced effect. The increasing trend in the NO_X/BC ratio shown in both near road and urban UK locations indicates that the correlation is likely based on seasonality—which further

shows that they are from the same source—while the similarities in R^2 values can conclude that the ratio of diesel to gasoline cars is similar.

Figure 12: Comparison of NOx and BC correlation for urban locations. Inset shows a higher resolution view of "Urban CA"

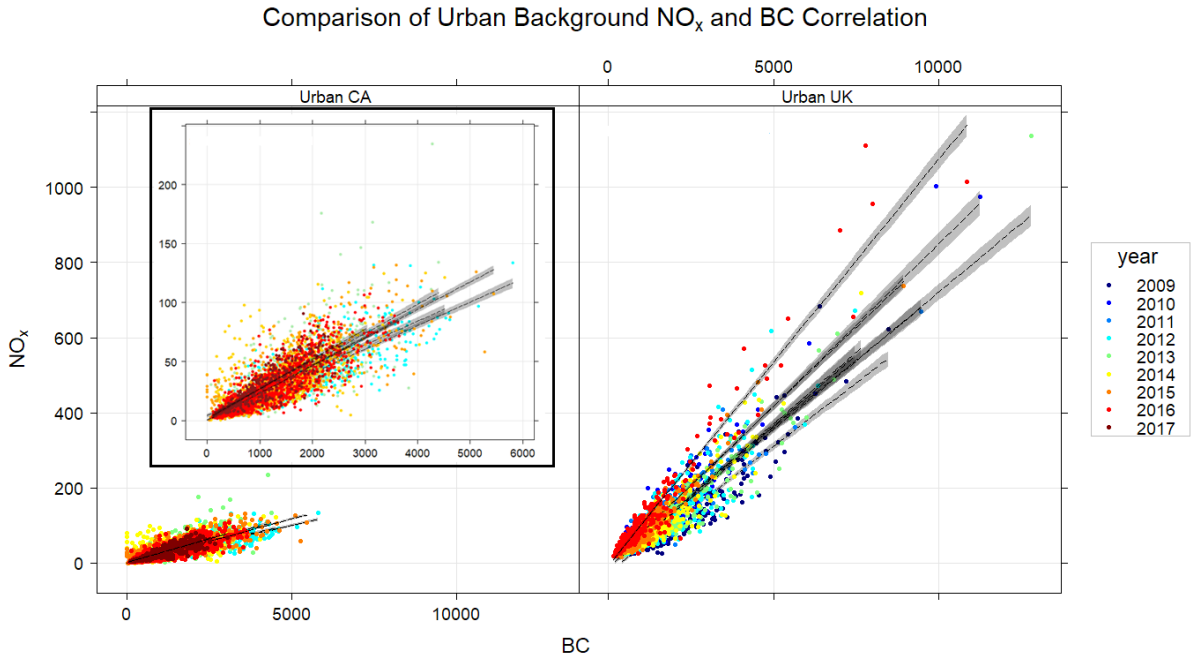


Table 5: Values corresponding to Figure 12 (CA: combination of ANAH, CELA, FONT, and RIVR; UK: N. Kensington, London)

Urban Background						
Year	CA			UK		
	m	b	R^2	m	b	R^2
2009	-	-	-	0.067	-23	0.84
2010	-	-	-	0.086	-12	0.9
2011	-	-	-	0.071	8.7	0.88
2012	0.02	0.28	0.71	0.075	-12	0.76
2013	0.025	-0.5	0.59	0.073	-9.6	0.9
2014	0.02	4.9	0.49	0.076	-11	0.85
2015	0.023	0.36	0.72	0.084	-2.4	0.92
2016	0.023	-0.046	0.71	0.11	-4.9	0.93
2017	0.025	1.6	0.75	-	-	-
Year	m	b	R^2	m	b	R^2
[NOx] = m [BC] + b						

Rural locations do not have similar correlations across the board, as shown below. The lack of correlation shown here indicates that a NO_X and BC correlation is indicative of some level of proximity to vehicular traffic, as rural DE and UK sites show relatively poor R^2 values and small NO_X/BC ratios. NR NO_X values are consistently above 100 ppb at the two EU near road locations, compared to rural, which are consistently lower than 70 ppb with no corresponding high (greater than 1200 ng/m^3) BC reading. While having low NO_X values is not indicative of a rural location (as is the case of NR and Urban CA where NO_X levels are on par with those of Rural UK) having low NO_X values with corresponding low BC values is.

These correlations—and lack thereof—indicate that the presence of NO_X is a good indicator of BC at roadside locations within close proximity to diesel traffic.

Figure 13: Comparison of NOx and BC correlation for rural locations. Inset shows higher resolution view of "Rural DE"

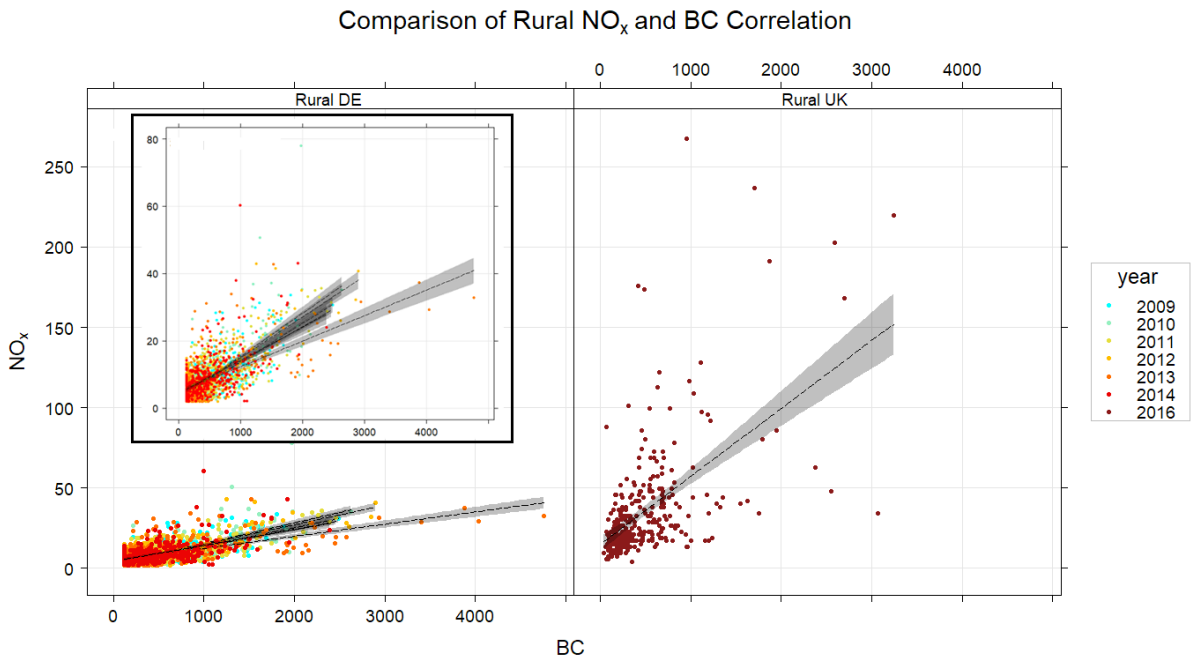
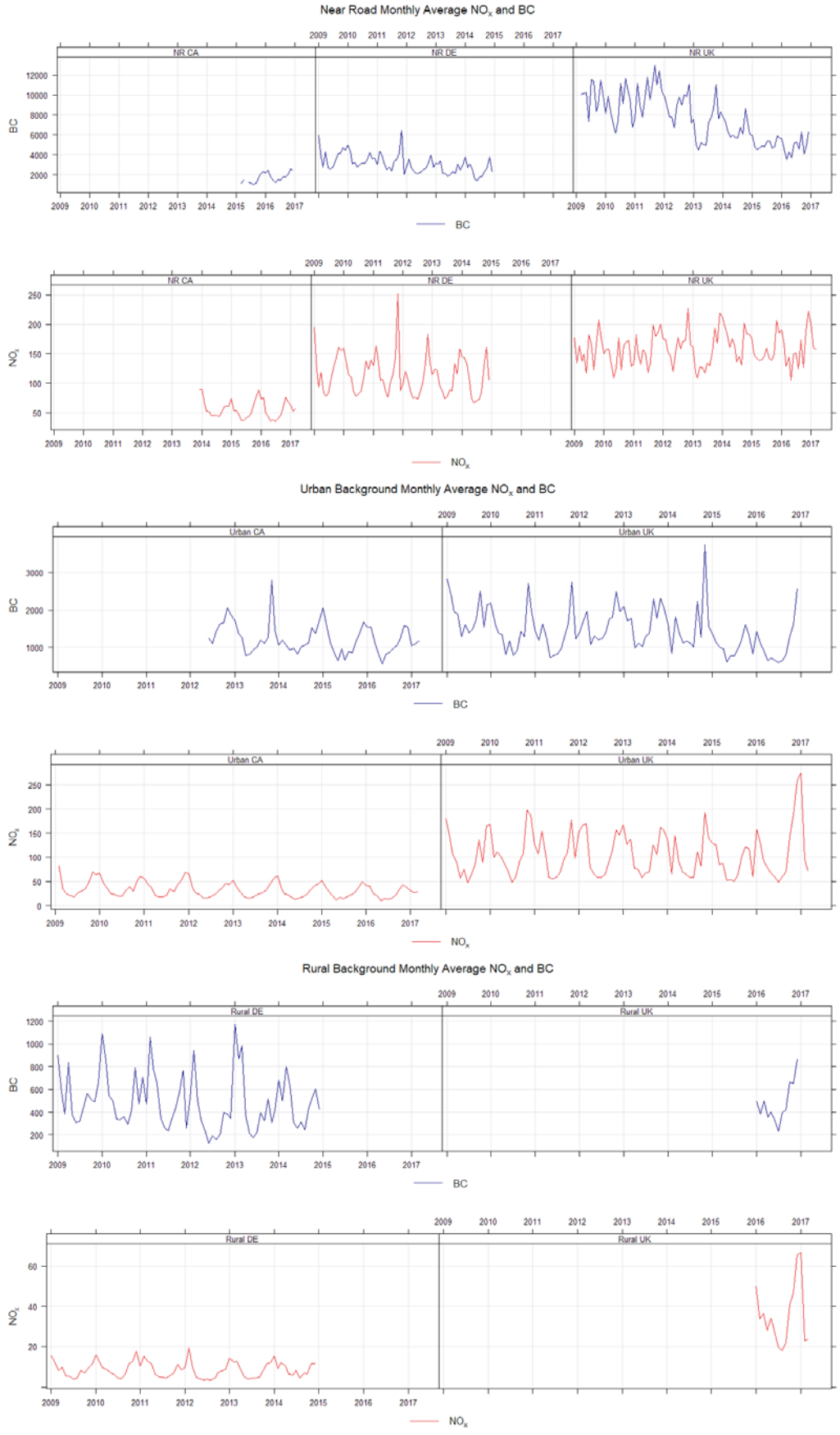


Table 6: Values corresponding to Figure 13 (DE: Neuhaus am Rennweg, Thüringen, Germany; UK: Chilbolton Observatory, Hampshire, England)

Rural Background						
Year	DE			UK		
	m	b	R^2	m	b	R^2
2009	0.011	2.4	0.5	-	-	-
2010	0.013	2.6	0.52	-	-	-
2011	0.011	3.2	0.55	-	-	-
2012	0.012	2.9	0.61	-	-	-
2013	0.0076	4.8	0.45	-	-	-
2014	0.0098	4.4	0.32	-	-	-
2015	-	-	-	-	-	-
2016	-	-	-	0.042	15	0.32
2017	-	-	-	-	-	-
Year	m	b	R^2	m	b	R^2
[NOx] = m [BC] + b						

Figure 14: Comparison of near road (top), urban (middle), and rural (bottom) monthly averaged NOx and BC levels at all locations. Interestingly, UK Urban and Rural NOx levels both increase significantly at the end of 2016.



7 Results and Conclusion

7.1 DPM estimation

DPM is a TAC of increasing importance in a time of rising global temperatures, heightened air quality awareness, and intensified climate-related effects on health. Previous methods of DPM estimation for the MATES III period, namely CMB and $PM_{2.5}$ Ratio, and DPM-to-NO_X Ratio and EI, provided DPM estimates within 10% of each other. Combining the two methods of DPM-to-NO_X Ratio and DPM-to-EC Ratio into the Combined Alpha Method, as discussed in Section 5, estimated DPM to values similar to the EI and CMB methods.

While uncertainty still lingers over whether the Combined Alpha Method of DPM estimation is more accurate than the previous DPM estimation methods, it is and has been highly recommended to use a combination of methods for a more accurate DPM estimation for a more comprehensive approach.

The method presented in this paper can be improved with more updated numbers to further assess for accuracy. To complement the accuracy assessment, correlation between NO_X and BC was examined. BC is currently used as a surrogate for DPM, but declining concentrations in California make for an increasingly less reliable tracer. Thus, the NO_X-to-BC correlation will be telling in whether the Combined Alpha method of DPM estimation can be considered.

7.2 NO_X to BC ratio

A study was performed on three sets of data at the three geographically different locations of SoCAB, London (area), and Thüringen, Germany. NO_X and BC were compared at near road sites for all three locations, urban sites for SoCAB and London, and rural locations in London and Thüringen.

It was discovered that near road and urban sites display a strong NO_X-to-BC correlation, and have an even stronger correlation where diesel powered vehicles are more prominent (such as at the two EU locations compared to CA, and near heavily HDDT trafficked freeways compared to urban areas, especially on days that typically see more truck traffic), whereas rural sites have almost no correlation. Traffic count and vehicle separation data would provide additional insight on this correlation.

For both NO_X and BC, rural sites consistently had the lowest concentration and near road the highest. And, for both species, the average values in SoCAB for both near road and urban were within two standard deviations from the average rural value. This highlights that the correlation does not depend on concentration nor average NO_X/BC values.

7.3 Outlook

Although NO_X alone is not telling of DPM, the NO_X-to-BC correlation indicates that at near road sites, especially those known to have high diesel traffic, NO_X is a good indicator of BC from diesel. This makes DPM estimations using NO_X and another species—such as EC in the Combined Alpha Method—a valid method. Interestingly, recent research[74] has discovered that, regardless of temperature, gasoline vehicles (of Euro 5 standard) emit more carbonaceous aerosols and are more sensitive to cold starts than are modern diesel vehicles equipped with proper technology. This highlights the increasing importance to steer away from BC or EC in future methods of estimating DPM.

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Appendix A: California Regulations

List of key regulations related to cleaner air quality and diesel reduction starting from 2000.

2000	• Regulations introduced to reduce air pollution from transit buses • Comprehensive plan approved to reduce PM emissions from diesel equipment
2001	• Standards passed reducing diesel soot and smog-forming emissions by 90% from new diesel engines, to take into effect in 2007 MY engines
2002	• Lower PM standards adopted o PM_{10} annual average: 20 µg/m^3 o PM_{10} 24h average: 50 µg/m^3 o $PM_{2.5}$ annual average: 12 µg/m^3 o $PM_{2.5}$ 24h average: 25 µg/m^3
2003	• Sulfur content in diesel fuel required to have 95% reduction
2004	• Low sulfur rule adopted for intrastate locomotives and harbor crafts • Idling time for HDDT limited to five minutes of non-essential idling
2005	• Regulation adopted requiring installation of diagnostic systems on all HDDT starting at engine MY 2010, which will reduce NO_X emissions by 100 tons/day • Memorandum of Understanding (MOU) signed with Union Pacific and Burlington Northern Santa Fe Railroads to reduce diesel emissions in and around rail yards
2006	• Diesel fuel switched to new Ultra Low Sulfur Diesel fuel (ULSD) • Comprehensive plan (Prop 1B) developed by POLA, POLB, US EPA, CARB, and SCAQMD to reduce air pollution and associated risks from port- and trade-related activities
2007	• Stricter NO_2 standards adopted o 1h average: 0.18 ppm o Annual average: 0.030 ppm • Statewide Drayage Truck Regulation approved, requiring lower emissions from port and rail bound or originated drayage trucks
2008	• Truck and Bus Rule approved, requiring installation of DPF or engine replacements and retrofits • Clean Truck Program launched at POLA/POLB
2009	• Regulation mandated ocean-going vessels (OGV) within 24 nautical miles of California's coastline to burn cleaner fuel which reduces SO_X and NO_X and DPM • Comprehensive Truck Management Plan approved at Port of Oakland
2010	• Diesel emissions reduced from four of the busiest railyards in the state • Diesel regulations are amended to further protect public health
2011	• Shore power made available for docked ships so idling is no longer needed • Funding assistance offered to truckers and buyers of on- and off-road clean vehicles

Appendix B: EC v. BC

Elemental carbon (EC) and black carbon (BC) have been loosely interchanged in the literature. While they both refer to non-organic carbon, BC is defined[75] as the optical measurement of light absorbing carbon, whereas EC is defined as the refractory measurement from thermal/optical carbon analyzers. Consequently, BC is typically measured with optical, and EC with thermal-optical methods.

At the SCAQMD, BC measurements were carried out using Aethalometers, whereas EC measurements were collected using $PM_{2.5}$ filters and subsequently analyzed in a carbon analyzer using the IMPROVE thermal optical transmittance method.

Aethalometers measure BC in real time, and its function is described elsewhere in the literature. Briefly, suspended particulates in ambient air are trapped in a filter material, creating a deposit. Light projected through the deposit is absorbed by the "black" particles. Measurements are made at regular intervals, and the increasing absorption is proportional to the increasing density of optically absorbing material on the filter, which is proportional to the concentration of material in the air stream. At a pre-set density limit, the filter tape advances and the measurements continue.

Carbon analyzers essentially monitor the evolution of carbon on filters through a series of increasing temperature steps to determine the concentration of EC, OC (organic carbon), and TC (total carbon). Filters sampling for 24 hours tend to provide a sufficient sample mass for analysis. In the analyzer, in an atmosphere of pure He, the temperature is raised to 550 °C – 850 °C, depending on method used. During this first temperature step, OC volatilizes or undergoes pyrolysis. Volatilized OC is measured; pyrolyzed OC produces char, which is light absorbing. This decreases the transmittance/reflectance of the sample (monitored by a He-Ne laser, 633 nm), and will be accounted for in the next step. EC in this stage remains bound on the filter because it requires an oxidant to combust. Next, in a 2% O_2 in He atmosphere, O_2 oxidizes EC and the pyrolyzed OC, consequently increasing the transmittance/reflectance. When the transmittance/reflectance returns to the baseline value, that determines the pyrolyzed OC, and the "split point" is set. From this point on, the EC detected is EC originally on the filter.

There are two different methods used for analysis, and the difference lies in their temperature steps. For the IMPROVE method, the highest temperature in the He phase is 580°C. For the NIOSH method, the highest temperature in the He phase is 850 °C - 870 °C, but light absorbing substances prematurely evolve at this temperature, leading to an inaccurate OC/EC split.

B.1 EC-to-BC Correlation

At the SCAQMD, while the aethalometers produce hourly readings of BC, filter-based EC measurements are taken on a 1-in-6 day basis—a mere 60 samples a year; thus, in an effort to both cut costs and to have a more comprehensive set of data, a study was conducted to examine the correlation between EC and BC. If readings and measurements were highly correlated, EC measurements could be largely replaced by BC for short term study purposes.

In the study conducted, EC to BC readings were, for the most part, correlated. Anaheim had a near 1:1 ratio with an R^2 value of 0.84. Central LA, Fontana, and Rubidoux displayed at least a slope of 0.8 with R^2 values around 0.7. See Figure B1. This data was from MATES IV, spanning a one year period from July 2012 to July 2013.

However, after repeating the correlation with additional data, spanning July 2012 through the end of 2015, the correlation was not so great. Table B1 lists the slopes and R^2 values showing that while the slopes are similar to those shown in Figure B1, the R^2 values are much lower, in the 0.5 range.

One explanation for the low R^2 values may be explained in Figure B2. The EC and BC readings tend to match one another until August 2015 when the EC values take a dip and the BC readings increase, diverging from one another. The bottom graph of Figure B2 also indicates that the percent difference between the two readings jump significantly during that period. When the August – December 2015 period is removed, the R^2 values increase slightly, as indicated by the “7/2012 – 7/2015” rows in Table B1.

However, as a more conclusive explanation for the divergence has not been proven yet, BC measurements will not be the only measure of carbon in SoCAB for the upcoming MATES V study.

Figure B1: EC-to-BC correlation from July 2012 - July 2013. Circled station names are continuous monitoring stations, whose measurements are continued after the MATES period. They are analyzed in a following study shown in Figure B2. In Table B1, Inland Valley SB corresponds to Fontana, and Rubidoux to Riverside.

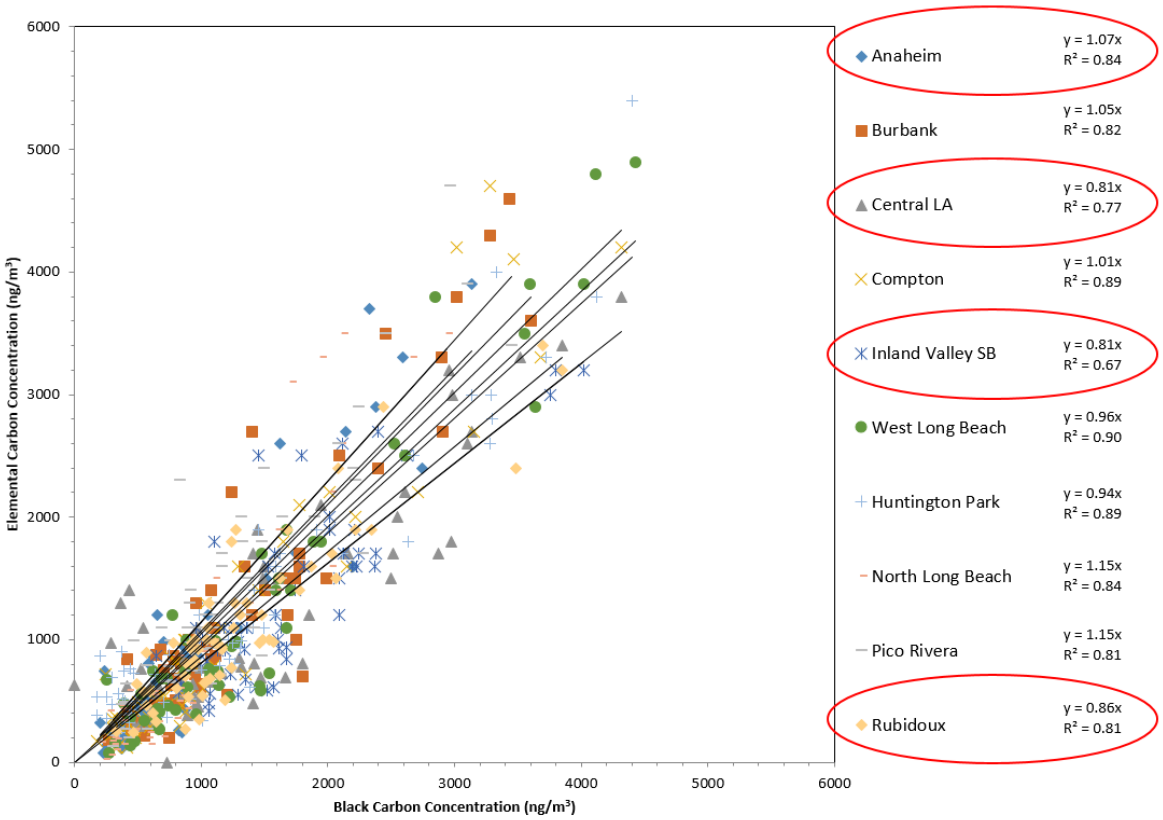
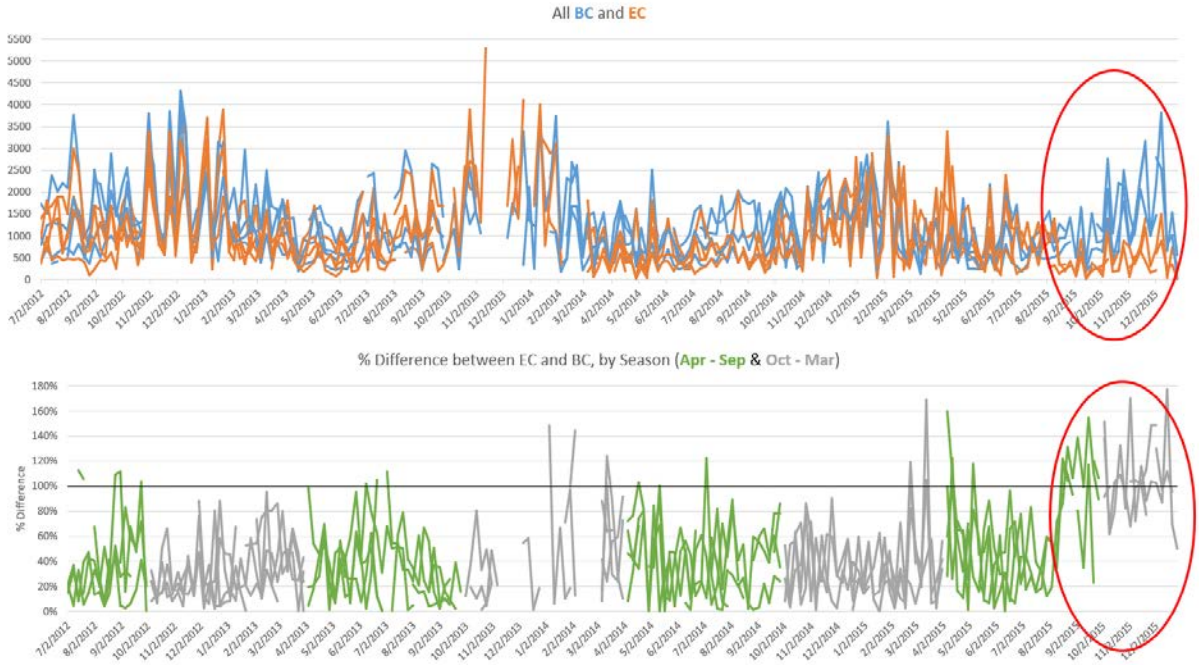


Table B1: Comparison of slopes and R^2 values of the four continuous monitoring stations at different time periods. Removing August to December 2015 improves the correlation slightly.

Station Name	Time Frame	m	R^2
ANAH	MATES IV	1.07	0.84
	7/2012 - 12/2015	0.91	0.59
	7/2012 - 7/2015	1.09	0.77
CELA	MATES IV	0.81	0.77
	7/2012 - 12/2015	0.80	0.50
	7/2012 - 7/2015	0.85	0.56
FONT	MATES IV	0.81	0.67
	7/2012 - 12/2015	0.82	0.58
	7/2012 - 7/2015	0.83	0.60
RIVR	MATES IV	0.86	0.81
	7/2012 - 12/2015	0.84	0.57
	7/2012 - 7/2015	0.89	0.65

Figure B2: Comparison of EC and BC values over time. Values tend to match until 8/2015 when they start to diverge from each other. The top graph is a time series of all four sites' measured EC (orange) and BC (blue) values. The bottom graph plots the percent difference between the two values, color coded by two loosely defined seasons, representative of the climate of the Basin, in hopes to attribute the diversion to season, which is not the case.



Appendix C: DPM Estimation

This section combines CARB's DPM-to- NO_X Ratio method and SCAQMD's DPM-to-EC Ratio method to estimate DPM, essentially taking the DPM estimate calculated with the DPM-to-EC Ratio method and plugging it in to the DPM term in α in the DPM-to- NO_X Ratio method; because after all, the DPM term in α was also an estimate.

The DPM-to-NO_X Ratio method is:

$$DPM_{annual\ average} = \alpha\, NO_{X\ annual\ average}$$

where

$$\alpha = \frac{DPM}{NO_{X\ total\ ambient}}$$

DPM in α, above, is determined using the DPM-to-EC Ratio method, as follows:

$$DPM = \frac{PM_{diesel}}{EC_{diesel\ speciation\ profiles}} \times \frac{EC_{diesel}}{EC_{total\ measured\ basin-wide\ average}}$$

Using this approach, DPM can be estimated as listed in Figure C1. The colored location headers correspond to the line colors in Figure 4, showing calculated DPM estimations. AQMIS DPM values are calculated with NO_x data from all 27 monitoring stations on the AQMIS database; "Select Sites" DPM values are calculated with seven, three, or four monitoring stations' data, depending on the location subset.

To calculate α, the DPM estimate value from MATES IV (0.95 µg/m^3) was divided by 32.8 ppb, the average 2012 NO_X concentration from the Select Sites—because those NO_X values are more representative of the Basin—to get to get 0.029. Average annual NO_X, multiplied by α to calculate DPM, is the average of NO_X from each respective year's respective database.

Figure C1: Estimates of DPM using the combined methods of DPM-to-NOx Ratio and DPM-to-EC Ratio, compared to DPM estimates reported in Propper et al.

Year	α	AQMIS		Select Sites						Propper et al.		% Difference (Propper et al. and...)	
		SoCAB		SoCAB		Near Road		Urban		SoCAB			
		NOx	DPM	NOx	DPM	NOx	DPM	NOx	DPM	α	DPM	AQMIS	Select
2004		95.091	2.750	-	-	-	-	-	-	0.0216	1.97	33.0%	-
2005		92.348	2.670	-	-	-	-	-	-	0.0228	2.01	28.2%	-
2006		89.495	2.588	-	-	-	-	-	-	0.0227	1.92	29.6%	-
2007		82.244	2.378	-	-	-	-	-	-	0.0220	1.76	29.9%	-
2008		76.873	2.223	-	-	-	-	-	-	0.0214	1.39	46.1%	-
2009		70.010	2.024	37.914	1.096	-	-	37.914	1.096	0.0193	1.20	51.1%	9.0%
2010	0.02892	62.804	1.816	38.215	1.105	-	-	38.215	1.105	0.0180	0.96	61.7%	14.0%
2011		60.150	1.739	37.101	1.073	-	-	37.101	1.073	0.0187	1.11	44.2%	3.4%
2012		52.148	1.508	32.773	0.948	-	-	32.773	0.948	0.0180	0.89	51.5%	6.3%
2013		52.164	1.508	32.181	0.931	-	-	31.616	0.914	-	-	-	-
2014		61.464	1.777	34.884	1.009	56.146	1.624	29.382	0.850	-	-	-	-
2015		72.508	2.097	38.300	1.108	55.677	1.610	28.250	0.817	-	-	-	-
2016		70.840	2.048	37.936	1.097	53.416	1.545	26.425	0.764	-	-	-	-

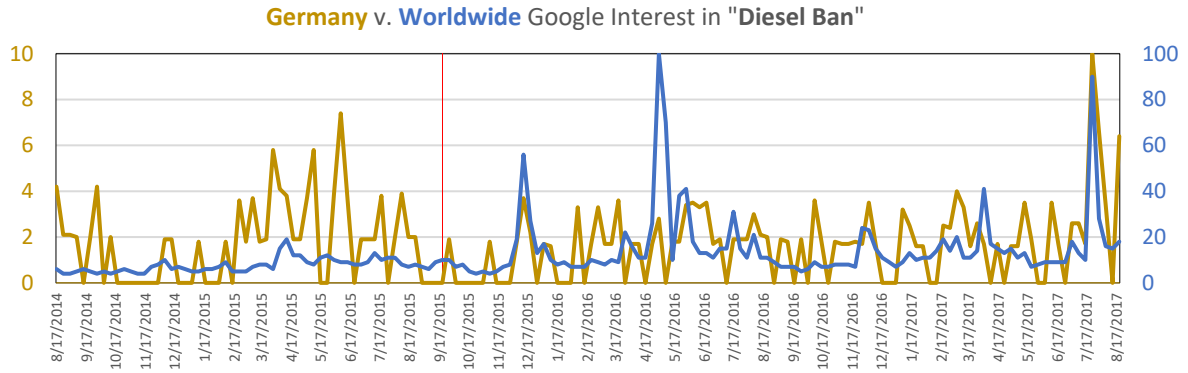
Appendix D: Emissions Scandal

The 2015 Volkswagen emissions scandal refers to the difference in emissions from model year 2009 – 2015 Volkswagen diesel cars during emissions testing and under normal driving conditions. The Volkswagen group had installed a “defeat device”—prohibited under the Clean Air Act—to affected vehicles, which was programmed to activate different emissions controls under laboratory emissions testing conditions so they would meet the stricter emissions standards of the State of California. But, during in real-world driving conditions, emissions of up to 40 times more pollution than standards allow were recorded.[76]

The software targeted components that reduce NO_X emissions, such as catalytic converters, EGR components, and the NO_X trap—all of which require the use of more fuel (and thus decrease vehicular performance in torque and acceleration) to function.[76]

This scandal initiated efforts on many levels to reevaluate NO_X levels and subsequent diesel bans in cities, which is significant considering Germany is home to many automakers. In Stuttgart, home to Porsche and Mercedes-Benz, diesel cars that do not meet the latest emissions standards will be banned on days of heavy pollution.[77] While a court ruling has proposed a complete diesel ban in Stuttgart, adding that software retrofits were insufficient, automakers support using incentives to promote sales of lower emissions vehicles. These ongoing events are rallying the mayors of cities such as Paris, Madrid, Mexico City, and Athens to propose a city-center diesel ban by 2025 in their own respective cities; while French and British governments mention a phase out of new gasoline and diesel vehicular sales by 2040.[77] Figure D1 shows Google Trends data for search interest in “diesel ban”. Germany’s interest was 10% of the worldwide interest, but both interests have piqued in recent months.

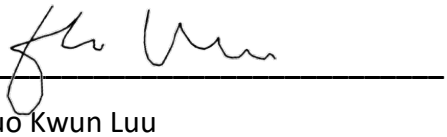
Figure D1: Comparison of Google search interest for "Diesel Ban". German interest is 10% of worldwide interest. Vertical red line is 9/18/2015, the day the scandal surfaced (9/18/2015). Data from Google Trends.



Declaration of Academic Honesty

I hereby confirm that the presented thesis work has been done independently and used only the sources and resources as listed. This thesis has not previously been submitted elsewhere for purposes of assessment.

München, 11-Oktober 2017



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