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Quantifying On-Road Emissions from Gasoline-Powered Motor Vehicles: Accounting for the Presence of Medium- and Heavy-Duty Diesel Trucks

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Supporting Information

ABSTRACT: Vehicle emissions of nitrogen oxides (NO_x), carbon monoxide (CO), fine particulate matter ($PM_{2.5}$), organic aerosol (OA), and black carbon (BC) were measured at the Caldecott tunnel in the San Francisco Bay Area. Measurements were made in bore 2 of the tunnel, where light-duty (LD) vehicles accounted for >99% of total traffic and heavy-duty trucks were not allowed. Prior emission studies conducted in North America have often assumed that route- or weekend-specific prohibitions on heavy-duty truck traffic imply that diesel contributions to pollutant concentrations measured in on-road settings can be neglected. However, as light-duty vehicle emissions have declined, this assumption can lead to biased results, especially for pollutants such as NO_x, OA, and BC, for which diesel-engine emission rates are high compared to corresponding values for gasoline engines. In this study, diesel vehicles (mostly medium-duty delivery trucks with two axles and six tires) accounted for <1% of all vehicles observed in the tunnel but were nevertheless responsible for (18 ± 3)%, (22 ± 6)%, and (45 ± 8)% of measured NO_x, OA, and BC concentrations. Fleet-average OA and BC emission factors for light-duty vehicles are, respectively, 10 and 50 times lower than for heavy-duty diesel trucks. Using measured emission factors from this study and publicly available data on taxable fuel sales, as of 2010, LD gasoline vehicles were estimated to be responsible for 85%, 18%, 18%, and 6% of emissions of CO, NO_x, OA, and BC, respectively, from on-road motor vehicles in the United States.

INTRODUCTION

On-road gasoline- and diesel-powered motor vehicles are major emission sources of nitrogen oxides (NO_x) and fine particulate matter ($PM_{2.5}$).[1] Light-duty (LD) gasoline vehicles are also the largest anthropogenic source of carbon monoxide (CO) emissions in the United States.[2] Gasoline- and diesel-engine contributions to total on-road vehicle emissions are functions of traffic volumes and vehicle exhaust emission rates, which are both subject to variations in space and time. An accurate understanding of the relative emissions contributions from these sources is needed for assessing their effects on air quality and human health. However, large uncertainties remain in current inventories of on-road vehicle emissions, particularly in the case of particulate black carbon (BC) and primary organic aerosol (OA).

A recent assessment of mobile sources of air pollution indicated that diesel engines are the dominant on-road source of primary particulate matter emissions.[1] Similarly, an emissions inventory for California estimated that 76% and 54% of BC and particulate organic carbon (OC), respectively, emitted by on-road sources come from diesel engines.[3] However, a broader reading of the relevant literature provides widely divergent findings about the relative importance of exhaust from gasoline versus diesel engines as sources of $PM_{2.5}$, BC, and OA emissions. For example, Gertler[4] concluded that gasoline vehicles are the dominant source of on-road PM emissions, based on emission factors measured in a tunnel study. Likewise, recent near-roadway measurements of vehicle emissions reported a significantly higher BC emission factor for LD vehicles than has been found in other field studies and suggested that current inventories might greatly underestimate BC emissions from gasoline engines.[5] There are also major disagreements about the relative importance of contributions from gasoline and diesel vehicles to ambient fine-particle concentrations, as inferred from receptor modeling studies.[6,7]

The sparsity of data on exhaust PM emissions from motor vehicles contributes to the uncertainty in current assessments of the relative importance of on-road sources to the overall burden of air pollution. Dynamometer testing is limited by the small numbers of vehicles that can be tested and by test cycles that do not fully represent real-world driving conditions.[8] Roadside

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remote-sensing techniques have provided snapshot measurements of hydrocarbon, NO_x, and CO emission factors for many thousands of in-use vehicles. However, this approach is more limited in its ability to characterize exhaust PM emissions.[9−12] Vehicle-chase and plume-capture methods have been used to measure BC and OA emission factors for individual heavy-duty diesel vehicles.[13−16] The application of similar methods to quantify LD vehicle emissions has been limited.[17] To date, in-use emissions data for LD vehicles have been derived mainly from tunnel and near-road studies. In such studies, emission factors are measured directly on roadways where heavy-duty (HD) diesel trucks are not allowed[18−20] or through the use of various statistical methods to separate or extrapolate the LD vehicle contributions to overall pollutant loadings measured on mixed-use roadways.[5,21,22] We plan to show that the presence of diesel trucks, even at seemingly low levels, affects inferred LD vehicle emission rates significantly, particularly for pollutants for which emission rates from diesel engines are much higher than those from gasoline engines.[21,23]

The overall objective of this study was to determine current emission rates of gaseous and particulate pollutants from on-road light-duty vehicles, accounting for pollutant contributions due to diesel trucks that were present to a small degree in the on-road setting where vehicle emissions were measured. Past studies of exhaust PM emissions at the Caldecott tunnel in the San Francisco Bay Area focused on separating out gasoline-engine contributions to pollutant concentrations measured in a mixed-traffic bore of the tunnel with larger numbers of trucks present in the mix (~5% of total traffic). In contrast, in the present study, we relied on emission factors for HD diesel trucks inferred from captures of exhaust plumes for hundreds of individual trucks, reported previously by Dallmann et al.[15] Apportionment techniques were used in this study to determine emission factors for LD gasoline vehicles by separating out diesel contributions to pollutant concentrations in bore 2 of the tunnel, where the diesel truck fraction was much lower. A further objective of this study was to map, in a general way, the relative contributions of gasoline and diesel engines to overall on-road vehicle emissions, as functions of fuel sales and emission factor ratios.

■ METHODS

Field Measurement Site. Motor vehicle emissions were measured in July 2010 at the Caldecott tunnel, on highway 24, in Oakland, CA. This site has been used extensively for vehicle emissions research.[18,24,25] The tunnel is 1 km long and consists of three two-lane traffic bores. This study focused on measurements made in bore 2 (middle bore) during the commuter peak period from 4 to 6 p.m. on eight weekdays (July 6−9, July 12−15) when vehicles traveled eastbound on an uphill roadway grade of 4%. Although this bore is nominally reserved for light-duty vehicles, small numbers of medium- and heavy-duty trucks also use it.

Measurement Methods. Gas and particle-phase pollutant concentrations were measured simultaneously in bore 2 near the tunnel exit and in ambient air outside of the tunnel. Instruments were positioned either in the fan building at the east end of the tunnel or in a tunnel ventilation duct located directly above vehicle traffic. For tunnel air measurements, sampling inlets extended through a ventilation aperture directly into the traffic bore approximately 50 m prior to the tunnel exit at the east end. Ambient measurements were made using sampling lines extending ~0.5 m through an open window in the fan building. A more detailed description of sampling and analytical methods used in this study is included in the Supporting Information. Briefly, gas-phase measurements were made using online analyzers for NO_x, CO, and CO_2. The tunnel NO_x and CO_2 analyzers were operated at 1-s time resolution, whereas tunnel CO and ambient data were averaged to provide 1-h integrated measurements. For each 2-h sampling period, integrated filter samples were collected to characterize $PM_{2.5}$ mass and particulate carbon concentrations in tunnel and ambient air. $PM_{2.5}$ mass concentrations were calculated from gravimetric analysis of Teflon filter samples, and BC and OC concentrations were derived from thermal-optical analysis of quartz filter samples. OC concentrations were multiplied by a factor of 1.25 to evaluate OA concentrations.[26] Additional high-time-resolution (1-s) measurements of tunnel BC concentrations were made using an aethalometer.

Manual traffic counts were collected to characterize vehicle activity during each 2-h sampling period. Vehicles were counted for 6 min of each 10-min interval every hour, and these counts were aggregated to obtain hourly averages. Vehicles were counted according to the number of axles and the number of tires on the rear axle and were classified in three separate categories: light-duty (LD; two-axle/four-tire), medium-duty (MD; two-axle/six-tire), and heavy-duty (HD; three or more axles). Light-duty vehicles consist of passenger cars and light-duty trucks, which, in California, are mostly powered by gasoline engines. Heavy-duty vehicles encompass trucks used for goods movement (e.g., tractor−trailer combinations), construction (e.g., cement mixers and dump trucks), and other heavy-duty applications (e.g., trash hauling) and are almost exclusively powered by diesel engines.[27] Medium-duty vehicles include both gasoline and diesel-powered trucks. Examples of MD vehicles observed at the Caldecott tunnel include delivery trucks, flat-bed trucks, and some large pick-up trucks with four tires on the rear axle. Vehicle counts were supplemented with a video recording of traffic on July 12. The video was analyzed to determine the times at which individual MD and HD trucks passed beneath tunnel sampling inlets. This analysis supported efforts (discussed below) to quantify contributions from these vehicles to measured pollutant concentrations in bore 2 of the tunnel.

Data Analysis. In prior studies at the Caldecott tunnel, fleet-average emission factors for LD vehicles were calculated using a carbon-balance method[18]

$$EF_P = \left(\frac{\Delta[P]}{\Delta[CO_2] + \Delta[CO]} \right) w_g \quad (1)$$

where EF_P is the fuel-specific emission factor for pollutant P [in units of g of P (kg of fuel burned)$^{-1}$]; $\Delta[P]$ (μg m^{-3}), $\Delta[CO_2]$ (mg of C m^{-3}), and $\Delta[CO]$ (mg of C m^{-3}) are background-subtracted (tunnel minus ambient) mass concentrations; and w_g is the carbon weight fraction of gasoline. Emission factors calculated using eq 1 represent average values for large numbers of vehicles passing through the tunnel in a given sampling period. Traffic in bore 2 of the tunnel consists almost entirely of LD vehicles (>99% of total vehicle counts during the 4−6 p.m. commute period), so previous studies used eq 1 and pollutant measurements from bore 2 of the tunnel to determine emission factors for LD vehicles directly. An implicit assumption was that small numbers of MD and HD trucks driving through bore 2 did not contribute significantly to measured pollutant concentrations. If pollutant emission factors for LD vehicles and diesel trucks are comparable, then this assumption is valid. However, as LD vehicle emissions have decreased over time, emission factors for some species (e.g., $PM_{2.5}$, BC, NO_x) are now an order of magnitude higher for diesel trucks relative to LD gasoline vehicles.[18] In such cases, the presence of even small numbers of MD and HD trucks in bore 2 of the tunnel might bias the determination of LD vehicle emission factors.

Results from concurrent measurements of emission factors from individual diesel trucks at the Caldecott tunnel[15] were used in this study for the apportionment of measured pollutant concentrations to determine contributions from LD gasoline vehicles and MD/HD diesel trucks. This approach explicitly accounts for the presence of diesel trucks in bore 2 of the tunnel and more accurately characterizes emission factors for LD vehicles. The data analysis methods applied here follow previous efforts to apportion emissions in mixed-use traffic lanes with much higher diesel truck fractions.[5,18] In past studies at the Caldecott tunnel,[18,25] apportionment efforts focused on deducing the diesel contribution to pollutant emissions in a mixed traffic bore of the tunnel, for midday sampling periods when diesel trucks were more abundant. Here, the goal was to determine contributions to pollution in bore 2 of the tunnel, for which MD/HD vehicle contributions were previously neglected. The relative contribution of gasoline vehicles ($\Delta[CO_2]_g$) to measured tunnel CO_2 concentrations was estimated using traffic count data and fuel and vehicle properties

$$\frac{\Delta[CO_2]_g}{\Delta[CO_2]} = \frac{\rho_g w_g[f_{LD}U_{LD} + f_{MD}(1-F)U_{MD,g}]}{\rho_g w_g[f_{LD}U_{LD} + f_{MD}(1-F)U_{MD,g}] + \rho_d w_d(f_{HD}U_{HD} + f_{MD}FU_{MD,d})} \quad (2)$$

where ρ and w are the fuel density and carbon weight fraction, respectively, for gasoline and diesel fuel (subscripts g and d, respectively); U is the fuel consumption (L/100 km) for each vehicle type; and F is the fraction of MD trucks powered by diesel engines. Values for these parameters are summarized in Table 1. f represents the fractions of observed vehicles that fall into the LD, MD, and HD categories; these values varied somewhat from day to day throughout the study.

The contribution of MD and HD diesel trucks ($\Delta[CO_2]_d$) to the measured CO_2 enhancement was subsequently calculated as

Table 1. Vehicle and Fuel Parameters Used in Eq 2

parameter	units	value
U_{LD}[a]	L (100 km)$^{-1}$	10.3
$U_{MD,g}$[a]	L (100 km)$^{-1}$	28.4
$U_{MD,d}$[a]	L (100 km)$^{-1}$	27.0
U_{HD}[a]	L (100 km)$^{-1}$	49.5
ρ_g[b]	kg L^{-1}	0.742
ρ_d[b]	kg L^{-1}	0.852
w_g[b]	kg of C (kg of fuel)$^{-1}$	0.824
w_d[b]	kg of C (kg of fuel)$^{-1}$	0.866
F[c]	–	0.7

[a]Fuel consumption rates from Ban-Weiss et al.[18] [b]Fuel properties from analysis of gasoline and diesel fuel samples collected in California in summer 2010.[37] [c]Diesel fraction of MD vehicles estimated using California Air Resources Board EMFAC2011 model data[45] and calculated as weighted average by fuel consumption of LHDT2 and MHD vehicle categories.

$$\Delta[CO_2]_d = \Delta[CO_2] - \Delta[CO_2]_g \quad (3)$$

The LD gasoline contribution to background-subtracted concentrations of other species measured in the tunnel ($\Delta[P]_g$) was then calculated as

$$\Delta[P]_g = \Delta[P] - \Delta[CO_2]_d\left(\frac{\Delta[P]_{HD}}{\Delta[CO_2]_{HD}}\right) \quad (4)$$

Here, the ratio in parentheses represents the emission ratio of pollutant P to CO_2 for HD diesel trucks. With the exception of $PM_{2.5}$, values for this ratio were derived from measurements of emission factors for individual HD diesel trucks conducted as part of this field campaign and reported elsewhere.[15,26] Note that OA emission factors for HD diesel trucks were derived from measurements of individual truck exhaust plumes, which are less dilute than vehicle exhaust measured in bore 2 of the tunnel. The reduced dilution could enhance partitioning of semivolatile organic compounds in diesel exhaust to condensed phases and result in an overestimate of the HD diesel OA emission factor relative to dilution levels prevailing for LD vehicle emissions in bore 2 of the tunnel.[28−30] Fine particulate-matter emission factors for HD diesel trucks were not measured directly but were calculated here as the sum of BC and OA emission factors. Supporting measurements at the Caldecott tunnel indicate that these carbonaceous species account for greater than 90% of $PM_{2.5}$ mass emissions in motor vehicle exhuast.[26] In eq 4, HD truck emission factors are assumed to apply to both MD and HD diesel trucks. Exhaust emission standards, expressed in mass of pollutant emitted per unit of useful work output by the engine, for both MD and HD diesel trucks have historically been set at similar levels for the pollutants considered here, so similar emission factors are expected.[31]

Results from eqs 2 and 4 were then used to calculate adjusted pollutant emission factors ($EF_{P,LD}$) for LD gasoline vehicles

$$EF_{P,LD} = \left(\frac{\Delta[P]_g}{\Delta[CO_2]_g + \Delta[CO]_g}\right)w_g \quad (5)$$

Emission factors calculated using eq 5 explicitly account for the presence of MD and HD trucks in bore 2 and better represent actual emission factors for LD vehicles. For pollutants that were measured at high time resolution (i.e., BC, NO_x, and CO), 1-h average data were used in eq 5 to provide two discrete emission factor results per day, yielding a larger sample of 16 1-h average values over the eight-day sampling campaign. For filter-based measurements of $PM_{2.5}$ and OA, only one LD emission factor could be calculated for each of the 2-h sampling periods. Other carbon-containing species accounted for less than 1% of the total vehicle-derived carbon emissions measured in bore 2 and were thus excluded from the denominator of eq 5.

In addition to the vehicle count apportionment method described above, a second method utilizing high-time-resolution data from one day of sampling (July 12) was used to investigate further the contribution of MD and HD trucks to measured pollutant concentrations in bore 2 of the tunnel. Times at which individual MD and HD trucks passed by the sampling inlet were identified from video recordings of tunnel traffic. For each truck, a corresponding exhaust plume was identified, where possible, in the 1 Hz BC, NO_x, and CO_2 concentration data. Periods with a high influence of diesel exhaust were often readily identifiable using BC concentration data, for which clear increases in BC concentration above tunnel baseline levels corresponded to the passage of individual trucks. These plume events were integrated and background-corrected for each pollutant and were compared against the entire 2-h sampling period total to infer the relative contributions from diesel trucks and LD vehicles. Lower-time-resolution measurements of other species did not permit use of this alternative analytical approach for CO, $PM_{2.5}$, or OA. Results from this additional apportionment method were compared to apportioned emissions evaluated based on observed vehicle counts for the July 12 sampling period.

■ RESULTS AND DISCUSSION

Vehicle Activity. For the weekday 4−6 p.m. sampling periods considered here, LD vehicles accounted for greater than 99% of total vehicles observed, averaging 3625 veh hr^{-1}. Of the trucks observed in bore 2, most were medium-duty (two-axle/six-tire) vehicles, observed at an average rate of 23 veh hr^{-1}. Heavy-duty trucks were observed in bore 2 on only four of the eight days of sampling, with a maximum influence on July 14 when eight HD trucks were identified during the 2-h sampling period.

Light-duty vehicle activity in the tunnel was stable from day to day, with little variation in total vehicle counts observed across sampling days. Traffic was relatively free-flowing once vehicles entered the tunnel, at typical speeds of 60 km hr^{-1} on a 4% uphill grade. Measurements reported here reflect emissions from vehicles operating in warmed up, stabilized modes. Excess emissions associated with cold engine starting, which can be an important contributor to total emissions from LD gasoline vehicles,[32,33] were not measured in this study.

Influence of Individual Truck Exhaust Plumes. Time-series plots of tunnel BC, NO_x, and CO_2 concentrations measured on July 12 are shown in Figure 1. For each species, corresponding background air concentrations were subtracted

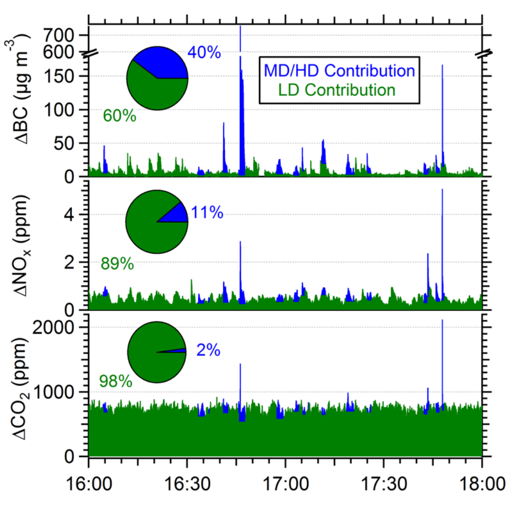

Figure 1. Ambient-background-subtracted tunnel concentrations of CO_2 (bottom), NO_x (middle), and BC (top) during the 7/12/2010 sampling period apportioned between LD vehicles (green) and MD and HD trucks (blue). Apportionment is based on an analysis of video recording of tunnel traffic and identification of passing times for individual MD and HD trucks. Inset pie charts show relative contributions of each vehicle type to measured pollutant concentrations for the 2-h sampling period. Average ambient concentrations of CO_2, NO_x, and BC were 394 ppm, 0.024 ppm, and 0.7 $\mu g\ m^{-3}$, respectively.

to isolate the emissions signal from vehicles traveling through the tunnel. Contributions from individual MD and HD trucks to measured pollutant concentrations are shown in blue, whereas green shading denotes contributions from much larger numbers of LD vehicles. During this 2-h sampling period, 20 MD and 3 HD trucks were noted driving through bore 2 of the tunnel. Although MD and HD trucks accounted for less than 1% of total vehicle counts, their contributions to pollutant concentrations are clearly noticeable in Figure 1.

The impact of diesel truck emissions is most clearly highlighted in the data recorded at 16:46, when an HD truck drove through the tunnel. Sharp increases in pollutant concentrations above typical tunnel levels are apparent in Figure 1 and correspond to the time period when the exhaust plume from this truck was being sampled. The peak BC concentration was nearly 100 times higher than typical tunnel concentrations, whereas smaller increases (factors of 6 and 2, respectively) were observed for NO_x and CO_2. This single HD diesel truck accounted for 19% of the total BC measured during the entire 2-h sampling period and 2% of the total NO_x signal. When normalized to fuel consumption, BC and NO_x emission factors for this truck were found to be similar to fleet-average values for HD trucks reported by Dallmann et al.[15] Thus, this truck was not an especially high emitter relative to the HD truck population at large. Rather, the disproportionate contributions to measured BC and NO_x are indicative of the large differences in emission factors for these pollutants from HD diesel trucks when compared to those for LD gasoline vehicles. Another contributing factor might be preferential sampling of emissions from trucks with elevated exhaust stacks, given the location of the air sampling inlets in the tunnel ventilation system above the traffic lanes.

In general, the presence of diesel trucks had the most pronounced effect on BC concentrations, accounting for 40% of the total BC measured during the 2-h sampling period (Figure 1). A similar response to MD and HD trucks was observed for NO_x, although concentration increases observed for truck exhaust plume events were not as large as those for BC. For this sampling period, diesel trucks were estimated to contribute 11% of total NO_x emissions. In contrast to BC and NO_x, CO_2 concentrations in exhaust plumes for most trucks were not noticeably different from the baseline tunnel concentrations. Light-duty vehicles accounted for nearly all of the CO_2 measured in the tunnel, with minor (2%) contributions from MD and HD trucks. In this case, the attributed CO_2 concentration was approximately proportional to the relative fraction of each vehicle type present in the tunnel.

These results demonstrate the substantial impact that relatively small numbers of MD and HD trucks can have on time-averaged concentrations of air pollutants measured in a mixed-use roadway setting. That diesel engines have considerably higher NO_x and BC emission factors than gasoline engines is not surprising and has been documented extensively elsewhere.[17,18,22,25] However, the data reported here indicate that these emission differences are of such a magnitude that even small numbers of diesel trucks can contribute substantially to overall emissions of these pollutants, even in cases that appear to be heavily dominated by LD vehicle traffic.

LD Vehicle Emission Factors. The relative contribution of diesel trucks to measured species concentrations in bore 2 was assessed over each of the eight sampling days using eqs 2−4. Here, the apportionment of measured species concentrations in the tunnel was based on measured vehicle counts and fleet-average pollutant emission factors for HD trucks. Background-subtracted tunnel concentrations for each sampling period are shown in Figure 2, with calculated contributions from MD and HD trucks shown in blue and LD vehicle contributions shown in green. Particle-phase emissions were the most sensitive to the presence of diesel trucks in the vehicle mix. The mean (±95% confidence interval) diesel contributions to measured $PM_{2.5}$, OA, and BC concentrations were $(24 \pm 4)\%$, $(22 \pm 6)\%$, and $(45 \pm 8)\%$, respectively. The two days with the highest levels of diesel truck activity, July 8 and July 14, also had the highest measured tunnel concentrations of OA and $PM_{2.5}$. Similarly, relatively high levels of NO_x were also measured on these days. The average diesel contribution to NO_x concentrations was $(18 \pm 3)\%$. Emissions of CO and CO_2 were dominated by LD vehicles, with diesel contributions of less than 2%. A comparison of the two apportionment methods for July 12 shows generally good agreement in the apportionment of emissions between vehicle types. Both methods attributed 37−40% of BC and 1−2% of CO_2 emissions to diesel trucks. The exhaust plume analysis estimated a lower NO_x contribution from trucks (11%) relative to the vehicle count apportionment method (17%), possibly because the HD-truck-derived emission factor might overestimate actual NO_x emission factors for MD trucks.

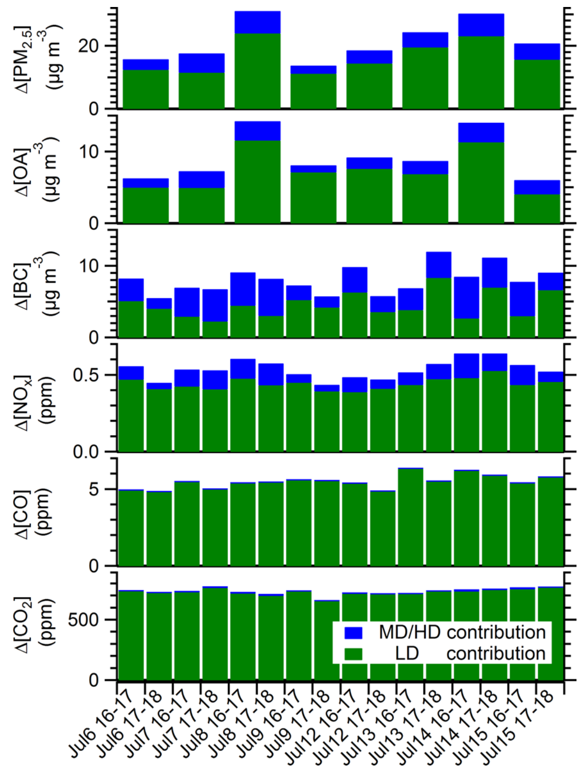

Figure 2. Measured increase in species concentration above ambient levels apportioned to LD gasoline vehicles (green) and HD and MD trucks (blue). Hourly time-resolved data were not available for OA and $PM_{2.5}$; therefore, 2-h average values for these species are presented here.

Once vehicle contributions to tunnel pollutant concentrations had been quantified, LD vehicle emission factors were calculated using eq 5. The results are summarized in Table 2 and compared with unadjusted emission factors that were calculated without accounting for diesel truck contributions using eq 1. With the exception of CO, LD vehicle emission factors were all found to be lower than the unadjusted values calculated using eq 1. The largest relative effect was seen for the BC emission factor, which was reduced by $(43 \pm 13)\%$ after accounting for diesel truck contributions. Likewise, the adjusted $PM_{2.5}$ and OA emission factors decreased relative to unadjusted values, although these changes have larger associated uncertainties. The reduction in the NO_x emission factor for LD vehicles was smaller, although still significant. Diesel trucks were an insignificant source of CO when compared to emissions from the large numbers of gasoline vehicles in the tunnel, and the adjusted CO emission factor was found to be similar to the unadjusted value.

Table 2. Unadjusted and Adjusted Emission Factors for LD Gasoline Vehicles

pollutant	N	unadjusted emission factor (EF_P)[a] ($g\ kg^{-1}$)	adjusted emission factor ($EF_{P,LD}$)[a] ($g\ kg^{-1}$)	relative change[a] (%)
NO_x[b]	16	2.29 ± 0.12	1.90 ± 0.08	-17 ± 5
CO	16	14.2 ± 0.7	14.3 ± 0.7	$+1 \pm 7$
$PM_{2.5}$	8	0.048 ± 0.012	0.038 ± 0.010	-22 ± 28
BC[c]	16	0.018 ± 0.002	0.010 ± 0.002	-43 ± 14
OA	8	0.021 ± 0.006	0.017 ± 0.005	-20 ± 34

[a]Unadjusted values calculated using eq 1; adjusted values calculated using eq 5 to exclude pollutant contributions from MD and HD diesel trucks present in bore 2 of the tunnel. Uncertainty estimates provide 95% confidence intervals. [b]NO_x emission factors reported as NO_2 equivalents. [c]BC emission factors calculated using Aethalometer BC concentration data for tunnel measurements and filter-derived BC concentration data for ambient-background subtractions.

For all species considered here, LD vehicle emission factors were lower than those measured at the same location in 2006.[14,18] These reductions resulted from both continued long-term downward trends in emissions from the LD vehicle fleet as new, lower-emitting vehicles replace older vehicles and the new methods for calculating emission factors used here that address a positive bias in previous estimates of LD NO_x, $PM_{2.5}$, BC, and OA emission factors. The light-duty NO_x and CO emission factors reported here are, respectively, 54% and 21% lower than the values measured in a 2010 remote-sensing study of LD vehicles in Los Angeles, CA.[10] For NO_x, this relation is consistent with previous comparisons of LD emission factors measured at the Caldecott tunnel and remote-sensing measurements, with differences in emission factors likely influenced by vehicle fleet age and operating mode differences.[10,34,35] The mean LD vehicle fleet age at the Caldecott tunnel has historically been approximately 3 years lower than the mean fleet age for vehicles operating at the Van Nuys tunnel in Los Angeles.[10,35] The mean vehicle fleet age at the Caldecott tunnel was 6.3 years in 2006,[18] although the fleet in 2010 might have been slightly older because of the effects of the economic recession. The relatively new vehicle fleet likely contributes to the lower NO_x and CO emission factors observed at the Caldecott tunnel.

After adjustments to account for diesel-engine contributions to tunnel concentrations measured in this study, there are large differences in resulting BC emission factors when compared to emission factors from other North American cities. The BC emission factor for LD vehicles estimated here is 7 times lower than the mean BC emission factor derived from on-road measurements in Los Angeles[20] and 11 times lower than the

LD vehicle emission factor inferred from near-road measurements along a highway running north of Toronto.[5] In both of these studies, emissions measurements were made for vehicles traveling on highways, and operating modes for the sampled vehicle population did not differ substantially from those observed at the Caldecott tunnel. The differences in BC likely arise from the inherent difficulties in characterizing emission factors based on measurements on or near mixed-use roadways. In the Los Angeles study, LD emission factors were calculated from measurements made from a highway with <1% truck activity, assuming that the diesel contribution was negligible. The Toronto study used a method similar to that used here to apportion BC concentrations between HD and LD vehicles. It is not clear whether MD truck contributions were addressed in that study. Results from the Caldecott tunnel indicate that even small numbers of diesel trucks can strongly influence measured on- and near-road BC concentrations. Thus, uncertainties in emission factors derived from mixed-use roadway measurements are expected to increase as the fraction of diesel trucks increases. Tunnel, on-road, and near-road measurement studies are attractive in that emissions from large numbers of vehicles can be measured in an efficient manner. However, the results presented here suggest that caution is needed when interpreting results and calculating emission factors for specific vehicle types, particularly for cases in which pollutant emission factors for diesel trucks are much greater than those for gasoline vehicles.

Emission Inventory Contributions from On-Road Gasoline and Diesel Engines. Exhaust emissions can be estimated as the products of fuel-based emission factors and the total amount of fuel burned.[1,34] This approach was applied using Caldecott-tunnel-derived emission factors for 2010 to map out the relative importance of gasoline versus diesel contributions to overall emissions from on-road motor vehicles. In this case, the relative contribution of diesel trucks to on-road emissions of a given pollutant ($E_{d,P}$) can be described by two parameters: (1) the ratio of diesel to gasoline emission factors for the pollutant (ER_P) and (2) the diesel fraction of total taxable fuel use by on-road motor vehicles (FC_d), expressed on a mass basis so that differences in fuel density are taken into account

$$E_{d,P} = \frac{ER_P}{ER_P + \left(\frac{1}{FC_d} - 1\right)} \times 100\% \qquad (6)$$

Increasing ER_P or FC_d results in a larger diesel contribution to overall emissions of pollutant P. Whereas ER_P extends over a wide range of values and depends on pollutant, FC_d is constrained to values between 0 and 1 and increases with the prevalence of diesel fuel use in the region of interest.

Equation 6 was used to estimate diesel contributions to total on-road vehicle emissions of various pollutants as shown in Figure 3. The shaded horizontal bands in Figure 3 show 95% confidence intervals for the mean emission factor ratios (ER_P) for the various pollutants. The labeled curves show diesel contributions as percentages of total on-road vehicle emissions. In general, the upper right corner of the diagram is diesel-dominated as a result of a high proportion of diesel fuel use and a high diesel-to-gasoline emission-factor ratio. In the lower left part of the diagram, gasoline-engine contributions dominate total emissions. The influence of cold-start effects on gasoline-engine emission contributions is not shown but will lead to higher relative contributions from gasoline engines. Including

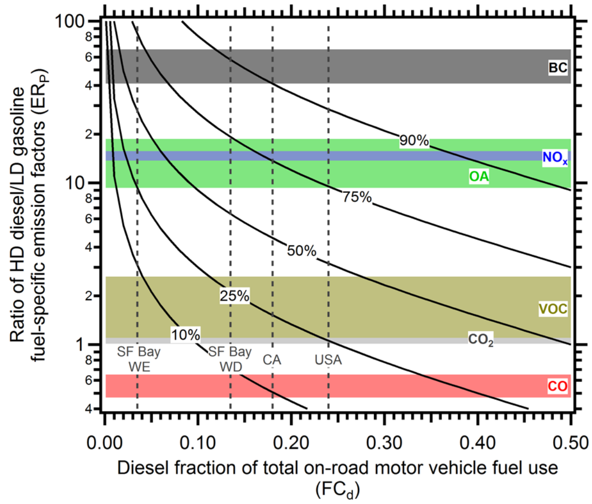

Figure 3. Contributions of diesel vehicles to total on-road motor vehicle exhaust emissions for varying levels of diesel consumption. Isopleth lines show percentages of on-road exhaust emissions attributable to diesel engines. Fuel-use data from McDonald et al.[34] (CA and USA) and Gentner et al.[37] (SF Bay). SF Bay weekday (WD) and weekend (WE) diesel fuel fractions calculated following methods of Marr et al.[44]

cold-start effects does not have much effect on the outcome in cases in which the diesel contribution is already above ~70%. In contrast, including start emissions further strengthens the conclusion in cases where gasoline-engine emissions are already the dominant source of running emissions for a given pollutant. There is evidence that BC emissions from gasoline vehicles might be magnified during start and hard acceleration operating modes, when the combustion mixture ratio is more fuel-rich than normal.[36] However, a recent on-road plume-capture study of individual LD gasoline vehicles found that variations in BC emissions due to changes in engine operating mode are small relative to intervehicle variability in BC emission rates.[17]

Fuel-specific emission factors for LD gasoline and HD diesel vehicles presented in Table 2 and in related publications[15,26,37] were used to define mean ER_P values for a range of pollutants as shown in Figure 3. For CO_2, ER_{CO_2} was calculated using the carbon weight fractions for gasoline and diesel fuel reported in Table 1, assuming complete oxidation of fuel carbon to CO_2. Note that, for organic aerosol, only primary emissions are considered here. Motor vehicles are also important sources of emissions of volatile organic compounds (VOCs) that can lead to atmospheric formation of secondary organic aerosol.[37,38] The ER_P values defined here are representative of the fleet of vehicles operating at the Caldecott tunnel in 2010. Differences in vehicle fleet age, particularly for the LD fleet, and vehicle operating modes might result in a broader range of ER_P values when considering other geographic areas and vehicle fleets.

A main feature of Figure 3 is the wide range of values of ER_P, which span several orders of magnitude, and the resulting implications for the importance of emissions from key sectors that make up the on-road motor vehicle fleet. For CO_2 and VOCs, for which fuel-specific emission factors for gasoline and diesel vehicles are similar ($ER_P \approx 1$), the contribution of exhaust emissions from diesel trucks is approximately proportional to fuel consumption. Because gasoline use tends to be much higher than corresponding diesel fuel sales in most parts of North America, gasoline engines also tend to dominate emissions of these species. For CO_2, the diesel contribution to total on-road motor vehicle emissions follows diesel fuel consumption. Reference values for the diesel-fuel share of total on-road fuel consumption are ∼10% for the San Francisco Bay Area and 25% in the United States as a whole. Of the pollutants shown in Figure 3, gasoline vehicles showed higher emission factors compared to diesel for CO only. When combined with fuel sales data, the conclusion that gasoline engines are the dominant on-road source of CO is very clear. This finding is consistent with those of other studies indicating that diesel trucks remain a minor source of CO emissions.[39]

Diesel engines are considerably more important as a source of other pollutants shown in Figure 3. Emission factors of NO_x and OA measured at the Caldecott tunnel were an order of magnitude higher for diesel trucks than for LD gasoline vehicles, and BC emission factors were approximately a factor of 50 higher for diesel engines. These differences in emission factors offset the relatively small (when compared to gasoline) amounts of diesel fuel consumed at regional, state, and national scales. As a result, we conclude that, as of 2010, diesel engines were the dominant on-road source of BC, OA, and NO_x.

Figure 3 shows that diesel engines contribute greater than 50% of total on-road BC emissions, even at very low relative levels of diesel fuel consumption. In urban areas, reductions in ambient concentrations of BC observed on weekends have been attributed to large reductions in the amount of diesel truck activity.[40,41] For an estimated diesel fuel sales fraction of 3.5% on weekends in the San Francisco Bay area, diesel engines still contribute ∼60% of total BC emissions. Thus, even though emissions of BC from diesel vehicles are reduced on weekends because of lower levels of activity and fuel consumption, diesel engines remain the dominant source of BC emissions. In general, these results suggest that, as of 2010, gasoline vehicles were a minor source of BC emissions relative to diesel trucks.

Future emissions from the on-road vehicle fleet will be strongly affected by the introduction of advanced emission control technologies for the diesel truck fleet. New control technologies such as diesel particle filters and selective catalytic reduction systems are now standard equipment for new HD diesel trucks. These systems are designed to reduce emissions of particulate matter and NO_x. Newer trucks are often also equipped with an oxidation catalyst that is effective in reducing emissions of CO and VOC.[11,42] As a result of in-use truck engine retrofit/replacement programs in California, most HD diesel trucks are expected to be equipped with exhaust particle filters by 2014.[43] As a result, the relative contributions of gasoline versus diesel engines to overall emissions of pollutants such as BC and OA might change rapidly in the coming years. Continued measurements of emissions from the on-road vehicle fleet are needed to track these changes and the resultant influences on the absolute and relative emission contributions from gasoline and diesel engines.

■ ASSOCIATED CONTENT

Supporting Information

Description of sampling and analytical methods. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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