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On-Road Measurement of Gas and Particle Phase Pollutant Emission Factors for Individual Heavy-Duty Diesel Trucks

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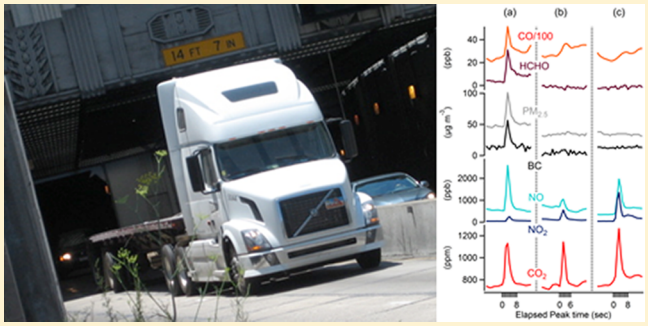
Supporting Information

ABSTRACT: Pollutant concentrations in the exhaust plumes of individual diesel trucks were measured at high time resolution in a highway tunnel in Oakland, CA, during July 2010. Emission factors for individual trucks were calculated using a carbon balance method, in which pollutants measured in each exhaust plume were normalized to measured concentrations of carbon dioxide. Pollutants considered here include nitric oxide, nitrogen dioxide (NO_2), carbon monoxide, formaldehyde, ethene, and black carbon (BC), as well as optical properties of emitted particles. Fleet-average emission factors for oxides of nitrogen (NO_x) and BC respectively decreased 30 ± 6 and 37 ± 10% relative to levels measured at the same location in 2006, whereas a 34 ± 18% increase in the average NO_2 emission factor was observed. Emissions distributions for all species were skewed with a small fraction of trucks contributing disproportionately to total emissions. For example, the dirtiest 10% of trucks emitted half of total NO_2 and BC emissions. Emission rates for NO_2 were found to be anticorrelated with all other species considered here, likely due to the use of catalyzed diesel particle filters to help control exhaust emissions. Absorption and scattering cross-section emission factors were used to calculate the aerosol single scattering albedo (SSA, at 532 nm) for individual truck exhaust plumes, which averaged 0.14 ± 0.03.



INTRODUCTION

Heavy-duty (HD) diesel trucks have long been recognized as an important source of air pollution.[1,2] In the United States, on-road diesel engines are estimated to be the single largest anthropogenic source of nitrogen oxide (NO_x) emissions, accounting for 27% of total anthropogenic NO_x emissions in 2005.[3] Diesel trucks also contribute significantly to emissions of fine particulate matter ($PM_{2.5}$), of which black carbon (BC) is a major component. Recent emission inventories highlight the importance of diesel engines as a source of BC.[4,5] Emissions of carbon monoxide (CO) and volatile organic compounds (VOC), particularly aldehydes, also contribute to the air quality impact of diesel exhaust.[6,7]

Recognizing these impacts, the U.S. Environmental Protection Agency (EPA) implemented emission standards effective for new engines in 2007 for PM and 2010 for NO_x.[8] Whereas previous emission standards were met primarily through engine modifications and combustion improvements, EPA's new and much lower emission limits compel the use of exhaust after-treatment technologies such as diesel particle filters (DPF) and selective catalytic reduction (SCR). To realize air quality benefits from new control technologies as quickly as possible, California introduced a rule requiring nearly all on-road HD diesel trucks to have PM filters installed by 2014, and to meet stringent emission standards for NO_x by 2023.[9] This rule is likely to promote retrofit of pre-2007 model year (MY) engines with exhaust filters, as well as accelerated replacement of the oldest trucks in the state fleet. These measures are expected to significantly reduce air pollutant emissions from on-road diesel trucks.

DPF systems typically employ a wall-flow filter to remove particles from the exhaust gas stream. To avoid excessive pressure drop across the filter, accumulated particles must be removed through some kind of regeneration process. Active regeneration systems employ an external energy source (e.g., fuel injection, electric heating) to raise the temperature of the filter and promote oxidation of trapped carbonaceous particles. In passive or continuously regenerated systems, catalysts are used to oxidize nitric oxide (NO) present in the exhaust to nitrogen dioxide (NO_2), which is then used to oxidize trapped carbon particles. NO_2 is capable of oxidizing trapped particles at

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temperatures typical of diesel exhaust and, thus, exhaust filters can be regenerated continuously.[10]

The capacity of DPF systems to remove >90% of PM mass from diesel exhaust has been well established through dynamometer testing.[11−13] The degree of oxidation catalyst loading present in DPF systems, as well as exhaust gas temperatures, can influence gaseous emissions from diesel engines. For example, oxidation catalysts help to lower CO and VOC emissions but may increase the fraction of NO_x emitted as NO_2.[12,14] Whereas the NO_2/NO_x mass emission ratio for untreated diesel exhaust is typically less than 0.10,[15,16] elevated NO_2/NO_x emission ratios (>0.30) have been reported for DPF-equipped engines in dynamometer studies,[12,13,17] as well as during in-use testing of diesel passenger buses and trucks equipped with particle filters.[18,19] Increased primary NO_2 emissions may be of concern due to the toxicity of NO_2, as well as potential for increases in ozone production.[20] Expanded use of new control technologies is also expected to increase the skewness of emissions distributions, where a small number of high-emitting vehicles are responsible for a disproportionately large fraction of total emissions.[16,21]

The objective of this research was to quantify pollutant emission factors from individual on-road diesel trucks and characterize the distribution of emissions across a large number of trucks. Remote sensing techniques have been effectively used to measure emissions of gaseous species from large numbers of individual trucks, but the number of species measured is limited and particle emissions are not well characterized. In contrast, tunnel studies often include a wider range of measured species but historically provided only fleet-average emission factors. With the advent of fast-time response instrumentation for measuring individual exhaust plumes, distributions of emission factors can be measured.[22,23]

This study measured a large number of gaseous species, featuring novel fast-response measurements of ethene (C_2H_4) and formaldehyde (HCHO), and also includes characterization of emitted particles. These measurements are used to characterize distributions of emission factors for individual pollutants as well as correlations among species in the exhaust of individual trucks. New data reported here track emission impacts of increased use of particle filters. Emissions measurements also provide baseline data just prior to the introduction of NO_x after-treatment control technologies such as SCR systems, which are anticipated in the U.S. after 2010.

METHODS

Measurement Site. Measurements of exhaust plumes from individual diesel trucks were made at the Caldecott tunnel. The Caldecott tunnel is located in the San Francisco Bay area on Highway 24 connecting Oakland with cities further inland to the east. This site has been used for on-road vehicle emission studies for many years.[24,25] The tunnel is 1 km in length and consists of three two-lane traffic bores. The two outer bores are reserved exclusively for eastbound and westbound traffic and accommodate all vehicle types including trucks. The middle bore handles westbound traffic in the morning, eastbound traffic in the afternoon, and is reserved for light-duty traffic at all times. Sampling for this study was performed in the eastbound traffic bore, which has a 4% uphill grade. Measurements reported here were made from 1000 to 1800 h on each of four weekdays in July 2010.

Air Pollutant Measurements. The suite of instrumentation deployed to characterize gaseous pollutants and physical and optical properties of particles emitted from trucks is listed in Table S1 of the Supporting Information. All instruments operated at a time resolution of 1 s, which is sufficiently fast to measure pollutant concentration peaks (typically 5 to 20 s in duration) associated with truck exhaust plumes. Instruments were placed in two locations: in the tunnel ventilation duct directly above the traffic and in the Aerodyne mobile laboratory parked outside the tunnel.[26] In both cases, air was drawn from the same aperture in the ventilation duct approximately 50 m prior to the tunnel exit. Sampling lines extended ∼0.1 m into the tunnel traffic bore above vertical exhaust stacks of HD trucks passing on the roadway below. The majority of trucks travel in the right-hand lane, so sampling inlets were placed above this lane to maximize the capture efficiency of truck exhaust plumes.

Short (2 m) perfluoroalkoxy (PFA) and conductive silicone sampling lines were used to continuously deliver tunnel air samples to the gas and particle instruments located in the ventilation duct. A cyclone (URG Corporation, Chapel Hill, NC; model 2000−30EN) with a cut-point diameter of 2.5 μm was connected in-line upstream of the particle instruments. Significantly longer (35 m) sampling lines were required to deliver tunnel air to instruments located in the mobile laboratory. A 0.95 cm inner diameter PFA sampling line was used for measurements of gas-phase species, with an air flow rate of 10 to 14 L per minute. This flow was filtered through a PTFE filter (nominal pore size 1−2 μm) that was changed daily. Aerosol instruments sampled tunnel air through a 1.6 cm outside diameter copper tube at 16.7 L per minute. Particle losses in the copper sampling line were characterized through a combination of transmission efficiency testing and theoretical calculations. Results suggest significant losses (>50%) of particles less than 50 nm in diameter, with minor losses (<10%) of particles greater than 100 nm in diameter. The loss of small particles is not expected to significantly affect measured optical properties, which are dominated by larger particles.

Multipoint calibrations were performed prior to field sampling for all instruments used for measurement of gas-phase species. During the field study, calibrations were validated with daily zero and span checks. Uncertainties in CO_2 measurements were estimated to be ±1% and ±2% for the LiCor LI-6262 and LI-820 analyzers, respectively. Raw NO concentrations reported by the chemiluminescence instrument were multiplied by a factor of 1.06 to account for quenching of electronically excited NO_2 by water vapor (present at ∼1% in tunnel air). The uncertainty of final NO measurements is estimated to be ±10% based on unresolved discrepancies between the multiple NO calibration sources examined.

Quantum cascade tunable infrared laser differential absorption spectrometers (QC-TILDAS) were used to measure CO, NO_2, HCHO, and C_2H_4 at high time resolution.[27] Although the QC-TILDAS method is fundamentally an absolute Beers-law absorption technique that does not require calibration, the nonideal line shapes of pulsed quantum cascade lasers (as used for this study) can lead to low readings. Readings for each instrument were therefore verified with diluted calibration gas standards (from cylinders for CO and C_2H_4, from a permeation tube for HCHO, and from ozonation of NO for NO_2). The uncertainty of QC-TILDAS measurements was estimated as ±6% for CO, ± 10% for NO_2, ±13% for HCHO, and ±3.5% for C_2H_4. Losses of gas-phase species through the PTFE filter and 35 m PFA sampling tube were negligible (Figure S1 of the Supporting Information).

Multiple instruments were used to characterize the light-absorbing component of $PM_{2.5}$ including a photoacoustic spectrometer, an aethalometer, and a multiangle absorption photometer (MAAP). The aethalometer and MAAP measure the attenuation of light by particles collected in a filter (ATN), which is then related to black carbon concentration. BC data from the aethalometer is subject to various systematic errors.[28−31] When sampling highly absorbing particles, a filter-loading artifact that diminishes the aethalometer's response to BC is the dominant source of error.[29] For this study, raw BC concentrations reported by the aethalometer were adjusted following Kirchstetter and Novakov:[30]

$$BC_{adj} = \frac{BC_{raw}}{1.5 \times \left[0.73 \times \exp\left(\frac{-ATN}{100}\right) + 0.27\right]} \quad (1)$$

The bracketed expression in the denominator adjusts BC concentrations for the filter loading effect. Coefficients used here, which differ slightly from those presented by Kirchstetter and Novakov,[30] were derived specifically for HD truck emissions by comparing BC concentrations measured with the aethalometer and absorption coefficients measured with the photoacoustic spectrometer (Figure S2 of the Supporting Information). The factor 1.5 in the denominator of eq 1 was included because aethalometer BC concentrations were consistently 50% higher than BC concentrations determined by thermal−optical analysis of particles collected on quartz fiber filters (Figures S3 and S4 of the Supporting Information).

The MAAP[32] and photoacoustic spectrometer[33] reported aerosol absorption coefficients at 630 and 532 nm respectively, which were converted to BC concentrations assuming mass absorption cross sections of 6.6 and 7.5 $m^2\ g^{-1}$, respectively.[34] As shown in Figure S4 of the Supporting Information, MAAP and photoacoustic derived BC concentrations agree to within 10% of filter-based BC measurements. Data from the MAAP, which explicitly accounts for filter-induced sampling artifacts,[32] did not require any adjustment. The photoacoustic spectrometer measures in situ absorption coefficient and is therefore free of filter-induced artifacts. The photoacoustic spectrometer responds to NO_2, but the high levels of absorbing aerosol in the tunnel overwhelmingly dominate the response of the instrument (Figures S5 and S6 of the Supporting Information).

Two DustTrak instruments were used to measure $PM_{2.5}$ mass concentrations. Because of reported uncertainties in using the DustTrak for quantitative measurements of $PM_{2.5}$ mass in motor vehicle exhaust,[23,35,36] the DustTraks are used in this study only to make qualitative comparisons between $PM_{2.5}$ and other pollutants emitted in diesel exhaust.

A reciprocal nephelometer, collocated in the same instrument with the photoacoustic spectrometer, was used to measure particle scattering coefficients at 532 nm. Absorption and scattering coefficients together yield particle extinction and enable definition of single scattering albedo (SSA), the ratio of light scattering to extinction for the sampled particles. An Aerodyne cavity attenuation phase-shift extinction monitor (CAPS PM_{ex}) was used to measure particle extinction at 630 nm in conjunction with the MAAP instrument's absorption measurements.[37] The CAPS PM_{ex} monitor employed an automatic filtered baseline technique to account for instrument drift and tunnel background gas phase absorption (e.g., NO_2).

Emission Factor Calculations. Video recordings of vehicle activity were analyzed to link trucks passing below the air sampling inlets with the rise and fall (peaks) in measured pollutant concentrations. Peaks in CO_2 concentrations that were 3 and 6% above baseline levels measured with the LI-6262 and LI-820 analyzers, respectively, were used to specify successful plume captures. This threshold corresponds to CO_2 rises of 30 and 60 ppm above a baseline of ∼1000 ppm measured in the tunnel. Emission factors were not calculated for trucks where CO_2 peaks could not be identified or did not meet these thresholds. Additionally, emission factors were not calculated in instances where multiple trucks passed the sampling inlet in close succession such that individual exhaust profiles could not be discerned.

For successful truck plume captures, pollutant emission factors expressed per unit of fuel burned were calculated using a carbon balance method:[23]

$$EF_P = \frac{\int_{t_1}^{t_2}([P]_t - [P]_{t_1})dt}{\int_{t_1}^{t_2}([CO_2]_t - [CO_2]_{t_1})dt} w_c \quad (2)$$

Here EF_P is the emission factor for pollutant P ($g\ kg^{-1}$) and w_c = 0.87 is the carbon content of diesel fuel. For particle optical properties, EF_P represents optical cross-section emitted per mass of fuel burned ($m^2\ kg^{-1}$). The interval $t_1 \le t \le t_2$ represents the time period that instruments were sampling the exhaust plume of an individual truck (typically ∼5−20 s), with t_1 and t_2 determined separately for each species. $([P]_t - [P]_{t_1})$ is the baseline-subtracted concentration of pollutant P at time t (expressed in units of $\mu g\ m^{-3}$ or $Mm^{1-} = 10^{-6}\ m^{-1}$), and the denominator expresses the carbon associated with the pollutant peak (estimated from CO_2, mg C m^{-3}). As noted above, three analyzers were used to measure CO_2 concentrations in three sampling lines. Eq 2 was applied using CO_2 and pollutant concentrations measured with collocated analyzers.

Although other carbon-containing species were measured in this study, these species are excluded from the carbon balance in eq 2 because they are present at low concentrations relative to CO_2 in diesel exhaust.[38] For example, CO contributed less than 2% of the total carbon measured in the exhaust of the highest (top 10%) CO-emitting trucks. Concentrations of BC, HCHO, and C_2H_4 measured in truck exhaust accounted for <1% of total carbon.

RESULTS AND DISCUSSION

Truck Activity and Plume Captures. Successful plume captures were recorded for 809 out of 1396 HD trucks observed during the four days of field sampling. Figure S7 of the Supporting Information shows NO, NO_2, BC, $PM_{2.5}$, HCHO, CO, and CO_2 concentrations measured in the exhaust plumes of three diesel trucks. Emission factors are not available for all pollutants for every truck because pollutant analyzers were occasionally offline for calibration. Emission factors were calculated for 37 to 48% of total trucks for all pollutants considered here with the exception of BC and absorption from the MAAP, which was offline for one entire day of sampling.

Large numbers of light-duty gasoline vehicles in the tunnel resulted in an elevated background C_2H_4 concentration, above which small C_2H_4 increases due to emissions from individual trucks were difficult to discern. A similar problem was encountered for CO. For other pollutants considered here, such as HCHO and NO_x, emission rates from diesel vehicles are generally much higher than from gasoline vehicles, and so background levels were not problematic. C_2H_4 emission factor measurements were further complicated by a relatively low

Table 1. Fleet-Average Emission Factors for Heavy-Duty Diesel Trucks

species	number of trucks	emission factor ±95% confidence interval	emission factor units	high-emitter contribution[a] (%)
BC (aethalometer)	667	0.54 ± 0.07	g kg^{-1}	47
BC (photoacoustic)	521	0.58 ± 0.09	g kg^{-1}	47
BC (MAAP)[b]	445	0.59 ± 0.11	g kg^{-1}	52
b_{abs} (λ=532 nm)	521	4.38 ± 0.69	m^2 kg^{-1}	47
b_{scat} (λ=532 nm)	521	0.68 ± 0.13	m^2 kg^{-1}	56
b_{abs} (λ=630 nm)[b]	445	3.90 ± 0.69	m^2 kg^{-1}	52
b_{ext} (λ=630 nm)[c]	616	4.53 ± 0.68	m^2 kg^{-1}	52
NO	612	17.0 ± 0.9	g kg^{-1}	24
NO_2	567	1.97 ± 0.25	g kg^{-1}	50
NO_x[d]	557	28.0 ± 1.5	g kg^{-1}	23
CO	553	8.0 ± 1.2	g kg^{-1}	51
HCHO	558	0.065 ± 0.006	g kg^{-1}	33
C_2H_4[e]	276	0.081 ± 0.009	g kg^{-1}	30

[a]Contribution to total emissions from 10% of trucks with the highest measured emission rates for each pollutant. [b]MAAP instrument offline during one day of sampling (see text). [c]b_{ext} concentrations in the exhaust plumes of two trucks exceeded the upper range of the CAPS instrument. b_{ext} emission factors for these trucks were calculated using the corresponding b_{abs} emission factor measured at 630 nm and the SSA measured at 532 nm. [d]NO_x mass emission factor reported in NO_2 equivalents (i.e., NO mass multiplied by 46/30). [e]Because of elevated C_2H_4 background and instrument sensitivity, only trucks with associated CO_2 peak rises greater than the median value (230 ppm) are considered for C_2H_4 analysis (see text).

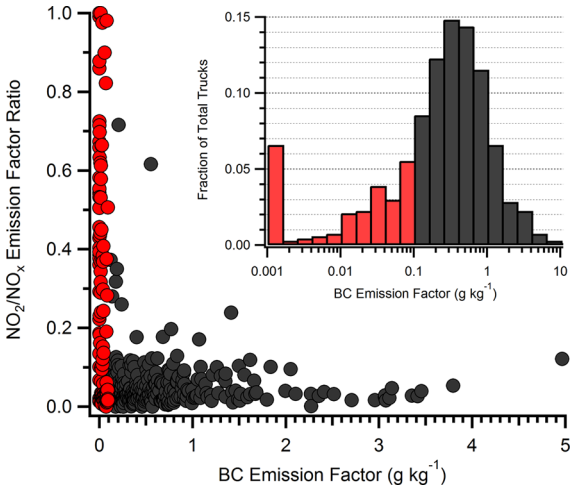

Figure 1. Relationship between NO_2/NO_x emission ratio and BC emission factor. Each data point represents a single truck, red points correspond to trucks with BC emission factor <0.1 g kg^{-1}. Insert plot shows BC emission factor distribution.

signal-to-noise ratio. Consequently, application of eq 2 to calculate C_2H_4 emission factors for more dilute truck plume captures (i.e., small CO_2 rise above baseline level) yielded potentially erroneous results. When grouped according to CO_2 peak rise, distributions of emission factors above and below the median CO_2 peak rise were similar for other species. However, a distinct shift was observed in the C_2H_4 emission factor distribution for trucks with CO_2 peak rises below the median level relative to the distribution for trucks with CO_2 peak rises

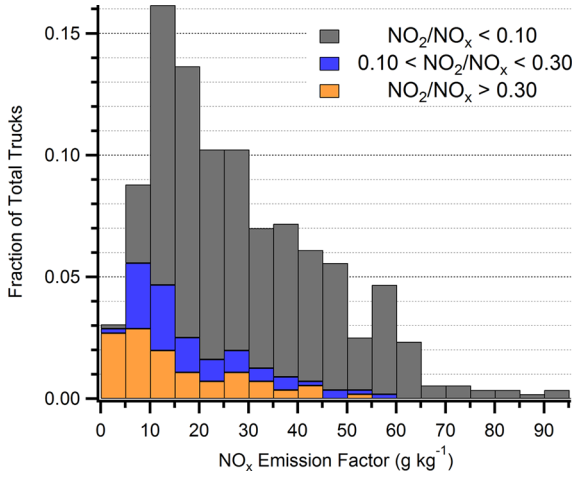

Figure 2. NO_x emission factor distribution with associated ranges of NO_2/NO_x emission ratio.

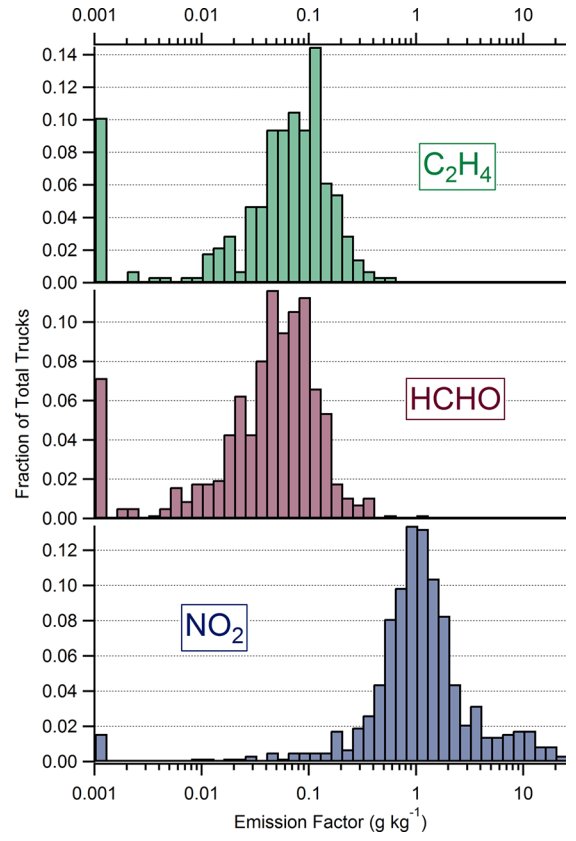

Figure 3. Emission factor distributions for ethene, formaldehyde, and nitrogen dioxide.

above the median level. Because of these complications, only trucks with CO_2 peak rises above the median level (230 ppm) are considered in the C_2H_4 analysis.

The most common HD truck types observed were tractor and trailer or container chassis combinations, which accounted for 39% of trucks. Ongoing construction of a fourth traffic bore at the Caldecott tunnel led to increased numbers of construction vehicles, with dump trucks, cement mixers, and tractors pulling hoppers accounting for 32% of trucks. Average vehicle speeds in the tunnel were approximately 65 km hr^{-1}. Thus, emissions data presented here are representative of

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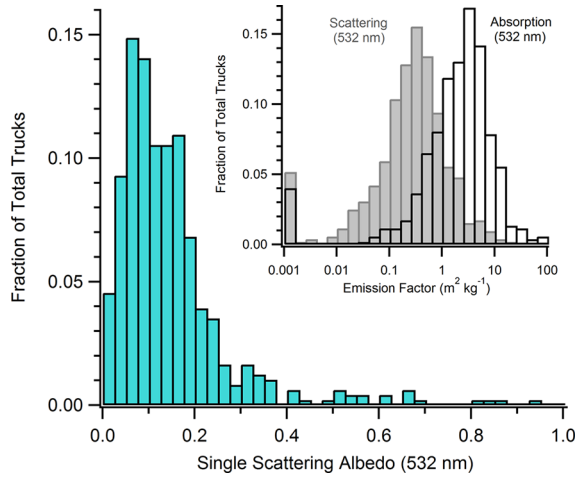

Figure 4. Distribution of single scattering albedo for PM emissions from individual trucks, with underlying emission rates of light-scattering and light-absorbing particles (insert plot).

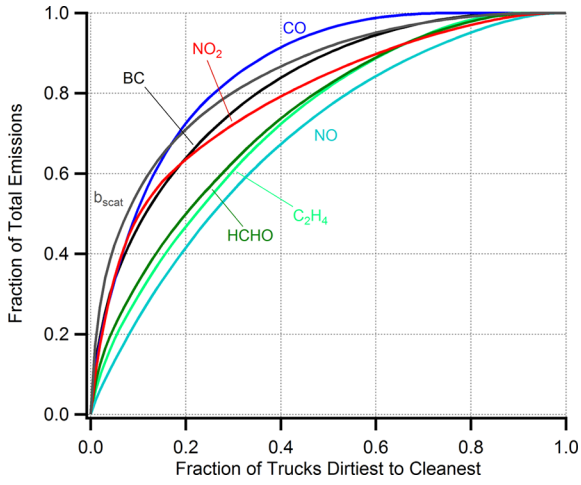

Figure 5. Cumulative emission distributions for pollutants measured in heavy-duty truck exhaust plumes. Any *y* value on this plot indicates the fraction of total emissions coming from the corresponding highest-emitting fraction (*x*) of all on-road trucks.

trucks traveling at relatively constant speeds and do not cover the entire spectrum of truck operating modes.

BC Emissions. Average BC emission factors calculated using data from the aethalometer, photoacoustic spectrometer, and MAAP are presented in Table 1. The results were similar for each instrument. The slightly higher emission factors for the MAAP and photoacoustic spectrometer relative to the aethalometer are consistent with comparisons with filter-based BC measurements (Figure S4 of the Supporting Information). The average BC emission factor measured in this 2010 study is 37 ± 10% lower than the average emission factor measured at the same location for medium and HD diesel trucks four years prior in 2006.[25] This rate of reduction is comparable to or possibly larger than the rate of reduction observed between 1997 and 2006.[25] The BC emission factor distribution is shown in the insert plot of Figure 1. Trucks with zero or negative BC emission factors calculated using eq 2 are included in the leftmost bin of the distribution and account for 7% of total trucks. With the exception of these very low-emitting trucks, the emission factor distribution is log-normal with a peak at ~0.3 g kg^{-1}. The distribution measured at the tunnel is similar to that measured for drayage trucks at the Port of Oakland in 2010, although a higher frequency of low BC emitting trucks was observed due to accelerated cleanup efforts at the Port.[23]

NO_x Emissions. The average NO_x emission factor for diesel trucks in 2010 decreased by 30 ± 6% relative to the emission factor measured in 2006.[25] Whereas total NO_x emissions declined during this period, the NO_2 emission factor increased from 1.47 ± 0.06 g kg^{-1} in 2006 to 1.97 ± 0.25 g kg^{-1} in 2010. Consequently, the NO_2/NO_x mass emission ratio increased from 0.037 ± 0.003 to 0.070 ± 0.010. The increased NO_2/NO_x ratio is attributed to a greater number of trucks with catalyzed DPF systems that oxidize NO to NO_2 in 2010. Remote sensing of NO and NO_2 emission factors from individual trucks in the Los Angeles area show similar NO_x emission trends: Bishop et al.[19] report a 10 ± 3% reduction in the fleet-average NO_x emission factor between 2008 and 2010 with no significant change in the NO_2 emission factor.

Effects of DPFs on NO_2 Emissions. Figure 1 shows a comparison of the NO_2/NO_x mass emission ratios and BC emission factors for individual diesel trucks. Red data points are used to represent trucks with BC emission factors <0.1 g kg^{-1} and correspond to the shaded portion of the insert plot. Whereas the majority of trucks had much higher emissions of NO than NO_2 (NO_2/NO_x < 0.10), trucks with the lowest BC emissions had higher NO_2/NO_x emission ratios. The average

Table 2. Degree of Overlap (0 = None, 100 = Maximum) among Trucks That Were Flagged As High-Emitters of Various Pollutants

	$PM_{2.5}$	BC[a]	Abs_{532}	Abs_{630}	$Scat_{532}$	Ext_{630}	NO	NO_2	CO	HCHO	C_2H_4
$PM_{2.5}$	100										
BC[a]	78	100									
Abs_{532}	72	88	100								
Abs_{630}	73	86	81	100							
$Scat_{532}$	81	76	73	67	100						
Ext_{630}	77	82	74	95	74	100					
NO	19	12	18	9	18	14	100				
NO_2	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**100**			
CO	23	26	38	32	32	31	11	**0**	100		
HCHO	27	27	17	25	35	27	15	**2**	13	100	
C_2H_4	34	25	17	25	23	31	22	**0**	22	37	100

[a]BC emission factors calculated using aethalometer data.

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NO_2 emission factor and NO_2/NO_x ratio for the lowest 7% of BC emitting trucks (shown in leftmost bin of BC emission factor distribution in Figure 1) are 6.00 ± 1.72 g kg^{-1} and 0.28 ± 0.12, respectively. These values are both much higher than fleet-average values shown in Table 1. The anticorrelation between NO_2/NO_x emission ratio and BC emissions is indicative of DPF-equipped trucks in the vehicle fleet sampled at the tunnel. Similar increases in NO_2 emissions relative to NO have been documented for DPF equipped trucks in the Los Angeles area [19] and transit buses equipped with continuously regenerating DPF systems in New York City.[18]

High NO_2/NO_x ratios measured here may be of concern insofar as they lead to higher NO_2 emissions for the diesel truck fleet. Figure 2 shows the NO_x emission factor distribution for diesel trucks measured at the Caldecott tunnel. The distribution is separated according to NO_2/NO_x ratio: greater than 0.30, between 0.10 and 0.30, and less than 0.10. The majority of trucks with NO_x emission factors less than 10 g kg^{-1} were found to have NO_2/NO_x ratios greater than 0.10. For these trucks, the effect of relatively high NO_2/NO_x ratios is offset by low total NO_x emissions resulting in only small increases in NO_2 emissions. In contrast, increased NO_2/NO_x ratios in trucks with higher total NO_x emissions have a much more pronounced effect on NO_2 emissions. For example, the subset of trucks with a NO_x emission factor greater than 25 g kg^{-1} and a NO_2/NO_x ratio greater than 0.10 accounted for 32% of total NO_2 emissions. These high NO_2-emitting trucks are evident in the NO_2 emission factor distribution, shown in Figure 3, which has a primary peak of ∼1 g kg^{-1} and a secondary peak at ∼10 g kg^{-1}. In light of current accelerated retrofit and replacement programs underway in California, it will be important to track changes in primary NO_2 emissions from the HD diesel truck fleet as greater numbers of vehicles are equipped with DPF systems.

HCHO and C_2H_4 Emissions. HCHO and C_2H_4 have been identified as two of the most abundant VOC in diesel exhaust.[6,39,40] To date, characterization of emissions of these species from diesel engines has largely been performed through dynamometer testing[6,17,39] and tunnel studies where emissions are apportioned between gasoline and diesel vehicles.[7,41] Whereas remote sensing systems have proven effective in measuring concentrations of other gaseous species (e.g., NO, NO_2, CO) in exhaust plumes of diesel vehicles, they are relatively insensitive to HCHO and C_2H_4.[42] Vehicle chase studies enable the measurement of emissions from individual in-use vehicles, but their application thus far has been limited to the characterization of HCHO emission factors for in-use passenger buses.[43] Thus, emission factors presented here represent novel measurements of HCHO and C_2H_4 emissions from individual in-use HD diesel trucks.

Emission factor distributions for HCHO and C_2H_4 are shown in Figure 3. The distributions show similar shapes, with high frequencies of very low-emitting trucks which are included in the leftmost bin. For C_2H_4, these low-emitting trucks account for ∼10% of total measurements. The average C_2H_4 mass emission factor for diesel trucks measured here is slightly greater than the value for HCHO. Previous studies report similar or higher emission rates of HCHO than C_2H_4 in diesel exhaust.[6,39,40] No clear explanation for these differences is apparent. The average HCHO emission factor measured in this study is approximately 50% lower than it was at the Caldecott tunnel in 2006.[7] This reduction may be expected given the introduction of diesel particle filters as oxidation catalysts typically found in these systems can be effective at reducing VOC emissions.[12,13]

Particle Optical Properties. Average optical cross-section emission factors are presented in Table 1. On the basis of these values, the average SSA for diesel exhaust plumes was 0.14 ± 0.03 and 0.14 ± 0.22 at wavelengths of 532 and 630 nm, respectively. A direct scattering measurement (smallest optical signal) was not available at 630 nm, and thus the SSA measured at this wavelength has more uncertainty. This low SSA is similar to previous values reported for measurements of fresh diesel exhaust.[34,44] The distribution of particle SSA at 532 nm in individual exhaust plumes is shown in Figure 4 as are the emission factor distributions for absorption and scattering cross sections. Note that trucks with negative absorption or scattering cross-section emission factors as calculated by eq 1 are excluded from the SSA distribution. Most trucks have exhaust SSA values of less than 0.20, consistent with a high fraction of BC in the emitted PM, although the high tail of the distribution extends to SSA values up to 0.94, with approximately 4% of truck exhaust plumes having SSA greater than 0.50. Some of these high SSA values may be sampling artifacts, particularly in instances where particle extinction emissions are low. However, several of the high SSA truck plumes had clear absorption and scattering signals, suggesting that a minority of trucks have a relatively high PM light-scattering organic carbon to light-absorbing black carbon emission ratio.

Cumulative Distributions and High-Emitter Correlations. Cumulative emissions distributions for selected species considered in this study are presented in Figure 5. These plots show the relative skewness of emissions for each species with the vertical axis indicating the fraction of total emissions coming from corresponding fractions of trucks plotted on the horizontal axis. A 1 to 1 line on this plot would indicate all trucks have the same emission factor. The distribution for scattering cross-section emissions is the most highly skewed. This distribution was heavily influenced by two extremely high-emitting trucks, which accounted for 9% of total emissions. The cumulative distribution of BC emissions (20% of trucks accounted for 64% of total emissions), which was similar to that of particle mass and absorption and extinction cross-section emissions, is slightly more skewed than the BC distribution measured in 2006 when 20% of trucks accounted for 60% of total BC emissions.[22] The relative importance of high-emitting trucks is expected to continue to increase in future years as more trucks are equipped with DPFs. The effect of increased DPF use is also apparent in the NO_2 cumulative emissions distribution, which shows that 50% of total NO_2 is emitted by just 10% of trucks. Remote sensing measurements of diesel truck exhaust in Colorado prior to the use of DPFs show the top 10% of trucks contributed 37% of total NO_2 emissions.[16] Of the other gaseous species, CO emissions are the most highly skewed, whereas NO emissions are the least skewed of all pollutants considered in this study.

The degree of overlap among high-emitting trucks of pollutants considered in this study is analyzed in Table 2. Each table entry represents the percentage of trucks that are common to the highest-emitting 10% of trucks for two species. A score of 100 signifies complete commonality among the highest emitters for two pollutants. A score of 0 signifies no overlap among the high-emitting truck subpopulation. In general there is very high correspondence among high-emitters of BC, $PM_{2.5}$, and light-scattering/absorbing particles. Combustion conditions that maximize formation of NO_x (i.e., high

temperatures and lean air/fuel ratios) tend to limit emissions of PM. This is evidenced here by the low degree of overlap (<20%) among trucks with the highest emission factors of NO and PM species. A similar lack of correspondence between high NO_x and high BC-emitting trucks was reported for diesel truck fleets in two Chinese cities.[45] There is a moderate degree of overlap in the highest emitting trucks for C_2H_4 and HCHO. With the exception of NO_2, there is some overlap in the highest-emitting trucks for all pollutant pairs considered here. The highest NO_2 emitting trucks did not rank in the top 10% for any of the other species measured in this study, except for one truck that was found to have both high NO_2 and HCHO emissions. Trucks having the highest NO_2 emissions are likely equipped with DPFs, and these systems can be quite effective in reducing emissions of CO and organic gases in addition to PM.

■ ASSOCIATED CONTENT

Supporting Information

Table of measured species and analytical instrumentation, and numerous figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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