Contribution of Lubricating Oil to Particulate Matter Emissions from Light-Duty Gasoline Vehicles in Kansas City

Darrell B. Sonntag,[†] Chad R. Bailey,*,[†] Carl R. Fulper,[†] and Richard W. Baldauf[†,‡]

[†]National Vehicle and Fuel Emissions Laboratory, Office of Transportation and Air Quality, U.S. Environmental Protection Agency, Ann Arbor, Michigan 48105, United States

[‡]National Risk Management Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711, United States

Ⓢ Supporting Information

ABSTRACT: The contribution of lubricating oil to particulate matter (PM) emissions representative of the in-use 2004 light-duty gasoline vehicles fleet is estimated from the Kansas City Light-Duty Vehicle Emissions Study (KCVES). PM emissions are apportioned to lubricating oil and gasoline using aerosol-phase chemical markers measured in PM samples obtained from 99 vehicles tested on the California Unified Driving Cycle. The oil contribution to fleet-weighted PM emission rates is estimated to be 25% of PM emission rates. Oil contributes primarily to the organic fraction of PM, with no detectable contribution to elemental carbon emissions. Vehicles are analyzed according to pre-1991 and 1991−2004 groups due to differences in properties of the fitting species between newer and older vehicles, and to account for the sampling design of the study. Pre-1991 vehicles contribute 13.5% of the KC vehicle population, 70% of oil-derived PM for the entire fleet, and 33% of the fuel-derived PM. The uncertainty of the contributions is calculated from a survey analysis resampling method, with 95% confidence intervals for the oil-derived PM fraction ranging from 13% to 37%. The PM is not completely apportioned to the gasoline and oil due to several contributing factors, including varied chemical composition of PM among vehicles, metal emissions, and PM measurement artifacts. Additional uncertainties include potential sorption of polycyclic aromatic hydrocarbons into the oil, contributions of semivolatile organic compounds from the oil to the PM measurements, and representing the in-use fleet with a limited number of vehicles.

INTRODUCTION

Estimating the contribution of lubricating oil to particulate matter (PM) emissions from the in-use fleet is critical in estimating PM mobile-source emission inventories, projecting trends over time, and informing vehicle emission control policies. Poorly constrained estimates of the impacts of high-emitting and oil-burning vehicles have been identified as key drivers of uncertainty in inventory development and receptor modeling.[1,2] The widespread use of such methods in local, national, and global policy settings highlights the importance of comprehending the major role oil consumption plays in vehicle emissions.[3,4]

Light-duty gasoline vehicle (LDGV) PM is primarily carbonaceous matter formed by gasoline and lubricating oil from (1) unburned components and additives, (2) incomplete combustion, and (3) pyrolysis in fuel-rich pockets within the cylinder.[5−7] Lubricating oil (also known as engine oil, motor oil, and engine lubricant) coats the piston and cylinder walls, from which semivolatile organic compounds (SVOC) desorb during the exhaust stroke, providing a major pathway for oil consumption and PM emissions for properly functioning LDGVs. SVOCs are higher molecular weight hydrocarbons that partition between the gaseous and particle phases. Some SVOCs nucleate or condense onto particles as exhaust dilutes.[8] Positive crankcase ventilation (PCV) systems prevent the direct emissions of oil vapors from the engine crankcase, but oil reintroduced into intake air by PCVs can still increase PM emissions.[6] Older, poorly maintained vehicles consume excessive oil due to engine wear and malfunction, such as leaking piston rings, gaskets, and valve guides.[6,9,10]

PM emission rates from properly maintained LDGVs are significantly higher directly following oil changes,[10] and used oil is enriched with low-volatility compounds as compared to fresh oil.[11,12] This suggests that as oil ages, its light ends volatize and contribute to PM and SVOC emissions. Oil consumption also increases fuel-derived PM and hydrocarbon emissions, as unburned fuel vapors desorb from oil films on the piston and cylinder walls,[13] and additives in the lubricating oil poison and deactivate the catalytic converter.[14]

Table 1. Overview of Stratified Design of Kansas City Study: Strata Definitions, Strata Population, Individual and Composite Samples, and Sample Weights

vehicle type[a]	strata	model year group	strata vehicle population[c]	% of KC LDGV vehicle population[b]	summer vehicles tested	summer chemical samples	summer sample weights[d]	winter vehicles tested	winter chemical samples	winter sample weights[d]
truck	1	pre-1981	12 956	1.1%	2	2	3239	3	3	2159
	2	81−90	43 579	3.7%	4	4	5447	3	3	7263
	3	91−95	84 803	7.2%	6	2	21 201	7	3	14 134
	4	96−2005	336 855	28.6%	8	2	84 214	11	3	56 142
car	5	pre-1981	15 312	1.3%	5	5	1531	4	3	2552
	6	81−90	87 158	7.4%	4	4	10 895	5	4	10 895
	7	91−95	157 827	13.4%	7	4	19 728	9	4	19 728
	8	96−2005	439 325	37.3%	15	3	73 221	9	3	73 221
		sum =	1 177 814	100%	51	26		51	26	

[a]Cars are defined as coups, sedans, and wagons; trucks are defined as minivans, sport-utility vehicles, and pickups. [b]Population percentages estimated from the 2004 Kansas City Travel Behavior Survey.[26] [c]The number of vehicles in the Kansas City Area based on the 2000 census.[27,28] [d]The number of vehicles that each chemical sample represents, assuming the vehicle population is equally split between the summer and the winter.

Lubricating oil emissions are likely important contributors to the exposure and health, and climate impacts of vehicle emissions. Per unit mass, the relative toxicity of exhaust PM increases with oil-associated species, including hopanes, zinc, phosphorus, and calcium.[15,16] SVOCs associated with engine oil are suggested as the primary components of high particle number concentrations near high-traffic roadways.[17−19] Atmospheric oxidation of SVOCs results in secondary organic aerosols (SOA), which may contribute to high PM concentrations worldwide.[20] Oil-derived organic aerosols, mixed with light-absorbing carbon, also can enhance the absorption of solar radiation.

Estimating lubrication oil's contribution to PM emissions from the in-use fleet is complicated by the disproportionate contribution of oil emissions from a small percentage of malfunctioning, poorly maintained vehicles. Previous studies report PM emissions from specially recruited smoking and high emitting vehicles at 70−600 times larger than vehicles meeting EPA Tier 1 emission standards.[9,12,21,23] Such approaches cannot estimate the prevalence of such vehicles in the real fleet. Further, the PM from high-oil emitters differs compositionally from normal vehicles, with higher OC/PM ratios, and higher emissions of oil markers used as fitting species in receptor models, including hopanes, steranes, and additive inorganics such as zinc, calcium, and phosphorus.[9,12,21,23] The in-use prevalence and variable composition of PM from high oil-emitting vehicles may be key sources of uncertainty in estimating the ambient PM contribution of LDGVs in receptor modeling.[1,21]

Rather than develop separate prevalence and emission rates of high and normal emitters, this Article estimates the mean contribution of lubricating oil to PM emission in the in-use fleet using a large representative vehicle sample, the Kansas City Light-Duty Vehicle Emissions Study (KCVES). This Article extends on prior research using multiple regression to estimate the contribution of fuel and oil to PM, by using survey analysis methods to account for the representative fleet in the KCVES. Kleeman et al.[22] and Fujita et al.[12], respectively, developed and applied multiple linear regression methods to estimate oil and fuel contributions to vehicle exhaust PM. This Article extends their methods by developing an approach to estimate the representative oil contribution to average PM by the chemical analysis subset in the KCVES, and applying survey analysis methods to assess the uncertainty associated with modeling the fleet-average contribution from a limited number of samples.

■ METHODS

Data. The KCVES tested 496 vehicles in two rounds. Round 1 (summer) ran from July to September 2004, and round 2 (winter) ran from January to April 2005. Using stratified random sampling, vehicles were recruited within eight strata representing vehicle types (passenger car or light-duty truck) and four model-year groups representing technology differences: carburetors, early fuel injectors, phase-in Tier-1 standards, and Tier-1 and National Low Emission Vehicles. The KCVES recruited vehicles from a cohort of owners designed to represent the population of the Kansas City Metropolitan Area according to household size, number of vehicles, income, type of residency, ethnicity, age, and geographic dispersion.[24] The design was optimized to estimate mean PM emissions while accounting for varying dispersion among the strata. Because ambient temperature significantly affects PM rates on the cold-start of the LA92 cycle,[25] the vehicles are differentiated by season, as outlined in Table 1. An overview of relevant aspects of the KCVES is provided herein with details covered in Fulper et al.[24] and EPA.[26]

The data used to estimate the lubricating oil and fuel contributions to PM were collected from 102 vehicle tests (99 separate vehicles, with three repeat tests) that were selected for chemical analysis. The data were collected in two stages: (1) PM measurements from each vehicle, and (2) chemical analysis. In the first stage, the emission rates, including PM (gravimetric mass), elemental carbon (EC), organic carbon (OC), and total carbon (TC), were sampled from each vehicle as it performed the California Unified Cycle or "LA92" driving cycle. The LA92 includes a cold-start (phase 1), hot-running (phase 2), and a hot-start (phase 3), covering 9.8 miles of driving representative of arterial and freeway driving in Los Angeles, CA. Vehicles were tested on a chassis dynamometer at ambient temperatures in a garage with open bay doors after soaking there overnight. The gasoline and lubricating oil were left "as received" during testing.

An overview of the PM sampling system is provided in the Supporting Information. Briefly, exhaust was diluted with a Positive Displacement Pump-Constant Volume Sampler (PDP-CVS), and drawn through a $PM_{2.5}$ cyclone and 47 mm Teflon membrane and quartz fiber filters (QFF). Filter face temperatures were maintained at constant 47 ± 1 F by adiabatic dilution. Teflon filters were weighted pre- and post-tests to calculate the mass emission rates. EC, OC, and TC emission

rates were measured from QFFs by thermal optical reflectance (TOR) using the IMPROVE (Interagency Monitoring of Protected Visual Environments) procedures.[26] In addition to filter measurements, a photoacoustic spectrometer measured light-absorbing carbon reported as black carbon (BC).[24]

In the second stage of analysis, the chemical species were analyzed for 102 selected vehicle tests. Emissions were sampled with Teflon-impregnated glass filters with backup glass cartridges with Amberlite XAD-4 adsorbent resins (TIGF/XAD) over the entire LA92 cycle. The organic material collected on the TIGF/XAD was then solvent extracted, and analyzed for speciation by gas chromatography and mass spectrometry (GC/MS). Speciation vehicles were sampled from each stratum, dependent on obtaining sufficient organic aerosol loadings for GC/MS, estimated from continuous PM instruments. For pre-1991 vehicles, each speciation sample included a single vehicle. For newer vehicles (1991−2004), samples from 2 to 5 vehicle tests were extracted and composited together. Although the composite chemical samples contained PM emissions from more than one vehicle, the vehicles contributing to each composite sample were from the same strata and had similar estimated OC/PM ratios.[26] Compositing reduced the 102 individual vehicle tests selected for speciation to 52 individual and composite samples (26 in each season) as shown in Table 1.

Given the limited sample size within older strata, where emission composition is likely quite heterogeneous due to multiple emission failure modes (i.e., overfueling, bad catalyst, oil consumption), selection of a few samples for speciation could result in a less than representative depiction of those strata. To ensure that the speciated vehicles are representative of the whole KCVES vehicle population, the gravimetric PM emission rates and the BC/PM ratios from the chemical samples are compared to those from the full KCVES data set. Figure 1 plots LA92 p.m. emission rates from the full KCVES sample (522 tests) and the 102 chemical analysis tests. The fleet-weighted mean gravimetric mass emission rate (12.85 mg/
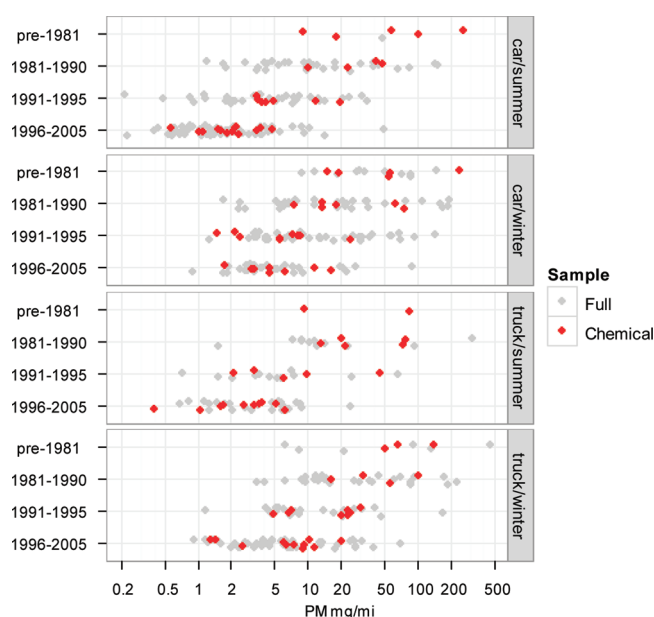

Figure 1. Comparison of the gravimetric mass (mg/mi) emission rates measured in the KCVES for the vehicles selected for chemical analysis and the full sample.

mi) for the entire fleet is slightly higher than the mean of speciation vehicles (10.77 mg/mi), but the difference is not statistically significant. The slight underestimation of the fleet PM emission rates by the chemical sample appears to be more pronounced in the newest vehicles (1996−2005), which make up the large percentage of the KC vehicle population (66%). The mean PM emission rates for the newest speciation vehicle strata are consistently lower than those of the full KCVES sample by 12−36% (Figure S2). However, the differences are not significantly different at the strata level. The fleet-weighted mean BC/PM ratio calculated from the full sample (0.21) is slightly smaller than when calculated with the chemical samples (0.25), but the BC/PM ratios are within the statistical variability of one another. The BC/PM ratios by strata are shown in Figure S3, with no systematic bias observed for vehicle type or season. Overall, the chemical subsample appears to be a sufficient representation of the full sample.

Survey Regression Model. Kleeman et al.[22] introduced a multiple linear regression approach to quantify vehicle exhaust PM emissions from oil or fuel using a single hopane and polycyclic aromatic hydrocarbon (PAH) compound. Fujita et al.[12] validated using the sum of hopanes and steranes, biomarkers found in lubricant, as tracers of oil-derived PM, by comparing apportionment with two other markers for lubricant, additive metals, and C_{20}−C_{35} alkanes and cyclo-alkanes measured as the unresolved complex mixture from GC/MS measurements. Fujita et al.[12] also estimated oil's contribution to PM in 12 KCVES vehicles tested in the KCVES, which were not representative of the in-use fleet.

This Article extends the basic method introduced by Kleeman et al.[22] by accounting for the stratified sampling framework in the KCVES to estimate oil's contribution to PM for the real-world fleet, and to quantifying uncertainty in the estimates. The basic form of regression is:

$$y = b + m_1 x_1 + m_2 x_2 + e \quad (1)$$

where y is EC, OC, TC, or gravimetric mass (MASS) emissions; b is the intercept; x_1 is the fuel markers' emission rate (ug/mi); and x_2 is the oil markers' rate (ug/mi); m_1 is the slope of the fuel-associated emissions; m_2 is the slope of oil-associated emissions; and e is the residual error. For each of the chemical samples, EC, OC, TC, and MASS emission rates were computed from the individual LA92 phases and vehicle-test measurements as shown in Tables S3,S4.[26] The regression model predicts the total or carbonaceous PM emission rates of the 52 chemical samples with the corresponding fuel and oil markers measurements. The intercept term is retained to ensure that the coefficients are unbiased, to preserve the validity of standard regression diagnostics, and to acknowledge that the simple linear regression model is unlikely to account for the totality of variability in PM emissions.

Gasoline Fuel Markers. The sum of three high molecular weight PAHs (benzo(*ghi*)perylene, indeno[123-*cd*]pyrene, and coronene) measured from each chemical sample is used to represent PM emissions formed from gasoline fuel in the engine. Gasoline contains trace amounts of these PAHs, and their emissions result overwhelmingly from formation during combustion.[5,29] Zielinska et al.[30] previously identified these PAHs as effective gasoline markers because they are emitted at higher concentrations than in diesel exhaust and are not present in fresh lubricant oil.[11]

One of the uncertainties of using PAHs to apportion gasoline is that PAHs partition into the lubricating oil and can be

Table 2. Estimated Coefficients, 95% Confidence Intervals, and R^2 Values from Model 1 Used To Predict EC, OC, TC, and MASS Emissions for the Data Weighted According to the KC Population Fleet

MY group	PM component	intercept (b)		fuel tracer (m_1)		oil tracer (m_2)		R^2
		estimate	p-value	estimate	p-value	estimate	p-value	
pre-1991	EC	2.16 ± 1.91	0.03	0.07 ± 0.02	<0.0001			0.83
	OC	7.55 ± 6.34	0.02	0.01 ± 0.03	0.68	0.15 ± 0.04	<0.0001	0.74
	TC	10.42 ± 6.60	0.004	0.09 ± 0.04	0.0001	0.13 ± 0.04	<0.0001	0.83
	MASS	13.02 ± 7.48	0.002	0.10 ± 0.04	0.0002	0.16 ± 0.07	<0.0001	0.79
1991−2004	EC	0.52 ± 0.59	0.08	0.18 ± 0.05	<0.0001			0.80
	OC	0.99 ± 0.29	<0.0001	0.11 ± 0.03	<0.0001	0.11 ± 0.05	0.0004	0.86
	TC	1.58 ± 0.69	0.0002	0.30 ± 0.06	<0.0001	0.08 ± 0.12	0.18	0.87
	MASS	1.43 ± 1.09	0.01	0.35 ± 0.07	<0.0001	0.18 ± 0.24	0.12	0.83

emitted with oil emissions.[6,30,31] Fujita et al.[11] analyzed 15 oil samples from the winter round of the KCVES and determined that PAHs absorbed in the oil contributed less than 1% of the PAH markers measured on corresponding composite samples. The three PAH species are assumed to be valid markers for the fuel contribution to PM in the regression model, but the contribution from absorbed PAHs in oil in all 52 chemical samples is likely small, but nonetheless uncertain.

Lubricating Oil Markers. Lubricating oil is a complex hydrocarbon mixture ranging from approximately C_{14} to C_{45}.[5] Hopanes and steranes are polycyclic high-molecular weight petroleum compounds ($\sim C_{27}−C_{35}$) that geochemically derived from cell membranes of prokaryotes and eukaryotes, respectively. They are useful oil markers because they are not expected to be present in the lighter boiling point ranges of gasoline ($\sim C_4−C_{10}$).[5,30] Fujita et al.[12] measured trace hopanes and steranes in gasoline, but they were unrelated to the measurement of PM emissions. Fujita et al.[11] identified the sum of the most abundant hopanes and steranes as effective oil markers in the KCVES (Table S2). These compounds were summed from the GC/MS measurements and used as the oil markers in this study (Tables S3,S4).

Application to the Kansas City Light-Duty Gasoline Fleet. Equation 1 assumes linear relationships between the markers and particulate emissions (m_1 and m_2). However, the relationship between the markers and particulate emissions is anticipated to vary considerably among individual vehicles and classes. Kleeman et al.[22] estimated significantly different slope coefficients for a hopane oil marker and a PAH fuel marker among five groups of LDGVs classified according to the technology, age, and emissions characteristics. Unlike Kleeman et al.,[22] the KCVES does not have repeated chemical measurements on individual vehicles and has limited chemical measurements for vehicles with similar characteristics. Despite the limited sample size, to yield unbiased and interpretable results, the linear model should be applied to groups of samples where the relationship between the markers and particulate emissions is linear across particulate emission levels. The ratios of (hopanes and steranes)/(organic carbon) and (PAH markers)/(elemental carbon) are used to group strata with similar relationships between markers and emissions, as shown in the Supporting Information (Figures S4 and S5). The samples are grouped into two model year groups, pre-1991 and 1991−2004, because the within-group ratios of markers to PM emission ratios are relatively constant in these model years groups, while being large enough to estimate statistically significant relationships. Separate models are estimated to the observations in the two model year groups for each measure of particulate matter (EC, OC, TC, and MASS).

A survey regression model is implemented by incorporating the statistical weights as presented in Table 1 into the regression estimates. The sample weights are calculated as the ratio of the vehicle strata population to the number of chemical samples in the strata. The statistical weighting corrects for the oversampling of older vehicles and trucks in the KCVES as compared to their population in the KC fleet. Variances of the coefficients are estimated using jackknife repeated replication (JRR), a nonparametric resampling method that removes one observation with each replication. JJR is implemented to evaluate the robustness of the model results, to ensure that the model coefficients are not dependent on one or two influential observations in each group of samples. The weighted-regression model parameters and JJR variances are estimated using SAS 9.2 Proc SurveyReg.[32]

Model Diagnostics. The statistical tests of coefficients in the standard linear regression are based on the assumptions of normal, independently distributed residuals with mean of zero. Standard statistical tests of normality generally support the normality assumption of the model residuals to the pre-1991 chemical samples, but not the residuals from the 1991−2004 chemical samples (Table S5). However, linear regression estimates are generally robust to departures of normality as long as the residuals are symmetric around zero.[32] The model residuals are evaluated in Figures S6,S7 in the Supporting Information, and the residual errors of the model are approximately symmetric around 0, and do not give strong evidence of heterogeneity of variances or misspecification of the model form (i.e., trends in the residuals, suggestive of nonlinear effects or missing variables). The model assumptions and model form are deemed acceptable representations for the data.

■ RESULTS

Model Coefficients. The coefficients and the model terms from the multiple linear regression models are displayed in Table 2, along with 95% confidence intervals for each coefficient estimated by the JJR. As expected, the fuel tracer coefficients (m_1) are significantly higher in the 1991−2004 group as compared to the pre-1991 vehicles in each of the EC, OC, TC, and MASS models, reflecting the smaller (PAH markers)/(elemental carbon) ratio observed for the 1991−2004 vehicle samples. The oil tracer coefficients (m_2) are not significantly different between the two model-year groups, reflecting a relatively consistent contribution of oil particulate with emissions of hopanes and steranes across vehicle technologies.

The intercept is significant at the 95% confidence level in all but one of the models and is significantly larger in the models for the pre-1991 vehicles. Unlike Kleeman et al.[22] and Fujita et

al.,[12] the intercept is retained in the model to enable unbiased estimates of the mean emission rates, prevent misfits of the model at low PM levels, and to avoid placing strong assumptions on the data. However, if the ratios of (hopanes and steranes)/(organic carbon) and (PAH markers)/(elemental carbon) monotonically increase with emissions within each model year group (pre-1991 and 1991−2004), the model will retain an intercept term as a byproduct of the misfit of the constant slope coefficients (m_1 and m_2) to the pooled data. The large intercept for the pre-1991 vehicles is attributed to the slight increase in the (hopanes and steranes)/(organic carbon) ratio (Figure S5) within the samples in the group. The samples were split into smaller groups (by season, pre-1981 and 1981−1990 model year groups, and truck vs car) in an attempt to improve the homogeneity of the particulate to marker ratios in a way that the intercept was no longer significant to the model predictions. When the data were fit to smaller groups, the intercept retained its high significance, and the model coefficients for the gasoline and oil markers became largely dependent on one or two observations.

In-Use Fleet Apportionment. Figure 2 displays the estimated apportionment of the fleet-average EC, OC, TC,
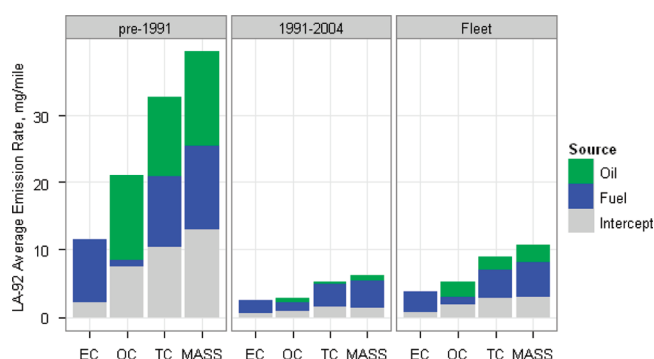

Figure 2. Estimated contributions of elemental carbon (EC), organic carbon (OC), total carbon (TC), and gravimetric mass (MASS) emission rates for the pre-1991, 1991−2004, and fleet-average emission rates calculated from eq 2.

and MASS emission rates to the intercept, fuel, and oil by model year groups. The linear regression coefficients are unbiased estimators of the average emission rates for each model year group:

$$\overline{y} = b + m_1\overline{x}_1 + m_2\overline{x}_2 \qquad (2)$$

The $m_1\overline{x}_1$ term estimates the fuel contribution, $m_2\overline{x}_2$ estimates the oil contribution, and b estimates the emissions that are explained by the intercept term.

Table 3 displays the uncertainty of the contributions based on the 95% confidence levels of the regression parameters estimated from the JJR. In calculating the confidence levels of the fuel and oil contributions, the uncertainty of the model parameters is used, while assuming fixed mean emission rates of the fuel and oil markers. The confidence intervals for the fuel and oil contributions are estimated by the range of the 2.5 and 97.5 percentile slope coefficients multiplied by the mean marker concentrations $(m_{1(0.025)}\overline{x}_1, m_{1(0.975)}\overline{x}_1)$ and $(m_{2(0.025)}\overline{x}_2, m_{2(0.975)}\overline{x}_2)$. The percentage contribution to the total EC, OC, TC, and MASS is calculated by dividing the estimated contributions and confidence intervals by the fleet-average EC, OC, TC, and MASS emissions. The fleet-average

parameters and associated uncertainties are calculated by the linear combination of the pre-1991 and 1991−2004 groups using the weights in Table 1. The degrees of freedom for the confidence intervals for the fleet-average contributions are calculated using the Satterthwaite approximation.[33]

Elemental Carbon. The EC emission rates are much larger for the older vehicles, but the relative contribution attributed to gasoline is similar for both groups of vehicles. Gasoline is estimated to contribute 81% of the pre-1991 EC emission rates, and 79% of the 1991−2004 EC emission rates, with the upper confidence levels extending to 99% and 100% for the two groups, respectively. Elemental carbon formation is favored in fuel-rich conditions, which occur in LDGV during cold-starts and large accelerations. Further, at high loads, LDGV vehicles can intentionally run rich to protect the catalyst from high temperatures.[7] The oil tracers had a slightly negative and insignificant effect in both the pre-1991 and the 1991−2004 EC models and were removed from the EC model to estimate source contributions. Kleeman et al.[22] also estimated that light-duty gasoline EC emissions are formed primarily from the fuel, with little or no significant contributions from the oil.

Organic Carbon. The relative contribution of oil and gasoline to OC emissions shifts dramatically between the model year groups. For the pre-1991 vehicles, the oil contributes 60% of the OC emissions, with a minor fuel contribution (4%). For the 1991−2004 vehicles, the fuel contribution (44%) is significantly larger than the oil contribution (21%). The large oil contribution (12.75 mg/mi) for the pre-1991 vehicles is expected to be due to their older technologies and increased wear and deterioration. Kleeman et al.[22] also estimated that the lubricating oil contribution to OC increased with three-way catalyst vehicle (1991−1999) and oxygen catalyst (1977−1980) vehicles as compared to LEV vehicles (1996−2003), and was the dominant OC source for two visibly smoking vehicles (1968 and 1993 model years).

The magnitude of fuel derived OC emissions is estimated to be statistically similar between the model year groups (0.88 and 1.21 mg/mi). The fuel coefficients are not significant at any reasonable confidence level for the pre-1991 vehicles, but were kept in the model because gasoline is a known source of OC emissions. LDGV vehicles emit particle-phase PAHs, n-alkanes, and isoprenoids, from unburned, partially oxidized, or combusted components of the gasoline fuel, although these resolved organic compounds comprise a minor portion of the total measured organic particulate in most studies.[29]

The intercept explains a relatively large percentage of OC emissions for both the pre-1991 and the 1991−2004 groups (36%). The larger intercept relative to the OC emissions could be due to the higher propensity of OC to have positive measurement artifacts. Because of high internal surface areas and potential for intermolecular bonding, QFFs are prone to positive particle-phase OC artifacts from adsorbed SVOCs.[34,35] In fact, large positive-artifacts from SVOC emissions were detected on 10 KCVES winter vehicles that were tested with QFFs behind Teflon filters.[36] The positive artifact can be a significant contribution for OC measurements from low-emitting vehicles and could result in persistent OC measurements on vehicles, despite low levels of the particle-phase fuel and oil markers.

Total Carbon. For the pre-1991 vehicles, the TC model estimates a 10.65 mg/mi contribution from fuel, which corresponds well with the summed contributions from the EC and OC models (10.22 mg/mi). Likewise, for the 1991−

Table 3. Estimated Contributions of the Intercept, Fuel, and Oil to the Elemental Carbon (EC), Organic Carbon (OC), Total Carbon (TC), and Gravimetric Mass (MASS) for the pre-1991, 1991−2004 Vehicle Group Emission Rates, mg/mi, and the Percentage Contributions, with 95% Confidence Intervals

MY group	PM component	intercept (b), mg/mi		fuel ($m_1\bar{x}_1$), mg/mi		oil ($m_2\bar{x}_2$), mg/mi	
pre-1991	EC	2.16	(0.25 to 4.07)	9.34	(7.29 to 11.4)		
	OC	7.55	(1.21 to 13.89)	0.88	(−3.48 to 5.23)	12.75	(9.07 to 16.43)
	TC	10.42	(3.82 to 17.01)	10.65	(6.04 to 15.26)	11.62	(7.82 to 15.42)
	MASS	13.02	(5.54 to 20.5)	12.46	(6.89 to 18.04)	13.98	(8.14 to 19.83)
1991−2004	EC	0.52	(−0.07 to 1.11)	2.00	(1.42 to 2.58)		
	OC	0.99	(0.7 to 1.28)	1.21	(0.91 to 1.51)	0.57	(0.3 to 0.85)
	TC	1.58	(0.89 to 2.27)	3.30	(2.64 to 3.96)	0.41	(−0.21 to 1.03)
	MASS	1.43	(0.34 to 2.53)	3.91	(3.12 to 4.71)	0.94	(−0.29 to 2.18)
fleet	EC	0.74	(0.19 to 1.29)	2.99	(2.43 to 3.55)		
	OC	1.87	(0.98 to 2.76)	1.17	(0.54 to 1.79)	2.22	(1.68 to 2.75)
	TC	2.77	(1.71 to 3.83)	4.29	(3.47 to 5.11)	1.92	(1.2 to 2.65)
	MASS	3.00	(1.64 to 4.35)	5.07	(4.08 to 6.06)	2.70	(1.4 to 4.01)
		intercept ($b/\bar{y}$), %		fuel ($m_1\bar{x}_1/\bar{y}$), %		oil ($m_2\bar{x}_2/\bar{y}$), %	
pre-1991	EC	19%	(2% to 35%)	81%	(63% to 99%)	0%	
	OC	36%	(6% to 66%)	4%	(0% to 25%)	60%	(43% to 78%)
	TC	32%	(12% to 52%)	33%	(18% to 47%)	36%	(24% to 47%)
	MASS	33%	(14% to 52%)	32%	(17% to 46%)	35%	(21% to 50%)
1991−2004	EC	21%	(0% to 44%)	79%	(56% to 100%)	0%	
	OC	36%	(25% to 46%)	44%	(33% to 55%)	21%	(11% to 31%)
	TC	30%	(17% to 43%)	62%	(50% to 75%)	8%	(0% to 19%)
	MASS	23%	(5% to 40%)	62%	(50% to 75%)	15%	(0% to 35%)
fleet	EC	20%	(5% to 35%)	80%	(65% to 95%)	0%	
	OC	36%	(19% to 53%)	22%	(10% to 34%)	42%	(32% to 52%)
	TC	31%	(19% to 43%)	48%	(39% to 57%)	21%	(13% to 29%)
	MASS	28%	(15% to 40%)	47%	(38% to 56%)	25%	(13% to 37%)

2004 vehicles, the TC model fuel contributions and summed EC+OC model fuel contributions are roughly equivalent (3.30 and 3.21 mg/mi). The TC model also estimates oil contributions comparable to those of the OC model for both model year groups. The consistency of the TC model with the summed results of the EC and OC models gives additional validation to the results from the regression models.

Gravimetric Mass. For the pre-1991 vehicles, the MASS model estimates similar contributions from the fuel and oil. For the 1991−2004 vehicles, fuel exceeds the oil contribution to total PM. In the fleet-average PM emission rates, the fuel contribution is 47% of the PM, and the oil contribution is 25%. While only contributing 13.5% of the vehicle population, the pre-1991 vehicles contribute 70% of the fleet-wide oil-derived PM emissions, and contribute 33% of the fuel-derived PM emissions.

The estimates of oil-derived total PM are slightly larger than the oil-derived OC and TC, which is likely explained by noncarbonaceous additives in the oil. The sum of zinc, calcium, manganese, phosphate, and sulfate emission rates from the pre-1991 vehicles is 1.45 mg/mile and 0.51 mg/mi from the 1991−2004 vehicles (Table S6). The emission rates of these inorganic oil-based compounds compare well with the difference in oil-derived MASS and OC estimates for the pre-1991 and 1991−2004 vehicles (1.23 and 0.37 mg/mi). However, noncarbon elements within organic particles may also explain some of the difference.

Metal emissions from engine and exhaust part wear (aluminum, iron, copper, chromium, and silicon) are potential sources of PM other than the fuel and lubricating oil. When these metal emissions are adjusted for their common oxidation states (Al_2O_3, Fe_2O_3, CrO_3, and SiO_2)[30,37,38], the metal oxides contribute 2.22 and 0.51 mg/mi of the PM for the pre-1991 and 1991−2004 model year groups. The metal masses constitute 17% of the PM intercept term in the pre-1991 model year groups, and 35% of the intercept in the 1991−2004 groups.

Uncertainties and Limitations. Through careful consideration of the fuel and oil markers, data structure, survey regression model assumptions, and quantitative assessment of uncertainty, the model provides robust estimates of the lubricating oil and fuel contributions to PM emissions. However, there are additional sources of uncertainty and limitations that cannot be quantified by the modeling approach, which include:

(1) The model is based on a cross-sectional "snapshot" of vehicles in the KCVES. The estimated impact of lubricating oil on LDGV PM emissions only considers the emissions measured at the time of the KCVES. The increase in fuel-derived PM emissions that occurs from excessive oil consumption during long-term vehicle operation cannot be estimated with these data. Likewise, the model assumes that the PAHs are emitted directly as a byproduct of gasoline combustion and does not consider that PAHs absorbed and emitted in the oil may be a significant source of PAHs for some vehicles. PAH partitioning into oil likely takes place over time frames longer than each vehicle was retained in the KCVES.

(2) The model assumes that the oil markers are consistent, well-correlated markers with the full range of oil-derived PM emissions. Because the hopanes and sterane compounds are relatively nonvolatile compounds, the markers could underestimate the contribution of the

lighter SVOCS from lubrication oil that contribute to the PM measurements, including absorbed PM filter artifacts.

(3) Inclusion of the intercept likely causes the contribution of the fuel and lubricating oil to be underestimated. The metal wear emissions and positive measurement artifact are physical rationale behind a portion of the intercept. However, these are unable to explain much of the intercept, particularly for the pre-1991 vehicles, which had an intercept of ~13 mg/mi. As explained earlier, the intercept is an outcome of fitting a pooled data set by a relatively simple linear model. Thus, some of the intercept emissions are in reality contributed by the lubricant and/or the fuel; however, the contribution attributable to each source is unknown. Even though the intercept prevents the complete allocation of PM to the fuel and lubricating oil, the intercept is retained to maintain transparency regarding the uncertainties and limitations involved in the apportionment of the PM emissions.

(4) Significant effort in both the KCVES study design and the selection of the chemical samples was made to ensure the samples are representative of the in-use fleet. Through the use of the JRR resampling method, the impact of excluding observations from the sample was quantified. Despite these efforts, the number of vehicles tested for chemical analysis are still limited, and uncertainties exist about the representation of the sample to both the Kansas City Metropolitan Area and other areas of the United States. For example, the vehicles selected for chemical analysis may be slightly under-represented by higher emitters in the newer vehicle strata (1996−2004), which could lead to an underestimation of the lubrication oil contribution.

(5) An advantage and disadvantage of the study is that the estimates of fuel and oil contributions to PM are based on aggregated measurements from vehicles tested on the LA92 driving cycle. However, better understanding of the relative impacts of specific driving conditions (i.e., cold-start vs high-load conditions) on the contribution of oil-derived PM emissions from LDGVs is needed, such as has been done for light-duty diesel engines.[39]

(6) The relative oil contribution to PM emissions of the in-use vehicle fleet has likely changed since 2004 due to fleet-turnover, new vehicle technologies, changes in fuel properties, and implementation of the Tier 2 Vehicle & Gasoline Sulfur Program Final Rule (Tier 2). The average fuel sulfur content for a subsample of 40 vehicles in round 2 of the KCVES was 203 ppm,[26] far above the average fuel sulfur content of 30 ppm set by the Tier 2.[40] Additionally, Tier 2 tightened the PM and gaseous criteria emission standard for LDGVs. Tier 2 compliant vehicles started phase-in to the vehicle fleet in 2004, although none were tested in the KCVES. The introduction of new LDGV technologies may have a mixed impact on the contribution of oil-derived PM emissions. Vehicle manufacturers continue to recommend longer oil change intervals, which imply reductions in oil-consumption in new vehicles through oil formulations and improved engine and manufacturing technologies.[41] Conversely, gasoline direct injection engines can increase the PM emissions with higher soot formation, and turbochargers may provide additional pathways for lubricating oil to contribute to PM emissions.[7] More work is needed to assess the impacts of these changes on PM emissions from in-use vehicles. Notwithstanding its uncertainties and limitations, this study provides an important baseline estimate of the lubricating oil contribution to PM emissions from the in-use LDGV fleet in the United States.

■ ASSOCIATED CONTENT

⑤ Supporting Information
Details on PM sampling, measured PM and marker emission rates of individual and composite samples, comparison of PM means and BC/PM ratios between chemical subset and all KCVES tests, and model diagnostic tests and plots. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: bailey.chad@epa.gov.

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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