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Lubricating Oil Dominates Primary Organic Aerosol Emissions from Motor Vehicles

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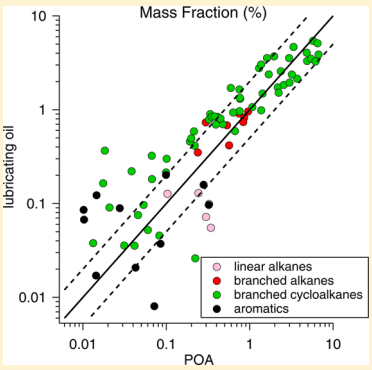
Supporting Information

ABSTRACT: Motor vehicles are major sources of primary organic aerosol (POA), which is a mixture of a large number of organic compounds that have not been comprehensively characterized. In this work, we apply a recently developed gas chromatography mass spectrometry approach utilizing "soft" vacuum ultraviolet photoionization to achieve unprecedented chemical characterization of motor vehicle POA emissions in a roadway tunnel with a mass closure of >60%. The observed POA was characterized by number of carbon atoms (N_C), number of double bond equivalents (N_{DBE}) and degree of molecular branching. Vehicular POA was observed to predominantly contain cycloalkanes with one or more rings and one or more branched alkyl side chains (≥80%) with low abundances of *n*-alkanes and aromatics (<5%), similar to "fresh" lubricating oil. The gas chromatography retention time data indicates that the cycloalkane ring structures are most likely dominated by cyclohexane and cyclopentane rings and not larger cycloalkanes. High molecular weight combustion byproducts, that is, alkenes, oxygenates, and aromatics, were not present in significant amounts. The observed carbon number and chemical composition of motor vehicle POA was consistent with lubricating oil being the dominant source from both gasoline and diesel-powered vehicles, with an additional smaller contribution from unburned diesel fuel and a negligible contribution from unburned gasoline.



INTRODUCTION

Motor vehicles are major sources of organic carbon in urban areas with implications for human health and air quality.[1,2] The emitted organic carbon is in the form of both primary particulate matter (PM) and gas phase organic compounds spanning a wide range of volatilities that can be oxidized in the atmosphere to form secondary organic aerosol (SOA).[3−5] The majority of fine PM from vehicles is carbonaceous in the form of either black (BC) or organic carbon, the latter of which is directly emitted as primary organic aerosol (POA).[6] Heavy duty (HD) diesel trucks are responsible for a disproportionate amount of BC and POA relative to light duty (LD) vehicles due to emission factors that are ∼50 and ∼15 times larger, respectively.[7−9]

In contrast to BC, POA contains many thousands of organic compounds that are thought to be derived from unburned fuel, unburned lubricating oil, and as byproducts of incomplete combustion.[10,11] Previous chassis dynamometer studies have estimated the contributions of unburned fuel and unburned lubricating oil to POA emissions for a small number of vehicles (<100 per study).[12−15] These studies showed a wide range in the contribution of unburned lubricating oil to POA emissions (20−80%). A substantial fraction of POA has been shown to be semivolatile under atmospheric conditions.[16−18] Following emission these organics can evaporate due to dilution to form low volatility vapors that can be oxidized to form SOA. Characterizing the chemical composition of POA and apportioning the contribution of these sources to the total POA mass is important as the chemical composition affects the rate and composition of SOA formation following evaporation,[19−23] as well as the physical properties and toxicity of the aerosol.[24,25]

The number of possible hydrocarbon isomers increases exponentially with increasing carbon number, which results in a very high number of constitutional isomers at large carbon numbers.[26] Due to the large number of hydrocarbon compounds present in POA, many of which are constitutional isomers, the vast majority of the mass cannot be resolved by conventional separation techniques and are present as part of

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an unresolved complex mixture (UCM).[10,27] As a result, previous studies have used tracer compounds considered representative of the different sources, for example, four and five ring polycyclic aromatic hydrocarbons (PAHs) for light duty gasoline engines, three ring PAHs for heavy duty diesel engines, and hopanes and steranes for unburned lubricating oil.[10,11,28,29] However, these tracers typically represent a very small fraction of the total emitted mass and this approach assumes that all the fuel based PAH tracers are emitted directly and do not partition into the lubricating oil within the engine to be later emitted as constituents of the unburned oil. Absorption and accumulation of fuel and combustion-derived PAHs in engine lubricating oil has previously been reported suggesting that the use of PAHs in tracer-based source apportionment methods may underestimate the importance of lubricating oil as a source of POA.[14,15]

Recent work has demonstrated the utility of coupling conventional gas chromatography (GC) or comprehensive gas chromatography (GC × GC) to high resolution time-of-flight mass spectrometry with 'soft' vacuum ultraviolet photoionization (VUV-HRTOFMS) to characterize large numbers of chromatographically unresolvable constituent isomers by carbon number, degree of unsaturation and degree of branching.[19,20,30] In this work, we determine the comprehensive chemical composition of POA for a much larger number of vehicles than is possible with dynamometer testing (N = 4000−7500 light duty, 50−200 medium, and 0−150 heavy duty) by analyzing filter samples collected in a highway tunnel using GC × GC/VUV-HRTOFMS. It is important to note that these data represent composites of a high number of vehicles and while they are representative of real world fleet and driving conditions high emitting vehicles can make a disproportionate contribution to these composite samples. Here we use this comprehensive analysis to better determine the contributions of unburned gasoline fuel, unburned diesel fuel, lubricating oil, and combustion byproducts to motor vehicle POA compared to tracer based methods.

■ EXPERIMENTAL SECTION

Measurement Site. Filter samples were collected between July 6−27, 2010 at the Caldecott Tunnel on Highway 24 in the San Francisco Bay Area. The tunnel is 1 km long and eastbound traffic is uphill on a 4% grade, which is helpful for providing engine load for the purposes of emissions testing. This site has been used for many years for studying on-road vehicle emissions and traffic conditions have been well characterized in previous studies.[31,32] In 2010, the tunnel consisted of three two-lane traffic bores; the outer bores accommodate a mixture of light and heavy duty traffic (bore 1) with one dedicated for eastbound traffic and the other for westbound traffic. The middle bore accommodates westbound traffic in the morning and eastbound traffic in the afternoon and is reserved exclusively for light duty vehicles (bore 2) at all times. However, there are a small number of medium and heavy duty trucks in that bore, which contribute ∼20% of the observed POA.[8] Sampling was conducted at the uphill end of both the eastbound traffic bores between 16:00 and 18:00 in bore 2 from July 6 to 15 and between 12:00−14:00 and 16:00−18:00 in bore 1 from July 19 to 27, 2010.

Filter Collection. Filter samples were collected downstream of sharp cut cyclones (BGI) at a flow rate of 16.7 L min^{-1} to remove particles with diameters greater than 2.5 μm from the sampled air. In order to remove positive sampling artifacts, samples were collected using the tandem filter sampling method where two quartz filters (47 mm, Pallflex Tissuquartz 2500 QAT-UP) were collected in parallel with one being collected in series behind a Teflon filter (Gelman Sciences, Teflon membrane, 2.0 μm pore size).[33] Here we assume negligible adsorption of semivolatile gases onto the Teflon filters, and use the quartz behind Teflon (QBT) signal to correct for positive gas phase artifacts from the other quartz filter as described in previous work (Figures S1 and S2, Supporting Information).[7,8,31,34] Evaporation of organics from the Teflon filter can also contribute to organic mass on the QBT filter, which can result in an overcorrection for the positive artifact, though this is estimated to be <20% and has not been accounted for in this work.[35] In total, 48 filter samples were collected: 24 quartz and 24 QBT. Prior to sampling, quartz filters were baked at 800 °C for 6 h to remove carbonaceous impurities.

Filter Analysis. Portions of all the filters (1.1 cm^2) were analyzed for total organic carbon (OC) and black carbon (BC) using a thermal optical technique, as described in previous work.[7,8,31] A subset of 18 filter samples (nine quartz and the corresponding nine quartz behind Teflon) were analyzed by GC × GC/HRTOFMS. This subset of samples was selected to span a range of diesel vehicle influence; 1−7% of the total vehicle counts (Table S1, Supporting Information).

Filter punches were subsampled for organic analysis using punches (1.2 cm^2) loaded into a thermal desorption and autosampler system (TDS3 and TDSA2; Gerstel Inc.) heated to 300 °C under helium flow, focused at 20 °C on a quartz wool liner in a cooled inlet (CIS4; Gerstel Inc.) then introduced by rapid heating in helium to the gas chromatograph (GC, Agilent 7890). Samples of "fresh" unused lubricating oil (SAE-10W30 and SAE-15W40), typically used in light duty passenger vehicles and heavy duty diesel trucks, respectively, were diluted in chloroform and directly injected with a syringe into the CIS4 inlet. Analytes were separated on a nonpolar primary column (60 m × 0.25 mm ×250 μm Rxi-5Sil-MS; Restek) and a moderate polarity secondary column connected in series (1 m × 0.25 mm ×250 μm Rtx-200MS; Restek). A cryogenic dual-stage thermal modulator (Zoex Corporation) consisting of guard column (1.5 m × 0.25 mm, Siltek; Restek) was the interface between the two columns. The modulation period was 2.3 s. The carrier gas flow rate was 2 mL min^{-1} of helium and the GC temperature program was 40 °C hold for 2 min, 3.5 °C min^{-1} until 320 °C and hold for 10 min. Analytes were ionized using traditional 70 eV electron ionization (EI) or 10.5 eV vacuum ultraviolet photoionization (VUV) always using a high resolution (m/Δm ∼ 4000) time-of-flight mass spectrometer (HTOF, Tofwerk). All filter samples were analyzed twice, once using EI and once with VUV. To minimize fragmentation in VUV the ion source and transfer line from the GC were operated at lower temperatures of 150 °C (EI; 270 °C). The VUV beam (tunable from 8−30 eV but typically 10.5 ± 0.2 eV, ∼10^{15} photons s^{-1}) was generated by the Chemical Dynamics Beamline 9.0.2 of the Advanced Light Source at Lawrence Berkeley National Laboratory.

Characterizing Complex Hydrocarbon Mixtures. With the 'softer' VUV photoionization, fragmentation of the molecular ion is substantially lower relative to traditional electron ionization (EI). In this work, as in previous work, the molecular ion mass was used to classify compounds comprising the UCM by carbon number (N_C), number of double bond

equivalents in their structure (N_{DBE}) and degree of branching.[30] Each N_{DBE} decreases the molecular ion mass by two (loss of two hydrogen atoms) compared to the fully saturated alkane of the same carbon number indicating the presence of a double bond or alkyl ring structure in the molecule, while N_{DBE} of four or more could also indicate an aromatic ring.

Figure 1a shows an example of a retention time versus ion mass chromatogram obtained using GC × GC/VUV-HRTOFMS for a late-afternoon tunnel filter sample of POA collected on July 22, 2010 (sample 2216, see Table S1, Supporting Information). In this plot the second dimension separation is not visible. Molecular ion mass is observed to increase as a function of increasing GC retention time, indicating increasing molecular mass with decreasing volatility as expected. This pattern is not evident in GC/EI-MS analyses where substantial fragmentation of the molecular ion typically occurs, leading to overlapping fragmentation patterns that cannot be deconvoluted.[19] Figure 1b shows all compounds with 28 carbon atoms as a function of unsaturation with N_{DBE} from 0 (alkanes) to 6 (hexacycloalkanes and/or octahydro-3-ring PAHs). Higher N_{DBE} ≥7 corresponding to PAHs were also observed albeit in much lower abundances (Table S2, Supporting Information), but are not shown here for simplicity.

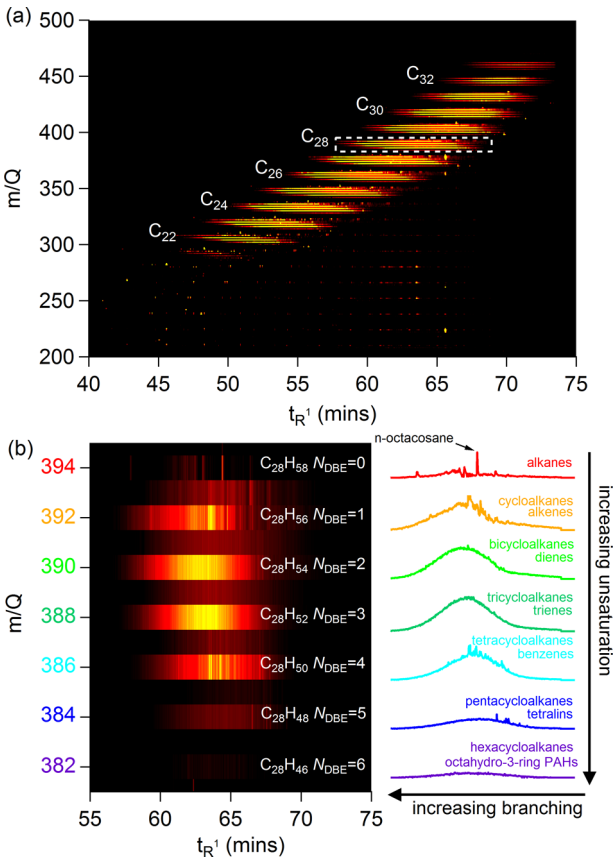

Figure 1. (a) GC × MS chromatogram of POA sample (quartz–quartz behind Teflon) collected on July 22, 16:00–18:00 in bore 1 obtained using VUV ionization illustrating the separation of hydrocarbon isomers by GC retention time (t_R^1) and ion mass-to-charge ratio (m/Q). Carbon number (evens labeled) can be assigned based on the apparent molecular ion. The dashed square shows the area that is enlarged in (b). (b) Close up of the C_{28} group of isomers showing their classification by number of double bond equivalents (N_{DBE}) or degree of unsaturation and degree of branching.

The GC retention time separation is critical for distinguishing between alkyl and PAH compounds of equal mass but different N_C (e.g., N_{DBE} = 0 versus N_{DBE} = 7).[30] Additionally, because molecular branching increases volatility, the GC retention time also provides information on the degree of branching. For example, compounds detected on the same molecular ion (m/Q 394) as *n*-octacosane but eluting earlier from the GC column correspond to more volatile and more branched $C_{28}H_{58}$ isomers.

Following previous work we use the relationship between GC retention time and the effective saturation vapor concentration (C^o) for known compounds to "bin" the chemically characterized POA data into the "volatility basis set" (VBS) framework.[36,37] Transfer efficiency and changes in the response of the mass spectrometer were corrected based on a suite of deuterated internal standards coinjected with every sample. Similar to previous work, a broad suite of authentic standards (>100) were used to calibrate the response of the mass spectrometer and to account for differences in fragmentation between the observed compound classes.[19,20,30] All data processing was performed using custom written analysis software in IGOR pro 6.31 (Wavemetrics).

RESULTS AND DISCUSSION

Chemical Composition of POA and Similarity to Lubricating Oil. Figure 2 shows the average chemically characterized POA mass distributions for low HD (BC < 15 μg m^{-3}) and high HD (BC > 15 μg m^{-3}) influence (Table S2, Supporting Information) as a function of N_c and N_{DBE}. The low HD influence samples were measured in bore 2 (two samples) and during the weekend in bore 1 (one sample) and during these sampling periods >98% of the traffic was light duty vehicles. All the high HD influenced samples were collected in bore 1 during weekdays (six samples) when MD and HD vehicles comprised 2–8% of the total traffic compared with <2% for the low HD influenced samples (Table S1, Supporting Information). The mass fraction distributions of two "fresh" unused lubricating oils (SAE-10W30 and SAE-15W40) are also shown in Figure 2. The lower ion source and transfer line temperatures used to minimize fragmentation of the molecular ion in the VUV analysis limited the volatility range of analytes that could reliability be measured to compounds with ≤30 carbon atoms. The EI analysis was not subjected to the same temperature constraints and lower volatility compounds (≥C_{30} or log C^o < 0) were observed (Figure S3, Supporting Information). The total hydrocarbon signal, derived from high mass resolution peak fitting of the C_xH_y fragments,[20] was converted to mass through a linear regression against the sum of the components from the VUV analysis and was apportioned to specific carbon numbers based on the observed EI distribution of total hydrocarbons (Figure S3, Supporting Information).

The POA mass distributions were consistent between the different samples (Figure 2; Table S2, Supporting Information) with a mass-weighted standard deviation of ~30%. The total speciated mass from the VUV analyses was in good agreement with the total OC measured from the same filter samples using thermal-optical analysis (Figure S4, Supporting Information). The slope indicated a mass closure of 60 ± 20%, substantially better than the ~5% reported in previous work.[10,27] This mass closure improved to 80 ± 30% when the OC data was corrected to exclude organic mass desorbed from the filters at temperatures above 300 °C, the thermal desorption temper-

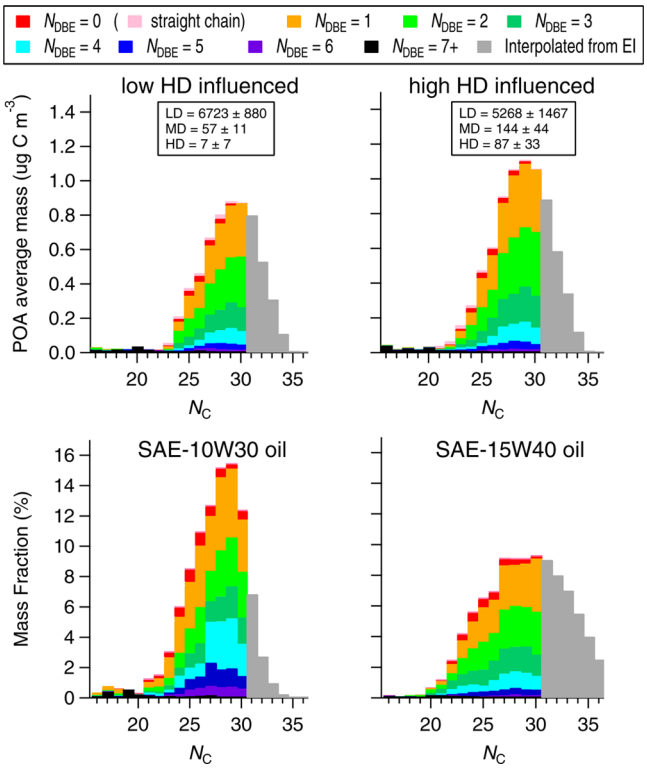

Figure 2. Averaged chemically characterized distributions of motor vehicle POA, separated into low HD (BC <15 μg m^{-3}) and high HD influence (BC>15 μg m^{-3}), and SAE-10W30 and SAE-15W40 lubricating oils. Distributions are shown as a function of carbon number (N_C) and number of double bond equivalents (N_{DBE}). The POA distributions are shown as mass concentrations in μg C m^{-3} while the lubricating oils are shown as mass fraction. Also shown is the average number of vehicles (±1 standard deviation) observed during filter collection periods separated by type (light duty, LD; medium duty, MD; and heavy duty, HD).

ature of the GC analyses (Figure S4, Supporting Information). Total averaged POA mass was ~30% higher for the high HD influenced samples relative to the low HD influenced samples, consistent with the vehicle count data and emission factors for LD (0.017 g OA kg^{-1}) and HD (0.24 g OA kg^{-1}) vehicles measured concurrently at the Caldecott tunnel.[8,9] Following the work of Dallmann et al.,[8] we estimated, using these emission factors, vehicle count data and fuel and vehicle properties, that on average 75 ± 10% of the observed POA mass in low HD influenced samples was attributed to gasoline vehicles, while for the high HD influenced samples gasoline vehicles contributed 25 ± 10% of the POA mass (For further details of the methodology used to attribute POA between gasoline and diesel vehicles see the Supporting Information).

N_{DBE} = 1 and 2 dominate the mass of POA making up >60% in both bores while aromatics and *n*-alkanes were substantially less abundant, making up <2 and <5%, respectively. This is in contrast to gasoline and diesel fuel, which both contain larger fractions of *n*-alkanes (>7%) and aromatics (>20%)[5] but is remarkably similar in both volatility distribution and composition to lubricating oil (Figure 3). The predominance of cycloalkanes in lubricating oil is consistent with their desirable properties, low viscosity and high viscosity index, which make them efficient lubricants across a wide range of operating temperatures. For example, *n*-alkanes crystallize at lower temperatures while the viscosity of aromatic compounds becomes too low at typical engine temperatures to effectively reduce friction. Aromatic compounds also have a tendency to increase soot formation at high temperatures. As such, all of these undesirable components are selectively targeted for removal during the processing of lubricating oil feedstocks.[38]

Evaporation of lubricating oil from hot surfaces in the engine would be expected to shift the distribution of the emitted unburned oil toward more volatile components, such a shift would not be expected for oil leaking from the engine through crankcase emissions or into the exhaust manifold via worn valve seals. The observed distributions are consistent with oil leaking from the engine and not from evaporation although it is not possible from these measurements to discern the fraction of the emissions that originate from the crankcase versus the tailpipe.

Volatility Distribution of Gasoline and Diesel Fuels, Lubricating Oil and POA. Gasoline is predominantly composed of branched alkanes and single ring aromatic compounds with less than 12 carbon atoms (C_{12}) and has a relatively narrow distribution around C_8[5]. High molecular

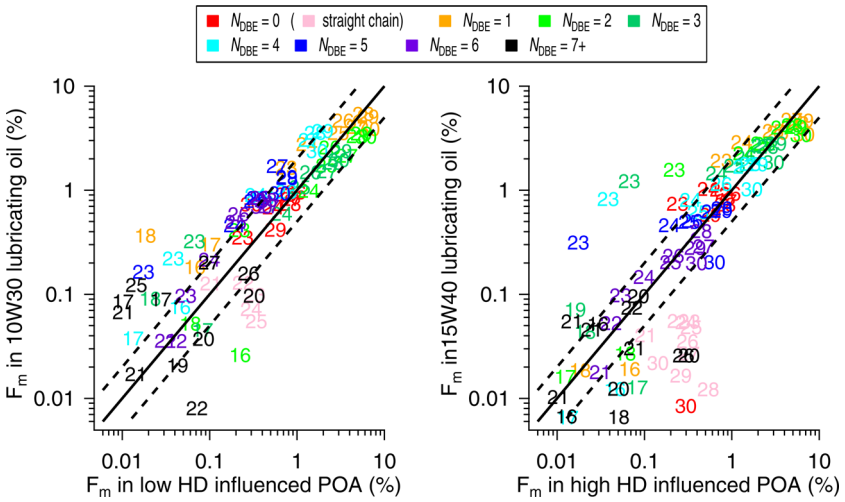

Figure 3. Comparison plot showing mass fractions (F_m) of chemically characterized components of low and high HD influenced POA versus "fresh" SAE-10W30 and SAE-15W40 lubricating oils, respectively. Text symbols show the carbon numbers (N_C) and color represents the number of double bond equivalents (N_{DBE}). Values are shown with 1:1 (solid), 1:2 and 2:1 (dashed) lines.

weight PAHs are known to be present in gasoline fuel following reformulation[28] but these are present at very low levels and do not contribute significant mass. Diesel fuel is comprised of about half branched alkanes and single ring aromatics and half cyclic compounds with 1 or more rings and has a broad distribution (C_6–C_{25}) that peaks around C_{10}–C_{12}[5]. Combustion of both gasoline and diesel fuel results in formation of byproducts from incomplete combustion (e.g., alkenes, aromatics, and oxygenates) that comprise ∼30% of the total measured gas phase emissions, though these products are volatile and unlikely to contribute to POA.[39]

As a result, the major pathway for gasoline fuel derived contributions to POA can only be through the formation of higher molecular weight combustion byproducts, for example, PAHs, which can be formed during incomplete combustion.[40] Low molecular weight alkenes, aromatics, and oxygenates (e.g., carbonyls) are known to be produced as byproducts of gasoline and diesel fuel combustion[39,41] but little is known about whether high molecular weight alkene, aromatic, or oxygenated compounds are generated during the combustion process. The similarity in the volatility distribution of POA and lubricating oil indicates that, in the absence of higher molecular weight combustion byproducts, unburned lubricating oil is likely the dominant source of vehicular POA.

Evidence for the Absence of Significant Combustion Byproducts in POA. The classification of compounds by N_{DBE} introduces some ambiguity regarding the characterization of N_{DBE} = 1−3 as cycloalkane versus alkene and N_{DBE} = 4 − 6 as cycloalkane versus aromatic (e.g., alkyl benzenes, tetralins and octahydro three ring PAHs). This ambiguity can be resolved by applying differing VUV energies and by comparing GC retention times for compounds whose molecular formulas overlap but whose chemical structures result in differing volatilities, polarities and/or ionization energies.

Aromatics. The aromatic components of N_{DBE} = 4−6 can be distinguished from the aliphatic components by reducing the VUV photon energy because the ionization energies of aromatic compounds are lower than aliphatic compounds.[42] Figure S6a (Supporting Information) shows the effect of varying the VUV photon energy from 10.5 to 9.0 eV on detector response for m/Q 386 (the molecular ion of $C_{28}H_{50}$; N_{DBE} = 4). Figure S6b (Supporting Information) shows a comparison of the signal response at 9.0 eV relative to 10.5 eV ($R_{9.0}$ eV/$R_{10.5}$ eV) for known authentic standards with N_{DBE} = 4 to the mass weighted average for POA. It is clear that for compounds >C_{20} N_{DBE} = 4 is predominantly aliphatic in composition. Interestingly, the $R_{9.0\ eV}/R_{10.5\ eV}$ is not constant across carbon numbers and values are close to ∼1 at the smaller observed carbon numbers (C_{16}–C_{20}) indicating that the signal was mostly aromatic. However, the observed mass at these carbon numbers was low resulting in a negligible contribution of N_{DBE} = 4 aromatics to POA.

The mass weighted $R_{9.0}$ eV/$R_{10.5}$ eV ratios were 0.30 ± 0.05 and 0.50 ± 0.3 for N_{DBE} = 5 and 6, respectively. Assuming that aromatic and aliphatic components of N_{DBE} = 5 and 6 ionize at the same VUV photon energies as the equivalent N_{DBE} = 4 species, it is possible to estimate, using a linear combination of the N_{DBE} = 4 aliphatic and aromatic $R_{9.0}$ eV/$R_{10.5}$ eV ratios (Figure S6, Supporting Information), that 0−10% and 0−100% of N_{DBE} = 5 and 6, respectively, could be aromatic. However, as a result of the low abundances of N_{DBE} = 5 (∼ 4%) and 6 (∼ 2%) in POA (Table S2, Supporting Information), these results indicate that the single ring aromatic mass fraction is <3% of the POA mass. This is similar to the observed PAH contribution to POA mass (<2%) and indicates that combustion derived aromatic compounds are a negligible fraction of POA mass.

Alkenes. The alkene and cycloalkane components of N_{DBE} = 1 − 3 differ in ionization energies by less than the photon energy bandwidth,[42,43] so variations in VUV photon energy cannot be used to distinguish between them. GC retention times for alkenes and cycloalkanes of the same molecular mass are not identical owing to differences in their volatilities. Figure S7a (Supporting Information) shows the Kovats retention indices relative to the *n*-alkane of the same molecular mass (ΔI_K)[44] for the observed detector signal for m/Q 308, the molecular ion of $C_{22}H_{44}$ (N_{DBE} = 1). The reported ranges in the measured Kovats retention indices for cycloalkanes and alkenes normalized to the *n*-alkane of the same molecular mass ((ΔI_K) show that straight chain alkenes elute almost a carbon number earlier than *n*-cyclohexanes and *n*-cyclopentanes and could not contribute to the later eluting N_{DBE} = 1 mass.

The *n*-cyclohexanes and *n*-cyclopentanes, similar to the *n*-alkanes, represent the least volatile end members and elute after all the more volatile branched isomers. The peaks identified as *n*-hexadecyl cyclohexane and *n*-heptadecyl cyclopentane were confirmed by the prevalence of m/Q 82, 83 and 68, 69 (mass fragments corresponding to the cyclohexane and cyclopentane rings), respectively, from the EI mass spectra at these retention times. The most likely cycloalkane ring structures present in N_{DBE} = 1−3 are cyclopentane and cyclohexane, five and six membered rings, respectively, due to the minimal ring strain of these configurations,[45] which is supported, for N_{DBE} = 1 at least, by the retention data for these compounds versus larger cycloalkanes (Figure S7a, Supporting Information).

The averaged EI mass spectral fragmentation patterns for alkenes and cyclohexanes from the NIST library are shown in Figure S7b (Supporting Information).[43] The difference spectra indicates that m/Q 56, 70 and 82, 83 are characteristic of alkenes and cyclohexanes, respectively. Lubricating oil, which is produced from high-boiling distilled fractions of crude oil, is not expected to contain significant amounts of compounds containing the alkene moiety and this has been confirmed by previous work.[46] The similarity between the ratio of the TIC normalized sum of m/Q 56 + 70 to the sum of m/Q 82 + 83 for POA compared to lubricating oil would suggest that N_{DBE} = 1 is predominantly cycloalkanes (Figure S7c, Supporting Information). Dienes (N_{DBE} = 2) have reportedly lower ionization energies than alkenes and cycloalkanes.[42,43] Therefore, the similarity in the observed $R_{9.0\ eV}/R_{10.5\ eV}$ ratio between N_{DBE} = 1 (0.05 ± 0.01) and N_{DBE} = 2 (0.07 ± 0.01) indicated that dienes are not an important component of N_{DBE} = 2 and it is likely dominated by bicyclic alkanes with various branched alkyl chains. Much less is known about retention times and ionization energies for trienes and tricycloalkanes (N_{DBE} = 3) although, based on the observations for N_{DBE} = 1 and 2, it seems likely that tricycloalkanes are dominant, for example, adamantanes or diamondoid hydrocarbons are a type of tricycloalkane that are known to be present in crude oils and are likely also present in lubricating oils.[47]

Oxygenates. To evaluate the possible contribution of high molecular weight oxygenated organics to POA mass, the high mass resolution data were peak fitted.[20] With the resolution of the HR-TOFMS (Δm/m = 4000), hydrocarbon and oxygenated mass spectral fragments can be fully resolved (full width at half-maximum height, fwhm) up to an m/Q of 140. To

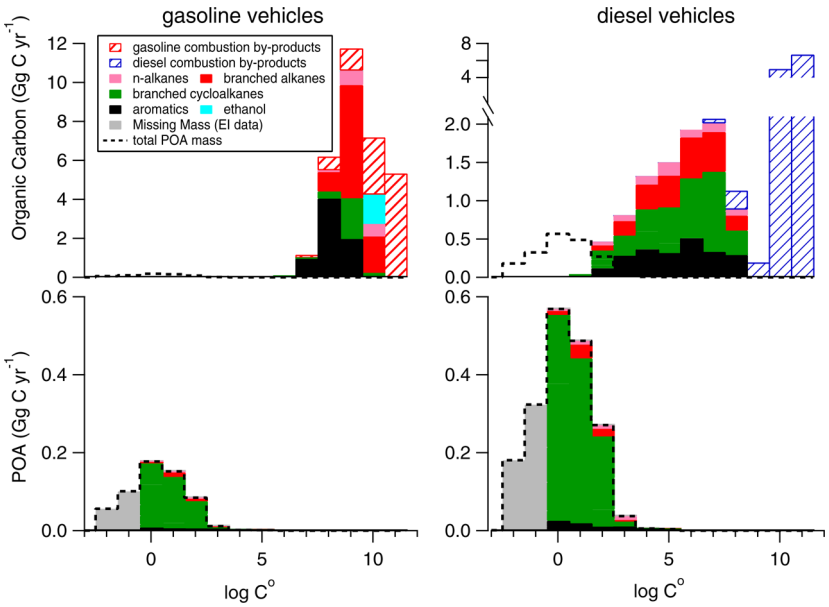

Figure 4. Volatility distributions of total primary organic carbon emissions for California in 2010 from on-road motor vehicles separated into simplified chemical classes (*n*-alkanes, branched alkanes, branched cycloalkanes, and aromatics that includes PAHs). Combustion byproducts from gasoline and diesel vehicles and ethanol emissions are also shown. The organic carbon, combustion byproducts and ethanol data were adapted from Gentner et al.[5,39]

improve the confidence in the assignment of the oxygenated contribution, the EI data was used preferentially to VUV data due to the larger fraction of mass fragments observed below m/Q = 140. Here we assume that hydrocarbons and oxygenated hydrocarbons have a similar fraction of their mass in fragments below m/Q = 140, which is consistent with the observed fragmentation patterns of aliphatic ketones, aldehydes, cycloalkanes and alkanes.[43] Aromatic oxygenates were not present in significant amounts from analysis of the GC × GC chromatograms, they are retained on the second column and would appear at longer second dimension retention times if present. High resolution peak fitting was performed for all the EI fragment data (m/Q <140) from the POA and lubricating oil analyses using all the carbonaceous fragments ($C_xH_yO_zN_w$) reported in the aerosol mass spectrometer (AMS) peak integration by key analysis (PIKA) fragmentation tables.[48] Additional specific fragments for siloxanes, deuterated internal standards and perfluoromethyldecalin (PFMD; mass calibration compound) known to be present in the GC system were also used.

The high resolution peak fitting analysis revealed that ∼2% of the total EI fragments in POA were oxygenated, consistent with lubricating oil and within the error of the high resolution peak fitting procedure. Even after accounting for different response factors for oxygenated compounds relative to hydrocarbons, typically less than a factor of 2 from injection of known authentic standard compounds, oxygenated compounds accounted for a small fraction of the observed POA mass. It is important to note that many oxygenated compounds, typically those that are highly oxygenated, are not GC amenable and would not been detected such that this figure likely represents the lower limit of the oxygenated fraction.

Chemical and Volatility Resolved Organic Carbon Emission Inventory. Figure 4 shows estimates of the annual mass emissions of organic carbon for California in 2010 as a function of volatility (C° = saturation vapor concentration, μg m^{-3}) for unburned gasoline, unburned diesel fuel, combustion byproducts from gasoline and diesel engines, and POA from light-duty gasoline passenger and heavy-duty diesel vehicles. Species originating from unburned fuel and oil are separated into simplified compound classes: *n*-alkanes, branched alkanes, branched cycloalkanes, and aromatics. These compound classes would be appropriate for inclusion in atmospheric models that use the volatility basis set (VBS) approach. Here we assume that 10% of observed N_{DBE} = 5 and all of N_{DBE} = 6 were aromatic, which provides an upper bound estimate for the aromatic content of vehicular POA emissions. The average POA mass distribution (average of all data from both traffic bores) was normalized to mass fraction and converted to emissions using reported emission factors for the same study.[8,9] The unburned diesel and gasoline fuel and combustion byproducts emission data was taken from Gentner et al.,[5,39] and apportioned into the VBS framework using GC retention times.[36] All emissions were converted to annual mass emissions for California by multiplying emission factors by taxable (on-road) fuel sales in 2010.[5] Figure 4 clearly shows that organic carbon emissions of unburned gasoline fuel and byproducts derived from gasoline and diesel fuel combustion are too volatile to contribute any mass to POA, consistent with our observations. POA emissions from diesel-powered vehicles were three times higher than for gasoline vehicles despite lower sales of diesel fuel in California as a result of the substantially higher diesel POA emission factor. The broad volatility distribution of diesel fuel indicates that tailpipe emissions of unburned diesel fuel could contribute up to ∼20% of the POA mass based on mass loadings of ∼10 μg m^{-3}.

■ ATMOSPHERIC IMPLICATIONS

In this work, the chemical composition of vehicular derived POA was characterized using GC × GC/VUV-HRTOFMS, with a mass closure of >60%, demonstrating the utility of the technique for resolving the UCM of organic aerosol samples. Observed POA mass was dominated by branched cycloalkanes with one or more rings and one or more branched alkyl side

chains (≥80%). The remaining mass was comprised of branched alkanes (<5%), *n*-alkanes (<3%), single ring aromatics (<3%), PAHs (<2%) and oxygenates (∼2%). Based on the similar observed carbon number (volatility) and chemical composition of POA and lubricating oil, and in the absence of significant high molecular weight material formed through the combustion process, we conclude that lubricating oil is the dominant constituent of vehicular POA emissions. This conclusion is consistent with related results from the same tunnel study that simultaneously used a soot particle aerosol mass spectrometer (SP-AMS) to measure mineral ash components in POA, and detected various trace metals at levels that were consistent with their use as lubricating oil additives.[9]

The dominance of cycloalkanes in vehicular POA emissions has implications for the atmospheric behavior of POA, as a result of the structural dependence of hydrocarbon reaction rates and SOA yields.[21,22] Heterogeneous oxidation rates for cycloalkanes are slower than *n*-alkanes of the same carbon number by ∼20% per addition of each nonaromatic ring.[20] SOA yields from large cycloalkanes (e.g., cyclooctane and cyclodecane) are reportedly comparable to yields from linear alkanes three to four carbon numbers larger in size but SOA yields from branched cyclohexanes were similar to branched alkanes of similar carbon number.[22] Cycloalkane ring-opening was not observed in the heterogeneous oxidation of cholestane, a four fused ring hydrocarbon, minimizing the formation of fragmentation products.[23] It is not clear whether this is a result of the low ring strain in the cyclohexane and cyclopentane rings or the fused nature of the cholestane structure. More oxidation studies targeting additional cycloalkane structures are necessary to determine what prevents ring-opening and to what extent this observation is constrained to heterogeneous chemistry. Taken together, these data suggest that evaporated POA components, which are likely dominated by cyclohexane and cyclopentane rings, will react slower and form less fragmentation products than if it were assumed to be purely branched alkane material. Gas phase oxidation of relevant cycloalkanes is less well studied and further work to characterize the fate of branched cyclohexanes and cyclopentanes is important to improve our understanding of the processing of atmospheric POA in regions downwind of urban centers.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional tables and 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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■ REFERENCES

(1) Subramanian, R.; Donahue, N. M.; Bernardo-Bricker, A.; Rogge, W. F.; Robinson, A. L. Contribution of motor vehicle emissions to organic carbon and fine particle mass in Pittsburgh, Pennsylvania: Effects of varying source profiles and seasonal trends in ambient marker concentrations. *Atmos. Environ.* **2006**, *40* (40), 8002−8019.

(2) Brook, J. R.; Graham, L.; Charland, J. P.; Cheng, Y.; Fan, X.; Lu, G.; Li, S. M.; Lillyman, C.; MacDonald, P.; Caravaggio, G.; MacPhee, J. A. Investigation of the motor vehicle exhaust contribution to primary fine particle organic carbon in urban air. *Atmos. Environ.* **2007**, *41* (1), 119−135.

(3) Hallquist, M.; Wenger, J. C.; Baltensperger, U.; Rudich, Y.; Simpson, D.; Claeys, M.; Dommen, J.; Donahue, N. M.; George, C.; Goldstein, A. H.; Hamilton, J. F.; Herrmann, H.; Hoffmann, T.; Iinuma, Y.; Jang, M.; Jenkin, M. E.; Jimenez, J. L.; Kiendler-Scharr, A.; Maenhaut, W.; McFiggans, G.; Mentel, T. F.; Monod, A.; Prevot, A. S. H.; Seinfeld, J. H.; Surratt, J. D.; Szmigielski, R.; Wildt, J. The formation, properties and impact of secondary organic aerosol: Current and emerging issues. *Atmospheric Chemistry and Physics* **2009**, *9* (14), 5155−5236.

(4) Kroll, J. H.; Seinfeld, J. H. Chemistry of secondary organic aerosol: Formation and evolution of low-volatility organics in the atmosphere. *Atmos. Environ.* **2008**, *42* (16), 3593−3624.

(5) Gentner, D. R.; Isaacman, G.; Worton, D. R.; Chan, A. W. H.; Dallmann, T. R.; Davis, L.; Liu, S.; Day, D. A.; Russell, L. M.; Wilson, K. R.; Weber, R.; Guha, A.; Harley, R. A.; Goldstein, A. H. Elucidating secondary organic aerosol from diesel and gasoline vehicles through detailed characterization of organic carbon emissions. *Proc. Natl. Acad. Sci.* **2012**, *109* (45), 18318−18323.

(6) Sawyer, R. F.; Harley, R. A.; Cadle, S. H.; Norbeck, J. M.; Slott, R.; Bravo, H. A. Mobile sources critical review: 1998 NARSTO assessment. *Atmos. Environ.* **2000**, *34* (12−14), 2161−2181.

(7) Dallmann, T. R.; DeMartini, S. J.; Kirchstetter, T. W.; Herndon, S. C.; Onasch, T. B.; Wood, E. C.; Harley, R. A. On-road measurement of gas and particle phase pollutant emission factors for individual heavy-duty diesel trucks. *Environ. Sci. Technol.* **2012**, *46* (15), 8511−8518.

(8) Dallmann, T. R.; Kirchstetter, T. W.; DeMartini, S. J.; Harley, R. A. Quantifying on-road emissions from gasoline-powered motor vehicles: Accounting for the presence of medium and heavy-duty diesel trucks. *Environ. Sci. Technol.* **2013**, *47*, 13873−13881.

(9) Dallmann, T. R.; Onasch, T. B.; Kirchstetter, T. W.; Worton, D. R.; Fortner, E. C.; Herndon, S. C.; Wood, E. C.; Franklin, J.; Worsnop, D. R.; Goldstein, A. G.; Harley, R. A. Characterization of particulate matter emissions from on-road gasoline and diesel vehicles using a soot particle aerosol mass spectrometer. *Atmos. Chem. Phys. Discuss.* **2014**, *14*, 4007−4049.

(10) Schauer, J. J.; Kleeman, M. J.; Cass, G. R.; Simoneit, B. R. T. Measurement of emissions from air pollution sources. 2. C-1 through C-30 organic compounds from medium duty diesel trucks. *Environ. Sci. Technol.* **1999**, *33* (10), 1578−1587.

(11) Schauer, J. J.; Kleeman, M. J.; Cass, G. R.; Simoneit, B. R. T. Measurement of emissions from air pollution sources. 5. C-1-C-32 organic compounds from gasoline-powered motor vehicles. *Environ. Sci. Technol.* **2002**, *36* (6), 1169−1180.

(12) Kleeman, M. J.; Riddle, S. G.; Robert, M. A.; Jakober, C. A. Lubricating oil and fuel contributions to particulate matter emissions from light-duty gasoline and heavy-duty diesel vehicles. *Environ. Sci. Technol.* **2008**, *42* (1), 235−242.

(13) Sonntag, D. B.; Bailey, C. R.; Fulper, C. R.; Baldauf, R. W. Contribution of lubricating oil to particulate matter emissions from light-duty gasoline vehicles in Kansas City. *Environ. Sci. Technol.* **2012**, *46* (7), 4191−4199.

(14) Brandenberger, S.; Mohr, M.; Grob, K.; Neukomb, H. P. Contribution of unburned lubricating oil and diesel fuel to particulate emission from passenger cars. *Atmos. Environ.* **2005**, *39* (37), 6985−6994.

(15) Fujita, E. M.; Zielinska, B.; Campbell, D. E.; Arnott, W. P.; Sagebiel, J. C.; Mazzoleni, L.; Chow, J. C.; Gabele, P. A.; Crews, W.; Snow, R.; Clark, N. N.; Wayne, W. S.; Lawson, D. R. Variations in speciated emissions from spark-ignition and compression-ignition motor vehicles in California's south coast air basin. *J. Air Waste Manage. Assoc.* **2007**, *57* (6), 705−720.

(16) Robinson, A. L.; Donahue, N. M.; Shrivastava, M. K.; Weitkamp, E. A.; Sage, A. M.; Grieshop, A. P.; Lane, T. E.; Pierce, J. R.; Pandis, S. N. Rethinking organic aerosols: Semivolatile emissions and photochemical aging. *Science* **2007**, *315* (5816), 1259−1262.

(17) May, A. A.; Presto, A. A.; Hennigan, C. J.; Nguyen, N. T.; Gordon, T. D.; Robinson, A. L. Gas-particle partitioning of primary organic aerosol emissions: (1) Gasoline vehicle exhaust. *Atmos. Environ.* **2013**, *77*, 128−139.

(18) May, A. A.; Presto, A. A.; Hennigan, C. J.; Nguyen, N. T.; Gordon, T. D.; Robinson, A. L. Gas-particle partitioning of primary organic aerosol emissions: (2) Diesel vehicles. *Environ. Sci. Technol.* **2013**, *47* (15), 8288−8296.

(19) Chan, A. W. H.; Isaacman, G.; Wilson, K. R.; Worton, D. R.; Ruehl, C. R.; Nah, T.; Gentner, D. R.; Dallman, T. R.; Kirchstetter, T. W.; Harley, R. A.; Gilman, J. B.; Gouw, J. A. d.; Offenberg, J. H.; Lin, Y. H.; Rubitschun, C. L.; Surratt, J. D.; Goldstein, A. H. Detailed chemical characterization of unresolved complex mixtures (UCM) in atmospheric organics: Insights into emission sources and atmospheric processing and secondary organic aerosol formation. *J. Geophys. Res.* **2013**, in press.

(20) Isaacman, G.; Chan, A. W. H.; Nah, T.; Worton, D. R.; Ruehl, C. R.; Wilson, K. R.; Goldstein, A. H. Heterogeneous OH oxidation of motor oil particles causes selective depletion of branched and less cyclic hydrocarbons. *Environ. Sci. Technol.* **2012**, *46* (19), 10632−10640.

(21) Lim, Y. B.; Ziemann, P. J. Effects of molecular structure on aerosol yields from OH radical-initiated reactions of linear, branched, and cyclic alkanes in the presence of NO_x. *Environ. Sci. Technol.* **2009**, *43* (7), 2328−2334.

(22) Tkacik, D. S.; Presto, A. A.; Donahue, N. M.; Robinson, A. L. Secondary organic aerosol formation from intermediate-volatility organic compounds: Cyclic, linear, and branched alkanes. *Environ. Sci. Technol.* **2012**, *46* (16), 8773−8781.

(23) Zhang, H.; Ruehl, C. R.; Chan, A. W. H.; Nah, T.; Worton, D. R.; Isaacman, G.; Goldstein, A. G.; Wilson, K. R. OH-iniated heterogenous oxidation of Cholestane: A model system for understanding the photochemical aging of cyclic alkane aerosols. *J. Phys. Chem.* **2013**, just accepted.

(24) Duplissy, J.; DeCarlo, P. F.; Dommen, J.; Alfarra, M. R.; Metzger, A.; Barmpadimos, I.; Prevot, A. S. H.; Weingartner, E.; Tritscher, T.; Gysel, M.; Aiken, A. C.; Jimenez, J. L.; Canagaratna, M. R.; Worsnop, D. R.; Collins, D. R.; Tomlinson, J.; Baltensperger, U. Relating hygroscopicity and composition of organic aerosol particulate matter. *Atmos. Chem. Phys.* **2011**, *11* (3), 1155−1165.

(25) McDonald, J. D.; Eide, I.; Seagrave, J.; Zielinska, B.; Whitney, K.; Lawson, D. R.; Mauderly, J. L. Relationship between composition and toxicity of motor vehicle emission samples. *Environ. Health Perspect.* **2004**, *112* (15), 1527−1538.

(26) Goldstein, A. H.; Galbally, I. E. Known and unexplored organic constituents in the earth's atmosphere. *Environ. Sci. Technol.* **2007**, *41* (5), 1514−1521.

(27) Fraser, M. P.; Cass, G. R.; Simoneit, B. R. T. Gas-phase and particle-phase organic compounds emitted from motor vehicle traffic in a Los Angeles roadway tunnel. *Environ. Sci. Technol.* **1998**, *32* (14), 2051−2060.

(28) Marr, L. C.; Kirchstetter, T. W.; Harley, R. A.; Miguel, A. H.; Hering, S. V.; Hammond, S. K. Characterization of polycyclic aromatic hydrocarbons in motor vehicle fuels and exhaust emissions. *Environ. Sci. Technol.* **1999**, *33* (18), 3091−3099.

(29) Rogge, W. F.; Hildemann, L. M.; Mazurek, M. A.; Cass, G. R.; Simoneit, B. R. T. Sources of fine organic aerosol. 2. Noncatalyst and catalyst-equipped automobiles and heavy duty diesel trucks. *Environ. Sci. Technol.* **1993**, *27* (4), 636−651.

(30) Isaacman, G.; Wilson, K. R.; Chan, A. W. H.; Worton, D. R.; Kimmel, J. R.; Nah, T.; Hohaus, T.; Gonin, M.; Kroll, J. H.; Worsnop, D. R.; Goldstein, A. H. Improved resolution of hydrocarbon structures and constitutional isomers in complex mixtures using gas chromatography-vacuum ultraviolet-mass spectrometry. *Anal. Chem.* **2012**, *84* (5), 2335−2342.

(31) Ban-Weiss, G. A.; McLaughlin, J. P.; Harley, R. A.; Lunden, M. M.; Kirchstetter, T. W.; Kean, A. J.; Strawa, A. W.; Stevenson, E. D.; Kendall, G. R. Long-term changes in emissions of nitrogen oxides and particulate matter from on-road gasoline and diesel vehicles. *Atmos. Environ.* **2008**, *42* (2), 220−232.

(32) Kirchstetter, T. W.; Singer, B. C.; Harley, R. A.; Kendall, G. R.; Traverse, M. Impact of California reformulated gasoline on motor vehicle emissions. I. Mass emission rates. *Environ. Sci. Technol.* **1999**, *33* (2), 318−328.

(33) Turpin, B. J.; Saxena, P.; Andrews, E. Measuring and simulating particulate organics in the atmosphere: Problems and prospects. *Atmos. Environ.* **2000**, *34* (18), 2983−3013.

(34) Kirchstetter, T. W.; Corrigan, C. E.; Novakov, T. Laboratory and field investigation of the adsorption of gaseous organic compounds onto quartz filters. *Atmos. Environ.* **2001**, *35* (9), 1663−1671.

(35) Subramanian, R.; Khlystov, A. Y.; Cabada, J. C.; Robinson, A. L. Positive and negative artifacts in particulate organic carbon measurements with denuded and undenuded sampler configurations. *Aerosol Sci. Technol.* **2004**, *38*, 27−48.

(36) Presto, A. A.; Hennigan, C. J.; Nguyen, N. T.; Robinson, A. L. Determination of volatility distributions of primary organic aerosol emissions from internal combustion engines using thermal desorption gas chromatography mass spectrometry. *Aerosol Sci. Technol.* **2012**, *46* (10), 1129−1139.

(37) Donahue, N. M.; Robinson, A. L.; Stanier, C. O.; Pandis, S. N. Coupled partitioning, dilution, and chemical aging of semivolatile organics. *Environ. Sci. Technol.* **2006**, *40* (8), 2635−2643.

(38) Gary, J. H.; Handwerk, G. E.; J., K. M. *Petroleum Refining Technology and Economics*, 5th ed.; CRC Press, 2007.

(39) Gentner, D. R.; Worton, D. R.; Isaacman, G.; Davis, L. C.; Dallman, T. R.; Wood, E. C.; Herndon, S. C.; Goldstein, A. H.; Harley, R. A. Chemical composition of gas-phase organic carbon emissions from motor vehicles and implications for ozone production. *Environ. Sci. Technol.* **2013**, *47*, 11837−11848.

(40) Fetzer, J. Polycyclic aromatic hydrocarbons and combustion. In *Handbook of Combustion*, Wiley-VCH Verlag GmbH & Co. KGaA: 2010.

(41) Harley, R. A.; Hannigan, M. P.; Cass, G. R. Respeciation of organic gas emissions and the detection of excess unburned gasoline in the atmosphere. *Environ. Sci. Technol.* **1992**, *26* (12), 2395−2408.

(42) Adam, T.; Zimmermann, R. Determination of single photon ionization cross sections for quantitative analysis of complex organic mixtures. *Anal. Bioanal. Chem.* **2007**, *389* (6), 1941−1951.

(43) NIST Chemistry WebBook, NIST Standard Reference Database Number 69 (http://webbook.nist.gov/).

(44) Kovats, E. Gas-chromatographische charakterisierung organischer verbindungen 0.1. Retentionsindices aliphatischer haolgenide, alkohole, aldehyde und ketone. *Helv. Chim. Acta* **1958**, *41* (7), 1915−1932.

(45) Anslyn, E. V.; Dougherty, D. A., Chapter 2: Strain and stability. In *Modern Physical Organic Chemistry*; University Science: Sausalito, CA, 2006.

(46) Mao, D.; Van De Weghe, H.; Lookman, R.; Vanermen, G.; De Brucker, N.; Diels, L. Resolving the unresolved complex mixture in motor oils using high-performance liquid chromatography followed by comprehensive two-dimensional gas chromatography. *Fuel* **2009**, *88* (2), 312−318.

(47) Wingert, W. S. GC-MS analysis of diamondoid hydrocarbons in smackover petroleums. *Fuel* **1992**, *71* (1), 37−43.

(48) DeCarlo, P. F.; Kimmel, J. R.; Trimborn, A.; Northway, M. J.; Jayne, J. T.; Aiken, A. C.; Gonin, M.; Fuhrer, K.; Horvath, T.; Docherty, K. S.; Worsnop, D. R.; Jimenez, J. L. Field-deployable, high-resolution, time-of-flight aerosol mass spectrometer. *Anal. Chem.* **2006**, *78* (24), 8281−8289.