Review of Urban Secondary Organic Aerosol Formation from Gasoline and Diesel Motor Vehicle Emissions

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S *Supporting Information*

ABSTRACT: Secondary organic aerosol (SOA) is formed from the atmospheric oxidation of gas-phase organic compounds leading to the formation of particle mass. Gasoline- and diesel-powered motor vehicles, both on/off-road, are important sources of SOA precursors. They emit complex mixtures of gas-phase organic compounds that vary in volatility and molecular structure—factors that influence their contributions to urban SOA. However, the relative importance of each vehicle type with respect to SOA formation remains unclear due to conflicting evidence from recent laboratory, field, and modeling studies. Both are likely important, with evolving contributions that vary with location and over short time scales. This review summarizes evidence, research needs, and discrepancies between top-down and bottom-up approaches used to estimate SOA from motor vehicles, focusing on inconsistencies between molecular-level understanding and regional observations. The effect of emission controls (e.g., exhaust aftertreatment technologies, fuel formulation) on SOA precursor emissions needs comprehensive evaluation, especially with international perspective given heterogeneity in regulations and technology penetration. Novel studies are needed to identify and quantify "missing" emissions that appear to contribute substantially to SOA production, especially in gasoline vehicles with the most advanced aftertreatment. Initial evidence suggests catalyzed diesel particulate filters greatly reduce emissions of SOA precursors along with primary aerosol.
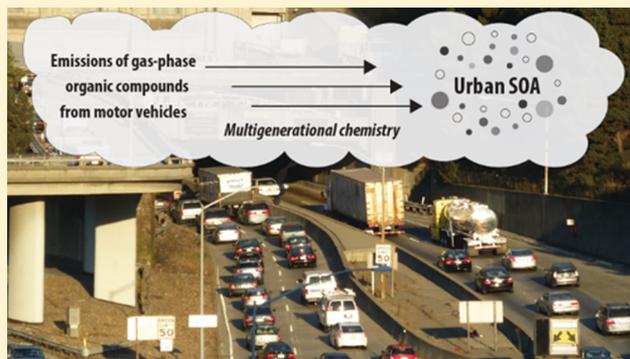
INTRODUCTION: GAS- AND PARTICLE-PHASE ORGANIC COMPOUNDS IN URBAN AREAS

With more than 1.6 billion vehicles globally, motor vehicle emissions are major contributors to ambient concentrations of, and human exposure to, air pollutants, including airborne particles less than 2.5 μm in diameter (i.e., $PM_{2.5}$). These
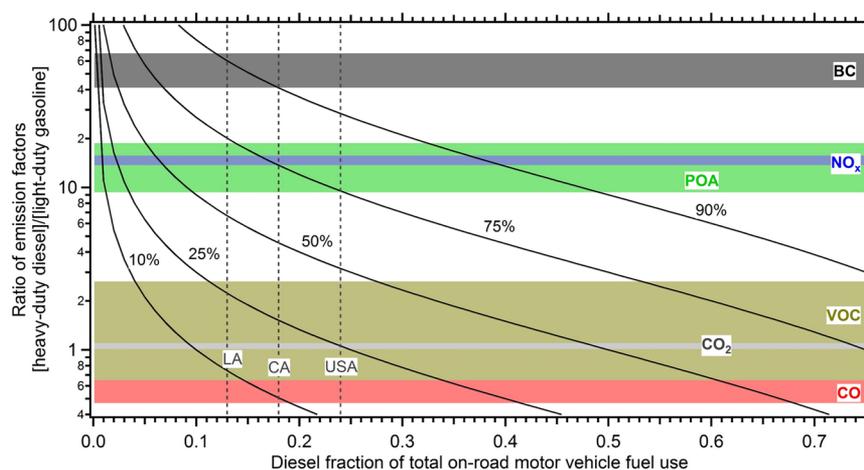
Figure 1. Contributions of pre-DPF diesel vehicles to total on-road motor vehicle exhaust emissions for varying levels of diesel consumption in the U.S., ca. 2010 (relative emission factors (g kg^{-1}) will change substantially with penetration of control technologies such as catalyzed DPF filters, the composition (i.e., age) of the light-duty gasoline vehicle fleet, and in regions with a larger fleet of light-duty diesel vehicles (e.g., Europe)). Labeled curves show percentages of on-road exhaust emissions attributable to diesel engines, with the remainder attributed to gasoline vehicles. The percentages vary with fuel use and air pollutant of interest. The intersection of the diesel fuel use fraction and the colored horizontal bands corresponds to ranges of values for the curved contours that specify diesel emission contributions to overall on-road emissions of that pollutant. For example, at the U.S. average of 24% diesel fuel use, the percentage of POA from diesel ranges 75−85% based on likely values for diesel/gasoline ratios of corresponding emission factors. See Dallmann et al.[197] for source data. Note: the lower VOC range has been adjusted based on variance in VOC EFs in Table 1.

atmospheric aerosols have important implications for human health.[1−5] Toxicological and epidemiological studies have shown the multifaceted, detrimental health effects (e.g., cardiovascular, pulmonary, and cognitive) linked to aerosol exposure, which is a dominant factor in the 3−4 million global deaths annually attributed to outdoor air pollution.[1,3−6]

PM$_{2.5}$ is predominantly comprised of organic carbon, elemental (i.e., black) carbon, sulfate, nitrate, ammonium, and other inorganic constituents such as metals.[7−9] Organic aerosol (OA) comprises a significant and variable fraction (20−90%) of PM$_{2.5}$.[7,8,10,11] Primary organic aerosol (POA) is directly emitted by sources such as biomass burning, cooking, and internal combustion engines that run on gasoline or diesel fuel. Secondary organic aerosol (SOA) is formed via the atmospheric oxidation of both biogenic and anthropogenic gas-phase organic compounds (e.g., volatile organic compounds (VOCs)).[12−15] SOA, sometimes quantified as the surrogate oxidized organic aerosol (OOA), typically comprises a greater fraction of OA, especially after longer atmospheric processing times in urban areas and in downwind plumes.[7,8,11] On urban and regional scales, emissions from on- and off-road motor vehicles are prominent contributors to observed concentrations of PM$_{2.5}$ and OA, via both direct primary emissions and through emissions of reactive organic gases that are SOA precursors.

Organic compounds in the atmosphere exist over a wide range of molecular weights and functionalities (e.g., carbonyl or acid groups), which together determine their volatility (i.e., vapor pressure) and other properties.[13,14] Both gas- and particle-phase compounds can be classified by volatility, which governs their partitioning between the gas- and particle-phase. Organic compounds are generally divided by effective saturation concentrations (C*) into volatile organic compound (VOC), intermediate-volatility organic compound (IVOC), semivolatile organic compound (SVOC), low-volatility organic compound (LVOC), and extremely low-volatility organic compound (ELVOC) ranges.[9] The exact

breakdown of compounds is dependent on total organic aerosol concentrations, but the compounds in each range are roughly as follows: VOC ($\leq C_{12}$), IVOC ($\sim C_{13}−C_{19}$), and SVOC ($\sim C_{20}$-C_{26}). The primary and secondary organic compounds that comprise organic aerosol are on the lower end of this volatility spectrum including ELVOCs and LVOCs, as well as SVOCs, which exist in both phases.[9] A large fraction of IVOCs and SVOCs have only recently been measured with any chemical detail due to difficulties with sampling and analysis.[15−17] Yet, IVOCs and SVOCs have substantial SOA yields (i.e., g SOA g^{-1} reactant) and are considered important contributors to SOA in urban and downwind environments.[12,15,18−22]

A CONCISE HISTORY OF KNOWLEDGE ON URBAN SOA

SOA was first reported in Los Angeles by Haagen-Smit (1952)[23] in conjunction with tropospheric ozone formation, colloquially known together as "photochemical smog." Subsequent research using photochemical oxidation "smog" chambers and studies of air pollution events in the South Coast air basin identified precursors and chemical mechanisms of SOA formation.[24−29] This included an emphasis on aromatic compounds, which were identified as key anthropogenic precursors with prevalent emissions from motor vehicles.[24,26,30−32] Odum et al. (1997)[30] examined the SOA formation potential of vaporized gasoline and attributed the observed SOA to C$_{7−10}$ aromatic precursors.

A systematic underprediction of SOA in models was identified in studies of urban environments and downwind plumes in the mid-2000s, as highlighted by Volkamer et al. (2006).[33] Here, we define "urban SOA" as SOA formed from VOC precursors emitted within the urban area. SOA formed outside the urban area (e.g., from regional BVOC emissions) may be present within the urban area, but it is not part of the "urban SOA" discussed in this paper. With a growing understanding of the prevalence and chemical/physical processes occurring across the spectrum of volatilities, Donahue

Table 1. Summary of Gas-Phase Organic Compound Emission Factors from Motor Vehicles[a]

U.S.				Units	Method, Notes, Source
Gasoline: *Fleet-wide*	*Pre-LEV* (1967−1993)	*LEV-1* (1994−2003)	*LEV-2* (2004−2012)		
	5.3 ± 4.4	1.6 ± 1.4	0.44 ± 0.36	g/L	Dynomometer, geometric avg (N = 15, 23, 25 vehicles)[46,49,67]
0.78	5.6 (3.8−24)	0.81 (0.56−3.1)	0.09 (0.07−0.18)	g/L	EMFAC (fleet averages with ranges across model year averages)[166]
	5.2 ± 6.2	1.1 ± 0.9	0.47 ± 0.48	g/L	EPA Kansas City Study (summer), geometric average ± std. deviation (N = 88, 143, 6 vehicles)[67,191]
	5.9 ± 5.9	1.6 ± 1.1	0.40 ± 0.07	g/L	EPA Kansas City Study (winter), geometric average ± std. deviation (N = 137, 144, 5 vehicles)[67,191]
0.68 ± 0.2				g/L	2010, Tunnel[103]
4.2 ± 0.4, 3.4 ± 0.2				g/L	1994, Tunnel (Aug., Oct.)[69]
2.5−4.0				g/L	1994−1997, Tunnel[192]
Diesel: *Fleet-wide*	*non-DPF[b]* (−2010)	*DPF-equipped* (2010−)			
	0.61−1.1	ND−0.011		g/L	Medium- and heavy-duty diesel vehicles (N = 3, 2 vehicles), Dynomometer[45,67], MD and HD
	0.09−0.85			g/mile	Transit buses, N = 4 vehicles,[67,193]
1.3 ± 0.4				g/L	2010, Tunnel[103]

Europe	Units	Method, Notes, Source
Gasoline: *Euro-5*		
0.19 ± 0.07	g/L	N = 7 vehicles,[194] geometric average (running + cold start emissions)
0.82	g/L	N = 1 vehicle,[47] (running + cold start emissions)
0.13	g/L	N = 1 vehicle[195] (running + cold start emissions)

[a]Running emission factors unless otherwise noted. [b]Non-DPF (diesel particulate filter) diesel includes DOC and 3-way catalysts.

et al. (2006)[34] developed the volatility basis set (VBS), and Robinson et al. (2007)[12] applied it to diesel exhaust emissions to better model urban SOA and parametrize the dynamic partitioning and chemical aging of IVOCs and SVOCs. This framework allowed for mass closure between observed and predicted SOA but with issues reproducing observed diurnal dynamics and SOA properties.[35−37] Improved laboratory experiments spurred revised, increased SOA yields of VOCs.[38] Yet, chamber yields from all types of compounds may still be significantly underestimated due to losses of vapors to Teflon chamber walls.[39−41]

Comprehensive chemical characterization of diesel fuel provided unprecedented detail on the VOCs, IVOCs, and SVOCs, which included straight, branched, monocyclic, bicyclic, and tricyclic alkanes, as well as aromatic and polycyclic aromatic hydrocarbons (PAHs).[15,42] This highlighted the broad spectrum of understudied SOA precursors and the necessity of further experiments and modeling studies on SOA yields for a diversity of atmospherically relevant chemical classes.[15] It also emphasized the value of whole emissions photochemical oxidation experiments to better characterize the SOA formation potential of the complex mixture of precursors in motor vehicle emissions.[12]

Meanwhile, field measurements in Los Angeles during the CalNex 2010 study observed little change in ambient SOA concentrations with large decreases in diesel traffic over the weekend—a surprising result considering the current understanding of SOA yields and the prevalence of potential SOA precursors in diesel emissions.[15,43,44] Contemporary smog chamber studies with emissions from newer, low emission gasoline vehicles (LEV) have shown a marked increase in the effective SOA yield of gasoline vehicle exhaust (Table 2) despite large decreases in the magnitude of gas-phase organic compound emissions (Note: LEV-1 and LEV-2 meets U.S. Tier

1 and 2 standards, respectively, with Tier 2 broadly similar to Euro 5 standards, Figure S1).[45−48]

The contributions from varying types of motor vehicles to urban SOA remains an active field of research with major implications for air quality management policies worldwide, with recent papers highlighting the growing importance of emissions beyond the on-road vehicle fleet in the developed world.[49,50] In the following sections of this review, we summarize and synthesize relevant research that has been published over the past 5−10 years and provide insights into the remaining questions, challenges, and greatest uncertainties, as well as trends and impacts with a global perspective.

MOTOR VEHICLE EMISSIONS: DIVERSITY IN VEHICLE CLASSES AND EMISSIONS OF ORGANIC COMPOUNDS

In addition to organic gases and aerosols, on- and off-road motor vehicles (and similar mobile sources) are major sources of nitrogen oxides (NO_X = NO + NO_2), carbon monoxide (CO), black carbon (BC), and carbon dioxide (CO_2).[50−57] Motor vehicles are also significant sources of ammonia (NH_3) and sulfur dioxide (SO_2), as well as other metals and other inorganic chemical species (Figure 1).[58−60] There is considerable variability in emission rates and composition between vehicles and vehicle types, with major differences based on vehicle class, size, fuel type (gasoline, diesel, biofuel), operation mode, model year, engine/post-combustion control technology, and differences in regulations between on- and off-road vehicles (and other off-road equipment) (Table 1). Furthermore, the chemical composition of gasoline and diesel emissions has evolved with changes in engine and post-combustion control technologies over the past several decades.[15,61−68]
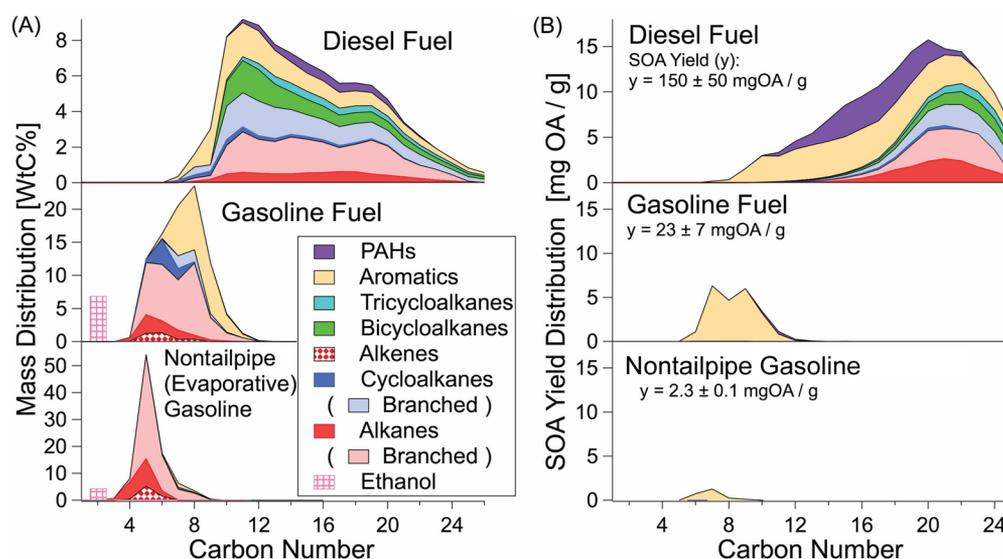
Figure 2. (A) Chemical composition of diesel fuel, gasoline, and evaporative gasoline emissions, with (B) SOA yield of each emission profile shown as a sum of SOA contributions; both are shown as a function of compound class and carbon number. Partitioning of oxidation products is calculated at an organic aerosol concentration of 10 μg m^{-3} after ~6 h of photochemical aging. Note: "branched cycloalkanes" refers to those with more than a single linear alkyl substituent.[15]

Fuel composition, engine design/technology (including computerized control), and exhaust aftertreatment technology are all determining factors in the composition of emissions. Gasoline engines use spark ignition of a lower molecular weight fuel with compounds in the C_4–C_{10} range (premixed with air) compared to diesel engines with compression ignition of heavier fuels (C_9–C_{25}) at higher temperatures and fuel-lean conditions to achieve greater efficiencies (Figure 2A).[51] The organic composition of gasoline and diesel fuel has been intentionally controlled over the past 50 years in the U.S. and elsewhere via several regulated reformulations. They were modified to improve engine performance, fuel efficiency, and compatibility with catalytic converters, and also to reduce emissions (organic gases/aerosols, CO, NO$_X$, BC, SO$_2$, lead) and to minimize the ambient photochemical production of ozone (O$_3$) from emissions of reactive VOCs and NO$_X$.[51,61,68,69] Reformulations have reduced volatility, reactivity, trace impurities, and/or propensity for forming NO$_X$, CO, or BC in the exhaust.[61,68–70]

Historically, gasoline engines have been identified as the major on-road source of VOC emissions in urban areas and have been a principal focus of VOC emission control efforts.[50–54] This was justified because fuel sales of gasoline greatly exceeded diesel in the U.S., and combustion of diesel fuel occurs with excess air (i.e., under overall fuel-lean conditions), leading to relatively low VOC emission rates in diesel exhaust.[51] Also the vapor pressure of diesel fuel is low compared to gasoline, so non-tailpipe, evaporative emissions of VOC are inherently low for diesel vehicles.[15] These assumptions have influenced emission control policy decisions around the world; historically, VOC control has prioritized of gasoline vehicle emissions, and efforts focused on diesel emissions have emphasized control of primary PM$_{2.5}$ and NO$_X$ emissions.[71–74] Additionally, IVOCs or SVOCs have never been directly regulated.

Both gasoline and diesel vehicles use lubricating motor oils that contain a complex mixture of high molecular weight hydrocarbons from 20 to 36 carbon atoms that are regularly observed in exhaust.[75] Several studies with a variety of methods have shown that the components of motor oil dominate POA emissions from the in-use motor vehicle fleet.[75–77] Several other studies suggest that for individual gasoline vehicles POA derived from fuel components can contribute half to most of POA in exhaust, albeit with considerable vehicle-to-vehicle heterogeneity.[78–80] For tested light-duty gasoline vehicles, the POA formed from fuel during combustion were in the LVOC or ELVOC range (C* ~ 10^{-2}–10^{-3}), while contributions from motor oil are concentrated in the SVOC range with a small fraction in the LVOC range.[79] All POA emissions can strongly influence gas-particle partitioning and remain an important area of research concurrent with this review's focus on SOA and their precursors.

New on-road diesel vehicle emissions standards effectively require exhaust aftertreatment technologies, including diesel particulate filters (DPF) and diesel oxidation catalysts (DOC) (Euro 6/VI, Tier 2 U.S., and the U.S. EPA 2007 diesel truck rule), and retrofits are required or incentivized dependent on location (e.g., California, select megacities).[73,74] Their impacts are discussed in this review.

The relative use of gasoline and diesel fuel varies regionally and temporally (Table S1, Figure S2).[15,81] The dominance of gasoline-related VOC emissions has been especially notable in the U.S., where gasoline has been and remains the fuel of choice for nearly all light-duty passenger vehicles. The situation differs in Europe where diesel-powered passenger vehicles are much more common following a rapid expansion in their usage in the 1990s. In both locations, the diesel contribution to overall VOC emissions has been increasing over time due to (1) substantial progress in reducing VOC emissions from gasoline engines and (2) more rapid growth in diesel fuel sales compared to gasoline.[52,53,57,82]

Past VOC source apportionment studies have used speciated measurements of ambient VOC concentrations in urban air.[83–85] The diesel contribution to ambient VOCs has been difficult to discern and is rarely reported in such studies. This is because most speciated hydrocarbon measurements, especially routine monitoring data, typically focus on lighter compounds in the C_2–C_8 range. This excludes most of the hydrocarbons

found in unburned diesel fuel, whereas gasoline contributions are strongly represented in the list of measured hydrocarbons. New measurements of VOCs and IVOCs allowed for the examination of the relative prevalence of gas-phase organics from diesel and gasoline in urban environments.[15,86,87] Diesel vehicles were found to contribute 24 ± 14% and 56 ± 18% of uncombusted VOCs + IVOCs from motor vehicle exhaust at two near/on-road Californian field sites; both are consistent with regional fuel sales data multiplied by emission factors for gasoline and diesel.[15]

Laboratory and in-use estimates of gas- and aerosol-phase organic compound emission factors span several orders of magnitude (Table 1), from as high as ~50 g kg-fuel^{-1} to as low as ~0.001 g kg-fuel^{-1} with some dependence on engine design and operation mode (e.g., 2- vs 4-stroke gasoline engines or emissions during cold starts).[67,88] Cold starts, which occur after several hours of nonoperation, are a major source of emissions for gasoline vehicles and have greater emissions due to two issues: (1) Low engine temperatures lead to incomplete combustion that allow non/partially combusted fuel compounds to exit engine cylinders. (2) Effective operation of the catalytic converter requires a warm-up period to reach sufficient catalyst operating temperatures.[89] The magnitude of cold-start emissions increases greatly in cold weather conditions and varies with vehicle type and year.[90,91] Studies have recently drawn attention to the large differences between 4-stroke and 2-stroke gasoline engines. The 2-stroke engines, such as in scooters and lawn/gardening equipment, emit large quantities of VOCs, CO, and PM$_{2.5}$ due to incomplete combustion and fuel/oil that escapes the engine without ever being ignited.[67,88,92,93,124] These off-road mobile sources and other engines are becoming relatively more important due to successful regulation of the on-road fleet.[50]

CONTRIBUTION OF MOTOR VEHICLES TO URBAN SOA

The chemical composition of urban aerosol varies considerably with location and season, with OA typically comprising a major fraction in addition to sulfate, nitrate, and BC aerosols.[11] Emissions of POA and gas-phase SOA precursors from motor vehicles have historically been major contributors to urban OA and remain major contributors (Figure 3).[50,94,95] The relative
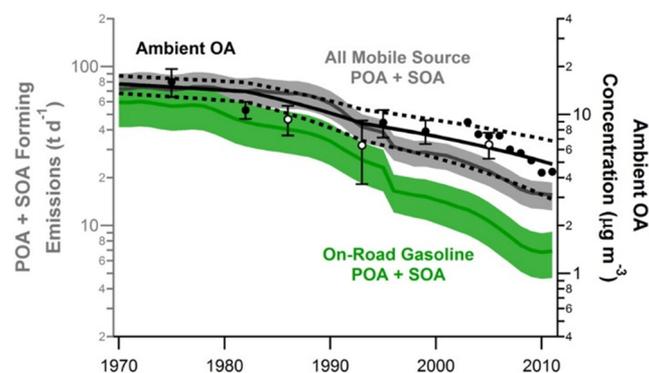
Figure 3. Trends in primary and potential secondary organic aerosol emissions for all mobile sources and on-road gasoline only in Los Angeles (lines with shaded 95% confidence intervals, left axis), shown with observed concentrations of organic aerosol (black solid and dashed lines, right axis) constrained by ambient measurements (markers).[50]

importance of motor vehicles for urban SOA depends on the magnitude and distribution of all anthropogenic and biogenic sources of SOA precursors. Following multiple generations of oxidation chemistry, motor vehicles are currently estimated to contribute 2.9 ± 1.6 Tg SOA yr^{-1} in the U.S.[96] compared to a total of 3.1 Tg SOA yr^{-1} from all urban emissions in the U.S.,[22] both of which are uncertain and considerably smaller than total biogenic contributions.[14] SOA formed from biogenic VOC emissions within the urban area is typically small, but urban SOA exists in a regional background that often has a large biogenic contribution (e.g., southeastern U.S.) that are enhanced by anthropogenic nitrogen and sulfur emissions.[22,97]

Observations of fossil and contemporary isotope abundances in aerosol samples provide evidence that nonfossil (non-vehicular) sources (e.g., cooking, biomass burning, and biogenic emissions) comprise a substantial fraction of observed OA in some but not all urban locations.[98−101]

There are several pieces of relevant evidence supporting the importance of motor vehicle SOA in most urban areas. First, motor vehicles are major sources of gas-phase organic compounds (including VOCs) that are known to be efficient SOA precursors (e.g., aromatics) are emitted in large quantities from motor vehicles (shown in both inventories and observations).[50,62,63,68,102−104] Second, long-term trends in primary emissions of POA and SOA precursors are consistent with OA concentration trends in Los Angeles (Figure 3).[50] Third, oxidation chamber results demonstrate that motor vehicle exhaust is efficient at forming SOA,[45,46] which implies large concentrations of predicted SOA when combined with observed precursors and their emission inventories.[15,105] Fourth, oxidation flow reactor results of traffic exhaust in a tunnel result in a similar magnitude of SOA formation as in urban air using the same reactor (Figure S3).[96,106,107] Fifth, source apportionment of urban OA identify major contributions that are interpreted as dominated by SOA from motor vehicles as opposed to other sources.[44,108] Lastly, ambient observations of urban aerosol composition via AMS are similar to both POA and oxidized aerosol in laboratory/tunnel studies (Figure 4), and similar results have been observed for Fourier transform infrared spectroscopy (FTIR) and radiocarbon measurements suggesting a dominance of fossil fuel sources for SOA from urban sources.[11,12,22,96,99,109,110]

SYNTHESIS OF APPROACHES: LOOKING FROM THE TOP-DOWN AND THE BOTTOM-UP

Several approaches have been used to estimate or constrain the quantity of SOA that can form from the complex mixtures of organic compounds emitted from gasoline and diesel vehicles. Estimation methods include top-down approaches based primarily on ambient air quality measurements and bottom-up methods that focus on in-depth characterization of fuels/emissions and individual vehicle testing, which includes the oxidation of fresh exhaust from single vehicles in chambers to simulate potential SOA formation in the ambient atmosphere. Here, we review these different approaches and synthesize their results, identifying key points of uncertainty and directions for future research.
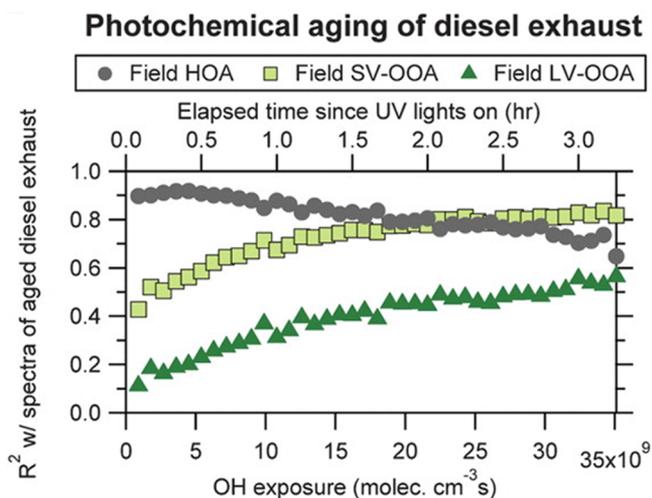
Figure 4. Statistical comparison of aerosol mass spectra observed from chamber oxidation of diesel exhaust to mass spectra from urban observations of hydrocarbon-like organic aerosol (HOA), and semivolatile- (SV) and low-volatility- (LV) oxidized organic aerosol (OOA). Coefficients of determination (R^2) between mass spectra show similarities between urban secondary organic aerosol and oxidized diesel vehicle exhaust with increased OH exposure.[11]

BOTTOM-UP METHOD #1: UNDERSTANDING SOA FORMATION POTENTIAL USING UNBURNED GASOLINE AND DIESEL FUEL AS EMISSION SURROGATES

Overview. Recent studies have provided near-comprehensive chemical characterization of diesel and gasoline liquid fuels with the necessary detail to probe the complex mix of organic gas-phase compounds that comprise the majority of gasoline and diesel emissions.[15,42] Along with an understanding of the relationship between the composition of organics in liquid fuels and emissions, fuel composition provides a useful avenue to predict the overall SOA yields of these complex mixtures and identify the SOA precursors responsible for the greatest fraction(s) of potential SOA.

Source apportionment via chemical mass balance receptor models (with *a priori* source profiles constructed from fuel speciation) has been used with ambient concentration data to estimate the relative contributions of SOA precursors from motor-vehicle sources at multiple field sites.[15,103] Average fuel composition is reported to be relatively consistent within a region at a given time but was only explicitly studied during summer in California when formulations are more tightly controlled.[15] Thus, a very detailed offline hydrocarbon speciation with a statistically significant number of fuel samples is representative of the regional fuel supply. With the exception of typical products of incomplete combustion (see below), the relative concentrations of unburnt fuel components in exhaust have been shown to be largely statistically consistent with liquid fuel (Figure S4).[15,103,111] Studies have confirmed the abundances of gas-phase SOA precursors from unburnt fuel at urban sites.[15,86,103] They have also successfully apportioned gas-phase organic compound emissions from motor vehicle sources; results from a 2010 Caldecott (Oakland, CA) tunnel study were shown to be consistent with those from Bakersfield, CA, in terms of the composition of uncombusted fuel in gasoline (and diesel) exhaust emissions and the relative

magnitude of gasoline vs diesel emission rates adjusted by relative fuel sales.[15]

Fuel composition data can be used to estimate SOA formation from the exhaust. The overall SOA yield of the complex mixture of organic gases in either diesel or gasoline emissions was estimated as the sum of the potential SOA of each fuel component. The fuel composition-weighted potential SOA for each species was estimated using published yield data for individual compounds (OH-initiated oxidation with NO_X) where available; otherwise, best estimates of yields and uncertainties were derived for unstudied compound types based on existing experimental and theoretical studies of SOA yields (e.g., see references within ref 15 and refs 112 and 113). Only 66% and 25% of the unburnt fuel components in gasoline and diesel exhaust (by mass) had published yield data, respectively.[15]

Method Results. On the basis of fuel composition, measured emission factors, relative fuel sales, source apportionment results from ambient sites, and estimated overall SOA yields, the results of this method suggest that both gasoline and diesel are important sources of SOA precursors. Unburnt fuel in diesel exhaust was estimated to have an effective SOA yield of 0.15 ± 0.05 gOA g^{-1}, larger than the yield of unburnt fuel components in gasoline exhaust (0.023 ± 0.007 gOA g^{-1}) (Figure 2).[15] The chemical composition of evaporative gasoline emissions (non-tailpipe) contains a minor concentration of SOA precursors (0.0024 ± 0.0001 gOA g^{-1}). Predicted yields are consistent with chamber oxidation of unburnt liquid gasoline and diesel fuel in Jathar et al. (Figure S5), very closely for gasoline and within the uncertainties for diesel.[19]

A clear result from this approach is that C_{6-12} aromatics are responsible for virtually all of the SOA from unburnt fuel components in gasoline exhaust, with 96% of SOA estimated to arise from single-ring aromatics and 3% from PAHs, which is consistent with Odum et al.[15,30] This revealed that 20−30% of the potential SOA from these precursors are not included in traditional compound-explicit SOA models.[15] For diesel fuel, single-ring and polycyclic aromatics were estimated to be responsible for 36% and 17% of SOA respectively, while alkanes were responsible for 47%.[15] The results highlight the importance of IVOCs for diesel SOA, yet found that the C_{9-11} aromatics (VOCs) (Figure S6) contribute almost 30% of the mass and 5% of diesel potential SOA.[15] There are significant differences in the SOA formation potential of alkanes depending on carbon number, degree of branching, and presence of cyclic structure.[15,112,114] The dominant alkane SOA precursors were IVOCs and SVOCs from the larger half of the diesel fuel mass range—C_{16} and above (Figure 2).[15] This precursor size dependence for SOA formation potential is largely responsible for the 7 times difference between the overall SOA yields of unburnt fuel between gasoline and diesel.

Advantages. This method utilizes a molecular level understanding of fuels and atmospheric oxidation, which enables the identification of compound-specific uncertainties and development of reformulation strategies. The comprehensive speciation of fuels provides the ability to predict the composition of unburnt fuel emissions that have historically been unspeciated due to a lack of resolution in the unresolved complex mixture or low concentrations of individual minor isomers. The results can be translated to other areas through the analysis of regional fuel samples and data on fuel sales and accurate, validated emission factors, or inventories for the region.

Table 2. Reported SOA Yields for Gasoline and Diesel Vehicles

	SOA Yield of Motor Vehicle Emissions [g SOA produced g^{-1} precursor reacted]	
Method	Gasoline	Diesel
Fuel composition-based estimates[a,15]	0.023 ± 0.07	0.15 ± 0.05
Chamber oxidation of vaporized unburned fuel[a,19]	0.01−0.04	0.07−0.2
Chamber oxidation of dilute emissions[45,46] U.S. vehicles[b]	Pre-LEV: 0.008	0.10 ± 0.05
	LEV-1: 0.03−0.17	
	LEV-2: 0.07−0.25	

[a]SOA yields are normalized to OA loading 10 μg m^{-3}. [b]SOA yields are calculated with mass loadings ranging 3−45 μg m^{-3}, see references for details.

Key Uncertainties and Standing Questions. One key assumption of this approach is that SOA precursors emitted by motor vehicles are overwhelmingly due to unburnt fuel components, and products of incomplete combustion are responsible for negligible amounts of potential SOA. There is uncertainty with the extent that fuel composition can be used as a proxy for SOA precursors in vehicle exhaust, which is also discussed in the following approach and the synthesis section as the predicted SOA based on fuels does not always match observations. Fuel-based SOA precursors that are emitted unburnt in exhaust are compositionally consistent with fuels, but there are enhancements in benzene, cyclohexane and cyclopentane that are intermediate species formed during the combustion of larger molecules.[15,69,103,111] Large differences tend to occur with products of incomplete combustion. However, it has been suggested that the composition of organics in exhaust can also be skewed by the enrichment of larger compounds with the lowest combustion efficiency.[115,116]

Commonly measured products of incomplete combustion (e.g., light alkanes, alkenes, small oxygenated species) comprise a significant fraction (30−50%)[67,103] of exhaust emissions, but based on the current state of knowledge they have only minor direct implications on SOA formation via gas-phase chemistry.[117,118] This has been shown for gasoline exhaust, both historically[69,111] and more recently.[67,103] In addition to small alkane/alkene products of incomplete combustion, diesel exhaust also contains a significant fraction of carbonyls as byproducts of pyrolysis, the prominent smaller species of which are not known to form SOA via gas-phase chemistry.[64,67,103,117] A key standing question is quantifying the potential SOA production from combustion or exhaust aftertreatment by-products. However, they have not been characterized, only inferred based on individual vehicle tests (next section). Recent research has highlighted the importance of SOA precursors in fresh gasoline exhaust that have gone unspeciated by available measurement techniques and are not present in liquid fuels. Jathar et al. reports that a substantial fraction of SOA precursors are unidentified and not resolved by traditional gas chromatography.[119] (See further discussion below in the synthesis section.)

This approach does not account for emissions related to lubricating oil hydrocarbons, which have large contributions to diesel and gasoline POA (including 2-stroke engines with premixed oil and fuel) but are only minor contributors to new aerosol formation.[75−77] Miracolo et al. report that contributions of motor oil to new OA are minor compared to exhaust (Figure S7).[120] However, they can change the composition of measured SOA through the oxidation of POA.[121] The theoretical SOA yields used from the literature for individual fuel components are limited by the current state of knowledge at ~3−6 h of oxidation. Furthermore, the SOA yields used in this method are currently irreversible and need to be refined to be consistent with the current understanding of SOA partitioning and aging. It is important to note that the published yields for individual compounds used in this method are subject to underestimation and uncertainty due to recently observed losses of condensing IVOCs and SVOCs to smog chamber walls during oxidation experiments.[40] Similar to the uncertainty issues of the bottom-up method #2, the underlying smog chamber experiments, and interconnected theoretical modeling, is hampered by these wall losses and underestimated SOA yields.

■ BOTTOM-UP METHOD #2: OXIDATION CHAMBER EXPERIMENTS WITH DILUTE VEHICLE EMISSIONS

Overview. SOA production from the exhaust of individual vehicles can be investigated by directly sampling and then photochemically aging actual emissions in reaction chambers. There have been 10 such independent studies, comprising light-duty gasoline vehicles (LDGV);[46−48,122] light-, medium-, and heavy-duty diesel vehicles (LDDV, MDDV, HDDV);[45,123,124] small (<50 cm^3 engine displacement) gasoline scooters (GS); lawn and garden equipment;[46,125] and gas turbines.[126,127] The tested vehicles incorporate a range of prominent engine and exhaust aftertreatment technologies, including DPFs and DOCs.

Method Results. Several conclusions emerge across multiple studies. First, SOA dominates the OA fraction in all the gasoline vehicle chamber studies even after relatively short OH exposures.[96,128] However, the ratios of SOA/POA vary dramatically (from 1 to >500) with vehicle age, engine load, and dilution in the chambers. Nordin et al. observed large OA enhancements (5−50 mg SOA kg-fuel^{-1}) during six experiments with emissions from three different idling LDGV (Euro 2, 3 and 4) after OH exposures of ~5 × 10^6 molecules cm^{-3} h.[48] These results are consistent with Gordon et al.[46] who report 20 to 60 mg-SOA kg-fuel^{-1} (although with somewhat lower SOA/POA ratios) after the same OH exposure; however, comparisons between the studies is complicated by differences in engine load (idle[48] vs urban driving[46]). Platt et al. report ~250 mg kg-fuel^{-1} of SOA (and SOA/POA ~ 10) from Euro 5 LDGV emissions or about 5 times more SOA than in the other LDGV studies.[47] This disparity may be due in part to the much higher chamber C$_{OA}$ in Platt et al. compared to other studies or the formation of ammonium nitrate from ammonia in the exhaust.[47]

Second, effective SOA yields observed in experiments with dilute exhaust from modern gasoline vehicles (i.e., LEV-1/2) are much higher (up to a factor of 10; Table 2) than those predicted or observed for unburnt gasoline.[15,19] This implies that gasoline vehicle exhaust is enriched in SOA precursors relative to fuel. In contrast, exhaust from older (pre-LEV) gasoline vehicles and diesel vehicles had similar SOA yields as predicted/observed from unburnt fuels.[15,19] The net effect of

these results is that the SOA production from diesel emissions per unit fuel is roughly comparable to SOA produced with emissions from LDGV conforming to modern emissions standards.

Third, the SOA formed in smog chamber experiments with dilute gasoline and diesel vehicle exhaust generally cannot be explained by the oxidation of VOC precursors that are included in traditional compound-explicit models (e.g., single-ring aromatics).[45−47,119] The one exception is that better mass balance closure is found for exhaust from older, higher-emitting gasoline vehicles.[46,48] The SOA formation from diesel exhaust is adequately explained by the IVOCs present in the fuel, but the observed SOA formation from gasoline exhaust cannot be explained by fuel composition (Table 2). The chemical composition of these "missing" gasoline exhaust precursors is not yet known nor is it clear if they are formed/enriched in the engine as products of incomplete combustion or during exhaust aftertreatment, highlighting the need to apply more advanced characterization techniques to actual emissions.

These chamber experiments suggest that traditional aromatic emissions still play an important role in SOA formation, but alone, they are no longer a sufficient predictor of SOA production from gasoline vehicles. However, the use of aromatic-free fuel replacements for gasoline decreased SOA formation by a factor of 10+ in two studies. One study used two scooters (with low emissions standards) with an aromatic-free alkylate fuel and ultraclean oil, and another study used a gas turbine engine to compare Fischer−Tropsch synthetic jet fuel to conventional military jet fuel (JP-8).[125,126] Aromatic fuel content appears to be only partially responsible for diesel exhaust SOA. For example, Gordon et al. found that SOA production from HDDV emissions remains constant regardless of whether 9%, 12%, or 28% aromatic diesel fuel is used, which confirms the shared role of aromatic and aliphatic precursors in ambient diesel SOA (Figure 2).[15,45]

Fourth, SOA does not dominate total carbonaceous $PM_{2.5}$ (POA + BC + SOA) from non-DPF-equipped diesel exhaust. This is due to large BC emissions from non-DPF diesel and because SOA production from diesel emissions per unit fuel is roughly comparable to that from LDGV emissions. SOA production from the emissions of two LDDV with and without a deactivated oxidation catalyst (254−461 mg kg-fuel^{-1})[123] is comparable to the 250 mg-SOA kg-fuel^{-1} produced from LDGV emissions in Platt et al.[47] Median SOA production from one HDDV and two MDDV without a DPF was 35 mg kg-fuel^{-1}—close to the median from experiments with 15 different LDGV (spanning model years 1987−2011)—while diesel BC was 20 times greater than LDGV BC.[45,46]

Fifth, catalyzed aftertreatment, especially DOC + DPF, is extremely effective at eliminating SOA from diesel combustion emissions. Gordon et al. found nearly zero SOA production from emissions from two different DOC + DPF-equipped HDDV operated over an urban driving cycle.[45] In addition, SOA from the emissions of a single LDDV were dramatically reduced from 461 to 19 mg kg-fuel^{-1} after a DOC was installed.[123] Furthermore, SOA production for warm and cold idle experiments with the active DOC-equipped LDDV were identical, which suggests that the DOC (rather than changes to the engine temperature/load) mitigates SOA formation.[123]

Advantages. The primary advantage of the chamber-based approach is that it provides a direct measurement of the SOA production from actual emissions. This is important given the often poor performance of SOA models, which is due to the complexity of the SOA chemistry and incomplete characterization of SOA precursors. Chamber experiments with dilute exhaust also enable direct evaluation of models that use emission surrogates like unburned fuel to estimate SOA production. In fact, model evaluation using chamber data with dilute exhaust played an important role in expanding the range of SOA precursors beyond single-ring aromatics.[12] Chamber experiments with dilute exhaust also provide a straightforward approach to explore the effect of different driving cycles, fuel composition, engines, and exhaust after-treatment technologies on SOA production.

Key Uncertainties and Standing Questions. While the chambers allow for testing of individual vehicles, it is challenging to develop large enough data sets to represent the entire in-use fleet, with studies limited to a small number of vehicles. In particular, sample sizes are likely too small to capture high-emitters that are responsible for the bulk of fleetwide emissions.[52,65,129−131]

All chamber oxidation studies, both dilute-exhaust studies and single-precursor experiments used to derive yield data for models, impart some uncertainty based on how well they represent atmospheric oxidation conditions (radical branching, VOC/NO$_X$ ratios, mixture of organics). There are potential losses of emitted IVOCs and SVOCs in transfer lines or exhaust dilution manifolds prior to the chamber. Experimental yields may be systematically and variably low due to losses of semivolatile precursors and gas-phase oxidation products to chamber walls.[39−41] These chamber-related concerns are somewhat reduced by studies that directly compare SOA formation between vehicles.

A challenge with the chamber experiments with dilute exhaust is that the complexity of exhaust makes it difficult to understand which component(s) of the exhaust are driving SOA formation (i.e., SOA mass closure). An excellent example of this issue is the unexpectedly high SOA yields of LEV-1/2 vehicle exhaust. SOA mass closure studies have demonstrated large uncertainty regarding the precursors responsible for SOA production in the chamber tests. In general, bottom-up, model-based SOA estimates based on compound-specific SOA yields cannot explain the measured SOA production in dilute exhaust.[12,45,46,48,115,119] This is especially true for vehicles manufactured over the past two decades that meet LEV-1/2 or Euro 5 standards. For example, both Platt et al. and Gordon et al. report that emitted aromatics ($\leq C_9$ plus naphthalene) accounted for <20% of the observed SOA production from LDGV.[45,47] While Nordin et al. found that a much higher fraction (60%) of the SOA produced in their LDGV experiments could be explained by aromatic emissions, they still were unable to account for 100% of the observed SOA production with idling old model vehicles.[48] They hypothesize that the balance of SOA (40%) was due primarily to unmeasured midweight VOCs such as C_{10} and C_{11} aromatics and naphthalene, while the fuel-based approach (bottom-up method #1) only attributes 21% of SOA from gasoline to C_{10} and larger aromatics.[15,48] Yet, Zhao et al.[116] shows that alkylated benzene contributes substantially to unspeciated IVOCs in gasoline vehicle exhaust, pointing again to the need to apply advanced characterization techniques to actual exhaust.

The key remaining question is why effective SOA yields of gasoline exhaust from newer vehicles (LEV-1/2) is higher than older vehicles, despite lower NMOG and traditional SOA precursor emissions, tighter emissions standards, and no observed changes in the measured organic composition of

emissions. This has led to an emphasis on unspeciated emissions and their importance for gasoline SOA, which is discussed further in the synthesis section.[119]

■ TOP-DOWN METHODS

Top-down methods #1−#3 all use ambient measurements of some type and are largely focused on the composition of organic aerosols. These composition data are often augmented by activity information and temporal or spatial variability (top-down methods #2 and #3). Direct analysis of chemical composition data (#1) has largely been insufficient to yield conclusions on the relative importance of motor vehicle types on SOA, so the results of methods #2 and #3 are discussed in more detail.

■ TOP-DOWN METHOD #1: CHEMICAL COMPOSITION OF AMBIENT OA

Overview. The chemical composition of ambient OA is commonly measured by multiple techniques (with different goals and priorities) and presents a potential way to estimate the contribution of gasoline and diesel precursors to SOA when combined with source apportionment analysis.[94,132−134] For example, Aerosol Mass Spectrometry (AMS) is commonly used to measure the total mass concentration of OA by vaporizing and directly ionizing the collected aerosol, with less compound-specific resolution relative to GC-MS.[11,135,136] Thermal-desorption gas chromatography (GC) or GC-MS is among the standard methods in analysis of ambient OA to quantify concentrations of specific primary and secondary components of OA.

Note: The ratios of SOA formed from motor vehicle emissions to total OA or BC in motor vehicle emissions can also be used to examine their influence on urban areas; they have been surveyed in several recent papers and change over time, with strong dependence on vehicle model year and exhaust aftertreatment.[45,46,67,88] Yet, these ratios systematically underestimated the role of SOA in urban areas in the past due to method assumptions.[137]

Method Results. The very complex nature of ambient OA means that detailed molecular speciation can only be achieved for a subset of species, leading to direct quantification of only a small fraction of OA mass.[94,95,137] Furthermore, full closure between the measured OA mass and results of source apportionment by CMB is not achieved in most studies.[134,138] Studies have used a few specific SOA tracers as proxies to assess SOA from chemical compound classes (e.g., aromatics, monoterpenes) but not source-specific tracers.[139−143] This chemically speciated data has been insufficient to discriminate SOA from different fossil sources and as specific oxidized tracers have not been identified yet.

Bulk characterization of OA using methods that do not provide detailed molecular composition also provides insight into SOA concentrations. One approach uses off-line FTIR analysis of OA, in which organic functional group composition of POA and SOA is determined.[144,145] Recent work has reported that FTIR spectra can be analyzed with positive matrix factorization (PMF) to quantify SOA components with different compositions of functional groups, but the different components are not specific to either gasoline or diesel emissions.[146] AMS spectra can also be analyzed with PMF to quantify total SOA as well as contributions of different sources to SOA, with more success at present for some biogenic SOA

sources.[44,97,147] Quantification of diesel vs gasoline SOA separately from ambient AMS data has not been reported to our knowledge. Yet, AMS measurements have been used to estimate the amount of SOA from diesel and gasoline emissions by examining the weekly cycle in SOA concentrations, and this analysis is described in more detail in the next section.

Advantages. This approach directly analyzes all atmospheric OA, its properties, and chemical dynamics in the ambient atmosphere.

Key Uncertainties and Standing Questions. In general, source apportionment of SOA using tracer composition measurements is difficult due to incomplete speciation of the entire SOA mass, possible atmospheric transformations (e.g., oxidation, oligomerization, gas-particle partitioning, deposition) of SOA tracers, and potential variability of tracer/SOA ratios. Quantification of SOA contributions using functionalized SOA tracers may also be affected by sampling inefficiencies, variability in oxidation conditions between lab and field studies (incl. chamber losses), atmospheric oxidation of tracers, or instability of these compounds during analysis with a variety of methods.[138,139,148] Further research in the area of tracer identification and characterization is thus required, especially studies that evaluate individual tracer oxidation pathways in comparison to overall oxidation and SOA formation, as well as tracer gas-particle partitioning. The development of more sophisticated analytical techniques, for example, the thermal desorption aerosol gas chromatograph (TAG),[95] two-dimensional TAG,[149,150] GC coupled with soft ionization,[42] and very high or ultra high resolution MS, are promising instruments for measurement of tracers that could not be detected by more traditional techniques as well as quantification of such tracers in laboratory-generated and ambient OA. Improved characterization of existing bulk techniques such as FTIR and AMS in terms of their response to specific SOA sources,[147] as well as development of new techniques such as those based on chemical ionization mass spectrometry (CIMS) (e.g., FIG-AERO-HRToF-CIMS[151]) may also lead to improvements in this area.

■ TOP-DOWN METHOD #2: DAY OF WEEK ANALYSES UTILIZING INTRA-WEEK VARIABILITY IN DIESEL FUEL USE AND TOTAL OA OR SOA CONCENTRATION DATA (FROM FACTOR ANALYSIS)

Overview. In many urban environments, lower diesel vehicle traffic volume is observed on weekends compared to weekdays, whereas light-duty gasoline vehicles have more consistent traffic activity throughout the week.[55,152] For example, in the Los Angeles Basin where there are minimal influxes of regional pollution, there is a very strong weekday/weekend pattern in BC concentrations, which is emitted predominantly by diesel vehicles. In contrast, there is little weekday/weekend pattern in mixing ratios of CO and benzene, emitted mainly from gasoline-fueled vehicles.[43,44,153] Using fuel-use data and vehicular BC emission factors, it was estimated that diesel emissions were 54% lower on the weekends compared to weekdays.[43] Such regular perturbations to emissions from diesel vehicles have been used in recent studies to estimate the contributions of gasoline and diesel emissions to SOA.[43,44]

Urban VOC emissions are from a mix of vehicular and nonvehicular sources, but urban NO_X emissions are dominated

Table 3. Observed Concentrations of Elemental Carbonaceous Aerosol (i.e., Black Carbon), Fossil Fuel-Derived Primary Organic Aerosol, and Fossil Fuel-Derived Secondary Organic Aerosol[a]

	Black Carbon[ug/m3]	Fossil Fuel-Derived POA[ug/m3]	Fossil Fuel-Derived SOA[ug/m3]
Marseilles, France	1.8	0.82	0.65
Barcelona, Spain	1.4	0.9	1
Paris, France	1.1	0.87	0.57
Zurich, Switzerland	1.3	0.51	0.55
Bakersfield, U.S.	0.31	0.61	2.5
Pasadena, U.S.	0.63	1.4	2.9

[a]Determined using carbon isotopes in $PM_{2.5}$ measurements. Data from refs 98, 99, and 196.

by diesel vehicles. So, less diesel activity over the weekend results in significantly lower NO_X concentrations, altering ambient VOC/NO_X ratios and, in many cases, increasing the rate of atmospheric processing by increasing the OH concentration.[153−155] This "weekend effect" with increased ozone concentrations over the weekend has long been observed in different cities.[55,152,153,156,157] In 1995, Turpin et al. reported some of the first evidence of a SOA weekend effect, where SOA concentrations in Los Angeles were greatest on Saturday.[29] When comparing SOA formation on weekends and weekdays, it is thus critical to account for both differences in chemical processing of precursors during weekdays versus weekends and differences in source emissions. Analyses have corrected for this using weekday and weekend data from air masses with similar degrees of photochemical aging determined from the observed ratios of vehicle-dominated hydrocarbons with different OH-oxidation rates (e.g., benzene vs toluene) or the NO_x/NO_y ratio.[43,44,49,158]

Two recent studies in LA used this effect to determine source impacts on SOA formation using ambient total OA and urban SOA enhancement measurements normalized to CO (i.e., ΔOA/ΔCO and ΔSOA/ΔCO) with airborne and ground site data.[43,44] In the airborne study (with OA mass measurements), contributions of POA to ambient measured OA were accounted for using ΔPOA/ΔCO values from other urban areas with adjustments made for weekend ratios to account for changes in emissions from diesel vehicles or other sources (e.g., cooking).[44,105,159,160] Weekday ΔSOA/ΔCO ratios were then compared to weekend ratios while controlling for photochemical processing to determine the relative contribution of diesel vehicles across the six flights. For the ground site study, AMS data obtained over 6 weeks from Pasadena, CA, were also analyzed using PMF to determine the contribution of urban sources to SOA.[44] The weekday vs Sunday concentration of urban SOA enhancements (normalized by ΔCO) were then similarly compared for air parcels with similar photochemical ages.[44] This removes the need for assumptions about weekday/ weekend differences in ΔPOA/ΔCO emissions. A follow-up study reported the ratios from the same data sets for Saturdays, as well as for the urban-dominated SV-OOA PMF component, and found a similar lack of difference between weekdays and weekend days.[49]

Method Results. From the average difference between weekday to weekend ΔSOA/ΔCO regressions with similar photochemical ages, the aircraft-based study estimated a range of diesel contributions to SOA in the LA Basin: 0−20% and 0−47% depending on the assumed POA/CO ratio.[43] In the ground AMS-based study, the rates of increase in the total SOA-to-ΔCO ratio (per unit photochemical age) were determined to be 108 ± 5 and 98 ± 8 $\mu g \ sm^{-3} \ ppmv^{-1} \ day^{-1}$ for weekdays and Sundays, respectively, with no

significant difference between the weekday and Sunday data.[44] These slopes are also similar to those observed when oxidizing air dominated by vehicle emissions in a tunnel.[96] Using the ratio of the ambient slopes (1.1 ± 0.1), the diesel vehicle contribution to the urban SOA budget was estimated to be 19(+17/−21)%. A follow-up study on Pasadena apportioned SOA using a box model incorporated several recent SOA parametrizations and was constrained by measurements (where possible); they reported a similar percentage of SOA from diesel, 16−27%,[22] consistent with the two field studies.

Advantages. This method allows for an experiment on the scale of urban atmospheres due to well-known changes in diesel activity and emissions. The airborne data used in Bahreini et al.[43] provided a basin-wide view of SOA formation.

Key Uncertainties and Standing Questions. The primary weakness of this top-down approach is the assumption that precursor emissions for urban SOA in Los Angeles are dominated by motor vehicles. However, there is a possibility of important and unidentified SOA precursors from nonvehicular sources. On the basis of the California Air Resources Board's 2010 inventory, mobile sources contribute only ∼50% of total reactive organic gases (ROG) emissions in the South Coast Air Basin, while area-wide and stationary sources contribute ∼38%.[49] Yet, ambient measurements in Pasadena (2010) suggest that gasoline emissions explain much of the variability in anthropogenic $C_2−C_{10}$ hydrocarbons (i.e., NMHC) and oxygenated VOC concentrations, along with a clear source of light alkanes from oil and gas production/use.[161,162] Zhao et al. found minimal weekday−weekend variation in IVOC concentrations and emphasized the importance of nondiesel vehicle sources.[87] Fossil-fuel driven emissions appear to contribute 75% of the afternoon increase in SOA mass formed from urban sources and observed in Pasadena with the remaining 25% from nonfossil sources.[99] A key question is the attribution of fossil SOA in the LA Basin, while the nonfossil fraction may be mostly due to SOA from in-basin cooking emissions.[22,99]

The weekend reduction in NO_X emissions appears to have less of an effect on oxidation rates in Los Angeles than expected, highlighting that large changes in weekend NO_X-driven oxidation conditions are not ubiquitous.[163] Yet, OH and HO_2 concentrations are still higher during the weekend due to the decrease in NO_X.[164] Additional uncertainties include the limited representation of urban areas with these two studies in LA, and the short duration of sample collection (i.e., six flights and six weeks, respectively). However, the SOA formation rates in LA were similar to those observed at other locations such as the NE U.S. and Mexico City.[44] Currently, the VOC/NO_X ratios in most urban environments are in the high-NO_X SOA formation regime.[37,44] Large future changes in NO_X concentrations could affect VOC/NO_X on weekends and weekend SOA formation due to changes in the branching ratio of RO_2

reactions (NO vs HO$_2$ channels) during weekends compared to weekdays and changing SOA formation potentials, complicating the interpretation of this top-down method.

■ TOP-DOWN METHOD #3: COMPARING OA COMPOSITION ACROSS URBAN AREAS WITH DIFFERENT RELATIVE GASOLINE−DIESEL FUEL USAGE

Overview. There are large differences in diesel fuel use in the U.S. and Europe (Table S1). Carbon isotope measurements can also provide an additional constraint for top-down analysis on regional scales by assessing how the fossil to nonfossil fraction of SOA varies with regional variations in fuel use. Zotter et al. compared fossil vs contemporary SOA from several European cities with greater diesel passenger car use.[99] They observed 2−3 times higher BC concentrations but 20% less SOA compared to LA.[99]

Method Results. Table 3 compares the relative contribution of vehicular emission components—including BC, POA and SOA—in major modern European cities and in the LA Basin (Bakersfield and Pasadena). In European cities where the fraction of diesel passenger cars is much larger than in the U.S., BC constitutes a larger fraction of PM$_{2.5}$ (1.2−1.8 μg m^{-3} vs ~0.5 μg m^{-3} in the LA Basin; Table 3). Conversely, in the LA Basin, the average levels of fossil SOA are 4−5 times higher than in European cities (~3 μg m^{-3}), despite lower fossil BC concentrations.[99] Combined with the higher proportions of gasoline cars in the U.S. compared to Europe, this suggests that gasoline emissions may dominate over diesel in the formation of fossil SOA.

Advantages. This method capitalizes on strong fuel use differences between Europe and the U.S. to provide a novel perspective to evaluate OA contributions.

Key Uncertainties and Standing Questions. There are known issues and uncertainties with the carbon isotope analytical method.[99,165] One uncertainty is that the data analysis method assumes that the photochemical ages of sampled air masses at the different locations are comparable. Additional analysis of photochemical ages are required to confirm the observed trends, especially considering potential differences in photochemical conditions between the studied cities. Possible differences between other nonvehicular sources presents uncertainty with such a comparative analysis, so it is best done in connection with an AMS−PMF analysis.

■ RECONCILING EVIDENCE ACROSS METHODS

In summary, using fuel as surrogate for the chemical composition of emissions (bottom-up method #1) suggests that gasoline and diesel vehicles both contribute to urban SOA, with diesel comprising a greater fraction. Chamber experiments (bottom-up method #2) with dilute gasoline exhaust find SOA yields from post-1993 (U.S.) vehicles are much higher than expected from unburned gasoline, but the underlying cause is unclear. Analysis of weekday vs weekend OA in Los Angeles (top-down method #2) suggests that diesel vehicles are not the dominant source, which is consistent with the chamber experiments showing enhanced SOA yields in modern gasoline vehicles. However, the SOA predicted from gasoline vehicles alone is not enough to explain the observed fossil SOA in LA. This contributes to a broader uncertainty about the overall importance of vehicles to urban SOA budget since contribu-

tions from vehicles have been decreasing due to tightening emission standards.

There are several areas where the methods are in agreement but also some key uncertainties within and between methods that we review as points of future research.

Synthesizing Bottom-Up Methods #1 and #2. Both bottom-up methods predict that aromatics and high molecular weight alkanes (>C$_{10}$) are important SOA precursors for diesels. These appear to be primarily unburned fuel components.[15,115] There is less agreement between the two methods for gasoline vehicles, especially for newer generation gasoline vehicles (LEV-1 (Tier 1) and Euro 5 onward), which affect the interpretation of results from the top-down methods. Chamber experiments with dilute exhaust are much higher than just unburned fuel, which may not be a good surrogate for SOA precursors in exhaust from modern gasoline vehicles. Currently (2016), CARB's emission factor model estimates that pre-LEV, LEV-1, and LEV-2 vehicles make up 5%, 26%, and 69% of the greater-LA vehicle population, which equates to 4%, 21%, and 75% of fuel consumption and 38%, 42%, and 20% of the ROG emissions from light-duty gasoline vehicles, respectively.[166] This suggests highly variable exhaust composition and SOA yields across the fleet.

To investigate the unexpectedly high SOA yields of LEV-1/2 gasoline vehicle exhaust, a carbon mass balance was used to estimate emissions of "unspeciated" gas-phase organics in motor vehicle exhaust (in that study unspeciated = compounds larger than C$_{12}$ or oxygenated compounds of any size).[119] Unspeciated organic compounds accounted for 30 ± 15% of gas-phase organic emissions from LEV-1/2 gasoline vehicles. Jathar et al. attributed the vast majority of SOA mass (roughly of 80%) to these unspeciated organics.[46,119] To explain the measured SOA mass, the effective SOA yield of these unspeciated organic emissions was equivalent to that of a C$_{13}$ n-alkane. Yet, gas-phase organic compounds larger than a C$_{12}$ are minor in gasoline fuels or existing speciated exhaust studies, with the exception of POA emissions of motor oil.[15,46,75,103] Studies should consider the possibility that the "missing" SOA precursors are partially oxidized fuel (or oil) components emitted as polar compounds that go undetected by typical measurement techniques. This could occur due to engine chemistry with changes in engine technology or exhaust aftertreatment, especially oxidation catalysts (driven by stricter emissions standards) may cause a fraction of the fuel components to be emitted as highly oxidized organics in tailpipe emissions of light-duty gasoline vehicles. Studies should also confirm that select fuel or oil components are not selectively enriched during combustion. Zhao et al. observed IVOC emissions from gasoline vehicles, but they increased proportionally with total NMHCs, which does not explain the LEV-1/2 increase in SOA yield.[116] Similarly, May et al. observed the same distribution of VOC compound classes between pre-LEV, LEV-1, and LEV-2.[67]

Uncertainties and Considerations Across All Methods. In addition to the uncertainties pointed out within each method, we discuss key points here.

Motor vehicle emissions are an important source for urban SOA in the developed world, but it is possible that it no longer dominates due to the dramatic reduction in emissions over the past few decades in response to strict vehicle emission standards. For example, Ensberg et al. could not reproduce observed SOA formation in Los Angeles with motor vehicle emission alone, although this may be due, in part, to low biases

in chamber yields and/or the lack of inclusion of important precursors in their model (Figure S8).[49] Furthermore, the speciated composition and sources of primary IVOCs are still highly uncertain, and recent analysis suggests that there is little weekday–weekend variation in the mixing ratios of primary IVOCs in Pasadena and hypothesizes fossil sources other than on-road vehicles as the dominant source of these species.[87,161]

The discussed studies define "unspeciated" precursors differently depending on the available instrumentation. The bottom-up method #2 studies refer to all hydrocarbons above C_{12} as unspeciated,[46,67,167] while the bottom-up method #1 studies refer to speciated IVOCs and SVOCs with resolution by carbon number and compound class and some prominent isomers.[15,103] The degree of resolution in studies is increasing,[116] but there remains a clear need for enhanced chemical characterization with molecular insight at the isomer level of actual vehicle exhaust. This will empower oxidation studies, source apportionment, and discernment of gasoline, diesel, and nonmotor vehicle sources necessary for comprehensive air quality management plans.

Cold-start emissions are a major source of gasoline vehicle emissions. Historical and recent studies report cold-start emissions resemble unburned fuel along with variable amounts (35–50%) of products of incomplete combustion, sometimes similar to running emissions.[48,89] If true, then cold-start emissions would be captured by the VOC source apportionment approaches (e.g., bottom-up method #1). Gasoline running emission factors from tunnels could have a low bias due to the exclusion of cold-start, idling, or low-load emissions, although Ensberg et al. included a distribution of drive cycles, all of which under-predicted SOA in LA (Figure S8), but this may have been due to other causes (above).[15,49,116,168] Conversely, recent work compared the observed ambient SOA formation to PAM chamber oxidation of tunnel air and found good agreement between SOA/ΔCO ratios as a function of photochemical age (Figure S3).[96,107]

The bottom-up methods and results are based on the assumption that environmental reactors and chambers that have been used to simulate SOA formation from individual precursors and motor vehicle emissions are representative of urban oxidation chemistry. There is certainly potential for experimental artifacts introduced through differences in oxidant exposure, organic aerosol loadings, vapor/particle wall losses in transfer lines and reactors/chambers, and relative abundance of NO_X. It is critical to point out that the body of work presented here does not fully account for aqueous processing, which may alter the relative importance of precursors for SOA (e.g., aldehydes). The assumption is made that both our chambers and ambient studies are not largely impacted by aqueous processing given the relatively dry field sites, other aqueous SOA studies in urban areas,[169,170] and the lack of observed differences in OA/ΔCO between days with cloudy and clear mornings over downtown LA.[22]

Pieber et al.[171] report that ammonium nitrate (NH_4NO_3) or other nitrate salts can lead to overestimation of OA with AMS measurements in chamber or ambient environments. This effect is particularly pronounced when concentrations of NH_4NO_3 are much greater than OA; yet is correctable and is not ubiquitous across AMS instruments.[171] Yields from some of the vehicle studies where nitrate ≫ OA may need some correction for this effect; however, most published SOA yields use scanning mobility particle sizer (SMPS) measurements in experiments with low nitrate/OA ratios.[38] Future studies

should consider this effect since newer gasoline vehicles with advanced NOx post-combustion control technology have higher ammonia emission factors.[59,172,173]

The impacts of gasoline and diesel emissions on urban SOA should be viewed in the context of all emitted organic and inorganic chemical species in urban areas, especially considering recent advancements in our understanding of the enhancement of biogenic SOA in the presence of anthropogenic emissions.[97] There may be synergistic effects between gasoline and diesel emissions, such that SOA formation in an air mass is not necessarily the sum of potential SOA in that same air mass.

■ IMPLICATIONS AND CHALLENGES FOR THE DEVELOPED AND DEVELOPING WORLD

Vehicular emissions and motor vehicle SOA have been declining for decades in the U.S., Canada, Europe, and Japan due to tightening regulations and the resulting improvements in vehicle technology. On the basis of the collection of evidence, it is likely that both gasoline and diesel are, and will continue to be, important sources of SOA precursors in urban areas but not the only sources of concern in the developed world. Decades of gasoline-focused VOC emission regulations have likely increased the importance of diesel precursors, but changes in modern gasoline emissions and the recent requirements for diesel exhaust aftertreatment technologies (e.g., DPF) may have shifted the balance back to gasoline. Future developments will continually change the importance of gasoline vs diesel emissions for SOA and their overall impact.

In the next 40 years, China, India, Brazil, and Russia will add more than 1.5 billion vehicles globally with 5–10% annual growth in sales. Motor vehicle emission standards and compliance in the developing world (Brazil, Russia, India, China, South Africa) lag behind those in the U.S., Canada, Europe, and Japan by roughly one equivalent standard (i.e., LEV-2 rather than LEV-3 or Euro 5 rather than Euro 6, Figure S1). Regulatory gaps between developed and developing nations continue to narrow, but location-dependent heterogeneity in vehicle fleets due to fuel use/formulation, regulations, and/or technology penetration will likely persist.

Several key takeaways and challenges emerge from this review:

Existing U.S. regulations will create a new generation of vehicles (LEV-3/Tier 3) with even lower VOC emissions. Yet, across developed and developing regions, SOA from gasoline vehicles appears to be caused by a combination of known emissions of unburned fuel components across the fleet and unspeciated SOA precursors in new vehicle models, as well as large contributions from outlier high emitters that comprise a small fraction of the in-use vehicles. Fuel reformulation is an option to reduce known SOA precursor components (i.e., aromatics), but existing evidence is unclear on how effective reformulation will be for SOA control since the precursors to the majority of SOA formed from LEV-1/2 exhaust are unknown, and it is unclear if (and how) the SOA precursors are derived from fuel components. Internationally, fuel composition standards (including aromatic content) varies for gasoline (and diesel fuel),[15,174,175] which could potentially affect potential SOA per liter of fuel burned.

In areas with more diesel vehicles (Europe and some parts of the developing world), existing emissions standards would suggest that on-road diesels contribute significantly to SOA and air pollution in urban environments. Since the vast majority of SOA precursors in diesel exhaust are unburned fuel, stricter

VOC emissions standards requiring the use of catalyzed aftertreatment technologies will likely reduce SOA formation. The newest standards in the developed world require diesel exhaust aftertreatment for all on-road (and soon off-road) vehicles;[176] diesel particulate filters and diesel oxidation catalysts dramatically reduce POA emissions, gas-phase SOA precursors, and diesel-derived SOA. However, there are concerns regarding emissions of ultrafine particles (mixed organic/inorganic) from DPF-equipped vehicles, depending on sulfur content of fuels.[177−179] Real-world tests on technology efficacy over their lifetime are key to answer questions about durability in the real world when deployed on large numbers of vehicles and low-speed operation emissions.

Stricter VOC and NOx emissions standards for all motor vehicles are intended to provide benefits for SOA and overall air quality. However, nonroad anthropogenic sources, off-road sources (e.g., construction/agricultural equipment), and outlier high-emitting on-road vehicles likely also have significant air quality impacts. This includes small off-road engines (e.g., lawn equipment, generators). Two-stroke vehicles are popular in Asia, Africa, and parts of Southern Europe. Given their very high VOC emissions, 2-stroke engines likely have a disproportionate effect on SOA formation. Already, several city and national governments (e.g., Lahore, Pakistan, Dhaka, Bangladesh, Taiwan) are considering, or have implemented, 2-stroke bans in metropolitan areas.

■ FUTURE RESEARCH PRIORITIES

We identify several areas related to emissions, oxidation, and urban chemistry:

- *Characterizing the unspeciated ∼30% of LEV-1/2 gasoline emissions:* The identities and formation mechanisms of the unspeciated gasoline emissions observed in chamber studies are key to unraveling the relative importance of gasoline and diesel sources on urban SOA (and gas-phase organics). The application of novel measurement techniques (e.g., chemical ionization[151,180,181]) is promising given the possible oxidized/polar nature.

- *New vehicles:* How will VOC emissions and SOA yields from emerging LEV-3 vehicles (Tier 3 standards, starting 2017) compare to their predecessors? How will new technologies such as gasoline direct injection (GDI) influence SOA precursor emissions?

- *Real-world emissions and conditions:* Bottom-up studies need to include a range of realistic vehicle operating modes (including idle, creep),[116,168] test vehicles that are representative of the fleet's population, and sampling/analytical instrumentation and methods that minimizes the loss of organic analytes. Lab and field studies are needed to evaluate the lifetime efficacy of exhaust aftertreatment technologies (e.g., DPF) and to monitor vehicle compliance, potentially with on-board sensors.

- *Emerging fuels and/or fuel formulation:* Existing differences in conventional fuel composition may have impacts on SOA yield; the effects of further strategic reformulation or alternative fuels require further study. Sustainable practices and issues related to energy security have led to an increase in use and research on synthetic (e.g., Fischer−Tropsch fuels) and biofuels (e.g., ethanol, biodiesel).[182−184] These fuels are radically different from conventional gasoline and diesel in terms of their molecular composition and thus SOA formation

potential. Aromatic-free fuels appear to significantly reduce gasoline SOA production,[125] while the use of soy-based biodiesel has resulted in negligible differences in SOA production in a gas-turbine engine.[126]

- *Chamber studies:* SOA formation resolved by dynamometer driving cycle (especially cold starts) with oxidation flow reactors (e.g., PAM chamber[185]) and experiments using real-world vehicle exhaust (from a roadway tunnel or busy roadside[96]) are valuable in characterizing SOA formation in the laboratory from actual emissions. Additionally, the effect of co-emitted sulfur species on oxidation chemistry/products and nighttime oxidation with NO_3 radical are important avenues of further research.

- *SOA yield studies on understudied SOA precursors:* There is a lack of experimental or theoretical studies on SOA yields for several known classes of compounds, including C_{9+} aromatics (single-ring and PAH), C_5/C_6 cycloalkanes, bicycloalkanes, and tricycloalkanes. Similar studies will also be needed for uncharacterized gasoline exhaust.

- *Multigenerational SOA formation occurring after the initial stages of oxidation:* SOA yields are limited in their treatment of increasing photooxidation. Individual SOA yields are limited to only a few generations of oxidation and need to be parametrized in a way that accounts for higher degrees of oxidation or a reversible equilibrium with revolatilization of highly aged organics following reactions that result in fragmentation. One option, oxidation flow reactors, may allow reaching higher oxidation levels.[96,186]

- *Measure/correct chamber yields for losses of precursor and oxidation products to walls and determine how yield underestimates change with compound class, size, and oxidation conditions:* Experimental yields can be biased low due to wall losses of gases but will vary for aromatics vs aliphatics and other precursors that require several generations of oxidation chemistry to condense.[39−41] This effect could lead to the underestimation of yields for chamber experiments with individual compounds and the complex mixtures in gasoline or diesel exhaust.

- *Past and future changes in urban chemistry:* Research should explore indirect effects of motor vehicle emissions on SOA formation chemistry in addition to direct effect as SOA precursors. This includes changes in POA mass for partitioning, changes in radical and oxidant production (e.g., OH, O_3, NO_3) that affect rates of photochemical processing of not only urban air but also of biogenic emissions downwind of urban areas, and the effect of aqueous processing in a variety of regions/climates. Furthermore, the effect of changing urban VOC/NOx ratios on SOA from motor vehicle precursors needs to be evaluated.

- *Auto-oxidation of unsaturated, nonaromatic hydrocarbons:* C_{10} and smaller alkenes have recently been shown to quickly form highly oxidized "extremely-low" volatility organic compounds (ELVOCs) and SOA.[187,188] Research on the propensity of unsaturated hydrocarbons in gasoline and diesel exhaust to auto-oxidize in urban air is necessary since the addition of this chemistry may change the apportionment of motor vehicle SOA.

- *Modeling SOA from motor vehicles:* Advancements in chemical modeling capabilities are necessary to better

represent/parametrize the complex organic mixtures in vehicle emissions. Partially or fully explicit chemical modeling (master chemical mechanism (MCM)[189] or Generator of Explicit Chemistry and Kinetics of Organics in the Atmosphere (GECKO-A)[190]) that incorporates greater detail on motor vehicle SOA oxidation precursors/yields/mechanisms will likely better represent/parametrize the complex organic mixtures. A simple parametrization includes speciation by compound class within the volatility bins of dynamic VBS-based models (Figure S6) to describe emissions, SOA potential, and oxidation products with a limited, but useful, amount of chemical detail.[15] The precursor chemical structure will inform fragmentation vs functionalization and product volatilities.

- *Comprehensive emissions data:* The next generation of chemistry models will need more comprehensive emissions data. Historically, inventories have focused on including VOC because of their contribution to atmospheric reactivity and ozone formation. However, lower volatility species (e.g., IVOC) with lower emission rates disproportionally contribute to SOA formation. More measurements are needed of these emissions, and they need to be formally included in inventories.

- *Largest molecular weight compounds in the VOC range from diesel vehicles:* These need to be included in either chemically explicit or VBS models, especially the aromatics, which are efficient SOA precursors (Figure S6).

- *Further examination of field data from more cities for weekend—weekday effects:* This needs to be studied in organic aerosol and tracer species and for long-term trends in time series of organic aerosol, especially in several locations with varied motor vehicle sources.

ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b04509.

Table S1 and Figures S1–S8(PDF)

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REFERENCES

(1) Schwartz, J.; Laden, F.; Zanobetti, A. The concentration-response relation between PM(2.5) and daily deaths. *Environ. Health Perspect.* **2002**, *110* (10), 1025−1029.

(2) Smith, K. R.; Frumkin, H.; Balakrishnan, K.; Butler, C. D.; Chafe, Z. A.; Fairlie, I.; Kinney, P.; Kjellstrom, T.; Mauzerall, D. L.; McKone, T. E.; et al. Energy and human health. *Annu. Rev. Public Health* **2013**, *34* (March), 159−188.

(3) Schlesinger, R. B.; Kunzli, N.; Hidy, G. M.; Gotschi, T.; Jerrett, M. The health relevance of ambient particulate matter characteristics: Coherence of toxicological and epidemiological inferences. *Inhalation Toxicol.* **2006**, *18* (2), 95−125.

(4) Pope, C. A. I.; Dockery, D. W. Health effects of fine particulate air pollution: lines that connect. *J. Air Waste Manage. Assoc.* **2006**, *56* (6), 709−742.

(5) Lim, S. S.; Vos, T.; Flaxman, A. D.; Danaei, G.; Shibuya, K.; Adair-Rohani, H.; Amann, M.; Anderson, H. R.; Andrews, K. G.; Aryee, M.; et al. A comparative risk assessment of burden of disease and injury attributable to 67 risk factors and risk factor clusters in 21 regions, 1990−2010: a systematic analysis for the Global Burden of Disease Study 2010. *Lancet* **2012**, *380* (9859), 2224−2260.

(6) World Health Organization. Burden of Disease from Ambient and Household Air Pollution: Database Estimates. http://www.who.int/phe/health_topics/outdoorair/databases/en/ (accessed July 2, 2015).

(7) Zhang, Q.; Jimenez, J. L.; Canagaratna, M. R.; Ulbrich, I. M.; Ng, N. L.; Worsnop, D. R.; Sun, Y. Understanding atmospheric organic aerosols via factor analysis of aerosol mass spectrometry: a review. *Anal. Bioanal. Chem.* **2011**, *401* (10), 3045−3067.

(8) Zhang, Q.; Jimenez, J. L.; Canagaratna, M. R.; Allan, J. D.; Coe, H.; Ulbrich, I.; Alfarra, M. R.; Takami, A.; Middlebrook, A. M.; Sun, Y. L.; et al. Ubiquity and dominance of oxygenated species in organic aerosols in anthropogenically-influenced Northern Hemisphere midlatitudes. *Geophys. Res. Lett.* **2007**, *34* (13), L13801.

(9) Donahue, N. M.; Robinson, A. L.; Pandis, S. N. Atmospheric organic particulate matter: From smoke to secondary organic aerosol. *Atmos. Environ.* **2009**, *43* (1), 94−106.

(10) Kanakidou, M.; Seinfeld, J. H.; Pandis, S. N.; Barnes, I.; Dentener, F. J.; Facchini, M. C.; Van Dingenen, R.; Ervens, B.; Nenes, A.; Nielsen, C. J.; et al. Organic aerosol and global climate modelling: a review. *Atmos. Chem. Phys.* **2005**, *5* (4), 1053−1123.

(11) Jimenez, J. L.; Canagaratna, M. R.; Donahue, N. M.; Prevot, A. S. H.; Zhang, Q.; Kroll, J. H.; DeCarlo, P. F.; Allan, J. D.; Coe, H.; Ng, N. L.; et al. Evolution of organic aerosols in the atmosphere. *Science* **2009**, *326* (5959), 1525−1529.

(12) 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.

(13) Goldstein, A. H.; Galbally, I. E. Known and Unexplored Organic Constituents in the Earth's Atmosphere. *Environ. Sci. Technol.* **2007**, *41* (5), 1514−1521.

(14) Hallquist, M.; Wenger, J. C.; Baltensperger, U.; Rudich, Y.; Simpson, D.; Claeys, M.; Dommen, J.; Donahue, N. M.; George, C.; Goldstein, A. H.; et al. The formation, properties and impact of secondary organic aerosol: current and emerging issues. *Atmos. Chem. Phys.* **2009**, *9* (14), 5155−5236.

(15) 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.; et al. Elucidating secondary organic aerosol from diesel and gasoline vehicles through detailed characterization of organic carbon emissions. *Proc. Natl. Acad. Sci. U. S. A.* **2012**, *109* (45), 18318−18323.

(16) Williams, B. J.; Goldstein, A. H.; Kreisberg, N. M.; Hering, S. V. An In-Situ Instrument for Speciated Organic Composition of

Atmospheric Aerosols: T hermal Desorption A erosol G C/MS-FID (TAG). *Aerosol Sci. Technol.* **2006**, *40* (8), 627−638.

(17) Williams, B. J.; Goldstein, A. H.; Kreisberg, N. M.; Hering, S. V. In situ measurements of gas/particle-phase transitions for atmospheric semivolatile organic compounds. *Proc. Natl. Acad. Sci. U. S. A.* **2010**, *107* (15), 6676−6681.

(18) de Gouw, J. A.; Middlebrook, A. M.; Warneke, C.; Ahmadov, R.; Atlas, E. L.; Bahreini, R.; Blake, D. R.; Brock, C. A.; Brioude, J.; Fahey, D. W.; et al. Organic aerosol formation downwind from the Deepwater Horizon oil spill. *Science* **2011**, *331* (6022), 1295−1299.

(19) Jathar, S. H.; Miracolo, M. A.; Tkacik, D. S.; Donahue, N. M.; Adams, P. J.; Robinson, A. L. Secondary organic aerosol formation from photo-oxidation of unburned fuel: experimental results and implications for aerosol formation from combustion emissions. *Environ. Sci. Technol.* **2013**, *47* (22), 12886−12893.

(20) Dzepina, K.; Cappa, C. D.; Volkamer, R. M.; Madronich, S.; DeCarlo, P. F.; Zaveri, R. A.; Jimenez, J. L. Modeling the multiday evolution and aging of secondary organic aerosol during MILAGRO 2006. *Environ. Sci. Technol.* **2011**, *45* (8), 3496−3503.

(21) Presto, A. A.; Miracolo, M. A.; Kroll, J. H.; Worsnop, D. R.; Robinson, A. L.; Donahue, N. M. Intermediate-volatility organic compounds: A potential source of ambient oxidized organic aerosol. *Environ. Sci. Technol.* **2009**, *43* (13), 4744−4749.

(22) Hayes, P. L.; Carlton, A. G.; Baker, K. R.; Ahmadov, R.; Washenfelder, R. A.; Alvarez, S.; Rappenglück, B.; Gilman, J. B.; Kuster, W. C.; de Gouw, J. A.; et al. Modeling the formation and aging of secondary organic aerosols in Los Angeles during CalNex 2010. *Atmos. Chem. Phys.* **2015**, *15* (10), 5773−5801.

(23) Haagen-Smit, A. J. Chemistry and Physiology of Los Angeles Smog. *Ind. Eng. Chem.* **1952**, *44* (6), 1342−1346.

(24) Pandis, S. N.; Harley, R. A.; Cass, G. R.; Seinfeld, J. H. Secondary organic aerosol formation and transport. *Atmos. Environ., Part A* **1992**, *26* (13), 2269−2282.

(25) Grosjean, D.; Seinfeld, J. H. Parameterization of the formation potential of secondary organic aerosols. *Atmos. Environ.* **1989**, *23* (8), 1733−1747.

(26) Izumi, K.; Fukuyama, T. Photochemical aerosol formation from aromatic hydrocarbons in the presence of NOx. *Atmos. Environ., Part A* **1990**, *24* (6), 1433−1441.

(27) McMurry, P. H.; Grosjean, D. Photochemical formation of organic aerosols: Growth laws and mechanisms. *Atmos. Environ.* **1985**, *19* (9), 1445−1451.

(28) Turpin, B. J.; Huntzicker, J. J.; Larson, S. M.; Cass, G. R. Los Angeles summer midday particulate carbon: primary and secondary aerosol. *Environ. Sci. Technol.* **1991**, *25* (10), 1788−1793.

(29) Turpin, B. J.; Huntzicker, J. J. Identification of secondary organic aerosol episodes and quantitation of primary and secondary organic aerosol concentrations during SCAQS. *Atmos. Environ.* **1995**, *29* (23), 3527−3544.

(30) Odum, J. R.; Jungkamp, T. P.; Griffin, R. J.; Flagan, R. C.; Seinfeld, J. H. The Atmospheric Aerosol-Forming Potential of Whole Gasoline Vapor. *Science (Washington, DC, U. S.)* **1997**, *276* (5309), 96−99.

(31) Odum, J. R.; Hoffmann, T.; Bowman, F.; Collins, D.; Flagan, R. C.; Seinfeld, J. H. Gas/Particle Partitioning and Secondary Organic Aerosol Yields. *Environ. Sci. Technol.* **1996**, *30* (8), 2580−2585.

(32) Stern, J. E.; Flagan, R. C.; Grosjean, D.; Seinfeld, J. H. Aerosol formation and growth in atmospheric aromatic hydrocarbon photo-oxidation. *Environ. Sci. Technol.* **1987**, *21* (12), 1224−1231.

(33) Volkamer, R.; Jimenez, J. L.; San Martini, F.; Dzepina, K.; Zhang, Q.; Salcedo, D.; Molina, L. T.; Worsnop, D. R.; Molina, M. J. Secondary organic aerosol formation from anthropogenic air pollution: Rapid and higher than expected. *Geophys. Res. Lett.* **2006**, *33* (17), L17811.

(34) 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.

(35) Grieshop, A. P.; Logue, J. M.; Donahue, N. M.; Robinson, A. L. Laboratory investigation of photochemical oxidation of organic aerosol from wood fires 1: measurement and simulation of organic aerosol evolution. *Atmos. Chem. Phys.* **2009**, *9* (4), 1263−1277.

(36) Hodzic, A.; Jimenez, J. L.; Madronich, S.; Canagaratna, M. R.; DeCarlo, P. F.; Kleinman, L.; Fast, J. Modeling organic aerosols in a megacity: potential contribution of semi-volatile and intermediate volatility primary organic compounds to secondary organic aerosol formation. *Atmos. Chem. Phys.* **2010**, *10* (12), 5491−5514.

(37) Dzepina, K.; Volkamer, R. M.; Madronich, S.; Tulet, P.; Ulbrich, I. M.; Zhang, Q.; Cappa, C. D. Evaluation of recently-proposed secondary organic aerosol models for a case study in Mexico City. *Atmos. Chem. Phys.* **2009**, *1*, 5681−5709.

(38) Ng, N. L.; Kroll, J. H.; Chan, A. W. H.; Chhabra, P. S.; Flagan, R. C.; Seinfeld, J. H. Secondary organic aerosol formation from m-xylene, toluene, and benzene. *Atmos. Chem. Phys.* **2007**, *3*, 3909−3922.

(39) Matsunaga, A.; Ziemann, P. J. Gas-Wall Partitioning of Organic Compounds in a Teflon Film Chamber and Potential Effects on Reaction Product and Aerosol Yield Measurements. *Aerosol Sci. Technol.* **2010**, *44* (10), 881−892.

(40) Zhang, X.; Cappa, C. D.; Jathar, S. H.; McVay, R. C.; Ensberg, J. J.; Kleeman, M. J.; Seinfeld, J. H. Influence of vapor wall loss in laboratory chambers on yields of secondary organic aerosol. *Proc. Natl. Acad. Sci. U. S. A.* **2014**, *111* (16), 5802−5807.

(41) Krechmer, J. E.; Pagonis, D.; Ziemann, P. J.; Jimenez, J. L. Quantification of Gas-Wall Partitioning in Teflon Environmental Chambers Using Rapid Bursts of Low-Volatility Oxidized Species Generated in Situ. *Environ. Sci. Technol.* **2016**, *50* (11), 5757−5765.

(42) 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.; et al. 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.

(43) Bahreini, R.; Middlebrook, A. M.; de Gouw, J. A.; Warneke, C.; Trainer, M.; Brock, C. A.; Stark, H.; Brown, S. S.; Dube, W. P.; Gilman, J. B.; et al. Gasoline emissions dominate over diesel in formation of secondary organic aerosol mass. *Geophys. Res. Lett.* **2012**, *39* (6), L060805.

(44) Hayes, P. L.; Ortega, A. M.; Cubison, M. J.; Froyd, K. D.; Zhao, Y.; Cliff, S. S.; Hu, W. W.; Toohey, D. W.; Flynn, J. H.; Lefer, B. L.; et al. Organic aerosol composition and sources in Pasadena, California, during the 2010 CalNex campaign. *J. Geophys. Res. Atmos.* **2013**, *118*, 9233−9257.

(45) Gordon, T. D.; Presto, A. A.; Nguyen, N. T.; Robertson, W. H.; Na, K.; Sahay, K. N.; Zhang, M.; Maddox, C.; Rieger, P.; Chattopadhyay, S.; et al. Secondary organic aerosol production from diesel vehicle exhaust: impact of aftertreatment, fuel chemistry and driving cycle. *Atmos. Chem. Phys.* **2014**, *14* (9), 4643−4659.

(46) Gordon, T. D.; Presto, A. A.; May, A. A.; Nguyen, N. T.; Lipsky, E. M.; Donahue, N. M.; Gutierrez, A.; Zhang, M.; Maddox, C.; Rieger, P.; et al. Secondary organic aerosol formation exceeds primary particulate matter emissions for light-duty gasoline vehicles. *Atmos. Chem. Phys.* **2014**, *14* (9), 4661−4678.

(47) Platt, S. M.; El Haddad, I.; Zardini, A. A.; Clairotte, M.; Astorga, C.; Wolf, R.; Slowik, J. G.; Temime-Roussel, B.; Marchand, N.; Ježek, I.; et al. Secondary organic aerosol formation from gasoline vehicle emissions in a new mobile environmental reaction chamber. *Atmos. Chem. Phys.* **2013**, *13* (18), 9141−9158.

(48) Nordin, E. Z.; Eriksson, A. C.; Roldin, P.; Nilsson, P. T.; Carlsson, J. E.; Kajos, M. K.; Hellén, H.; Wittbom, C.; Rissler, J.; Löndahl, J.; et al. Secondary organic aerosol formation from idling gasoline passenger vehicle emissions investigated in a smog chamber. *Atmos. Chem. Phys.* **2013**, *13* (12), 6101−6116.

(49) Ensberg, J. J.; Hayes, P. L.; Jimenez, J. L.; Gilman, J. B.; Kuster, W. C.; de Gouw, J. A.; Holloway, J. S.; Gordon, T. D.; Jathar, S.; Robinson, A. L.; et al. Emission factor ratios, SOA mass yields, and the impact of vehicular emissions on SOA formation. *Atmos. Chem. Phys.* **2014**, *14* (5), 2383−2397.

(50) McDonald, B. C.; Goldstein, A. H.; Harley, R. A. Long-term trends in California mobile source emissions and ambient concentrations of black carbon and organic aerosol. *Environ. Sci. Technol.* **2015**, *49* (8), 5178−5188.

(51) de Nevers, N. The Motor Vehicle Problem. In *Air Pollution Control Engineering*, second ed.; Waveland Press, 2010; Chapter 13, pp 471−506.

(52) McDonald, B. C.; Gentner, D. R.; Goldstein, A. H.; Harley, R. A. Long-term trends in motor vehicle emissions in U.S. urban areas. *Environ. Sci. Technol.* **2013**, *47* (17), 10022−10031.

(53) McDonald, B. C.; Dallmann, T. R.; Martin, E. W.; Harley, R. A. Long-term trends in nitrogen oxide emissions from motor vehicles at national, state, and air basin scales. *J. Geophys. Res. Atmos.* **2012**, *117*, D00V18.

(54) Warneke, C.; de Gouw, J. A.; Holloway, J. S.; Peischl, J.; Ryerson, T. B.; Atlas, E.; Blake, D.; Trainer, M.; Parrish, D. D. Multiyear trends in volatile organic compounds in Los Angeles, California: Five decades of decreasing emissions. *J. Geophys. Res. Atmos.* **2012**, *117* (D21), D00V17.

(55) Harley, R. A.; Marr, L. C.; Lehner, J. K.; Giddings, S. N. Changes in Motor Vehicle Emissions on Diurnal to Decadal Time Scales and Effects on Atmospheric Composition. *Environ. Sci. Technol.* **2005**, *39* (14), 5356−5362.

(56) 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.

(57) Bishop, G. A.; Stedman, D. H. A Decade of On-road Emissions Measurements. *Environ. Sci. Technol.* **2008**, *42* (5), 1651−1656.

(58) Nowak, J. B.; Neuman, J. A.; Bahreini, R.; Middlebrook, A. M.; Holloway, J. S.; McKeen, S. A.; Parrish, D. D.; Ryerson, T. B.; Trainer, M. Ammonia sources in the California South Coast Air Basin and their impact on ammonium nitrate formation. *Geophys. Res. Lett.* **2012**, *39*, D00F16.

(59) Kean, A. J. J.; Littlejohn, D.; Ban-Weiss, G. A. A.; Harley, R. A. A.; Kirchstetter, T. W. W.; Lunden, M. M. M. Trends in on-road vehicle emissions of ammonia. *Atmos. Environ.* **2009**, *43* (8), 1565−1570.

(60) Grieshop, A. P.; Lipsky, E. M.; Pekney, N. J.; Takahama, S.; Robinson, A. L. Fine particle emission factors from vehicles in a highway tunnel: Effects of fleet composition and season. *Atmos. Environ.* **2006**, *40*, 287−298.

(61) Kirchstetter, T. W.; Singer, B. C.; Harley, R. A.; Kendall, G. R.; Traverse, M. Impact of California Reformulated Gasoline on Motor Vehicle Emissions. 1. Mass Emission Rates. *Environ. Sci. Technol.* **1999**, *33* (2), 318−328.

(62) Schauer, J. J.; Kleeman, M. J.; Cass, G. R.; Simoneit, B. R. T. Measurement of Emissions from Air Pollution Sources. 5. C1-C32 Organic Compounds from Gasoline-Powered Motor Vehicles. *Environ. Sci. Technol.* **2002**, *36* (6), 1169−1180.

(63) 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.

(64) Ban-Weiss, G. A.; McLaughlin, J. P.; Harley, R. A.; Kean, A. J.; Grosjean, E.; Grosjean, D. Carbonyl and Nitrogen Dioxide Emissions From Gasoline- and Diesel-Powered Motor Vehicles. *Environ. Sci. Technol.* **2008**, *42* (11), 3944−3950.

(65) 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.

(66) Dallmann, T. R.; Harley, R. A.; Kirchstetter, T. W. Effects of diesel particle filter retrofits and accelerated fleet turnover on drayage truck emissions at the Port of Oakland. *Environ. Sci. Technol.* **2011**, *45* (24), 10773−10779.

(67) May, A. A.; Nguyen, N. T.; Presto, A. A.; Gordon, T. D.; Lipsky, E. M.; Karve, M.; Gutierrez, A.; Robertson, W. H.; Zhang, M.; Brandow, C.; et al. Gas- and particle-phase primary emissions from in-use, on-road gasoline and diesel vehicles. *Atmos. Environ.* **2014**, *88*, 247−260.

(68) Kirchstetter, T. W.; Singer, B. C.; Harley, R. A.; Kendall, G. R.; Hesson, J. M. Impact of California Reformulated Gasoline on Motor Vehicle Emissions. 2. Volatile Organic Compound Speciation and Reactivity. *Environ. Sci. Technol.* **1999**, *33* (2), 329−336.

(69) Kirchstetter, T. W.; Singer, B. C.; Harley, R. A.; Kendall, G. R.; Chan, W. Impact of Oxygenated Gasoline Use on California Light-Duty Vehicle Emissions. *Environ. Sci. Technol.* **1996**, *30* (2), 661−670.

(70) Gentner, D. R.; Harley, R. A.; Miller, A. M.; Goldstein, A. H. Diurnal and Seasonal Variability of Gasoline-Related Volatile Organic Compounds in Riverside, CA. *Environ. Sci. Technol.* **2008**, *1*, 78.

(71) European Comission. Directives and Regulations on Motor Vehicles, Their Trailers, Systems and Components. http://ec.europa.eu/growth/sectors/automotive/legislation/motor-vehicles-trailers/index_en.htm (accessed December 2016).

(72) U.S. EPA. Emission Standards Reference Guide for On-Road and Nonroad Vehicles and Engines. https://www.epa.gov/emission-standards-reference-guide (accessed December 2016).

(73) Sanchez, F. P.; Bandivadekar, A.; German, J. *Estimated Cost of Emission Reduction Technologies for LDVs*; International Council on Clean Transportation: Washington, DC, 2012. http://www.theicct.org/estimated-cost-emission-reduction-technologies-ldvs (accessed December 2016).

(74) Posada, F.; Chambliss, S.; Blumberg, K. *Costs of Emission Reduction Technologies for Heavy-Duty Diesel Vehicles*; International Council on Clean Transportation: Washington, DC, 2016. http://www.theicct.org/costs-emission-reduction-tech-hdvs (accessed December 2016)

(75) Worton, D. R.; Isaacman, G.; Gentner, D. R.; Dallmann, T. R.; Chan, A. W. H.; Ruehl, C.; Kirchstetter, T. W.; Wilson, K. R.; Harley, R. A.; Goldstein, A. H. Lubricating Oil Dominates Primary Organic Aerosol Emissions from Motor Vehicles. *Environ. Sci. Technol.* **2014**, *48* (7), 3698−3706.

(76) Canagaratna, M. R.; Jayne, J. T.; Ghertner, D. A.; Herndon, S.; Shi, Q.; Jimenez, J. L.; Silva, P. J.; Williams, P.; Lanni, T.; Drewnick, F.; et al. Chase Studies of Particulate Emissions from in-use New York City Vehicles. *Aerosol Sci. Technol.* **2004**, *38* (6), 555−573.

(77) Sakurai, H.; Tobias, H. J.; Park, K.; Zarling, D.; Docherty, K. S.; Kittelson, D. B.; McMurry, P. H.; Ziemann, P. J. On-line measurements of diesel nanoparticle composition and volatility. *Atmos. Environ.* **2003**, *37* (9−10), 1199−1210.

(78) 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.

(79) Kuwayama, T.; Collier, S.; Forestieri, S.; Brady, J. M.; Bertram, T. H.; Cappa, C. D.; Zhang, Q.; Kleeman, M. J. Volatility of Primary Organic Aerosol Emitted from Light Duty Gasoline Vehicles. *Environ. Sci. Technol.* **2015**, *49* (3), 1569−1577.

(80) 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.

(81) Klaassen, G.; Berglund, C.; Wagner, F. The GAINS Model for Greenhouse Gases, Version 1.0: Carbon Dioxide (CO_2). http://pure.ltu.se/portal/files/588121/IR-05-053.pdf (accessed February 8, 2015).

(82) Parrish, D. D.; Kuster, W. C.; Shao, M.; Yokouchi, Y.; Kondo, Y.; Goldan, P. D.; de Gouw, J. A.; Koike, M.; Shirai, T. Comparison of air pollutant emissions among mega-cities. *Atmos. Environ.* **2009**, *43* (40), 6435−6441.

(83) Gentner, D. R.; Harley, R. A.; Miller, A. M.; Goldstein, A. H. Diurnal and Seasonal Variability of Gasoline-Related Volatile Organic Compound Emissions in Riverside, California. *Environ. Sci. Technol.* **2009**, *43* (12), 4247−4252.

(84) Rubin, J. I.; Kean, A. J.; Harley, R. A.; Millet, D. B.; Goldstein, A. H. Temperature dependence of volatile organic compound evaporative emissions from motor vehicles. *J. Geophys. Res.* **2006**, *111* (D3), D03305.

(85) Larsen, R. K.; Baker, J. E. Source apportionment of polycyclic aromatic hydrocarbons in the urban atmosphere: a comparison of three methods. *Environ. Sci. Technol.* **2003**, *37* (9), 1873−1881.

(86) Dunmore, R. E.; Hopkins, J. R.; Lidster, R. T.; Lee, J. D.; Evans, M. J.; Rickard, A. R.; Lewis, A. C.; Hamilton, J. F. Diesel-related hydrocarbons can dominate gas phase reactive carbon in megacities. *Atmos. Chem. Phys. Discuss.* **2015**, *15* (6), 9541−9571.

(87) Zhao, Y.; Hennigan, C. J.; May, A. A.; Tkacik, D. S.; de Gouw, J. A.; Gilman, J. B.; Kuster, W.; Borbon, A.; Robinson, A. L. Intermediate-volatility organic compounds: a large source of secondary organic aerosol. *Environ. Sci. Technol.* **2014**, *48* (23), 13743−13750.

(88) Platt, S. M.; El Haddad, I.; Pieber, S. M.; Huang, R.-J.; Zardini, A. A.; Clairotte, M.; Suarez-Bertoa, R.; Barmet, P.; Pfaffenberger, L.; Wolf, R.; et al. Two-stroke scooters are a dominant source of air pollution in many cities. *Nat. Commun.* **2014**, *5*, 3749.

(89) George, I. J.; Hays, M. D.; Herrington, J. S.; Preston, W.; Snow, R.; Faircloth, J.; George, B. J.; Long, T.; Baldauf, R. W. Effects of Cold Temperature and Ethanol Content on VOC Emissions from Light-Duty Gasoline Vehicles. *Environ. Sci. Technol.* **2015**, *49* (21), 13067−13074.

(90) Weilenmann, M.; Soltic, P.; Saxer, C.; Forss, A.-M.; Heeb, N. Regulated and nonregulated diesel and gasoline cold start emissions at different temperatures. *Atmos. Environ.* **2005**, *39* (13), 2433−2441.

(91) Weilenmann, M.; Favez, J.-Y.; Alvarez, R. Cold-start emissions of modern passenger cars at different low ambient temperatures and their evolution over vehicle legislation categories. *Atmos. Environ.* **2009**, *43* (15), 2419−2429.

(92) Volckens, J.; Braddock, J.; Snow, R. F.; Crews, W. Emissions profile from new and in-use handheld, 2-stroke engines. *Atmos. Environ.* **2007**, *41* (3), 640−649.

(93) Volckens, J.; Olson, D. A.; Hays, M. D. Carbonaceous species emitted from handheld two-stroke engines. *Atmos. Environ.* **2008**, *42* (6), 1239−1248.

(94) Schauer, J. J.; Rogge, W. F.; Hildemann, L. M.; Mazurek, M. A.; Cass, G. R.; Simoneit, B. R. T. Source apportionment of airborne particulate matter using organic compounds as tracers. *Atmos. Environ.* **1996**, *30* (22), 3837−3855.

(95) Williams, B. J.; Goldstein, A. H.; Kreisberg, N. M.; Hering, S. V.; Worsnop, D. R.; Ulbrich, I. M.; Docherty, K. S.; Jimenez, J. L. Major components of atmospheric organic aerosol in southern California as determined by hourly measurements of source marker compounds. *Atmos. Chem. Phys.* **2010**, *10* (23), 11577−11603.

(96) Tkacik, D. S.; Lambe, A. T.; Jathar, S.; Li, X.; Presto, A. A.; Zhao, Y.; Blake, D.; Meinardi, S.; Jayne, J. T.; Croteau, P. L.; et al. Secondary Organic Aerosol Formation from in-Use Motor Vehicle Emissions Using a Potential Aerosol Mass Reactor. *Environ. Sci. Technol.* **2014**, *48* (19), 11235−11242.

(97) Xu, L.; Guo, H.; Boyd, C. M.; Klein, M.; Bougiatioti, A.; Cerully, K. M.; Hite, J. R.; Isaacman-VanWertz, G.; Kreisberg, N. M.; Knote, C.; et al. Effects of anthropogenic emissions on aerosol formation from isoprene and monoterpenes in the southeastern United States. *Proc. Natl. Acad. Sci. U. S. A.* **2015**, *112* (1), 37−42.

(98) Minguillón, M. C.; Perron, N.; Querol, X.; Szidat, S.; Fahrni, S. M.; Alastuey, A.; Jimenez, J. L.; Mohr, C.; Ortega, A. M.; Day, D. A.; et al. Fossil versus contemporary sources of fine elemental and organic carbonaceous particulate matter during the DAURE campaign in Northeast Spain. *Atmos. Chem. Phys.* **2011**, *11* (23), 12067−12084.

(99) Zotter, P.; El-Haddad, I.; Zhang, Y.; Hayes, P. L.; Zhang, X.; Lin, Y.-H.; Wacker, L.; Schnelle-Kreis, J.; Abbaszade, G.; Zimmermann, R.; et al. Diurnal cycle of fossil and nonfossil carbon using radiocarbon analyses during CalNex. *J. Geophys. Res. Atmos.* **2014**, *119*, 6818−1835.

(100) Huang, R.-J.; Zhang, Y.; Bozzetti, C.; Ho, K.-F.; Cao, J.-J.; Han, Y.; Daellenbach, K. R.; Slowik, J. G.; Platt, S. M.; Canonaco, F.; et al. High secondary aerosol contribution to particulate pollution during haze events in China. *Nature* **2014**, *514* (7521), 218−222.

(101) Beekmann, M.; Prévôt, A. S. H.; Drewnick, F.; Sciare, J.; Pandis, S. N.; Denier van der Gon, H. A. C.; Crippa, M.; Freutel, F.; Poulain, L.; Ghersi, V.; et al. In situ, satellite measurement and model evidence on the dominant regional contribution to fine particulate matter levels in the Paris megacity. *Atmos. Chem. Phys.* **2015**, *15* (16), 9577−9591.

(102) Hasheminassab, S.; Daher, N.; Ostro, B. D.; Sioutas, C. Long-term source apportionment of ambient fine particulate matter (PM2.5) in the Los Angeles Basin: a focus on emissions reduction from vehicular sources. *Environ. Pollut.* **2014**, *193*, 54−64.

(103) Gentner, D. R.; Worton, D. R.; Isaacman, G.; Davis, L. C.; Dallmann, 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* (20), 11837−11848.

(104) 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.

(105) de Gouw, J. A.; Brock, C. A.; Atlas, E. L.; Bates, T. S.; Fehsenfeld, F. C.; Goldan, P. D.; Holloway, J. S.; Kuster, W. C.; Lerner, B. M.; Matthew, B. M.; et al. Sources of particulate matter in the northeastern United States in summer: 1. Direct emissions and secondary formation of organic matter in urban plumes. *J. Geophys. Res.* **2008**, *113* (D8), D08301.

(106) Weitkamp, E. A.; Sage, A. M.; Pierce, J. R.; Donahue, N. M.; Robinson, A. L. Organic aerosol formation from photochemical oxidation of diesel exhaust in a smog chamber. *Environ. Sci. Technol.* **2007**, *41* (20), 6969−6975.

(107) Ortega, A. M.; Hayes, P. L.; Peng, Z.; Palm, B. B.; Hu, W.; Day, D. A.; Li, R.; Cubison, M. J.; Brune, W. H.; Graus, M.; et al. Real-time measurements of secondary organic aerosol formation and aging from ambient air in an oxidation flow reactor in the Los Angeles area. *Atmos. Chem. Phys.* **2016**, *16* (11), 7411−7433.

(108) Liu, S.; Ahlm, L.; Day, D. A.; Russell, L. M.; Zhao, Y.; Gentner, D. R.; Weber, R. J.; Goldstein, A. H.; Jaoui, M.; Offenberg, J. H.; et al. Secondary organic aerosol formation from fossil fuel sources contribute majority of summertime organic mass at Bakersfield. *J. Geophys. Res. Atmos.* **2012**, *117*, D00V26.

(109) Russell, L. M.; Bahadur, R.; Ziemann, P. J. Identifying organic aerosol sources by comparing functional group composition in chamber and atmospheric particles. *Proc. Natl. Acad. Sci. U. S. A.* **2011**, *108* (9), 3516−3521.

(110) Ortega, J.; Helmig, D.; Daly, R. W.; Tanner, D. M.; Guenther, A. B.; Herrick, J. D. Approaches for quantifying reactive and low-volatility biogenic organic compound emissions by vegetation enclosure techniques - part B: applications. *Chemosphere* **2008**, *72* (3), 365−380.

(111) Leppard, W. R.; Rapp, L. A.; Burns, V. R.; Gorse, R. A.; Knepper, J. C.; Koehl, W. J. Effects of Gasoline Composition on Vehicle Engine-Out and Tailpipe Hydrocarbon Emissions - The Auto/Oil Air Quality Improvement Research Program. SAE International Congress & Exposition, February 24, *SAE Tech. Pap. Ser.*1992, No. 920329, 10.4271/920329.

(112) Hunter, J. F.; Carrasquillo, A. J.; Daumit, K. E.; Kroll, J. H. Secondary organic aerosol formation from acyclic, monocyclic, and polycyclic alkanes. *Environ. Sci. Technol.* **2014**, *48* (17), 10227−10234.

(113) Aumont, B.; Camredon, M.; Mouchel-Vallon, C.; La, S.; Ouzebidour, F.; Valorso, R.; Lee-Taylor, J.; Madronich, S. Modeling the influence of alkane molecular structure on secondary organic aerosol formation. *Faraday Discuss.* **2013**, *165*, 105.

(114) 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 NOx. *Environ. Sci. Technol.* **2009**, *43* (7), 2328−2334.

(115) Zhao, Y.; Nguyen, N. T.; Presto, A. A.; Hennigan, C. J.; May, A. A.; Robinson, A. L. Intermediate Volatility Organic Compound Emissions from On-Road Diesel Vehicles: Chemical Composition,

Emission Factors, and Estimated Secondary Organic Aerosol Production. *Environ. Sci. Technol.* **2015**, *49* (19), 11516−11526.

(116) Zhao, Y.; Nguyen, N. T.; Presto, A. A.; Hennigan, C. J.; May, A. A.; Robinson, A. L. Intermediate Volatility Organic Compound Emissions from On-road Gasoline Vehicles and Small Off-road Gasoline Engines. *Environ. Sci. Technol.* **2016**, *50* (8), 4554−4563.

(117) Atkinson, R.; Arey, J. Gas-phase tropospheric chemistry of biogenic volatile organic compounds: a review. *Atmos. Environ.* **2003**, *37* (2), 197−219.

(118) Volkamer, R.; Ziemann, P. J.; Molina, M. J. Secondary Organic Aerosol Formation from Acetylene (C_2H_2): seed effect on SOA yields due to organic photochemistry in the aerosol aqueous phase. *Atmos. Chem. Phys.* **2009**, *9* (6), 1907−1928.

(119) Jathar, S. H.; Gordon, T. D.; Hennigan, C. J.; Pye, H. O. T.; Pouliot, G.; Adams, P. J.; Donahue, N. M.; Robinson, A. L. Unspeciated organic emissions from combustion sources and their influence on the secondary organic aerosol budget in the United States. *Proc. Natl. Acad. Sci. U. S. A.* **2014**, *111* (29), 10473−10478.

(120) Miracolo, M. a; Presto, A. a; Lambe, A. T.; Hennigan, C. J.; Donahue, N. M.; Kroll, J. H.; Worsnop, D. R.; Robinson, A. L. Photo-oxidation of low-volatility organics found in motor vehicle emissions: production and chemical evolution of organic aerosol mass. *Environ. Sci. Technol.* **2010**, *44* (5), 1638−1643.

(121) Miracolo, M. A.; Presto, A. A.; Lambe, A. T.; Hennigan, C. J.; Donahue, N. M.; Kroll, J. H.; Worsnop, D. R.; Robinson, A. L. Photo-oxidation of low-volatility organics found in motor vehicle emissions: production and chemical evolution of organic aerosol mass. *Environ. Sci. Technol.* **2010**, *44* (5), 1638−1643.

(122) Liu, T.; Wang, X.; Deng, W.; Hu, Q.; Ding, X.; Zhang, Y.; He, Q.; Zhang, Z.; Lü, S.; Bi, X.; et al. Secondary organic aerosol formation from photochemical aging of light-duty gasoline vehicle exhausts in a smog chamber. *Atmos. Chem. Phys.* **2015**, *15* (15), 9049−9062.

(123) Chirico, R.; DeCarlo, P. F.; Heringa, M. F.; Tritscher, T.; Richter, R.; Prevot, A. S. H.; Dommen, J.; Weingartner, E.; Wehrle, G.; Gysel, M.; Laborde, M.; Baltensperger, U. mpact of aftertreatment devices on primary emissions and secondary organic aerosol formation potential from in-use diesel vehicles: results from smog chamber experiments. *Atmos. Chem. Phys.* **2010**, *10* (23), 11545−11563.

(124) Gordon, T. D.; Tkacik, D. S.; Presto, A. A.; Zhang, M.; Jathar, S. H.; Nguyen, N. T.; Massetti, J.; Truong, T.; Cicero-Fernandez, P.; Maddox, C.; et al. Primary Gas- and Particle-Phase Emissions and Secondary Organic Aerosol Production from Gasoline and Diesel Off-Road Engines. *Environ. Sci. Technol.* **2013**, *47* (24), 14137−14146.

(125) Zardini, A. A.; Platt, S. M.; Clairotte, M.; El Haddad, I.; Temime-Roussel, B.; Marchand, N.; Ježek, I.; Drinovec, L.; Močnik, G.; Slowik, J. G.; et al. Effects of alkylate fuel on exhaust emissions and secondary aerosol formation of a 2-stroke and a 4-stroke scooter. *Atmos. Environ.* **2014**, *94*, 307−315.

(126) Miracolo, M. A.; Drozd, G. T.; Jathar, S. H.; Presto, A. A.; Lipsky, E. M.; Corporan, E.; Robinson, A. L. Fuel composition and secondary organic aerosol formation: gas-turbine exhaust and alternative aviation fuels. *Environ. Sci. Technol.* **2012**, *46* (15), 8493−8501.

(127) Miracolo, M. A.; Hennigan, C. J.; Ranjan, M.; Nguyen, N. T.; Gordon, T. D.; Lipsky, E. M.; Presto, A. A.; Donahue, N. M.; Robinson, A. L. Secondary aerosol formation from photochemical aging of aircraft exhaust in a smog chamber. *Atmos. Chem. Phys.* **2011**, *11* (9), 4135−4147.

(128) de Gouw, J. A. Budget of organic carbon in a polluted atmosphere: Results from the New England Air Quality Study in 2002. *J. Geophys. Res.* **2005**, *110* (D16), D16305.

(129) Bishop, G. A.; Schuchmann, B. G.; Stedman, D. H.; Lawson, D. R. Multispecies remote sensing measurements of vehicle emissions on Sherman Way in Van Nuys, California. *J. Air Waste Manage. Assoc.* **2012**, *62* (10), 1127−1133.

(130) Park, S. S.; Kozawa, K.; Fruin, S.; Mara, S.; Hsu, Y.-K.; Jakober, C.; Winer, A.; Herner, J. Emission Factors for High-Emitting Vehicles Based on On-Road Measurements of Individual Vehicle Exhaust with a Mobile Measurement Platform. *J. Air Waste Manage. Assoc.* **2011**, *61*, 1046−1056.

(131) Beaton, S. P.; Bishop, G. A.; Zhang, Y.; Stedman, D. H.; Ashbaugh, L. L.; Lawson, D. R. On-road vehicle emissions: regulations, costs, and benefits. *Science* **1995**, *268* (5213), 991−993.

(132) Kleindienst, T. E.; Jaoui, M.; Lewandowski, M.; Offenberg, J. H.; Lewis, C. W.; Bhave, P. V.; Edney, E. O. Estimates of the contributions of biogenic and anthropogenic hydrocarbons to secondary organic aerosol at a southeastern US location. *Atmos. Environ.* **2007**, *41* (37), 8288−8300.

(133) Lough, G. C.; Christensen, C. G.; Schauer, J. J.; Tortorelli, J.; Mani, E.; Lawson, D. R.; Clark, N. N.; Gabele, P. A. Development of Molecular Marker Source Profiles for Emissions from On-Road Gasoline and Diesel Vehicle Fleets. *J. Air Waste Manage. Assoc.* **2007**, *57* (10), 1190−1199.

(134) Stone, E. A.; Zhou, J.; Snyder, D. C.; Rutter, A. P.; Mieritz, M.; Schauer, J. J. A Comparison of Summertime Secondary Organic Aerosol Source Contributions at Contrasting Urban Locations. *Environ. Sci. Technol.* **2009**, *43* (10), 3448−3454.

(135) Canagaratna, M. R.; Jayne, J. T.; Jimenez, J. L.; Allan, J. D.; Alfarra, M. R.; Zhang, Q.; Onasch, T. B.; Drewnick, F.; Coe, H.; Middlebrook, A.; et al. Chemical and microphysical characterization of ambient aerosols with the aerodyne aerosol mass spectrometer. *Mass Spectrom. Rev.* **2007**, *26* (2), 185−222.

(136) Ng, N. L.; Canagaratna, M. R.; Zhang, Q.; Jimenez, J. L.; Tian, J.; Ulbrich, I. M.; Kroll, J. H.; Docherty, K. S.; Chhabra, P. S.; Bahreini, R.; et al. Organic aerosol components observed in Northern Hemispheric datasets from Aerosol Mass Spectrometry. *Atmos. Chem. Phys.* **2010**, *10* (10), 4625−4641.

(137) Docherty, K. S.; Stone, E. A.; Ulbrich, I. M.; DeCarlo, P. F.; Snyder, D. C.; Schauer, J. J.; Peltier, R. E.; Weber, R. J.; Murphy, S. M.; Seinfeld, J. H.; et al. Apportionment of Primary and Secondary Organic Aerosols in Southern California during the 2005 Study of Organic Aerosols in Riverside (SOAR-1). *Environ. Sci. Technol.* **2008**, *42* (20), 7655−7662.

(138) Rutter, A. P.; Snyder, D. C.; Stone, E. A.; Shelton, B.; DeMinter, J.; Schauer, J. J. Preliminary assessment of the anthropogenic and biogenic contributions to secondary organic aerosols at two industrial cities in the upper Midwest. *Atmos. Environ.* **2014**, *84*, 307−313.

(139) Lewandowski, M.; Piletic, I. R.; Kleindienst, T. E.; Offenberg, J. H.; Beaver, M. R.; Jaoui, M.; Docherty, K. S.; Edney, E. O. Secondary organic aerosol characterisation at field sites across the United States during the spring−summer period. *Int. J. Environ. Anal. Chem.* **2013**, *93* (10), 1084−1103.

(140) Baker, K. R.; Carlton, A. G.; Kleindienst, T. E.; Offenberg, J. H.; Beaver, M. R.; Gentner, D. R.; Goldstein, A. H.; Hayes, P. L.; Jimenez, J. L.; Gilman, J. B.; et al. Gas and aerosol carbon in California: comparison of measurements and model predictions in Pasadena and Bakersfield. *Atmos. Chem. Phys.* **2015**, *15* (9), 5243−5258.

(141) Nah, T.; Zhang, H.; Worton, D. R.; Ruehl, C. R.; Kirk, B. B.; Goldstein, A. H.; Leone, S. R.; Wilson, K. R. Isomeric Product Detection in the Heterogeneous Reaction of Hydroxyl Radicals with Aerosol Composed of Branched and Linear Unsaturated Organic Molecules. *J. Phys. Chem. A* **2014**, *118* (49), 11555−11571.

(142) Ruehl, C. R.; Nah, T.; Isaacman, G.; Worton, D. R.; Chan, A. W. H.; Kolesar, K. R.; Cappa, C. D.; Goldstein, A. H.; Wilson, K. R. The Influence of Molecular Structure and Aerosol Phase on the Heterogeneous Oxidation of Normal and Branched Alkanes by OH. *J. Phys. Chem. A* **2013**, *117* (19), 3990−4000.

(143) Schilling Fahnestock, K. A.; Yee, L. D.; Loza, C. L.; Coggon, M. M.; Schwantes, R.; Zhang, X.; Dalleska, N. F.; Seinfeld, J. H. Secondary Organic Aerosol Composition from C12 Alkanes. *J. Phys. Chem. A* **2015**, *119* (19), 4281−4297.

(144) Gilardoni, S.; Russell, L. M.; Sorooshian, A.; Flagan, R. C.; Seinfeld, J. H.; Bates, T. S.; Quinn, P. K.; Allan, J. D.; Williams, B.; Goldstein, A. H.; et al. Regional variation of organic functional groups in aerosol particles on four U.S. east coast platforms during the International Consortium for Atmospheric Research on Transport and

Transformation 2004 campaign. *J. Geophys. Res.* **2007**, *112* (D10), D10S27.

(145) Maria, S. F.; Russell, L. M.; Turpin, B. J.; Porcja, R. J. FTIR measurements of functional groups and organic mass in aerosol samples over the Caribbean. *Atmos. Environ.* **2002**, *36* (33), 5185–5196.

(146) Guzman-Morales, J.; Frossard, A. A.; Corrigan, A. L.; Russell, L. M.; Liu, S.; Takahama, S.; Taylor, J. W.; Allan, J.; Coe, H.; Zhao, Y.; et al. Estimated contributions of primary and secondary organic aerosol from fossil fuel combustion during the CalNex and Cal-Mex campaigns. *Atmos. Environ.* **2014**, *88*, 330–340.

(147) Hu, W. W.; Campuzano-Jost, P.; Palm, B. B.; Day, D. A.; Ortega, A. M.; Hayes, P. L.; Krechmer, J. E.; Chen, Q.; Kuwata, M.; Liu, Y. J.; et al. Characterization of a real-time tracer for isoprene epoxydiols-derived secondary organic aerosol (IEPOX-SOA) from aerosol mass spectrometer measurements. *Atmos. Chem. Phys.* **2015**, *15* (20), 11807–11833.

(148) Williams, B. J.; Zhang, Y.; Zuo, X.; Martinez, R. E.; Walker, M. J.; Kreisberg, N. M.; Goldstein, A. H.; Docherty, K. S.; Jimenez, J. L. Organic and inorganic decomposition products from the thermal desorption of atmospheric particles. *Atmos. Meas. Tech.* **2016**, *9* (4), 1569–1586.

(149) Goldstein, A. H.; Worton, D. R.; Williams, B. J.; Hering, S. V.; Kreisberg, N. M.; Panić, O.; Górecki, T. Thermal desorption comprehensive two-dimensional gas chromatography for in-situ measurements of organic aerosols. *J. Chromatogr. A* **2008**, *1186* (1–2), 340–347.

(150) Worton, D. R.; Kreisberg, N. M.; Isaacman, G.; Teng, A. P.; McNeish, C.; Górecki, T.; Hering, S. V.; Goldstein, A. H. Thermal Desorption Comprehensive Two-Dimensional Gas Chromatography: An Improved Instrument for In-Situ Speciated Measurements of Organic Aerosols. *Aerosol Sci. Technol.* **2012**, *46*, 380–393.

(151) Lopez-Hilfiker, F. D.; Mohr, C.; Ehn, M.; Rubach, F.; Kleist, E.; Wildt, J.; Mentel, T. F.; Lutz, A.; Hallquist, M.; Worsnop, D.; et al. A novel method for online analysis of gas and particle composition: description and evaluation of a Filter Inlet for Gases and AEROsols (FIGAERO). *Atmos. Meas. Tech.* **2014**, *7* (4), 983–1001.

(152) Marr, L. C.; Harley, R. A. Spectral analysis of weekday–weekend differences in ambient ozone, nitrogen oxide, and non-methane hydrocarbon time series in California. *Atmos. Environ.* **2002**, *36* (14), 2327–2335.

(153) Pollack, I. B.; Ryerson, T. B.; Trainer, M.; Parrish, D. D.; Andrews, A. E.; Atlas, E. L.; Blake, D. R.; Brown, S. S.; Commane, R.; Daube, B. C.; et al. Airborne and ground-based observations of a weekend effect in ozone, precursors, and oxidation products in the California South Coast Air Basin. *J. Geophys. Res. Atmos.* **2012**, *117*, D00V05.

(154) Ahmadov, R.; McKeen, S. A.; Robinson, A. L.; Bahreini, R.; Middlebrook, A. M.; de Gouw, J. A.; Meagher, J.; Hsie, E.-Y.; Edgerton, E.; Shaw, S.; Trainer, M. A volatility basis set model for summertime secondary organic aerosols over the eastern United States in 2006. *J. Geophys. Res.* **2012**, *117* (D6), D06301.

(155) Warneke, C.; de Gouw, J. A.; Edwards, P. M.; Holloway, J. S.; Gilman, J. B.; Kuster, W. C.; Graus, M.; Atlas, E.; Blake, D.; Gentner, D. R.; et al. Photochemical aging of volatile organic compounds in the Los Angeles basin: Weekday-weekend effect. *J. Geophys. Res. Atmos.* **2013**, *118* (10), 5018–5028.

(156) Marr, L.; Harley, R. Modeling the effect of weekday-weekend differences in motor vehicle emissions on photochemical air pollution in central California. *Environ. Sci. Technol.* **2002**, *36* (19), 4099–4106.

(157) Murphy, J. G.; Day, D. A.; Cleary, P. A.; Wooldridge, P. J.; Cohen, R. C. Observations of the diurnal and seasonal trends in nitrogen oxides in the western Sierra Nevada. *Atmos. Chem. Phys.* **2006**, *6* (12), 5321–5338.

(158) Roberts, J. M.; Fehsenfeld, F. C.; Liu, S. C.; Bollinger, M. J.; Hahn, C.; Albritton, D. L.; Sievers, R. E. Measurements of aromatic hydrocarbon ratios and NOx concentrations in the rural troposphere: Observation of air mass photochemical aging and NOx removal. *Atmos. Environ.* **1984**, *18* (11), 2421–2432.

(159) Crippa, M.; DeCarlo, P. F.; Slowik, J. G.; Mohr, C.; Heringa, M. F.; Chirico, R.; Poulain, L.; Freutel, F.; Sciare, J.; Cozic, J.; et al. Wintertime aerosol chemical composition and source apportionment of the organic fraction in the metropolitan area of Paris. *Atmos. Chem. Phys.* **2013**, *13* (2), 961–981.

(160) Mohr, C.; DeCarlo, P. F.; Heringa, M. F.; Chirico, R.; Slowik, J. G.; Richter, R.; Reche, C.; Alastuey, A.; Querol, X.; Seco, R.; et al. Identification and quantification of organic aerosol from cooking and other sources in Barcelona using aerosol mass spectrometer data. *Atmos. Chem. Phys.* **2012**, *12* (4), 1649–1665.

(161) Borbon, A.; Gilman, J. B.; Kuster, W. C.; Grand, N.; Chevaillier, S.; Colomb, A.; Dolgorouky, C.; Gros, V.; Lopez, M.; Sarda-Esteve, R.; et al. Emission ratios of anthropogenic volatile organic compounds in northern mid-latitude megacities: Observations versus emission inventories in Los Angeles and Paris. *J. Geophys. Res. Atmos.* **2013**, *118* (4), 2041–2057.

(162) Peischl, J.; Ryerson, T. B.; Brioude, J.; Aikin, K. C.; Andrews, A. E.; Atlas, E.; Blake, D.; Daube, B. C.; de Gouw, J. A.; Dlugokencky, E.; et al. Quantifying sources of methane using light alkanes in the Los Angeles basin, California. *J. Geophys. Res. Atmos.* **2013**, *118* (10), 4974–4990.

(163) Baidar, S.; Hardesty, R. M.; Kim, S.; Langford, A. O.; Oetjen, H.; Senff, C. J.; Trainer, M.; Volkamer, R. Weakening of the weekend ozone effect over California's South Coast Air Basin. *Geophys. Res. Lett.* **2015**, *42*, 9457–9464.

(164) Griffith, S. M.; Hansen, R. F.; Dusanter, S.; Michoud, V.; Gilman, J. B.; Kuster, W. C.; Veres, P. R.; Graus, M.; de Gouw, J. A.; Roberts, J.; et al. Measurements of hydroxyl and hydroperoxy radicals during CalNex-LA: Model comparisons and radical budgets. *J. Geophys. Res. Atmos.* **2016**, *121* (8), 4211–4232.

(165) Szidat, S.; Bench, G.; Bernardoni, V.; Calzolai, G.; Czimczik, C.; Derendorp, L.; Dusek, U.; Elder, K.; Fedi, M.; Genberg, J. Intercomparison of 14C Analysis of Carbonaceous Aerosols: Exercise 2009. *Radiocarbon* **2013**, *55* (3–4), na DOI: 10.2458/azu_js_rc.55.16314.

(166) California Air Resources Board. EMFAC2014 Web Database (v1.0.7), 2014. http://www.arb.ca.gov/emfac/2014/ (accessed December 2016).

(167) Jathar, S. H.; Gordon, T. D.; Hennigan, C. J.; Pye, H. O. T.; Pouliot, G.; Adams, P. J.; Donahue, N. M.; Robinson, A. L. Unspeciated organic emissions from combustion sources and their influence on the secondary organic aerosol budget in the United States. *Proc. Natl. Acad. Sci. U. S. A.* **2014**, *111* (29), 10473–10478.

(168) Cross, E. S.; Sappok, A. G.; Wong, V. W.; Kroll, J. H. Load-Dependent Emission Factors and Chemical Characteristics of IVOCs from a Medium-Duty Diesel Engine. *Environ. Sci. Technol.* **2015**, *49* (22), 13483–13491.

(169) Washenfelder, R. A.; Young, C. J.; Brown, S. S.; Angevine, W. M.; Atlas, E. L.; Blake, D. R.; Bon, D. M.; Cubison, M. J.; de Gouw, J. A.; Dusanter, S.; et al. The glyoxal budget and its contribution to organic aerosol for Los Angeles, California, during CalNex 2010. *J. Geophys. Res. Atmos.* **2011**, *116*, D00V02.

(170) Dzepina, K.; Volkamer, R. M.; Madronich, S.; Tulet, P.; Ulbrich, I. M.; Zhang, Q.; Cappa, C. D.; Ziemann, P. J.; Jimenez, J. L. Evaluation of recently-proposed secondary organic aerosol models for a case study in Mexico City. *Atmos. Chem. Phys.* **2009**, *9* (15), 5681–5709.

(171) Pieber, S. M.; El Haddad, I.; Slowik, J. G.; Canagaratna, M. R.; Jayne, J. T.; Platt, S. M.; Bozzetti, C.; Daellenbach, K. R.; Fröhlich, R.; Vlachou, A.; et al. Inorganic Salt Interference on CO_2^+ in Aerodyne AMS and ACSM Organic Aerosol Composition Studies. *Environ. Sci. Technol.* **2016**, *50* (19), 10494–10503.

(172) Borillo, G. C.; Tadano, Y. S.; Godoi, A. F. L.; Santana, S. S. M.; Weronka, F. M.; Penteado Neto, R. A.; Rempel, D.; Yamamoto, C. I.; Potgieter-Vermaak, S.; Potgieter, J. H.; et al. Effectiveness of selective catalytic reduction systems on reducing gaseous emissions from an engine using diesel and biodiesel blends. *Environ. Sci. Technol.* **2015**, *49* (5), 3246–3251.

(173) Sun, K.; Tao, L.; Miller, D. J.; Khan, M. A.; Zondlo, M. A. On-road ammonia emissions characterized by mobile, open-path measurements. *Environ. Sci. Technol.* **2014**, *48* (7), 3943−3950.

(174) *China V − Gasoline and Diesel Fuel Quality Standards*; International Council on Clean Transportation: Washington, DC, 2014. http://www.theicct.org/sites/default/files/publications/ICCTupdate_ChinaVfuelquality_jan2014.pdf (accessed December 2016).

(175) *Technical Background on India BS VI Fuel Specifications*; International Council on Clean Transportation: Washington, DC, 2016. http://www.theicct.org/technical-background-india-BS-VI-fuel-specifications (accessed December 2016).

(176) Miller, J. D.; Facanha, C. *The State of Clean Transport Policy − A 2014 Synthesis of Vehicle and Fuel Policy Developments*; International Council on Clean Transportation: Washington, DC, 2014. http://www.theicct.org/sites/default/files/publications/ICCT_StateOfCleanTransportPolicy_2014.pdf (accessed December 2016).

(177) Herner, J. D.; Hu, S.; Robertson, W. H.; Huai, T.; Chang, M.-C. O.; Rieger, P.; Ayala, A. Effect of Advanced Aftertreatment for PM and NOx Reduction on Heavy-Duty Diesel Engine Ultrafine Particle Emissions. *Environ. Sci. Technol.* **2011**, *45* (6), 2413−2419.

(178) Herner, J. D.; Hu, S.; Robertson, W. H.; Huai, T.; Collins, J. F.; Dwyer, H.; Ayala, A. Effect of Advanced Aftertreatment for PM and NOx Control on Heavy-Duty Diesel Truck Emissions. *Environ. Sci. Technol.* **2009**, *43* (15), 5928−5933.

(179) Ma, H.; Jung, H.; Kittelson, D. B. Investigation of Diesel Nanoparticle Nucleation Mechanisms. *Aerosol Sci. Technol.* **2008**, *42* (5), 335−342.

(180) Bertram, T. H.; Kimmel, J. R.; Crisp, T. A.; Ryder, O. S.; Yatavelli, R. L. N.; Thornton, J. A.; Cubison, M. J.; Gonin, M.; Worsnop, D. R. A field-deployable, chemical ionization time-of-flight mass spectrometer. *Atmos. Meas. Tech.* **2011**, *4* (7), 1471−1479.

(181) Yatavelli, R. L. N.; Lopez-Hilfiker, F.; Wargo, J. D.; Kimmel, J. R.; Cubison, M. J.; Bertram, T. H.; Jimenez, J. L.; Gonin, M.; Worsnop, D. R.; Thornton, J. A. A chemical ionization high-resolution time-of-flight mass spectrometer Coupled to a micro orifice volatilization impactor (MOVI-HRToF-CIMS) for analysis of gas and particle-phase organic species. *Aerosol Sci. Technol.* **2012**, *46* (12), 1313−1327.

(182) U.S. Energy Information Administration. Monthly Energy Review, May 2016.

(183) Atabani, A. E.; Silitonga, A. S.; Badruddin, I. A.; Mahlia, T. M. I.; Masjuki, H. H.; Mekhilef, S. A comprehensive review on biodiesel as an alternative energy resource and its characteristics. *Renewable Sustainable Energy Rev.* **2012**, *16* (4), 2070−2093.

(184) Suarez-Bertoa, R.; Zardini, A. A.; Platt, S. M.; Hellebust, S.; Pieber, S. M.; El Haddad, I.; Temime-Roussel, B.; Baltensperger, U.; Marchand, N.; Prévôt, A. S. H.; et al. Primary emissions and secondary organic aerosol formation from the exhaust of a flex-fuel (ethanol) vehicle. *Atmos. Environ.* **2015**, *117*, 200−211.

(185) Karjalainen, P.; Timonen, H.; Saukko, E.; Kuuluvainen, H.; Saarikoski, S.; Aakko-Saksa, P.; Murtonen, T.; Bloss, M.; Dal Maso, M.; Simonen, P.; et al. Time-resolved characterization of primary particle emissions and secondary particle formation from a modern gasoline passenger car. *Atmos. Chem. Phys.* **2016**, *16* (13), 8559−8570.

(186) Peng, Z.; Day, D. A.; Stark, H.; Li, R.; Lee-Taylor, J.; Palm, B. B.; Brune, W. H.; Jimenez, J. L. HOx radical chemistry in oxidation flow reactors with low-pressure mercury lamps systematically examined by modeling. *Atmos. Meas. Tech.* **2015**, *8* (11), 4863−4890.

(187) Ehn, M.; Thornton, J. A.; Kleist, E.; Sipilä, M.; Junninen, H.; Pullinen, I.; Springer, M.; Rubach, F.; Tillmann, R.; Lee, B.; et al. A large source of low-volatility secondary organic aerosol. *Nature* **2014**, *506* (7489), 476−479.

(188) Crounse, J. D.; Nielsen, L. B.; Jørgensen, S.; Kjaergaard, H. G.; Wennberg, P. O. Autoxidation of Organic Compounds in the Atmosphere. *J. Phys. Chem. Lett.* **2013**, *4* (20), 3513−3520.

(189) Master Chemical Mechanism, MCM v3.2. http://mcm.leeds.ac.uk/MCM (accessed December 2016).

(190) Lee-Taylor, J.; Madronich, S.; Aumont, B.; Baker, A.; Camredon, M.; Hodzic, A.; Tyndall, G. S.; Apel, E.; Zaveri, R. A. Explicit modeling of organic chemistry and secondary organic aerosol partitioning for Mexico City and its outflow plume. *Atmos. Chem. Phys.* **2011**, *11* (24), 13219−13241.

(191) Kishan, S.; Burnette, A.; Fincher, S.; Sabisch, M.; Crews, W.; Snow, R.; Zmud, M.; Santos, R.; Bricka, S.; Fujita, E.; et al. *Kansas City PM Characterization Study Final Report*; Report No. EPA420-R-08e009; U.S EPA: Washington, DC, 2008.

(192) Kirchstetter, T. W.; Singer, B. C.; Harley, R. A.; Kendall, G. R.; Hesson, J. M. Impact of California reformulated gasoline on motor vehicle emissions. 2. Volatile organic compound speciation and reactivity. *Environ. Sci. Technol.* **1999**, *33* (2), 329−336.

(193) Hesterberg, T. W.; Lapin, C. A.; Bunn, W. B. A Comparison of Emissions from Vehicles Fueled with Diesel or Compressed Natural Gas. *Environ. Sci. Technol.* **2008**, *42* (17), 6437−6445.

(194) Dardiotis, C.; Martini, G.; Marotta, A.; Manfredi, U. Low-temperature cold-start gaseous emissions of late technology passenger cars. *Appl. Energy* **2013**, *111*, 468−478.

(195) Clairotte, M.; Adam, T. W.; Zardini, A. A.; Manfredi, U.; Martini, G.; Krasenbrink, A.; Vicet, A.; Tournié, E.; Astorga, C. Effects of low temperature on the cold start gaseous emissions from light duty vehicles fuelled by ethanol-blended gasoline. *Appl. Energy* **2013**, *102*, 44−54.

(196) El Haddad, I.; D'Anna, B.; Temime-Roussel, B.; Nicolas, M.; Boreave, A.; Favez, O.; Voisin, D.; Sciare, J.; George, C.; Jaffrezo, J.-L.; et al. Towards a better understanding of the origins, chemical composition and aging of oxygenated organic aerosols: case study of a Mediterranean industrialized environment, Marseille. *Atmos. Chem. Phys.* **2013**, *13* (15), 7875−7894.

(197) 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* (23), 13873−13881.