Long-Term Trends in California Mobile Source Emissions and Ambient Concentrations of Black Carbon and Organic Aerosol

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Ⓢ Supporting Information

ABSTRACT: A fuel-based approach is used to assess long-term trends (1970−2010) in mobile source emissions of black carbon (BC) and organic aerosol (OA, including both primary emissions and secondary formation). The main focus of this analysis is the Los Angeles Basin, where a long record of measurements is available to infer trends in ambient concentrations of BC and organic carbon (OC), with OC used here as a proxy for OA. Mobile source emissions and ambient concentrations have decreased similarly, reflecting the importance of on- and off-road engines as sources of BC and OA in urban areas. In 1970, the on-road sector accounted for ~90% of total mobile source emissions of BC and OA (primary + secondary). Over time, as on-road engine emissions have been controlled, the relative importance of off-road sources has grown. By 2010, off-road engines were estimated to account for $37 \pm 20\%$ and $45 \pm 16\%$ of total mobile source contributions to BC and OA, respectively, in the Los Angeles area. This study highlights both the success of efforts to control on-road emission sources, and the importance of considering off-road engine and other VOC source contributions when assessing long-term emission and ambient air quality trends.
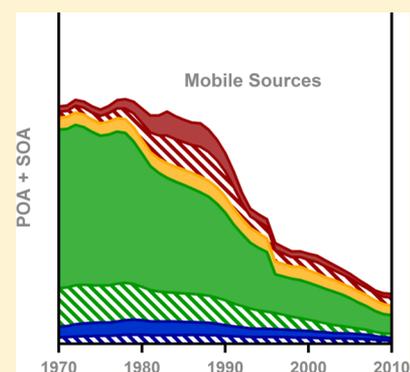
INTRODUCTION

Two major constituents of airborne fine particulate matter are black carbon (BC) and organic aerosol (OA). Bond et al.[1] report BC as the second largest contributor to anthropogenic climate forcing after carbon dioxide globally. In North America, the two largest sources of BC are on-road and off-road diesel engines, which together accounted for about half of total BC emissions in the year 2000.[1] Because BC is abundant in diesel particulate matter emissions,[2] BC is sometimes used as a tracer for diesel sources.[3] BC present in diesel exhaust provides solid particle surface area upon which other compounds may condense or adsorb, including volatile, semivolatile, and low-volatility organics.[4] Diesel exhaust has been classified as a known human carcinogen by the International Agency for Research on Cancer. Short-term exposure to diesel exhaust has been associated with impaired vascular function.[5−7]

OA has been found to comprise a major fraction of submicrometer airborne particle mass at urban and rural/remote measurement sites around the world.[8,9] OA exerts a negative radiative forcing that affects global climate.[10] Unlike BC, which is emitted directly from sources into the atmosphere,

OA arises due to both direct emissions of primary organic aerosol (POA) as well as in situ atmospheric formation of secondary organic aerosol (SOA) from volatile or semivolatile organic precursors. Many of these organics can be oxidized in the atmosphere to form condensable low-volatility products.[9,11]

Over time, there has been increasing recognition of the importance of SOA relative to POA. High relative abundances of SOA were reported in the Los Angeles area as early as 1973,[12] and SOA is thought to be especially dominant during summertime air pollution episodes.[13−15] Other studies have found POA to dominate over SOA during less polluted time periods[15,16] and during wintertime.[17] Recent studies[8,9,18−20] have generally concluded that SOA is the dominant contributor, responsible for about two-thirds of submicrometer OA mass in urban areas around the world, and for even higher fractions of OA in downwind/remote locations.

Another area of debate has been the relative importance of gasoline versus diesel engine sources of POA emissions. Schauer et al.[16] found diesel exhaust emissions dominated the on-road contribution to POA in Los Angeles, whereas Watson et al.[21] concluded the opposite was true in Denver. There is further debate as to the relative importance of volatile organic compound (VOC) emissions from gasoline versus diesel engines as precursors to formation of anthropogenic SOA.[22,23] Gentner et al.[23] estimate that the fraction of VOC emissions converted to SOA from diesel fuel-related emissions is about 7 times greater than for gasoline engines, and found that diesel engines are the dominant source of vehicular SOA in Los Angeles. In contrast, Bahreini et al.[22] found that gasoline vehicles dominated SOA formation in Los Angeles during the Calnex field study in 2010. Recent laboratory measurements suggest that SOA production from passenger vehicle exhaust VOC emissions is higher than aerosol yields calculated based on the composition of unburned gasoline.[24,25] Major questions also remain about whether SOA formation from VOC emitted by motor vehicles and other sources have been underestimated in smog chamber studies as compared to real atmospheric conditions.[26,27]

The objectives of this study are to describe long-term trends in (1) ambient BC and organic carbon (OC) concentrations, and (2) mobile source emissions relevant to the abundances of primary and secondary carbonaceous aerosols. Mobile sources include on-road and off-road engines, both gasoline and diesel powered. Emissions and ambient trends are compared to reconcile observed changes in atmospheric concentrations with long-term emission trends. The present study examines the historical record of ambient BC and OC concentrations for the Los Angeles area, using data from both special field studies and routine monitoring, spanning a time period of more than 4 decades. A complementary analysis of long-term trends in emissions and ambient concentrations of BC is also presented for the San Francisco Bay Area. A national ambient air quality standard for fine particulate matter ($PM_{2.5}$) was first established in the U.S. in 1997, and the resulting record of ambient air monitoring data is still relatively short (~15 years). Other studies reporting long-term trends in carbonaceous aerosols[28−31] have typically focused on BC, though some studies also include trends for OC.[32]

■ MATERIALS AND METHODS

Fuel Sales Data. We use taxable sales of gasoline and diesel fuel as measures of passenger vehicle and diesel truck activity, respectively. In the U.S., on-road consumption of diesel fuel occurs primarily in the engines of medium- and heavy-duty trucks rather than in passenger vehicles. Diesel fuel sales for use in off-road engines are exempt from excise taxes and are tracked separately from fuel sales for on-road engines. For the period from 1990 to 2010, we use available estimates of on-road gasoline and diesel fuel consumption for the Los Angeles Basin reported by McDonald et al.,[33] and apply the same approach to estimate fuel consumption in the San Francisco Bay Area. To extend gasoline and diesel engine emission trends further back in time (Figure 1), ratios of fuel sales in earlier years relative to 1990 were estimated from state-level fuel sales reports.[34] These ratios were then used to extrapolate back in time based on gasoline and diesel fuel use as of 1990 for the two air basins of interest here (Tables S1 and S2, Supporting Information).

Separate estimates of fuel use by off-road diesel engines are also shown in Figure 1. Off-road uses of diesel fuel include
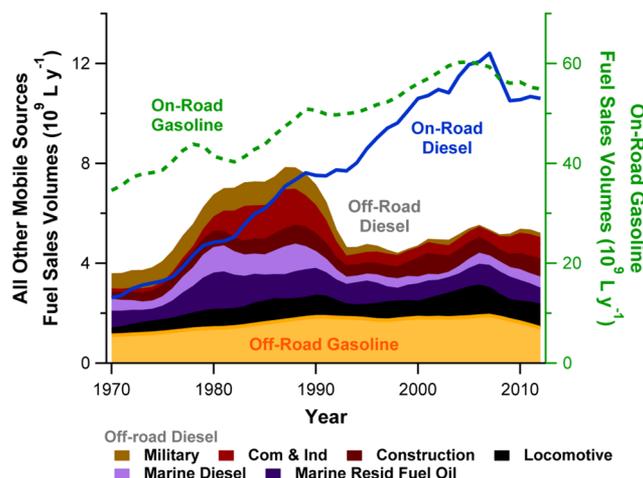
Figure 1. Long-term trends in fuel use by mobile sources in California. All sources shown here use gasoline or diesel fuel, except for large ocean-going vessels, which burn residual fuel oil. Residual fuel that is consumed in international waters has been excluded. Also, farm equipment emissions occur predominantly in rural areas, so agricultural use of diesel fuel is not shown. Fuel use by heavy equipment is broken down into military, commercial/industrial (Com & Ind), and construction sectors. The secondary *y*-axis indicates a separate scale for on-road use of gasoline, which dominates liquid fuel sales in California.

construction and farm equipment, railroad locomotives, marine vessels such as fishing boats, tugboats and ferries, and other commercial and industrial engines. Also shown is heavy residual fuel oil consumed by ocean-going marine vessels. Results from surveys of distillate fuel wholesalers conducted by the U.S. Energy Information Administration (EIA) that resolve fuel sales by end use sector were used to define activity by off-road engine type;[35] this dataset has been available since 1984. Based on previous work by Kean et al.[36] we excluded distillate fuel sales intended for use in furnaces, boilers, and for electric power generation, where combustion air and fuel are typically premixed, and resulting particle emissions are much lower than for diesel engines. Prior to 1984, trends in off-road engine activity were estimated using economic sector data[37,38] and the EIA's State Energy Data System[39] (Figures S1 and S2, Supporting Information). We considered carefully which proxies best replicated trends in off-road engine activity; more details are presented in the Supporting Information.

Estimates of fuel use in off-road gasoline engines are taken from California's OFFROAD model.[40] Off-road gasoline engines include lawnmowers, hedge trimmers, leaf blowers, small generators, recreational vehicles and watercraft, and other two- and four-stroke engines.

On-Road Diesel Engine Emission Factors. Emission factors for exhaust particulate matter (PM), expressed in units of grams of pollutant emitted per kg of diesel fuel burned, are derived from on-road measurements. Table S3 (Supporting Information) provides details on the data sources used for this analysis, which include measurements at the Tuscarora and Allegheny Mountain Tunnels in Pennsylvania,[41,42] and the Caldecott Tunnel in Oakland.[43−49] Additional measurements have been made in roadway tunnels in Baltimore,[41] Houston,[50] and Pittsburgh.[51] Only the Tuscarora (1976−1999) and Caldecott (1996−2010) tunnels have long-term measurements. We account for engine load differences between these two tunnels, which leads to a steeper rate of decrease in exhaust PM

emission factors over time, as compared to a simple regression across all tunnel observations (Table S4, Supporting Information).

Other pollutants (BC, OC, and total VOC emissions) from heavy-duty trucks are estimated by ratio to PM, using results from tunnel studies (Table S3, Supporting Information) and chassis dynamometer emissions testing (Table S5, Supporting Information).[52−56] All three pollutants are well correlated with PM ($R^2 > 0.70$, see Figures S3−S5, Supporting Information). An OA/OC ratio of 1.25, appropriate for hydrocarbon-like POA emissions, is used to convert OC to POA mass[57] for all mobile sources considered in this study.

On-Road Gasoline Engine Emission Factors. Light-duty vehicle emissions of PM, BC, OC, and total VOC are estimated by ratio to carbon monoxide (CO). McDonald et al.[58] have reviewed and compiled CO emission factor data from roadway tunnel and roadside emission spectrometer ("remote sensing") studies conducted between 1990 and 2010. A regression analysis of additional tunnel studies (Table S6, Supporting Information) and McDonald et al.[58] was used to characterize changes in fleet-averaged CO emission factors between 1970 and 2010 (see Table S7, Supporting Information, and Figure 2b).

Estimates of excess emissions associated with cold engine starting are included based on predictions from the EMFAC model,[59] which predicts increasing start-related contributions to tailpipe emissions over time, from 16% in 1990 to 26% in 2010. A similar trend is assumed prior to 1990. Early vehicle fleets included high fractions of automobiles not equipped with catalysts, which would not contribute to cold start emissions.

Emission ratios of other pollutants to CO were derived from on-road emission studies (Table S6, Supporting Information) and based on results of laboratory emission testing (Table S8, Supporting Information).[55,60−63] Engines tested span a range of model years from 1965 to 2012. Both VOC (Figure S6, Supporting Information) and PM (Figure S7, Supporting Information) are well correlated with CO, with similarly large decreases in emission factors of all three pollutants over time. Particle emissions from gasoline engine exhaust are mostly carbonaceous, with OC being the dominant fraction. Both OC and BC are well correlated with total exhaust PM emissions (Figure S8, Supporting Information). Over time, the relative abundance of BC in PM has been increasing, as PM emission factors have been decreasing. Rogge et al.[61] found noncatalyst vehicles emitted much higher amounts of OC relative to BC, as compared to catalyst-equipped vehicles.

Off-Road Engine Emission Factors. PM emission factors from Dallmann et al.[64] are used for off-road heavy-equipment, marine vessels, and locomotives. To estimate carbonaceous aerosol components from overall PM, we use OC/PM and BC/PM mass fractions from Chow et al.[65] specific to each off-road sector (see Tables S9 and S10, Supporting Information). We note that PM emission factors for off-road heavy diesel equipment tend to be significantly higher than for heavy-duty trucks when emissions are expressed on a per unit of fuel burned basis, and hence off-road engines can be an important source of particle emissions even at relatively low fuel consumption levels. To estimate VOC emissions from off-road diesel engines, we assume the same VOC/PM ratio as for on-road diesel engines. Off-road gasoline emission factors of primary OC and VOC are taken from laboratory tests,[66−68] reported on mass of fuel burned basis, separately for two- and four-stroke engines (Table S11, Supporting Information). More
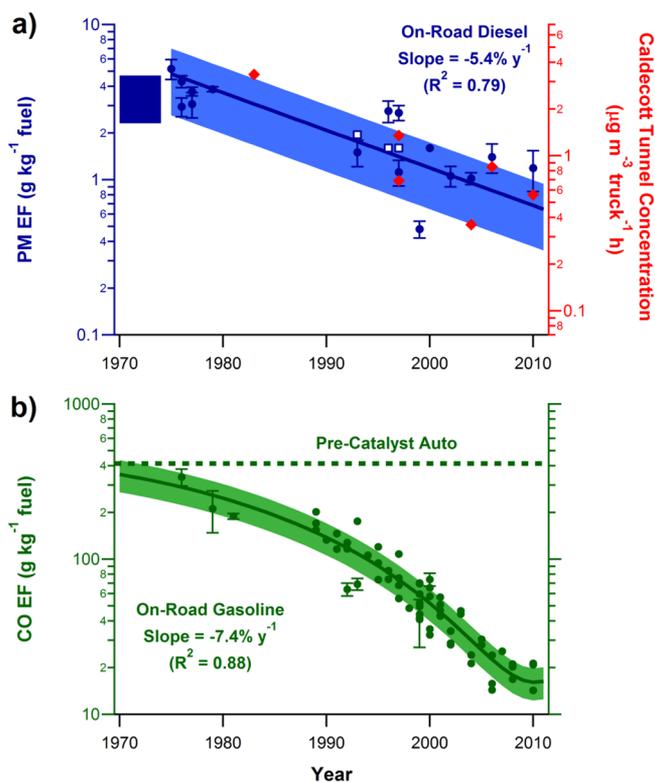
Figure 2. (a) Trends in heavy-duty diesel (blue) running exhaust emission factors for PM derived from regression analysis of tunnel studies. Early Tuscarora and Allegheny Mountain tunnel measurements are shown for comparison (dark band at left). Three fleet-averaged PM emission factors for selected calendar years (open squares) from chassis dynamometer emission tests are shown, but were not included in the regression. Plotted against the right axis are measured PM concentrations in a mixed-traffic bore of the Caldecott Tunnel (red diamonds). Shaded bands show 95% confidence interval for the regression. (b) Trends in light-duty gasoline running exhaust emission factors for CO derived from all on-road emission studies (green circles). Cold start emissions are not included. Emission factor for an uncontrolled precatalyst vehicle is shown for comparison as the dashed line. Shaded bands show 95% confidence interval for the regression.

details on methods and uncertainties can be found in the Supporting Information.

SOA Yields. We merge SOA yields for emissions of unburned gasoline and diesel fuel with laboratory measurements of tailpipe exhaust, on the basis of μg SOA μg VOC reacted^{-1}, where VOC reacted refers to all gas-phase organic emissions from tailpipe exhaust (Table S12, Supporting Information). The calculated SOA yields are then combined with corresponding VOC emissions to estimate contributions to SOA formation. For gasoline vehicles, we use aerosol yields reported by Gentner et al.,[23] Gordon et al.,[24] and Jathar et al.[25]

Between 1995 and 1996, gasoline was reformulated to reduce content of heavy/aromatic hydrocarbons in California.[69] For years prior to 1996, we recalculated bulk SOA yields following Gentner et al.,[23] using different fuel speciation profiles.[69] The result was an aerosol mass yield for pre-1996 conditions that was 60% higher than for reformulated gasoline. Aerosol yields in Gentner et al.[23] are for individual hydrocarbons derived from laboratory chamber studies, and overall yields were calculated assuming SOA formation was due to emissions of unburned fuel under high nitrogen oxide (NO_x) conditions. The yields

are representative of the first several generations of oxidation products (∼6 h of processing), and are expected to under-estimate contributions to ambient SOA, especially in aged air masses.[23]

Aerosol yields are also affected by environmental factors. An important factor that we take into account is the effect of decreasing OA concentrations in the Los Angeles atmosphere over time, which reduces partitioning of semivolatile organics to the particle-phase. We use an SOA parametrization described by Jathar et al.[25] to quantify the effect of changing OA concentrations on both gasoline and diesel yields of SOA. The yields are predicted to be 1.5 and 2 times higher, respectively, in 1970 relative to 2010. Another environmental factor that could also lead to lower aerosol yields with time, are decreasing levels of VOC/NO$_x$.[70,71] In the Los Angeles Basin, the VOC/NO$_x$ ratio has fallen significantly over the past few decades.[58,72] Changes in VOC/NO$_x$ ratios are not accounted for in this analysis.

Another consideration is the increased production efficiency of SOA per amount of VOC emitted from modern passenger vehicles.[24] Old vehicles that predate California's Low-Emitting Vehicle (LEV-I) emission standard, have aerosol yields that can be well-described based on the composition of unburned gasoline. However, automobiles designed to meet LEV-I and LEV-II standards produce higher SOA than would be expected, despite substantially lower total VOC emissions. These vehicles have significant fractions of intermediate volatility organics, that are unresolved by standard gas chromatography techniques, and which have a high potential to form SOA in the atmosphere once emitted.[73] Following the introduction of LEV-I vehicles, we calculate aerosol yields based on tailpipe exhaust rather than unburned fuel for the whole vehicle fleet in calendar years 1994 and later, similar to Ensberg et al.[26] The result is an SOA yield that is ∼3 times higher in the year 2010 than from unburned gasoline reported by Gentner et al.[23]

For on-road and off-road diesel engines, we take a composite average of aerosol yields reported in the literature for both unburned fuel and diesel exhaust.[23,25,74] Diesel fuel contains much greater abundance of intermediate volatility organics than gasoline, and these organics form SOA in higher yields compared to the lighter and more volatile compounds present in gasoline. Jathar et al.[25] show that SOA yields for diesel exhaust can be understood based on the composition of unburned fuel. SOA yields for off-road gasoline engine emissions are based on work of Gordon et al.[66]

Gas−Particle Partitioning of POA. A complicating factor is that partitioning of POA between the gas and particle phases varies depending on organic aerosol mass loadings, the extent to which POA emissions have been diluted with ambient air, and ambient temperature.[75] In tunnel studies and in chassis dynamometer tests, POA emission factors are biased high because aerosol concentrations are many times higher than in the ambient environment, and which, in turn, favors partitioning of low volatility organics into the particle phase. Using estimates of gasoline and diesel POA partitioning from May et al.,[76,77] we estimate that ∼30% of gasoline and diesel POA emissions (Table S13, Supporting Information) measured in laboratory and tunnel studies (Table S14, Supporting Information) will evaporate upon dilution to ambient conditions at 25 °C (see the Supporting Information for more details). Upon oxidation, the evaporated POA, which includes semivolatile organic compounds (SVOCs), can readily form SOA. We estimate contributions of evaporated POA to

SOA assuming an aerosol yield of 0.50 μg SOA μg SVOC reacted^{-1} from Zhao et al.,[78] as determined in the Los Angeles area during Calnex in 2010. We assume SOA yields for evaporated POA change similarly to those for unburned gasoline and diesel fuel over time with respect to decreases in ambient OA concentrations.

Ambient BC and OC Concentrations. Ambient trends in BC are estimated for both Los Angeles and the San Francisco Bay Area. In the Bay Area, routine measurements of the coefficient of haze for ambient air are available from 1967 to 2003, and these measurements are closely related and can be converted to BC.[30] In Los Angeles, a combination of reflectance-tape based samplers[31] and filter samples are used to estimate BC concentrations. Filter data are also used to estimate ambient OC for Los Angeles only.

Table S15 (Supporting Information) summarizes filter-based datasets used to describe ambient carbon particle concen-trations (cutpoint diameter = 2.1 or 2.5 μm depending on the study) in the Los Angeles area. Data sources include a series of yearlong field studies by Cass and co-workers,[32,79,80] more recent studies by the South Coast Air Quality Management District,[81,82] and routine monitoring data from the Speciation Trends Network (STN) and National Air Surveillance Network.[83] These studies used filters to measure PM mass, BC, and OC. Filter samples were typically collected over 24 h time periods and subsequently analyzed in a central laboratory. Thermal optical analysis techniques were used to differentiate and quantify black and organic carbon contributions to total carbon mass on each filter.

In Los Angeles, average BC concentrations from 1960 to 1982 are derived from reflectance-based tape samplers that operated at seven locations measured across the basin. The tape samplers were shown to be well-correlated with BC.[31] From 1993 to 2010, a linear regression is performed on filter samples described in Table S15 (Supporting Information). In the intervening years, ambient BC concentrations are interpolated, as discussed below in the section on BC Trends. To derive ambient OC concentrations, correlations between filter-based measurements of OC and BC were developed, and more extensive records of measured BC concentrations were thereby used to estimate OC. The similarity of slopes inferred from regression analyses involving OC and BC measured in multiple studies (Figure S9, Supporting Information) implies similar long-term trends in ambient BC and OC concentrations.

A key reason why we infer OC from measured BC concentrations is that there is a potentially large OC sampling artifact due to adsorption of gas-phase organics onto quartz filters, which can lead to systematic biases of up to +50%.[84−86] A negative sampling artifact due to volatilization of particle-phase organics collected on the filter sample is also possible, and can occur when there is a large pressure drop over the filter.[85] Turpin et al.[87] concluded that the dominant sampling artifact in the Los Angeles Basin was due to adsorption of gas-phase organics. Adsorbed carbon is often estimated by difference between a front and back-up filter, using either quartz-behind-quartz (QBQ) or quartz-behind-Teflon (QBT) filter configurations. However, measurements of OC are not always adjusted to account for sampling artifacts. For measurements that are not corrected, face velocity (air flow rate divided by filter cross-sectional area) is known to influence OC measurements. At higher face velocity, the importance of the OC adsorption artifact tends to be reduced.[87] For three studies where organic carbon was not corrected using back-up
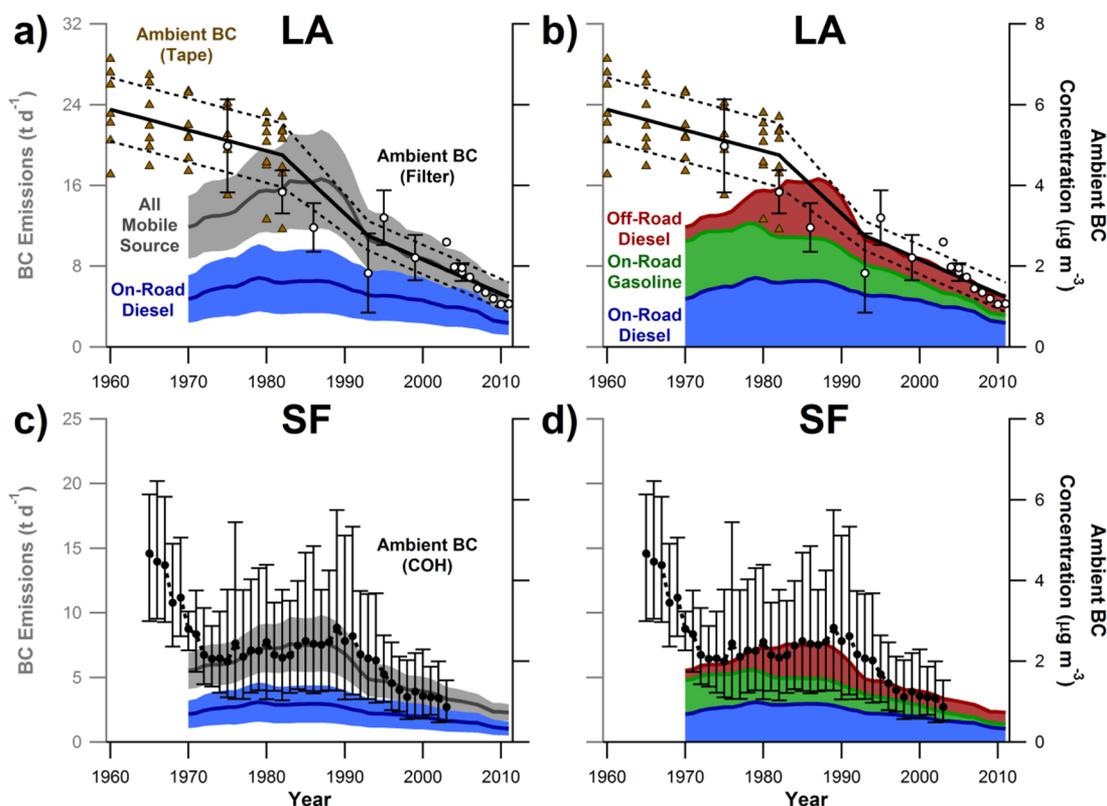
Figure 3. (a) Trends in ambient BC concentrations (right axis) for the Los Angeles area, compared with fuel-based inventory trends for BC emissions from on-road diesel (blue) and all mobile sources (gray). The latter is the sum of on-road diesel, on-road gasoline, and off-road diesel BC emissions. The ambient trend from 1960 to 1982 is derived from reflectance tape data (brown), and from 1993 to 2011 from filter samples listed in Table S15 (Supporting Information). Ambient values in between are interpolated. Error bars on the ambient data show the 95% confidence interval for basin-average concentrations, and reflect spatial variability. Shaded bands for the fuel-based inventory also represent 95% confidence intervals. (b) Trends in mobile source emissions of BC broken down by major source category and shown as stacked area contributions to the total. (c) Same as panel a for the San Francisco Bay Area. Trends in annual average ambient BC concentrations (right axis) derived from coefficient of haze monitoring in the San Francisco Bay Area. Error bars show the minimum and maximum values of annually averaged BC concentrations across COH monitoring locations. (d) Same as panel b for the San Francisco Bay Area.

filter data, and where sampling was done at low air flow rates, the OC to BC ratio is clearly elevated compared to other studies (Figure S9, Supporting Information). To avoid biasing OC estimates, we derive a relationship between OC and BC from the other studies where the adsorption artifact is already corrected for using either QBQ or QBT paired filter configurations, or where the adsorption artifact was mitigated by use of high sample air flow rates.

Measurements of OC are the best available proxy for how ambient levels of organic aerosol have changed over time. Similar OA/OC mass ratios have been reported across various urban areas, even though ambient OA levels vary substantially. OA/OC ratios in Mexico City,[88] Los Angeles,[19] and Pittsburgh[89] have been reported to range from 1.6 to 1.8. In contrast, absolute OA concentrations vary by a factor of 4 across these cities.[19,89,90] A reanalysis of early carbonaceous aerosol samples collected in the Los Angeles Basin during 1982,[91] found similar OA/OC ratios ranging from 1.6 to 1.8 across three urban sites.[92] We use a constant OA/OC mass ratio of 1.7 to convert ambient concentrations of OC to OA.

■ RESULTS AND DISCUSSION

BC Trends. Over a 40 year period between 1970 and 2010, heavy-duty diesel truck exhaust PM emission factors decreased by a factor of ~7, as shown in Figure 2a. Our PM emission factor of 0.68 ± 0.31 g kg^{-1} fuel as of 2010 agrees well with

measurements of diesel truck emissions at a weigh station on Interstate Highway 5 near Redding, California.[93] To evaluate the slope of the emission factor trend line, we compare emission factor trends with results of repeated measurements of pollutant concentrations at the Caldecott tunnel in the San Francisco Bay Area.[43−49] The evolution of measured PM concentrations normalized to truck traffic flow at this location (Table S14, Supporting Information) is plotted on the secondary vertical axis of Figure 2a; the trend is a proxy for changes in diesel truck emission factors shown on the same plot and is consistent with our regression. Tunnel concentrations are shown on the secondary axis because an early study by Hering et al.[47] reported PM but not carbon dioxide, which is needed to calculate emission factors.

The first organized emission inspections for heavy-duty trucks started in 1970 and were aimed to reduce visible smoke under steady state engine operation.[3] The first diesel exhaust emission standards specifically for PM were implemented much later, for 1988 and newer engines.[44,53] Initial efforts to lower diesel PM emissions involved changes to engine design to reduce lubricating oil emissions and to improve air–fuel mixing (thereby lowering BC emissions), rather than installing aftertreatment control technologies.[3] Starting with the 2007 model year, allowable PM emission rates for heavy-duty diesel engines were lowered by an order of magnitude. Diesel particle filters (DPF) are now included as standard equipment on most new

engines, and large resulting decreases in BC emission factors have been observed.[94,95] The effects of large numbers of DPF-equipped engines entering into service is not accounted for in this analysis, so emission factor trends in Figure 2a may show a change in slope when projected forward in time beyond ∼2010.

When evolving values of taxable diesel fuel sales and emission factors are combined for the period 1970−2010, a resulting trend in BC emissions can be derived, as shown in Figure 3. The spatial domains for which emissions were estimated include the South Coast/Los Angeles (top) and San Francisco Bay Area (bottom) air basins. The sum of all mobile source emissions, including on-road gasoline, on-road diesel, and off-road diesel is shown in Figure 3b,d for these air basins, and compared with trends in ambient BC concentrations. Off-road gasoline engines are not shown because they are a very minor contributor to BC emissions[66,68] (most of the PM emissions from these engines consist of lubricating oil/POA rather than BC).

A surprising result is that on-road heavy-duty diesel trucks have never accounted for more than half of the total BC emissions from all mobile sources (Figure 3a,c). In 1970, passenger vehicles were of similar importance as sources of BC emissions. In 2010, gasoline vehicles are now a relatively minor source of BC (only 15 ± 7% of the total), and diesel trucks are the largest contributor (48 ± 27%). However, off-road heavy diesel engines are also a significant source of BC emissions (37 ± 20%). Fuel volumes consumed by off-road diesel engines were much less than for on-road diesel trucks as of 2010 (Figure 1). However, BC emission factors are twice as high in off-road versus on-road diesel engines when expressed per unit of fuel burned basis. Differences in emission factors arise from delayed implementation of emission standards for off-road diesel engines, which began in 1996, decades after the first visible smoke regulations were implemented on on-road diesel engines in 1970.[3]

Figure 1 shows how diesel fuel use in off-road heavy equipment has changed over time. Between 1975 and 1980, there was a ∼50% increase in off-road sales of diesel fuel in California. This was followed by a similar decrease between 1987 and 1992. The large fluctuations in California off-road fuel purchases were seen in the commercial and industrial sectors; much less variability was seen at the national level (Figure S1, Supporting Information). The large differences between California and the U.S. diesel fuel sales trends likely resulted from different limits on sulfur content in diesel fuel. The decrease in fuel sales in California occurred when use of high-sulfur diesel (fuel with over 500 ppm sulfur content used to be allowed) was being phased-out in off-road engines, a statewide rule that was specific to California (see Figure S1, Supporting Information).[36] BC emissions from off-road diesel engines are shown in Figure 3b,d. Because emission standards for off-road diesel engines had not been established yet, changes in activity (i.e., fuel sales) were the dominant factor affecting off-road diesel emissions prior to the mid-1990s. Reduced off-road engine activity appears to explain, at least in part, why ambient concentrations of BC were decreasing more rapidly around 1990, which is evident in both the Los Angeles Basin (Figure 3b) and the San Francisco Bay Area (Figure 3d). The noticeable drop in off-road fuel purchases around 1990 is not affected by interpolation methods used in this study for extrapolating off-road activity in earlier years. State-level fuel survey data are available beginning in 1984 and capture the downturn in California off-road diesel engine activity.[35]

Between 1970 and 2010, overall mobile source emissions of black carbon decreased by a factor of 2 (Figure 3). We attribute ∼70% of the decrease to on-road gasoline vehicles, and the other ∼30% to efforts to control PM emissions from diesel trucks. Off-road diesel emissions of BC grew rapidly and then dropped (Figure 1). In contrast to the present study, the presumption in the literature has been that BC decreases in California have been driven by control of on-road diesel emission sources.[29,30]

In the San Francisco Bay Area, there is good agreement between our mobile source inventory and coefficient of haze-derived BC concentrations (Figure 3c). Prior to 1970, there is a very sharp decrease in ambient BC concentrations, possibly due to decreased emissions from stationary sources. Ambient BC concentrations in Los Angeles exhibit many of the same features as the San Francisco Bay Area, but lack the sudden drop in BC concentrations around 1970 (Figure 3a). The ambient BC concentration trend also exhibits a slight decrease rather than increase between 1970 and 1980. The differences between Los Angeles and San Francisco Bay Area also may reflect regional differences in pollution sources and/or policies to control stationary source emissions.

After 1980, mobile sources are expected to be a dominant contributor to BC. First, other potentially important sources of BC, including industrial uses of coal, residential heating, and open burning are no longer expected to be significant in California cities.[1] Second, ambient BC concentrations are known to exhibit day-of-week cycles,[30] consistent with decreases in diesel truck activity on weekends compared to weekdays.[96] Passenger vehicles[96] and stationary/residential sources[97] do not exhibit strong day-of-week cycles in activity patterns. Lastly, the consistency of our emissions inventory with ambient trends corroborates the importance of mobile sources to BC.

OA Trends. The OA analysis focuses only on the Los Angeles Basin. It is well documented that tailpipe emissions of CO and VOC from passenger vehicles have decreased rapidly due to widespread deployment of catalytic converters along with supportive changes in fuel properties.[58,98] Between 1970 and 2010, gasoline engine emission factors of CO were found to decrease by 7.4% per year (Figure 2b). In 1970, our regression estimate is in agreement with an emission factor for precatalyst vehicles (model years 1957−1965) calculated by Harley et al.[99] After accounting for ∼60% increase in gasoline sales, and a growing contribution to overall emissions associated with cold engine starting, on-road gasoline engine emissions of CO still decreased by a factor of 10 between 1970 and 2010. In this study, CO provides a baseline from which we estimate emissions of POA and VOC, with VOC emissions, in turn leading to the formation of SOA. All three pollutants have trended similarly to CO, and exhibited order of magnitude reductions between 1970 and 2010. Estimates of SOA production from gasoline emissions account for effects of decreasing aerosol mass loadings in the atmosphere, decreased aromatic content of gasoline, and higher SOA produced per unit mass of VOC emitted from newer vehicles.

It is of interest to reconcile changes in emissions of VOC and POA with long-term trends in ambient concentrations of organic aerosol. As described above, we infer ambient OC concentrations in the Los Angeles Basin using relationships shown in Figure S9 (Supporting Information) combined with measured BC concentrations, and then multiply OC in all cases by an OA/OC mass ratio of 1.7.[19] Our analysis indicates that

the constructed OA concentrations in the Los Angeles Basin decreased from 15.5 ± 2.7 μg m^{-3} in 1970 to 5.1 ± 1.4 μg m^{-3} in 2010 (Figure 4).
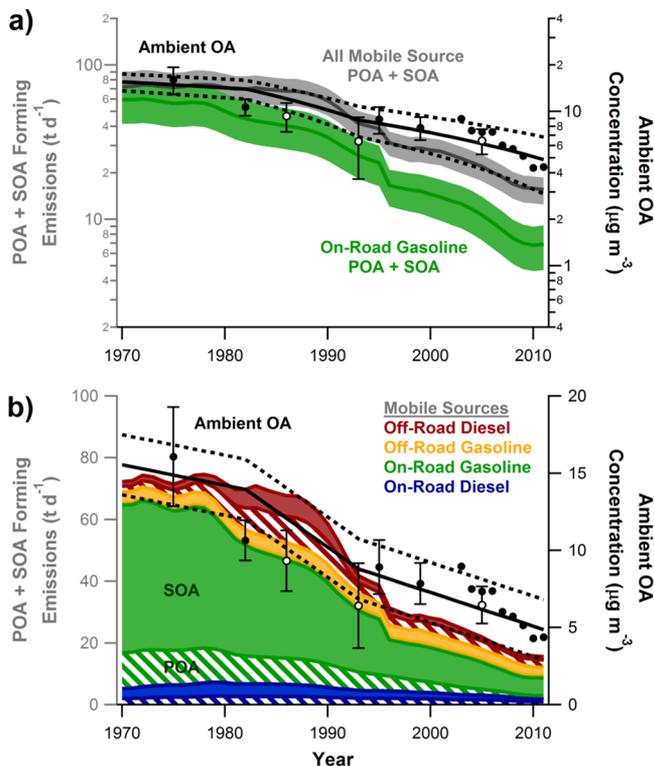
Figure 4. (a) Trends in ambient organic aerosol concentrations (right axis) inferred from filter samples for the Los Angeles area, compared with estimated emission contributions to OA from on-road gasoline vehicles (green) and from all mobile sources (gray). Total OA emissions are calculated as the sum of both primary and secondary contributions. SOA-forming emissions equals gas-phase VOC and evaporated semivolatile POA emissions, multiplied by an aerosol yield for each (see text). Shaded bands for the emissions inventory represent a 95% confidence interval. Ambient OA values are scaled from OC measurements that are shown as reported (closed circles) or estimated using OC to BC relationships derived in Figure S9 (Supporting Information) (open circles). Error bars for ambient organic aerosol denote 95% confidence intervals for basin-average concentrations, and reflect spatial variability. Note the logarithmic scale. (b) Trend in mobile source emissions of OA as in the top panel, broken down by major source category and plotted on a linear scale.

Estimated on-road and off-road contributions to OA (including both primary and secondary sources) and ambient OA concentrations are compared in Figure 4a on a logarithmic scale. The step change seen in Figure 4a for gasoline-related SOA between 1995 and 1996 is due to a statewide program requiring use of reformulated gasoline, which lowered the aromatic and heavy hydrocarbon content of gasoline as well as the SOA-forming potential of related VOC emissions.[100] It is clear that on-road gasoline contributions to POA and SOA formation are decreasing at a much faster rate than ambient OA. When other mobile sources are included, the emissions trend becomes flatter, with OA decreasing by a factor of 4–5 between 1970 and 2010, in agreement with the constructed record of ambient OA concentrations. A slower rate of decrease in OA is expected when contributions from on-road diesel and off-road engines are included. There is now near-universal use

of catalytic converters to treat on-road gasoline exhaust, with resulting large reductions in VOC emissions that lead to SOA formation. Exhaust after-treatment devices have not been widely used in other mobile source sectors until recently.

Emissions are broken down by on-road and off-road engine, fuel categories, and by POA and SOA separately in Figure 4b. As of 1970, on-road gasoline engines accounted for 82 ± 32% of mobile source contributions to OA (POA + SOA), and clearly dominated over all other mobile source contributions. By 2010, on-road gasoline engines accounted for 43 ± 16% of the mobile source contribution to OA, followed by off-road diesel and gasoline equipment accounting for ∼20% each. Off-road gasoline equipment are increasingly becoming an important source of precursor emissions to ozone and SOA. Platt et al.[101] suggest that in many cities around the globe, two-stroke scooters are the largest source of vehicular PM and SOA. We estimate that VOC emission factors on a fuel basis are 170 ± 40 times higher in off-road gasoline engines (e.g., lawn and garden equipment) than for the 2010 on-road light-duty vehicle fleet. As control of on-road pollution sources was an early focus of air quality management efforts, other sources of POA and SOA-forming emissions are likely to have grown in relative importance over time.

As shown in Figure 4a, mobile source contributions to OA (including both primary and secondary sources) and constructed OA concentrations show similar long-term downward trends. The similarity between mobile source emissions and the ambient OA trends reflects the historical importance of on-road and off-road engines as air pollution sources in the Los Angeles Basin. Note that the two independent vertical axes of Figure 4b are aligned in a similar manner as in Figure 3. The relative scaling of the axes aligns primary pollutant emissions with resulting ambient concentrations (1 μg m^{-3} corresponds to 4–5 tons per day of primary emissions under annual average conditions). The lack of a gap between emissions and ambient trend lines in Figure 4b suggests that our inventory-based approach applying SOA yields to gasoline and diesel VOC emissions is giving reasonable results.

There are also other potentially important stationary and area source emissions, which we have not considered in this analysis, but may also be making noteworthy contributions to OA. These other sources of OA include cooking, wood smoke and forest fires, as well as SOA due to biogenic VOC emissions.[13,16,17,19,20] Zotter et al.[102] suggest that 58 ± 15% of OC measured at Pasadena during CalNex in 2010 was nonfossil. Including these other sources of organic aerosol would be likely to flatten the overall OA emissions trend, and bring it into better agreement with the ambient OA concentration trend.

In summary, we found consistent pictures of long-term trends in mobile source emissions of carbon particles and corresponding ambient concentrations for two major urban areas in California. This suggests that mobile sources in the past have dominated contributions to carbonaceous aerosols (including primary emissions plus secondary formation). As of 1970, mobile source emissions were dominated by on-road sources for both BC and OA (∼90%). By 2010, off-road engines accounted for 37 ± 20% and 45 ± 16% of mobile source-related BC and OA, respectively. Emission uncertainties for individual mobile source categories are summarized in Table S16 (Supporting Information). For the urban areas considered in this study, it appears to be increasingly important that air quality management plans consider and address the air

pollution burdens associated with off-road engines and other possible sources of VOCs with high SOA formation potential, in addition to regulating emissions from on-road motor vehicles.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information
Supplementary tables (S1–S16) and figures (S1–S9) as referenced in the text. This material is available free of charge via the Internet at http://pubs.acs.org/.

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Notes
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