Environmental Science & Technology

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Long-Term Trends in Motor Vehicle Emissions in U.S. Urban Areas

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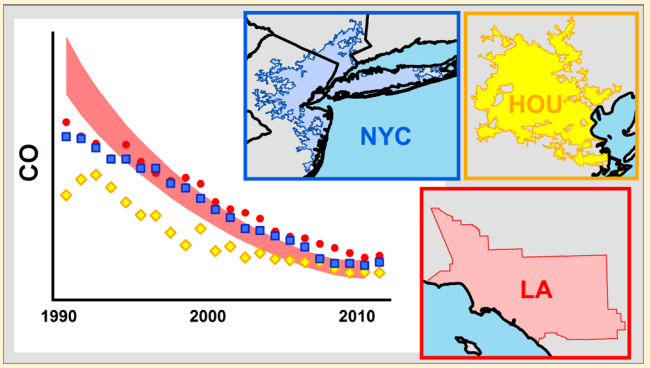
Supporting Information

ABSTRACT: A fuel-based approach is used to estimate long-term trends (1990−2010) in carbon monoxide (CO) emissions from motor vehicles. Non-methane hydrocarbons (NMHC) are estimated using ambient NMHC/CO ratios after controlling for nonvehicular sources. Despite increases in fuel use of ∼10−40%, CO running exhaust emissions from on-road vehicles decreased by ∼80−90% in Los Angeles, Houston, and New York City, between 1990 and 2010. The ratio of NMHC/CO was found to be 0.24 ± 0.04 mol C/mol CO over time in Los Angeles, indicating that both pollutants decreased at a similar rate and were improved by similar emission controls, whereas on-road data from other cities suggest rates of reduction in NMHC versus CO emissions may differ somewhat. Emission ratios of CO/NO_x (nitrogen oxides = NO + NO_2) and $NMHC/NO_x$ decreased by a factor of ∼4 between 1990 and 2007 due to changes in the relative emission rates of passenger cars versus diesel trucks, and slight uptick thereafter, consistent across all urban areas considered here. These pollutant ratios are expected to increase in future years due to (1) slowing rates of decrease in CO and NMHC emissions from gasoline vehicles and (2) significant advances in control of diesel NO_x emissions.



INTRODUCTION

Non-methane hydrocarbons (NMHC), nitrogen oxides (NO_x = NO + NO_2), and carbon monoxide (CO) are coemitted with carbon dioxide (CO_2) during combustion. These pollutants are important to tropospheric ozone (O_3) and secondary organic aerosol (SOA) formation,[1,2] which have impacts on health[3−5] and climate.[6] In urban settings, motor vehicles are among the most important sources of emissions for NMHC, NO_x, and CO. In the U.S., motor vehicles can be divided between light-duty passenger vehicles which are mostly gasoline powered, and heavy-duty trucks and buses which are mostly diesel powered. Emission reduction measures in the U.S. have been implemented over a period stretching back to the 1960s. Control efforts on gasoline engines include adjustments to air/fuel ratios, changes in the way fuel is metered into engines, changes to fuel properties, and use of catalytic converters that oxidize CO and NMHC and reduce NO_x.[7] For diesel engines, installation of exhaust gas recirculation (EGR) and more recently the use of selective catalytic reduction (SCR) systems have lowered NO_x. Tailpipe CO and hydrocarbon emissions can be reduced with diesel oxidation catalysts and particle filters along with particulate matter.[8] Initial control efforts emphasized achieving reductions in NMHC and CO emissions, before shifting to NO_x.[9] Additionally, emissions from light-duty vehicles were controlled earlier than heavy-duty diesel trucks. This has had important consequences for NO_x, as heavy-duty truck emissions have become an increasing share of emissions in the U.S.[10,11]

Emission inventories are central to air quality planning and atmospheric modeling studies, but inventories are subject to large uncertainties.[12,13] In estimating motor vehicle emissions,

Received: March 6, 2013
Revised: June 5, 2013
Accepted: August 5, 2013
Published: August 5, 2013

dx.doi.org/10.1021/es401034z | Environ. Sci. Technol. 2013, 47, 10022−10031

challenges arise in accurately representing traffic volumes and driving conditions as a function of location and time and in specifying appropriate emission factors.[14] As fleet-average emissions decrease over time, it is becoming increasingly important to account for skewness in emission factor distributions and, in particular, to include the contributions to overall emissions from high-emitting vehicles.[15] As emission factor distributions become more tail-heavy, larger and larger vehicle sample sizes are required in emission studies to maintain the same level of accuracy in estimates of population mean values. Fleet-average emission factors that reflect emissions from thousands of in-use vehicles are available from roadside remote sensing,[16] roadway tunnel studies,[17,18] and inspection and maintenance program data.[19] Similarly large and unbiased vehicle samples are very difficult to obtain and costly to test in laboratory settings.

A related challenge is controlling for effects of driving mode (e.g., vehicle speed, acceleration, and roadway grade) on emission factors, which can vary by pollutant.[16,20,21] Measurements taken at any single location are unlikely to represent the full range of emission factors and driving conditions observed on the road. Also excess emissions associated with cold engine starting are not usually captured in on-road emission studies. In laboratory testing, the cold start phase that includes the first few minutes of vehicle operation can be the dominant source of pollutant emissions for many vehicles, this is especially true for exhaust emissions of NMHC.[22] Evaporative NMHC emissions from vehicles are also difficult to describe, in part because these emissions vary with changes in ambient temperature, and because some of the emissions occur while vehicles are parked.

The main goal of this study is to evaluate long-term trends (1990−2010) in motor vehicle emissions for major urban areas in the U.S. New estimates for CO and NMHC emissions are developed in this study, and these values are compared with available estimates for NO_x.[10] An important feature of this work is the use of both source-oriented (bottom-up) and ambient air (top-down) measurements to constrain NMHC emission factors. Previous evaluations of emission inventories indicate that bottom-up and top-down studies of vehicle emissions have not converged.[12,13] Only a few of the top-down evaluations have considered changes in emissions over a long time period. Ambient air measurement studies reporting selected individual hydrocarbon species in urban air have highlighted the importance of motor vehicle contributions,[23−25] but total mass emissions are not estimated, and many hydrocarbons known to be present in liquid fuels are missing (i.e., unmeasured or not reported) from ambient air studies. This paper focuses on three major U.S. metropolitan areas: Los Angeles, New York City, and Houston. These metropolitan areas have large populations (6−22 million), violate ambient air quality standards, and have been focal points for field studies and air pollution control efforts.

METHODS

Activity Data. A fuel-based approach is used in this study to estimate motor vehicle emissions, where on-road vehicle activity is measured by fuel consumed rather than distance traveled, and emission factors are expressed per unit of fuel burned. In the U.S., gasoline is consumed primarily by light-duty passenger vehicles, whereas diesel is consumed mostly by heavy trucks and buses. Fuel sales are reported at national and state levels and are allocated in this study to finer spatial scales using traffic count data.

The spatial domain for Los Angeles was the South Coast air basin. New York City and Houston were represented as urban areas as defined by the U.S. Census Bureau (Figures S2−S4). For the South Coast air basin, McDonald et al.[10] have estimated gasoline and diesel fuel use, and these estimates are used here. For New York City and Houston, only gasoline fuel use is estimated. Annual reports of fuel sales and traffic data are available from the Federal Highway Administration.[26] Vehicle travel is reported for individual urban areas as well as by state and is used as a spatial surrogate for gasoline use. The amount of vehicle travel in each urban area as a fraction of state totals is calculated for each year and multiplied by statewide gasoline sales to arrive at estimates of fuel consumption in each metropolitan area of interest.

Because ambient measurements were selected only for weekdays (see below), inventory estimates were adjusted to reflect weekday emissions for comparison. Heavy-duty truck fuel use is known to decrease by 70−80% on weekends, and day-of-week specific truck count data reported by Marr et al.[27] were used to derive weekday-specific estimates of diesel emissions.

Bottom-up CO Emission Factors. We use CO running exhaust emission factors measured in tunnel and remote sensing studies, expressed in grams of CO emitted per kilogram of fuel burned. Remote sensing measurements of light-duty vehicle emissions in the Los Angeles area span a period of 20 years and have been made at multiple locations.[15,16,28−33] Vehicle emissions have also been measured at a tunnel in Van Nuys, CA, spanning a similar time period.[15,17,34] Multiyear studies of vehicle emissions in other U.S. and California cities are available for comparison, including remote sensing studies in Chicago,[16,35] Denver,[16,35−38] Phoenix,[16] and San Jose[31] and tunnel measurements in Oakland[18,39−41] (Table S1). We focus on studies with sample sizes larger than 10 000 vehicles, to capture contributions from high-emitting vehicles (in the earliest years of field sampling in Denver, vehicle sample sizes were smaller, on the order of several thousand vehicles). Since both emission factors and fuel economy vary with vehicle age, emission factors for each vehicle model year were weighted by corresponding estimates of fuel economy,[42] following an approach described by Singer et al.[29] Further fuel economy differences between cars and light-duty trucks were also taken into account. This places greater weight on emissions from vehicles with lower fuel economies in calculating fleet-average emissions. Fuel economy-related adjustments are less influential after 2000, as new vehicle fuel economy standards did not change significantly between the mid-1980s and 2010. Typical uncertainties of the remote sensor for CO are ±5%.[16] The uncertainty of the regression analysis in this study reflects differences in fleet characteristics between remote sensing locations, such as vehicle fleet age and driving mode.

Emission values can be affected by seasonal differences in fuel formulation, especially in earlier years when CO emission rates were higher and oxygenates were added to gasoline during winter months only.[18,43] In most cases, field sampling of vehicle emissions took place during the summer or fall and therefore exclude wintertime oxygenate effects on emissions. For Denver, both summer and wintertime measurements were taken. To ensure consistency in comparison of trends across cities, only summer emissions results were included in the analysis in earlier years.

A multivariate regression of CO running exhaust emission factors with time is performed on the aforementioned studies

using a second-order polynomial fit (Table S2). Differences in vehicle fleet age across on-road studies are controlled for and included as an additional independent variable to account for (1) California having an older vehicle fleet than the national average and (2) aging of the vehicle fleet in recent years due to recession-related effects on new vehicle sales. The mean vehicle age is estimated from the National Household Travel Survey (NHTS) (Figure S5).[44−46] These values are then input into the regression model for each urban domain. Age distributions at remote sensing locations are similar to the U.S. and California vehicle fleets (Figure S6). Because California vehicles were certified to meet *less* stringent CO emission standards during the 1980s and early 1990s,[47] we include a dummy variable to account for differences between California vehicles and those from other states. This effect diminishes over time: since 1993, CO emission standards for new California vehicles have been the same as or more restrictive than national standards. Cold engine starting emissions are estimated for California only. The ratio of start to running emissions is taken from the EMFAC model[48] and multiplied with running exhaust emissions from this study.

For heavy-duty diesel trucks, we use linear regression to describe CO emission factor trends (Figure S1). Data points include remote sensing measurements of truck exhaust plumes in Anaheim, CA,[49] and San Marcos, TX.[50] We exclude port locations where truck fleets may not be representative and also exclude high-elevation sites that show increases in CO emissions but that are not relevant for the cities that are the focus of this study. Tunnel measurements of CO emissions from Tuscarora, PA in 1992[51] and Oakland, CA in 2010[52] are included in the regression. To augment CO emissions data for the 1990s to support the regression analysis, we calculated fleet-average emission factors for calendar years 1992−1998, based on heavy-duty vehicle chassis dynamometer emission tests summarized by Yanowitz et al.[53]

Top-Down Gasoline NMHC/CO. Light-duty NMHC emission factors are estimated using a top-down approach by determining ratios of gasoline-related NMHC to CO in ambient air using a combination of literature values and monitoring data (Table S4). Gasoline-related NMHC are emitted as evaporated fuel and tailpipe exhaust from vehicles in use or at rest or from storage tanks.[54] To isolate gasoline-related emissions, we either use an overconstrained chemical mass balance (CMB) method or scale the sum of unburned fuel species predominantly emitted by motor vehicles by their mass fraction in liquid fuel samples. Ambient NMHC/CO reported here include evaporative and fugitive emissions in addition to tailpipe exhaust, because tracer species are emitted via each of these pathways.[54]

CMB was applied to hourly ambient air measurements (N = 57; morning rush hour samples only) from the 1987 Southern California Air Quality Study[55] and PAMS monitoring network data from downtown Los Angeles between 1994 and 2001 (N = 357). A detailed description of CMB analysis can be found in Gentner et al.[56] PAMS samples were collected every third day from July to August at 5 a.m. and also at noon from 1994 to 1999. Tracer compounds whose emissions are mainly due to motor vehicles were selected and scaled up to reflect other unmeasured fuel-derived species, based on the content of the measured ambient species in liquid gasoline samples collected over the same time period.[56,57] Compounds used included isopentane, 3-methylpentane, 3-methylhexane, methylcyclohexane, and isooctane (as well as n-butane in 1987). Based on results of Kirchstetter et al.,[18] we estimate that 24 ± 2% of exhaust NMHC emissions by mass are products of incomplete combustion (e.g., ethane, ethene, acetylene, propene), which are not captured by the CMB analysis. This value is used to adjust upward results for the gasoline source contribution in ambient air. The motor vehicular contribution to ambient NMHC is then regressed with concentrations of CO to derive the ambient ratio of NMHC/CO.

For field measurements where ambient results are reported as study averages,[23−25] we scaled up each tracer species individually based on corresponding mass fractions in unburned fuel and used averages of the ensemble of the results. This resulting value was adjusted to include products of incomplete combustion as described above. NMHC emission factors were obtained by multiplying bottom-up CO running exhaust emission factors for each calendar year by the average ambient NMHC/CO ratio resulting from the analyses described above.

Bottom-up Diesel NMHC. For heavy-duty diesel trucks, a regression analysis of remote sensing,[49,50] tunnel,[56] and chassis dynamometer[53] measurements was used to estimate bottom-up fleet-averaged NMHC emission factors (Figure S1). Infrared (IR) remote sensors calibrated using propane are known to underestimate NMHC emissions from gasoline engines by a factor of ∼2 when compared to flame ionization detectors (FID).[58] Because the mix of hydrocarbons present in exhaust emissions differs between gasoline and diesel engines, a separate NMHC scaling factor was derived based on comprehensive diesel fuel speciation profiles published by Gentner et al.[56] and generalized IR/FID response factors reported by Singer et al.[58] The IR/FID response for alkanes and cycloalkanes is approximately equal to 1. For single-ring aromatics we estimate the response to be $(n - 6)/n$, where n is the number of carbon atoms in the molecule (i.e., the aromatic ring and associated C−H bonds are invisible at the IR wavelengths used for remote sensing). For polycyclic aromatics we assumed zero response. We included diesel emissions of ethene reported by Dallmann et al.,[52] which Singer et al. report to have IR/FID response of ∼0. Overall, a scaling factor of ∼1.2 applies for diesel exhaust, in contrast to the higher value of ∼2 for gasoline engine NMHC emissions. The differences in IR/FID response between fuels are driven by the higher alkane/cycloalkane and lower aromatic fractions in diesel fuel compared to gasoline and the presence of longer alkyl constituents on aromatics present in diesel fuel. Oxygenated products of incomplete combustion are not included in these calculations, such as formaldehyde which is an important species in diesel exhaust.[52] If included, the scaling factor would increase to reflect nonmethane organic carbon (NMOC) rather than NMHC mass.

Ambient Air Monitoring Data. We compare bottom-up CO emission trends derived in this study with top-down trends in surface observations of CO and CO/NO_x ratios derived from ambient air monitoring networks. To isolate motor vehicle emissions, comparisons are made during the morning commuter peak period, on weekdays from 0500 to 0800 h local standard time over the entire year.[12,13] Cold start effects are included in ambient data. To reduce effects of year-to-year meteorological variations in extreme values of the distribution, we calculated the annual mean of the daily 3-h morning average of weekday CO levels, rather than using absolute maxima for each year. For Southern California, we used long-term records (1990−2011) of measured CO concentrations at 9 urban sites located in Los Angeles and Orange Counties where CO mixing

ratios are highest (Figure S2). In New York City, data from 7 to 14 monitoring sites were available in each year and for Houston 3−4 (Figures S3 and S4). For CO/NO_x, we limit the analysis to Los Angeles and include four additional monitoring sites located further inland. Ambient CO/NO_x molar ratios were computed by regression analysis of daily 0500−0800 average concentrations for each year (see Figure S11 for example).

RESULTS AND DISCUSSION

CO Emission and Ambient Trends. Significant progress has been made in controlling motor vehicle CO running exhaust emissions over the last twenty years (Figure 1a). For gasoline-powered vehicles since 1990, there were 10-fold and 7-fold reductions in CO emission factors of running exhaust measured in California and the US, respectively. During the early 1990s, California vehicles consistently emitted CO at higher amounts, due to emission control trade-offs that were made to enable more effective control of NO_x.[47] In terms of CO emission factors, California vehicles appear to have converged with the US fleet by around 2005. The large decreases in CO running exhaust emission factors observed both in California and at the national scale can be attributed to improved performance and durability of catalytic converters[16] and associated improvements in control of air-fuel ratios in gasoline engines.

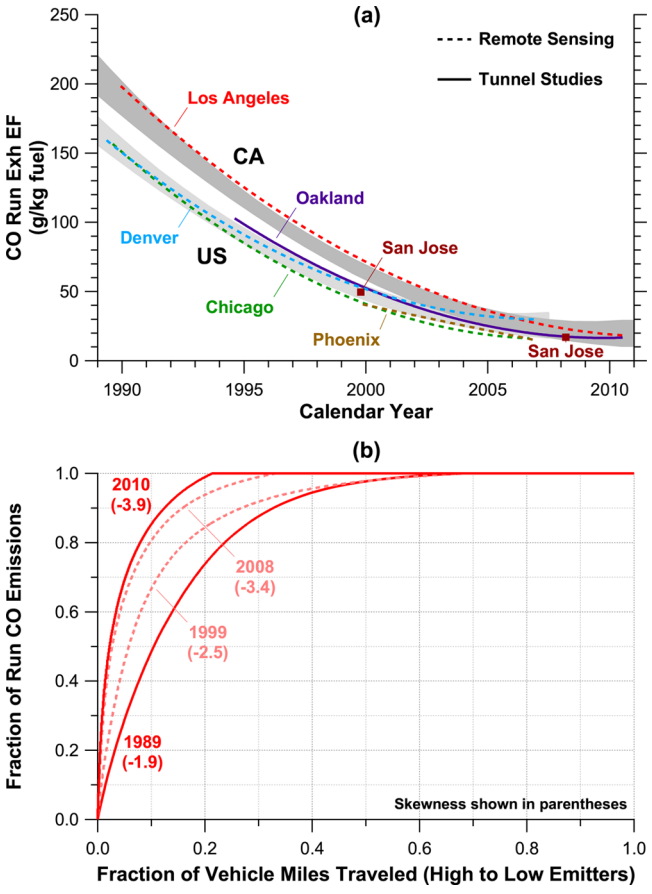


Figure 1. (a) Carbon monoxide stabilized (running) emission factor trends for light-duty gasoline-powered vehicles. All trends shown here are derived from remote sensing data, except for California tunnel measurements made in Oakland, and are reflective of long-term changes in summertime emissions (see text). Gray bands show 95% confidence intervals of the regression for California (upper band) and US (lower band). City trends reflect local vehicle mixes across model years. (b) Cumulative distributions of stabilized CO emissions from gasoline-powered vehicles in Los Angeles, based on remote sensing measurements of many individual vehicle exhaust plumes. The fraction of total CO emissions coming from the highest-emitting 10% of vehicles on the road increased from ∼50 to ∼90% between 1989 and 2010. The skew of emissions shown in panel b were not incorporated in the emission factor regression shown in panel a.

As a result of the notable success in CO emission control, the distribution of running exhaust emission factors is becoming increasingly skewed, such that a smaller and smaller proportion of vehicles on the road are accounting for the majority of overall emissions (Figure 1b). The distribution is based on the assumption that remote sensing captures a representative sample of vehicles for the region on a distance traveled basis (Figure S6). In 1989, the highest-emitting 10% of vehicles in Los Angeles accounted for ∼50% of running CO emissions,[28] whereas by 2010, the top 10% of vehicles were responsible for ∼85% of the emissions.[15] Similarly, ∼80% of vehicles contributed negligible amounts of CO in 2010. This suggests that further reductions in light-duty CO emissions should target high-emitters rather than the vehicle fleet as a whole, which are ∼5−7 years older than the rest of the fleet (Figure S8). Emission factor distributions are also skewed for other pollutants (Figure S9). The skewness for light-duty NMHC, CO, and NO_x emissions is −4.9, −3.9, and −2.9, respectively. The distribution of NO_x emission factors for heavy-duty trucks is currently much less skewed (skewness = −0.6 to −0.7)[49,52] than for gasoline-powered vehicles (skewness = −2.9) and results because most trucks at present are not equipped with advanced systems for NO_x control (Figure S9).

Bottom-up running exhaust emissions and ambient concentrations of CO are compared in Figure 2 for the three metropolitan areas. The long-term trends in emissions are reflective of changes during summertime. Because gasoline vehicles heavily dominate the on-road inventory of CO emissions in Los Angeles (Tables S5 and S6), only gasoline is shown. The large reductions in CO running exhaust emission factors are more than enough to offset 10−40% increases in gasoline sales from 1990 to 2010. Los Angeles and New York City saw growth in gasoline use near the lower end of this range, while Houston saw a larger increase in gasoline use. Running CO emissions from on-road vehicles decreased by 80−90%, despite increases in the number of vehicles on the road and the amount of fuel burned. The results of this study are consistent with trends in ambient CO concentrations measured in all three cities. Comparisons of fuel-based emission estimates for the Los Angeles area with estimates from the most recent version of the EMFAC model[48] are also in reasonable agreement, though our rate of CO reduction may be slightly steeper than EMFAC.

The fuel-based trend of decreasing CO running emissions appears to be slowing and may have stopped completely in recent years. This emissions-related finding is consistent with ambient observations that show little change in CO concentrations in the most recent years, which is true in all three cities (Figure 2). Federal tailpipe emission standards for CO have not been lowered since Tier 0 standards were first implemented on 1981 model year vehicles (Figure S7).[59] The slowdown in the ambient trend is also due to aging of the vehicle fleet (Figure S5) and the growing importance of cold start emissions. In California, start emissions have accounted for an increasing fraction of CO emissions: from 15% in 1990

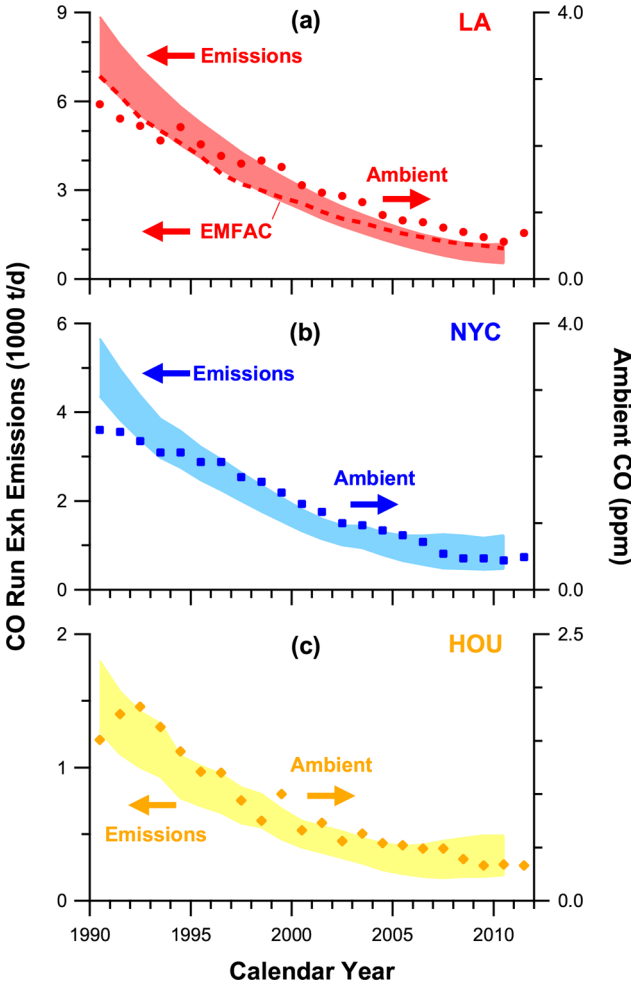


Figure 2. Ambient concentration and on-road gasoline vehicle trends for stabilized (running) CO emissions in (a) Los Angeles, (b) New York City, and (c) Houston metropolitan areas. Emission estimates shown as bands give 95% confidence intervals, and the long-term emission changes are reflective of summertime. EMFAC model predictions (dashed line) are shown for Los Angeles. Ambient CO data reflect morning rush hour conditions on weekdays when CO levels are high and vehicle emissions dominate and are shown as the annual average (see text). Start emissions are not shown but have accounted for an increasing share of on-road gasoline emissions in California from 15% to 27% between 1990 and 2010.

to 27% in 2010. The influence of deterioration on ambient trends may depend on the extent to which model year vehicles 1991−2000 remain in the fleet. A decade analysis of remote sensing data found deterioration rates were near zero for model year vehicles 1990 and earlier and 2001 and later.[16]

Running emission factors for CO are known to vary depending on engine load.[16,20,21] When expressed per unit of fuel burned, the CO emission factor increases both at idle and especially when accelerating while driving at high speed. Engine load can be described using a normalized measure known as vehicle specific power (VSP = engine power output divided by vehicle mass, in W kg^{-1} or kW t^{-1}) which is a function of vehicle speed, acceleration, and roadway grade.[60] For the West Los Angeles remote sensing site,[16] we calculated VSP for each vehicle and compared the resulting distribution of engine load with the corresponding fuel use distribution derived from the Unified LA92 drive cycle,[61] which is used to represent the full range of in-use driving conditions observed on-road in California. Driving conditions at the West Los Angeles site encompass most of the range of the Unified cycle, but idle and high engine load operating conditions are under-represented (Figure S10). For VSP values between 0 and 25 kW t^{-1}, which accounts for ~95% of the fuel use in the Unified cycle, the CO emission factor is relatively stable. For comparison, driving conditions are similar at the Denver site, while engine loads are lower in Chicago but predominantly between 0 and 25 kW t^{-1}.[16] This suggests that effects of engine load on CO emission rates do not introduce substantial bias in the fleet-average results reported here, though some high load driving may be missing in this analysis.

NMHC Emission and Ambient Trends. Figure 3a shows a stable top-down ambient NMHC/CO ratio of 0.24 ± 0.04 mol C/mol CO in Los Angeles. Units are shown as molar ratios to be consistent with prior studies reporting ambient species relative to CO.[23,25] Given reductions in CO described above, this result suggests that vehicular emissions of NMHC and CO have been decreasing at a similar rate and that gasoline powered vehicles dominate the emissions of NMHCs used in this study (Tables S5 and S6). This is consistent with pollutant concentration trends observed in the Los Angeles area over a 50-year period.[23] Note that the ambient-derived trend includes evaporated fuel in addition to tailpipe emissions. The EMFAC model also shows similar reductions in CO and

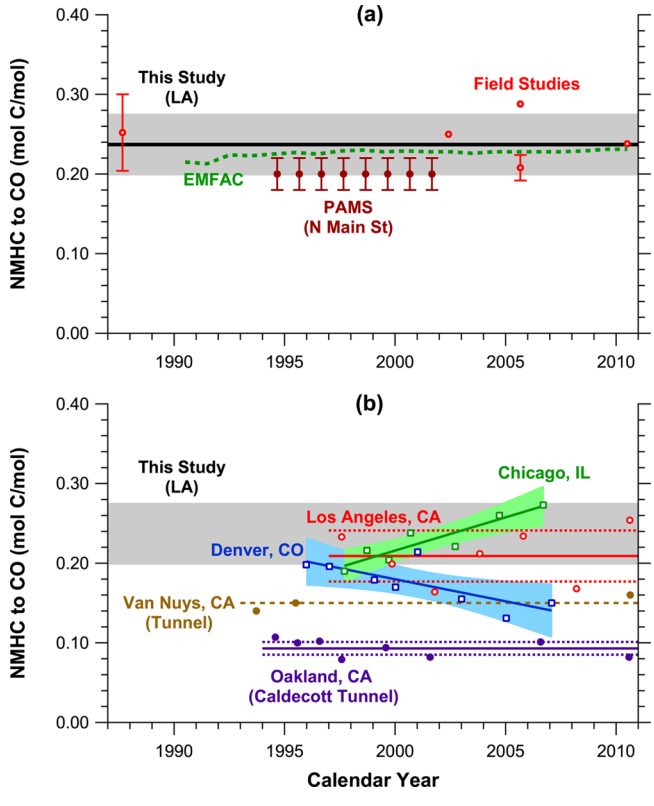


Figure 3. (a) Trends of ambient NMHC/CO in Los Angeles derived from special field studies and Photochemical Assessment Monitoring Stations (PAMS) data during summertime. NMHC data have been adjusted to exclude nonvehicular emissions (see text). Comparisons to ratios from EMFAC are also shown. (b) Measured NMHC/CO emission ratios derived from remote sensing (open symbols) and tunnels (solid symbols). Uncertainty bands reflect 95% confidence intervals in both panels. Note that "This Study (LA)" is the same in both panels.

dx.doi.org/10.1021/es401034z | Environ. Sci. Technol. 2013, 47, 10022−10031

NMHC emissions over time and a roughly constant emission ratio that is similar to our estimate.

When compared to on-road diesel engines, hydrocarbon emission factors for gasoline engines have historically been much higher when expressed per unit of fuel burned (Figure S1). Diesel engines operate with excess oxygen, and these fuel-lean conditions are conducive to oxidation of CO and NMHC. While near-stoichiometric combustion conditions typical in gasoline engines lead to higher engine-out CO and NMHC emissions, widespread use of the three-way catalytic converter has proved very effective at reducing these emissions from gasoline engines. Diesel CO and NMHC emissions have also declined over time, but the reductions have not been as great, such that for NMHC especially the gap between gasoline and diesel emission factors has narrowed considerably. Gasoline engines still dominate in terms of overall NMHC mass emissions, because of larger volumes of gasoline sold and used compared to diesel fuel. Looking ahead, trucks will increasingly be equipped with diesel particulate filters and associated upstream oxidation catalysts used for regeneration of the filter, and this is expected to reduce diesel NMHC emissions significantly.[62]

Bottom-up NMHC/CO emission ratios from remote sensing studies and tunnel measurements in Oakland (Caldecott) and Los Angeles (Van Nuys) are shown for comparison in Figure 3b. A key result is that the on-road studies in California also show NMHC/CO emission ratios that are stable over time, consistent with trends in top-down pollutant ratios derived from ambient air studies discussed above. However, the absolute ratios in on-road studies differ by a factor of 2, with the Caldecott tunnel measurements on the lower end, remote sensing on the upper end, and Van Nuys tunnel study results in the middle. A potential explanation is systematic differences in driving conditions and engine load among study sites. Vehicles inside the Caldecott tunnel are driving uphill on a 4% grade at speeds of 60−100 km h^{-1}.[20] Vehicles traveling through the Van Nuys tunnel move at a uniform speed of ∼65 km h^{-1} with a small net downhill grade of ∼0.1% in the eastbound direction.[17,34] It has been suggested that higher NMHC/CO ratios measured by remote sensing, when compared to tunnel measurements at Van Nuys, could be due to differences in driving conditions between two nearby sampling locations.[15] Differences in NMHC/CO ratios appear to arise primarily due to engine load effects on NMHC as opposed to CO emissions. A methodological difference between approaches shown in Figure 3b is that remote sensing captures tailpipe emissions only, tunnel studies include evaporative running loss emissions,[15,18] and ambient ratios include the full range of evaporative and exhaust emissions. The lowest NMHC/CO ratio should be from remote sensing, but the magnitude is comparable to the ambient-derived ratio, highlighting the need for checking bottom-up estimates of NMHC with top-down measurements.

We did not estimate NMHC in New York City and Houston in this analysis, and we recommend caution in applying the ambient NMHC/CO ratios discussed above outside of California. Local conditions including temperature, humidity, altitude, and characteristics of vehicle fleets can all influence emissions. NMHC/CO ratios derived from remote sensing are increasing over time in Chicago, and decreasing in Denver, although in an absolute sense the emission ratios from other cities are in rough agreement with Los Angeles (Figure 3b).

CO/NO_x and $NMHC/NO_x$ Trends. Bottom-up CO and top-down derived NMHC emission results reported here are compared with NO_x emission results reported by McDonald et al.[10] for the South Coast air basin (Figure 4). In this section of

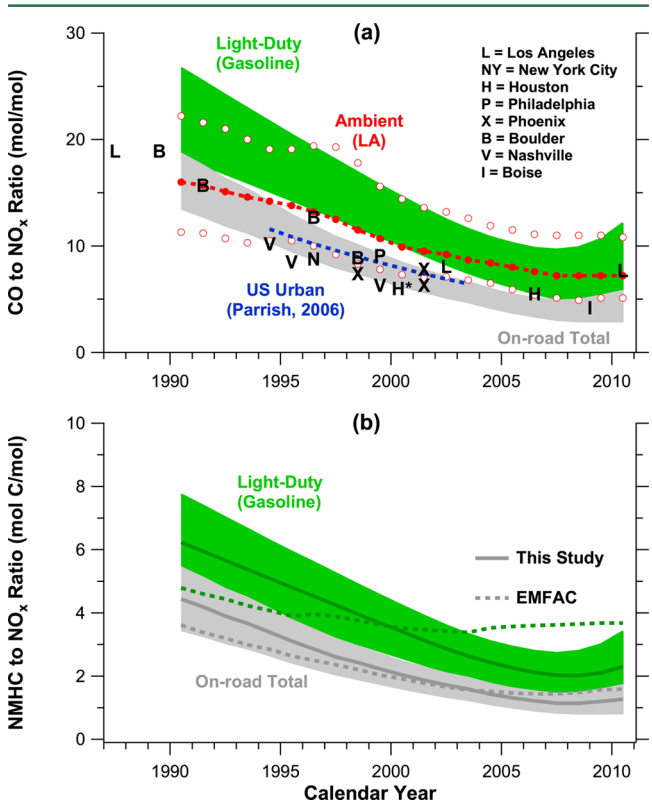


Figure 4. (a) Trends in CO/NOx emission ratios. Ratios for Los Angeles shown as bands reflect emissions from light-duty vehicles only (including running + start; upper band in green) and total emissions from all on-road vehicles (including diesel; lower band in gray). The mean, maximum, and minimum values from the ambient monitoring data are shown as a 3-year moving average for the morning commute period (0500 to 0800 PST). City abbreviations are shown for ambient literature values. (b) Trends in NMHC/NOx emission ratios. Results from this study are compared with EMFAC (including running + start). Uncertainty bands reflect 95% confidence intervals in both panels, see the Supporting Information for details. NOx emissions were taken from McDonald et al.[10]

the analysis, cold start emissions are included with running exhaust. Results are reported with NO_x in the denominator to be consistent with prior work.[12,63] Between 1990 and 2007, the bottom-up CO/NO_x emissions ratio from on-road vehicles decreased by ∼4, with slight increases after 2007. The same result is true for emissions of NMHC to NO_x, since the ambient NMHC/CO remained unchanged. The large decreases in on-road emissions of CO/NO_x and $NMHC/NO_x$ ratios are a result of two factors: (1) larger decreases in gasoline CO and NMHC emissions relative to gasoline NO_x and (2) increases in diesel NO_x emissions during the 1990s. The flattening of the CO/NO_x emissions ratio after 2002 and the uptick after 2007 appear to be a result of diminishing returns on efforts to control CO and NMHC emissions from light-duty vehicles as well as decreases in diesel NO_x emissions since 2007 due to recession-related reductions in goods movement. We expect that CO/NO_x and $NMHC/NO_x$ emission ratios for on-road motor vehicles will continue to

dx.doi.org/10.1021/es401034z | Environ. Sci. Technol. 2013, 47, 10022−10031

increase. Advanced systems for NO_x emission control are now required on new heavy-duty diesel trucks nationwide, and a California rule will further require replacement of all pre-2010 heavy-duty truck engines over the next ten years. Significant further reductions in NO_x emissions are therefore expected. In contrast, decreases in gasoline CO and NMHC emissions are not expected to be as large over the coming decade, so ratios to NO_x should increase.

Mean ambient CO/NO_x are also shown from the monitoring network in the South Coast air basin in Figure 4a. The monitoring ratio is ~25% higher than bottom-up emissions of CO to NO_x, which represent the California on-road vehicle fleet (gasoline + diesel), though the trend appears consistent. This suggests underestimation of CO and/or overestimation of NO_x emissions using a fuel-based approach. The comparison could also be complicated by the influence of start emissions as ambient monitoring ratios are for the morning commute. Additionally, spatial heterogeneity of the vehicle mix (gasoline vs diesel) could affect the comparison. In the Supporting Information, we show that the ambient ratio of CO/NO_x varies by a factor of 2 across 13 urban sites in southern California, due to spatial differences in the local mix of gasoline versus diesel vehicles (Figures S2 and S11). Areas with lower CO/NO_x ratios are more diesel-dominated on average, since even a small amount of diesel traffic can add significantly to NO_x emissions. Comparisons between basin-wide emission inventory ratios and ambient CO/NO_x or $NMHC/NO_x$ ratios derived from sites within the air basin are increasingly subject to uncertainties due to spatial and temporal variations in diesel NO_x sources. This emphasizes the need for motor vehicle emission inventories that provide high spatial and temporal resolution.

Figure 4a compares our bottom-up emission results with ambient CO/NO_x ratios reported in the literature based on measurements made by either ground-based ambient monitors or by aircraft in Los Angeles,[55,64,65] New York City,[66] Houston,[67,68] Atlanta,[13] Philadelphia,[69] Phoenix,[70] Boulder,[63] Nashville,[63] and Boise.[71] Most of the literature values for ambient CO/NO_x are for weekdays during the morning commute period. Also shown in Figure 4a is an ambient CO/NO_x trend derived by Parrish,[13] representing a US urban average from 300 monitoring sites. A key finding is that, both in absolute terms and in trend over time, measurements in other US cities appear to show consistent CO/NO_x ambient ratios and trends that are consistent with results for Los Angeles. This suggests general similarity in motor vehicle emission trends across US urban areas.

The EMFAC model (running + start) provides a different explanation for trends in CO/NO_x and $NMHC/NO_x$ for Los Angeles (Figure 4b). The trend in overall emissions (gasoline + diesel vehicles) agrees with fuel-based emission estimates of the present study, but there is a difference for light-duty vehicles. EMFAC indicates that the CO/NO_x and $NMHC/NO_x$ emission ratios for light-duty vehicles have remained constant over the period 1990–2010, while this study suggests that the corresponding emission ratios decreased through the 1990s especially and have leveled off since then. Because there was good agreement between this study and EMFAC in bottom-up CO emissions and top-down NMHC/CO ratios, the discrepancy is mainly due to NO_x emissions.[10] The ambient data also suggest a decreasing trend in CO/NO_x emission ratios from passenger vehicles, as represented by the maximum value of ambient CO/NO_x from the monitoring network shown in Figure 4a. The maximum value represents a location with a predominantly gasoline vehicle mix. As an offsetting effect in the estimation of total emissions from on-road vehicles, the EMFAC model predicts larger increases in diesel NO_x emissions as compared to a fuel-based estimate,[10] and hence why $NMHC/NO_x$ from total on-road is in better agreement with this study.

Policy Implications. In the greater Los Angeles area, peak ozone concentrations decreased by a factor of 2 between 1980 and 2000, but ozone reductions appear to have slowed greatly since 2000.[9] Slow decreases in peak ozone have also been observed in Houston and New York City since 2000. The hydrocarbon to NO_x emissions ratio is one of several important factors that determine NO_x and hydrocarbon-sensitivity regimes that govern urban and regional ozone formation.[72] Given that motor vehicles are a major source of ozone precursors in urban environments, changes in the effects of emission control strategies during the 1990s (Δ% NMHC > Δ% NO_x) versus since 2000 (Δ% NMHC ≈ Δ% NO_x) are likely to have affected atmospheric chemistry and ozone formation regimes, although other sources (e.g., industry, solvents, biogenics) of O_3 precursors may also be important. In the period 2010–2020, another shift is predicted in decadal emission changes: Δ% NMHC < Δ% NO_x, due mainly to installation of SCR systems on heavy-duty trucks.

In this study, running CO and evaporative and tailpipe NMHC emissions from gasoline-powered vehicles are shown to have decreased by almost an order of magnitude over the last twenty years using a fuel-based approach. However, decreases in emissions of these pollutants appear to be slowing down and may have leveled off. As shown, the success in control of emission from gasoline vehicles has led to greater skew in emission factor distributions, such that the highest-emitting 10% of vehicles are now responsible for the overwhelming majority of running CO (skewness = −3.9), NMHC (skewness = −4.9), and NO_x (skewness = −2.9) (Figure S9). If progress in reducing emissions is to continue, vigorous efforts will be needed to identify and repair or replace high-emitting vehicles. Fuel economy improvements are an alternative approach being pursued over the coming decade that could help to reduce overall emissions of CO and NMHC, even if fleet-averaged emission factors (in g/kg fuel) do not change. High-emitting engines can also be expected to increasingly dominate emissions from the heavy-duty truck fleet in the future, especially as the use of diesel particle filters and selective catalytic reduction (SCR) systems becomes more widespread[8] (Figure S9).

■ ASSOCIATED CONTENT

Supporting Information

Supplementary figures (S1–S11) and tables (S1–S7) referenced in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This paper is a result of work supported by the California Air Resources Board under contract 10-776. Results and discussion

presented in this paper are solely the responsibility of the authors and do not necessarily represent the views of the sponsor.

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