Title
Trends in Exhaust Emissions from In-Use California Light-Duty Vehicles, 1994-2001

Authors
Kean, Andrew J
Sawyer, Robert F
Harley, Robert A
et al.

Publication Date
2002

2002-01-1713

Trends in Exhaust Emissions from In-Use California Light-Duty Vehicles, 1994-2001

Andrew J. Kean, Robert F. Sawyer, and Robert A. Harley
University of California, Berkeley

Gary R. Kendall
Bay Area Air Quality Management District

ABSTRACT

Major efforts to control motor vehicle emissions have been made in recent years, both through improved emission control technologies and through gasoline reformulation. Our assessment of the impacts of these efforts was conducted in the San Francisco Bay Area, in lanes of a highway tunnel where heavy-duty vehicles are not allowed. This study focuses on the afternoon rush hour, during which over 4000 vehicles per hour travel uphill through the tunnel. Concentrations of CO, CO_2, NO_x, and total and speciated non-methane organic compounds (NMOC) have been measured during summers 1994-1997, 1999, and 2001. Emission factors for CO, NMOC, and NO_x decreased by factors of 2-3 over the 7-year period between 1994 and 2001, with CO and NMOC showing greater percentage reductions than NO_x. From our data, fleet turnover appears to have a greater overall impact on exhaust emissions than fuel changes for most pollutants. However, emissions of benzene have been greatly affected by changes in fuel composition.

INTRODUCTION

Motor vehicles are known to be a major source of air pollution problems throughout the world. In industrial nations, gasoline-powered vehicles are the primary source of carbon monoxide (CO) and are major sources of oxides of nitrogen (NO_x = NO + NO_2) and volatile organic compounds (VOC) [1]. Motor vehicle emissions are particularly problematic in urban areas, where the concentrations of vehicles, emissions, and people are highest.

These species can be directly hazardous to human health [2]. For example, CO bonds readily to hemoglobin, reducing the supply of oxygen to body tissues. NO is non-toxic, but it is readily oxidized to NO_2 in the atmosphere, and NO_2 is a respiratory irritant. Some VOC, such as formaldehyde, benzene, and polycyclic aromatic hydrocarbons can be toxic and/or carcinogenic. CO, NO_x, and VOC in the presence of sunlight are also promoters of the formation of tropospheric ozone, which is another respiratory irritant. While all these species are hazardous to human health at high concentrations over short time periods, less is known about their long-term toxicity or their effects on those with compromised cardiovascular systems.

Because of the human health concerns associated with vehicle-related air pollution, there has been much effort to reduce vehicle emissions over the past 30 years, particularly in California. These efforts have included both improved emission control technologies (i.e., catalytic converters, feedback control of air/fuel ratio through use of an oxygen sensor, positive crankcase ventilation, electronic fuel injection, and exhaust gas recirculation), and gasoline reformulation (i.e., modified distillation properties, addition of oxygenated species, reduction of sulfur content, etc.). Improvements to emission control devices include improving both their initial effectiveness, and their durability. The use of reformulated gasoline was mandated by the 1990 Clean Air Act Amendments for areas with severe ozone problems [3]. The National Research Council [4] has reviewed many of the numerous studies addressing the effects of reformulation of gasoline on vehicle emissions. In general, reformulated/oxygenated gasoline is expected to reduce CO and VOC emissions, while the direction of the impact on NO_x emissions will depend on the details of the reformulation. While reformulated gasoline is not required throughout California under federal regulations, the California Air Resources Board has implemented its own statewide reformulated gasoline program. Phase 1 of the California reformulated gasoline program took effect in 1992. The Reid vapor pressure (RVP) of summer gasoline was reduced from 9.0 to 7.8 psi, leaded gasoline was eliminated, and detergents to reduce engine deposits were required [5]. Phase 2 of California's program took effect in early 1996, and included eight changes to gasoline. Use of oxygenated species, reductions of benzene, total aromatic, alkene, and sulfur contents in fuel, reduced T_{50}

and T_{90} distillation temperatures, and a further decrease in the summer RVP to 7.0 psi were all required [6,7]. The program's developers anticipated a 17% reduction in VOC, 11% reduction in both CO and NO_x, and a 30% reduction in toxic air contaminant emissions due to the use of phase 2 gasoline in its first year [7].

Typically, emissions from motor vehicles are determined from tests performed on chassis dynamometers. While laboratory dynamometer testing has provided many useful insights into vehicle emissions and fuel effects, the numbers of vehicles tested in laboratory studies are small, and these studies usually emphasize relatively new vehicles having low emissions. The contributions of deteriorated and malfunctioning vehicles to total fleet emissions are difficult to capture in laboratory tests, due to the skewed distribution of emissions across the fleet. To complement dynamometer studies, it is important to assess the changes of emissions due to gasoline reformulation and improved emission control technologies during vehicle operation on-road.

The objective of this study was to determine the impact of efforts to reduce emissions from in-use automobiles in California between 1994 and 2001. New data for summer 2001 are reported here, together with previous data for summers 1994-1997 [8,9] and summer 1999 [10].

EXPERIMENTAL SECTION

FIELD SAMPLING SITE

Vehicle emissions were measured at the Caldecott tunnel, which is located near Berkeley in the San Francisco Bay area of California. It is a highway tunnel on state highway 24 which connects Berkeley, Oakland, and San Francisco with the inland communities of Contra Costa County. The tunnel consists of three bores, each with two traffic lanes. The center bore was the sampling location for this study because heavy-duty vehicles are restricted from using these lanes. The direction of traffic through this bore is changed to accommodate the dominant rush-hour direction of traffic flow (westbound towards Berkeley in the morning and eastbound in the afternoon/evening). The tunnel is roughly 1000 m long and has a grade of ~4% with eastbound traffic heading uphill. Ventilation is accomplished through use of adjustable speed fans situated at both ends of the tunnel. During this investigation, these fans were turned off, so there was only longitudinal ventilation induced by the flow of traffic and by prevailing winds. A diagram of the tunnel can be found in Kirchstetter et al. [11].

SAMPLING TIMES

For this study, we have focused on weekday afternoon rush-hour periods (4-6 pm PDT), when traffic is headed eastbound and uphill. Sampling at the Caldecott tunnel took place during summers in 1994-1997, 1999, and 2001. Approximately 10 days of sampling were performed each year to obtain representative information about emissions for that year.

POLLUTANT MEASUREMENTS

Fleet-averaged emissions of CO, CO_2, NO_x, and speciated VOC were determined from the background-corrected pollutant concentrations at the tunnel exit (east end of tunnel). Subtracting background concentrations from measured concentrations at the tunnel exit results in the amount of pollution that was emitted while vehicles traveled through the tunnel. In 1994-1997, the background pollutant concentrations were determined from sampling in the fresh air outside of the tunnel at the tunnel exit. For 1999 and 2001, the experimental design was improved by measuring background pollutant concentrations at the tunnel entrance (i.e., west end of tunnel during afternoon hours). During all years, CO and CO_2 concentrations were measured continuously with infrared absorption gas filter correlation spectrometers. NO_x was also measured continuously using chemiluminescent analyzers. Calibration of these analyzers was performed at least every other day, using NIST-traceable gas standards. Total and speciated VOC concentrations were obtained from laboratory analysis of two-hour integrated air samples collected in evacuated stainless steel canisters. Analysis was performed by the Bay Area Air Quality Management District using a gas chromatograph with a flame ionization detector and photoionization detector [9].

TRAFFIC MONITORING

The fleet of vehicles traveling through the center bore of the Caldecott tunnel was characterized during all days on which pollutant data were obtained. The types and total volume of vehicles through the tunnel were determined from visual counts. Traffic was categorized into 3 categories: cars, light-duty trucks, and heavy-duty trucks. The age distribution of the fleet was determined from license plate surveys performed in 1995-1997 and 2001. In 1995-1997, the speed of vehicles through the tunnel was determined by repeatedly following traffic through the tunnel with a chase car. In 2001, average vehicle speed was determined using video cameras with synchronized clocks filming at both ends of the tunnel. By identifying the same vehicle on both tapes, the time needed for that vehicle to travel through the tunnel was determined. An instrumented vehicle that logged speed at 1-second intervals completed 26 trips through the tunnel in 1996 to measure the speed characteristics as a function of position inside the tunnel.

GASOLINE SAMPLING AND ANALYSIS

Each summer, gasoline samples from San Francisco and Concord, CA were collected and analyzed by Southwest Research Institute. Approximately 30 samples were obtained from major brand service stations each year in July and August. Measured fuel properties included density, RVP, sulfur content,

speciation by hydrocarbon class, oxygen content, and distillation properties.

RESULTS AND DISCUSSION

GASOLINE PROPERTIES

Average fuel properties determined from the gasoline sampling discussed above are presented in Table 1. As expected, there were major changes in fuel characteristics between 1995 and 1996, corresponding to the introduction of California phase 2 reformulated gasoline. Based on these fuel changes, one might expect lower evaporative emissions (due to reduced RVP), lower CO and VOC emissions (due to oxygenate), reduced atmospheric reactivity of VOC emissions (due to alkene and aromatic reduction), reduced benzene emissions (due to reduced benzene and total aromatic content), enhanced catalytic converter performance (from reduction in sulfur content), and a reduction in fleet fuel economy (due to reduced gasoline density and the lower energy content of MTBE compared to hydrocarbons found in gasoline). After 1996, the use of MTBE in gasoline decreased somewhat, as refiners began using more of other oxygenates such as ethanol and tert-amyl methyl ether (TAME), and gasoline formulations that did not contain oxygenates. Due to tighter requirements for gasoline, there was also less brand-to-brand variability in gasoline sulfur and alkene contents after 1995.

TRAFFIC CHARACTERISTICS

The bore of the Caldecott tunnel used for this investigation is not accessible via any nearby on-ramps, so vehicles traveling through this bore have been on the highway for sufficient time to reach a hot stabilized operating mode. As a result, the measurements presented here are not influenced by cold-start emissions. There is a traffic bottleneck upstream of the tunnel, after which traffic gradually accelerates to 40-65 km h^{-1} (25-40 mph) by the tunnel entrance. Vehicles continue to accelerate gradually through the tunnel, and reach 60-80 km h^{-1} (40-50) mph by the tunnel exit. Speed as a function of position in the tunnel as measured by an instrumented vehicle is presented elsewhere [8]. Year to year variability in traffic volume and speed is small, because the bottleneck upstream of the tunnel has effectively “choked” the traffic flow. This is demonstrated in the histogram given in Figure 1, which shows the fraction of average speeds observed in various speed ranges for 1995 to 2001. The average vehicle speed is between 59 and 63 km h^{-1} (37 and 39 mph) for all years. As a result, changes in emissions from one year to the next are not due to changing driving conditions at the tunnel.

Traffic volume through the tunnel has been 4200 ± 200 vehicles per hour for all years of this study. Traffic consisted almost entirely of light-duty vehicles due to the time of day (afternoon commuter peak) and the requirement that heavy-duty vehicles stay out of the center bore. In 1994, the fleet of vehicles sampled included 31% light-duty trucks. This value has been rising gradually, and reached 38% in 2001 due to the increasing popularity of pickups and SUVs. The contribution of heavy-duty trucks was 0.3% or less for all years. The mean age of the vehicle fleet is ~6 years for all years studied.

EMISSION TRENDS

Background corrected concentrations of CO, CO_2, NO_x, and speciated VOC were used to determine light-duty vehicle emission factors using a carbon balance method. The fuel-based emission factors (mass of pollutant emitted per volume of gasoline consumed) were calculated using the following equation

$$E_p = \left(\frac{\Delta[P]}{\Delta[CO_2] + \Delta[CO]} \right) \left(\frac{MW_p}{MW_c} \right) w_c \rho_f \qquad (1)$$

where $\Delta[P]$ is the increase in concentration of pollutant P measured between tunnel inlet and outlet, MW_P is the molecular weight of pollutant P (g mol^{-1}), MW_C = 12 g mol^{-1}, w_c = 0.85 is the weight fraction of carbon in gasoline, and gasoline density ρ_f = 740 g L^{-1} (w_c = 0.87 and ρ_f = 760 g L^{-1} before 1996). VOC have been ignored in the denominator of eq. 1; the hydrocarbon contribution to total carbon concentrations in the tunnel is known to be negligible compared to CO_2. Emission factors determined from summer 2001 measurements are: 4.1 ± 0.1 g L^{-1} for NO_x as NO_2 (i.e., using a molecular weight of 46 g mol^{-1}), 32 ± 1 g L^{-1} for CO, and 1.3 ± 0.1 g L^{-1} for non-methane organic compounds (NMOC). The uncertainty bounds provide a 95% confidence interval for the mean based on run-to-run variability in the results over 9 days of sampling.

As shown in Figures 2-4, emissions of NO_x, CO, and NMOC have declined significantly at this site from 1994 to 2001. Since 1994, emissions factors have decreased 49 ± 4% for NO_x, 62 ± 5% for CO, and 67 ± 7% for NMOC. Note that the major fuel change in California occurred between 1995 and 1996; since 1996, gasoline properties have not changed dramatically. Emission reductions since 1996 can be attributed primarily to fleet turnover; new, cleaner cars replacing older, more polluting vehicles. Over the period 1994-2001, gasoline sales for highway use in California have grown 13% due to the growth in the number of vehicles and distance traveled per vehicle [12,13]. Therefore growth in vehicle usage has been more than offset by emission factor reductions during this period. Because the fuel economy of the light-duty fleet remained about the same from 1994 to 2001 [14], distance-based emission factors (mass of pollutant per distance traveled) have decreased by similar percentages to those stated above.

Examining Figure 2, we see a fairly uniform decrease in NO_x emission factors over time, except

between 1996 and 1997 when there was little change in the measured emission factor. In Figures 3 and 4, we see that the rates of emission reductions for CO and NMOC are greatest in the early years of this study, though significant reductions are still being observed. Assessing the contribution of gasoline reformulation to these trends is confounded by the fact that refiners may have begun meeting some phase 2 reformulated gasoline specifications prior to its required introduction in 1996. Nevertheless, the contribution of turnover in the vehicle fleet to the overall reductions between 1994 and 2001 is greater than that of gasoline reformulation, which should be apparent as a larger reduction between 1995 and 1996, compared to what would be expected based on long-term trends.

The trend in the benzene emission factor is shown in Figure 5. Between 1994 and 2001, the benzene emission factor decreased by 82 ± 12%. In contrast to the trends discussed previously, the impact of gasoline reformulation on benzene emissions is clear. A large reduction is observed between 1995 and 1996, with only modest reductions since 1996. Phase 2 reformulated gasoline contains less benzene and other aromatic hydrocarbons in the fuel, which are precursors to benzene. Trends for other NMOC will be presented in a future publication.

This study was designed to assess the trends over time in light-duty vehicle emissions under similar operating conditions. Because this study focuses on vehicles in a warmed-up operating mode driving on a highway, our results may not represent emission trends for other driving conditions or emission modes (e.g., cold start emissions, evaporative emissions, stop-and-go driving, idling emissions, etc.).

CONCLUSIONS

Reductions of ~50-70% in CO, NO_x, and NMOC emission factors were observed over a 7-year period, with CO and NMOC showing greater percentage reductions than NO_x. These reductions include effects of both vehicle fleet turnover and gasoline reformulation. From our data for 1994-2001, fleet turnover appears to have had a greater overall impact on emissions than fuel changes for most pollutants. The reduction in emissions due to the replacement of old vehicles with less polluting, new vehicles is expected to continue. In addition, the use of MTBE and other ethers in gasoline is currently planned to be phased out in California by the end of 2002. Therefore further changes in vehicle emissions are expected in future years.

ACKNOWLEDGMENTS

This research was supported by the U.S. Department of Transportation and the CA Department of Transportation through the University of California Transportation Center. Major in-kind support contributions to this research were provided by the Bay Area Air Quality Management District. We thank Rory McArthur and David Kohler of Chevron, and the Caltrans staff at the Caldecott tunnel for their support.

REFERENCES

1. Urban Traffic Pollution; edited by Dietrich Schwela and Olivier Zali, World Health Organisation; E & FN Spon, London, England, 1999.
2. Automobiles and Pollution; Paul Degobert; Society of Automotive Engineers, Inc.; Warrendale, PA, 1995.
3. Code of Federal Regulations, Title 40, Part 80.
4. Ozone-Forming Potential of Reformulated Gasoline; National Research Council; National Academy Press, Washington, D.C., 1999.
5. Reformulated Gasoline: proposed phase 1 specifications. California Air Resources Board, Sacramento, CA, 1990
6. Proposed regulations for California phase 2 reformulated gasoline. California Air Resources Board, Sacramento, CA, 1991.
7. Proposed amendments to the California phase 2 reformulated gasoline regulations, including amendments providing for the use of a predictive model. California Air Resources Board, Sacramento, CA 1994.
8. Kirchstetter, T.W.; Singer, B.C.; Harley, R.A.; Kendall, G.R.; Traverse, M.; Environ. Sci. Technol. 1999, 33, 318-328.
9. Kirchstetter, T.W.; Singer, B.C.; Harley, R.A.; Kendall, G.R.; Hesson, J.M..; Environ. Sci. Technol. 1999, 33, 329-336.
10. Kean, A.J.; Harley, R.A.; Littlejohn, D.; Kendall, G.R.; Environ. Sci. Technol. 2000, 34, 3535-3539.
11. Kirchstetter, T.W.; Singer, B.C.; Harley, R.A.; Kendall, G.R.; Chan, W.; Environ. Sci. Technol. 1996, 30, 2843-2849.
12. Highway Statistics 1994; Office of Highway Policy Information; Federal Highway Administration; National Technical Information Service; Springfield, VA, 1995.
13. Highway Statistics 2000; Office of Highway Policy Information; Federal Highway Administration; National Technical Information Service; Springfield, VA, 2001.
14. Transportation Energy Data Book: Edition 21; Stacy C. Davis, Oak Ridge National Laboratory; Oakridge, TN, 2001.

Table 1. Summary of San Francisco Bay Area gasoline properties[a] (mean ± 1σ) during summers 1994-2001.

gasoline property	1994	1995	1996	1997	1998	1999	2000	2001
RVP[b] (kPa)	51 ± 1	51 ± 1	48 ± 1	49 ± 1	48 ± 1	49 ± 1	49 ± 1	49 ± 1
(psi)	7.4 ± 0.1	7.4 ± 0.1	7.0 ± 0.1	7.1 ± 0.1	7.0 ± 0.1	7.1 ± 0.1	7.0 ± 0.1	7.0 ± 0.1
sulfur (ppmw)	131 ± 41	81 ± 36	16 ± 9	12 ± 11	16 ± 8	10 ± 8	9 ± 2	10 ± 4
oxygen (wt%)	0.5 ± 0.3	0.2 ± 0.2	2.0 ± 0.3	1.6 ± 0.6	1.6 ± 0.6	1.7 ± 0.6	1.8 ± 0.3	1.5 ± 0.9
MTBE[c] (vol%)	2.7 ± 1.7	1.0 ± 0.9	10.7 ± 1.7	8.2 ± 3.7	7.4 ± 4.3	8.0 ± 4.0	7.8 ± 4.3	5.9 ± 5.6
TAME[d] (vol%)	N/A	N/A	N/A	N/A	0.5 ± 0.8	0.1 ± 0.1	0.1 ± 0.8	0.2 ± 0.5
ethanol (vol%)	N/A	N/A	N/A	N/A	0.5 ± 1.6	0.7 ± 2.1	0.0 ± 0.0	0.5 ± 1.3
alkane (vol%)	57.4 ± 4.8	56.6 ± 5.1	62.6 ± 2.5	65.4 ± 3.7	64 ± 3	66 ± 5	63 ± 5	65 ± 4
alkene (vol%)	7.9 ± 4.4	8.8 ± 3.5	3.3 ± 0.9	3.4 ± 1.2	3.6 ± 1.2	3.2 ± 2.1	4.5 ± 1.8	4.3 ± 1.7
aromatic (vol%)	31.9 ± 2.1	33.7 ± 3.3	23.5 ± 1.4	22.7 ± 1.4	24 ± 2	22 ± 3	25 ± 3	24 ± 2
benzene (vol%)	1.6 ± 0.4	1.5 ± 0.4	0.4 ± 0.1	0.4 ± 0.1	0.51 ± 0.08	0.52 ± 0.08	0.55 ± 0.07	0.48 ± 0.06
T_{50} (°C)	101 ± 4	103 ± 2	93.8 ± 2.2	93.3 ± 1.7	93.3 ± 1.7	93.3 ± 1.1	94.7 ± 2.7	94.4 ± 1.1
(°F)	214 ± 8	218 ± 4	199 ± 4	200 ± 3	200 ± 3	200 ± 2	202 ± 5	202 ± 2
T_{90} (°C)	168 ± 4	172 ± 4	149 ± 2	148 ± 3	151 ± 4	152 ± 6	151 ± 4	149 ± 2
(°F)	334 ± 8	341 ± 8	300 ± 4	299 ± 6	304 ± 8	306 ± 10	305 ± 7	301 ± 3
density (g L^{-1})	761 ± 8	760 ± 4	743 ± 2	741 ± 5	746 ± 5	742 ± 6	742 ± 6	743 ± 7

[a]Sales-weighted average of regular, mid-grade and premium gasoline. Service station samples collected during July in Concord and August in San Francisco, and analyzed by Southwest Research Institute. [b]RVP is Reid Vapor Pressure. [c]MTBE is methyl tertiary butyl ether. [d]TAME is tert-amyl methyl ether.

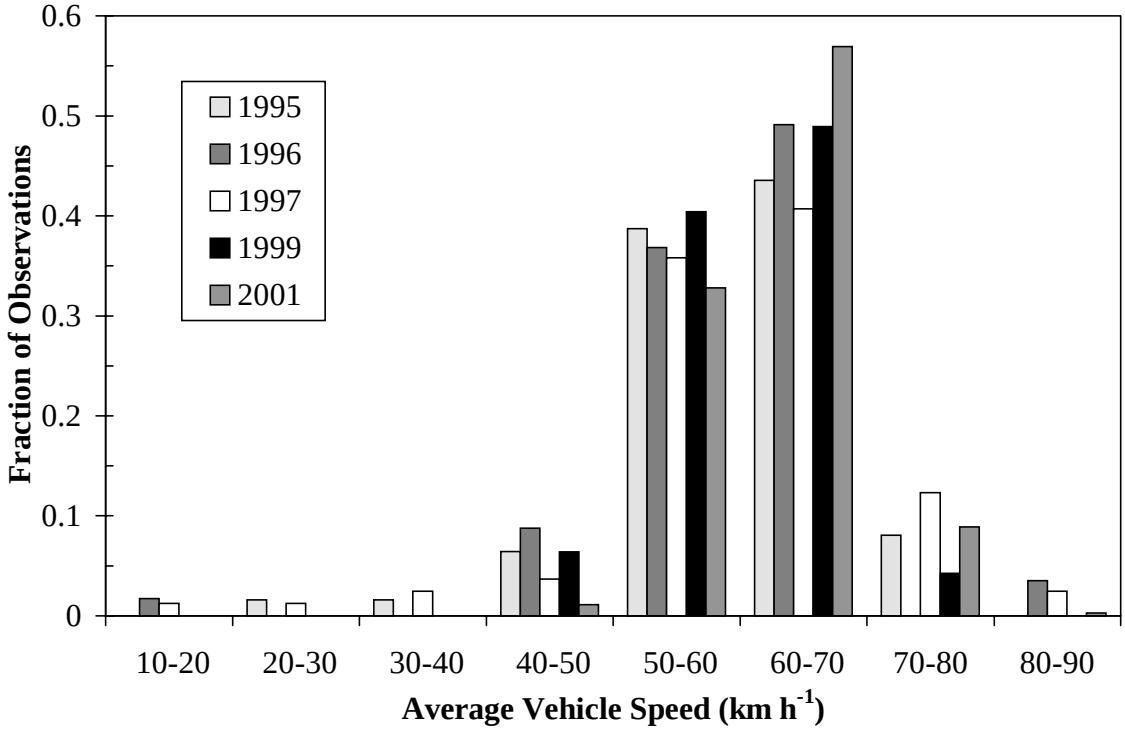

Figure 1. Histogram of average vehicle speeds measured at the Caldecott tunnel from 4 to 6 pm PDT. Speed data was not measured in 1994.

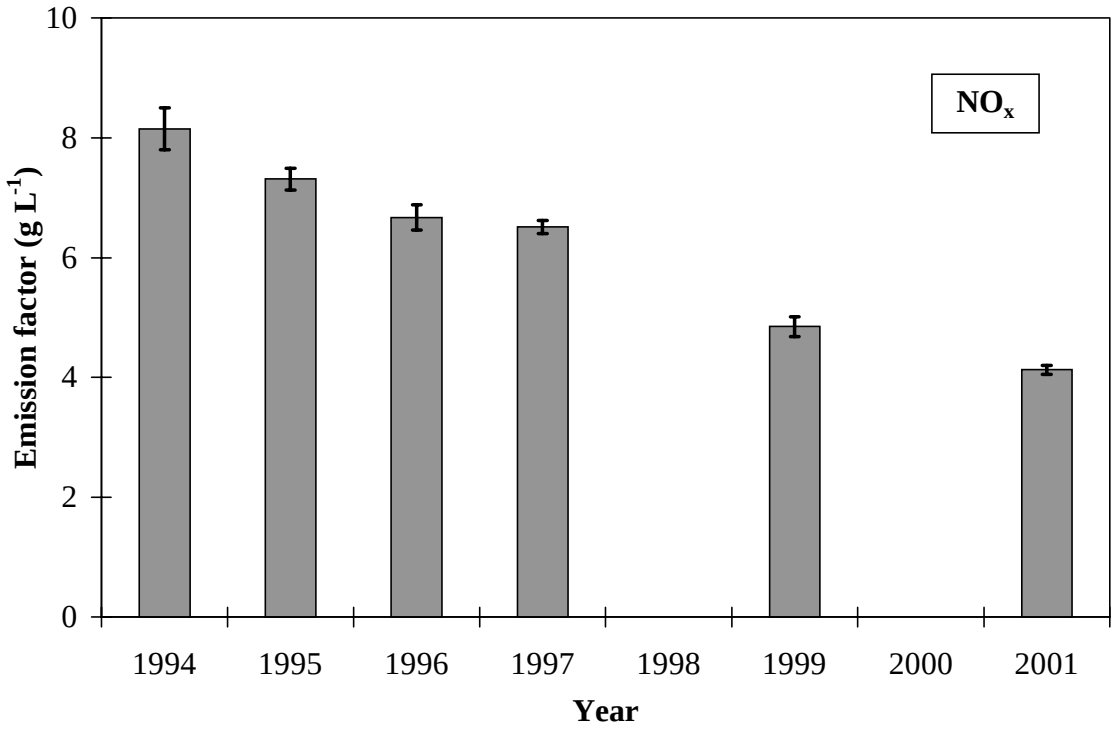

Figure 2. Average (± 95% C.I.) light-duty emission factor for NO_x measured during summers 1994-2001. No measurements were made in 1998 and 2000. The emission factors are expressed per unit volume of fuel burned. California reformulated gasoline phase 2 took effect in early 1996.

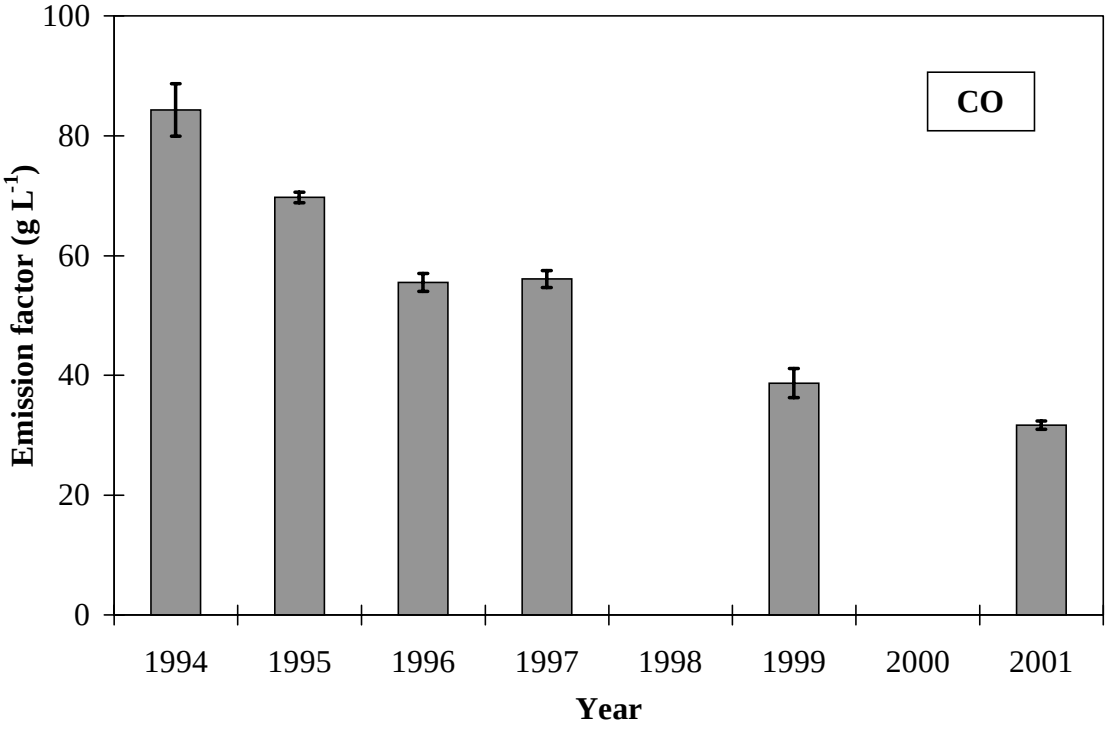

Figure 3. Average (± 95% C.I.) light-duty emission factor for CO measured during summers 1994-2001.

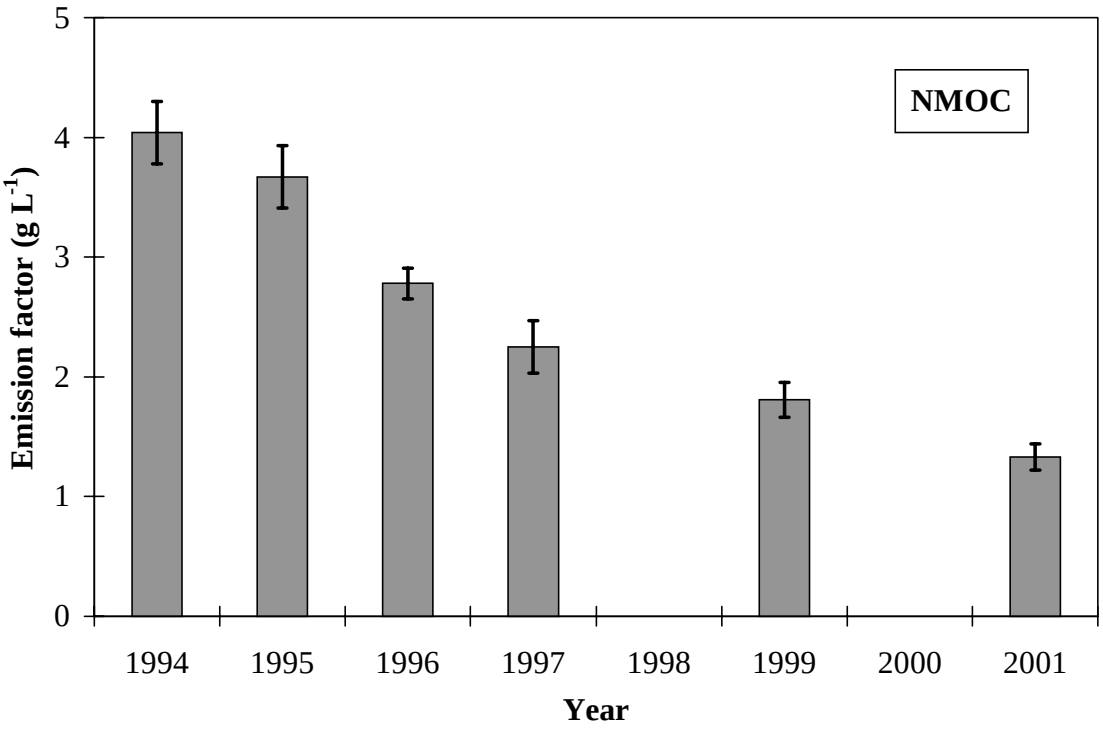

Figure 4. Average (± 95% C.I.) light-duty emission factor for NMOC measured during summers 1994-2001.

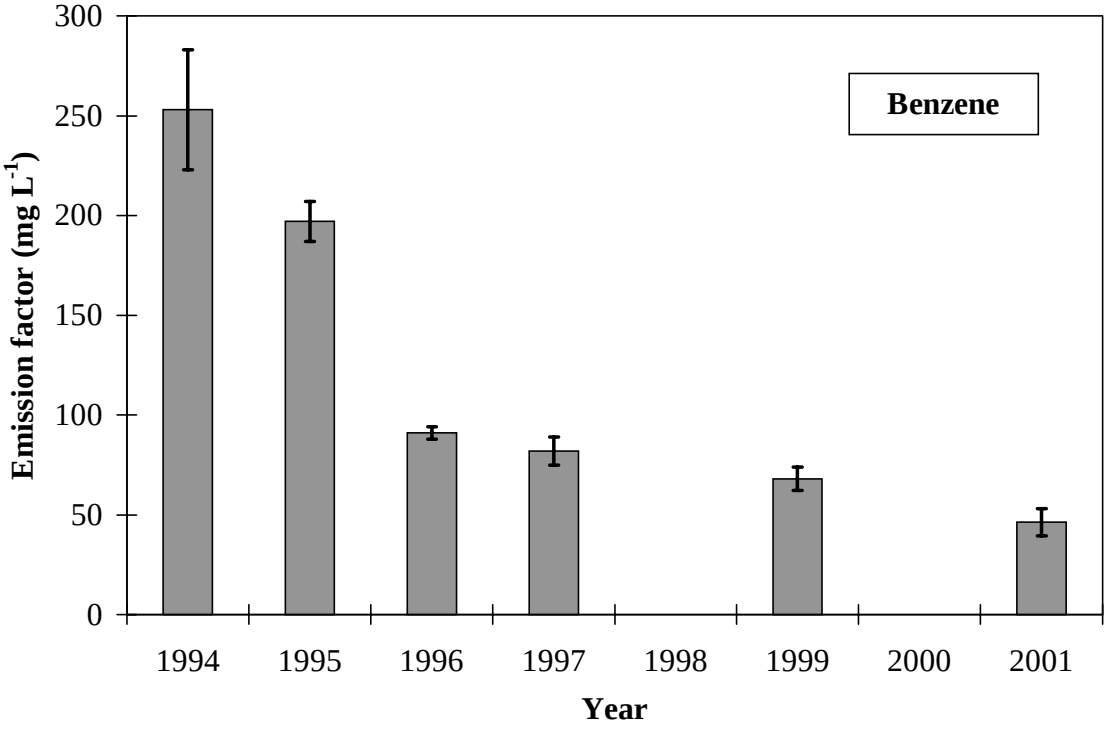

Figure 5. Average (± 95% C.I.) light-duty emission factor for benzene measured during summers 1994-2001.