

# UC Berkeley

## Earlier Faculty Research

### Title

On-Road Measurement of Ammonia and Other Motor Vehicle Exhaust Emissions

### Permalink

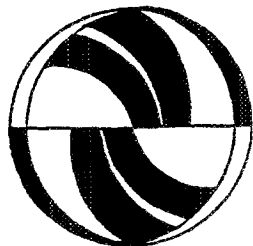
<https://escholarship.org/uc/item/9gf1q2x3>

### Authors

Kean, Andrew J.  
Harley, Robert A  
Littleton, David  
[et al.](#)

### Publication Date

2001



**On-Road Measurement of Ammonia and  
Other Motor Vehicle Exhaust Emissions**

Andrew J Kean  
Robert A Harley  
David Littlejohn  
Gary R Kendall

Reprint  
UCTC No 491

**The University of California  
Transportation Center**

University of California  
Berkeley, CA 94720

**The University of California  
Transportation Center**

The University of California Transportation Center (UCTC) is one of ten regional units mandated by Congress and established in Fall 1988 to support research, education, and training in surface transportation. The UC Center serves federal Region IX and is supported by matching grants from the U.S. Department of Transportation, the California Department of Transportation (Caltrans), and the University.

Based on the Berkeley Campus, UCTC draws upon existing capabilities and resources of the Institutes of Transportation Studies at Berkeley, Davis, Irvine, and Los Angeles; the Institute of Urban and Regional Development at Berkeley, and several academic departments at the Berkeley, Davis, Irvine, and Los Angeles campuses. Faculty and students on other University of California campuses may participate in

Center activities. Researchers at other universities within the region also have opportunities to collaborate with UC faculty on selected studies.

UCTC's educational and research programs are focused on strategic planning for improving metropolitan accessibility, with emphasis on the special conditions in Region IX. Particular attention is directed to strategies for using transportation as an instrument of economic development, while also accommodating to the region's persistent expansion and while maintaining and enhancing the quality of life there.

The Center distributes reports on its research in working papers, monographs, and in reprints of published articles. It also publishes *Access*, a magazine presenting summaries of selected studies. For a list of publications in print, write to the address below.



University of California  
Transportation Center

108 Naval Architecture Building  
Berkeley, California 94720  
Tel. 510/643-7378  
FAX. 510/643-5456

**DISCLAIMER**

The contents of this report reflect the views of the authors, who are responsible for the facts and the accuracy of the information presented herein. This document is disseminated under the sponsorship of the Department of Transportation, University Transportation Centers Program, in the interest of information exchange. The U.S. Government assumes no liability for the contents or use thereof.

The contents of this report reflect the views of the author who is responsible for the facts and accuracy of the data presented herein. The contents do not necessarily reflect the official views or policies of the State of California or the U.S. Department of Transportation. This report does not constitute a standard, specification, or regulation.

# **On-Road Measurement of Ammonia and Other Motor Vehicle Exhaust Emissions**

**Andrew J. Kean  
Robert A. Harley**

Department of Mechanical Engineering and  
Department of Civil and Environmental Engineering  
University of California  
Berkeley, CA 94720

**David Littlejohn**

Environmental Energy Technologies Division  
Lawrence Berkeley National Laboratory  
Berkeley, CA 94720

**Gary A. Kendall**

Technical Services Division  
Bay Area Air Quality Management District  
San Francisco, CA 94109

Reprinted from  
*Environmental Science & Technology*  
Vol 34, no 17, pp 3535-3539 (2000)

UCTC No 491

The University of California Transportation Center  
University of California at Berkeley

# On-Road Measurement of Ammonia and Other Motor Vehicle Exhaust Emissions

ANDREW J. KEAN<sup>†</sup> AND  
ROBERT A. HARLEY<sup>\*,\*</sup>

*Department of Mechanical Engineering and Department of  
Civil and Environmental Engineering, University of  
California, Berkeley, California 94720*

DAVID LITTLEJOHN

*Environmental Energy Technologies Division, Lawrence  
Berkeley National Laboratory, Berkeley, California 94720*

GARY R. KENDALL

*Technical Services Division, Bay Area Air Quality  
Management District, 939 Ellis Street,  
San Francisco, California 94109*

Ammonia is the primary alkaline gas in the atmosphere and contributes to fine particle mass, visibility problems, and dry and wet deposition. The objective of this research was to measure ammonia and other exhaust emissions from a large sample of on-road vehicles using California phase 2 reformulated gasoline with low sulfur content (~10 ppm by weight). Vehicle emissions of ammonia, NO<sub>x</sub>, CO, and CO<sub>2</sub> were measured in the center bore of a San Francisco Bay area highway tunnel on eight 2-h afternoon sampling periods during summer 1999. Ammonia concentrations were divided by total carbon (mainly CO<sub>2</sub>) concentrations to compute an emission factor of 475 ± 29 mg L<sup>-1</sup> (95% C.I.). The molar ratio of nitrogen emitted in the tunnel in the form of ammonia to that emitted in the form of NO<sub>x</sub> was 0.27 ± 0.01. Emissions of NO<sub>x</sub> and CO have been measured at this tunnel sampling location since 1994. From 1994 to 1999, emissions decreased by 41 ± 4% for NO<sub>x</sub> and 54 ± 6% for CO. These reductions include the impacts of turnover in the vehicle fleet and the use of reformulated gasoline. Between 1997 and 1999, when fuel properties did not change significantly, emissions of NO<sub>x</sub> and CO decreased by 26 ± 2% and 31 ± 3%, respectively. While use of three-way catalytic converters has contributed to decreases in NO<sub>x</sub> and CO emissions, their use, in combination with fuel-rich engine operation, is the likely cause of the ammonia emissions from motor vehicles observed during this study.

## Introduction

Motor vehicle emissions contribute significantly to air pollution problems on local, regional, and national scales (1). Despite increasing numbers of vehicles on the road and increasing vehicle travel, progress has been made in lowering

vehicle emissions in the United States (2). Catalytic converters play an important role in controlling emissions by oxidizing carbon monoxide (CO) and volatile organic compounds (VOC) and reducing oxides of nitrogen (NO<sub>x</sub>) present in vehicle exhaust. An unintended consequence of the use of three-way catalytic converters has been increased emissions of nitrous oxide (3, 4) and ammonia (5, 6).

Ammonia (NH<sub>3</sub>) is the third most abundant nitrogen-containing compound, after N<sub>2</sub> and N<sub>2</sub>O, and is the primary alkaline gas in the atmosphere (7). An important role of ammonia in the atmosphere is neutralizing compounds such as nitric and sulfuric acids, formed as products of the atmospheric oxidation of NO<sub>x</sub> and SO<sub>2</sub> emissions, respectively. Ammonium nitrate and sulfate contribute significantly to fine particle mass and visibility problems (8, 9). Ammonia, along with NO<sub>x</sub> and SO<sub>2</sub>, is one of the primary pollutants involved with acidifying deposition (7, 10). The transport of nitric acid is aided by the formation and condensation of ammonium nitrate on accumulation mode particles. In addition, dry and wet deposition of ammonia and ammonium is an important source of nutrients to some ecosystems (7, 10).

Major sources of ammonia emissions identified in past assessments include animal waste, biological processes in soils, ammonia-based chemical fertilizers, biomass burning, and sewage treatment plants (11, 12). Most internal combustion processes also produce ammonia, though the amount of ammonia produced is typically small compared to the other sources mentioned above (11-13).

Ammonia emissions from catalyst equipped vehicles have been shown in laboratory dynamometer studies to be dramatically higher than for precatalyst vehicles (5, 14, 15). The production of ammonia can be increased further if the engine runs fuel-rich, because that condition favors reducing processes on the catalyst surface (5, 14, 15). On-road measurements of ammonia emissions from motor vehicles have been reported by three groups of investigators. Pierson and Brachaczek (16) determined the on-road emission rate of ammonia from gasoline-powered vehicles to be 1.3 ± 3.5 mg km<sup>-1</sup> in the Allegheny Mountain Tunnel in Pennsylvania. In 1981, when these measurements were made, less than 10% of vehicles were equipped with three-way catalytic converters. Moeckh et al. (17) reported ammonia emissions of 15 ± 4 mg km<sup>-1</sup> for vehicles traveling through the Gubrist Tunnel in Switzerland in 1995. This vehicle fleet was made up of mostly light-duty vehicles but also included 4-4% large trucks. Fraser and Cass (6) made measurements during 1993 in the Sherman Way tunnel in Van Nuys, CA, and found an average emission factor of 380 mg L<sup>-1</sup> (equivalent to about 60 mg km<sup>-1</sup>) for a fleet in which 76% of the fuel was consumed by three-way catalyst equipped vehicles. These results suggest that on-road vehicle ammonia emissions increased significantly following the introduction of three-way catalytic converters. Furthermore, turnover in the on-road vehicle fleet continues to replace older vehicles with new three-way catalyst-equipped vehicles. Major reformulation of gasoline that occurred in California in 1996 (18) may have also affected ammonia emissions, for example because fuel sulfur levels decreased. Sulfur is known to adversely affect catalytic converter efficiency for regulated pollutants (19), but its impact on ammonia emissions is uncertain. In laboratory flow reactors, it has been shown that decreasing the SO<sub>2</sub> concentration in a simulated exhaust stream increases ammonia production over a catalyst (20, 21). On the other hand, a recent chassis dynamometer study of two vehicles

\* Corresponding author phone (510)643-9168, fax (510)642-7483; e-mail: harley@ce.berkeley.edu.

<sup>†</sup> Department of Mechanical Engineering, University of California.

<sup>‡</sup> Department of Civil and Environmental Engineering, University of California.

found that decreasing the fuel sulfur content caused lower ammonia emissions for one vehicle and had little effect on ammonia emissions for the second vehicle (22).

The objective of this study was to measure ammonia and other exhaust emissions from a large sample of on-road vehicles using California reformulated gasoline.

## Experimental Section

**Field Sampling Site.** Vehicle emissions were measured in the Caldecott Tunnel, which is situated on California state highway 24 near Berkeley in the San Francisco Bay area. The tunnel connects the inland communities of Contra Costa County with Oakland, Berkeley, and San Francisco. The tunnel is 1100 m long and has three traffic bores of two lanes each. The center bore was used as the sampling location for this study as heavy-duty vehicles are restricted from using these lanes. The tunnel grade is 4.2% with eastbound traffic headed uphill. Ventilation in the tunnel is accomplished with adjustable speed fans located at each end of the tunnel. During this study, the ventilation fans were turned off at both ends of the tunnel, so there was only longitudinal airflow caused by the flow of traffic through the tunnel and prevailing winds. A diagram of the tunnel can be found in Kirchstetter et al. (23)

**Pollutant Measurements.** Pollutant concentrations were measured at sampling points located 11 m from the entrance (west end) and about 50 m from the exit (east end) inside the center bore of the tunnel on 8 weekdays between July 21 and August 5, 1999. Measurements were made during the afternoon rush hour between 1600 and 1800 h PDT, when traffic was traveling eastbound and uphill. Pollutants that were measured included ammonia,  $\text{NO}_x$ , CO,  $\text{CO}_2$ , and speciated VOC. Results for VOC will be presented elsewhere.

Ammonia sampling was performed using glass annular denuders (University Research Glassware, Chapel Hill, NC; model 2000-30B). Denuders were coated with a solution of 4% w/v citric acid and 2% v/v glycine mixture in methanol and dried with nitrogen. Three annular denuders in series were used for sampling at the east end (exit) of the tunnel. The primary denuder was expected to collect gas-phase ammonia present in the sample air stream. The second denuder was used to check for breakthrough, and the final denuder was used as a field blank. Two annular denuders in series were used at the west end (entrance) of the tunnel. The concentration of ammonia at the tunnel entrance was expected to be low, so no breakthrough of ammonia was anticipated. A 24 cm long Teflon sampling tube (1.7 cm ID) and a fluorinated ethylene-propylene copolymer-coated cyclone were placed upstream of the denuders in the sampling train. Samples were collected over 2 h periods at a constant nominal flow rate of 10 LPM. At this flow rate, the cyclone cutpoint was approximately 2.5  $\mu\text{m}$ .

Following sampling, the denuders were extracted with deionized water and analyzed for ammonium using an ion chromatograph (Dionex, Sunnyvale, CA, model 2010i) with a Wescan conductivity detector (Alltech, Deerfield, IL; model 269-004) and Dionex cation micromembrane suppressor column. The eluent and regenerant used in the analyses were 0.004 M HCl and 0.05 M KOH, respectively. The amount of deionized water used to extract and dilute the samples varied between 5 and 100 mL to maintain the sample in the linear range of the ion chromatograph, which was 0–200  $\mu\text{M}$  of ammonium ion. The detection limit of the system used was approximately 25  $\mu\text{M}$ , which corresponds to ~3 ppb of ammonia in a 2-h integrated air sample collected at 10 LPM when the minimum amount (5 mL) of deionized water was used to extract the denuder samples. Peak heights were compared with a five point calibration curve to determine molar concentration of ammonium ion. At both tunnel

entrance and exit, the amount of ammonia present on the last denuder present in series (field blank) was subtracted from ammonia measured on the primary denuder as described below, this adjustment was minor at the tunnel exit where ammonia concentrations were high. Ammonia concentrations determined in  $\mu\text{g m}^{-3}$  were converted to parts per billion by volume (ppb) assuming a constant air temperature of 25 °C and 1 atm pressure.

$\text{NO}_x$  concentrations inside the tunnel were monitored continuously using chemiluminescent analyzers (Thermo Environmental Instruments (TECO), Franklin, MA, model 42 at the tunnel exit and model 14A at the tunnel entrance). Similarly, CO concentrations were monitored continuously at both ends of the tunnel by infrared absorption using gas filter correlation spectrometers (TECO model 48). Pollutant concentrations were recorded as 5-min averages using dataloggers (Environmental Systems Corporation, Knoxville, TN; model 8800). Calibration checks of the gas analyzers were performed daily using  $\pm 1\%$  NIST traceable gas mixtures. The Bay Area Air Quality Management District performed audits of the  $\text{NO}_x$  and CO analyzers used at both ends of the tunnel. The  $\text{NO}_x$  analyzer at the exit of the tunnel was accurate within  $\pm 3\%$ , and the  $\text{NO}_x$  analyzer at the entrance read 9% low. Both tunnel CO analyzers were accurate within  $\pm 4\%$ . A second audit was performed on the analyzers at the tunnel exit by the California Air Resources Board. This audit showed the CO analyzer was accurate to within  $\pm 3\%$ , and the  $\text{NO}_x$  analyzer read 7% low for NO and 15% low for  $\text{NO}_2$ . Typically, the  $\text{NO}_x$  measured in the tunnel consisted of only 3%  $\text{NO}_2$ , so inaccuracy in the  $\text{NO}_2$  measurements did not impact the results significantly.

Two-hour integrated air samples were collected in evacuated 6 L stainless steel canisters using mass flow controllers to maintain a constant sample air flow rate of 85  $\text{cm}^3 \text{min}^{-1}$  (XonTech, Inc., Van Nuys, CA, model 910A).  $\text{CO}_2$  concentrations in these air samples were determined using gas chromatography (Perkin-Elmer, Wellesly, MA; model 8700) with thermal conductivity detector and Carbosieve II packed column (Supelco, Bellefonte, PA).

**Traffic Monitoring.** The types and total volume of vehicles traveling through the center bore of the tunnel were monitored during each sampling period. The average speed of vehicles inside the tunnel was also calculated by driving through the tunnel repeatedly during the sampling periods and recording travel time for a known distance. The instantaneous speed of the vehicle at major points along the tunnel was recorded along with the elapsed time for each tunnel drivethrough.

## Results

The average traffic volume was  $4200 \pm 80$  vehicles per hour over all 8 sampling days. Traffic consisted almost entirely of light-duty vehicles due to the time of day (afternoon commuter peak) and the requirement for heavy-duty vehicles to stay out of the center bore. On average, the vehicle fleet in the center bore consisted of 62% cars, 37% light-duty trucks (pickups, sport utility vehicles, and minivans), 0.8% motorcycles, and 0.1% heavy-duty vehicles.

Typical vehicle speeds at the tunnel entrance and exit were  $52 \pm 14$  and  $71 \pm 5 \text{ km h}^{-1}$ , respectively. Note greater variability in vehicle speed was observed at the tunnel entrance. No stalled vehicles were observed within the center bore, and the general pattern of driving involved steady, gradual acceleration throughout the tunnel. Stop-and-go driving conditions and heavy accelerations were rarely observed. The location of the Caldecott Tunnel is such that cars in the center bore will be in a warmed, or hot-stabilized, operating mode. These traffic conditions are similar to those observed at the tunnel in previous years (18).

TABLE 1. Average Pollutant Concentrations in the Center Bore of the Caldecott Tunnel from 4 to 6 p.m. during Summer 1999

date	NH <sub>3</sub> (ppb)		NO <sub>x</sub> (ppm)		CO (ppm)		CO <sub>2</sub> (ppm)	
	entrance	exit	entrance	exit	entrance	exit	entrance	exit
7/20/99	26	403	0.16	1.53	2.5	18.7	472	1111
7/21/99	34	344	0.19	1.50	2.9	19.7	466	1097
7/27/99	21	333	0.18	1.37	2.5	18.3	472	1069
7/28/99	36	370	0.22	1.51	2.7	18.5	472	1135
7/29/99	35	403	0.21	1.55	2.4	19.3	486	1097
8/3/99	37	355	0.23	1.42	2.7	19.7	500	1054
8/4/99	40	360	0.22	1.41	2.8	18.8	486	1081
8/5/99	51	384	0.28	1.48	3.9	21.2	486	1081

Pollutant concentrations measured at the entrance and exit of the tunnel are presented in Table 1. For all pollutants, concentrations at the tunnel exit were significantly above the entrance concentrations. Ammonia showed the greatest relative increase in concentration from entrance to exit, a factor of over 10. NO<sub>x</sub> and CO both increased by a factor of about 7, and CO<sub>2</sub> increased by a factor of 2.3 above background (tunnel entrance) levels.

At the tunnel exit, the quantity of ammonia collected on the second and third denuders in series were typically 2 and 3%, respectively, of the amount collected on the primary denuder. At the tunnel entrance where ammonia concentrations were lower, the mass of ammonia collected on the second denuder was typically 25% of that found on the primary denuder. The molar ratio of nitrogen emitted in the tunnel in the form of ammonia to nitrogen emitted in the form of NO<sub>x</sub> was 0.27 ± 0.01, indicating that ammonia emissions contribute significantly to total nitrogen-containing pollutant emissions from gasoline powered light-duty vehicles.

Light-duty vehicle emission factors  $E_p$  for pollutant P were calculated by carbon balance, using the following equation

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

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  $\rho_f = 740\ g\ L^{-1}$ . Hydrocarbons 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<sub>2</sub> (18). Emission factors determined from summer 1999 measurements are as follows: 475 ± 29 mg L<sup>-1</sup> for NH<sub>3</sub>, 4.85 ± 0.17 g L<sup>-1</sup> for NO<sub>x</sub> (as NO<sub>2</sub>), and 38.7 ± 2.5 g L<sup>-1</sup> for CO. The uncertainty bounds provide a 95% confidence interval for the mean based on run-to-run variability in the results over 8 days of sampling.

## Discussion

**Ammonia Emission Factor.** License plate surveys carried out at this site in recent years have shown that typically ~99% of vehicles in the center bore are gasoline-powered, and the average vehicle age is about 6 years old (18, 24). In 1997, 96% of the vehicles traveling through the tunnel were 1981 and newer models, and 93% were 1984 and newer. These percentages are estimated to have increased to 97 and 95%, respectively, between summers 1997 and 1999, given 2 additional years of fleet turnover. 1981 is an important model year because this was when three-way catalysts were introduced in mass on cars sold in California. By 1984, almost all new cars sold in California were equipped with three-way catalysts (25). Less stringent NO<sub>x</sub> emission standards apply to light-duty trucks compared to cars, so the installation of three-way catalyst systems in the light-duty truck fleet

occurred later in the 1980s (26). As a result, the fleet of vehicles observed in the Caldecott Tunnel in 1999 included a high proportion (>94%) of vehicles originally outfitted with three-way catalyst systems.

The ratio of the exit to entrance concentration was approximately 10 for ammonia, compared to and about 7 for both NO<sub>x</sub> and CO. The somewhat larger relative increase in ammonia concentrations compared to NO<sub>x</sub> and CO suggests that the emission characteristics of vehicles before entering the tunnel differed from those inside the tunnel due to differences in driving conditions. By focusing on the difference between tunnel entrance and exit concentrations, the influence of emissions occurring before vehicles entered the tunnel is removed from the emission factors reported here.

Based on measurements made at the Sherman Way tunnel in Van Nuys, CA, during 1993, Fraser and Cass (6) reported an ammonia emission factor of 380 mg L<sup>-1</sup>, which is 20% lower than the value of 475 ± 29 mg L<sup>-1</sup> found in the present study. Important factors that are likely to contribute to differences in ammonia emission factors between the two studies include a higher proportion of three-way catalyst-equipped vehicles on the road in 1999 compared to 1993 and the presence of 3% heavy-duty diesel trucks in the 1993 vehicle fleet studied by Fraser and Cass. Diesel trucks would be expected to contribute to CO<sub>2</sub> but do not contribute as significantly to ammonia concentrations (16) and thereby lower the fleet-average ammonia emission factor. Fraser and Cass estimated from their data that the ammonia emission rate from a fleet composed entirely of dual-bed and three-way catalyst-equipped vehicles would be 480 mg L<sup>-1</sup>, which is nearly identical to the result reported in the present study.

Other differences between the two studies may include the fraction of vehicles operating in cold start mode, differences in driving conditions and engine load, and the low sulfur content (~10 ppm by weight) characteristic of the reformulated gasoline being used in 1999. A summary of Bay Area gasoline properties measured during summers 1994–1999 is presented in Table 2.

An estimate of the ammonia emission factor on a g km<sup>-1</sup> basis can be made using vehicle fuel efficiencies measured at another tunnel. Pierson et al. (27) measured light-duty vehicle fuel consumption for uphill traffic (average grade = 3.3%) in the Fort McHenry tunnel in 1992 to be 9.8 km L<sup>-1</sup> (23 mpg). If this rate of fuel consumption is assumed to apply to the present study, the average ammonia emission factor would be approximately 49 mg km<sup>-1</sup>. Given the uncertainty in fuel consumption involved in these calculations, we conclude that our value is similar to Fraser and Cass' estimate of 61 mg km<sup>-1</sup> but significantly higher than the values reported by Moeckli et al. (17) in Switzerland and by Pierson and Brachaczek (16) in the Allegheny Mountain tunnel. The fleet of vehicles in the Caldecott Tunnel had more three-way catalysts than the vehicles from Switzerland. Moeckli et al. state the fleet of vehicles in the district of Zurich was about 75% three-way catalyst equipped during their study. The 1981 study by Pierson and Brachaczek was performed before a

**TABLE 2. Summary of San Francisco Bay Area Gasoline Properties<sup>a</sup> (Mean ± 1σ) during Summers 1994–1999**

gasoline property	1994	1995	1996	1997	1998	1999
RVP <sup>b</sup> (kPa)	51 ± 1	51 ± 1	48 ± 1	49 ± 1	48 ± 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
sulfur (ppmw)	131 ± 41	81 ± 36	16 ± 9	12 ± 11	16 ± 8	10 ± 8
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
MTBE <sup>c</sup> (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
TAME <sup>d</sup> (vol %)	N/A	N/A	N/A	N/A	0.5 ± 0.8	0.1 ± 0.1
ethanol (vol %)	N/A	N/A	N/A	N/A	0.5 ± 1.6	0.7 ± 2.1
alkane (vol %)	57.4 ± 4.8	56.6 ± 5.1	62.6 ± 2.5	65.4 ± 3.7	64 ± 3	66 ± 5
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
aromatic (vol %)	31.9 ± 2.1	33.7 ± 3.3	23.5 ± 1.4	22.7 ± 1.4	24 ± 2	22 ± 3
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
T <sub>50</sub> (°C)	101 ± 4	103 ± 2	93.8 ± 2.2	93.3 ± 1.7	93.3 ± 1.7	93.3 ± 1.1
(°F)	214 ± 8	218 ± 4	199 ± 4	200 ± 3	200 ± 3	200 ± 2
T <sub>90</sub> (°C)	168 ± 4	172 ± 4	149 ± 2	148 ± 3	151 ± 4	152 ± 6
(°F)	334 ± 8	341 ± 8	300 ± 4	299 ± 6	304 ± 8	306 ± 10
density (g L <sup>-1</sup> )	761 ± 8	760 ± 4	743 ± 2	741 ± 5	746 ± 5	742 ± 6

<sup>a</sup> 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. <sup>b</sup> RVP is Reid Vapor Pressure. <sup>c</sup> MTBE is methyl tertiary butyl ether. <sup>d</sup> TAME is tert-amyl methyl ether.

significant number of three-way catalyst equipped vehicles were on the road. As a consequence, that study should be treated as a base case to demonstrate how emissions of ammonia have changed as the prevalence of three-way catalysts has increased over the past 20 years.

Ammonia emissions have been shown to increase from three-way catalyst equipped vehicles when the engine runs fuel-rich, because this favors reducing processes on the catalyst (5, 14, 15). Well-maintained vehicles run at near-stoichiometric conditions during driving conditions defined in the Federal Test Procedure (FTP) used for emissions certification testing. The operation of three-way catalysts is optimized for these conditions, so that overall exhaust emissions are minimized. Under high load conditions, emissions of CO and ammonia from vehicles may increase dramatically due to commanded enrichment of the air-fuel mixture. This strategy is used to maximize engine torque, avoid engine knock, and protect the catalyst and exhaust valves from excessive temperatures while at the high load condition (28). As a predictor of conditions under which enrichment of the air-fuel mixture may occur, following Jiménez (28), vehicle power output  $P_r$ , in Watts, was estimated as follows:

$$P_r = \left( ma(1 + \epsilon_i) + mg \sin \theta + C_R mg + C_D A_f \frac{\rho_a v^2}{2} \right) \times v \quad (2)$$

where  $m$  is vehicle mass,  $a$  is acceleration,  $\epsilon_i$  is a mass factor which accounts for the acceleration of rotating components (this is gear-dependent),  $g = 9.81 \text{ m s}^{-2}$ ,  $\sin \theta \approx \tan \theta = 0.042$  for uphill traffic in the Caldecott Tunnel,  $C_R$  and  $C_D$  are rolling resistance and aerodynamic drag coefficients,  $A_f$  is the frontal area of the vehicle,  $\rho_a$  is air density, and  $v$  is vehicle speed. Equation 2 neglects additional contributions to engine load due to frictional losses in the drivetrain and use of accessories such as air conditioning. Vehicle specific power  $\bar{P}_r = P_r/m$  was then computed assuming  $C_R = 0.0135$ ,  $C_D A_f/m = 0.0005$ , and  $\epsilon_i = 0.1$  (see ref 28). The maximum value of  $\bar{P}_r$  calculated for FTP driving conditions is  $24 \text{ W kg}^{-1}$ . The onset of commanded enrichment is expected to occur at higher values of  $\bar{P}_r$  and may vary depending on vehicle make and model. Based on second-by-second measurements of vehicle speed collected inside the tunnel using a specially instrumented vehicle in summer 1996 (18), the average value of  $\bar{P}_r$  calculated for Caldecott Tunnel driving conditions is  $12 \text{ W kg}^{-1}$  with a standard deviation of  $7 \text{ W kg}^{-1}$  (average vehicle speeds in the center bore of the tunnel were similar in 1996 and 1999).

Therefore, the effect of the uphill grade on engine load does not appear to be large enough to lead to commanded enrichment, and the reported ammonia emissions are likely to result from malfunctioning catalyst-equipped vehicles that have lost their ability to control air-fuel ratio effectively.

**Sampling Artifacts.** Losses of ammonia to the tunnel walls may lead to a negative bias in the ammonia emission factor reported here. Simultaneous on-road measurement of ammonia, NO<sub>x</sub>, and CO emissions via remote sensing (27, 29, 30) is recommended to determine the distribution and inter-relationship of emissions across individual vehicles and model years. This approach would be less susceptible to wall loss effects that may be present in tunnel sampling for ammonia.

Additional losses of ammonia may have occurred in the 24 cm length of Teflon tube and the cyclone used upstream of the denuders when sampling ammonia. To quantify the magnitude of this effect, side-by-side ammonia measurements were made using identical sampling trains except the Teflon inlet tube and cyclone were removed from one sampling system. The relative increase in the quantity of ammonia collected on the system without the cyclone and sampling tube ranged from 13% to -1%, with an average of 7%. Although the losses of ammonia were not large in the sampling system used, a correction factor of 1.07 could be applied to the ammonia emission factor reported above. Concerns about losses of ammonia in sampler inlets have been raised before (31, 32). Sampler inlet losses of ammonia are expected to be more problematic in ambient air sampling, especially when low (sub-ppb) levels of ammonia are being measured. In contrast, high ammonia concentrations were measured in the tunnel, as shown in Table 1.

**Other Exhaust Emissions.** Emissions of other pollutants such as NO<sub>x</sub> and CO have been measured at this site since 1994 (18). The emissions trends are given in Figure 1 for NO<sub>x</sub> and Figure 2 for CO. Between 1994 and 1999, emissions reductions of  $41 \pm 4\%$  for NO<sub>x</sub> and  $54 \pm 6\%$  for CO have been observed. These reductions include the impacts of California phase 2 reformulated gasoline and turnover in the vehicle fleet. For comparison, California's EMFAC 7G emissions model predicts similar reductions in the emission factors of 34% for NO<sub>x</sub> and 53% for CO from 1994 to 1999 for light-duty gasoline powered vehicles. Vehicle speeds and the distribution of vehicle types observed at the Caldecott Tunnel were used in EMFAC 7G, it was not possible to simulate the effect of uphill grade using the model. The reductions predicted by EMFAC 7G were similar whether presented on an emissions



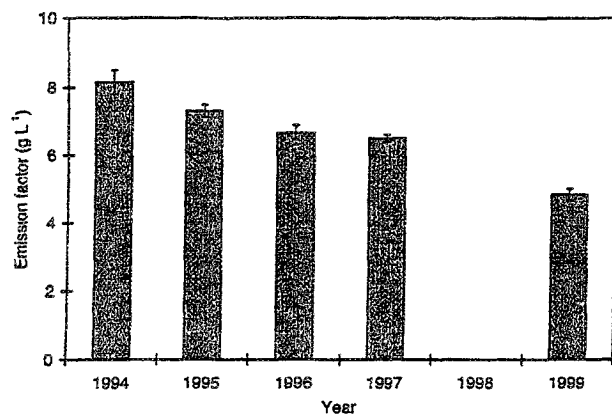


FIGURE 1. Measured NO<sub>x</sub> (as NO<sub>2</sub>) emission factors ( $\pm 95\%$  C.I.) for light-duty vehicles at the Caldecott Tunnel, 1994–1999. No measurements were made during summer 1998.

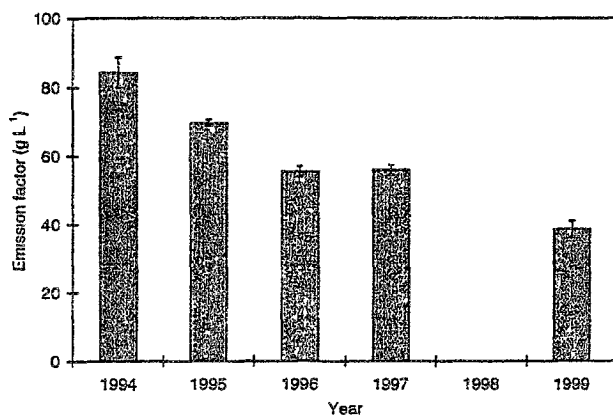


FIGURE 2. Measured CO emission factors ( $\pm 95\%$  C.I.) for light-duty vehicles at the Caldecott Tunnel, 1994–1999. No measurements were made during summer 1998.

per fuel burned or emissions per distance traveled basis. Between 1997 and 1999, emissions of NO<sub>x</sub> and CO decreased at the tunnel by  $26 \pm 2\%$  and  $31 \pm 3\%$ , respectively. During this period, there has been little change in fuel properties, as can be seen in Table 2. The reductions seen in the tunnel between 1997 and 1999 are roughly double the reductions of 14% for NO<sub>x</sub> and 16% for CO predicted by EMFAC 7G over the same 2-year period. Uncertainties in both EMFAC 7G model predictions and the tunnel measurements may contribute to these differences.

#### Acknowledgments

We thank Doug Black, Shannon Coulter-Burke, Linsey Marr, Greg Noblet, and Robert Sawyer of UC Berkeley, and the Caltrans staff at the Caldecott Tunnel for their assistance in this research. Financial support was provided by the University of California Transportation Center. Major in-kind contributions to this research were made by the Technical Services Division of the Bay Area Air Quality Management District. In addition, we thank Daniel Zucker, James Hesson, and Amir Fanai of BAAQMD and Michael Miguel of the California Air Resources Board for their assistance.

#### Literature Cited

- (1) Sawyer, R. F., Harley, R. A., Cadle, S. H., Norbeck, J. M., Slott, R. *Atmos Environ.* 2000, 34, 2161–2181
- (2) U.S. EPA. *National Air Pollutant Emissions Trends, 1900–1996*; Office of Air Quality Planning and Standards. Research Triangle Park, NC, 1997.
- (3) Berges, M. G. M., Hofmann, R. M., Scharffe, D., Crutzen, P. J. *J Geophys Res* 1993, 98(D10), 18527–18531
- (4) Sjödin, A.; Cooper, D. A.; Andreasson, K. J. *Air Waste Manage Assoc* 1995, 45, 186–190
- (5) Cadle, S. H., Nebel, G. J., Williams, R. L. *SAE Tech. Pap Ser* 1979, no. 790694
- (6) Fraser, M. P., Cass, G. R. *Environ Sci Technol* 1998, 32, 1053–1057.
- (7) Seinfeld, J. H., Pandis, S. N. *Atmospheric Chemistry and Physics From Air Pollution to Climate Change*; John Wiley & Sons: New York, 1998, pp 74–75, 1056–1057
- (8) Chow, J. C.; Watson, J. G.; Fujita, E. M.; Lu, Z.; Lawson, D. R., Ashbaugh, L. L. *Atmos. Environ.* 1994, 28, 2061–2080
- (9) Larson, S. M., Cass, G. R., Hussey, K. J., Luce, F. *Environ Sci Technol.* 1988, 22, 629–637.
- (10) Pearson, J., Stewart, G. R. *New Phytol.* 1993, 125, 283–305
- (11) Bouwman, A. F.; Lee, D. S., Asman, W. A. H., Dentener, F. J., Van Der Hoek, K. W., Olivier, J. G. J. *Global Biogeochemical Cycles* 1997, 11, 561–587
- (12) Asman, W. A. H., Sutton, M. A., Schjorring, J. K. *New Phytol.* 1998, 139, 27–48
- (13) Russell, A. G., Cass, G. R. *Atmos Environ.* 1986, 20, 2011–2025
- (14) Urban, C. M., Garbe, R. J. *SAE Tech. Pap Ser.* 1979, no. 790696
- (15) Cadle, S. H., Mulawa, P. A. *Environ Sci Technol.* 1980, 14, 718–723.
- (16) Pierson, W. R.; Brachaczek, W. W. *Environ. Sci Technol.* 1983, 17, 757–760.
- (17) Moeckli, M. A., Fierz, M., Sigrist, M. W. *Environ Sci Technol.* 1996, 30, 2864–2867
- (18) Kirchstetter, T. W., Singer, B. C., Harley, R. A., Kendall, G. R., Traverse, M. *Environ Sci Technol.* 1999, 33, 318–328
- (19) Benson, J. D., Burns, V. R., Gorse, R. A., Jr., Hochhauser, A. M., Koehl, W. J., Panter, L. J., Reuter, R. M. *SAE Tech. Pap Ser* 1991, no. 912323.
- (20) Summers, J. C., Baron, K. J. *Catal* 1979, 57, 380–389
- (21) Ghandhi, H. S., Yao, H. C., Stepien, H. K., Shelef, M. *SAE Tech. Pap Ser* 1978, no. 780606
- (22) Baromick, J., Heller, B., Lach, G., Ramacher, B. *SAE Tech. Pap Ser.* 2000, no. 2000-01-0857.
- (23) Kirchstetter, T. W., Singer, B. C.; Harley, R. A.; Kendall, G. R., Chan, W. *Environ Sci Technol.* 1996, 30, 661–670
- (24) Kirchstetter, T. W., Harley, R. A., Littlejohn, D. *Environ Sci. Technol.* 1996, 30, 2843–2849.
- (25) Long, J. Mobile Source Control Division, California Air Resources Board, El Monte, CA, personal communication, 1999
- (26) Heavenrich, R. M., Murrell, J. D., Cheng, J. P. *SAE Tech Ser* 1987, no. 871088
- (27) Pierson, W. R., Gertler, A. W., Robinson, N. F.; Sagebiel, J. C., Zielinska, B., Bishop, G. A., Stedman, D. H., Zweidinger, R. B., Ray, W. D. *Atmos Environ* 1996, 30, 2233–2256
- (28) Jiménez-Palacios, J. L. Ph.D. Dissertation, Massachusetts Institute of Technology, 1999
- (29) Nelson, D. D., Zahnser, M. S., McManus, J. B.; Kolb, C. E.; Jiménez, J. L. *Appl. Phys B—Lasers Optics* 1998, 67, 433–441.
- (30) Popp, P. J., Bishop, G. A., Stedman, D. H. *J Air Waste Manage Assoc* 1999, 49, 1463–1468
- (31) Sutton, M. A., Lee, D. S., Dollard, G. J., Fowler, D. *Atmos Environ* 1998, 32, 269–271.
- (32) Parrish, D. D., Fehsenfeld, F. C. *Atmos Environ.* 2000, 34, 1921–1957.

Received for review December 30, 1999 Revised manuscript received May 17, 2000 Accepted June 6, 2000.

ES991451Q