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MEASUREMENTS OF VEHICLE EMISSIONS OF SPECIATED CARBONYLS AND CARBOXYLIC ACIDS IN HIGHWAY TUNNELS

Final Report on CRC Project No. E-58

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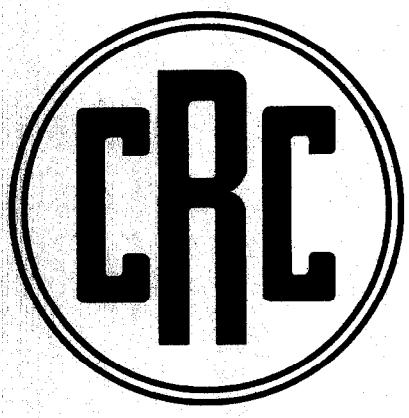

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The objective of this study has been met by carrying out measurements of carbonyls and carboxylic acids in two highway tunnels. Carbonyls have been measured at the Tuscarora Mountain Tunnel in Pennsylvania, and the results are described in Part 1 of the report. Carboxylic acids have been measured at the Caldecott Tunnel near San Francisco, California, and the results are described in Part 2 of the report.

Carboxylic acids play an important role in atmospheric acidity, long-range transport of airborne pollutants, and acid deposition. While vehicles are known to emit carboxylic acids, no information is available regarding the nature and magnitude of emissions of carboxylic acids by on-road vehicles. To identify carboxylic acids and measure their emission factors, a field study was carried out in July-August 1999 at the Caldecott Tunnel (a highway tunnel in the San Francisco, CA Bay Area).

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EXECUTIVE SUMMARY

PART 1: MEASUREMENTS OF VEHICLE EMISSIONS OF SPECIATED CARBONYLS IN THE TUSCARORA MOUNTAIN TUNNEL

PART 2: MEASUREMENTS OF VEHICLE EMISSIONS OF SPECIATED CARBOXYLIC ACIDS IN THE CALDECOTT TUNNEL

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EXECUTIVE SUMMARY

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EXECUTIVE SUMMARY

The objective of CRC Project E-58 was to measure on-road vehicle emission factors for speciated carbonyls (aldehydes and ketones) and speciated carboxylic acids. This objective has been met by carrying out measurements of carbonyls and carboxylic acids in two highway tunnels. Carbonyls have been measured at the Tuscarora Mountain Tunnel, PA, and the results are described in Part 1 of the report. Carboxylic acids have been measured at the Caldecott Tunnel near San Francisco, CA, and the results are described in Part 2 of the report. Results for Part 1 (carbonyls) and Part 2 (carboxylic acids) are summarized below.

On-road vehicle emissions of speciated carbonyls

To measure on-road vehicle emissions of carbonyls, we have carried out in May 1999 a field study at the Tuscarora Mountain Tunnel, PA. Samples were collected simultaneously at the tunnel inlet and tunnel outlet by drawing air through DNPH-coated silica gel cartridges downstream of a KI oxidant scrubber. The carbonyl-DNPH derivatives were analyzed by liquid chromatography with gradient elution and with detection by diode array ultraviolet-visible spectroscopy and by atmospheric pressure negative chemical ionization mass spectrometry.

Thirty-one carbonyls have been identified and their concentration measured (10 saturated aliphatic aldehydes, 4 saturated aliphatic ketones, 4 unsaturated aliphatic carbonyls, 4 aliphatic dicarbonyls and 9 aromatic carbonyls). Emission factors, calculated for each carbonyl and each tunnel experiment, averaged 16.8 mg / km for total carbonyls. Emission factors for light-duty vehicles (LD) and heavy-duty vehicles (HD) have been calculated from regression analysis of the measured emission factors vs. the fraction of HD vehicles in each experiment. Two sets of calculations were carried out, one using the fraction of total HD vehicles (weight

classes 4-8) and the other using the fraction of weight classes 7 and 8 HD vehicles (7-8 HD), which accounted for the majority of HD vehicles during this study.

For LD vehicles, total carbonyl emissions were ca. 6.4 mg / km, and the ten largest emission factors were, in decreasing order, those of formaldehyde (2.58 ± 1.05 mg / km, ca. 40% of total carbonyls), acetone, acetaldehyde, heptanal, crotonaldehyde, 2-butanone, propanal, acrolein, methacrolein and benzaldehyde. For 7-8 HD vehicles, total carbonyl emissions were ca. 26.1 mg / km, and the ten largest emission factors were, in decreasing order, those of formaldehyde (6.73 ± 2.05 mg / km, ca. 26% of total carbonyls), acetaldehyde, acetone, crotonaldehyde, m-tolualdehyde, 2-pentanone, benzaldehyde, a C_5 saturated aliphatic aldehyde isomer, 2,5-dimethylbenzaldehyde, and 2-butanone.

While formaldehyde, acetaldehyde and acetone were the three most abundant carbonyls in both LD and 7-8 HD vehicle emissions, the carbonyl source profile for 7-8 HD vehicles was different from that for LD vehicles. Emission factor ratios (7-8 HD / LD) varied from one carbonyl to the next and ranged from ca. 0.2 to ca. 40. Aromatic carbonyls (e.g., tolualdehydes and dimethylbenzaldehydes), unsaturated aliphatic aldehydes (e.g., crotonaldehyde, acrolein, methacrolein) and aliphatic dicarbonyls (e.g., glyoxal, methylglyoxal) represented larger fractions of the total carbonyl emissions for 7-8 HD vehicles than for LD vehicles.

Carbonyl emission factors have also been calculated on a fuel consumed basis (mg / L) using fuel economy data from the Tuscarora Mountain tunnel field study. For total carbonyls, emissions from 7-8 HD vehicles were ca. 4.0 times higher than those from LD vehicles on a distance traveled basis (mg / km), and were slightly lower (HD / LD ratio = 0.865) than those from LD vehicles on a fuel consumed basis (mg / L).

A brief comparison has been made of carbonyl, CO_2, CO, NO, total hydrocarbons (THC) and PM emission factors measured in May 1999 at the Tuscarora Mountain Tunnel. Emission factors of carbonyls are comparable in magnitude to those measured for particles (PM_{10} and $PM_{2.5}$). The carbonyl / CO_2 and carbonyl / THC emission factor ratios for LD vehicles are about the same as those for HD vehicles. This information may be of value to estimate on-road carbonyl emissions using data for the more commonly measured pollutants, e.g., CO, CO_2, THC and NO_X.

On-road emission factors for formaldehyde and acetaldehyde measured in this study are compared to the limited data available from past studies. For HD vehicles, the emission factors measured in this study are ca. 4-5 times lower than those measured in earlier work. For LD vehicles, emission factors measured in this study are generally lower than those measured in earlier work, although the emission factors measured in this study are about the same, within reported uncertainties, as those measured in 1992 at the Tuscarora Mountain and Fort McHenry Tunnels.

On-road emissions of speciated carboxylic acids

Carboxylic acids play an important role in atmospheric acidity, long-range transport of airborne pollutants, and acid deposition. While vehicles are known to emit carboxylic acids, no information is available regarding the nature and magnitude of emissions of carboxylic acids by on-road vehicles. To identify carboxylic acids and measure their emission factors, we have carried out in July-August 1999 a field study at the Caldecott Tunnel, a highway tunnel in the San Francisco, CA, Bay Area. The vehicle fleet studied was an urban-suburban commuter

fleet (ca. 6 years old on the average) and consisted almost entirely of light-duty vehicles equipped with 3-way catalysts and fueled with oxygenated California Phase 2 reformulated gasoline. Samples of 2 hr. duration (corresponding to 8,400 ± 160 vehicles) were collected at the tunnel entrance and tunnel exit, derivatized with pentafluorobenzyl bromide, and analyzed by liquid chromatography with detection by diode array ultraviolet spectroscopy and by atmospheric pressure negative chemical ionization mass spectrometry. Thirty-three monocarboxylic acids were identified including 22 saturated aliphatic acids (C_1-C_{12}), 5 unsaturated aliphatic acids and 6 aromatic acids. Emission factors were calculated using concentration differences between tunnel exit and tunnel inlet and were, in units of mg carboxylic acid emitted / L fuel consumed, 19.52 ± 1.10 for acetic acid, 5.96 ± 0.46 for formic acid, 1.25 for the sum of C_3-C_{12} saturated aliphatic acids, 0.892 for the sum of aromatic acids, 0.126 for the sum of unsaturated aliphatic acids and 27.75 mg / L for total measured carboxylic acids, of which acetic acid and formic acid together accounted for 92 percent. Ratios of emission factors were 5.2 for formaldehyde / formic acid, 0.41 for acetaldehyde / acetic acid, and 2.5 for total carbonyls / total carboxylic acids.

MEASUREMENTS OF VEHICLE EMISSIONS OF SPECIATED CARBONYLS IN THE TUSCARORA MOUNTAIN TUNNEL

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SUMMARY

To measure on-road vehicle emissions of carbonyls, we have carried out in May 1999 a field study at the Tuscarora Mountain Tunnel, PA. Samples were collected simultaneously at the tunnel inlet and tunnel outlet by drawing air through DNPH-coated silica gel cartridges downstream of a KI oxidant scrubber. The carbonyl-DNPH derivatives were analyzed by liquid chromatography with gradient elution and with detection by diode array ultraviolet-visible spectroscopy and by atmospheric pressure negative chemical ionization mass spectrometry.

Thirty one carbonyls have been identified and their concentration measured (10 saturated aliphatic aldehydes, 4 saturated aliphatic ketones, 4 unsaturated aliphatic carbonyls, 4 aliphatic dicarbonyls and 9 aromatic carbonyls). Emission factors, calculated for each carbonyl and each tunnel experiment, averaged 16.8 mg / km for total carbonyls. Emission factors for light-duty vehicles (LD) and heavy-duty vehicles (HD) have been calculated from regression analysis of the measured emission factors vs. the fraction of HD vehicles in each experiment. Two sets of calculations were carried out, one using the fraction of total HD vehicles (weight classes 4-8) and the other using the fraction of weight classes 7 and 8 HD vehicles (7-8 HD), which accounted for the majority of HD vehicles during this study.

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INTRODUCTION

Carbonyls play an important role in atmospheric chemistry and urban air quality. They are emitted by mobile and stationary sources, including indoor sources (1-4) and are formed as major reaction products in the atmospheric oxidation of many hydrocarbons and other volatile organic compounds (5-8). Carbonyls are important precursors to free radicals, ozone, and peroxyacyl nitrates (9-12). Carbonyls have received regulatory attention as toxic air contaminants, mutagens and carcinogens (13-16).

A major source of carbonyls in outdoor air is vehicle exhaust. Past studies have documented vehicle exhaust emission of carbonyls in dynamometer tests, where a limited number of vehicles can be studied under a prescribed set of operating conditions (17-20). Vehicle emissions can also be measured under real-world conditions, i.e., on roadways and in highway tunnels (21-34). Several roadway and highway tunnel studies have included measurements of carbonyls (24-34).

In this report, we describe the methods and results of a study in which airborne carbonyls have been measured in a highway tunnel, the Tuscarora Mountain Tunnel in Pennsylvania. Samples were collected on silica gel cartridges coated with 2,4-dinitrophenylhydrazine (DNPH) downstream of KI oxidant scrubbers, and the carbonyl-DNPH derivatives were identified using a recently published method (35) that involves liquid chromatography analysis with detection by diode array uv-visible spectroscopy and by atmospheric pressure negative chemical ionization mass spectrometry (LC-DAD-APCI-MS). Thirty-one carbonyls have been identified and their concentrations measured at the tunnel inlet and tunnel outlet. This information, together with information on vehicle traffic, vehicle fleet composition, air flow through the tunnel and other parameters (36), has been used to calculate carbonyl emission factors and to estimate emission factors for light-duty (LD) and heavy-duty (HD) vehicles.

Our study was motivated by several considerations. Past studies of on-road vehicle emissions of carbonyls have been limited to formaldehyde, acetaldehyde and, less frequently, several other low molecular weight carbonyls (24-34). Higher molecular weight carbonyls have seldom been identified and their vehicle emission factors have not been measured. The present study offered an opportunity to characterize on-road carbonyl emissions from heavy-duty diesel vehicles, for which little data are currently available. Recent studies indicate that carbonyls are a major component of diesel exhaust emissions and account for most of the ozone-forming potential of organic gases emitted by diesel vehicles (37-39). Detailed information on vehicle emissions of carbonyls is necessary to assess the contribution of vehicle emissions to ambient levels of carbonyls (e.g., source apportionment and receptor modeling studies), to estimate population exposure and possible adverse health effects, and to examine the role and importance of vehicle-emitted carbonyls in the photochemical formation of ozone, peroxyacyl nitrates, and secondary aerosols.

Of special interest with respect to mobile source emissions of carbonyls are recent and near-future changes in the composition and properties of gasolines and diesel fuels. These changes have a direct impact on the nature and magnitude of carbonyl emissions by vehicles. Examples of legislated changes in fuel composition are the 1990 Clean Air Act Amendments (40) that mandate the use of oxygenated additives to gasoline, e.g., ethanol and / or methyl-tert-butyl ether (MTBE), more recent federal and state reformulated fuel programs that affect gasoline and diesel fuel composition and exhaust reactivity (41), and the current phasing out, to be completed in 2002, of MTBE from reformulated gasolines sold in the State of California (42). The withdrawal of MTBE from gasolines is also being considered at the federal (U. S.) level, as is the possible replacement of MTBE by ethanol (43). The composition of diesel fuels is also likely to change and biodiesel, among other options, is currently receiving much attention (44-47). Past studies have shown that on-road emissions of carbonyls from diesel vehicles were higher than those from spark-ignition engines, and this by ca. one order of magnitude on a mass per distance traveled basis (22,24-26). As fuel

composition and vehicle technology continue to evolve, it is important to characterize current on-road emissions of carbonyls and to provide baseline data for comparison with future on-road studies.

EXPERIMENTAL METHODS

The Tuscarora Mountain Tunnel is a two-bore tunnel with two lanes in each bore, on the Pennsylvania Turnpike (Interstate 76) which runs east-west through Tuscarora Mountain (tunnel altitude = ca. 305 m) in south-central Pennsylvania (ca. 112 km west of Harrisburg, PA). The tunnel is 1623 m. long, straight, and flat (grades of + 0.3 percent towards the middle from either end). A schematic diagram of the tunnel is given by Pierson, et al., (22). Additional information regarding the Tuscarora Mountain Tunnel and the design and results of vehicle emission studies carried out in this tunnel in 1992 and 1999 can be found in Pierson, et al., (22) and Gertler, et al., (36), respectively.

The tunnel's supply ventilation system was not operated during our study, and air flow in the tunnel resulted entirely from the eastbound vehicle traffic and the prevailing westerly wind. Average air residence time within the tunnel was 5 ± 1 minute. Carbonyl samples were collected simultaneously at the tunnel inlet and tunnel outlet, a few meters in from each portal. In this way the inlet air was essentially ambient air (the air residence time from the portal to the inlet sampling location was ca. 1 second), and only tunnel air was sampled at the outlet location. Emissions of pollutants in the tunnel were from vehicles operated in the hot stabilized mode, and cold-start and hot-start operations were inconsequential in the eastbound direction chosen for the measurements (22, 36).

Ten experiments, each of one-hour duration, were carried out on May 18-21, 1999. The total number of vehicles was 192-814 per hour and the total number of weight class 4-8 heavy-duty (HD) vehicles was 108-225 per hour. The fraction of heavy-duty vehicles, which

consisted mostly of heavy-duty diesel trucks (weight classes 7 and 8, i.e., ≥ 26,000 lbs), ranged from 13.3 to 86.5 percent, and was ≥ 64.5 percent in six experiments. A summary of information is given in Table 1 which includes, for each experiment, the day and time carbonyl samples were collected, the total number of vehicles, the number of light-duty, class 4-6 HD and class 7-8 HD vehicles, the fraction of HD vehicles, the average model year for light-duty (LD) vehicles, the measured average vehicle speed, and the carbon dioxide and nitric oxide concentrations measured at the tunnel inlet and tunnel outlet.

Carbonyl samples were collected by drawing air through 2,4-dinitrophenylhydrazine (DNPH)-coated silica gel cartridges (Waters Corp.). All samples were collected downstream of a KI oxidant scrubber (Waters Corp.) connected to the cartridge by a 1 inch long, 1/4 inch diameter piece of Teflon tubing. The sampling duration was 60 min., the sampling flow rate was 0.407-0.700 L / min. (measured with flowmeters calibrated using a certified, NIST-traceable Humonics model 650 flow calibrator) and the volume of air sampled was 33-55 L. Samples and field controls were eluted with acetonitrile, and aliquots of the extracts were analyzed by liquid chromatography with detection by diode array ultraviolet spectroscopy and by atmospheric pressure negative chemical ionization mass spectrometry. The operating conditions and overall analytical protocol have been described in detail by Grosjean, et al., (35). Carbonyls were positively identified by matching the retention times, uv-visible absorption spectra and negative chemical ionization mass spectra of their DNPH derivatives to those of ca. 150 carbonyl-DNPH reference standards synthesized in our laboratory (35, 48-50). Quantitative analysis involved the use of response factors measured using carbonyl-DNPH reference standards (35, 48-50).

RESULTS AND DISCUSSION

Carbonyls identified and comparison with literature data

Thirty one carbonyls have been identified in all samples collected at the inlet and outlet of the Tuscarora Mountain Tunnel. The compounds identified are listed in Table 2 and included 10 saturated aliphatic aldehydes, 4 saturated aliphatic ketones, 4 unsaturated aliphatic carbonyls, 4 aliphatic dicarbonyls and 9 aromatic carbonyls. The three entries "isomer" in Table 2 (a C_5 saturated aliphatic carbonyl, a C_6 saturated aliphatic carbonyl, and, tentatively, a C_6 unsaturated aliphatic carbonyl) reflect the current limitation of our library of reference compounds, i.e., the molecular weight and chemical functionality (aromatic or aliphatic, and, for aliphatic compounds, saturated or not) of the compound could be determined from the uv-visible absorption spectrum and the negative chemical ionization mass spectrum but no reference standard was available for positive identification. Since isomers that have nearly identical retention times also have nearly identical response factors (35, 48-50), concentrations of the C_5 and the C_6 aliphatic carbonyls that were not positively identified could be reported using the measured response factor of the closest-eluting isomer for which a reference standard was available. The two entries "and/or isomers" in Table 2, one for 2,4-dimethylbenzaldehyde and the other for 2,4,6-trimethylbenzaldehyde, indicate that a reference standard was available for positive identification but that other isomers (which often have almost identical retention times, uv-visible spectra and mass spectra) could not be ruled out. For 2-pentanone, which was positively identified in all tunnel inlet samples, the possible presence of a co-eluting compound with the same uv spectrum could not be ruled out from the mass spectrometer data for samples collected at the tunnel outlet. Thus, tunnel outlet concentrations and vehicle emission factors for 2-pentanone may be upper limits for actual values.

Twenty five percent of the samples were analyzed twice, and the relative standard deviations (RSD) for these replicate analyses were 1-10% for all carbonyls. All cartridges were eluted

twice with acetonitrile, and no detectable amounts of carbonyls could be measured in aliquots of the second elution.

For comparison with our results, we have included in Table 2 a list of the carbonyls that have been identified in earlier studies carried out in highway tunnels. Of these studies, the most detailed are those of Kirchstetter et al., who reported 12-16 carbonyls in the Caldecott Tunnel, CA (27-29). Also included in Table 2 is a list of the carbonyls identified in the few measurements made on roadways (those of Zweidinger, et al., (21) in the U. S. and of Grosjean, et al., (35) in Brazil) and a list of carbonyls identified in recent dynamometer tests (those of Schauer (51) for catalyst-equipped LD vehicles and of Schauer, et al., (38) and Truex, et al., (39) for diesel trucks). The data in Table 2 indicate qualitative agreement between the present highway tunnel study and earlier work, and especially between the results of the present study and those obtained in recent dynamometer tests (38, 51).

Carbonyl concentrations

Concentrations measured in each experiment are listed in the Appendix (concentrations measured at the tunnel inlet are listed in Table A1; those measured at the tunnel outlet are listed in Table A2). Average concentrations measured at the tunnel inlet and tunnel outlet are summarized in Table 3 along with the corresponding RSD, which give a measure of variability from one tunnel experiment to the next. Also listed in Table 3 are the average differences between tunnel outlet and tunnel inlet concentrations.

At the tunnel inlet, the sum of the concentrations of the 31 carbonyls averaged 7.66 $\mu g\ m^{-3}$. Acetone was the most abundant carbonyl in all inlet samples, followed by formaldehyde and acetaldehyde (average concentrations = 2.43, 1.72 and 1.12 $\mu g\ m^{-3}$, respectively). Acetone accounted for 31.7% of the total measured carbonyls (mass basis), and acetone, formaldehyde and acetaldehyde together accounted for 68.7% of the total measured carbonyls. Other abundant carbonyls in tunnel inlet samples included, in decreasing order, benzaldehyde, 2-butanone, methylglyoxal and propanal, with average concentrations of ca.

0.16-0.24 μg m^{-3}. Carbonyls measured at the tunnel inlet may have diverse origins including in-situ oxidation of biogenic and anthropogenic hydrocarbons, as well as direct emissions from stationary and mobile sources (including vehicle emissions on Interstate 76 near the tunnel). The relative contribution of these sources may vary substantially from one tunnel experiment to the next, as is suggested by the large RSD associated with tunnel inlet average concentrations (range 31-96%, e.g., 49% for formaldehyde) and by the large RSD in the concentrations of other pollutants measured at the tunnel inlet, e.g., 83% for nitric oxide.

At the tunnel outlet, the sum of the concentrations of the 31 carbonyls averaged 16.44 μg m^{-3} (average outlet / inlet concentration ratio = 2.15). The relative abundance of carbonyls at the tunnel outlet was different from that at the tunnel inlet. Formaldehyde was the most abundant carbonyl in all outlet samples, followed by acetone and acetaldehyde (average concentrations = 4.59, 3.63 and 2.25 μg m^{-3}, respectively). Formaldehyde accounted for 27.9% of the total measured carbonyls (mass basis), and formaldehyde, acetone and acetaldehyde together accounted for 63.7% of the total measured carbonyls. Other abundant carbonyls in tunnel outlet samples included, in decreasing order, benzaldehyde, 2-butanone, crotonaldehyde, m-tolualdehyde, propanal, acrolein, methacrolein and methylglyoxal, with average concentrations of ca. 0.29-0.66 μg m^{-3}. With one exception (2-oxobutanal), RSDs for average carbonyl concentrations measured at the tunnel outlet were 11-35 percent (e.g., 19 percent for formaldehyde)i.e., they were much lower than those for average concentrations measured at the tunnel inlet. RSDs for other pollutants, e.g., 16% for nitric oxide, were also much lower at the tunnel outlet than at the tunnel inlet.

Differences between concentrations measured at the tunnel outlet and those measured at the same time at the tunnel inlet are summarized in Table 3. The three most abundant carbonyls emitted by vehicles were formaldehyde (average difference = 2.99 ± 1.30 μg m^{-3}), acetone (1.25 ± 0.78 μg m^{-3}) and acetaldehyde (1.18 ± 0.31 μg m^{-3}). The data in Table 3 indicate that all carbonyls identified in this study were emitted by vehicles in the Tuscarora Mountain

Tunnel. For 4-methyl-2-pentanone, anisaldehyde, 2,4-dimethylbenzaldehyde, 2-oxobutanal and biacetyl, outlet concentrations were higher than inlet concentrations in each tunnel experiment. However, the averages of the differences (outlet minus inlet) were comparable in magnitude (higher for anisaldehyde and 2,4-dimethylbenzaldehyde; lower for 4-methyl-2-pentanone, 2-oxobutanal and biacetyl) to the standard deviations of the averages of the tunnel inlet concentrations. More conclusive evidence for vehicle emissions of these five carbonyls has been obtained in the Caldecott Tunnel (34) where the vehicle traffic count was much higher than was the case in this study, as well as in dynamometer tests involving light-duty vehicles (51, 52) and medium-duty diesel trucks (38, 52) .

Parameters that influence carbonyl emissions from one tunnel experiment to the next include the total number of vehicles, the fraction of HD vehicles, and, for both LD vehicles and HD vehicles, the fleet composition, the fleet age, the average speed, and the number of vehicles that may be high emitters of carbonyls. Variability in carbonyl emissions from one tunnel experiment to the next is indicated by the large RSD, e.g., 43% for formaldehyde, associated with the averages of the differences between tunnel outlet concentrations and tunnel inlet concentrations (see Table 3). To examine similarities and differences among carbonyls emitted by vehicles, we have constructed, for each carbonyl and each experiment, scatterplots (not shown) of the difference between tunnel outlet and tunnel inlet concentrations versus that for formaldehyde. Least squares linear regressions of the data were carried out, and the corresponding correlation coefficients are listed in Table 3. Of the ten most abundant carbonyls (after formaldehyde) emitted by vehicles, three correlated reasonably well with formaldehyde (acetone, benzaldehyde and methacrolein, $R = 0.90$, 0.78 and 0.72, respectively), six correlated rather poorly (acetaldehyde, acrolein, crotonaldehyde, m-tolualdehyde, 2-butanone and 2-pentanone, $R = 0.41$-0.62) and one not at all (the C_5 saturated aliphatic isomer, $R = 0.16$). Of the less abundant carbonyls, six correlated reasonably well with formaldehyde ($R \geq 0.68$ for butanal, hexanal, methylglyoxal, 2-oxobutanal, biacetyl and heptanal), four did not correlate with formaldehyde ($R \leq 0.18$ for

glyoxal, pentanal, acetophenone and 2,5-dimethylbenzaldehyde) and the other carbonyls correlated poorly with formaldehyde ($0.2 < R < 0.7$).

Carbonyl emission factors

Carbonyl emissions factors were calculated as is described in detail by Pierson, et al., (22) for airborne pollutants measured in a highway tunnel, i.e.:

$$EF_i = (C_{out}V_{out} - C_{in}V_{in}) / NL \qquad \text{(Eq. 1)}$$

where EF_i is the emission factor for experiment i, N is the traffic count (number of vehicles per experiment), L is the tunnel length (distance between the inlet and outlet sampling locations), $C_{out}V_{out}$ and $C_{in}V_{in}$ are the fluxes at the tunnel outlet and inlet, respectively, C is the measured concentration of the carbonyl of interest, and V is the volume calculated from the measured cross-section of the tunnel and the measured wind speed.

Carbonyl emission factors have been calculated for each experiment and are not listed due to space limitations. The corresponding lowest values, highest values, averages and RSD are listed in Table 4. The average emission factor for formaldehyde was 5.41 mg / km (RSD = 41 percent). The sum of the averages of the emission factors for the 31 carbonyls measured was 16.79 mg / km, of which formaldehyde accounted for 32.2 percent (mass basis), formaldehyde, acetaldehyde and acetone together accounted for 58.0 percent, and the ten most abundant carbonyls (formaldehyde, and, in decreasing order, acetaldehyde, acetone, crotonaldehyde, m-tolualdehyde, 2-pentanone, the C_5 saturated aliphatic isomer, 2-butanone, benzaldehyde and methacrolein) together accounted for 79.2 percent.

Carbonyl emission factors for light-duty and heavy-duty vehicles

To estimate LD and HD carbonyl emission factors, we have constructed , for each carbonyl, plots of the measured emission factor vs. the fraction of HD vehicles according to the following equation (22, 25, 26):

$$EF_i = \alpha_i EF_{HD} + (1-\alpha_i) EF_{LD} \quad \text{(Eq. 2)}$$

where EF_i is the measured carbonyl emission factor in experiment i, α_i is the fraction of HD vehicles in experiment i, EF_{LD} is the carbonyl emission factor for HD vehicles and EF_{HD} is the carbonyl emission factor for LD vehicles. According to Equation 2, a plot of EF_i vs. α_i should yield a straight line with intercepts of EF_{LD} at $\alpha_i = 0$ and EF_{HD} at $\alpha_i = 1.0$. The limitations of this approach, in which it is assumed that each experiment involves the same mixtures of LD vehicles and HD vehicles and the same driving conditions, have been discussed previously (22, 25, 26).

Using Equation 2, we carried out linear least squares regressions of the experimental data using two values of α_i, one being the fraction of total HD vehicles (weight classes 4-8) and the other being the fraction of weight classes 7-8 HD vehicles (hereafter 7-8 HD) which accounted for most of the total HD vehicles in all tunnel experiments (see Table 1). The LD and HD carbonyl emission factors thus calculated are listed in the Appendix, Table A3 and Table A4, respectively. These tables include, for each carbonyl, the slope and its standard deviation, the intercept (i.e., the emission factor for LD vehicles) and its standard deviation, the sum of the slope and the intercept (i.e., the emission factor for HD vehicles), the corresponding standard deviation, and the correlation coefficient R. As discussed previously (22, 25, 26), the numerical value of R becomes lower as the slope of the plot of the experimental data according to Equation 2 decreases, i.e., R becomes lower for those carbonyls for which LD emission factors and HD emission factors are of the same magnitude. Thus, the values of R given in Table A3 and Table A4 are indicative of goodness of fit only for those carbonyls that have high HD / LD emission factor ratios.

We repeated the regression analysis with outliers deleted, and this again for α_i = fraction of total HD and α_i = fraction of 7-8 HD. Outliers (experimental data that were outside of the domain defined by ± one standard deviation of the regression slope) were identified by examination of the scatterplots of all experimental data for each carbonyl and for both values

of α_i. The number of outliers was zero for 5 carbonyls (including acetone), one for 8 carbonyls (including formaldehyde), two for 12 carbonyls (including acetaldehyde), three for 5 carbonyls, and four for 2-oxobutanal. There were more outliers for those carbonyls that had the lowest concentrations, as expected since the measurement uncertainty increases with decreasing carbonyl concentration. Carbonyl emission factors calculated after deleting outliers are listed in Table 5 for 7-8 HD vehicles and in Table A5 of the Appendix for total HD vehicles. These tables include, for each carbonyl, the same parameters as those listed above for Tables A3 and A4. They also include rankings of LD and HD carbonyl emission factors. Examples of scatterplots of carbonyl emission factor vs. fraction of 7-8 HD vehicles are given in Figure 1 and Figure 2. As indicated earlier, most HD vehicles were 7-8 HD vehicles in all tunnel experiments, and as a result the emission factors given in Table A5 for total HD vehicles are similar to those given in Table 5 for 7-8 HD vehicles. Thus, the following discussion focuses on the carbonyl emission factors calculated from plots of the experimental data vs. the fraction of 7-8 HD vehicles.

For LD vehicles, the sum of the carbonyl emission factors was ca. 6.4 mg / km. The ten carbonyls with the largest LD emission factors were, in decreasing order, formaldehyde (2.58 ± 1.05 mg / km), acetone, acetaldehyde, heptanal, crotonaldehyde, 2-butanone, propanal, acrolein, methacrolein and benzaldehyde. The emission factors of formaldehyde, acetone and acetaldehyde together accounted for ca. 76 percent of the sum of all LD carbonyl emission factors. This compares to 5.6 percent for unsaturated aliphatic aldehydes (acrolein + methacrolein + crotonaldehyde), 4.9 percent for aromatic carbonyls and 1.3 percent for aliphatic dicarbonyls (glyoxal, methylglyoxal, 2-oxobutanal and biacetyl). For 7-8 HD vehicles, the sum of the carbonyl emission factors was ca. 26.07 mg / km. The ten carbonyls with the largest 7-8 HD emission factors were, in decreasing order, formaldehyde (6.73 ± 2.05 mg / km), acetaldehyde, acetone, crotonaldehyde, m-tolualdehyde, 2-pentanone, benzaldehyde, the C_5 saturated aliphatic isomer, 2,5-dimethylbenzaldehyde and 2-butanone. The emission factors of formaldehyde, acetaldehyde and acetone together accounted for ca. 50 percent of the sum of all 7-8 HD emission factors. This compares to 9.5

percent for the unsaturated aliphatic aldehydes, 15.8 percent for aromatic carbonyls and 3.9 percent for aliphatic dicarbonyls.

There were similarities and differences between the carbonyl source profile for LD vehicles and that for 7-8 HD vehicles. Formaldehyde, acetaldehyde and acetone were the three major components in both LD and 7-8 HD emissions, although their relative abundance was different (e.g., the formaldehyde / acetaldehyde emission factors ratio was ca. 4.0 for LD vehicles and ca. 1.7 for 7-8 HD vehicles, and the acetone / acetaldehyde emission factors ratio was ca. 2.6 for LD vehicles and ca. 0.63 for 7-8 HD vehicles). Aromatic carbonyls accounted for a significant fraction of the total (15.8 percent) for 7-8 HD vehicles but not for LD vehicles (4.9 percent). Emission factors of unsaturated aliphatic aldehydes accounted for a larger fraction of the total for 7-8 HD vehicles than for LD vehicles (9.5 vs. 5.6 percent), and the same was observed for aliphatic dicarbonyls (3.9 vs. 1.3 percent). For one saturated aliphatic carbonyl, heptanal, the slope of the plot of the data according to Equation 2 was negative (see Table 5; slopes were positive for all other carbonyls) and the calculated LD vehicle emission factor was ca. five times higher than that calculated for 7-8 HD vehicles. Emission factor ratios (7-8 HD / LD vehicles) varied substantially from one carbonyl to the next, i.e., from 0.2 to ca. 4.0. Carbonyls with high 7-8 HD / LD emission factor ratios included several aromatic aldehydes (anisaldehyde, the three tolualdehydes, and the dimethylbenzaldehydes) and several aliphatic dicarbonyls (glyoxal, methylglyoxal and biacetyl). Speciated carbonyl emissions from LD vehicles are expected to be different from those for 7-8 HD vehicles: carbonyls are emitted as a result of incomplete oxidation of fuel components, and the composition of gasoline is substantially different from that of diesel fuel.

Comparison of carbonyl emission factors for LD and HD vehicles

Emissions of carbonyls by LD vehicles can be compared to those of HD vehicles in two ways, i.e., on a distance traveled basis or on a fuel consumed basis. Carbonyl emission factors measured in this study are listed in Table 6 in units of mg / km and in units of mg / L. The emission factors listed in mg / km are those calculated by regression analysis of the

experimental data, with outliers deleted, versus the fraction of 7-8 HD vehicles. The corresponding 7-8 HD / LD emission factor ratios are given in Table 6 for each carbonyl. We calculated the LD and 7-8 HD carbonyl emission factors in units of mg / L using the fuel economy data reported by Gertler, et al., (36) for this study, i.e., 14.75 km / L for LD vehicles and 3.15 km / L for HD vehicles. These emission factors and their ratios (7-8 HD / LD) are also listed in Table 6.

On a distance traveled basis (mg / km), total carbonyl emissions from 7-8 HD vehicles were ca. 4 times higher than those from LD vehicles. As discussed in the preceding section, 7-8 HD / LD emission factor ratios varied from one carbonyl to the next. For example, 7-8 HD / LD emission factor ratios were 2.6 for formaldehyde, 6.1 for acetaldehyde, 1.5 for acetone, 7.3 for crotonaldehyde, 15.9 for m-tolualdehyde and 14.2 for methylglyoxal. On a fuel consumed basis (mg / L), total carbonyl emissions from 7-8 HD vehicles were slightly less than those from LD vehicles, i.e., ca. 82 mg / L vs. ca. 95 mg / L. On a fuel consumed basis, the 7-8 HD / LD ratio was ca. 0.86 for total carbonyls and varied from one carbonyl to the next, e.g., 0.6 for formaldehyde, 1.3 for acetaldehyde, 0.3 for acetone, 1.6 for crotonaldehyde, 3.4 for m-tolualdehyde and 3.0 for methyl glyoxal.

Comparison with literature data

Of the several past studies that have included the identification of carbonyls in emissions from vehicles in highway tunnels (see Table 2), few have included calculations of carbonyl emission factors. A summary of literature data is given in Table 7 for formaldehyde and acetaldehyde (on-road emission factors for several other carbonyls have been reported in references 22, 25-29, 31 and 34). Of the several highway tunnel studies listed in Table 7, only one, carried out in 1992 by Pierson and co-workers in the Fort McHenry and Tuscarora Mountain Tunnels, has included calculations of carbonyl emission factors for LD and HD vehicles (22, 25, 26). Also included in Table 7 for comparison are data from this study and from recent dynamometer tests (38, 51).

For HD vehicles, the emission factors measured in this study are substantially lower than those measured in previous work, e.g., 4 times lower for formaldehyde (Tuscarora Mountain, 1999 vs. 1992) and 5 times lower for acetaldehyde (Tuscarora mountain, 1999 vs. Fort McHenry, 1992). For LD vehicles, emission factors measured in this study are lower than literature data, and this more so for acetaldehyde than formaldehyde. For formaldehyde, the LD emission factor measured in this study is lower than those measured in the Caldecott Tunnel (27-29, 34) and in recent dynamometer tests (38, 51) but is essentially the same, within the stated uncertainties, as those measured in 1992 in the Tuscarora Mountain and Fort McHenry Tunnels (22, 25, 26). No firm conclusions regarding long-term trends can be made due to the scarcity of literature data.

On-road emissions of carbonyls and other pollutants

It is of interest to compare on-road emissions of carbonyls to those of other pollutants, which were measured by Gertler, et al., (36, 55). Information on speciated carbonyls in emissions from on-road vehicles is limited, and this especially so for 7-8 HD vehicles. Thus, ratios of carbonyl emission factors to those of other pollutants measured in this study could be used to estimate carbonyl emissions using data for commonly measured pollutants such as CO_2, CO, NO and total hydrocarbons. These ratios may also be useful as indicators of the impact, on vehicle emissions, of future changes in fuel composition, engine technology and exhaust control devices. A summary of LD and HD emission factors measured in 1999 in the Tuscarora Mountain Tunnel is given in Table 8 for CO_2, CO, NO, total hydrocarbons (THC), PM_{10}, $PM_{2.5}$ and total carbonyls. Also given in Table 8 are the ratios of the emission factors of carbonyls to those of CO_2, CO, NO, THC and PM. The data in Table 8 indicate that on-road vehicle emissions of carbonyls are comparable in magnitude (mass basis) to those of particulate matter and are, as is expected, much lower than those of CO_2, CO, NO and THC. The data in Table 8 also indicate that the carbonyl / CO_2 and carbonyl / THC emission factor ratios for LD vehicles are essentially the same as those for HD vehicles, e.g., ca. 1.7 percent for the carbonyl / THC emission factor ratio. Carbonyls, like CO and a fraction of THC

(hydrocarbons are also emitted as unburned fuel), are incomplete combustion products. A more detailed examination of the relationship between speciated carbonyls in exhaust and speciated hydrocarbons in fuels is of interest and will be carried out in future work.

The results of this study provide, for the first time, detailed information on the nature and abundance of carbonyls emitted by LD and HD vehicles under real-world conditions. However, our study involved only one highway tunnel and as such provides only a snapshot of current vehicle emissions of carbonyls. For example, the majority of LD vehicles going through the non-urban Tuscarora Mountain Tunnel during our study were hot-stabilized with presumably little off-cycle emissions. Higher emissions of carbonyls may be observed in an urban setting where more vehicles are in cold start and off-cycle conditions. Differences in fuel composition are also expected to affect the magnitude and composition of carbonyl emissions. Additional studies are needed to provide a more complete assessment of on-road vehicle emissions of speciated carbonyls.

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Table 1. Summary of carbonyl experiments at the Tuscarora Mountain Tunnel

Date (May 1999)	Start time	End time	Number of vehicles: light-duty (LD)	heavy-duty (HD): class 4-6 (a)	heavy-duty (HD): class 7-8 (b)	Total	HD, percent of total	Avg. LD model year	Avg. speed, mph	nitric oxide, ppb: inlet	nitric oxide, ppb: outlet	carbon dioxide, ppm: inlet	carbon dioxide, ppm: outlet
Tue. 18	2200	2300	104	10	179	293	64.5	1993.5	57.0	292	1950	428	558
Wed. 19	0000	0100	31	4	171	206	85.0	1993.5	54.9	316	1968	451	568
	0200	0300	26	10	156	192	86.5	1991.1	55.1	459	2113	476	590
	1900	2000	240	14	200	454	47.1	1994.8	57.7	241	1714	387	506
	2100	2200	148	20	191	359	58.8	1994.3	54.4	49	2133	384	536
	2300	0000	70	4	178	252	72.2	1993.6	53.6	13	1999	384	515
Thu. 20	0100	0200	43	6	152	201	78.6	1994.3	55.0	12	1888	387	507
	1600	1700	505	23	202	730	30.8	1994.8	53.2	35	1975	371	541
Fri. 21	0500	0600	88	9	151	248	64.5	1993.7	58.1	574	2233	486	602
	1700	1800	706	16	92	814	13.3	1994.7	56.9	153	1223	385	534

(a) weight ≤ 26,000 lbs.

(b) weight class 7: 26,000-33,000 lbs.; weight class 8: > 33,000 lbs.

Table 2. Carbonyls identified at the inlet and outlet of the Tuscarora Mountain Tunnel and comparison with literature data for highway tunnels and for selected roadway dynamometer studies

Carbonyl	Highway tunnels		Roadway studies		Dynamometer tests		
					light-duty	diesel trucks	
	this study	previous work (a)	ref. 21, U. S. (b)	ref. 35, Brazil (c)	vehicles, ref. 51 (d)	ref. 38 (e)	ref. 39 (f)
Saturated aliphatic aldehydes:							
formaldehyde	•	22, 24-31, 33	•	•	•	•	•
acetaldehyde	•	22, 24-31, 33	•	•	•	•	•
propanal	•	27-29	•	•	•	•	•
butanal	•	27-29	•	•	•	•	•
isopentanal (3-methylbutanal)	•	29		•			
C5 isomer (g)	•						
pentanal	•	29, 30		•	•		•
C6 isomer (g)	•						
hexanal	•	29, 31		•	•	•	•
heptanal	•			•	•	•	
octanal		31		•	•	•	
nonanal				•	•	•	
decanal				•	•	•	
undecanal				•	•	•	
dodecanal				•	•	•	
tridecanal				•		•	
tetradecanal				•			
Saturated aliphatic ketones:							
acetone	•	27-30, 32	•	•	•	•	•
2-butanone (methyl ethyl ketone)	•	22, 25-29, 31		•	•	•	
2-pentanone	•	29					
4-methyl-2-pentanone (methyl isobutyl ketone)	•	29					
2-methyl-3-pentanone		29					
2-heptanone		29					

Table 2 (continued)

Carbonyl	Highway tunnels		Roadway studies		Dynamometer tests		
					light-duty vehicles,	diesel trucks	
	this study	previous work (a)	ref. 21, U. S. (b)	ref. 35, Brazil (c)	ref. 51 (d)	ref. 38 (e)	ref. 39 (f)
Unsaturated aliphatic carbonyls:							
acrolein	•	27-29, 33	•	•	•	•	•
crotonaldehyde	•	27-29, 31	•	•	•	•	•
methacrolein (h)	•	27-29		•	•	•	•
C6 isomer (g)	•						
Aliphatic dicarbonyls:							
glyoxal	•	31		•	•	•	
methylglyoxal	•	31		•	•	•	
2-oxobutanal	•			•			
biacetyl (2,3-butanedione)	•			•	•	•	
Aromatic carbonyls:							
benzaldehyde	•	27-31	•	•	•	•	•
anisaldehyde (methoxy benzaldehyde) (i)	•						
o-tolualdehyde	•		•	•	•		
m-tolualdehyde	•		•	•	•		
p-tolualdehyde	•			•	•		
tolualdehyde, isomer not specified		27-29					•
2,5-dimethylbenzaldehyde	•			•	•	•	
2,4-dimethylbenzaldehyde (and / or isomers) (j)	•	29					
2,4,6-trimethylbenzaldehyde (and / or isomers) (j)	•						
acetophenone	•				•	•	

Table 2 (continued)

(a) The reference number is that cited in the reference list. Data for references 28 and 29 were published as supplementary material. Acrolein, methacrolein, isopentanal and dimethylbenzaldehyde were not detected in the 1997 Caldecott Tunnel study (28, 29). The ketones 2-pentanone, 4-methyl-2-pentanone, 2-methyl-3-pentanone and 2-heptanone were not reported in the 1994, 95 and 96 Caldecott Tunnel studies (27-29).

(b) Data from samples collected in 1983 on U. S. Highway 70 near Raleigh, NC.

(c) Data from samples collected on divider strip of major highway in downtown Porto Alegre, RS, Brazil.

(d) Data are for catalyst-equipped cars. Carbonyls identified in emissions from cars without a catalytic converter also included isopentanal, 2-furaldehyde, tridecanal and tetradecanal (51, 52).

(e) Average of data for two 1995 medium-duty diesel trucks, hot start FTP urban driving cycle, California reformulatec diesel fuel.

(f) Cummins L10 engine, cold start and hot start tests with pre-1993, low aromatic content and California reformulatec diesel fuels.

(g) Compound tentatively identified, see text.

(h) o, m, and / or p-isomers, isomers not resolved.

(i) also ascribed to vehicle emissions (along with methyl vinyl ketone) from ambient air measurements made in Toron during the winter (53).

(j) other isomers possibly present, see text.

Table 3. Summary of carbonyl concentrations at the inlet and outlet of the Tuscarora Mountain Tunnel

Carbonyl	Tunnel inlet		Tunnel outlet		Outlet minus inlet		
	AVE (a)	RSD	AVE	RSD	AVE	RSD	R (b)
Formaldehyde	1.72	49	4.59	19	2.99	43	1.000
Acetaldehyde	1.12	58	2.25	22	1.18	26	0.413
Acetone	2.43	44	3.63	16	1.25	62	0.902
Propanal	0.161	51	0.345	11	0.185	40	0.622
Acrolein	0.102	36	0.315	13	0.217	21	0.623
Crotonaldehyde	0.119	36	0.435	13	0.322	19	0.563
Methacrolein	0.095	55	0.312	23	0.225	32	0.721
2-Butanone (MEK)	0.206	52	0.435	21	0.238	31	0.545
Butanal	0.124	39	0.214	17	0.096	31	0.742
Benzaldehyde	0.241	46	0.451	22	0.222	48	0.778
o/m/p-Anisaldehyde	0.0058	54	0.014	22	0.008	43	0.611
2-Pentanone	0.0055	44	0.277	21 (c)	0.282	18	0.596 (c)
C5 ALP ISM (d)	0.0026	65	0.248	13	0.249	13	0.163
Isopentanal	0.0011	65	0.031	13	0.030	15	0.206
Glyoxal	0.0003	65	0.093	13	0.094	13	0.150
Pentanal	0.0014	65	0.177	13	0.178	13	0.157
Acetophenone	0.0005	65	0.023	13	0.023	14	0.180
o-Tolualdehyde	0.011	58	0.105	23	0.096	21	0.499
m-Tolualdehyde	0.064	69	0.348	23	0.294	28	0.582
p-Tolualdehyde	0.014	69	0.147	23	0.138	23	0.473
C6 ALP ISM (d)	0.027	94	0.074	13	0.047	65	0.322
4-Methyl-2-Pentanone (MIBK)	0.112	38	0.140	28	0.028	12	0.563
C6 UNSAT ISM (TENT) (d)	0.150	31	0.213	15	0.067	81	0.521
Methyl Glyoxal	0.167	69	0.289	19	0.129	62	0.754
Hexanal	0.131	79	0.239	34	0.116	65	0.810
2,5-Dimethylbenzaldehyde	0.104	84	0.276	16	0.178	47	0.097
2,4-Dimethylbenzaldehyde/ISM (d)	0.131	34	0.180	19	0.051	84	0.348
2-Oxobutanal	0.049	96	0.062	65	0.016	65	0.695
Biacetyl	0.148	37	0.170	32	0.023	66	0.706
Heptanal	0.142	41	0.212	35	0.073	112	0.678
2,4,6-Trimethylbenzaldehyde/ISM (d)	0.079	61	0.141	23	0.062	50	0.480

(a) AVE: average concentration, micrograms per cubic meter. RSD: relative standard deviation, percent.

(b) R = correlation coefficient for linear regression of data for carbonyl vs. data for formaldehyde.

(c) Possible upper limits for actual values, see text.

(d) ALP = Aliphatic carbonyl; UNSAT = Unsaturated carbonyl; ISM = Isomer; /ISM = and/or isomers; TENT = tentative.

Table 4. Summary of measured carbonyl emission factors

Carbonyl	Emission factor, mg / km			
	lowest	highest	average	RSD, percent
Formaldehyde	3.11	9.93	5.41	41
Acetaldehyde	1.05	2.98	2.19	31
Acetone	0.95	3.75	2.14	38
Propanal	0.19	0.54	0.33	38
Acrolein	0.18	0.59	0.41	31
Crotonaldehyde	0.26	0.85	0.61	31
Methacrolein	0.16	0.70	0.43	41
2-Butanone (MEK)	0.17	0.79	0.46	45
Butanal	0.09	0.36	0.19	50
Benzaldehyde	0.17	0.90	0.44	66
o/m/p-Anisaldehyde	0.006	0.033	0.017	67
2-Pentanone (a)	0.240	0.98	0.56	46
C5 ALP ISM	0.192	0.73	0.49	37
Isopentanal	0.024	0.088	0.059	36
Glyoxal	0.072	0.276	0.184	37
Pentanal	0.137	0.523	0.35	37
Acetophenone	0.018	0.068	0.045	37
o-Tolualdehyde	0.088	0.37	0.19	50
m-Tolualdehyde	0.222	1.09	0.59	51
p-Tolualdehyde	0.126	0.53	0.28	51
C6 ALP ISM	0.0018	0.157	0.08	66
4-Methyl-2-Pentanone (MIBK)	0.022	0.090	0.054	41
C6 UNSAT ISM (TENT)	0.011	0.375	0.14	96
Methyl Glyoxal	0.042	0.516	0.23	73
Hexanal	0.074	0.600	0.21	74
2,5-Dimethylbenzaldehyde	0.085	0.700	0.34	60
2,4-Dimethylbenzaldehyde/ISM	0.0084	0.276	0.097	96
2-Oxobutanal	0.0076	0.070	0.029	71
Biacetyl	0.010	0.113	0.044	89
Heptanal	0.0045	0.183	0.098	68
2,4,6-Trimethylbenzaldehyde/ISM	0.026	0.200	0.115	56

(a) possible upper limit for actual values, see text.

Table 5. Carbonyl emission factors for LD and HD vehicles from regression of experimental data, with outliers deleted, vs. fraction of 7-8 HD vehicles

Carbonyl	n	m	sm	b=LD	sb	R^2	b+m=HD	s(b+m)	Rank LD	Rank HD
Formaldehyde	8	4.15	1.75	2.57	1.05	0.482	6.73	2.04	1	1
Acetaldehyde	7	3.30	0.53	0.64	0.27	0.886	3.95	0.59	3	2
Acetone	9	0.79	1.22	1.69	0.73	0.057	2.49	1.42	2	3
Propanal	7	0.50	0.11	0.11	0.06	0.787	0.62	0.13	7	13
Acrolein	7	0.61	0.11	0.10	0.05	0.861	0.71	0.12	8	11
Crotonaldehyde	7	0.92	0.13	0.14	0.07	0.898	1.07	0.15	5	4
Methacrolein	9	0.59	0.15	0.10	0.09	0.669	0.69	0.18	9	12
2-Butanone (MEK)	7	0.63	0.31	0.12	0.16	0.441	0.75	0.35	6	10
Butanal	7	0.15	0.01	0.06	0.01	0.947	0.22	0.01	13	23
Benzaldehyde	7	0.77	0.29	0.09	0.17	0.577	0.86	0.34	10	7
o/m/p-Anisaldehyde	7	0.03	0.00	0.00	0.00	0.778	0.03	0.00	31	30
2-Pentanone	9	0.93	0.18	0.04	0.11	0.783	0.97	0.21	17	6
C5 ALP ISM	8	0.78	0.08	0.07	0.04	0.933	0.86	0.09	11	8
Isopentanal	8	0.09	0.01	0.01	0.00	0.917	0.10	0.01	29	25
Glyoxal	8	0.30	0.03	0.02	0.01	0.937	0.32	0.03	21	18
Pentanal	8	0.56	0.06	0.05	0.03	0.935	0.61	0.07	15	14
Acetophenone	9	0.06	0.01	0.01	0.00	0.829	0.07	0.01	28	29
o-Tolualdehyde	8	0.28	0.04	0.02	0.02	0.861	0.30	0.05	22	19
m-Tolualdehyde	8	0.99	0.20	0.06	0.12	0.794	1.06	0.24	12	5
p-Tolualdehyde	8	0.49	0.10	0.01	0.06	0.794	0.50	0.12	23	17
C6 ALP ISM	7	0.13	0.06	0.03	0.03	0.458	0.17	0.07	20	24
4-Methyl-2-Pentanone (MIBK)	7	0.06	0.01	0.01	0.00	0.859	0.07	0.01	24	27
C6 UNSAT ISM (TENT)	6	0.26	0.19	0.03	0.12	0.321	0.30	0.23	18	20
Methyl Glyoxal	7	0.47	0.28	0.03	0.14	0.356	0.51	0.32	19	16
Hexanal	6	0.52	0.37	0.01	0.17	0.331	0.54	0.41	26	15
2,5-Dimethylbenzaldehyde	6	0.76	0.12	0.05	0.06	0.909	0.81	0.13	14	9
2,4-Dimethylbenzaldehyde/ISM	6	0.21	0.18	0.01	0.11	0.504	0.23	0.22	25	22
2-Oxobutanal	5	0.06	0.04	0.01	0.02	0.588	0.07	0.05	27	28
Biacetyl	7	0.08	0.08	0.00	0.05	0.301	0.09	0.10	30	26
Heptanal	9	-0.14	0.08	0.17	0.05	0.279	0.03	0.10	4	31
2,4,6-Trimethylbenzaldehyde/ISM	6	0.19	0.02	0.04	0.01	0.952	0.23	0.02	16	21

n = number of tunnel experiments; m = slope; b = intercept = LD emission factor, mg/km; b + m = 7-8 HD emission factor, mg/km; sm, sb and s(b + m) = one standard deviation; R = correlation coefficient; Rank LD (HD) = ranking of carbonyls in decreasing order of LD (HD) emission factors.

Table 6. Comparison of carbonyl emission factors for LD vehicles and 7-8 HD vehicles on a distance traveled basis and on a fuel consumed basis

Carbonyl	Emission Factor, mg/km (a)			Emission Factor, mg/L (b)		
	LD	HD	Ratio, HD/LD	LD	HD	Ratio, HD/LD
Formaldehyde	2.578	6.732	2.6	38.028	21.205	0.6
Acetaldehyde	0.643	3.951	6.1	9.488	12.445	1.3
Acetone	1.699	2.496	1.5	25.057	7.862	0.3
Propanal	0.117	0.626	5.4	1.721	1.971	1.1
Acrolein	0.108	0.718	6.7	1.593	2.263	1.4
Crotonaldehyde	0.148	1.072	7.3	2.177	3.376	1.6
Methacrolein	0.104	0.694	6.7	1.537	2.185	1.4
2-Butanone (MEK)	0.123	0.753	6.1	1.818	2.373	1.3
Butanal	0.062	0.220	3.5	0.916	0.693	0.8
Benzaldehyde	0.091	0.861	9.4	1.345	2.713	2.0
o/m/p-Anisaldehyde	0.001	0.035	28.9	0.018	0.110	6.2
2-Pentanone	0.043	0.973	22.7	0.632	3.063	4.8
C5 ALP ISM	0.071	0.860	12.1	1.049	2.710	2.6
Isopentanal	0.010	0.103	10.2	0.150	0.325	2.2
Glyoxal	0.026	0.326	12.7	0.377	1.026	2.7
Pentanal	0.050	0.617	12.4	0.736	1.943	2.6
Acetophenone	0.011	0.073	6.8	0.159	0.231	1.5
o-Tolualdehyde	0.023	0.305	13.5	0.335	0.962	2.9
m-Tolualdehyde	0.067	1.062	15.9	0.984	3.344	3.4
p-Tolualdehyde	0.016	0.506	31.4	0.238	1.594	6.7
C6 ALP ISM	0.034	0.171	5.1	0.497	0.537	1.1
4-Methyl-2-Pentanone (MIBK)	0.014	0.079	5.5	0.211	0.248	1.2
C6 UNSAT ISM (TENT)	0.038	0.304	7.9	0.565	0.958	1.7
Methyl Glyoxal	0.036	0.512	14.2	0.534	1.614	3.0
Hexanal	0.014	0.542	39.7	0.202	1.708	8.5
2,5-Dimethylbenzaldehyde	0.050	0.811	16.1	0.742	2.556	3.4
2,4-Dimethylbenzaldehyde/ISM	0.014	0.232	16.9	0.203	0.731	3.6
2-Oxobutanal	0.011	0.076	6.9	0.161	0.240	1.5
Biacetyl	0.008	0.096	11.5	0.124	0.303	2.4
Heptanal	0.179	0.034	0.2	2.633	0.106	0.0
2,4,6-Trimethylbenzaldehyde/ISM	0.045	0.235	5.2	0.668	0.741	1.1
All measured carbonyls	**6.434**	**26.075**	**4.05**	**94.898**	**82.136**	**0.865**

(a) from data in Table 5, standard deviations omitted for clarity.

(b) fuel economy = 14.75 km/L (LD) and 3.15 km/L (HD).

Table 7. Literature data for on-road vehicle emission factors for formaldehyde and acetaldehyde

	Formaldehyde, mg / km			Acetaldehyde, mg / km		
	Light-duty vehicles	Heavy-duty vehicles	Overall fleet	Light-duty vehicles	Heavy-duty vehicles	Overall fleet
Tauerntunnel near Salzburg, Austria, 1988 (33) (a)			24.6 ± 6.9			7.15 ± 2.26
Van Nuys Tunnel, urban Los Angeles, CA, area, 1993 (31) (b)			20.3			4.6
Fort McHenry Tunnel, Baltimore, MD, 1992 (22, 25, 26) (c)	4.31 ± 1.11	32.7 ± 5.82		1.30 ± 0.31	20.0 ± 1.7	
Tuscarora Mountain Tunnel, South central PA, 1992 (22, 25, 26) (c)	3.88 ± 1.37	26.87 ± 4.52				
Caldecott Tunnel, San Francisco Bay area, CA (d):						
1994, August (27) (e)	7.10 ± 0.29			1.65 ± 0.13		
1994, October (27) (e)	8.00 ± 0.29			1.72 ± 0.29		
1995 (28, 29)	7.06 ± 0.32			1.46 ± 0.10		
1996 (28, 29)	7.12 ± 0.51			1.20 ± 0.10		
1997 (28, 29)	4.17 ± 0.58			0.92 ± 0.13		
1999 (34)	3.73 ± 0.46			0.96 ± 0.10		
Dynamometer tests (38, 51)	8.69 (f)	22.3 (g)		3.94 (f)	41.8 (g)	
Tuscarora Mountain Tunnel, 1999 (this study)	2.58 ± 1.05 (h)	6.73 ± 2.05 (h, i)	5.41 ± 2.22 (j)	0.64 ± 0.27 (h)	3.95 ± 0.60 (h, i)	2.19 ± 0.68 (j)

(a) Results reported by the authors in gm / km, ± one standard deviation. The authors also reported emission factors for a weekday (Friday) and a weekend (Sunday). Emission factors (mg / kg) were 29.0 ± 7.5 (Sunday) and 20.2 ± 1.5 (Friday) for formaldehyde and 8.7 ± 2.0 (Sunday) and 5.6 ± 1.4 (Friday) for acetaldehyde.

(b) Mostly light-duty vehicles, results reported by the authors in mg / L of fuel consumed (no standard deviation given) and converted to mg / km using a fuel economy of 6.3 km / L (54).

(c) Results reported by the authors in mg / vehicle•mile, ± one standard deviation.

(d) Results reported by the authors in mg / L of fuel consumed, ± 95% confidence interval, and converted to mg / km using a fuel economy of 8.3 km / L (27-29).

(e) Before (August) and after (October) introduction of MTBE as the oxygenated additive to gasoline (27).

(f) Average of data for 9 catalyst-equipped cars (model year 1981-1994, engine displacement 1.5 - 5.0 L, 4-8 cylinders, vehicle mileage 17,500 - 106,700, cold start FTP urban driving cycle (51).

(g) Average of data for two 1995 medium-duty diesel trucks, hot start FTP urban driving cycle, California reformulated diesel fuel (38).

(h) Calculated using Equation 2, data for other carbonyls are given in Table 5.

(i) For class 7-8 HD vehicles.

(j) From Table 4.

Table 8. On-road vehicle emission factors for carbonyls and other pollutants

(Tuscarora Mountain Tunnel, 1999)

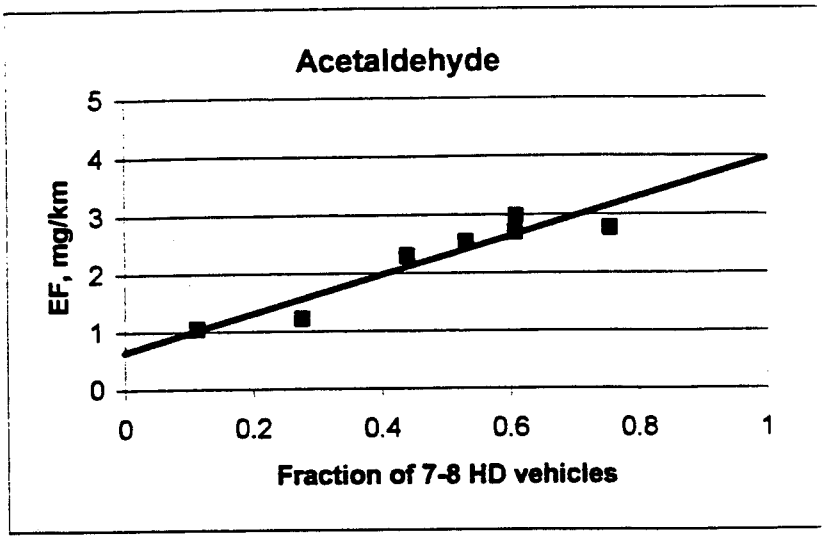
	Emission factor (a)		Emission factor ratio, total carbonyls / other pollutant, percent	
	LD	HD	LD	HD
CO_2, g / km	155 ± 15	744 ± 13	4.1×10^{-3}	3.5×10^{-3}
CO, g / km	1.93 ± 0.68	—	0.33	—
NO (as NO_2), g / km	0.422 ± 0.068	11.87 ± 1.93	1.52	0.22
Total hydrocarbons, g / km	0.404 ± 0.211	1.49 ± 0.81	1.58	1.77
PM_{10}, mg / km	13 ± 13	178 ± 13	49.2	14.6
$PM_{2.5}$, mg / km	9 ± 11	132 ± 17	71.1	19.8
Total measured carbonyls, mg / km	6.40	26.07	(100)	(100)

(a) data for CO_2, CO, NO, THC and PM are from Gertler, et al., (36, 55).

Figure Captions

Figure 1. Examples of scatterplots of measured carbonyl emission factors vs. fraction of weight classes 7-8 HD vehicles (outliers omitted). Top: acetaldehyde, middle: crotonaldehyde, bottom: 2,5-dimethylbenzaldehyde. Regression parameters are given in Table 5.

Figure 2. Examples of scatterplots of measured carbonyl emission factors vs. fraction of weight classes 7-8 HD vehicles (outliers omitted). Top: glyoxal, middle: butanal, bottom: 2,4,6-trimethylbenzaldehyde. Regression parameters are given in Table 5.


Acetaldehyde
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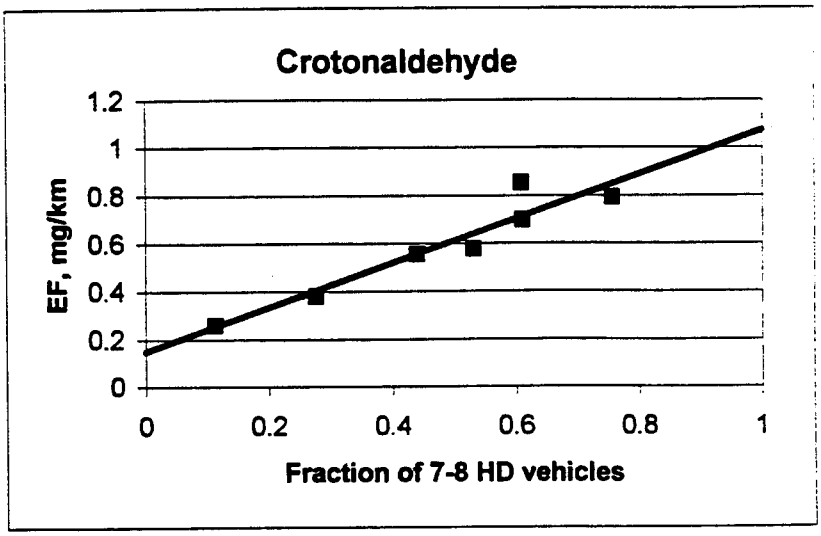
1
2
3
4
5
0
0.2
0.4
0.6
0.8
1
Fraction of 7-8 HD vehicles


Crotonaldehyde
EF, mg/km
0
0.2
0.4
0.6
0.8
1
1.2
0
0.2
0.4
0.6
0.8
1
Fraction of 7-8 HD vehicles

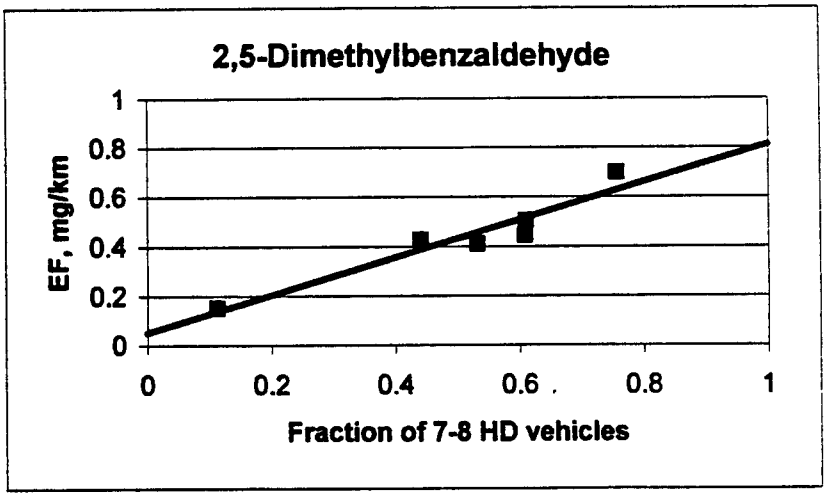
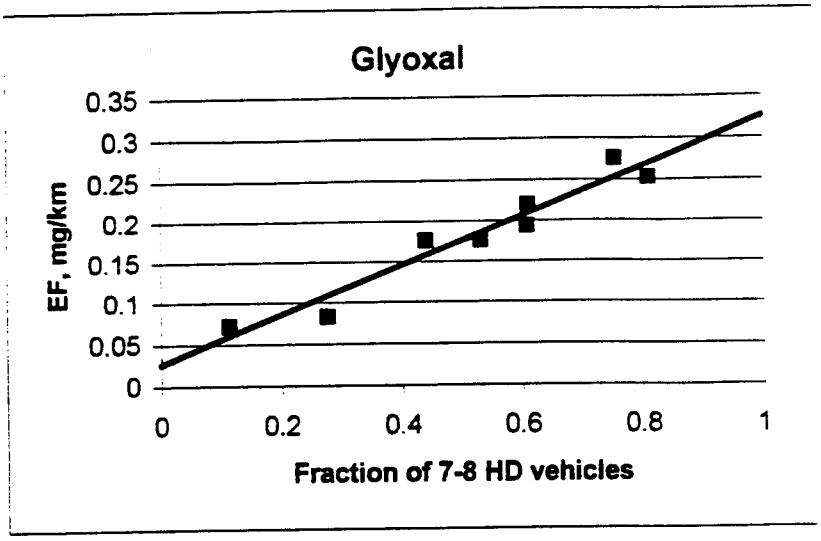
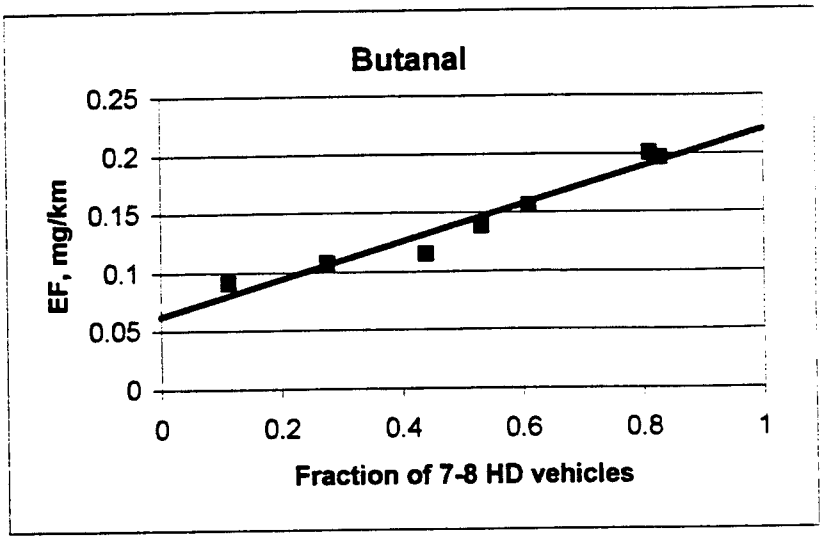

2,5-Dimethylbenzaldehyde
EF, mg/km
0
0.2
0.4
0.6
0.8
1
0
0.2
0.4
0.6
0.8
1
Fraction of 7-8 HD vehicles

Figure 1


Glyoxal
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
EF, mg/km
0
0.2
0.4
0.6
0.8
1
Fraction of 7-8 HD vehicles


Butanal
0.25
0.2
0.15
0.1
0.05
0
EF, mg/km
0
0.2
0.4
0.6
0.8
1
Fraction of 7-8 HD vehicles

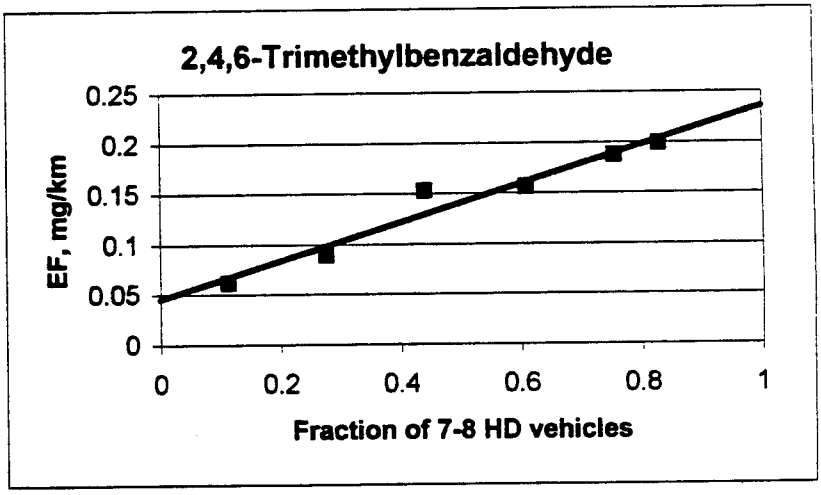

2,4,6-Trimethylbenzaldehyde
0.25
0.2
0.15
0.1
0.05
0
EF, mg/km
0
0.2
0.4
0.6
0.8
1
Fraction of 7-8 HD vehicles

Figure 2

APPENDIX

Table A1. Concentrations of carbonyls measured at the inlet of the Tuscarora Mountain Tunnel.

Table A2. Concentrations of carbonyls measured at the outlet of the Tuscarora Mountain Tunnel.

Table A3. Emission factors for LD and HD vehicles, from regression of all experimental data vs. fraction of total HD vehicles.

Table A4. Emission factors for LD and HD vehicles, from regression of all experimental data vs. fraction of 7-8 HD vehicles.

Table A5. Emission factors for LD and HD vehicles, from regression of experimental data with outliers deleted, vs. fraction of total HD vehicles.

Table A1. Concentrations of carbonyls measured at the inlet of the Tuscarora Mountain Tunnel

Sample	12-1-C18	11-2-SG	11-3-SG	11-5-SG	11-6-SG	11-7-SG	11-8-SG	11-9-SG	11-10-SG	11-13-SG
Start Date	5/18/99	5/19/99	5/19/99	5/19/99	5/19/99	5/19/99	5/20/99	5/20/99	5/21/99	5/21/99
Stop Date	5/18/99	5/19/99	5/19/99	5/19/99	5/19/99	5/20/99	5/20/99	5/20/99	5/21/99	5/21/99
Start Time	22:00	0:00	2:00	19:00	21:00	23:00	1:00	16:00	5:00	17:00
Stop Time	23:00	1:00	3:06	20:13	22:00	0:00	2:05	17:07	6:03	18:00
					Carbonyl, ug/m^3					
Formaldehyde	2.28	3.10	2.25	1.61	1.88	Void*	1.16	2.03	0.767	0.378
Acetaldehyde	1.48	1.78	2.33	0.80	1.22		0.813	0.722	0.736	0.193
Acetone	2.67	3.40	4.31	1.91	2.20		2.41	2.82	1.60	0.55
Propanal	0.180	0.225	0.337	0.138	0.148		0.142	0.112	0.106	0.056
Acrolein	0.140	0.118	0.139	0.072	0.115		0.093	0.134	0.067	0.035
Crotonaldehyde	0.163	0.137	0.162	0.084	0.134		0.109	0.156	0.079	0.041
Methacrolein	0.082	0.187	0.160	0.044	0.067		0.121	0.088	0.068	0.031
2-Butanone (MEK)	0.191	0.379	0.362	0.103	0.157		0.250	0.200	0.145	0.067
Butanal	0.133	0.182	0.193	0.111	0.110		0.138	0.130	0.071	0.042
Benzaldehyde	0.369	0.350	0.372	0.214	0.304		0.152	0.203	0.118	0.081
o/m/p-Anisaldehyde	0.010	0.007	0.008	0.004	0.008		0.003	0.004	0.002	0.001
2-Pentanone	0.006	0.007	0.009	0.004	0.004		0.005	0.006	0.003	0.001
C5 ALP ISM	0.002	0.004	0.005	0.001	0.001		0.003	0.002	0.001	0.000
Isopentanal	0.000	0.002	0.002	0.000	0.000		0.001	0.001	0.000	0.000
Glyoxal	0.000	0.000	0.000	0.000	0.000		0.000	0.000	0.000	0.000
Pentanal	0.001	0.002	0.003	0.000	0.000		0.001	0.001	0.000	0.000
Acetophenone	0.000	0.000	0.001	0.000	0.000		0.000	0.000	0.000	0.000
o-Tolualdehyde	0.011	0.021	0.018	0.006	0.009		0.005	0.016	0.011	0.001
m-Tolualdehyde	0.064	0.106	0.112	0.123	0.053		0.023	0.077	0.013	0.003
p-Tolualdehyde	0.013	0.022	0.243	0.026	0.011		0.005	0.016	0.003	0.000
C6 ALP ISM	0.008	0.021	0.054	0.012	0.007		0.074	0.052	0.013	0.002
4-Methyl-2-Pentanone (MIBK)	0.168	0.120	0.127	0.139	0.138		0.110	0.119	0.040	0.046
C6 UNSAT ISM (TENT)	0.207	0.148	0.157	0.172	0.170		0.177	0.171	0.069	0.079
Methyl Glyoxal	0.226	0.286	0.384	0.117	0.186		0.106	0.091	0.092	0.016
Hexanal	0.109	0.290	0.310	0.060	0.090		0.070	0.148	0.090	0.008
2,5-Dimethylbenzaldehyde	0.054	0.211	0.239	0.032	0.044		0.025	0.131	0.177	0.016
2,4-Dimethylbenzaldehyde/ISM	0.203	0.143	0.149	0.134	0.167		0.112	0.091	0.127	0.049
2-Oxobutanal	0.038	0.127	0.122	0.020	0.031		0.071	0.014	0.002	0.014
Biacetyl	0.206	0.142	0.231	0.151	0.170		0.078	0.165	0.126	0.058
Heptanal	0.158	0.171	0.120	0.237	0.130		0.107	0.205	0.098	0.047
2,4,6-Trimethylbenzaldehyde/ISM	0.163	0.111	0.048	0.055	0.134		0.020	0.037	0.096	0.048

* Sample 11-7-SG was not started.

Table A2. Concentrations of carbonyls measured at the outlet of the Tuscarora Mountain Tunnel

Sample	10-1-C18	9-2-SG	9-3-SG	9-5-SG	9-6-SG	9-7-SG	9-8-SG	9-9-SG	9-10-SG	9-13-SG
Start Date	5/18/99	5/19/99	5/19/99	5/19/99	5/19/99	5/19/99	5/20/99	5/20/99	5/21/99	5/21/99
Stop Date	5/18/99	5/19/99	5/19/99	5/19/99	5/19/99	5/20/99	5/20/99	5/20/99	5/21/99	5/21/99
Start Time	22:00	0:00	2:00	19:00	21:00	23:00	1:00	16:00	5:00	17:00
Stop Time	23:00	1:00	3:00	20:00	22:00	0:00	2:00	17:00	6:00	18:00
					Carbonyl, ug/m^3					
Formaldehyde	4.47	4.88	5.02	4.44	3.92	3.52	3.19	5.32	4.95	6.18
Acetaldehyde	2.94	2.49	3.08	2.25	2.59	1.82	1.77	2.01	1.87	1.70
Acetone	3.47	4.15	4.94	3.50	3.05	3.12	3.37	3.82	3.18	3.67
Propanal	0.372	0.308	0.408	0.321	0.326	0.335	0.315	0.405	0.333	0.325
Acrolein	0.367	0.287	0.278	0.315	0.322	0.278	0.276	0.405	0.317	0.300
Crotonaldehyde	0.507	0.397	0.384	0.436	0.445	0.383	0.382	0.559	0.438	0.415
Methacrolein	0.318	0.443	0.347	0.225	0.280	0.241	0.265	0.259	0.328	0.414
2-Butanone (MEK)	0.464	0.646	0.507	0.329	0.408	0.352	0.386	0.378	0.478	0.404
Butanal	0.210	0.253	0.262	0.184	0.184	0.159	0.245	0.244	0.221	0.173
Benzaldehyde	0.453	0.567	0.645	0.351	0.398	0.343	0.358	0.438	0.498	0.452
o/m/p-Anisaldehyde	0.013	0.017	0.019	0.010	0.012	0.010	0.011	0.013	0.014	0.013
2-Pentanone	0.242	0.325	0.344	0.288	0.213	0.184	0.213	0.312	0.301	0.345
C5 ALP ISM	0.289	0.201	0.232	0.298	0.254	0.219	0.254	0.235	0.219	0.276
Isopentanal	0.036	0.025	0.029	0.037	0.031	0.027	0.031	0.029	0.027	0.034
Glyoxal	0.108	0.075	0.087	0.111	0.095	0.082	0.095	0.088	0.082	0.103
Pentanal	0.206	0.143	0.166	0.212	0.181	0.156	0.181	0.168	0.156	0.197
Acetophenone	0.027	0.019	0.022	0.028	0.024	0.020	0.024	0.022	0.020	0.026
o-Tolualdehyde	0.102	0.128	0.145	0.079	0.900	0.077	0.080	0.110	0.102	0.129
m-Tolualdehyde	0.340	0.426	0.484	0.264	0.299	0.258	0.269	0.366	0.034	0.431
p-Tolualdehyde	0.144	0.180	0.205	0.111	0.126	0.109	0.114	0.155	0.144	0.182
C6 ALP ISM	0.085	0.059	0.069	0.088	0.075	0.065	0.075	0.069	0.065	0.082
4-Methyl-2-Pentanone (MIBK)	0.191	0.143	0.158	0.164	0.167	0.144	0.137	0.150	0.067	0.078
C6 UNSAT ISM (TENT)	0.220	0.284	0.231	0.213	0.193	0.166	0.213	0.183	0.204	0.215
Methyl Glyoxal	0.294	0.359	0.398	0.268	0.258	0.223	0.283	0.216	0.308	0.281
Hexanal	0.214	0.339	0.361	0.202	0.188	0.162	0.118	0.226	0.343	0.232
2,5-Dimethylbenzaldehyde	0.301	0.283	0.293	0.301	0.265	0.228	0.265	0.221	0.365	0.234
2,4-Dimethylbenzaldehyde/ISM	0.215	0.244	0.196	0.139	0.189	0.163	0.185	0.149	0.139	0.176
2-Oxobutanal	0.042	0.135	0.130	0.049	0.037	0.032	0.087	0.034	0.032	0.040
Biacetyl	0.211	0.148	0.269	0.179	0.186	0.160	0.086	0.196	0.172	0.091
Heptanal	0.247	0.193	0.121	0.260	0.217	0.187	0.142	0.327	0.114	0.310
2,4,6-Trimethylbenzaldehyde/ISM	0.175	0.183	0.091	0.152	0.154	0.133	0.085	0.131	0.163	0.137

Table A3. Emission factors for LD and HD vehicles, from regression of all experimental data vs. fraction of total HD vehicles

Carbonyl	n	m	sm	b=LD	sb	R^2	b+m=HD	s(b+m)	Rank LD	Rank HD
Formaldehyde	9	4.69	2.91	2.66	1.84	0.271	7.34	3.44	1	1
Acetaldehyde	9	1.86	0.76	1.10	0.48	0.462	2.95	0.89	3	2
Acetone	9	0.74	1.20	1.70	0.76	0.052	2.45	1.43	2	3
Propanal	9	0.15	0.18	0.24	0.12	0.086	0.39	0.22	4	15
Acrolein	9	0.41	0.12	0.17	0.07	0.632	0.58	0.14	8	11
Crotonaldehyde	9	0.66	0.15	0.22	0.10	0.732	0.88	0.18	5	6
Methacrolein	9	0.57	0.16	0.09	0.10	0.655	0.67	0.19	12	10
2-Butanone (MEK)	9	0.55	0.24	0.13	0.15	0.427	0.68	0.29	11	9
Butanal	9	0.23	0.11	0.05	0.07	0.382	0.28	0.13	16	18
Benzaldehyde	9	0.72	0.35	0.01	0.22	0.383	0.73	0.41	22	8
o/m/p-Anisaldehyde	9	0.03	0.01	0.00	0.01	0.497	0.03	0.01	26	31
2-Pentanone	9	0.91	0.18	0.02	0.12	0.776	0.93	0.22	19	5
C5 ALP ISM	9	0.67	0.11	0.09	0.07	0.845	0.76	0.13	13	7
Isopentanal	9	0.08	0.01	0.01	0.01	0.812	0.09	0.02	23	25
Glyoxal	9	0.26	0.04	0.03	0.03	0.853	0.29	0.05	18	17
Pentanal	9	0.48	0.08	0.06	0.05	0.848	0.55	0.09	15	12
Acetophenone	9	0.06	0.01	0.01	0.01	0.834	0.07	0.01	24	27
o-Tolualdehyde	9	0.34	0.07	-0.01	0.04	0.786	0.33	0.08	27	16
m-Tolualdehyde	9	1.05	0.23	-0.03	0.15	0.741	1.02	0.28	30	4
p-Tolualdehyde	9	0.51	0.10	-0.02	0.07	0.773	0.48	0.12	28	13
C6 ALP ISM	9	0.02	0.08	0.07	0.05	0.013	0.09	0.10	14	24
4-Methyl-2-Pentanone (MIBK)	9	0.08	0.01	0.01	0.01	0.849	0.09	0.02	25	26
C6 UNSAT ISM	9	0.30	0.17	-0.03	0.11	0.299	0.26	0.20	31	20
Methyl Glyoxal	9	0.12	0.25	0.16	0.16	0.031	0.28	0.30	10	19
Hexanal	9	0.07	0.23	0.17	0.15	0.012	0.24	0.28	7	21
2,5-Dimethylbenzaldehyde	9	0.30	0.29	0.17	0.18	0.132	0.46	0.34	9	14
2,4-Dimethylbenzaldehyde/ISM	9	0.20	0.12	-0.02	0.08	0.287	0.18	0.14	29	22
2-Oxobutanal	9	0.01	0.03	0.02	0.02	0.022	0.03	0.04	20	30
Biacetyl	9	0.05	0.06	0.02	0.04	0.083	0.06	0.07	21	28
Heptanal	9	-0.14	0.09	0.18	0.05	0.278	0.04	0.10	6	29
2,4,6-Trimethylbenzaldehyde/ISM	9	0.13	0.08	0.04	0.05	0.250	0.17	0.10	17	23

n = number of tunnel experiments; m = slope; b = intercept = LD emission factor, mg/km; b + m = HD emission factor, mg/km; sm, sb and s(b + m) = one standard deviation; R = correlation coefficient; Rank LD (HD) = ranking of carbonyls in decreasing order of LD (HD) emission factors.

Table A4. Emission factors for LD and HD vehicles, from regression of all experimental data vs. fraction of 7-8 HD vehicles

Carbonyl	n	m	sm	b=LD	sb	R^2	b+m=HD	s(b+m)	Rank LD	Rank HD
Formaldehyde	9	4.72	2.97	2.80	1.78	0.265	7.52	3.46	1	1
Acetaldehyde	9	1.85	0.78	1.16	0.47	0.448	3.02	0.91	3	2
Acetone	9	0.80	1.22	1.70	0.73	0.057	2.50	1.42	2	3
Propanal	9	0.15	0.19	0.24	0.11	0.086	0.40	0.22	4	15
Acrolein	9	0.42	0.12	0.18	0.07	0.637	0.59	0.14	7	11
Crotonaldehyde	9	0.67	0.15	0.24	0.09	0.736	0.91	0.18	5	6
Methacrolein	9	0.59	0.16	0.10	0.09	0.669	0.69	0.18	13	10
2-Butanone (MEK)	9	0.57	0.24	0.15	0.15	0.438	0.71	0.28	11	9
Butanal	9	0.24	0.11	0.05	0.07	0.389	0.29	0.13	16	18
Benzaldehyde	9	0.74	0.35	0.03	0.21	0.389	0.77	0.41	20	8
o/m/p-Anisaldehyde	9	0.03	0.01	0.00	0.01	0.508	0.03	0.01	27	31
2-Pentanone	9	0.93	0.18	0.04	0.11	0.783	0.97	0.22	17	5
C5 ALP ISM	9	0.68	0.11	0.11	0.07	0.840	0.79	0.13	12	7
Isopentanal	9	0.08	0.01	0.02	0.01	0.807	0.09	0.02	23	24
Glyoxal	9	0.26	0.04	0.04	0.02	0.848	0.30	0.05	18	17
Pentanal	9	0.49	0.08	0.08	0.05	0.843	0.57	0.09	14	12
Acetophenone	9	0.06	0.01	0.01	0.01	0.829	0.07	0.01	24	27
o-Tolualdehyde	9	0.35	0.07	0.00	0.04	0.784	0.35	0.08	26	16
m-Tolualdehyde	9	1.06	0.24	0.00	0.14	0.741	1.06	0.28	28	4
p-Tolualdehyde	9	0.51	0.11	-0.01	0.06	0.772	0.51	0.12	29	13
C6 ALP ISM	9	0.02	0.08	0.07	0.05	0.011	0.09	0.10	15	25
4-Methyl-2-Pentanone (MIBK)	9	0.08	0.01	0.01	0.01	0.834	0.09	0.02	25	26
C6 UNSAT ISM	9	0.31	0.17	-0.03	0.10	0.319	0.28	0.20	31	20
Methyl Glyoxal	9	0.13	0.26	0.16	0.15	0.037	0.29	0.30	10	19
Hexanal	9	0.07	0.24	0.17	0.14	0.011	0.24	0.28	9	21
2,5-Dimethylbenzaldehyde	9	0.30	0.29	0.17	0.18	0.132	0.48	0.34	8	14
2,4-Dimethylbenzaldehyde/ISM	9	0.21	0.12	-0.02	0.07	0.315	0.19	0.14	30	22
2-Oxobutanal	9	0.01	0.03	0.02	0.02	0.025	0.03	0.04	21	29
Biacetyl	9	0.04	0.06	0.02	0.04	0.072	0.06	0.07	22	28
Heptanal	9	-0.14	0.09	0.18	0.05	0.279	0.03	0.10	6	30
2,4,6-Trimethylbenzaldehyde/ISM	9	0.14	0.08	0.04	0.05	0.276	0.18	0.10	19	23

n = number of tunnel experiments; m = slope; b = intercept = LD emission factor, mg/km; b + m = 7-8 HD emission factor, mg/km; sm, sb and s(b + m) = one standard deviation; R = correlation coefficient; Rank LD (HD) = ranking of carbonyls in decreasing order of LD (HD) emission factors.

Table A5. Emission factors for LD and HD vehicles, from regression of experimental data, with outliers deleted, vs. fraction of total HD vehicles

Carbonyl	n	m	sm	b=LD	sb	R^2	b+m=HD	s(b+m)	Rank LD	Rank HD
Formaldehyde	8	4.13	1.72	2.45	1.08	0.491	6.58	2.03	1	1
Acetaldehyde	7	3.25	0.51	0.56	0.28	0.892	3.81	0.58	3	2
Acetone	9	0.74	1.20	1.70	0.76	0.052	2.45	1.43	2	3
Propanal	7	0.49	0.12	0.11	0.07	0.775	0.60	0.14	6	13
Acrolein	7	0.59	0.11	0.10	0.06	0.852	0.69	0.13	8	11
Crotonaldehyde	7	0.90	0.14	0.13	0.08	0.891	1.03	0.16	5	4
Methacrolein	9	0.57	0.16	0.09	0.10	0.655	0.67	0.19	9	12
2-Butanone (MEK)	7	0.62	0.31	0.11	0.17	0.448	0.73	0.35	7	10
Butanal	7	0.15	0.02	0.06	0.01	0.941	0.21	0.02	12	23
Benzaldehyde	7	0.77	0.29	0.07	0.18	0.590	0.84	0.34	10	7
o/m/p-Anisaldehyde	7	0.03	0.01	0.00	0.00	0.789	0.03	0.01	31	31
2-Pentanone	9	0.91	0.18	0.02	0.12	0.776	0.93	0.22	20	6
C5 ALP ISM	8	0.76	0.09	0.06	0.06	0.919	0.82	0.11	11	8
Isopentanal	8	0.09	0.01	0.01	0.01	0.902	0.10	0.01	28	25
Glyoxal	8	0.29	0.03	0.02	0.02	0.923	0.31	0.04	21	18
Pentanal	8	0.55	0.07	0.04	0.04	0.921	0.59	0.08	14	14
Acetophenone	9	0.06	0.01	0.01	0.01	0.834	0.07	0.01	27	29
o-Tolualdehyde	8	0.28	0.05	0.02	0.03	0.840	0.29	0.06	22	19
m-Tolualdehyde	8	0.98	0.20	0.04	0.13	0.793	1.02	0.24	13	5
p-Tolualdehyde	8	0.48	0.10	0.00	0.07	0.793	0.49	0.12	30	16
C6 ALP ISM	7	0.14	0.06	0.03	0.04	0.477	0.17	0.07	19	24
4-Methyl-2-Pentanone (MIBK)	7	0.06	0.01	0.01	0.01	0.873	0.08	0.01	24	27
C6 UNSAT ISM (TENT)	6	0.26	0.19	0.04	0.13	0.311	0.29	0.23	17	20
Methyl Glyoxal	7	0.45	0.29	0.03	0.16	0.332	0.48	0.33	18	17
Hexanal	6	0.50	0.37	0.01	0.18	0.314	0.51	0.41	25	15
2,5-Dimethylbenzaldehyde	6	0.74	0.13	0.04	0.08	0.890	0.77	0.15	16	9
2,4-Dimethylbenzaldehyde/ISM	6	0.20	0.11	0.01	0.07	0.455	0.22	0.13	23	22
2-Oxobutanal	5	0.06	0.03	0.01	0.02	0.596	0.07	0.03	26	28
Biacetyl	7	0.09	0.06	0.01	0.03	0.306	0.09	0.07	29	26
Heptanal	9	-0.14	0.09	0.18	0.05	0.278	0.04	0.10	4	30
2,4,6-Trimethylbenzaldehyde/ISM	6	0.19	0.02	0.04	0.01	0.953	0.23	0.02	15	21

n = number of tunnel experiments; m = slope; b = intercept = LD emission factor, mg/km; b + m = HD emission factor, mg/km; sm, sb and s(b + m) = one standard deviation; R = correlation coefficient; Rank LD (HD) = ranking of carbonyls in decreasing order of LD (HD) emission factors.

MEASUREMENTS OF VEHICLE EMISSIONS OF SPECIATED CARBOXYLIC ACIDS IN THE CALDECOTT TUNNEL

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ABSTRACT

Carboxylic acids play an important role in atmospheric acidity, long-range transport of airborne pollutants, and acid deposition. While vehicles are known to emit carboxylic acids, no information is available regarding the nature and magnitude of emissions of carboxylic acids by on-road vehicles. To identify carboxylic acids and measure their emission factors, we have carried out in July-August 1999 a field study at the Caldecott Tunnel, a highway tunnel in the San Francisco, CA, Bay Area. The vehicle fleet studied was an urban-suburban commuter fleet (ca. 6 years old on the average) and consisted almost entirely of light-duty vehicles equipped with 3-way catalysts and fueled with oxygenated California Phase 2 reformulated gasoline. Samples of 2 hr. duration (corresponding to 8,400 ± 160 vehicles) were collected at the tunnel entrance and tunnel exit, derivatized with pentafluorobenzyl bromide, and analyzed by liquid chromatography with detection by diode array ultraviolet spectroscopy and by atmospheric pressure negative chemical ionization mass spectrometry. Thirty-three monocarboxylic acids were identified including 22 saturated aliphatic acids (C_1-C_{12}), 5 unsaturated aliphatic acids and 6 aromatic acids. Emission factors were calculated using concentration differences between tunnel exit and tunnel inlet and were, in units of mg carboxylic acid emitted / L fuel consumed, 19.52 ± 1.10 for acetic acid, 5.96 ± 0.46 for formic acid, 1.25 for the sum of C_3-C_{12} saturated aliphatic acids, 0.892 for the sum of aromatic acids, 0.126 for the sum of unsaturated aliphatic acids and 27.75 mg / L for total measured carboxylic acids, of which acetic acid and formic acid together accounted for 92 percent. Ratios of emission factors were 5.2 for formaldehyde / formic acid, 0.41 for acetaldehyde / acetic acid, and 2.5 for total carbonyls / total carboxylic acids.

INTRODUCTION

Carboxylic acids are ubiquitous in the atmosphere and are important as primary pollutants (emitted directly), as secondary pollutants (formed in-situ) and for their relevance to atmospheric acidity, acidic deposition, long-range transport of airborne contaminants on regional and global scales, and geochemical cycles. Carboxylic acids have received regulatory attention for their role in acid deposition, human exposure to acidic air pollutants and toxicity (e.g., as U. S. EPA Hazardous Air Pollutants). Direct sources of carboxylic acids in the atmosphere include vehicle exhaust (see below), biogenic emissions, biomass burning, bacterial action in soils, and wood combustion. Indirect sources of carboxylic acids include the gas phase reaction of ozone with anthropogenic and biogenic unsaturated compounds (alkenes, isoprene, terpenes, unsaturated oxygenates), the reactions of peroxyacyl radicals with HO_2 and organic peroxy radicals (RO_2), the OH-initiated oxidation of aromatic hydrocarbons (leading to aromatic acids, e.g., benzoic, and aliphatic acids, e.g., pyruvic), and the aqueous phase oxidation of organic compounds in clouds, fog, and rain. Ambient concentrations of gas phase and particulate phase carboxylic acids have been measured numerous times in settings ranging from urban centers to remote locations including marine and arctic air. Carboxylic acids have also been measured in cloudwater, rain, dew, fog, snow, and ice cores.

To assess the importance of vehicles as a source of carboxylic acids, it is necessary to measure the corresponding emission factors. Carboxylic acids may be present in vehicle fuels as corrosion inhibitors (1). They are emitted as incomplete oxidation products of fuel components (2, 3), and may also be present in used engine oil (2). Past studies have

documented the presence of several carboxylic acids in the exhaust of a single light-duty vehicle (2, 3) and the exhaust of a single light-duty diesel truck (3). Emission factors of high molecular weight acids (C_6 and higher) have been measured in dynamometer tests involving several light-duty gasoline vehicles and light-duty diesel trucks (4, 5). Dynamometer tests involve a limited number of vehicles studied under a prescribed set of operating conditions. Vehicle emissions can also be measured under real-world conditions, for example in highway tunnels (6). Two highway tunnel studies have documented vehicle emissions of formic acid and acetic acid, but vehicle emission factors were not measured (7-9). One study was carried out near Hampton, VA in the late 1980s (7) and the other in Sao Paulo, Brazil in the mid-1990s (8, 9). These two studies involved vehicle fuels, engine technology and exhaust control technology that were substantially different from those relevant to today's U. S. vehicle fleet. For example, light-duty vehicles in Sao Paulo use either ethanol fuel or a blend of ca. 22% ethanol and 78% gasoline, and the composition of the gasoline used in that blend is different from that of current U. S. gasolines.

We describe here the methods and results of a study in which airborne carboxylic acids have been measured in July-August 1999 in a highway tunnel, the Caldecott Tunnel in the San Francisco, CA, metropolitan area. The vehicle fleet studied (average vehicle age = about 6 years) was an urban-suburban commuter fleet (4200 ± 80 vehicles / hour) and consisted almost entirely of light-duty vehicles equipped with 3-way catalysts and fueled with oxygenated California Phase 2 reformulated gasoline. Samples were collected on KOH-impregnated filters and carboxylic acids were identified as their pentafluorobenzyl esters using a recently described method (10). This method involves liquid chromatography analysis with detection by diode array ultraviolet spectroscopy and by atmospheric pressure negative chemical ionization mass spectrometry (LC-DAD-APNCI-MS). Thirty-three monocarboxylic acids have been

identified and their concentrations measured at the tunnel entrance and tunnel exit. This information has been used to calculate on-road emission factors for C_1-C_{12} monocarboxylic acids emitted by light-duty vehicles.

As noted above, on-road emissions of speciated carboxylic acids have not been measured prior to this work. The results described here, together with data on CO_2, CO, NO_x, NH_3, speciated hydrocarbons and speciated carbonyls obtained at the same time in the same highway tunnel (11, 12) represent a comprehensive data base regarding mid-1999 on-road emissions of light-duty vehicles that use California Phase 2 reformulated gasoline. In addition, recently legislated changes in fuel composition, including the phasing out of MTBE from reformulated gasolines sold in California (13), may result in changes in the nature and magnitude of vehicle emissions of carboxylic acids and other pollutants. The withdrawal of MTBE from gasolines is also being considered at the federal (U. S.) level, as is the possible replacement of MTBE by ethanol (14). The incomplete combustion of ethanol in spark-ignition engines leads to acetaldehyde and other products including acetic acid (15). Thus, vehicle emissions of acetaldehyde and acetic acid may increase as a result of current and near-future changes in fuel composition. Our results may provide baseline data to which future measurements may be compared to assess the impact of changes in fuel composition (including the replacement of MTBE by ethanol), vehicle fleet and exhaust control measures on real-world emissions of light-duty vehicles.

EXPERIMENTAL METHODS

The Caldecott Tunnel 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 1,100 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 either lane in this bore. The grade in the tunnel is 4.2 percent with eastbound traffic headed uphill. The tunnel's ventilation fans were turned off during this study, and there was only longitudinal airflow caused by the flow of traffic through the tunnel and prevailing winds. Additional information regarding the Caldecott Tunnel and the design and results of the several vehicle emission studies carried out in this tunnel between 1994 and 1999 can be found elsewhere (11, 12, 16-18).

Pollutant concentrations were measured at sampling points located 11m from the entrance (west end) and about 50 m from the exit (east end) inside the center bore of the tunnel on eight weekdays (July 20, 21 and 27-29 and August 3-5, 1999). Temperatures were 17°C on July 20, 18°C on July 21 and August 5, 20°C on July 27, 28 and August 4, 21°C on July 29 and 22°C on August 3. Measurements were made during the afternoon rush hour between 1600 and 1800h (afternoon commuter peak) when vehicles were traveling eastbound and uphill. Organic acid samples, each of two-hour duration, were collected simultaneously at the tunnel entrance and at the tunnel exit. The average traffic count was 4,200 ± 80 vehicles per hour. The average fleet age was ca. 6 years. Traffic consisted almost entirely of light-duty vehicles, of which > 94% were equipped with 3-way catalytic converters. On average, the vehicle fleet in the center bore consisted of 62.4% cars, 37.4% other light-duty vehicles (pickup trucks, minivans, and sport utility vehicles) and 0.1% heavy-duty vehicles. Typical vehicle speeds at

the tunnel entrance and exit were 52 ± 4 and 71 ± 5 km h^{-1}, respectively, and the general pattern of driving involved steady acceleration throughout the tunnel. The location of the Caldecott Tunnel is such that cars in the center bore are in a hot-stabilized mode, and cold-start and hot start operations were inconsequential in all experiments (11, 16-18). Fuel properties in the San Francisco Bay Area during the summer of 1999 are given by Kean, et al. (11) and included the following (sales-weighted averages of regular, mid-grade and premium gasolines): RVP = 49 ± 1 kPa (7.1 ± 0.1 psi), sulfur content = 10 ± 8 ppm by weight, oxygen content = 1.7 ± 0.6 weight percent, density = 742 ± 6 g L^{-1}, and MTBE, alkane, alkene and aromatic content = 8.0 ± 4.0, 66 ± 5, 3.2 ± 2.1 and 22 ± 3 volume percent, respectively.

The sampling and analytical protocols employed to identify carboxylic acids and measure their concentrations are described in detail elsewhere (10), including methods validation and quality assurance, and only a brief summary is given here. Samples were collected on pre-cleaned quartz filters coated with potassium hydroxide (KOH). We used two KOH-coated filters in series to minimize breakthrough. We sought to measure total vehicle emissions of carboxylic acids, whether emitted as gases or as components of particles, and therefore no Teflon filter was used upstream of the KOH-coated filters. The sampling duration was 2 h, the sampling flow rate was ca. 9-10 L/min (measured in each experiment with a calibrated flowmeter) and the volume of air sampled was ca. 1.1 m^3. After addition of 4-bromobenzoic acid (used as an internal standard), the filter samples, including field blanks and field controls, were extracted and derivatized using acetone containing pentafluorobenzyl bromide ($C_6F_5CH_2Br$) and 18-crown-6-ether. The derivatization procedure has been described previously and has been used to measure carboxylic acids as their pentafluorobenzyl esters by gas chromatography with electron capture detection and by gas chromatography-mass spectrometry (19-21).

Separation and identification of the pentafluorobenzyl esters ($RC(O)OCH_2C_6F_5$) was achieved by liquid chromatography with detection by diode array ultraviolet spectroscopy and by atmospheric pressure negative chemical ionization mass spectrometry (LC-DAD-APNCI-MS). Positive identification of the pentafluorobenzyl esters in the tunnel samples was obtained by matching their retention times, diode array ultraviolet-visible spectra and APNCI mass spectra to those of pentafluorobenzyl esters of carboxylic acid standards. These standards were also used to optimize operating parameters for LC separation and for APNCI-MS detection (10) and to construct calibration curves for quantitative analysis.

RESULTS AND DISCUSSION

Carboxylic acids identified and their concentrations

Thirty-three monocarboxylic acids have been identified in samples collected at the exit of the Caldecott Tunnel (Table 1). They included 22 saturated aliphatic acids ranging from C_1 to C_{12} (from formic acid to dodecanoic acid), 5 unsaturated aliphatic acids (acrylic, vinylacetic, crotonic, methacrylic and trans-2-pentenoic) and 6 aromatic acids (benzoic, the three toluic acid isomers, and two C_2-substituted benzoic acid isomers). Butyric acid and isobutyric acid were not resolved. A reference standard was available for positive identification of trans-2-pentenoic acid but other isomers, for which no standards were prepared, could not be ruled out. The entries ALP ISM (aliphatic isomer) in Table 1 reflect the current limitation of our library of reference standards. These branched-chain isomers (1 C_6, 1 C_7, 1 C_{10} and 2 C_8, 2 C_9 and 2 C_{12} compounds) were well resolved from the n-alkyl-substituted isomers (for which reference standards were prepared) but no additional information could be obtained regarding the nature of the branched-chain alkyl substituent. In the same way, the two entries C2SUB-BZA ISM (C_2-substituted benzoic acid isomers) may be ethylbenzoic and / or dimethylbenzoic acid isomers.

Carboxylic acid concentrations measured at the exit of the tunnel in each of the 8 experiments are listed in Table 1 together with the corresponding averages and their relative standard deviations (RSD). Acetic acid was the most abundant acid in all samples followed by, in order of decreasing abundance, formic acid, benzoic acid, propionic acid and nonanoic acid. The RSD associated with the average concentrations listed in Table 1 reflect sampling and

analytical uncertainties as well as differences in fleet composition and driving patterns from one experiment to the next. This study, like previous studies carried out at the Caldecott Tunnel (16-18), was designed to minimize experiment-to-experiment variability in vehicle emissions (many of the vehicles commuting through the tunnel were the same every weekday). The low RSD given in Table 1, i.e., 8, 10 and 7 percent for the three most abundant acids (acetic, formic and benzoic, respectively), suggest that experiment-to-experiment differences in fleet composition, average vehicle speed, and other factors (e.g., vehicles that may be high emitters for one or more of the acids measured) were small with respect to vehicle emissions of carboxylic acids.

Carboxylic acid concentrations measured at the entrance of the tunnel are listed in Table 2. Three of the acids listed in Table 1 were not detected in any of the samples collected at the tunnel entrance: a C_6 aliphatic isomer, one of the C_2-substituted benzoic acid isomers, and one of the C_{12} aliphatic isomers. Formic acid was the most abundant acid in all samples, followed closely by acetic acid. The RSD associated with the average concentrations listed in Table 2 were larger than those given in Table 1; i.e., the experiment-to-experiment variability in the tunnel inlet concentrations was substantially larger than that associated with tunnel exit concentrations. Concentrations measured at the tunnel entrance, which are contributed by the highway as a line source (vehicle emissions) and by urban air (emissions from all sources plus *in-situ* formation), are expected to change from one experiment to the next as a result of day-to-day variations in meteorological conditions.

Vehicle emissions of monocarboxylic acids

Differences between tunnel exit and tunnel entrance concentrations can be ascribed to light-duty vehicle emission of carboxylic acids. These differences are listed in Table 3 for each experiment. The corresponding averages and their RSD are also listed in Table 3. The largest differences measured in all experiments were those for acetic acid, followed by, in decreasing order, those for formic acid, benzoic acid, propionic acid, nonanoic acid, butyric acid + isobutyric acid, hexanoic acid, p-toluic acid and acrylic acid. The RSD associated with the averages of the concentration differences were 7, 13 and 8 percent for acetic, formic and benzoic acid, respectively. Even though vehicle transit times and pollutant residence times in the tunnel were short, ca. 1 min. and 5 min., respectively, some loss of carboxylic acids inside the tunnel cannot be ruled out and the measured differences between tunnel exit and tunnel inlet concentrations may be lower limits for actual vehicle emissions.

To examine the variability of the carboxylic acid emission profiles from one experiment to the next, we have constructed, for each experiment, scatterplots of the concentration difference (tunnel exit-tunnel entrance) measured for each acid vs. the concentration difference measured for formic acid, used arbitrarily as a reference for comparison. The scatterplots (not shown) indicated reasonable correlation between a number of acids and formic acid, and linear least squares regressions of the data were carried out (unit-weighted, not forced through the origin). The corresponding correlation coefficients are listed in Table 3. Overall, vehicle emissions of other carboxylic acids appear to correlate reasonably with those of formic acid, with $R > 0.8$ for 22 acids and $R > 0.7$ for 5 acids. More scatter ($R = 0.57$-0.68) was observed for five acids: propionic acid, methacrylic acid, the two C_8 aliphatic isomers, and one C_{12} aliphatic isomer. The C_7 aliphatic isomer and one C_9 aliphatic isomer correlated poorly with

formic acid (R = 0.31 and 0.41, respectively). Tunnel entrance and tunnel exit concentrations of these two compounds were low (with large RSD on the corresponding averages) and the poor correlation with formic acid may be contributed in part by measurement uncertainty.

Light-duty vehicle emission factors for C_1-C_{12} monocarboxylic acids

From the data in Tables 1-3, carboxylic acid emission factors for on-road light-duty vehicles have been calculated on a fuel consumed basis using the following carbon balance equation (16):

$$EF_i = [(C_{ex} - C_{en}) / (\Delta CO_2 + \Delta CO)] \ (MW_i / MW_c) \ W_c d_g \qquad \text{(Equation 1)}$$

where EF_i is the emission factor for experiment i (in mg /L), C_{ex} and C_{en} are the carboxylic acid concentrations measured at the tunnel exit and tunnel entrance, respectively, ΔCO_2 and ΔCO are the increases in the concentrations of CO_2 and CO, respectively, measured between tunnel entrance and tunnel exit, MW_i is the molecular weight of the carboxylic acid (g mol^{-1}), MW_c = 12g mol^{-1} C, W_c = 0.85 is the weight fraction of carbon in gasoline, and d_g = 740 g L^{-1} is the gasoline density. Gas phase organic compounds (hydrocarbons, carbonyls, gas phase organic acids, and other compounds such as MTBE) can be ignored in the denominator of Equation 1 since their contribution to total carbon concentrations in the tunnel is negligible compared to that of CO_2 (11, 16).

Emission factors calculated using Equation 1 are listed in Table 4 for each carboxylic acid and each experiment. Also given in Table 4 are the range of measured emission factors, their

averages, the corresponding RSD%, the 95% confidence interval, the 95% confidence interval / average emission ratio, and the rank of each carboxylic acid in order of decreasing emission factor. Total measured carboxylic acid emission factors for LD vehicles averaged 27.75 mg/L. Acetic acid (emission factor = 19.52 ± 1.10 mg /L), and formic acid (emission factor = 5.96 ± 0.46 mg/L), accounted for ca. 70 and 21 percent, respectively, of the total carboxylic acid emissions. The acetic acid / formic acid ratio of emission factors was ca. 3.3. The six aromatic acids, of which benzoic acid was the most abundant, together accounted for ca. 3 percent of the total. The five unsaturated aliphatic acids, of which acrylic acid was the most abundant, together accounted for ca. 0.5 percent of the total, and the C_3-C_{12} saturated aliphatic acids accounted for the remaining 4.5 percent.

Comparison with literature data

On-road vehicle emission factors of carboxylic acids have not been measured prior to this work. The single car exhaust study of Kawamura et al. (2) included concentrations of 12 acids (eleven C_1-C_{10} saturated aliphatics and benzoic acid). Acetic acid was the most abundant followed by, in decreasing order, formic acid, propionic acid and benzoic acid. The acetic acid / formic acid concentration ratio (mass basis) was 4.5, vs. 3.3 in the present study. The abundance of propionic acid relative to that of benzoic acid (mass basis) was 4.5, vs. 0.7 in this study. The more recent dynamometer study of Schauer (5) includes data for catalyst-equipped cars and emission factors for several high MW acids, i.e., 12.2, 27.9, 9.3 and 124 μg /km for gas phase octanoic, nonanoic, decanoic and benzoic acid, respectively. Using a fuel economy of 8.3 km/L (11, 16) to convert our data from mg/L to μg/km, on-road emission factors for octanoic, nonanoic, decanoic and benzoic acid in this study are 4.8, 13.6, 7.2 and

84.3 μg/km, respectively; i.e., they are consistent in magnitude and in relative abundance with the data of Schauer (5). For the two previous highway tunnel studies, the acetic acid / formic acid concentration ratio (mass basis) was 2.6 in Hampton, VA (7) and 5.2 in the more recent study in Sao Paulo, Brazil (8, 9), vs. 3.3 in the present study. The highest ratio measured in Brazil is qualitatively consistent with the expectation, supported by laboratory experiments (15, 22) that the use of ethanol fuel and ethanol-gasoline blends results in higher emissions of acetic acid.

Comparison of carboxylic acid and carbonyl on-road emission factors for LD vehicles

We recently measured on-road LD vehicle emission factors for speciated carbonyls (12, 23), and it is of interest to compare emission factors for carbonyls to those measured in this study for speciated carboxylic acids. Emission factors for carbonyls and for carboxylic acids are summarized in Table 5. Data for carbonyls are from two highway tunnel studies, one carried out at the Caldecott Tunnel at the same time as the present study (12) and the other carried out in May 1999 at the Tuscarora Mountain Tunnel, PA (23). Carbonyl data for the Tuscarora Mountain Tunnel are LD vehicle emission factors that were calculated by plotting measured emission factors vs. the fraction of LD vehicles in each experiment (23). Data for the two highway tunnels illustrate similarities and differences in carbonyl emission factors as a function of LD vehicle fleet age and composition, driving pattern, and perhaps gasoline composition (older, urban commuter fleet, uphill grade, steady acceleration and California Phase 2 reformulated gasoline at Caldecott; more recent, interstate fleet at nearly constant speed in flat tunnel and federal reformulated gasoline at Tuscarora Mountain).

The data in Table 5 indicate that, on the average, total emissions of carbonyls at the Caldecott Tunnel were higher than those of carboxylic acids by a factor of ca. 2.5. There were substantial variations from one structural homologue and from one functional group to the next; e.g., the formaldehyde / formic acid (C_1 compounds) emission factor ratio was 5.2, the acetaldehyde / acetic acid (C_2 compounds) emission factor ratio was 0.41, emissions of unsaturated aliphatic acids were ca. 30 times lower than those of unsaturated aliphatic carbonyls, and emissions of aromatic acids were ca. 17 times lower than those of aromatic carbonyls. There were also differences among classes of structural homologues; e.g., benzoic acid accounted for 78 percent of total aromatic acid emissions and benzaldehyde accounted for only 33 percent of total aromatic carbonyl emissions.

Carbonyls and carboxylic acids are emitted as incomplete combustion products of fuel components and possibly as a result of oxidation of engine oil. The relationship between fuel composition, engine oil composition and vehicle emissions of carbonyls and carboxylic acids is a complex function of engine technology and exhaust control technology. For carboxylic acids, very little information exists regarding vehicle emissions and fuel composition. Taylor et al. (15) reported acetic acid as a product of the high temperature decomposition of ethanol and in the exhaust of one car fueled with E100. Zervas et al. (22) have carried out laboratory studies of exhaust emissions using test fuels and a monocylinder spark ignition engine. They reported formic acid from n-octane, toluene, ethylbenzene, MTBE, methanol and ethanol, acetic acid from ethanol, propionic acid from several aromatics (benzene, toluene, ethylbenzene and o-xylene), butyric acid from o-xylene, and isovaleric acid from o-xylene and ethylbenzene. Isooctane did not produce propionic acid. Studies of carboxylic acid emissions vs. fuel

composition using commercially relevant vehicle engines and / or fuels have yet to be carried out.

Study limitations and recommendations for future work

This study provides, for the first time, detailed information on the nature and magnitude of on-road emissions of carboxylic acids by light-duty vehicles. The limitations of our study are as follows: the light-duty vehicles studied used California Phase 2 reformulated gasoline, and our results are only representative of that fuel; only one highway tunnel has been studied, and additional studies are obviously needed, especially in view of the current regulatory changes in fuel composition and emission limits; driving patterns in highway tunnels are not necessarily representative of urban driving; the emission factors measured in this study are for vehicles operated in hot-stabilized mode, with little or no off-cycle emissions, and therefore may be lower limits for actual emissions of carboxylic acids in urban areas (cold starts, stop-and-go traffic on surface streets and congested freeways, etc); vehicles that may be high emitters of carboxylic acids have yet to be characterized. Regarding short-term regulatory issues, follow-up studies should be carried out to assess the impact of phasing out MTBE (to be possibly replaced by ethanol) on the on-road vehicle emissions of key indicators such as formaldehyde, formic acid, acetaldehyde and acetic acid. Emission factors for these four compounds are likely to continue to change with future regulations that affect gasoline composition and reactivity. With modest additional method development and validation work, the LC-DAD-APNCI-MS method employed in this study would also be suitable to measure vehicle emission factors for dicarboxylic acids, oxo-acids, hydroxyacids and other polar organics such as phenols and hydroxy-substituted polycyclic aromatic hydrocarbons. Information on vehicle emission rates for these compounds would be valuable in the context of $PM_{2.5}$ regulations.

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Table 1. Carboxylic acid concentrations at the tunnel exit

	Concentration, μg / m^3									
Date, 1999	7/20	7/21	7/27	7/28	7/29	8/3	8/4	8/5	AVE	RSD
Formic acid	6.6	7.1	7.2	8.8	8.3	8.0	7.8	8.6	7.79	10
Acetic acid	12.2	13.9	13.3	15.9	14.4	13.7	12.6	13.8	13.71	8
Benzoic acid	0.552	0.516	0.562	0.626	0.547	0.591	0.524	0.597	0.56	7
Acrylic acid	0.045	0.052	0.053	0.068	0.053	0.071	0.054	0.062	0.06	15
Propionic acid	0.370	0.484	0.452	0.632	0.591	0.413	0.502	0.569	0.50	18
Vinylacetic acid	0.004	0.006	0.005	0.006	0.005	0.004	0.004	0.005	0.005	21
Crotonic acid	0.018	0.024	0.021	0.028	0.025	0.021	0.023	0.025	0.023	13
Methacrylic acid	0.007	0.006	0.006	0.007	0.006	0.006	0.006	0.007	0.006	8
Butyric acid/Isobutyric acid	0.101	0.108	0.087	0.140	0.119	0.110	0.107	0.127	0.11	14
trans-2-Pentenoic acid/ISM	0.003	0.004	0.004	0.005	0.004	0.004	0.004	0.004	0.004	9
Isopentanoic acid	0.032	0.039	0.028	0.039	0.043	0.051	0.040	0.047	0.04	19
Pentanoic acid	0.057	0.064	0.057	0.067	0.070	0.090	0.062	0.074	0.07	16
C6 ALP ISM #1	0.0007	0.0009	0.0005	0.0008	0.0005	0.0003	0.0006	0.0007	0.001	27
Isohexanoic acid	0.004	0.007	0.006	0.008	0.007	0.010	0.008	0.009	0.01	25
Hexanoic acid	0.120	0.135	0.103	0.155	0.129	0.122	0.137	0.146	0.13	12
C7 ALP ISM #1	0.006	0.007	0.007	0.010	0.012	0.010	0.011	0.010	0.009	22
Heptanoic acid	0.058	0.063	0.061	0.070	0.061	0.069	0.063	0.067	0.064	7
o-Toluic acid	0.009	0.011	0.009	0.015	0.012	0.010	0.010	0.016	0.011	23
m-Toluic acid	0.043	0.045	0.046	0.045	0.049	0.047	0.043	0.057	0.047	10
p-Toluic acid	0.063	0.070	0.065	0.072	0.078	0.074	0.069	0.074	0.071	7
C8 ALP ISM #1	0.029	0.033	0.037	0.046	0.046	0.057	0.041	0.055	0.04	23
C8 ALP ISM #2	0.008	0.010	0.008	0.011	0.012	0.008	0.007	0.013	0.010	22
Octanoic acid	0.075	0.080	0.081	0.092	0.094	0.100	0.080	0.094	0.09	10
C2SUB-BZA ISM #1	0.003	0.004	0.002	0.004	0.004	0.003	0.002	0.005	0.003	29
C2SUB-BZA ISM #2	0.013	0.013	0.013	0.015	0.014	0.013	0.014	0.017	0.014	11
C9 ALP ISM #1	0.004	0.005	0.004	0.005	0.005	0.006	0.005	0.008	0.005	25
C9 ALP ISM #2	0.042	0.036	0.034	0.044	0.027	0.022	0.047	0.010	0.03	38
Nonanoic acid	0.122	0.128	0.126	0.160	0.184	0.212	0.156	0.214	0.16	23
C10 ALP ISM #1	0.014	0.019	0.016	0.019	0.014	0.011	0.013	0.014	0.015	19
Decanoic acid	0.045	0.055	0.044	0.059	0.060	0.061	0.066	0.075	0.06	18
C12 ALP ISM #1	0.008	0.009	0.010	0.011	0.010	0.011	0.008	0.012	0.010	16
C12 ALP ISM #2	0.004	0.005	0.004	0.005	0.004	0.003	0.003	0.003	0.004	17
Dodecanoic acid	0.031	0.032	0.030	0.037	0.033	0.040	0.032	0.040	0.034	13

AVE = average. RSD = relative standard deviation, percent. ISM = isomer. ALP = saturated aliphatic.
C2SUB-BZA = C2-substituted benzoic acid.

Table 2. Carboxylic acid concentrations at the tunnel entrance

	Concentration, $\mu g/m^3$									
Date (1999)	7/20	7/21	7/27	7/28	7/29	8/3	8/4	8/5	AVE	RSD
Formic acid	3.48	3.74	4.39	5.17	5.43	5.56	5.12	5.58	4.81	17
Acetic acid	2.88	3.61	4.05	4.69	4.84	4.21	3.48	4.02	3.97	16
Benzoic acid	0.19	0.16	0.22	0.21	0.22	0.26	0.20	0.26	0.21	15
Acrylic acid	0.01	0.01	0.02	0.02	0.02	0.04	0.02	0.03	0.02	40
Propionic acid	0.19	0.22	0.24	0.28	0.29	0.26	0.27	0.28	0.25	13
Vinylacetic acid	0.0011	0.0020	0.0023	0.0020	0.0029	0.0029	0.0021	0.0030	0.002	29
Crotonic acid	0.0038	0.0058	0.0058	0.0064	0.0074	0.0074	0.0063	0.0073	0.006	19
Methacrylic acid	0.0006	0.0009	0.0010	0.0015	0.0015	0.0018	0.0015	0.0021	0.001	36
Butyric acid/Isobutyric acid	0.034	0.036	0.041	0.057	0.064	0.086	0.058	0.076	0.056	33
trans-2-Pentenoic acid/ISM	0.001	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	18
Isopentanoic acid	0.015	0.016	0.012	0.014	0.026	0.042	0.026	0.033	0.023	47
Pentanoic acid	0.023	0.025	0.026	0.028	0.037	0.059	0.035	0.040	0.034	35
C6 ALP ISM #1	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Isohexanoic acid	0.004	0.004	0.005	0.006	0.007	0.010	0.007	0.008	0.006	35
Hexanoic acid	0.067	0.053	0.042	0.069	0.081	0.102	0.091	0.116	0.078	32
C7 ALP ISM #1	0.003	0.003	0.003	0.004	0.005	0.008	0.005	0.007	0.005	40
Heptanoic acid	0.032	0.036	0.038	0.040	0.041	0.051	0.040	0.046	0.041	14
o-Toluic acid	0.0016	0.0018	0.0022	0.0027	0.0035	0.0045	0.0033	0.0039	0.003	36
m-Toluic acid	0.0094	0.0102	0.0126	0.0117	0.0204	0.0260	0.0203	0.0272	0.017	42
p-Toluic acid	0.0123	0.0134	0.0164	0.0152	0.0266	0.0339	0.0235	0.0324	0.022	40
C8 ALP ISM #1	0.020	0.021	0.030	0.032	0.033	0.048	0.031	0.042	0.032	29
C8 ALP ISM #2	0.003	0.004	0.004	0.004	0.005	0.006	0.004	0.005	0.004	19
Octanoic acid	0.051	0.055	0.061	0.065	0.073	0.090	0.061	0.077	0.067	19
C2SUB-BZA ISM #1	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
C2SUB-BZA ISM #2	0.005	0.006	0.008	0.008	0.009	0.010	0.008	0.011	0.008	22
C9 ALP ISM #1	0.002	0.002	0.002	0.003	0.003	0.005	0.003	0.005	0.003	44
C9 ALP ISM #2	0.002	0.001	0.002	0.002	0.006	0.007	0.003	0.003	0.003	64
Nonanoic acid	0.053	0.070	0.074	0.088	0.131	0.171	0.103	0.156	0.106	41
C10 ALP ISM #1	0.002	0.003	0.003	0.003	0.004	0.004	0.003	0.004	0.003	21
Decanoic acid	0.015	0.016	0.020	0.024	0.032	0.046	0.029	0.043	0.028	42
C12 ALP ISM #1	0.004	0.004	0.005	0.005	0.006	0.006	0.004	0.007	0.005	25
C12 ALP ISM #2	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Dodecanoic acid	0.012	0.014	0.014	0.018	0.021	0.030	0.019	0.022	0.019	32

AVE = average.. RSD = relative standard deviation, percent. ISM = isomer. ALP = saturated aliphatic.
C2SUB-BZA = C2-substituted benzoic acid. BDL = below detection limit.

Table 3. Carboxylic acid concentration differences between tunnel exit and tunnel entrance

	Concentration, µg / m^3										
Date, 1999	7/20	7/21	7/27	7/28	7/29	8/3	8/4	8/5	AVE	RSD	R (C1)
Formic acid	3.1	3.4	2.8	3.6	2.9	2.4	2.7	3.0	2.99	13	1.000
Acetic acid	9.3	10.3	9.3	11.2	9.6	9.5	9.1	9.7	9.74	7	0.809
Benzoic acid	0.367	0.354	0.339	0.411	0.328	0.335	0.321	0.342	0.35	8	0.830
Acrylic acid	0.033	0.040	0.034	0.049	0.032	0.034	0.036	0.033	0.04	15	0.723
Propionic acid	0.180	0.259	0.216	0.356	0.305	0.151	0.232	0.291	0.25	27	0.677
Vinylacetic acid	0.0031	0.0039	0.0028	0.0043	0.0026	0.0006	0.0016	0.0016	0.003	48	0.888
Crotonic acid	0.0144	0.0186	0.0149	0.0213	0.0177	0.0131	0.0168	0.0176	0.017	16	0.789
Methacrylic acid	0.0065	0.0054	0.0048	0.0057	0.0044	0.0043	0.0049	0.0046	0.005	15	0.650
Butyric acid/Isobutyric acid	0.067	0.073	0.047	0.083	0.056	0.024	0.049	0.051	0.056	32	0.962
trans-2-Pentenoic acid/ISM	0.0023	0.0025	0.0016	0.0025	0.0019	0.0015	0.0016	0.0023	0.002	20	0.943
Isopentanoic acid	0.0174	0.0228	0.0157	0.0249	0.0173	0.0087	0.0140	0.0135	0.017	31	0.925
Pentanoic acid	0.0335	0.0392	0.0317	0.0391	0.0323	0.0310	0.0273	0.0340	0.034	12	0.870
C6 ALP ISM #1	0.0007	0.0009	0.0005	0.0008	0.0005	0.0003	0.0006	0.0007	0.001	27	0.945
Isohexanoic acid	0.0005	0.0031	0.0015	0.0025	0.0009	0.0003	0.0011	0.0010	0.001	72	0.735
Hexanoic acid	0.0525	0.0820	0.0617	0.0862	0.0488	0.0197	0.0457	0.0303	0.053	43	0.819
C7 ALP ISM #1	0.0035	0.0041	0.0042	0.0057	0.0067	0.0017	0.0061	0.0038	0.004	36	0.308
Heptanoic acid	0.0257	0.0269	0.0230	0.0299	0.0203	0.0176	0.0234	0.0209	0.023	17	0.889
o-Toluic acid	0.0076	0.0095	0.0065	0.0121	0.0085	0.0051	0.0068	0.0118	0.009	30	0.818
m-Toluic acid	0.0336	0.0349	0.0331	0.0334	0.0289	0.0210	0.0224	0.0300	0.030	18	0.801
p-Toluic acid	0.0508	0.0570	0.0489	0.0571	0.0516	0.0402	0.0450	0.0414	0.049	13	0.800
C8 ALP ISM #1	0.0093	0.0116	0.0065	0.0140	0.0125	0.0093	0.0107	0.0129	0.011	22	0.571
C8 ALP ISM #2	0.0052	0.0059	0.0040	0.0070	0.0075	0.0018	0.0030	0.0080	0.005	42	0.681
Octanoic acid	0.0240	0.0254	0.0194	0.0276	0.0210	0.0101	0.0189	0.0167	0.020	27	0.893
C2SUB-BZA ISM #1	0.0029	0.0045	0.0023	0.0044	0.0038	0.0026	0.0024	0.0048	0.003	29	0.700
C2SUB-BZA ISM #2	0.0073	0.0069	0.0053	0.0068	0.0048	0.0022	0.0057	0.0067	0.006	29	0.809
C9 ALP ISM #1	0.0020	0.0025	0.0020	0.0027	0.0024	0.0010	0.0014	0.0024	0.002	29	0.841
C9 ALP ISM #2	0.0407	0.0345	0.0318	0.0418	0.0211	0.0150	0.0439	0.0072	0.030	46	0.414
Nonanoic acid	0.0690	0.0586	0.0515	0.0720	0.0529	0.0405	0.0533	0.0579	0.057	18	0.893
C10 ALP ISM #1	0.0124	0.0163	0.0130	0.0162	0.0107	0.0069	0.0102	0.0099	0.012	27	0.886
Decanoic acid	0.0308	0.0392	0.0237	0.0348	0.0275	0.0147	0.0370	0.0324	0.030	26	0.705
C12 ALP ISM #1	0.0041	0.0047	0.0052	0.0059	0.0044	0.0044	0.0041	0.0049	0.005	13	0.573
C12 ALP ISM #2	0.0043	0.0048	0.0040	0.0048	0.0042	0.0030	0.0034	0.0034	0.004	17	0.842
Dodecanoic acid	0.0189	0.0180	0.0160	0.0194	0.0116	0.0101	0.0129	0.0184	0.016	23	0.852

AVE = average. RSD = relative standard deviation, percent. ISM = isomer. ALP = saturated aliphatic. C2SUB-BZA = C2-substituted benzoic acid. R(C1) = correlation coefficient for linear regression of data for carboxylic acid vs. formic acid.

Table 4. On-road LD vehicle emission factors for carboxylic acids

Date	7/19/99	7/20/99	7/26/99	7/27/99	7/28/99	8/2/99	8/3/99	8/4/99							
	Emission Factor, mg / L								MIN	MAX	AVE	RSD %	95% CI	95% CI/AVE	RANK
Formic acid	5.954	6.465	5.738	6.689	5.732	5.353	5.560	6.191	5.353	6.689	5.960	8	0.382	0.064	2
Acetic acid	17.646	19.826	19.016	20.811	19.263	20.983	18.724	19.879	17.646	20.983	19.518	6	0.919	0.047	1
Benzoic acid	0.697	0.682	0.697	0.763	0.660	0.743	0.661	0.698	0.660	0.763	0.700	5	0.030	0.043	3
Acrylic acid	0.063	0.077	0.070	0.090	0.065	0.076	0.074	0.067	0.063	0.090	0.073	12	0.007	0.101	9
Propionic acid	0.343	0.500	0.443	0.660	0.613	0.336	0.478	0.594	0.336	0.660	0.496	24	0.101	0.204	4
Vinylacetic acid	0.006	0.008	0.006	0.008	0.005	0.001	0.003	0.003	0.001	0.008	0.005	44	0.002	0.371	29
Crotonic acid	0.027	0.036	0.031	0.039	0.036	0.029	0.034	0.036	0.027	0.039	0.034	12	0.003	0.103	16
Methacrylic acid	0.012	0.011	0.010	0.010	0.009	0.010	0.010	0.009	0.009	0.012	0.010	11	0.001	0.088	24
Butyric acid/Isobutyric acid	0.127	0.140	0.096	0.154	0.112	0.054	0.101	0.104	0.054	0.154	0.111	28	0.026	0.231	6
trans-2-Pentenoic acid/ISM	0.004	0.005	0.003	0.005	0.004	0.003	0.003	0.005	0.003	0.005	0.004	16	0.001	0.134	31
Isopentanoic acid	0.033	0.044	0.032	0.046	0.035	0.019	0.029	0.028	0.019	0.046	0.033	26	0.007	0.220	17
Pentanoic acid	0.064	0.076	0.065	0.073	0.065	0.069	0.056	0.069	0.056	0.076	0.067	9	0.005	0.074	10
C6 ALP ISM #1	0.001	0.002	0.001	0.002	0.001	0.001	0.001	0.001	0.001	0.002	0.001	23	0.000	0.195	33
Isohexanoic acid	0.001	0.006	0.003	0.005	0.002	0.001	0.002	0.002	0.001	0.006	0.003	68	0.002	0.572	32
Hexanoic acid	0.100	0.158	0.127	0.160	0.098	0.044	0.094	0.062	0.044	0.160	0.105	40	0.035	0.330	7
C7 ALP ISM #1	0.007	0.008	0.009	0.011	0.014	0.004	0.012	0.008	0.004	0.014	0.009	36	0.003	0.298	26
Heptanoic acid	0.049	0.052	0.047	0.055	0.041	0.039	0.048	0.043	0.039	0.055	0.047	12	0.005	0.100	14
o-Toluic acid	0.015	0.018	0.013	0.022	0.017	0.011	0.014	0.024	0.011	0.024	0.017	27	0.004	0.223	21
m-Toluic acid	0.064	0.067	0.068	0.062	0.058	0.046	0.046	0.061	0.046	0.068	0.059	14	0.007	0.121	12
p-Toluic acid	0.097	0.110	0.101	0.106	0.104	0.089	0.093	0.085	0.085	0.110	0.098	9	0.007	0.075	8
C8 ALP ISM #1	0.018	0.022	0.013	0.026	0.025	0.021	0.022	0.026	0.013	0.026	0.022	21	0.004	0.171	20
C8 ALP ISM #2	0.010	0.011	0.008	0.013	0.015	0.004	0.006	0.016	0.004	0.016	0.011	41	0.004	0.341	23
Octanoic acid	0.046	0.049	0.040	0.051	0.042	0.022	0.039	0.034	0.022	0.051	0.040	23	0.008	0.189	15
C2SUB-BZA ISM #1	0.006	0.009	0.005	0.008	0.008	0.006	0.005	0.010	0.005	0.010	0.007	27	0.002	0.228	28
C2SUB-BZA ISM #2	0.014	0.013	0.011	0.013	0.010	0.005	0.012	0.014	0.005	0.014	0.011	26	0.002	0.220	22
C9 ALP ISM #1	0.004	0.005	0.004	0.005	0.005	0.002	0.003	0.005	0.002	0.005	0.004	26	0.001	0.216	30
C9 ALP ISM #2	0.077	0.067	0.065	0.077	0.042	0.033	0.090	0.015	0.015	0.090	0.058	44	0.022	0.368	13
Nonanoic acid	0.131	0.113	0.106	0.133	0.106	0.090	0.110	0.118	0.090	0.133	0.113	13	0.012	0.105	5
C10 ALP ISM #1	0.024	0.031	0.027	0.030	0.021	0.015	0.021	0.020	0.015	0.031	0.024	23	0.005	0.190	19
Decanoic acid	0.058	0.076	0.049	0.065	0.055	0.033	0.076	0.066	0.033	0.076	0.060	24	0.012	0.202	11
C12 ALP ISM #1	0.008	0.009	0.011	0.011	0.009	0.010	0.009	0.010	0.008	0.011	0.009	11	0.001	0.095	25
C12 ALP ISM #2	0.008	0.009	0.008	0.009	0.008	0.007	0.007	0.007	0.007	0.009	0.008	12	0.001	0.103	27
Dodecanoic acid	0.036	0.035	0.033	0.036	0.023	0.022	0.027	0.038	0.022	0.038	0.031	20	0.005	0.164	18

AVE = average. RSD = relative standard deviation, percent. ISM = isomer. ALP = saturated aliphatic. C2SUB-BZA = C2-substituted benzoic acid. MIN = lowest value. MAX = highest value. 95% CI = 95% confidence interval. 95% CI / AVE = ratio of 95% confidence interval and average emission factor. RANK = rank, in decreasing order.

Table 5. On-road LD vehicle emission factors for carboxylic acids and carbonyls

		Emission factor, mg / L			
	Carboxylic acids		Carbonyls		
		Caldecott Tunnel (this study)		Caldecott Tunnel (12)	Tuscarora Mountain Tunnel (23) (a)
Sum of all compounds		27.75		68.4 (b)	94.9
Saturated aliphatics					
C1	formic acid	5.96	formaldehyde	31.0	38.0
C2	acetic acid	19.52	acetaldehyde	8.0	9.5
C3	propionic acid	0.50	propanal	0.84	1.72
			acetone	4.0	25.1
Unsaturated aliphatics		0.126		3.94	5.88
Aromatics		0.892		14.81	4.69
C7	benzoic acid	0.700	benzaldehyde	4.89	1.35

(a) converted from mg/km to mg/L using measured LD vehicle fuel economy = 14.75 km/L (23).

(b) for comparison, emission factors for CO, NOx (as NO2) and NH3 in the same study were 38.7 ± 2.5, 4.85 ± 0.17 and 0.475 ± 0.029 g/L, respectively (11).