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On-Road Measurement of Carbonyls in California Light-Duty Vehicle Emissions

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Abstract

Emissions of carbonyls by motor vehicles are of concern because these species can be hazardous to human health and highly reactive in the atmosphere. The objective of this research was to measure carbonyl emission factors for California light-duty motor vehicles Measurements were made at the entrance and exit of a San Francisco Bay area highway tunnel, in the center bore where heavy-duty trucks are not allowed. During summer 1999, approximately 100 carbonyls were identified, including saturated aliphatic aldehydes and ketones, unsaturated aliphatic carbonyls, aliphatic dicarbonyls, and aromatic carbonyls. Concentrations were measured for 32 carbonyls and were combined with NMOC, CO and CO_2 concentrations to calculate by carbon balance emission factors per unit of fuel burned. The measured carbonyl mass emitted from light-duty vehicles was 68 ± 4 mg L^{-1}. Formaldehyde accounted for 45% of the measured mass emissions, acetaldehyde 12%, tolualdehydes 10%, benzaldehyde 7.2%, and acetone 5.9%. The ozone forming potential of the carbonyl emissions was dominated by formaldehyde (70%) and acetaldehyde (14%) Between 1994 and 1999, emission factors measured at the same tunnel for formaldehyde, acetaldehyde, and benzaldehyde decreased by 45-70%. Carbonyls constituted 3.9% of total NMOC mass emissions and 5 2% of NMOC reactivity A comparison of carbonyl

emissions with gasoline composition supports previous findings that aromatic aldehyde emissions are related to aromatics in gasoline Carbonyl concentrations in liquid gasoline were also measured Acetone and MEK were the most abundant carbonyls in unburned gasoline, 8 other carbonyls were detected and quantified

Introduction

Various carbonyls, including formaldehyde, acetaldehyde, acrolein (propenal), and methyl ethyl ketone (MEK), are known to be toxic, mutagenic and/or carcinogenic, and as a result have been identified as hazardous air pollutants (*1-3*) Carbonyls are also an important source of radicals in the chemistry of ozone production (*4, 5*). They are directly emitted by anthropogenic and natural sources, and also are formed *in situ* as the photochemical oxidation products of other directly emitted organic gases (*6, 7*) Therefore control programs should consider both primary and secondary sources of carbonyls Photochemical modeling studies (*8, 9*) show that during summer months, photochemical production of formaldehyde and acetaldehyde can be the dominant contributor to total concentrations of these compounds in urban air. However, the contribution from direct emissions is expected to dominate during winter months

Carbonyls are both reactants and products in a variety of important photochemical processes. Photolysis of formaldehyde can be an important source of HO_x radicals (*10*). These radicals control the rates of VOC oxidation and NO to NO_2 conversion in the atmosphere, which directly affects ozone production. Reaction of acetaldehyde with the hydroxyl radical and photolysis of acetone both form the peroxyacetyl radical, which reacts with NO_2 to form peroxyacetyl nitrate or PAN (*11*). PAN and its analogs are toxic to plants and are known to be eye irritants (*12*) PAN can also act as a reservoir for NO_x, allowing long-range transport of nitrogen Acetone is believed to play an important role in the chemistry of the upper troposphere, though sources of acetone are not well characterized at this time (*13-15*). Carbonyls form as oxidation products of other VOC in the atmosphere. For example, formaldehyde, methacrolein, and methyl vinyl ketone are formed during isoprene oxidation (*16, 17*). Concentrations of these product species are sometimes measured to help assess the role of biogenic VOC emissions in air quality problems (*16, 17*) The usefulness of methacrolein as a marker for oxidation of biogenic isoprene emissions may be compromised in some cases by direct emissions of methacrolein in motor vehicle exhaust (*18, 19*).

Fuel combustion is a well-known direct source of carbonyl emissions to the atmosphere (*19-23*). Carbonyls are intermediate species created during fuel oxidation and will be emitted to the atmosphere if combustion is unable to go to completion. Formaldehyde is typically the most abundant carbonyl in combustion exhaust emissions, although acetaldehyde, benzaldehyde, the sum of tolualdehyde isomers, and acetone can each be of similar magnitude (*20*) Addition of oxygenated compounds such as methyl tert-butyl ether (MTBE) and ethanol to reformulated gasoline is of special interest because these fuel changes are known to increase exhaust emissions of formaldehyde and acetaldehyde, respectively (*24, 25*). Aromatic hydrocarbons present in gasoline, especially toluene and xylenes, are known precursors to emissions of benzaldehyde and tolualdehydes (*26-28*) Cycloalkanes in fuel have been shown to create more aldehydes than the corresponding aromatic hydrocarbons, but highly branched alkenes and alkanes create the highest aldehyde emissions (*29*) Use of MTBE in California gasoline will be phased out by the end of 2002, and increased reliance on ethanol and/or alkylate (i.e , branched alkanes such as 2,2,4-trimethylpentane), and possible changes in the aromatic content of gasoline are anticipated These fuel changes are likely to affect the nature and emission rates of carbonyls in vehicle exhaust

While carbonyl emissions have been measured in previous laboratory (*24, 30-32*) and on-road (*33-37*) studies, a new analytical technique has been described (*38*) that greatly increases the number of carbonyls that can be identified and quantified. This technique has been applied recently to determine carbonyl emission factors for light- and heavy-duty vehicles in the Tuscarora Mountain tunnel in Pennsylvania (*39*) The main objective of the present study is to measure exhaust emission factors for carbonyls from California light-duty vehicles. Important differences between this study and that of Grosjean et al (*39*) include the use of California phase 2 reformulated gasoline, more stringent new-vehicle emission standards and emission control technologies, loaded mode driving on a ~4% uphill grade, and sampling in a tunnel bore with minimal heavy-duty diesel truck influence

Experimental Section

Field Sampling Site. Measurements were made at the Caldecott tunnel, which is located between Alameda and Contra Costa Counties in the San Francisco Bay area on California state highway 24 The tunnel is 1100 m long and has a total of six lanes of traffic contained in 3 separate bores. The roadway grade is 4.2%, uphill in the eastbound direction. Measurements were carried out in the center bore, where heavy-duty diesel trucks are not allowed. All ventilation fans were turned off during sampling, so the only ventilation was induced by the flow of traffic through the tunnel and prevailing winds. Vehicles driving through the center bore of the tunnel are operating in a fully warmed up mode.

Traffic Monitoring. Traffic volume and the composition of the vehicle fleet driving through the tunnel were observed visually on each day of sampling. Vehicle counts were accumulated separately for cars, light-duty trucks (pickups, small vans, and sport-utility vehicles), medium and heavy-duty trucks (all trucks with 2 axles and 6 tires, and all trucks with 3 or more axles), and motorcycles. Average traffic volume during the afternoon sampling periods was 4200 ± 80 vehicles per hour. Due to the time of day and the requirement that heavy-duty vehicles stay out of the center bore, traffic consisted of 62% cars, 37% light-duty trucks, 0.8% motorcycles, and 0.1% heavy-duty vehicles. License plate surveys performed in 1997 were used to estimate fleet characteristics in 1999. Most of the vehicles (>94%) in the center bore were originally equipped with three-way catalytic converters (*40*), and a small percentage (<2%) of the light-duty vehicles were diesel powered (*41*) A car was driven through the tunnel repeatedly during each afternoon sampling period to monitor driving conditions inside the tunnel Typically, vehicles entered the tunnel at 52 ± 14 km h^{-1}, accelerated gradually throughout the tunnel, and exited at 71 ± 5 km h^{-1}.

Pollutant Measurements. Pollutant concentrations were measured in the center bore of the tunnel at two sampling locations: the first was 11 m inside the tunnel from the entrance, and the second was about 50 m before the tunnel exit Sampling was performed during afternoon rush hour periods (1600 to 1800 h PDT) on 8 weekdays between July 21 and August 5, 1999. Traffic in the center bore was traveling eastbound and uphill. Concentrations of ammonia, NO_x, CO, CO_2, speciated hydrocarbons, speciated carbonyls, and speciated organic acids were measured in the tunnel. Results for ammonia, NO_x, CO, and CO_2 have been presented previously (40). 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 connected to the cartridge using a short piece of Teflon tubing. The sampling duration was 120 min, the sampling flow rate was 0.700 L min^{-1} (measured with flowmeters calibrated using a certified, NIST-traceable Humonics model 650 flow calibrator), and the volume of air sampled was 84 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. (*38*). Absence of carbonyl breakthrough during sampling has been verified previously (*42, 43*). 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 (*38, 42-44*). Quantitative analysis involved the use of response factors measured using carbonyl-DNPH reference standards (*38, 42-44*). 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.

Additional air samples were collected at the tunnel entrance and exit during each 2-hour sampling period in evacuated 6 liter stainless steel canisters. CO_2 concentrations in these samples were determined using gas chromatography (Perkin-Elmer, Wellesly, MA, model 8700) with thermal conductivity detector and Carbosieve II packed column (Supelco, Bellafonte, PA). Total and speciated organic compound concentrations were determined from the canister samples by gas chromatography using a flame ionization detector. Analytical methods are described in more detail elsewhere (*34, 45*). Carbon monoxide concentrations were monitored continuously at both ends of the tunnel using infrared gas filter correlation spectrometers (Thermo Environmental Instruments, Franklin, MA, model 48).

Gasoline Analysis. Gasoline sold in the Bay Area during 1999 contained 10 ± 8 ppm sulfur, 8.0 ± 4.0 vol% MTBE, and 0.7 ± 2.1 vol % ethanol; the total oxygen content was 1.7 ± 0.6 wt% (*40*). Further information on fuel composition was desired for this investigation, so regular and premium grade liquid gasoline samples from 5 high-volume service stations in Berkeley, CA were obtained in August 1999. These stations represented the 5 major gasoline vendors in the Bay Area The detailed composition of each sample was measured by gas chromatography with flame ionization detection as described previously (*45*) A composite fuel sample was obtained by weighting the individual fuel sample compositions by market share. Carbonyl concentrations were measured in 3 of the 10 Bay Area gasoline samples using liquid-chromatography-mass spectrometry, as described above Two additional gasoline samples were obtained in Ventura, CA, and analyzed for the presence of carbonyls Two derivatization protocols were used, one involving the injection of 300 µL of gasoline on a DNPH-coated silica gel cartridge, and the other the reaction of 300 µL of gasoline with a solution of acidic DNPH. In both cases, the reaction was allowed to proceed overnight (after which the cartridge was eluted) and the samples were blown down to dryness with ultra-high purity N_2 to remove some of the more volatile hydrocarbons and reconstituted with 2 mL acetonitrile. Two blanks were included for each derivatization method. The recovery of DNPH derivatives using these procedures was assumed to be identical to that of DNPH (100%) in all of the samples and of the DNPH derivatives of formaldehyde, acetaldehyde, and acetone (all at 100%) present in the blank samples Separate aliquots from each of the 3 gasoline samples were provided in glass and plastic vials and the results were identical showing no preferential loss or contamination of carbonyls using these vials. Also, no contamination was found on the blanks The two protocols gave essentially the same results. Concentrations were measured for 10 carbonyls (formaldehyde, acetaldehyde, propanal, butanal, benzaldehyde, o-tolualdehyde, acetone, MEK, 2-pentanone, and an unidentified carbonyl whose DNPH derivative had a molecular weight of 502 g mol^{-1}, which we suspect is a C_8 dicarbonyl of molecular weight 142 g mol^{-1}. Other carbonyls tentatively identified in the gasoline samples include cyclohexanone or other isomers. The absolute determination of these species was precluded by the co-elution of hydrocarbons from the gasoline. Future work will focus on separating the carbonyl fraction from the interfering hydrocarbons present in gasoline in order to identify and quantify more carbonyls and to compare the gasoline composition to the measured emission rates.

Results and Discussion

Carbonyl Emission Factors. Measured carbonyl concentrations at the tunnel exit exceeded those measured at the tunnel entrance by factors ranging from 1.7 to 30 for the carbonyls listed in Table 1. Emission factors shown in Table 1 were computed by carbon balance using the following equation

$$E_p = \left(\frac{\Delta[\mathrm{P}]}{\Delta[\mathrm{CO_2}] + \Delta[\mathrm{CO}] + \Delta[\mathrm{NMOC}]} \right) \left(\frac{\mathrm{MW_P}}{\mathrm{MW_C}} \right) w_c \rho_f$$

where $\Delta[\mathrm{P}]$ is the increase in concentration of pollutant P measured between tunnel inlet and outlet, $\mathrm{MW_P}$ is the molecular weight of pollutant P (g mol^{-1}), $\mathrm{MW_C}$=12 g mol^{-1} C, w_c=0.85 is the weight fraction of carbon in gasoline, and gasoline density ρ_f=740 g L^{-1} (*40*). Emission factors are presented as means over 8 days of sampling. The 95% confidence intervals quantify the extent of run-to-run variability across sampling periods. Even though vehicle transit times and air residence times in the tunnel were short, loss of carbonyls inside the tunnel could not be ruled out, and reported emission factors may therefore be lower limits for actual vehicle emissions.

Carbonyl emission factors are presented graphically in Figures 1 and 2, with comparisons to results from the 1999 Tuscarora, PA tunnel study (*39*) for each carbonyl. The Tuscarora tunnel has both light- and heavy-duty vehicles sharing the same bore and as a result, regression analysis was used to calculate emission factors for each of these vehicle categories. In order to facilitate the comparison with results of the present study, 95% confidence intervals for the Tuscarora light-duty emission factors were calculated by doubling the standard errors reported in the regression analysis (*39*). Heavy-duty vehicles are barred from using the center bore of the Caldecott tunnel, so regression analysis was not needed to calculate light-duty vehicle emissions. Caldecott tunnel sampling provided 95% confidence intervals on carbonyl emission factors for light-duty vehicles that were generally narrower than those determined from Tuscarora by regression analysis.

Figure 1 presents emission factors for saturated aliphatic aldehydes and aromatic carbonyls. The saturated aliphatic aldehydes with the highest mass emission rates were formaldehyde (31 ± 4 mg L^{-1}) and acetaldehyde (8.0 ± 0.8 mg L^{-1}). Emissions of saturated aliphatic aldehydes decreased with increasing molecular weight. This trend was observed for gasoline vehicles in the 1960s (*29*) and, as a result, appears to be independent of recent modifications to gasoline or vehicle technology. Results from the Tuscarora tunnel are generally of similar magnitude and show similar trends.

With the exception of benzaldehyde, the lowest molecular weight aromatic aldehyde, aromatic carbonyls also show a trend of decreasing emissions as molecular weight increases. The primary reason that total tolualdehyde emissions are greater than benzaldehyde is that xylenes, which are tolualdehyde precursors, are more abundant in gasoline than toluene, a precursor of benzaldehyde: measured sales-weighted average gasoline composition in summer 1999 was 7.7% by weight xylenes and 6.3% toluene. The conclusion that emissions of tolualdehydes depend directly on xylene content in the fuel is strengthened by examining the relative abundance of the tolualdehyde and xylene isomers. Emissions of m-tolualdehyde were approximately twice as high as emissions of o- or p-tolualdehyde, similarly m-xylene was 2-3 times more abundant in gasoline than o- and p-xylene. Emission factors for aromatic aldehydes determined in this study generally fall within the 95% confidence intervals reported for light-duty vehicles in the Tuscarora tunnel study (see Figure 1).

Figure 2 shows that the emissions of three unsaturated aliphatic aldehydes (acrolein, methacrolein, and crotonaldehyde) were similar, between 1.1 and 1.7 mg L^{-1}. Emissions measured in the Tuscarora Mountain tunnel for these three species were comparable to those measured in the present study. These results support the argument that motor vehicle emissions of methacrolein will complicate its use as a tracer for biogenic emissions, particularly in urban areas (*18, 19*).

Emission factors for aliphatic ketones are also presented in Figure 2. The only ketone with emissions greater than 1 mg L^{-1} was acetone, at 4.0 ± 0.5 mg L^{-1}. The study at Tuscarora found a nominally higher emission factor for acetone, 25 ± 22 mg L^{-1}, though the two acetone emission factors agree within their 95% confidence intervals. Figure 2 also presents emission factors for dicarbonyls. Methyl glyoxal was emitted at the Caldecott tunnel in significantly greater quantities than the other dicarbonyls, namely glyoxal, biacetyl, and 2-oxobutanal.

In addition to the 32 carbonyls for which emission factors were determined, approximately 70 less abundant carbonyl species were detected in the samples obtained at the Caldecott tunnel. These species are listed in Table 2.

Carbonyl Weight Fractions and Reactivities. The total mass of carbonyls emitted was 68 ± 4 mg L^{-1}, of which formaldehyde and acetaldehyde accounted for 45 and 12%, respectively. As shown in Table 1, other species that contributed more than 2% to total carbonyl mass emissions were the tolualdehydes, benzaldehyde, acetone, the dimethyl benzaldehydes, and methacrolein. These carbonyls together made up 86% of the total measured carbonyl mass emissions.

The ozone forming potential of the quantified carbonyl emissions was calculated using the maximum incremental reactivity (MIR) scale developed by Carter (*46*). For the carbonyls 2-oxobutanal, 3-pentene-2-one, unknown C_5 aliphatic carbonyl, unknown C_6 aliphatic carbonyls, and aromatic carbonyls except benzaldehyde and tolualdehydes, MIR values are not available and were estimated from structure-reactivity considerations The normalized reactivity was determined to be 5 9 ± 0 4 g O_3 per g carbonyl emitted This value does not reflect uncertainties in MIR values or the contributions of carbonyls listed in Table 2, which were not quantified Formaldehyde emissions were responsible for 70% of carbonyl reactivity Other species that contributed more than 2% to this total were acetaldehyde, methyl glyoxal, crotonaldehyde, and methacrolein. These 5 carbonyls together accounted for 92% of the ozone forming potential of the measured carbonyls. Methyl glyoxal was emitted at low levels, but due to its high MIR value, it made a significant contribution to total carbonyl reactivity.

Carbonyls constituted 3 9% of total NMOC emissions by mass and 5 2% of NMOC reactivity in 1999. These values are similar in magnitude because while some carbonyls are very reactive, the aromatic aldehydes have negative MIR values (*46*) Therefore as a group, carbonyls do not contribute disproportionately to the reactivity of exhaust emissions. In 1994 and 1995, prior to the introduction of California phase 2 reformulated gasoline, carbonyls accounted for 3.6% of NMOC mass emissions and 4 1-4.2% of NMOC reactivity (*45*). Following gasoline reformulation, the carbonyl contribution increased to 4.2% of NMOC mass and 6% of reactivity. After 1996, these values were below 4% of mass and approximately 5% of reactivity (*45*)

Emission Factor Trends, 1994-1999. In addition to measurements reported here for summer 1999, carbonyl emission factors have been measured at the Caldecott tunnel each summer from 1994 to 1997, with liquid gasoline sampling occurring in 1995 and 1996 (34,45). Between 1995 and 1996, California phase 2 reformulated gasoline program requirements took effect, and led to the addition of MTBE and reduced aromatic content in gasoline. Figure 3 presents carbonyl emission factor trends from 1994 to 1999. The list of carbonyls quantified has changed from year to year. To facilitate an appropriate comparison, solid tones with bold outlines are used in Figure 3 for species that have been measured since 1994. Patterns with light outlines are used for species that were not measured every year. The error bar given is the 95% confidence interval of the total measured carbonyl emission factor for each year Over the period 1994 to 1999, emissions decreased by 50±6% for formaldehyde, 45±7% for acetaldehyde, 71±5% for benzaldehyde, and 73±5% for tolualdehyde isomers Over this same 5-year time period, emission factors decreased by 55±8% for NMOC, 41±4% for NO_x, and 54±6% for CO at this same location (*40*). The overall reductions reported above include the combined effects of fuel changes and fleet turnover Direct evidence of the major fuel change between 1995 and 1996 is not obvious in Figure 3, though the reduced aromatic content in gasoline is the likely reason for the larger overall reduction in emissions of aromatic aldehydes compared to other carbonyls. Previous investigations at the Caldecott tunnel (*45, 47*) have shown an increase in formaldehyde emissions when MTBE was added to Bay Area gasoline, as would be expected

Cold Start Effects. Carbonyl formation is most pronounced during engine start-up, because under these conditions partial oxidation of fuel components is likely to occur and the catalyst is not yet warmed up enough to further oxidize the compounds (*20, 48*) Laboratory testing has shown that warmed-up catalysts oxidize carbonyls with efficiencies between 85 and 100% (*49, 50*). As stated previously, the emissions measured in the center bore of the Caldecott tunnel are from vehicles operating in a fully warmed up mode. Results of this investigation may underestimate overall carbonyl emissions from vehicles, because they do not include excess emissions associated with vehicle starting.

Emitted Carbonyls and Fuel Composition. Figure 4 compares the weight percentages of 4 emitted aldehydes with 4 likely precursor species found in gasoline (*23, 29, 31*) for the years 1995, 1996, and 1999. Formaldehyde in exhaust is compared with MTBE in gasoline, benzaldehyde with toluene, tolualdehydes with xylenes, and dimethylbenzaldehydes with trimethylbenzenes. Emissions of the three aromatic aldehydes generally track the changes in aromatic precursors in gasoline, whereas formaldehyde emissions do not track MTBE content in gasoline nearly as closely While use of MTBE increases formaldehyde emissions, there are numerous other precursors to formaldehyde in gasoline (*23, 28*).

Carbonyls in Gasoline. Studies of carbonyl emissions from engines have typically assumed that all carbonyl emissions resulted from partial oxidation of other compounds present in fuel, rather than being present in the gasoline to begin with. To test the validity of this assumption, the concentrations of carbonyls were measured in three Bay Area gasoline samples. Acetone (10-161 mg L^{-1} or 0 001-0.022 wt %) and MEK (7-22 mg L^{-1} or 0.001-0 003 wt %) were the most abundant carbonyls in liquid gasoline, and 8 other carbonyls were detected and quantified. Since carbonyls have not been reported previously in liquid gasoline, two additional fuel samples were obtained in southern California (Ventura) and analyzed for carbonyls As shown in Table 3, carbonyls are present in the Ventura gasoline samples at levels similar to those found in Bay Area gasoline. Though presence of carbonyls in California gasoline may be widespread, at these concentrations, the likely contribution of carbonyls present in gasoline to measured carbonyl emission factors will be minor.

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Literature Cited

(1) Skog, E. *Acta Pharmacologica et Toxicologica* **1950**, 6, 299.

(2) Feron, V J , Til, H.P., Devrijer, F , Woutersen, R A , Cassee, F R ; Vanbladeren, P.J ; *Mutation Research* **1991**, 259, 363

(3) U.S. 1990 Clean Air Act Amendments, Section 112, Hazardous Air Pollutants.

(4) Carter, W.P L., *Atmos. Environ* **1995**, 29, 2513.

(5) Lary, D.J ; Shallcross, D.E. *J Geophys Res* **2000**, 105, 19771.

(6) Grosjean, E , Grosjean, D.; Seinfeld, J H *Environ Sci Technol* **1996**, 30, 1038.

(7) Calvert, J G , Madronich, S *J Geophys Res* **1987**, 92, 2211.

(8) Harley, R A.; Cass, G R *Environ Sci Technol* **1994**, 28, 88

(9) Altshuller, A P *Atmos Environ* **1993**, 27A, 21

(10) Veyret, B ; Lesclaux, R ; Rayez, M T , Rayez, J C , Cox, R.A ; Moortgat, G K., *J Phys Chem* **1989**, 93, 2368

(11) Carter, W.P.L., Winer, A.M., Pitts, J.N., Jr. *Environ Sci Technol* **1981**, 15, 831.

(12) Vyskocil, A., Viau, C , Lamy, S. *Human & Experimental Toxicology* **1998**, 17, 212.

(13) Wohlfrom, K.H ; Hauler, T , Arnold, F , Singh, H. *Geophys Res Lett.* **1999**, 26, 2849.

(14) Arnold, F , Schneider, J.; Gollinger, K ; Schlager, H , Schulte, P , Hagen, D E.; Whitefield, P D , vanVelthoven, P *Geophys Res Lett* **1997**, 24, 57

(15) Henderson, G.S , McConnell, J.C ; Evans, W.F J *J Atmos. Chem* **1989**, 8, 277.

(16) Montzka, S.A.; Trainer, M.; Goldan, P.D., Kuster, W.C.; Fehsenfeld, F.C. *J. Geopys. Res* **1993**, 98, 1101.

(17) Lee, Y.N ; Zhou, X ; Kleinman, L I , Nunnermacker, L.J., Springston, S R.; Daum, P.H , Newman, L ; Keigley, W.G., Holdren, M W., Spicer, C W ; Young, V., Fu, B., Parrish,

D.D ; Holloway, J , Williams, J.; Roberts, J M , Ryerson, T.B ; Fehsenfeld, F C. *J Geophys. Res* **1998**, 103, 22449.

(18) Biesenthal, T.A.; Shepson, P B *Geophys Res Lett* **1997**, 24, 1375

(19) McLaren, R ; Singleton, D L.; Lai, Y.J K., Khouw, B ; Singer, E.; Wu, Z., Niki, H. *Atmos Environ.* **1996**, 30, 2219.

(20) Wagner, T., Wyszynski, M.L *Proc Instn Mech Engrs* **1996**, 210, 109.

(21) Zhang, J; Smith, K.R. *Environ Sci Technol* **1999**, 33, 2311

(22) Siegl, W O ; Hammerle, R H , Herrmann, H M , Wenclawiak, B W ; Luers-Jongen, B *Atmos Environ* **1999**, 33, 797.

(23) Schauer, J.J , Kleeman, M.J , Cass, G R., Simoneit, B R T. *Environ Sci Technol* **1999**, 33, 1578.

(24) Reuter, R M ; Gorse, R.A., Jr ; Painter, L J.; Benson, J D , Hochhauser, A M ; Rippon, B H.; Burns, V.R ; Koehl, W J., Rutherford, J.A. *SAE Tech Pap Ser* **1992**, paper no 920326

(25) Gorse, R.A., Jr ; Koehl, W.J.; Benson, J.D.; Painter, L.J ; Burns, V.R; Reuter, R.M ; Hochhauser, A.M ; Rippon, B.H. *SAE Tech Pap Ser* **1991**, paper no 912324.

(26) Wigg, E E. *SAE Tech Pap Ser* **1973**, paper no. 730196.

(27) Kaiser, E W.; Siegl, W.O.; Henig, Y.I.; Anderson, R W.; Trinker, F.H *Environ Sci Technol* **1991**, 25, 2005.

(28) Zervas, E , Montagne, X., Lahaye, J. *J Air & Waste Manage Assoc* **1999**, 49, 1304.

(29) Oberdorfer, P E *SAE Tech Pap. Ser.* **1967**, paper no 670123.

(30) Stump, F.D.; Knapp, K T.; Ray, W.D. *J Air & Waste Manage Assoc.* **1990**, 40, 872

(31) Hoekman, S.K. *Environ Sci Technol.* **1992**, 26, 1206

(32) Sigsby, J.E., Jr ; Tejada, S B.; Ray, W.; Lang, J M.; Duncan, J W. *Environ Sci Technol* **1987**, 21, 466.

(33) Schmid, H , Pucher, E , Ellinger, R., Biebl, P. Puxbaum, H *Atmos. Environ.* **2001**, 35, 3585

(34) Kirchstetter, T.W.; Singer, B C., Harley, R.A.; Kendall, G.R.; Traverse, M. *Environ Sci Technol* **1999**, 33, 318

(35) Fraser, M P.; Cass, G.R.; Simoneit, B.R T *Environ. Sci. Technol* **1998**, 32, 2051.

(36) Staehelin, J.; Keller, C.; Stahel, W.; Schlapfer, K.; Wunderli, S. *Atmos. Environ* **1998**, 32, 999.

(37) Zweidinger, R B.; Sigsby, J.E , Jr , Tejada, S.B., Stump, F D.; Dropkin, D L.; Ray, W D *Environ Sci Technol.* **1988**, 22, 956.

(38) Grosjean, E ; Green, P G , Grosjean, D. *Anal Chem* **1999**, 71, 1851.

(39) Grosjean, D , Grosjean, E , Gertler, A W. *Environ Sci. Technol.* **2001**, 35, 45

(40) Kean, A J.; Harley, R.A., Littlejohn, D ; Kendall, G.R *Environ Sci. Technol.* **2000**, 34, 3535.

(41) Kirchstetter, T.W.; Harley, R.A.; Kreisberg, N M.; Stolzenburg, M.R.; Hering, S.V. *Atmos. Environ* **1999**, 33, 2955.

(42) Grosjean, E.; Grosjean, D. *Int. J. Environ. Anal Chem* **1995**, 61, 343

(43) Grosjean, E ; Grosjean, D ; Fraser, M.P ; Cass, G R. *Environ. Sci Technol.* **1996**, 30, 2687.

(44) Grosjean, E.; Grosjean, D. *Int J Environ Anal. Chem.* **1995**, 61, 47.

(45) Kirchstetter, T.W.; Singer, B C.; Harley, R.A., Kendall, G.R ; Hesson, J.M. *Environ Sci. Technol* **1999**, 33, 329

(46) Carter, W.P.L. Additions and Corrections to the SAPRC-99 Maximum Incremental Reactivity (MIR) Scale, Report to the California Air Resources Board, Nov. 29 2000.

(47) Kirchstetter, T.W ; Singer, B C ; Harley, R.A , Kendall, G R , Chan, W *Environ Sci Technol* **1996**, 30, 661.

(48) Baugh, J.; Ray, W ; Black, F ; Snow, R *Atmos Environ.* **1987**, 21, 2077.

(49) Shore, P.R ; Humphries, D T., Hadded, O *SAE Tech Pap Ser.* **1993**, paper no. 930373.

(50) Leppard, W.R , Gorse, R.A , Rapp, L A , Knepper, J.C , Burns, V R., Koehl, W J. *SAE Tech Pap Ser.* **1992**, paper no 920329

Table 1. Carbonyls Measured at the Caldecott Tunnel, 1999.

Carbonyl Type	Ratio[a] (Exit/Entrance)	Emission Factor[b] (mg L^{-1})	rsd[c]	Mass Fraction[d], %	Reactivity Contribution[e], %
Saturated Aliphatic Aldehydes					
Formaldehyde	4.1	31 ± 4	0.15	45	70
Acetaldehyde	3.6	8.0 ± 0.8	0.12	12	14
Propanal	2.8	0.84 ± 0.09	0.13	1.2	1.6
Butanal	2.9	0.58 ± 0.13	0.28	0.84	0.97
Pentanal	3.9	0.34 ± 0.12	0.43	0.50	0.49
Isopentanal	2.4	0.34 ± 0.18	0.64	0.49	0.46
Hexanal	1.9	0.22 ± 0.12	0.67	0.32	0.27
Heptanal	2.0	0.11 ± 0.05	0.55	0.16	0.11
Subtotal		41		61	87
Unsaturated Aliphatic Carbonyls					
Acrolein	7.6	1.1 ± 0.1	0.10	1.5	2.0

Methacrolein	6.3	1.7 ± 0.2	0.12	2.4	2.6
Crotonaldehyde	3.4	1.1 ± 0.1	0.15	1.6	2.7
3-Pentene-2-one	1.8	0.15 ± 0.04	0.32	0.23	0.34
Subtotal		4.0		5.7	7.6
Aromatic Carbonyls					
Benzaldehyde	4.8	4.9 ± 0.6	0.16	7.2	–0.75
o-Tolualdehyde	18	1.5 ± 0.2	0.13	2.2	–0.21
m-Tolualdehyde	7.0	3.5 ± 0.3	0.12	5.1	–0.47
p-Tolualdehyde	17	1.9 ± 0.2	0.15	2.8	–0.26
2,5-Dimethylbenzaldehyde	6.9	1.2 ± 0.1	0.13	1.8	–0.12
2,4-Dimethylbenzaldehyde^f	6.8	0.81 ± 0.08	0.12	1.2	–0.08
2,4,6-Trimethylbenzaldehyde^f	7.2	0.42 ± 0.03	0.08	0.62	–0.04
o/m/p-Anisaldehyde	7.8	0.38 ± 0.07	0.22	0.55	–0.04
Acetophenone	4.5	0.097 ± 0.010	0.12	0.14	–0.01
Subtotal		15		22	–2
Aliphatic Ketones					

Acetone	1.7	4.0 ± 0.5	0.14	5.9	0.43
2-Butanone (MEK)	2.4	0.56 ± 0.08	0.17	0.82	0.21
2-Pentanone	7.9	0.40 ± 0.24	0.72	0.58	0.31
4-Methyl-2-Pentanone (MIBK)	3.1	0.49 ± 0.19	0.47	0.72	0.53
C_5 Aliphatic Carbonyl[g]	5.1	0.23 ± 0.09	0.45	0.33	0.18
C_6 Aliphatic Carbonyl #1[g]	30.2	0.88 ± 0.20	0.27	1.3	0.78
C_6 Aliphatic Carbonyl #2[g]	6	0.55 ± 0.17	0.38	0.81	0.49
Subtotal		7.1		10	2.9
Aliphatic Dicarbonyls					
Glyoxal	3.7	0.085 ± 0.031	0.43	0.12	0.30
Methyl Glyoxal	3.4	0.75 ± 0.15	0.24	1.1	3.0
Biacetyl	1.8	0.13 ± 0.03	0.24	0.19	0.67
2-Oxobutanal	2.2	0.035 ± 0.008	0.26	0.05	0.18
Subtotal		1.0		1.5	4.2

[a] Carbonyl concentration at the tunnel exit divided by the concentration at the entrance.

[b] Emission factors for light-duty vehicles given as mean values over 8 days of sampling, expressed per unit of volume of fuel burned, listed with associated 95% confidence interval.

[c] Relative standard deviation of the emission factors, $s/\bar{x}$.

[d] Percentage of total measured carbonyl mass emissions

[e] Percentage of total carbonyl reactivity

[f] These species were positively identified using a reference standard, although other isomers with almost identical retention times could not be ruled out.

[g] Concentrations of the C_5 and C_6 aliphatic carbonyls that were not positively identified were reported using the measured response factor of the closest-eluting isomer for which a reference standard was available.

Table 2. Other Carbonyls Identified in Caldecott Tunnel Samples

Carbonyl Species[a]
2-Pentenal/Isomer
Cyclopentanone (Tentative)
Methyl Vinyl Ketone
Aromatic Isomer #1
trans-Cinnamaldehyde
C_6 Aliphatic Isomer #3
Indanone
Dimethylbenzaldehyde Isomer #1
Dimethylbenzaldehyde Isomer #2
C_7 Aliphatic Isomer #1
C_7 Aliphatic Isomer #2
C_7 Aliphatic Isomer #3
C_7 Aliphatic Isomer #4
6-Methyl-5-Heptene-2-One (Tentative)
2-Heptanone
Aromatic Isomer #2
Trimethylbenzaldehyde Isomer #1
Trimethylbenzaldehyde Isomer #2
Unknown #1 (MW=236, Aliphatic)[b]
2-Oxopentanal

Carbonyl Species (continued)
2-Oxoheptanal/Isomer
C_4 Substituted Benzaldehyde
C_8 Dicarbonyl
Unknown #3 (MW=234, ARM)
C_9 Aliphatic Isomer #2
C_9 Aliphatic Isomer #3
C_9 Aliphatic Isomer #4
Nonanal
C_{10} Aliphatic Isomer #1
C_{10} Aliphatic Isomer #2
C_{10} Aliphatic Isomer #3
C_{10} Aliphatic Isomer #4
trans-2-Decenal/Isomer
2-Decanone
Decanal
Unknown #4 (MW=221, ARM)
Unknown #5 (MW=221, Aliphatic)
C_{11} Aliphatic Isomer #1
C_{10} Dicarbonyl
C_{11} Aliphatic Isomer #2

C_8 Aliphatic Isomer #1
2,3-Pentanedione
C_8 Aliphatic Isomer #2
Unknown #2 (MW=236, Aliphatic)[b]
C_8 Aliphatic Isomer #3
2-Oxohexanal
C_8 Aliphatic Isomer #4
C_8 Unsaturated Isomer #1
C_8 Aliphatic Isomer #5
C_8 Unsaturated Isomer #2
2,3-Hexanedione/Isomer
C_8 Aliphatic Isomer #6
Pinonaldehyde (Tentative)
Octanal
C_9 Aliphatic Isomer #1
Unknown #6 (MW=283, Aliphatic)
Undecanal
C_{12} Aliphatic Isomer #1
C_{12} Aliphatic Isomer #2
2-Dodecanone
Dodecanal
C_{13} Aliphatic Isomer #1
C_{13} Aliphatic Isomer #2
Unknown #7 (MW=285, Aliphatic)
Tridecanal
C_{14} Aliphatic Isomer #1
C_{14} Aliphatic Isomer #2
C_{14} Aliphatic Isomer #3
C_{14} Aliphatic Isomer #4
Tetradecanal

[a] Samples were analyzed by LC-DAD-APCI-MS and carbonyls are listed in order of elution. Carbonyls were identified by their retention time, DAD-UV spectrum and APCI mass spectrum Compound purity was >98% by MS for all carbonyls

[b] Unknowns #1 and #2 are isomers and may be compounds other than carbonyls. Their UV spectrum is consistent with an aliphatic carbonyl-DNPH and their mass spectrum indicates a DNPH group (m/z 182).

Table 3. Measured concentrations of carbonyls in liquid gasoline[a].

Species	Bay Area Sample #1	Bay Area Sample #2	Bay Area Sample #3	Ventura Sample #1	Ventura Sample #2
Formaldehyde	0.02	0 04	0 04	0.03	0.02
Acetaldehyde	0 12	0 14	0 17	0 22	0.12
Acetone	15 16	160 79	9.67	8 54	8 75
Propanal	0 30	0 25	0.27	0.31	0.25
MEK	13.90	22 49	7 23	5 33	1 90
Butanal	0 87	4 58	0 35	0 55	0 70
Benzaldehyde	0 05	0.07	0 04		
2-Pentanone	1 69	1 30	1 27		
o-Tolualdehyde	0 13	0 13	0 11		
Unknown[b]	3 96	0 16	2 80		

[a] Concentrations are reported in units of mg of carbonyl per liter of gasoline.

[b] Unknown species had a DNPH derivative of 502 g mol^{-1} and is likely a 142 g mol^{-1} C_8 dicarbonyl.

Figure Captions

Figure 1. Emission factors for saturated aliphatic aldehydes and aromatic carbonyls measured at the Caldecott tunnel with comparison to results from the Tuscarora tunnel in Pennsylvania. Uncertainty bars represent the 95% confidence intervals of the mean emission factor. [a]Although marked species were positively identified using a reference standard, other isomers could not be ruled out

Figure 2. Emission factors for unsaturated aliphatic carbonyls, aliphatic ketones, and dicarbonyls measured at the Caldecott tunnel with comparison to results from the Tuscarora tunnel in Pennsylvania Uncertainty bars represent the 95% confidence intervals of the mean emission factor. 3-pentene-2-one was not detected at the Tuscarora tunnel. [a]Concentrations of the C_5 and C_6 saturated aliphatic carbonyls (arbitrarily grouped here with ketones) that were not positively identified were reported using the measured response factor of the closest-eluting isomer for which a reference standard was available.

Figure 3. Trends in light-duty emission factors (±95% C I on the total) for carbonyls measured at the Caldecott tunnel between 1994 and 1999 No measurements were made during summer 1998. Formaldehyde, acetaldehyde, benzaldehyde, and 7 others (propanal, butanal, pentanal, hexanal, crotonaldehyde, acetone, and MEK) were measured each year. Total tolualdehydes were not measured in 1997 The group "Other carbonyls" includes some different species for each year, see text. California phase 2 reformulated gasoline was introduced between 1995 and 1996.

Figure 4. Changes in gasoline composition and in carbonyl emissions (as a percentage of total carbonyl mass emissions).

Figure 1

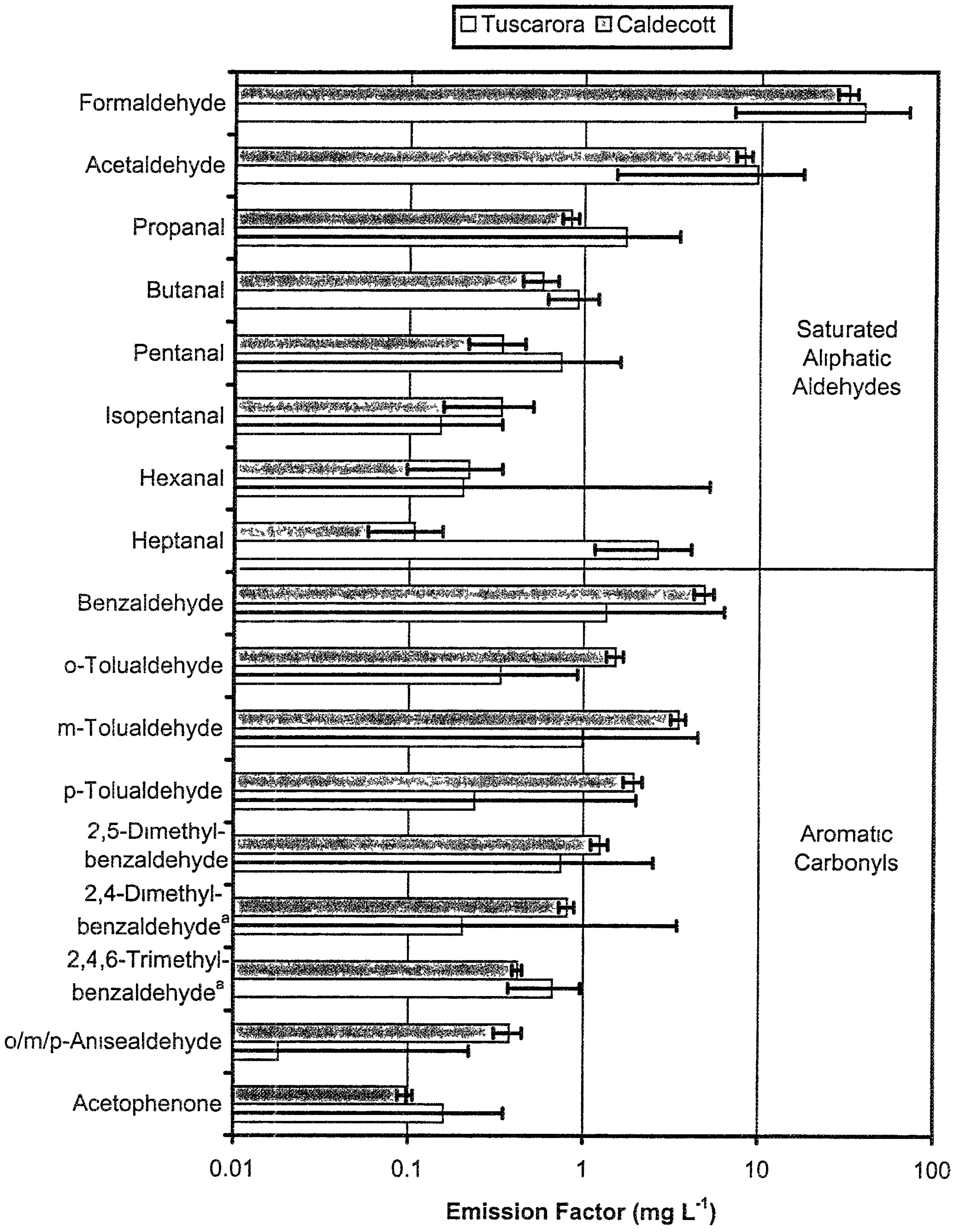
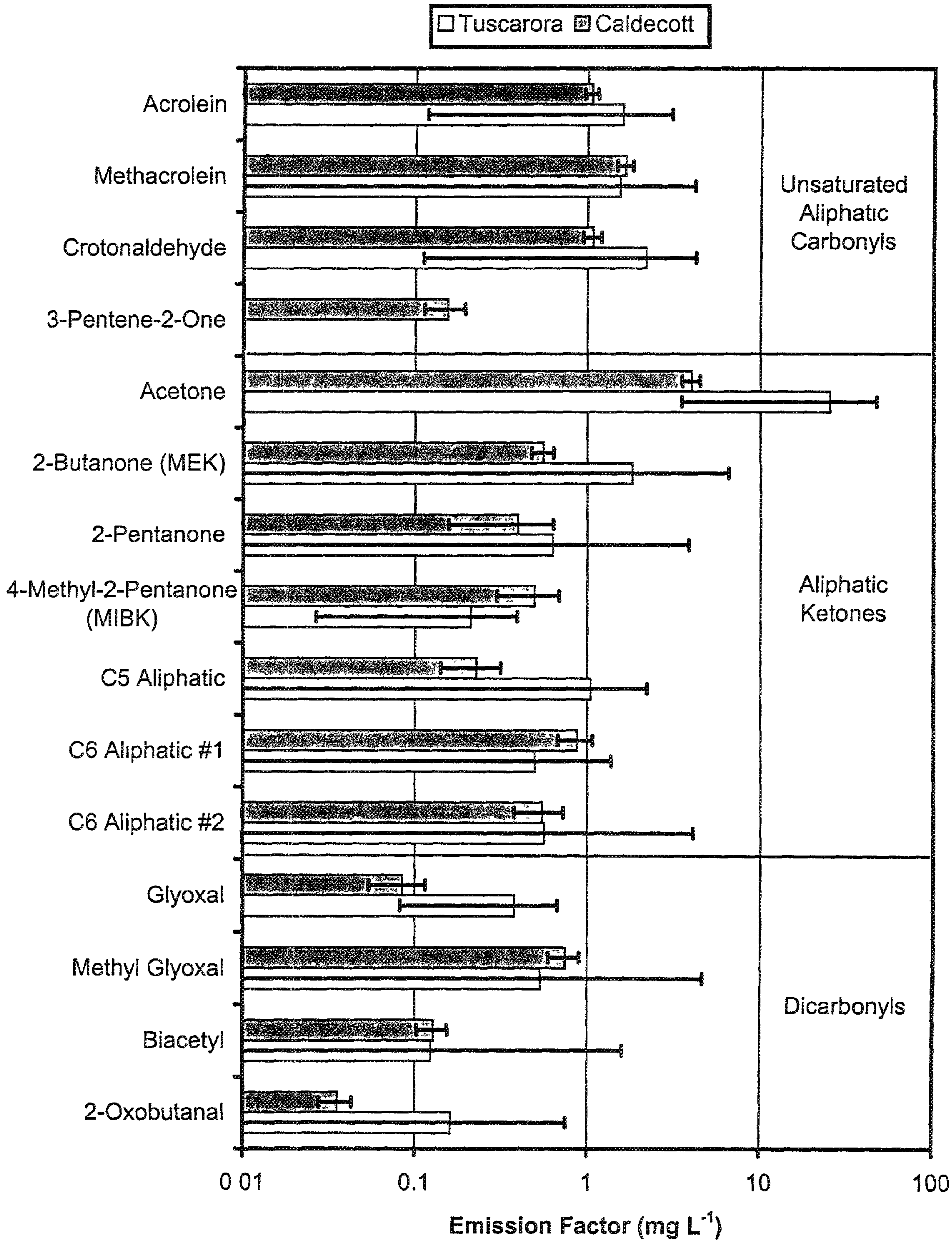
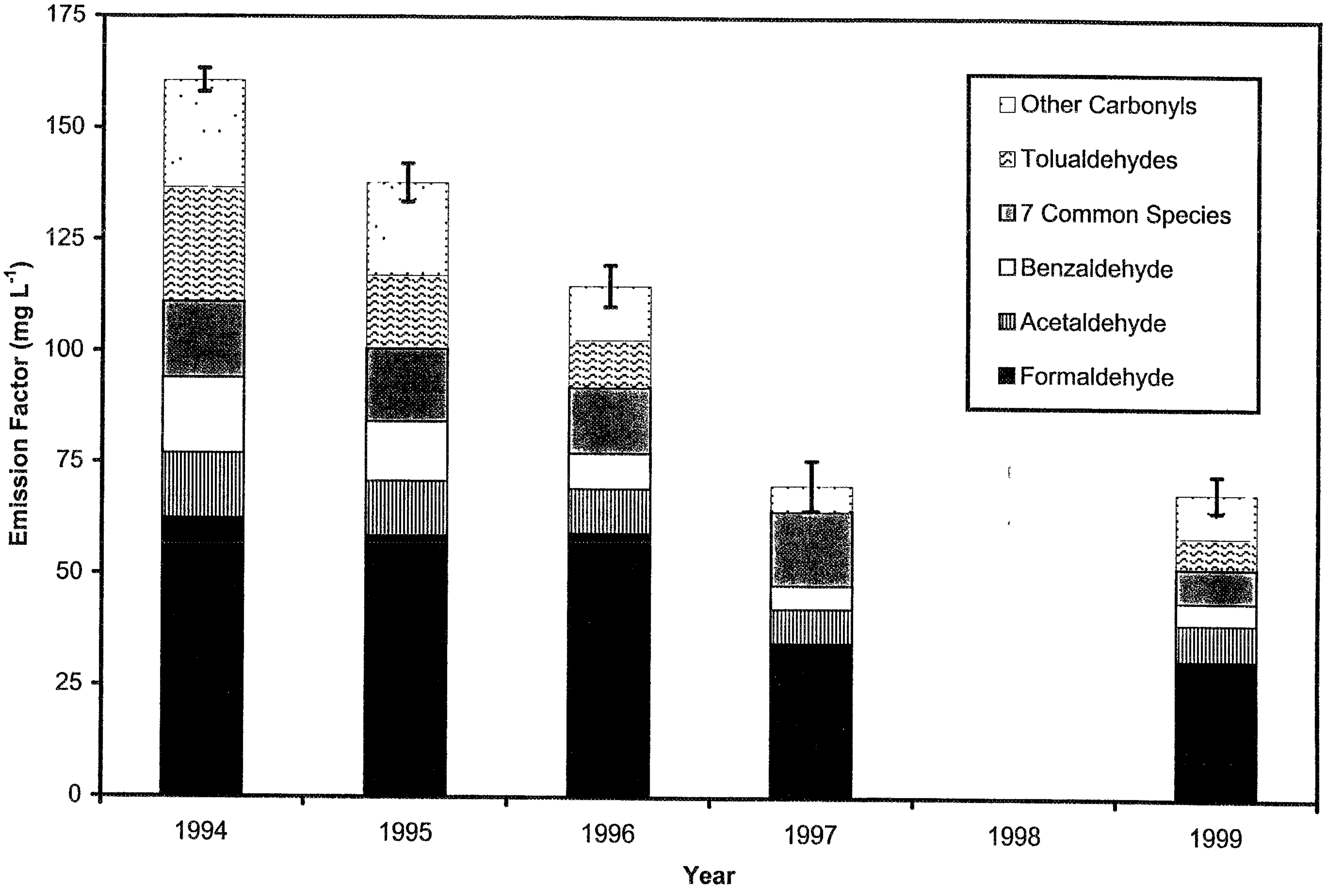

☐ Tuscarora ▨ Caldecott
Formaldehyde
Acetaldehyde
Propanal
Butanal
Pentanal
Isopentanal
Hexanal
Heptanal
Benzaldehyde
o-Tolualdehyde
m-Tolualdehyde
p-Tolualdehyde
2,5-Dimethyl-benzaldehyde
2,4-Dimethyl-benzaldehyde[a]
2,4,6-Trimethyl-benzaldehyde[a]
o/m/p-Anisealdehyde
Acetophenone
Saturated Aliphatic Aldehydes
Aromatic Carbonyls
0.01
0.1
1
10
100
Emission Factor (mg L-1)

Figure 2



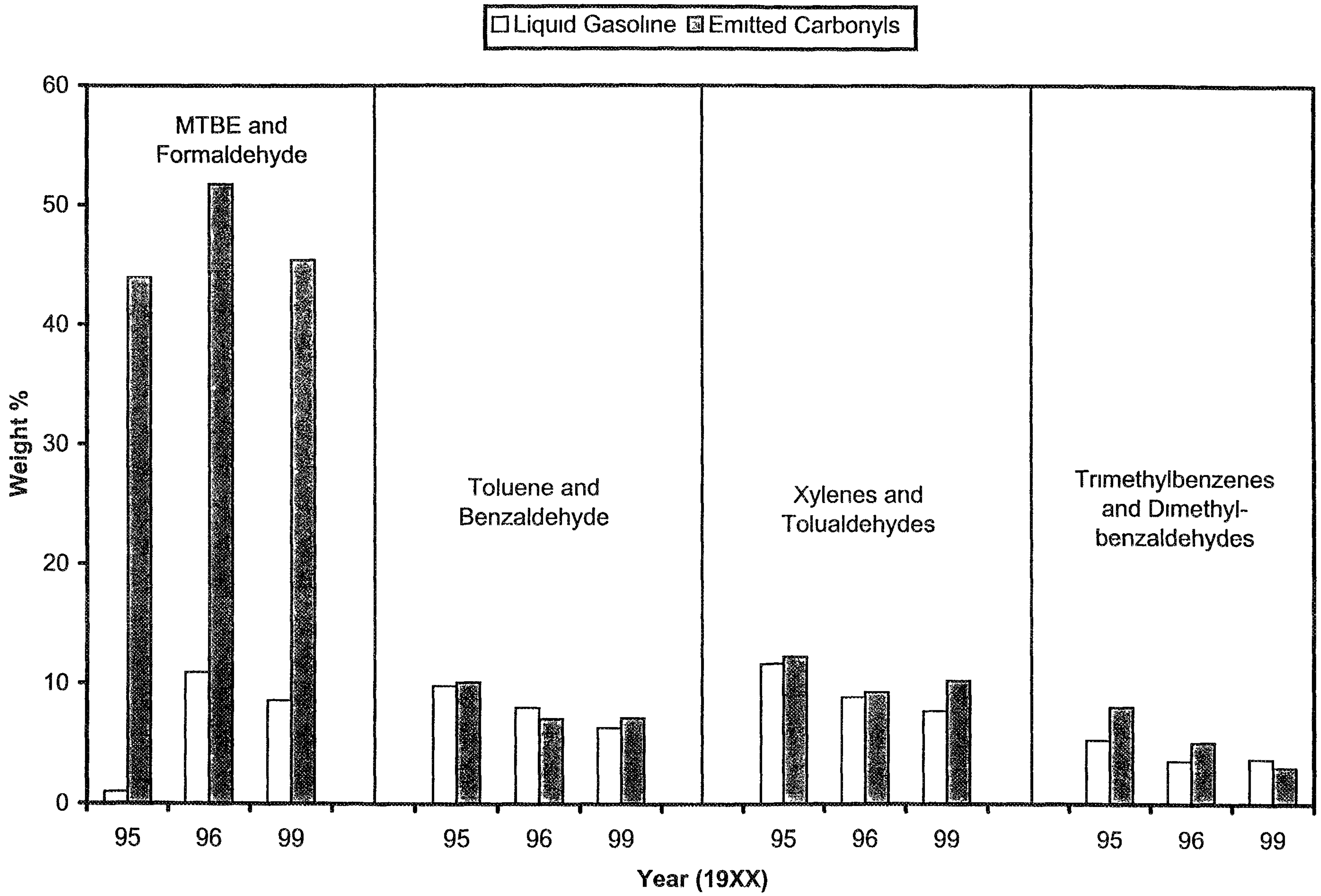
☐ Tuscarora ▨ Caldecott
Acrolein
Methacrolein
Crotonaldehyde
3-Pentene-2-One
Acetone
2-Butanone (MEK)
2-Pentanone
4-Methyl-2-Pentanone (MIBK)
C5 Aliphatic
C6 Aliphatic #1
C6 Aliphatic #2
Glyoxal
Methyl Glyoxal
Biacetyl
2-Oxobutanal
Unsaturated Aliphatic Carbonyls
Aliphatic Ketones
Dicarbonyls
0 01
0.1
1
10
100
Emission Factor (mg L^{-1})

Figure 3



Emission Factor (mg L^{-1})
175
150
125
100
75
50
25
0
Other Carbonyls
Tolualdehydes
7 Common Species
Benzaldehyde
Acetaldehyde
Formaldehyde
1994
1995
1996
1997
1998
1999
Year

Figure 4


☐ Liquid Gasoline ▨ Emitted Carbonyls
Weight %
60
50
40
30
20
10
0
MTBE and Formaldehyde
Toluene and Benzaldehyde
Xylenes and Tolualdehydes
Trimethylbenzenes and Dimethylbenzaldehydes
95
96
99
95
96
99
95
96
99
95
96
99
Year (19XX)