

Temperature dependence of volatile organic compound evaporative emissions from motor vehicles

Juli I. Rubin,¹ Andrew J. Kean,^{1,2} Robert A. Harley,¹ Dylan B. Millet,^{3,4} and Allen H. Goldstein³

Received 1 July 2005; revised 13 September 2005; accepted 8 November 2005; published 10 February 2006.

[1] A chemical mass balance approach is used to determine the relative contributions of evaporative versus tailpipe sources to motor vehicle volatile organic compound (VOC) emissions. Contributions were determined by reconciling time-resolved ambient VOC concentrations measured downwind of Sacramento, California, in summer 2001 with source speciation profiles. A composite liquid fuel speciation profile was determined from gasoline samples collected at Sacramento area service stations. Vapor-liquid equilibrium relationships were used to determine the corresponding headspace vapor composition. VOC concentrations measured in a highway tunnel were used to define the composition of running vehicle emissions. The chemical mass balance analysis indicated that headspace vapor contributions ranged from 7 to 29% of total vehicle-related VOC depending on time of day and day of week, with a mean daytime contribution of $17.0 \pm 0.9\%$ (mean \pm 95% CI). A positive association between the headspace vapor contribution and ambient air temperature was found for afternoon hours. We estimate a $6.5 \pm 2.5\%$ increase in vapor pressure-driven evaporative emissions and at least a $1.3 \pm 0.4\%$ increase in daily total (exhaust plus evaporative) VOC emissions from motor vehicles per degree Celsius increase in maximum temperature.

Citation: Rubin, J. I., A. J. Kean, R. A. Harley, D. B. Millet, and A. H. Goldstein (2006), Temperature dependence of volatile organic compound evaporative emissions from motor vehicles, *J. Geophys. Res.*, *111*, D03305, doi:10.1029/2005JD006458.

1. Introduction

[2] Motor vehicles are a major anthropogenic source of volatile organic compounds [Sawyer *et al.*, 2000]. VOC are important as precursors to formation of other air pollutants such as tropospheric ozone and secondary aerosols [National Research Council, 1991; Odum *et al.*, 1997]. Uncertainty in emission inventories has been a long-running concern in air quality research and management [National Research Council, 1991, 2000]. The situation with respect to vehicular VOC emissions is especially complex as there are contributions from both tailpipe exhaust and nontailpipe evaporative sources. Tailpipe emissions include running exhaust and excess emissions associated with cold engine starting. Evaporative sources include hot soak emissions that are driven by residual engine heat following vehicle operation, diurnal emissions associated with venting of fuel tank vapors as temperature increases during the day, running loss evapo-

rative emissions that occur while vehicles are operating, and resting losses that result from gasoline permeation through rubber and plastic components of the fuel system.

[3] EMFAC [California Air Resources Board (CARB), 2002] is a statistical model used in California to estimate on-road motor vehicle emissions. Figure 1 shows model-predicted contributions to vehicular VOC emissions in Sacramento during summer 2001. Additional gasoline-related VOC emissions not shown in Figure 1 occur at service stations, for example, because of liquid fuel spillage and vapor displacement during refueling [Morgester *et al.*, 1992]. As shown in Figure 1, diesel exhaust accounts for only 3% of total on-road vehicle VOC emissions, and is therefore excluded from further consideration in this study.

[4] It is important to assess the apportionment of VOC in emission inventories (as shown for example in Figure 1). From an analysis of ambient air samples and reconciliation with VOC source profiles, Pierson *et al.* [1999] conclude that $71 \pm 9\%$ of motor vehicle VOC emissions is emitted from tailpipes, $17 \pm 6\%$ result from nontailpipe liquid fuel emissions, and the remaining $12 \pm 4\%$ of emissions are due to headspace vapor emissions. Pierson *et al.* [1999] also review tailpipe and evaporative emission test results for various fleets of in-use vehicles. From the vehicle test data, it appears that nontailpipe sources exceed tailpipe VOC emissions by a wide margin, which is inconsistent with ambient air results discussed above.

[5] The source apportionment study of Pierson *et al.* [1999] and others reviewed by Watson *et al.* [2001], have

¹Department of Civil and Environmental Engineering, University of California, Berkeley, California, USA.

²Now at Department of Mechanical Engineering, California Polytechnic State University, San Luis Obispo, California, USA.

³Department of Environmental Science, Policy, and Management, University of California, Berkeley, California, USA.

⁴Now at Department of Earth and Planetary Sciences, Harvard University, Cambridge, Massachusetts, USA.

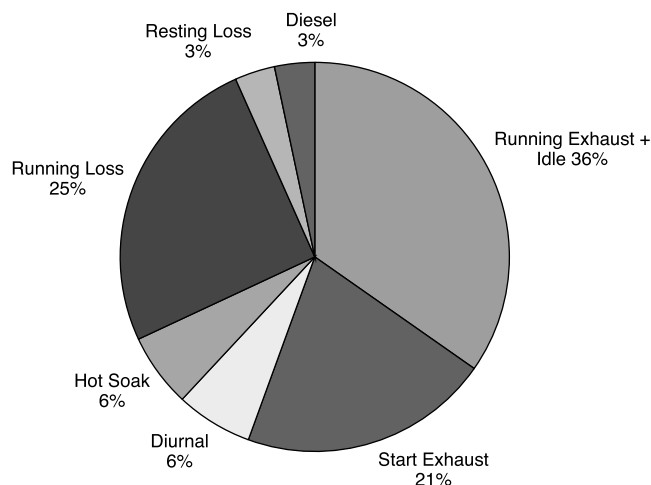


Figure 1. EMFAC model estimates [CARB, 2002] of relative contributions to on-road motor vehicle emissions (Sacramento, California; summer 2001).

been constrained by available methods for measuring ambient VOC concentrations. Semicontinuous online measurement methods [e.g., Millet *et al.*, 2005] now make it possible to conduct more comprehensive analyses using months of consecutive VOC concentration measurements with hourly or better time resolution.

[6] The relative importance of various emission modes may have changed as a result of vehicle and fuel changes that took place during the 1990s. The maximum allowed summer season vapor pressure (measured at 38°C) of California gasoline was reduced from 62 kPa prior to 1992, to 54 kPa for 1992–1995, and to 48 kPa from 1996 onward. These changes reduced vapor pressure-driven emissions of VOC. Also, increasingly stringent emission standards led to installation of more robust and durable tailpipe and evaporative emission control equipment on new vehicles sold during the 1990s.

[7] It is known that meteorological variability affects photochemical air pollution levels, and that high-ozone days are correlated with high temperatures [Sillman and Samson, 1995]. In addition to direct effects of temperature and sunlight on chemical reaction rates, and reduced ventilation due to light winds that often prevail on hot days, increased temperatures also can contribute to higher ozone through effects on natural and anthropogenic emissions. There are multiple mechanisms by which ambient temperature could affect vehicular VOC emissions. For example, increases in temperature can decrease excess emissions associated with cold engine starting; this effect is most

significant in winter [Braddock, 1981; Stump *et al.*, 1989]. Use of vehicle air conditioning on hot days leads to increased fuel consumption, carbon monoxide, and nitrogen oxide emissions [Welstand *et al.*, 2003]. However, tailpipe VOC emissions did not increase significantly with air conditioner use in these tests. Diurnal evaporative VOC emissions increase with increasing temperature, because of an exponential rise in gasoline vapor pressure and greater vapor flows out of fuel tanks.

[8] The objective of the present research is to determine source contributions to VOC emissions by reconciling emission source fingerprints with recent, time-resolved ambient concentration data. The sensitivity of evaporative emissions to changes in temperature from day to day is also examined.

2. Methods

2.1. Ambient VOC

[9] Ambient concentrations of 47 VOC listed in Table 1 were measured on school district property in the town of Granite Bay, California (38°N 44' 23"/121°W 12' 01"/277 m above sea level), located approximately 30 km northeast of Sacramento near Folsom Lake. Major highways are located ~10 km to the north and south. Continuous VOC measurements were recorded with time resolution of ~45 min over an 8-week period from 18 July through 15 September 2001 using online gas chromatographic methods described by Millet *et al.* [2005]. Ambient data were separated into weekday and weekend subsets to control for the effect of different driving patterns on weekends.

[10] Measured winds at the site [Cleary *et al.*, 2005] were consistent from day to day during the field study, with afternoon (1200–1700 LT) flows from the southwest bringing air directly from the Sacramento area to Granite Bay, and nighttime (2000–0600 LT) flows from the southeast, down-slope from the Sierra Nevada Mountains. During morning hours, wind direction transitioned smoothly from the nighttime to the afternoon flow regime, with an earlier and more abrupt transition to southwesterly flow on warmer days.

2.2. Liquid Gasoline

[11] The composition of liquid gasoline was quantified for five major gasoline brands for both regular and premium fuel grades. One-liter liquid fuel samples were collected at Sacramento area service stations in summer 2001. Samples were analyzed by gas chromatography on a Hewlett Packard model 5890 IT GC equipped with dual flame ionization detectors. Primary analysis was performed on a DB-1 capillary column with coeluting peaks resolved on a DB-5

Table 1. VOC Measured at Granite Bay During Summer 2001

VOC	
Alkanes	propane, n-butane, isobutane, n-pentane, isopentane, cyclopentane, 2,2-dimethylpropane, n-hexane, methylpentanes, ^a n-heptane
Alkenes	propene, trans-2-butene, 1-butene, 2-methylpropene, 1,3-butadiene, cyclopentene, 3-methyl-1-butene, trans-2-pentene, 1-pentene, 2-methyl-1-butene, cis-2-pentene, isoprene, α -pinene, d-limonene, 3-carene
Aromatics	benzene, toluene, ethylbenzene, o-xylene, m-xylene, p-xylene
Other	MTBE, acetaldehyde, acetone, methanol, ethanol, pentanal, hexanal, methyl ethyl ketone, methyl vinyl ketone, methacrolein, 3-methylfuran, propyne, methyl chloride, dichloromethane, trichloromethane, tetrachloroethylene

^aSum of 2- plus 3-methylpentane isomers.

column, as described in more detail elsewhere [Kirchstetter *et al.*, 1999]. A composite liquid fuel profile was calculated as a sales-weighted average of the 10 individual gasoline brand and grade samples.

2.3. Gasoline Headspace Vapors

[12] Partial pressures p_i of organic compounds in gasoline headspace vapors were calculated for each brand of gasoline using the following vapor-liquid equilibrium relationship:

$$p_i = \gamma_i x_i p_i^o \quad (1)$$

where γ_i is the liquid-phase activity coefficient of species i , x_i is the mol fraction of species i in liquid fuel, and p_i^o is the vapor pressure of compound i in pure liquid form. Fuel blends that did not contain ethanol were assumed to follow ideal solution behavior ($\gamma_i = 1$). Liquid-phase activity coefficients for ethanol-gasoline mixtures were defined as described by Harley *et al.* [2000]. As of summer 2001, only one gasoline refiner supplying fuel to the Sacramento area used ethanol instead of MTBE to supply the required 2 wt% fuel oxygen. Weight fractions w_i of each compound in headspace vapors were calculated from partial pressures of individual VOC:

$$w_i = \frac{y_i MW_i}{\sum_i y_i MW_i} \quad (2)$$

where MW_i is the molecular weight of compound i and $y_i = p_i \div \sum_i p_i$. A composite headspace vapor profile was computed as the sales-weighted average of individual gasoline brands and grades.

[13] Harley *et al.* [2000] compared predicted and measured headspace vapor composition using this method and found good agreement, within $\pm 15\%$. One exception was *n*-butane, which was overpredicted in the headspace by 22%. For isopentane and methylpentanes that are of interest in this work, agreement was within $\pm 4\%$.

2.4. Tunnel Emissions

[14] Vehicle emissions were measured in the center bore of the Caldecott tunnel in summer 2001 [Kean *et al.*, 2002]. The Caldecott tunnel is located in the San Francisco Bay area on highway 24 between Oakland and Orinda. Pollutant concentrations were measured in the traffic tube approximately 50 m before the tunnel exit and also in background air near the tunnel entrance. Two-hour integrated air samples were collected on 9 weekdays from 1600 to 1800 LT in 6-L stainless steel canisters. Hydrocarbon concentrations in these air samples were quantified using a Perkin-Elmer Model 8500 GC equipped with FID (for details, see Kirchstetter *et al.* [1999]). Vehicle emissions were determined by subtracting background values from concentrations measured at the tunnel exit.

2.5. Chemical Mass Balance

[15] Source contributions to ambient VOC were calculated by reconciling liquid fuel, headspace vapor, and tunnel emission speciation profiles with measured VOC concentrations at Granite Bay. Tracer compounds for this analysis were selected on the basis of the following criteria:

(1) measured at Granite Bay, (2) minimal oxidative loss in transit from source to receptor, (3) vehicle emissions overwhelmingly dominant as source of tracer, (4) low relative standard deviation for tracer in source profiles, and (5) clear signal above background in ambient VOC data. It was also desired to have similar atmospheric reactivity across tracers so that even small losses due to reaction do not affect the outcome. Source contributions s_j to ambient VOC were calculated by chemical mass balance:

$$c_i = \sum_j w_{ij} s_j \quad (3)$$

where c_i is the measured ambient concentration of species i , and w_{ij} is the weight fraction of species i in direct emissions from source j .

[16] Hourly temperature data were obtained from the nearby Fair Oaks station [California Irrigation Management Information System, 2004], and matched with Granite Bay VOC concentrations. Day-to-day variations in temperature coupled with 8 weeks of online VOC concentration measurements were used to examine the temperature dependence of source contributions. To eliminate the effect of day-to-day and diurnal changes in wind speed and mixing height on absolute VOC concentrations, relative source contributions are used in later parts of this analysis. Use of relative source contributions also reduces the influence of site-to-site differences in absolute VOC concentrations.

3. Results and Discussion

[17] A summary of the most abundant compounds in liquid gasoline, headspace vapors, and tunnel emissions is shown in Table 2. In subsequent analyses, tunnel and liquid fuel weight fractions were averaged together because of collinearity of these profiles: $\sim 50\%$ of VOC mass in tailpipe emissions consists of unburned gasoline [Leppard *et al.*, 1992].

[18] Isopentane is a useful tracer in our analysis because it is abundant in vehicle emissions, and vehicle emissions of isopentane overwhelm all other sources. While already abundant in liquid fuel and tunnel emissions, isopentane is greatly enriched in headspace vapors (see Table 2). The sum of 2- and 3-methylpentane was selected as the second tracer for this study. The methylpentanes are also abundant in gasoline and tunnel emissions, but in contrast to C_5 isopentane, the C_6 methylpentanes are only slightly enriched in headspace vapors relative to their abundance in liquid fuel. Using VOC mass emission estimates [CARB, 2004] and emission speciation profiles, $>99\%$ of isopentane and methylpentane emissions in central California were attributed to motor vehicles.

[19] Using a daytime OH concentration of 1.1×10^7 molecules cm^{-3} estimated for the Sacramento urban plume [Dillon *et al.*, 2002], characteristic times for the oxidation of isopentane and the methylpentanes are 6.8 and 4.7 hours, respectively. Both tracers react slowly compared to many of the other VOC listed in Table 1. Nevertheless, while in transit from source to Granite Bay, methylpentanes may be depleted because of reaction with OH to a greater extent than isopentane, which could lead us to overstate the importance of vapor-emitting sources of VOC.

Table 2. Summary of the Most Abundant Compounds (wt% of Total NMOC; Mean \pm 1 Standard Deviation) in Sacramento Gasoline and Caldecott Tunnel Emissions

Liquid Gasoline		Headspace Vapors		Tunnel Emissions	
Compound	wt%	Compound	wt%	Compound	wt%
MTBE	10.7 \pm 5.6	isopentane	26.6 \pm 3.1	toluene	9.4 \pm 0.6
toluene	7.8 \pm 1.8	MTBE	13.6 \pm 7.3	isopentane	8.6 \pm 1.4
isopentane	7.5 \pm 0.8	n-butane	8.0 \pm 1.3	ethene	5.9 \pm 1.2
m-xylene	5.0 \pm 0.3	n-pentane	7.7 \pm 0.4	m/p-xylene	4.8 \pm 0.3
2-methylpentane	3.6 \pm 0.5	2-methylpentane	4.2 \pm 0.8	2-methylpentane	4.1 \pm 0.5
n-pentane	2.8 \pm 0.2	methylcyclopentane	4.1 \pm 0.3	propene	3.8 \pm 0.8
methylcyclopentane	2.8 \pm 0.1	toluene	2.4 \pm 0.8	benzene	3.4 \pm 0.6
1,2,4-trimethylbenzene	2.8 \pm 0.2	3-methylpentane	2.3 \pm 0.4	2,2,4-trimethylpentane	2.8 \pm 0.3
o-xylene	2.4 \pm 0.2	2-methyl-2-butene	2.3 \pm 1.1	pentane	2.7 \pm 0.3
3-methylpentane	2.2 \pm 0.2	isobutane	2.2 \pm 0.5	3-methylpentane	2.3 \pm 0.1

[20] Table 3 compares the abundance of selected VOC in liquid gasoline and headspace vapors for Berkeley versus Sacramento in summer 2001. The individual abundances of isopentane and methylpentanes in liquid gasoline match in these two locations, to within 95% confidence limits. Because of well-matched fuel composition for these constituents, use of the Caldecott tunnel emissions profile is appropriate for Sacramento, given the tracers that we are using. Differences in isopentane in liquid gasoline are magnified in the headspace vapor composition profiles.

[21] While Table 1 shows that concentrations of many other VOC were measured at Granite Bay, these other compounds fail to meet one or more of our selection criteria for inclusion in the chemical mass balance analysis. For example, benzene could be a useful tracer to help distinguish between tailpipe emissions and nontailpipe emissions of liquid gasoline. Benzene levels in exhaust are enriched above levels in gasoline because of catalytic dealkylation of other aromatic hydrocarbons [Bruehlmann *et al.*, 2005]. However, because measured benzene concentrations were often close to background values at Granite Bay, benzene was not used here. Toluene levels are similarly abundant in tunnel emissions and liquid gasoline, and much lower in headspace vapors (see Table 2). Analysis of toluene emission inventory data indicates significant emissions from nonvehicular sources such as surface coatings and solvents

(vehicle sources were responsible for \sim 70% of total inventoried toluene emissions). Propyne, which is emitted in vehicle exhaust but is not present in unburned fuel, was not measured at the Caldecott tunnel. Other aromatics and all of the alkenes are too reactive to use as tracers. Light alkanes including propane and butanes have other sources such as liquefied petroleum gas (LPG). Butanes have been diverted from the summertime gasoline pool to help meet fuel vapor pressure limits and to make 2,2,4-trimethylpentane and other high-octane compounds through a refining process known as alkylation [Gary and Handwerk, 1984]. Acetylene was not measured at Granite Bay. Oxygenate use in gasoline is optional in the San Francisco Bay area where tunnel emission profiles were measured, but required in the Sacramento area where ozone air pollution problems are more severe. MTBE and 2,2,4-trimethylpentane levels in Bay area versus Sacramento gasoline differ significantly, and therefore Bay area tunnel-derived speciation profiles are not representative of Sacramento area emissions for these compounds. Use of ethanol in gasoline was at a low level as of summer 2001, though ethanol use has since increased greatly because of the phaseout of ethers from California gasoline.

[22] Average weekday and weekend source contributions calculated using equation (3) are shown in Figure 2. Contributions are expressed as concentrations and can be

Table 3. Comparison of Isopentane and Methylpentanes in Liquid Gasoline, Headspace Vapors, and Tunnel Emissions (wt% of Total NMOC; Mean \pm 1 Standard Deviation)

	Berkeley 2001	Sacramento 2001	CARB ^a
Liquid gasoline			
Isopentane	9.7 \pm 1.9	7.5 \pm 0.8	9.8
2-Methylpentane	4.8 \pm 1.1	3.6 \pm 0.5	5.6
3-Methylpentane	2.9 \pm 0.7	2.2 \pm 0.2	3.1
Isopentane/ Σ -methylpentanes	1.3	1.3	1.1
Headspace vapors			
Isopentane	37.6 \pm 7.2	26.6 \pm 3.1	34.9
2-Methylpentane	6.2 \pm 1.8	4.2 \pm 0.8	4.2
3-Methylpentane	3.4 \pm 0.9	2.3 \pm 0.4	2.3
Isopentane/ Σ -methylpentanes	3.9	4.1	5.4
Tunnel/tailpipe emissions			
Isopentane	8.6 \pm 1.4	NA	7.1
2-Methylpentane	4.1 \pm 0.5	NA	3.8
3-Methylpentane	2.3 \pm 0.1	NA	2.3
Isopentane/ Σ -methylpentanes	1.3	NA	1.2

^aCalifornia Phase 2 reformulated gasoline species profiles for liquid gasoline, diurnal evaporative emissions, and stabilized exhaust emissions from catalyst-equipped vehicles (P. D. Allen, personal communication, 1999).

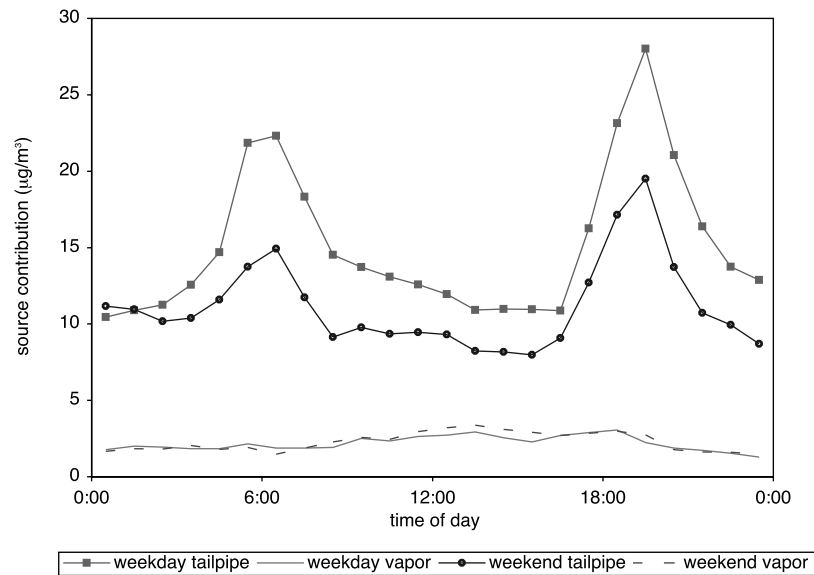


Figure 2. Weekday and weekend source contributions to ambient VOC due to tailpipe emissions and liquid fuel (combined source), and headspace vapor emissions. Hourly average values over an 8-week summertime period.

interpreted as the part of the total ambient VOC concentration that can be attributed to a specified source. As shown in Figure 2, weekend and weekday data produce similar diurnal patterns with higher tailpipe/liquid fuel source contributions on weekdays, and comparable headspace vapor contributions for all days of the week. The peaks in liquid fuel/tailpipe source contributions shown in Figure 2 occur at the same time on all days of the week despite different driving patterns on weekends, suggesting a common effect of atmospheric transport on the timing of the peaks on all days. The diurnal pattern in headspace vapor contributions shows an increase throughout the day despite enhanced dilution due to increasing mixed layer height. This increase in headspace vapors leads to the midday minimum observed in tailpipe/liquid fuel contributions.

[23] Relative contributions of headspace vapors to total vehicle-related VOC are presented in Table 4. Only daytime hours are shown, as wind direction is not from Sacramento and vehicle activity is low at night. As shown in Table 4, the

importance of headspace vapors increases throughout the day, reaching maximum values between 1400–1600 LT on weekdays and 1400–1500 LT on weekends. The average daytime contribution is $17.0 \pm 0.9\%$ on weekdays. Using alternate VOC emission speciation profiles shown in Table 3 has little effect on this result: average daytime headspace vapor contributions were 14% using Berkeley 2001 fuel profiles, and 16% using CARB profiles.

[24] Source contributions from this analysis were compared to predictions from California's EMFAC model for Sacramento. EMFAC values listed in Table 4 were calculated assuming that all diurnal emissions and half of running loss emissions resemble headspace vapors in terms of composition. The basis for this assumption is measurements of running loss emissions [Haskew *et al.*, 1999], in which roughly equal contributions from liquid fuel and vapor leaks were found. Overall EMFAC's headspace vapor contributions are higher at most hours (except 1500–1800 LT on weekdays and 1300–1800 LT on weekends) than the

Table 4. Percent Contributions (With 95% Confidence Intervals) of Headspace Vapors to VOC Emissions for 1-Hour Time Intervals

Time Interval	Weekday	Weekend	EMFAC ^a
0600–0700 LT	7 ± 3	9 ± 4	25
0700–0800 LT	9 ± 3	14 ± 6	20
0800–0900 LT	9 ± 3	17 ± 7	20
0900–1000 LT	14 ± 6	19 ± 3	23
1000–1100 LT	17 ± 6	16 ± 3	25
1100–1200 LT	16 ± 3	18 ± 2	23
1200–1300 LT	17 ± 2	20 ± 3	26
1300–1400 LT	19 ± 2	27 ± 5	26
1400–1500 LT	22 ± 3	29 ± 2	26
1500–1600 LT	22 ± 3	28 ± 4	25
1600–1700 LT	19 ± 2	27 ± 4	14
1700–1800 LT	16 ± 2	20 ± 4	14

^aCalifornia emission inventory model predictions for Sacramento in summer 2001: Headspace vapor contribution as a percent of vehicular VOC emissions is calculated using 100% of diurnal evaporative plus 50% of running loss emissions (see text).

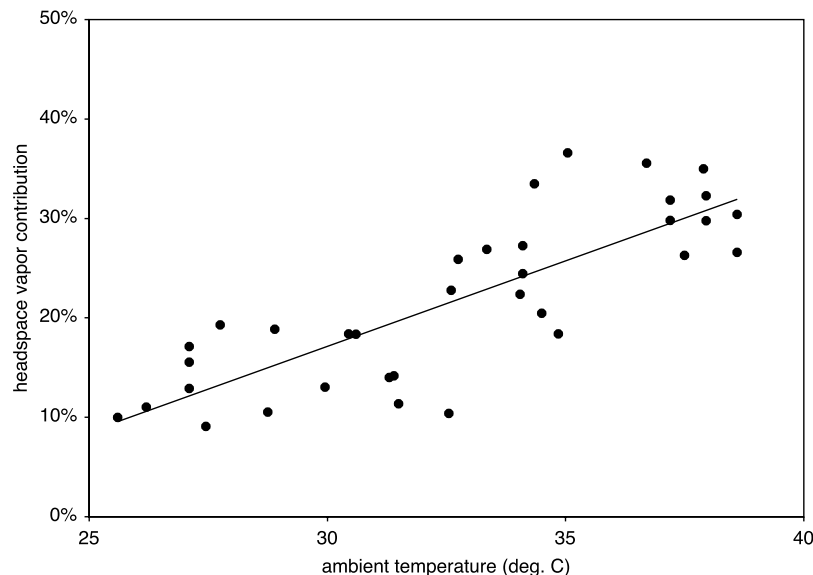


Figure 3. Headspace vapor contribution to vehicular VOC emissions on weekdays, 1500–1600 LT, as a function of ambient temperature.

Granite Bay data would suggest. The largest disagreement is seen at 0600–0900 LT on weekdays. A possible explanation could be that the relative importance of running loss emissions is overstated, and that of diurnal evaporative emissions understated, in the EMFAC model. Running loss evaporative emissions occur only while vehicles are operating and therefore peak during weekday commute hours. A source of uncertainty in these comparisons is the use of point measurements at Granite Bay to evaluate the regional emission inventory for the Sacramento area.

[25] Statistically significant dependencies were found between ambient temperature and the fraction of ambient VOC attributed to headspace vapor sources on weekday afternoons. The relationship for 1500–1600 LT when the headspace vapor contribution was highest is shown in Figure 3. A summary of slopes and correlation coefficients for afternoon hours is presented in Table 5. Little can be said about differences in sensitivities to temperature (slopes) from hour to hour because of overlapping confidence intervals. From Table 4, the average fraction of total VOC emissions attributed to headspace vapors during afternoon hours is $\sim 20\%$. The average change in the headspace vapor contribution (from Table 5) is $+1.3\%$ per $^{\circ}\text{C}$. Therefore, in absolute terms headspace vapor emissions (we believe mainly diurnal evaporative sources) increase by $6.5 \pm 2.5\%$ per $^{\circ}\text{C}$ over a temperature range of 25 to 38°C .

[26] Using the EMFAC model, the change in tailpipe/liquid fuel emissions with temperature was predicted, assuming that these emissions comprise exhaust (running, idle, and start), half of running evaporative losses, and all of hot soak and resting losses. The predicted change in this total was less than 0.5% per degree Celsius for summer conditions. Using an average slope for fractional contribution of evaporative emissions as a function of temperature and assuming that tailpipe emissions remain constant, a 1°C increase in temperature would result in a $1.3 \pm 0.4\%$ increase in vehicle-related VOC emissions. This represents a lower bound on the actual emission increase as other

vehicle-related VOC sources may also increase with temperature. Note that because of the low olefin content of California gasoline, the reactivity [Carter, 1994] of VOC in headspace vapors is $\sim 30\%$ less than that of liquid gasoline and tunnel emissions.

4. Conclusions

[27] The use of highly time resolved ambient VOC concentration data in this study showed a varying contribution from evaporative emission sources throughout the day. On weekdays, headspace vapor emissions were responsible for 7 to 22% of total motor vehicle VOC emissions, with somewhat higher relative contributions on weekends due to decreased tailpipe/liquid fuel emissions. Headspace vapors appear not to be the dominant source of vehicle-related VOC emissions, as reported previously by Pierson *et al.* [1999]. Compared to current EMFAC model predictions for California during summer months, analysis of hour-by-hour data points to a greater role for diurnal evaporative sources and less of a role for running loss evaporative emissions associated with vehicles in motion. This in turn could point to a need for changes in emphasis in control strategies for VOC emissions from the motor vehicle sector, such as increased attention to tailpipe sources. The strong relationship between evaporative VOC emissions and temperature

Table 5. Best Fit Slopes (With 95% Confidence Interval) for Weekday Headspace Vapor Contribution to Vehicle-Related VOC as a Function of Ambient Temperature

Time Interval	Slope, % contribution/ $^{\circ}\text{C}$	R
1300–1400 LT	1.0 ± 0.5	0.60
1400–1500 LT	1.7 ± 0.7	0.66
1500–1600 LT	1.7 ± 0.4	0.81
1600–1700 LT	1.3 ± 0.6	0.60
1700–1800 LT	1.0 ± 0.4	0.60

suggests that an overall increase in motor vehicle emissions will be observed on hot days.

[28] **Acknowledgments.** We thank David Kohler of ChevronTexaco Technology Center for detailed hydrocarbon analysis of liquid gasoline samples and James Hesson and Gary Kendall of the Bay Area Air Quality Management District for analysis of tunnel air samples. We gratefully acknowledge the U.S. Department of Energy for support of measurements at Granite Bay under contract AC03-76SF0009. Although the research described in this article has been funded wholly or in part by the U.S. Environmental Protection Agency through grant RD-83096401-0 to the University of California, Berkeley, it has not been subjected to the Agency's required peer and policy review and therefore does not necessarily reflect the views of the Agency and no official endorsement should be inferred.

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A. H. Goldstein, Department of Environmental Science, Policy, and Management, University of California, Berkeley, CA 94720-3110, USA.

R. A. Harley and J. I. Rubin, Department of Civil and Environmental Engineering, University of California, Berkeley, CA 94720-1710, USA. (harley@ce.berkeley.edu)

A. J. Kean, Department of Mechanical Engineering, California Polytechnic State University, San Luis Obispo, CA 93407, USA.

D. B. Millet, Department of Earth and Planetary Sciences, Harvard University, Cambridge, MA 02138, USA.