Research

Diurnal and Seasonal Variability of Gasoline-Related Volatile Organic Compound Emissions in Riverside, California

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On- and off-road mobile sources are the dominant contributors to urban anthropogenic volatile organic compound (AVOC) emissions. Analyses of gasoline samples from California for both summer and winter indicate significant differences in liquid fuel and vapor chemical composition due to intentional seasonal adjustments. Ambient concentrations of 55 VOCs were measured via in situ gas chromatography in the 2005 Study of Organic Aerosols at Riverside (SOAR) during both summer and fall. A chemical mass balance analysis was used to differentiate vapor pressure-driven VOC emissions from other motor vehicle-related emissions such as tailpipe exhaust. Overall, fuel vapor emissions accounted for $31 \pm 2\%$ of gasoline-related VOC in Riverside; California's emission factor model similarly estimates 31% of gasoline-related VOC emissions are fuel vapor. The diurnal pattern of vapor pressure-driven VOC source contributions is relatively stable around 10 μg/m^3, while whole gasoline (i.e., tailpipe) contributions peak at ~60 μg/m^3 during the morning commute. There is no peak in whole gasoline source contributions during the afternoon, due to rapid dilution associated with high mixing heights and wind speeds in the Riverside area. The relationship between estimated gasoline-related VOC and observed carbon monoxide concentrations in this study is similar to California's 2005 emission inventory; we calculated a VOC to CO mass ratio of 0.086 ± 0.006 (95% CI) compared to 0.097 in the emission inventory for all gasoline-related sources.

1. Introduction

Volatile organic compound (VOC) emissions, both biogenic and anthropogenic, are important precursors to the formation of ozone and secondary organic aerosols (1). Anthropogenic volatile organic compound (AVOC) emissions in urbanized areas are predominantly from gasoline-related sources (2). Gasoline use occurs in both on- and off-road engines, which together are responsible for the majority of both VOC and carbon monoxide (CO) emissions in urban environments (2). California actively regulates gasoline formulation to reduce environmental and human health effects of air pollution; recently methyl tert-butyl ether (MTBE) was replaced by ethanol as the main oxygenated additive in gasoline.

VOC emissions from the tailpipe contain compounds of all volatilities and include running exhaust, engine idling, and engine start up; these emissions are attributable to incomplete combustion of gasoline during various modes of vehicle operation. The composition of the resulting VOC emissions is a function of engine design, operating conditions, and vehicle maintenance. Evaporative emissions include the release of gasoline vapors resulting from diurnal temperature variations, hot soak (i.e., residual heat at the end of a trip), running losses, and resting losses. In contrast to diurnal and hot soak emissions from parked vehicles, running losses occur only during vehicle operation. Resting losses, due for example to permeation of fuel through plastic and rubber components of the fuel system, occur at all hours whether or not the vehicle is in operation. All forms of evaporative emissions are released into the ambient atmosphere due to leaks throughout the fuel system, and in the case of older vehicles, uncontrolled atmospheric vents on the gas tank. For emission inventories, liquid fuel leaks/spills originating from on-road vehicles are considered a form of running losses, while leaks/spills occurring at service stations are included under fuel storage and handling as an area source; in terms of our analysis both are grouped in with tailpipe emissions under the larger category of whole gasoline emissions. California regulations and control equipment have emphasized control of both tailpipe and vapor emissions from vehicles. Control technologies include catalytic converters, seasonal changes in gasoline formulation to reduce summertime vapor pressure, and vapor recovery systems on vehicles and at service stations.

Previous studies using dynamometer vehicle fleet tests conclude that 7−35% of motor vehicle nonmethane hydrocarbons are nontailpipe emissions (3). Similarly, an analysis of 2001 ambient data from Granite Bay, CA (near Sacramento) estimated $17.0 \pm 0.9\%$ of total daytime gasoline-related VOC emissions are vapor pressure-driven (4). This new work in Riverside, CA presents a valuable opportunity to study a different location with different geography and meteorological conditions while also considering seasonal variability. Another difference compared to previous work is the incorporation of ethanol into California gasoline, which may affect VOC emissions. A comprehensive understanding of VOC emissions at Riverside is of particular interest because this area has some of the highest levels of ozone and particulate matter (PM) pollution in the United States (5).

Methods for generating emissions estimates are subject to uncertainties. A review of mobile source emission modeling by the National Research Council stresses the importance of model evaluation studies using ambient observations to reduce uncertainties by identifying areas of agreement and those that deserve further study (6). In an effort to evaluate emission inventories, we compare ambient observations to inventories developed by the California Air Resources Board (CARB) for reactive organic gases and CO (7). These inventories are resolved by source category, county, and air basin. Table 1 summarizes VOC emissions estimates for the western

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TABLE 1. 2005 Gasoline-Related VOC Emission Inventory for Riverside County (South Coast Air Basin)[a]

source[b]	emissions [tons/day]	percent contribution
cars	11.0	26%
light duty trucks	8.4	20%
medium duty trucks	2.9	7%
heavy duty gasoline trucks & buses	3.3	8%
motorcycles	3.3	8%
recreational (off-road & boats)	4.6	11%
off-road equipment[c]	5.2	12%
gasoline distribution & marketing	2.1	5%
fuel storage and handling	1.4	3%

[a] Estimates are the annual average of daily emissions. [b] Train and aircraft emissions are excluded due to fuel differences (2.8 tons VOC/day). [c] Includes farm, lawn and garden, and other commercial/residential equipment.

portion of Riverside County that is included in the South Coast air basin (SoCAB). California's emission inventories (7) and EMFAC model (8) are the sources of the estimates shown in Table 1; EMFAC estimates on-road vehicle emissions by calendar year, season, and location.

The objectives of this research were to evaluate changes in AVOC emissions resulting from seasonal variations in gasoline formulation; to distinguish vapor pressure-driven AVOC emissions from other gasoline-related AVOC emission sources; to develop diurnal profiles of AVOC emissions, meteorology, and source contributions; and finally to examine the consistency of AVOC and CO emission inventories with measured ambient pollutant concentrations.

2. Methods

2.1. Ambient Measurements. Ambient concentrations of 55 VOCs (Table S1) were measured during the 2005 Study of Organic Aerosols at Riverside (SOAR) campaign in Riverside, CA. The measurement site (33°58'18'' N/117°19'17'' W) was located on the University of California, Riverside campus in an urban area within the South Coast air basin, east of Los Angeles and Orange County. The site was located 1 km east (typically downwind) of a major highway—Interstate 215. Month-long sampling campaigns were conducted in the summer (July 15–August 15) and in the fall (October 31–November 30).

Hourly resolved VOC concentrations were measured on-site using a gas chromatograph (HP model 5890) equipped with both a mass-selective detector (HP model 5971) and a flame ionization detector; example chromatograms can be found in the Supporting Information (Figure S1). The instrument preconcentrated 450 mL samples of ambient air on adsorbent traps over a 30 min period and thermally desorbed them onto capillary columns; the FID-analyzed sample was collected on a glass bead/Carbopak B/Carboxen 1000 adsorbent mix and injected onto a RT-Alumina Plot column, while the MSD-analyzed sample was collected on a glass bead/Carbopak B/Carbosieves SIII mix, then injected onto a DB-Wax column. Further detail on the GC/MS-FID system can be found in Millet et al. (9). Meteorological data, including ambient temperature and wind speed/direction, were recorded on-site throughout the campaign. CO was measured using nondispersive infrared absorption (TEI, model 48c) and ground-level ozone (O_3) was measured using an UV photometric analyzer (Dasibi Inc., model 1008-RS); CO and O_3 data were averaged to match the temporal resolution of the VOC data.

2.2. Liquid Gasoline. Liquid gasoline composition was measured by the California Air Resources Board during both summer and winter 2005–2006 by collecting fuel samples from the tanks of 20 in-use vehicles during both summer

(April–October) and winter (November–March) months. Individual gasoline samples were combined into aggregate samples for each season and then a detailed hydrocarbon analysis was performed to measure fuel composition (10). For specific compound weight fractions reported in this study, averages (and ranges) of the two seasonal mixtures were calculated.

2.3. Gasoline Headspace Vapors. Vapor–liquid equilibrium calculations were performed using speciated liquid gasoline measurements to predict gasoline vapor composition:

$$P_i = x_i \gamma_i P_i^o(T) \tag{1}$$

$$y_i = P_i \div \sum_i P_i \tag{2}$$

$$w_i = y_i MW_i \div \sum_i y_i MW_i \tag{3}$$

where P_i represents the partial pressure of compound i and $P_i^o(T)$ is the vapor pressure of the pure liquid i at a specified temperature ($T = 298$ K in this analysis). γ_i denotes the liquid phase activity coefficient of compound i. California gasoline now contains significant amounts of ethanol and behaves as a nonideal solution ($\gamma \neq 1$); liquid-phase activity coefficients were specified as described in Harley et al. (11). The vapor-phase mol fractions and weight fractions of species in the gasoline headspace vapor are represented by y_i and w_i, respectively. Vapor–liquid equilibrium calculations considered all species with up to 8 carbons; the heavier molecules are minor contributors to gasoline vapor pressure and headspace composition.

2.4. Chemical Mass Balance Analysis. Source-receptor modeling using a chemical mass balance method was performed following Rubin et al. (4). We used tracers present in both liquid gasoline and headspace vapors to distinguish between whole gasoline and vapor pressure-driven VOC emissions. Isopentane and the sum of methylpentane isomers were used as tracers in this study. Emissions of these VOC are dominated by gasoline-related sources, and they have defined and distinctly different signatures in vapor versus liquid fuel. Both tracers were measured at Riverside during SOAR and have similar atmospheric lifetimes. Tracer weight fractions in the headspace vapor represent vapor pressure-driven evaporative emissions, whereas whole gasoline emissions are estimated using the tracer weight fractions in liquid gasoline. The colinearity of vehicular tailpipe VOC emissions and liquid gasoline composition has been reported previously (12). This approach provides an upper bound on the vapor pressure-driven contribution as we neglect products of incomplete combustion such as ethane, ethene, propene, acetylene, isobutene, and all aldehydes in tailpipe emissions, which were not measured at Riverside. We estimate, from previous on-road measurements (13), that ~17% of the nonmethane organic carbon mass emissions are products of incomplete combustion, with the precise fraction varying depending on engine type, age, and operation mode. Isopentane's high vapor pressure makes it considerably more abundant in vapor pressure-driven emissions and changes in its abundance, relative to the heavier methylpentanes, allow us to differentiate vapor from liquid fuel sources.

The chemical mass balance equation can be written as follows:

$$C_i = \sum_j w_{ij} S_j \tag{4}$$

Hourly source contributions (S_j) were calculated from measured ambient concentrations (C_i) and the chemical fingerprint matrix (w_{ij}) generated from the liquid fuel and

TABLE 2. Most Abundant Compounds in Gasoline and Headspace Vapors [wt% (Range)][a]

compound	headspace vapor		liquid gasoline	
	summer	winter	summer	winter
isopentane	31.7 (30.9−32.6)	24.2 (23.6−24.8)	6.9 (6.7−7.1)	7.4 (7.2−7.5)
n-butane	4.7 (4.4−5.1)	24.2 (24.1−24.3)	0.5 (0.5−0.5)	3.4 (3.4−3.4)
2-methylpentane	6.5 (6.3−6.7)	4.0 (3.6−4.3)	3.9 (3.8−3.9)	3.3 (3.0−3.6)
3-methylpentane	3.5 (3.4−3.7)	2.5 (2.3−2.6)	2.4 (2.3−2.4)	2.3 (2.2−2.5)
ethanol	7.5 (7.5−7.6)	5.4 (5.4−5.5)	6.0 (6.0−6.1)	6.3 (6.2−6.4)
n-pentane	8.3 (8.2−8.3)	7.8 (7.1−8.4)	2.4 (2.4−2.4)	3.2 (2.9−3.5)
toluene	2.0 (1.9−2.1)	1.3 (1.2−1.4)	8.2 (7.7−8.6)	7.6 (7.0−8.3)
m-xylene	0.3 (0.3−0.3)	0.2 (0.2−0.2)	3.9 (3.9−4.0)	4.1 (4.0−4.3)
2,2,4-trimethylpentane	3.3 (3.2−3.4)	1.3 (1.0−1.7)	6.3 (6.0−6.7)	3.5 (2.6−4.5)
isobutane	0.7 (0.7−0.7)	6.2 (4.9−7.5)	0.05 (0.05−0.05)	0.6 (0.5−0.7)

[a] Liquid gasoline composition acquired from CARB and is based on 20 liquid gasoline samples collected each season and aggregated into 2 mixtures for detailed hydrocarbon analysis (ranges are over the two aggregates). Some individual liquid samples may have been affected by weathering in the fuel tank.

headspace vapor composition profiles described above. Source contribution results from this method were used to analyze the diurnal variations in fuel vapor and whole gasoline emissions as well as the vapor pressure-driven contribution to total gasoline-related VOC emissions. In addition, we examined variations in wind speed and direction to determine meteorological effects on ambient concentrations and source contributions. Measurements were separated into weekday and weekend subgroups to control for differences in traffic patterns (*14*).

2.5. Emission Inventories. County and air basin-resolved emission inventories for 2005 were compared to our ambient CO data and total gasoline-related VOC (the sum of fuel vapor and whole gasoline source contributions) (*7*). We evaluated the correlation of gasoline-related VOC to CO concentrations via linear regression using our data and compared them to model estimates developed using California's emission inventory tools. The model-based gasoline-related VOC/CO ratios were estimated by dividing the sum of on- and off-road gasoline-related VOC emissions by the total CO emissions in the region to be consistent with the sources included in our ambient sampling-based method. For the purposes of comparison, biogenic CO emissions were excluded due to the absence of forest fires during the field studies in 2005 and the relatively low biogenic VOC emissions in the Riverside and Los Angeles areas. VOC/CO emission inventory ratios were calculated for the portion of Riverside County within the South Coast air basin and the entire South Coast air basin for comparison to results derived using our ambient data.

The EMFAC model was used to generate daily and hourly resolved estimates of gasoline vapor contributions to total gasoline-related VOC emissions and VOC/CO ratios during summer 2005. One caveat to the ratios developed using EMFAC is that they are limited to on-road emissions for both VOC and CO, and do not include off-road emissions or any other sources of CO observed in ambient air. California's emission inventory suggests that ∼30% of gasoline-related VOC and ∼20% of CO emissions have therefore been excluded from the comparison. For comparison to the hourly EMFAC results, we also generated a diurnal profile of VOC/CO ratios by performing linear regressions over 3-h intervals of our data (Table S3 and Figure S5).

3. Results and Discussion

3.1. Gasoline Seasonality. Seasonal changes in gasoline formulation are reflected in differences between summer and winter headspace vapor composition. Isopentane comprises a smaller fraction of winter gasoline vapors compared to summer, while the n-butane vapor fraction increases significantly and the ethanol fraction decreases in winter.
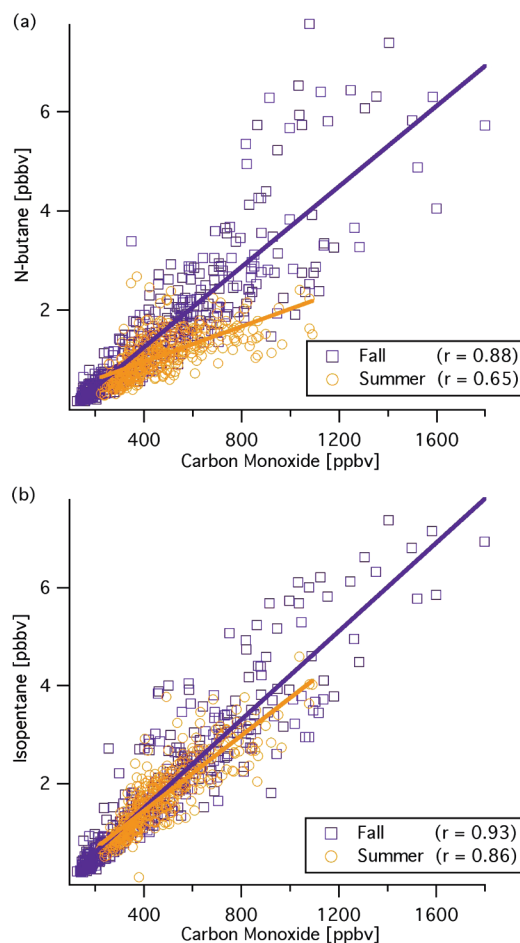
FIGURE 1. Plots of ambient concentrations of (a) n-butane and (b) isopentane versus carbon monoxide at Riverside for summer and fall 2005.

Table 2 summarizes the seasonal variation of abundant compounds in gasoline in both liquid fuel and headspace vapors. The inclusion of high-volatility compounds is intentionally limited during the summer to reduce AVOC emissions, which contributes to observed decreases in ambient mixing ratios of such VOCs in the summer (see Figure 1) (*15*). The molar ratio of n-butane to CO more than doubles from $(1.8 \pm 0.2) \times 10^{-3}$ in the summer to $(4.1 \pm 0.2) \times 10^{-3}$ in the fall, while the isopentane ratio to CO exhibits less variation, increasing modestly from 0.0038 ± 0.0002 in the summer to 0.0045 ± 0.0002 in the fall. Similar seasonality of ambient n-butane concentrations was observed by Lee et al.
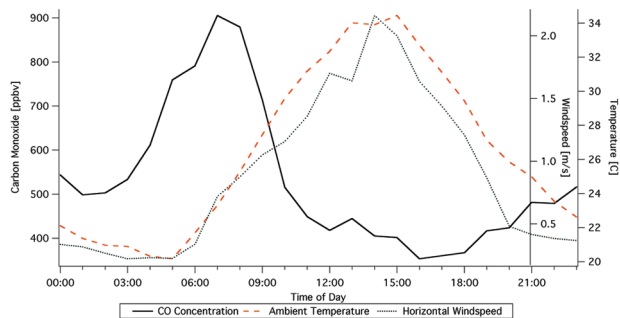
FIGURE 2. Diurnal variation of ambient CO concentration at Riverside (weekdays only during summer 2005) and collocated variations in ambient temperature and wind speed.

in the northeastern U.S. during much of the 1990s and isopentane concentrations were more stable with no statistically significant seasonal variation observed between summer and fall (*16*).

The most dramatic compositional effect of seasonal gasoline reformulation is the large variation of n-butane in the liquid fuel, headspace vapors, and ambient measurements. This result is expected since n-butane has a higher vapor pressure than isopentane and is preferentially removed by refiners during summer months due to seasonal limits on gasoline vapor pressure. Despite strong vapor/liquid and seasonal contrasts in n-butane abundance, we did not include this compound in the chemical mass balance analysis. Our primary concern is the presence of n-butane in other VOC emission sources (*17*). In summer especially, when n-butane is greatly reduced in liquid gasoline, it should not be assumed that gasoline-related sources will dominate the atmospheric concentration of n-butane. The high vapor pressure of n-butane and its very low abundance in summer gasoline also makes this compound especially susceptible to fuel weathering (aging) effects, which would be an added source of uncertainty in the analysis.

3.2. Dilution Effects. The diurnal concentration profile of vehicle-related pollutants during the summer sampling period consistently showed a large peak from morning commuter traffic and a gradual accumulation of pollution during nighttime hours in the shallow inversion layer. Riverside's location is far enough inland to not be limited by marine boundary layer effects, thus the afternoon concentration minima is attributed to atmospheric dilution associated with increased mixing heights and horizontal wind speeds. Figure 2 shows the concentration of CO plotted with wind speed and ambient temperature; increases in both correspond to enhanced dilution and vertical mixing. Even with this dilution, the summertime daily minimum in Riverside is significantly above background at ~400 ppbv CO compared to the hemispheric background of ~100 ppbv CO (*18*).

An analysis of wind speed and direction in the summer (Figure 3) indicates that the wind is consistently blowing from the west (LA/Orange County) during the afternoon. This precludes wind direction from being responsible for the lack of an afternoon peak in pollutant concentration by changing boundary inflow conditions with cleaner air. Dilution effects are responsible for attenuating local concentrations associated with the higher emissions during the afternoon commute. The same winds that dilute nearby primary emissions also transport ozone formed further upwind. The diurnal ozone cycle coincides with ambient temperature, peaking at an average of ~90 ppb around 15:00 PST (Figure S2).

3.3. Source Contributions. The chemical mass balance results for the summer sampling period showed a consistent diurnal pattern (Figure 4). Similar to the CO profile (Figure 2), the peak in tailpipe contributions (~60 $\mu g/m^3$) coincides with the morning commute, and the gradual increase in tailpipe
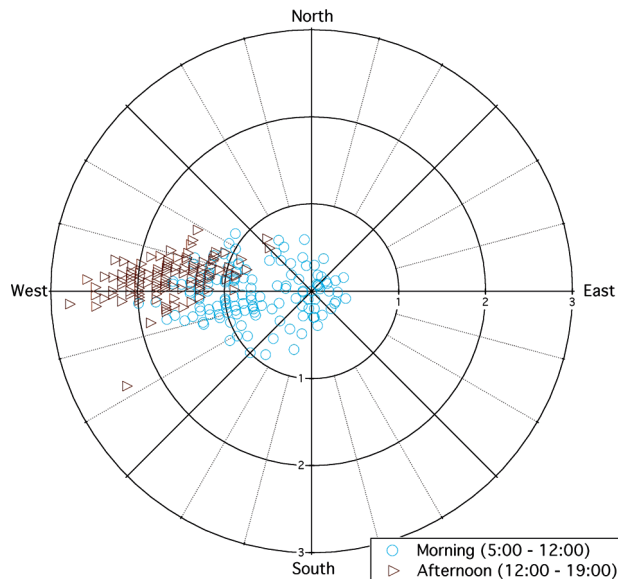

FIGURE 3. Distributions of summer wind speed (m/s) and direction at Riverside, CA. Displayed as individual hourly measurements for the morning and afternoon; overnight ground-level wind (not shown) was relatively calm with no dominant direction.
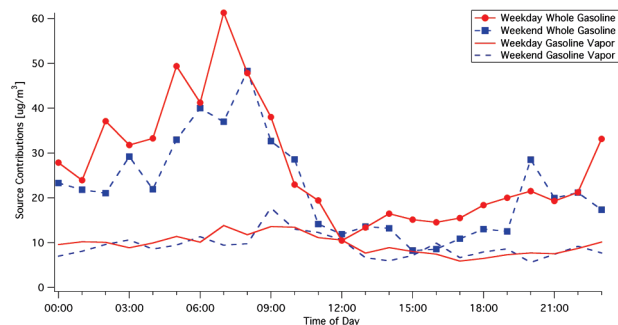
FIGURE 4. Source contributions to ambient VOC at Riverside from whole gasoline and gasoline vapor emissions.

contributions throughout the nighttime hours can be attributed to some nighttime traffic, but more importantly decreased dilution. In the afternoon, dilution offsets the expected increase in source contributions from both whole gasoline and fuel vapor VOC emissions, which we would expect due to increased traffic and temperature. The relatively stable vapor pressure-driven source contributions (~10 $\mu g/m^3$) with increasing temperatures throughout the day indicate a balance between evaporative emissions and atmospheric dilution in the South Coast air basin. A comparison of our temperature observations to evaporative emissions estimated using EFMAC yields an expected increase in evaporative emissions with temperature (Figure S3), which is offset in our ambient observations by enhanced afternoon dilution. Similar stability of vapor source contributions throughout the day was observed near Sacramento, CA, in a previous study (*4*).

Vapor pressure-driven contributions to gasoline-related VOC emissions averaged $31 \pm 2\%$ during the summer portion of SOAR 2005 and did not vary significantly from weekday to weekend ($30 \pm 2\%$ on weekdays versus $33 \pm 3\%$ during the weekend). Similar to previous results (*4*), the percent vapor contribution to total gasoline-related VOC is statistically stable after the morning commute. At Riverside, it peaks in the early afternoon (~40%) due to increased temperatures and reduced traffic volumes compared to commuter peak periods (Figure S4). The percent vapor contribution is lowest during the morning commute (~20%) due to the large volume
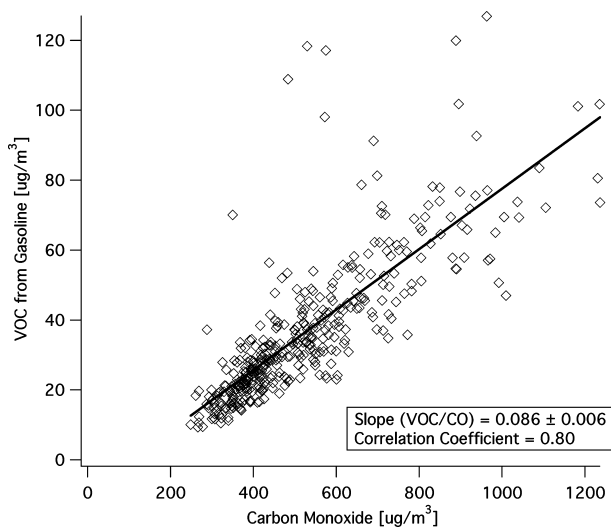
FIGURE 5. Plot of gasoline-related VOC concentrations versus carbon monoxide concentrations during summer 2005.

of whole gasoline (presumably tailpipe) emissions. Diurnal patterns of the vapor contribution exhibited statistically insignificant variation between weekdays and weekends (Table S2). The relative vapor contribution to total gasoline-related VOC is significantly higher than previous results from Granite Bay, which ranged from 7 to 22% during daytime hours on weekdays, compared to 19−44% during daytime hours on weekdays at Riverside in the present study; both sites had similar diurnal patterns in vapor fraction, and at similar afternoon temperatures the percent contribution of fuel vapor was greater at Riverside than Granite Bay (*4*). Possible contributing factors include reductions in tailpipe hydrocarbon emissions between 2001 and 2005, differences in emissions and meteorology at Granite Bay and Riverside, increases in evaporative emissions since 2001 due to the switch from MTBE to ethanol, and uncertainties in VOC source speciation profiles.

Simulations using the EMFAC emission factor model indicate 31% of total gasoline-related VOC is vapor pressure-driven, which is in agreement with our overall value of 31 ± 2%. The comparison of our data to the model's diurnal profile of percent vapor contribution (Figure S4) shows reasonable agreement during the day considering the uncertainties involved in both approaches.

Our results highlight the importance of VOC emission control for both tailpipe and vapor pressure-driven emissions. Both are significant contributors and will need to be controlled to successfully reduce ozone and secondary organic aerosol formation in the South Coast air basin.

3.4. Gasoline-Related VOC to Carbon Monoxide Emission Ratio. Our estimated mass emission ratio for Riverside is 0.086 ± 0.006 for gasoline-related VOC to CO emissions (Figure 5). Ratios estimated using California's emission inventory are slightly greater; ranging from 0.097 to 0.106 depending on the spatial scale considered. Our mass emission ratio is consistent with the 0.087 ratio estimated using EMFAC. One caveat to our inventory is that the ambient CO measurements may be greater than that expected from emissions due to inflow from upwind urban areas and formation of secondary CO from the oxidation of AVOC in the late morning and afternoon (*19*). This may explain why our value is slightly lower than values from the emission inventory.

A comparison of diurnal patterns in gasoline-related VOC to CO ratios between our data and the EMFAC model (Figure S5) indicates good agreement between the two, given that the model includes only 80% of CO emissions. Our results show no significant difference between weekdays and weekends, and the ratio is relatively stable as expected (Table S3).

3.5. Implications for Emissions Studies. A caveat to this and similar studies is that it assumes liquid gasoline composition is representative of actual combustion (i.e., whole gasoline) emissions and does not account for all products of incomplete combustion. In actuality, the compositional fraction of prominent hydrocarbons (e.g., tracers) in tailpipe exhaust is lower than in liquid fuel. This implies that analyses may underestimate contributions from exhaust and the total AVOC emissions from gasoline, and thus the percent contribution from vapor pressure-driven emissions is likely an upper bound. Accounting for this effect, we estimate that tailpipe source contributions may be underestimated by up to 20%. Additionally, designations for motor vehicle emission mechanisms merit reflection as it is not always clear if an evaporative pathway is vapor pressure-driven and thus temperature dependent or if all the components of the liquid gasoline are being evaporated. In some cases evaporative emissions may appear to be more representative of tailpipe emissions, for example with hot soak emissions and running losses from older vehicles, or liquid fuel spillage at service stations. Nevertheless, our upper-limit results are in agreement with California's emission factor model and their emission inventories.

Acknowledgments

Supporting Information Available

Supplementary figures (S1−S5) and tables (S1−S3) referenced in the text. This information is available free of charge via the Internet at http://pubs.acs.org.

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