Methodology for Speciation of Organic Gas Hot Soak Emissions California Light-Duty Vehicles

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July 23, 2003

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ACKNOWLEDGMENTS

This document was prepared by the staff of the
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Background

Speciation profiles are used in emission inventories, health risk assessments and photochemical modeling. The current hot soak speciation profile (# 420) is based on 1997 ARB Sealed Housing for Evaporative Determination (SHED) tests. The benzene mass fraction (3.43% of TOG) in the current gasoline vehicular hot soak profile may overestimate benzene emissions from motor vehicles. In response to benzene overestimation concerns, recent hot soak speciation data were requested from MSOD to update the hot soak profile (Jerry Ho, 2002). ARB staff went through a series of data analyses and discussions within PTSD, MSOD and MLD. We believe that the following methodology better characterizes the composition of statewide gasoline motor vehicle hot soak emissions and more accurately estimates benzene emissions from motor vehicles.

Overview of Hot Soak Emissions

Hot soak emissions are comprised of fuel vapors emitted from a vehicle after the engine is turned off. The elevated engine temperature causes fuel vaporization from different sources such as fuel delivery lines, purge line to the canister, and gas cap. EMFAC2000 Technical Support Documentation (EMFAC2000) defines the cutpoint for normal and moderate hot soak emitters at 2 g TOG/soak and 1 g TOG/soak for carbureted and fuel-injected vehicles, respectively. A high liquid leaker, 21 g TOG/soak, is defined as a vehicle with a fuel leak and is identified from either the US EPA or Auto/Oil Air Quality Improvement Research Program inspection report. A statewide average hot soak emission rate was estimated to be 0.4 g TOG/soak based on EMFAC 2002.

New Speciation Data Source The proposed new hot soak speciation profile is based on 19 hot soak SHED tests performed as part of surveillance program conducted in 1999 and 2000 at ARB Haagen-Smit laboratory in El Monte California. The new data provides one-hour hot soak TOG emission rates ranging from 0.1 g TOG/soak to 36 g TOG/soak and averaging 6.4 g TOG/soak. Samples were speciated for 192 chemicals including methane, non-methane hydrocarbons, alcohols, carbonyls and ethers.

From the 19 vehicles tested, the chemical compositions showed a trend where vehicles with higher hot soak emissions (larger than 20 g TOG/soak) were dominated by low molecular weight species, e.g., butane, and vehicles with lower hot soak emissions included both high and low molecular weight compounds. Similar emission compositions were also seen in the diurnal speciation profiles that followed immediately after each hot soak test (Table 1). This trend indicates that a methodology is needed to compile the new hot soak speciation profiles.

The new hot soak tests have a higher average emission rate (6.4 g TOG/soak) than EMFAC 2002 (0.4 g TOG/soak) (Figure 1). The highest three hot soak emitters (23 g TOG/soak, 24 g TOG/soak, 36 g TOG/soak) in the new SHED tests are not considered as outliers because studies show that there is a fraction of vehicles that emit high hot soak TOG (Figure 2).

The average hot soak and emission rate distribution show that the vehicles procured for the new hot soak speciation tests were not representative to the current fleet, which has prominently lower hot soak emissions (Figure 2). Based on these facts, weighting factors

are needed to accurately characterize the hot soak emissions when compiling the new speciation profiles.

The current hot soak profile was derived from evenly averaging the speciated hot soak profiles (Paul Allen, 2002). As stated above, evenly averaging the new tests bias the profile toward the high emitters compositions due to the weights of these high hot soak emission vehicles (~70-fold higher than the low emitters).

Methodology

The methodology used for compiling the speciation profiles is intended to be consistent with EMFAC 2002 and representative of California statewide emissions.

Emission Rate Distribution: Three data sets, ARB's In-Use Vehicle Surveillance Projects, Auto/Oil Air Quality Improvement Research Program, and EPA's hot soak emissions test program are used in EMFAC 2002 (Jeff Long, 2002). Hot soak emission rates were tested on 1209 vehicles. The population was disaggregated into four bins:

1. less than 1.0 g TOG/soak – weight: 773/1209
2. 1.0 – 2.0 g TOG/soak – weight: 182/1209
3. 2.0 – 20 g TOG/soak – weight: 239/1209
4. 20 – 50 g TOG/soak – weight: 15/1209

The breakdown of emission bins is based on the emission rates and species distribution patterns of the new 19 hot soak speciation profiles. The 19 hot soak speciation profiles were weighted accordingly. The final hot soak profile is then averaged from the weighted profiles. Due to the chemical composition trend in the new hot soak tests. The weighting factors reconstruct hot soak emissions and better characterize statewide hot soak TOG speciation profile than equally averaging the profiles.

Results and Discussion

After applying the weighting factors, the average hot soak emission rate is 0.5 TOG g/soak as opposed to 6.4 TOG g/soak without weighting. The weighted average hot soak emission rate is close to 0.4 TOG g/soak in EMFAC 2002.

A comparison of several related profiles is attached. Toluene, xylenes and benzene in the proposed new profile are considerably lower than in the current hot soak profile (Table 2). Butane and 2-methylbutane mass fractions in the proposed profile are higher than the current fractions by more than 10%. The proposed profile is similar to US EPA hot soak profile (Profile 1311) in toluene, xylenes, MTBE, butane and 2-methylbutane. Overall profile reactivities (Maximum Incremental Reactivity, MIR) of the current and proposed hot soak profiles decrease from 3.14 to 2.24 (Carter, 2002).

Fuel compositions: ARB staff questioned whether the composition differences in liquid gasoline might lead to the large variation in hot soak speciation profiles, or enhance hot soak emission rates. In response to this inquiry, six speciated liquid gasoline profiles

were collected from a subset of the same 19 vehicles were examined (Table 3). These liquid gasoline samples were collected from the vehicles as they were received by the laboratory. One of the samples was from the second highest hot soak emitter which was a model year 1994 fuel-injected vehicle. These fuels were similar in terms of the physical properties of vapor pressures, densities, and boiling points. Also, the fuels collected in the same season were comparable in molecular weights and chemical compositions of butane, benzene, toluene, MTBE etc. (Figure 3). There is no significant correlation between fuels, hot soak emission rates and speciation profiles. More fuel samples are needed for a definitive relationship analyses.

It has been suggested that liquid gasoline could be used to estimate the toxics inventory from hot soak emissions. This is not an appropriate approach since the diffusion mechanism enhances compounds with higher diffusivities. For example, n-butane and toluene mass fractions are close to 6% in some gasoline samples. Due to the diffusivities, the n-butane mass fraction should be much higher than toluene in hot soak emissions. Therefore, the ratio of butane and toluene in vapor should not be similar to liquid gasoline composition. By calculating the diffusivities of butane, benzene, and toluene in liquid gasoline, a trend was noticed that species emission rates during hot soak follow the magnitudes of diffusivities.

Seasonal hot soak profiles: Emissions in the summer are important for ozone photochemical modeling. With the limited data, determining seasonal profiles is not appropriate due to fuel changes and small sample size in each season. For example, seven vehicles were tested in April and May. Only low hot soak emitters were procured for this period. As discussed above, high emitters in the summer may have different compositions from the low hot soak vehicles.

Recommendation

We recommend that the TOG speciation profile in Attachment 1 be used as profile # 422 and replace the existing hot soak speciation profile # 420.

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Table 1. Hot Soak and Diurnal Evaporation Butane Emission Rates

Date Tested	Year/Make	Model	Butane in hot soak, mg/soak	Butane in diurnal, mg/24 hrs evap.
4/20	92/SUZU	Metro	8	88
4/6	86/Chey	Fifth Avenue	10	100
3/28	91/Honda	Accord	12	36
3/16	94/Ford	Mustang	229	1018
12/21	86/Toyota	Celica	7914	24369
2/9	94/Ford	Cougar	9465	62668
1/19	75/Chey	SportManVan	11392	61675

Table 2. Comparison of Toxic Compounds and Profile Reactivity in Proposed and Current Hot Soak Profiles

	Proposed New Hot Soak[1]	Current Hot Soak
Benzene fraction, %	0.84	3.43
Xylenes Fraction[2], %	2.67	12.01
Toluene Fraction, %	3.42	15.51
Profile Reactivity[3]	2.24	3.14

1. Based on Year 2001 California statewide inventory, the hot soak profile is applied to 147,997 tons/year of TOG emissions from hot soak and running evaporative sources.
2. Xylenes fraction is the sum of ortho, meta, and para xylene fractions.
3. Profile Reactivity is estimated based on Carter's Maximum Incremental Reactivity, http://pah.cert.ucr.edu/~carter/reactdat.htm.

Table 3. Comparison of Butane in Fuels and Hot Soak (HS) and Emission Rates from the Same Vehicles

Vehicle #	2	21	34	73	71	87
Date Tested	9/30	11/10	11/24	1/26	2/9	2/16
Butane in Fuel, %	0.72	3.48	5.71	6.17	5.87	3.19
Butane in HS, %	7.9	2.41	5.05	15.14	39.3	7.87
HS Emission, g/soak	10.4	0.66	0.5	0.74	24	0.2

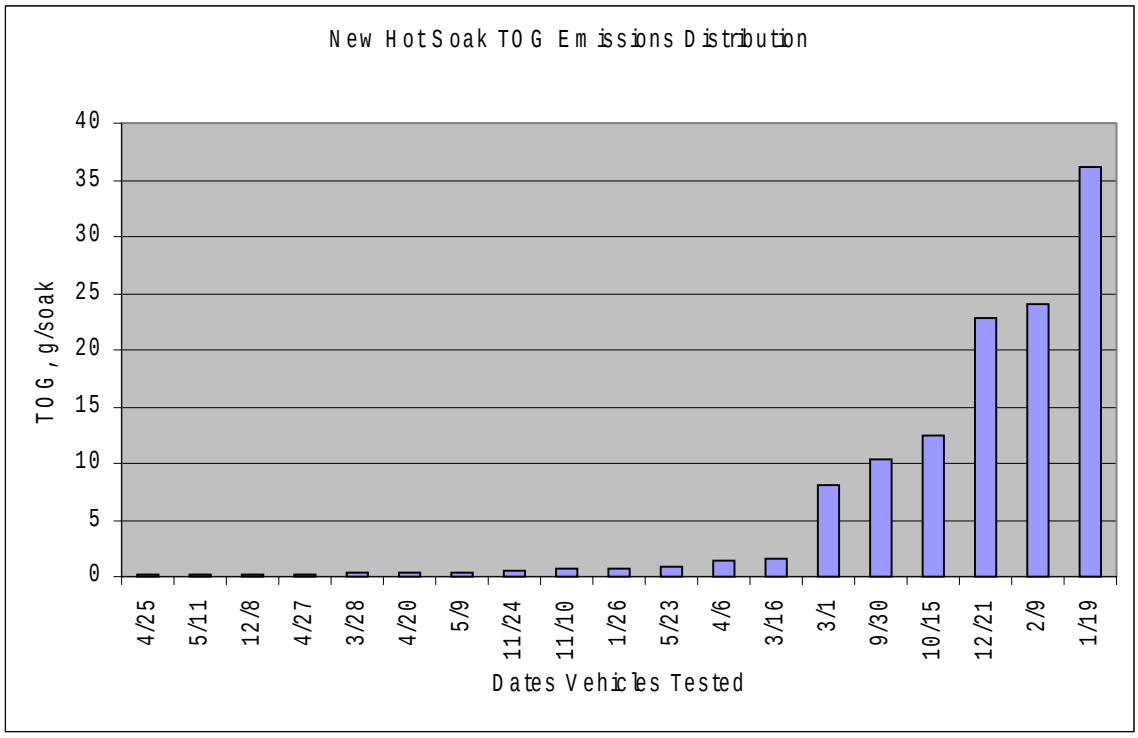

Figure 1. New Hot Soak TOG Emissions Tested for Chemical Speciation Profiles

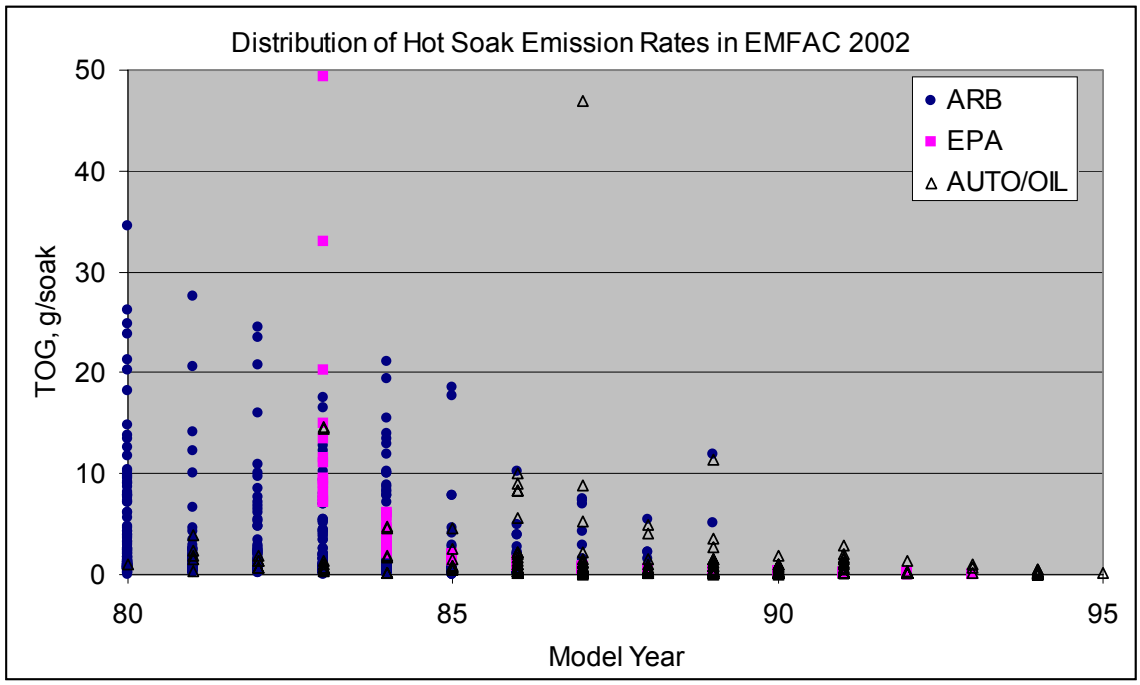

Figure 2. Distribution of Hot Soak Emission Rates in EMFAC 2002

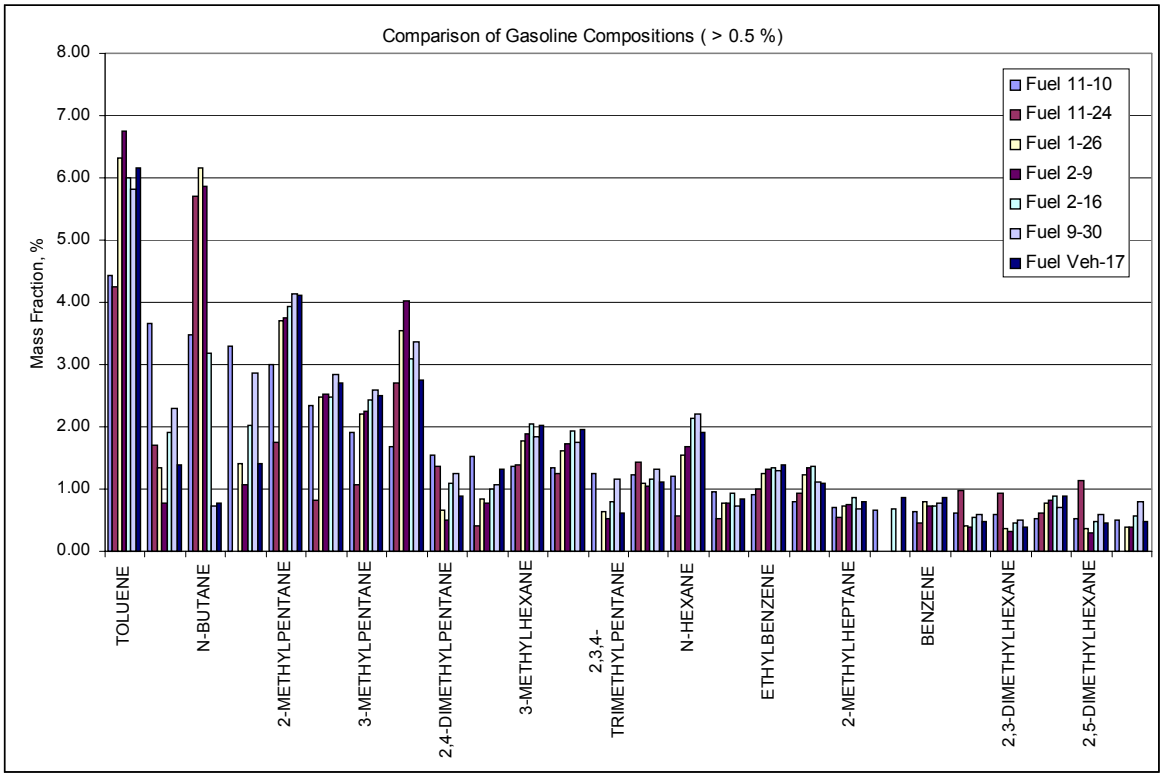

Figure 3. Comparison of Gasoline Compositions Collected from the Subset of Vehicles Tested for Hot Soak Emissions (only mass fractions larger than 0.5% shown).

References:

1. Jerry Ho, Personal conversation, 2002
2. Paul Allen, Personal conversation, 2002
3. Jeff Long, Personal conversation, provided three sets of hot soak emission rate test data and the 2002 California vehicular trips file.
4. Bill Carter, Maximum Incremental Reactivity, http://pah.cert.ucr.edu/~carter/reactdat.htm.
5. EMFAC2000 Technical Support Documentation, http://www.arb.ca.gov/msei/on-road/doctable_test.htm