

To: Steve Brisby
Stationary Source Division
California Air Resources Board

From: Robert Harley
Department of Civil and Environmental Engineering, UC Berkeley

Re: Testing of draft version of California predictive model

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Introduction

The predictive model starts with a gasoline formulation containing ethanol (2 wt% oxygen) and compares emissions to a reference fuel (2 wt% oxygen from MTBE). Predicted effects of the switch to ethanol for this case include a 5.8% increase in evaporative VOC emissions, a 3.0% increase in the ozone-forming potential of vehicle emissions, and a 0.2% increase in toxic pollutant emissions (the sum of benzene, formaldehyde, acetaldehyde and 1,3-butadiene).

It appears that the main challenge for refiners in using the predictive model to formulate gasoline will be to offset adverse effects of ethanol use on evaporative VOC emissions, without increasing NO_x emissions.

General Comments on Aggregation of Predictive Model Outputs

It was difficult to evaluate predictive model outputs in detail, as many results are reported in aggregated form. For example, fuel effects on toxic VOC emissions are reported as a (potency weighted?) sum of four compounds: benzene, 1,3-butadiene, formaldehyde, and acetaldehyde. Some fuel variables are known to affect specific compounds: benzene and aromatics in gasoline affect benzene emissions, olefins affect butadiene, and ethanol affects acetaldehyde. To evaluate the model more in depth, I would need to obtain from CARB the predicted changes in individual toxic VOC emissions in response to fuel changes, rather than just looking at the aggregated sum.

Likewise the 90% distillation temperature (T_{90}) is known to affect hydrocarbon emissions via increased engine-out emissions, which are especially important during cold engine starting when the catalytic converter has not warmed up and is not efficient in converting HC emissions. The predictive model does not output cold start effects separately from changes in running (stabilized) emissions.

Finally, the ozone-forming potential of vehicle emissions is aggregated to include reactivity-weighted measures of exhaust VOC, evaporative VOC, and carbon monoxide emissions. I recommend that the predictive model should first report individual emission effects **without** reactivity weighting, and then calculate the change in ozone-forming

potential separately as a final step. This would make it easier to understand and evaluate what the model is predicting in response to fuel variables such as ethanol content.

Oxygenate Effects

When fuel oxygenates were increased in steps of 0.5 wt% from 2.0 up to 3.5 wt%, the following % changes to predicted emissions were obtained.

Oxygen	NOx	Exh VOC	EvapVOC	OFP	toxics
2.0 wt%	0	0	+5.8	+3.0	+0.2
2.5 wt%	+1.5	-0.7	+5.8	+2.4	-0.1
3.0 wt%	+3.4	-1.4	+5.8	+1.9	-0.4
3.5 wt%	+5.7	-2.2	+5.8	+1.4	-0.7

Note: OFP = ozone-forming potential, a reactivity-weighted combination of exhaust and evaporative VOC emissions plus CO.

Refiners might consider a strategy of increasing oxygenates above 2 wt% to decrease CO and exhaust VOC emissions, seeking to offset the adverse effects of ethanol use on evaporative emissions. The predictive model indicates two problems with this strategy: NOx emissions increase and the decreases in exhaust VOC and CO are not large enough to offset fully the evaporative emissions increase.

Measurements of light-duty vehicle emissions at the Caldecott tunnel show the on-road effect of oxygenated gasoline use (Kirchstetter et al., ES&T 1996). The tunnel study results showed ~20% decreases in CO and VOC and no significant effect on NOx emissions. As fleet-average CO and VOC emissions decline, the effect of oxygenates on exhaust emissions may be reduced, as feedback controls on air/fuel ratio are better able to compensate for changes in fuel composition. If so, I could understand that CO and VOC benefits might decrease over time, but it doesn't make sense to me that NOx disbenefits remain while CO and VOC benefits die away. Are fuel economy effects of ethanol use important here?

In switching from MTBE to ethanol, the model predicts little change in toxic emissions overall (+0.2%). Formaldehyde emissions will decrease due to the phase-out of MTBE, and this should offset some of the increase in acetaldehyde emissions due to increased use of ethanol. Are evaporative emissions of benzene predicted to increase as well? My general concern about aggregation of model predictions is a factor here: it would be appropriate to evaluate predictions for each toxic VOC individually.

I do not understand why when the maximum oxygen content of gasoline is increased above 2 wt%, leaving the minimum at 2 wt%, I get changes in predicted emissions for both the min and the max oxygenate levels. This appears to be a bug in the draft version of the predictive model.

Aromatic Effects

For 1996 and later years, on-road vehicle emissions of toxics (formaldehyde, acetaldehyde, butadiene, and benzene) should be heavily dominated by exhaust emissions. Only for benzene would I expect the evaporative contribution to emissions to be significant; though even in the case of benzene, tailpipe emissions will dominate.

I considered effects of a 3×3 matrix of benzene and total aromatic levels in California gasoline. Percent changes in toxic emissions from California's draft predictive model are shown below. It would be preferable to examine these fuel effects on benzene emissions alone, rather than effects on the sum of 4 toxic pollutants shown below.

	0.8 vol% benzene	0.4 vol% benzene	0 vol% benzene
25 vol% aromatics	+0.2	-10.6	-21.1
20 vol% aromatics	-3.0	-13.5	-23.7
15 vol% aromatics	-5.8	-15.9	-25.8

It is not clear that the relative importance of benzene vs. heavier aromatics in gasoline as sources of toxic emissions is correctly represented. The sensitivity of toxic emissions (mainly benzene?) to reductions in non-benzene aromatic content is too small compared to the sensitivity to benzene. Also note that lowering heavy aromatics in gasoline could help to reduce polycyclic aromatic hydrocarbons (PAH), another class of toxic compounds that are not included currently in the predictive model's definition of toxic pollutant emissions.

Cyclohexane content of gasoline is not an input variable to the predictive model. However, there is evidence that this molecule in gasoline can lead to increased butadiene emissions in exhaust (Kaiser et al., *Environ. Sci. Technol.*, pp. 1581-1586, 1992). If refiners use their pentane/hexane isomerization reactors to convert benzene to cyclohexane (i.e., to lower the benzene content of gasoline), benefits of fuel benzene reductions may be offset by increased butadiene emissions. This effect has not been included in the predictive model, and is recommended for further study.

Reid Vapor Pressure (RVP) Effects

The predictive model indicates that ethanol effects on evaporative emissions could be offset at least in part by reducing gasoline Reid Vapor Pressure (RVP).

RVP (psi)	NOx	Exh VOC	EvapVOC	OFP	toxics
7.0	0	0	+5.8	+3.0	+0.2
6.8	0	0	+4.4	+2.3	-0.3
6.6	0	0	+3.1	+1.6	-0.7
6.4	0	0	+1.7	+0.9	-1.1

The sensitivity of total evaporative emissions to changes in RVP is not large. The evaporative emissions should be less reactive than exhaust emissions, by factors of ~20%

for liquid gasoline and ~40% for headspace vapors. Reiterating comment 2 above, I cannot assess the accuracy of predicted changes in OFP without knowing what the RVP effects were on mass emissions (the Evap VOC changes shown above were adjusted to account for reactivity differences). The toxics effect here is presumably due to reduced evaporation of all VOC including benzene.

Sulfur Effects

Sulfur effects are predicted to be larger for NO_x than for exhaust VOC emissions. As expected, sulfur in gasoline does not affect evaporative emissions.

S (ppmw)	NO _x	Exh VOC	EvapVOC	OFP	toxics
20	0	0	+5.8	+3.0	+0.2
10	-4.1	-0.6	+5.8	+2.6	-0.1
0	-8.2	-1.3	+5.8	+2.2	-0.4

Previous studies have reported larger sulfur effects for VOC than for NO_x, the opposite of what the predictive model is showing. For example, Benson et al. (SAE 912323) report 16 vs. 9% reductions in HC vs. NO_x when sulfur is reduced from 466 to 49 ppmw. Both of these sulfur levels are higher than what is currently found in California gasoline. A follow-on study (Koehl et al., SAE 932727) investigated the linearity of sulfur effects and considered effects of reducing gasoline sulfur level further from 50 down to 10 ppmw. Koehl et al found larger decreases in CO and HC than NO_x. Leppard et al. (SAE 952504) show large sulfur effects on exhaust HC emissions persist in 1993 Federal Tier 1 vehicles, as was found in earlier testing as part of the Auto/Oil study (1983-85 and 1989 model years).

Changes in underlying data used to develop predictive model relationships to changes in fuel properties were mentioned by CARB staff as the explanation for the larger sensitivity of NO_x to fuel sulfur levels in the updated predictive model. I recommend further study of the reasons for changes in NO_x vs. VOC emissions sensitivity to fuel sulfur levels.

T₅₀ and T₉₀ Effects

Previous studies (Hochhauser et al., SAE 912322; Rutherford et al., SAE 952510) have noted distillation temperature effects on exhaust HC emissions. The T₉₀ effect has been explained in terms of increased engine-out emissions that are passed through to the tailpipe and have an especially large influence on cold start emissions when the catalytic converter is not yet working efficiently.

Effects of gasoline distillation temperatures on exhaust VOC emissions were studied using a 3×3 matrix of T₅₀ and T₉₀ values. No large interactive effects between T₅₀ and T₉₀ levels were seen over a range of distillation temperatures typical of current California gasoline. A lack of significant interactions between T₅₀ and T₉₀ is consistent with results reported by Rutherford et al.

Exhaust VOC (% change)	T ₅₀ (°F)		
	206	213	220
298	-2.85	-0.35	3.14
T ₉₀ (°F)	305	312	
	-2.50	-1.85	0.67
			4.20

Previous Auto/Oil results for 1989 and 1993 vehicles (Figure 5 from Rutherford et al.) indicate similar sensitivity of exhaust NMHC to both T₅₀ and T₉₀: about 0.2% increase in emissions per °F. The predictive model here indicates different sensitivities of exhaust VOC emissions: 0.4% per °F for changes in T₅₀ versus 0.07-0.08% per °F for T₉₀.

NOx (% change)	T ₅₀ (°F)		
	206	213	220
298	0.24	-0.06	-0.57
T ₉₀ (°F)	305	312	
	0.30	0.36	0
			-0.51
			-0.45

In general NOx emissions are less sensitive to changes in T₅₀ and T₉₀ compared to exhaust VOC emissions. This result is consistent with prior studies. Also note that the predicted T₅₀ effect on NOx emissions is larger going from 213 to 220°F than from 206 to 213°F.

Application of Predictive Model to On-Road Study of Fuel Effects

The predictive model was used to study the effects of California Phase 2 RFG, matching the fuel changes as closely as possible to what was observed between 1995 and 1996 in on-road studies of vehicle emissions at the Caldecott tunnel in the San Francisco Bay area. This was not an intended use of the predictive model being reviewed here; the model was designed to predict fuel effects for a future (2010) rather than historical (1996) vehicle fleet, and presumes ethanol rather than MTBE as the gasoline oxygenate. Fuel variables from Table 1 of Kirchstetter et al. (ES&T 1999) were input to the model, and predicted reductions of 25% for NOx, 17% for exhaust VOC, and 64% for toxics were obtained. On-road emissions data from the Caldecott tunnel (Harley et al., ES&T 2005; Harley et al., ES&T 2006) show no significant RFG effect on NOx, a 14% reduction in NMOC, and a 50% reduction in benzene emissions.

Direct comparisons are difficult to make because the predictive model is based on laboratory studies of vehicles driven over a wide range of operating conditions (including cold engine starting, stop-and-go driving and freeway driving). In contrast the tunnel measurements reflect emissions from fully warmed up vehicles driving uphill on a 4% grade at ~40 mph. The tunnel measurements reflect composite emissions from more than 8000 vehicles driving through the tunnel from 4-6 PM each day, and are more likely to capture fuel effects on high-emitting vehicles which dominate total running emissions from the on-road fleet. Despite the foregoing caveats, I still question the larger fuel

effects on NO_x relative to exhaust VOC forecast by the predictive model. On-road data indicate past fuel and light-duty vehicle emission control technology effects have been larger for CO and VOC than for NO_x.