California Environmental Protection Agency

Air Resources Board

Air Quality Impacts of the Use of Ethanol in California Reformulated Gasoline

Appendix D

Responses to Scientific Peer Review and Public Comments

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D-1. Response to Professor Harley Scientific Peer Review

This section contains ARB responses to the scientific peer review of Professor Robert Harley of the University of California at Berkeley (see Attachment A1). The focus of Professor Harley review was on organic gas speciation profiles of exhaust and evaporative emissions from alternate gasoline formulations. Each comment by Professor Harley is presented in normal font and is followed by the ARB response inserted in italics.

Comment 1: CAT STABILIZED EXHAUST PROFILE FOR RFG w/MTBE. The stabilized exhaust profile for catalyst-equipped engines (profile 876) is compared in the attached Figure 1 with the on-road running emissions profile measured in the Caldecott tunnel in summer 1996 for 20 individual species that together account for >70% of non-methane organic compound emissions in profile 876 and in the tunnel. The tunnel profile is similar to profile 876 for all species except MTBE, which accounted for 5.0% of tunnel VOC (5.5% of tunnel NMOC), whereas profile 876 includes only 2.0% by weight MTBE. Methane is not shown in Figure 1; it accounted for 15.8% of VOC in profile 876 versus 9.1% of VOC in the Caldecott tunnel. A 1996 emissions-weighted average of the profiles for cat and non-cat stabilized exhaust should give around 10% methane to agree with on-road data.

Comment 2: CAT STABILIZED EXHAUST PROFILES FOR ALL 4 FUELS. The stabilized exhaust profiles for all 4 fuels for catalyst-equipped engines (profiles 876, 663, 673, and 653) are compared for selected species in Figure 2. Abundance of species shown in Figure 2 is similar across all profiles, except for five species shown at the right: isobutene, formaldehyde (HCHO), acetaldehyde (CCHO), MTBE, and ethanol. Changes for these species are expected if changes are made in gasoline oxygenate content.

While addition of MTBE to gasoline is expected to lead to increased emissions of isobutene in vehicle exhaust (Hoekman, 1992; Kirchstetter et al., 1999), further consideration should be given as to whether isobutene would increase as much as shown in Figure 2 when switching from RFG containing ethanol to RFG without any oxygenate.

Response to 2nd paragraph:

We have changed the isobutene content in the exhaust profiles in light of this comment.

The original isobutene content of the profiles was different for the two types of MTBE-free CaRFGs because they were derived from different experiments. The ARB's MTBE/EtOH study showed a 60% decline in isobutene in bag 2 between the EtOH- and MTBE-blended test fuels, while the A/O 17 study showed only a 32% decline between its oxygen-free and MTBE-blended test fuels. (In contrast, the two studies showed more similar declines in isobutene in the bag 1-bag 3 results, 53% and 43%.)

Isobutene is a known product of burning MTBE. It is not known to be produced by burning ethanol. From this information alone, one would not expect the presence or absence of ethanol in MTBE-free gasoline to affect the decline in isobutene from the removal of MTBE.

Since there is isobutene in the exhaust of oxygen-free gasoline, there obviously is some precursor in gasoline other than MTBE. Butenes are intuitive candidates, and they were more plentiful in the oxygen-free A/O fuel than in the MTBE-blended fuel. However, their combined fuel concentrations were too low (~0.1%) to explain the different declines in isobutene between the two studies.

Since MTBE is the only identified determinant of isobutene in the exhaust, it is reasonable to regard the ARB and A/O studies as providing equally valid data on the effect of removing MTBE from the fuel, regardless of whether or not ethanol is added. Then, the estimated decline in isobutene in bag 2 is (0.60 + 0.32)/2 = 46%. This is within the range between the two studies in the decline in the starts emissions (41% to 53%, mean 47%). Therefore, it is reasonable to use a common adjustment factor, 1 - 0.46 = 0.54, for creating the isobutene contents of both exhaust profiles for each CaRFG that does not contain MTBE.

Despite the use of a common adjustment factor, the final profiles will have somewhat different isobutene contents because the adjusted profiles must be separately normalized to 100% after different net changes in their oxygenate contents and in other species.

[Comment 2 resumed]

Given that ethanol accounts for 5.75 and 10.1% of gasoline mass (these values correspond to 2 and 3.5% by weight oxygen, respectively), it is surprising in profiles 663 and 673 that ethanol accounts for only 0.25 and 0.5% of exhaust VOC mass. I would predict that roughly half of the exhaust would be unburned fuel, and so would expect as much as an order of magnitude higher ethanol (3-5%) in exhaust emissions depending on fuel ethanol content. Further consideration of this issue is recommended.

Response to 3rd paragraph:

We changed the ethanol content in the exhaust profiles in light of this comment.

The ethanol content we had assigned to bag 2 exhaust was probably too low. Our algorithm is to directly insert the observed EtOH fraction from the chosen study (ARB's MTBE/EtOH study, in this case) into the emission profile being built. (For all other species, we multiply the content in ARB's existing MTBE-blended profile by the content ratio between fuels in an external study.) The ethanol content of bag 2 from the EtOH test fuel is very low, as is the MTBE content of bag 2 for the MTBE test fuel. In contrast, the MTBE content in ARB's in-use survey results is much higher, as are exhaust MTBE and EtOH contents in data from other sources. Probably, then, the bag 2 ethanol content we had directly inserted (from the MTBE/EtOH study) is unrealistic.

In this case, it is better to create the EtOH content of exhaust from ethanol-blended CaRFG as we do for other species, by applying an adjustment factor to the MTBE content in the existing profile. That adjustment factor (taken from the ARB study results) is 1.96 for gasoline with 3.9 wt% oxygen as ethanol. Linearly adjusted according to the oxygen content, it becomes 1.00 or 1.75 for oxygen at 2.0 or 3.5 wt%, respectively.

Comment 3: EXHAUST PROFILES FOR RFG w/MTBE. For gasoline containing 2% oxygen as MTBE, a comparison of exhaust profiles for catalyst/non-catalyst engines and stabilized/start emissions is presented in Figure 3. Isopentane is higher in the stabilized profiles than in the start profiles. Aromatics (toluene, ethylbenzene, xylenes, and 1,2,4-trimethylbenzene) are less abundant

in the catalyst stabilized exhaust profile (876) when compared to the other profiles shown in Figure 3. Acetylene in the non-catalyst stabilized exhaust profile (401) is the lowest of all profiles shown in Figure 3, which is unexpected because vehicles with catalytic converters are expected to have the lower acetylene levels. ARB staff should consider specifying a higher acetylene fraction in profile 401. I am concerned that using the highest-emitting vehicles from ARB in-use surveillance testing may not accurately represent non-catalyst engine emissions.

Response:

We did not modify the acetylene fraction. Acetylene is a negligible contributor to ozone and PAN formation.

Comment 4: LIQUID FUEL. In Figures 4 and 5, liquid fuel composition in profile 419 is compared against measured fuel composition in the SF Bay Area from summer 1996 (Kirchstetter et al., 1999). The profiles are similiar in terms of distribution of species across organic compound categories (Figure 4) and for the top 16 identified species listed in profile 419 (Figure 5). These 16 species account for >60% of the mass in profile 419. Profile 419 seems reasonable in comparison to the liquid fuel data from the Bay Area, although differences exist in the specific isomers and types of alkanes present. Further comparisons of profile 419 against Los Angeles area gasoline composition measured during summer 1996 (Norbeck et al., 1998) could be helpful.

Comment 5: HOT SOAK. Duplicate entries exist in the hot soak emission profile (420) for all 3 isomers of ethyltoluene (also called methyl-ethyl-benzene). ARB staff should consider deleting the entries for SAROAD codes 45211, 45212, and 98164 in profile 420, which duplicate entries for SAROAD codes 99915, 99912, and 99914, respectively. If this change is made, the profile will need to be renormalized to sum to 100%, and the hot soak profiles for other fuels (numbers 652, 662, and 672) should be rederived based on the revised profile 420.

The benzene content in hot soak emissions varies widely across fuels, from a low of 3.3% to a high of 4.9% by weight. Given the modest changes specified in fuel benzene content, the changes appear too large, and furthermore the highest hot soak benzene content is specified for the liquid fuel having the lowest benzene (profile 652). A large decrease in hot soak benzene occurs between profiles 662 and 672, while fuel benzene hardly changes.

Response to 2nd paragraph:

Four factors are involved in the benzene content:

- *Proportionality of evaporative emissions to fuel composition (e.g., Raoult's law).*
- *Use of MathPro's linear programming predicted fuels to derive adjustment factors for species in the various CaRFGs.*
- *ARB's model (like EPA's) that shows hot-soak benzene increasing when MTBE is removed.*
- *Normalization of each profile to total 100%, which alters the "raw" numbers.*

These have led to a complex set of benzene contents in the fuels and associated hot-soak profiles. Further consideration has led to a simpler approach that reduces the variation in the hot-soak profiles.

MathPro predicts 0.80 benzene content in both EtOH-blended and oxygen-free CaRFG vs. 0.67 percent benzene in MTBE-blended CaRFG. Per Raoults' law, the greater benzene content caused a

20% increase in the benzene content of the hot-soak profile compared to MTBE-blended CaRFG. However, both the .67 and .80 figures exceed the typical benzene content of current gasoline and probably will not be practical under upcoming changes to the ARB's gasoline regulations. Accordingly, there is no clear basis to predict any differences in the benzene contents of the various CaRFGs in the future. Therefore, it is advisable to fix the benzene contents of all CaRFGs at the value in the ARB's composition for MTBE-blended CaRFG.

This change leaves only the depressant effect of MTBE (6%) as the only factor to change the benzene content of hot-soak emissions. (It also changes some results for benzene in exhaust emissions as predicted with the Predictive Model.)

[Comment 5 resumed]

The composition of hot soak evaporative emissions may approach, in some cases, the composition of liquid gasoline, especially for older vehicles with carburetors. Large differences exist in the relative abundances of toluene (15.1% in profile 420 vs. 6.7% in liquid fuel), m- xylene (8.8% in profile 420 vs. 3.5% in liquid fuel), and 2,2,4-trimethyl-pentane (2.1% in profile 420 vs. 5.5% in liquid fuel).

Response:

We used the liquid fuel gasoline composition to represent hot soak evaporative emissions in the 2000 and 2003 scenarios.

Comment 6: DIURNAL. A gasoline headspace vapor profile (906) is used to represent the speciation of diurnal evaporative emissions. This profile was derived using vapor-liquid equilibrium theory and measured composition of liquid gasoline from the Bay Area in summer 1996 (see Kirchstetter et al., 1999). This profile is likely to describe the composition of displaced gasoline vapor emissions that occur during refueling (Furey and Nagel, 1986). For diurnal emissions from vehicles equipped with correctly-functioning activated carbon canister control systems, other factors such as differing uptake rates of individual VOC, canister carryover effects, and permeation of VOC through fuel system elastomers, can affect VOC composition (Urbanic et al., 1989; Burns et al., 1992). Therefore, an equilibrium headspace vapor composition profile may not represent all diurnal evaporative emissions correctly. Also the benzene levels in profile 906 were calculated from Bay Area liquid gasoline composition which included 0.58% benzene, as opposed to 1.00 wt% benzene in profile 419 (unburned fuel profile, RFG w/MTBE). Therefore profile 906 is likely to understate the benzene content of diurnal evaporative emissions relative to what is specified in the liquid fuel in profile 419.

The level of benzene in diurnal profile 651 (0.52% for RFG w/o oxygenate) is not consistent with benzene content in the liquid fuel, which is the lowest of all 4 fuels, whereas the corresponding diurnal profile has the highest benzene value.

Response to 2nd paragraph:

The response to the previous comment applies here, too; except that in the most recent version of the ARB model for evaporative benzene, MTBE is not a factor for diurnal benzene emissions.

[Comment 6 resumed]

The presence of ethanol in headspace vapor/diurnal evaporative emissions may not scale linearly with ethanol content in fuel, because ethanol exhibits non-ideal behavior in solution with

non-polar gasoline hydrocarbons (Bennett et al., 1993), and the activity coefficient increases as ethanol content decreases. Therefore, decreases in ethanol in the liquid may be offset in part by increases in its activity coefficient. Further analysis of profiles 661 and 671 is recommended.

Response to 3rd paragraph:

We dropped these profiles from our analysis and used the headspace calculation provided by Professor Harley (see Attachment A1).

[Comment 6 resumed]

ARB staff should move isomers of ethyltoluene listed in the diurnal evap profiles to list them under SAROAD codes 99915, 99912, and 99914, for consistent labeling of these species across all 7 profiles for each fuel.

Response:

We made this change.

Comment 7: BUTADIENE. 1,3-butadiene is present in exhaust emissions, but is not present in any of the evaporative emissions profiles supplied by ARB. This is appropriate. At present there are only minor differences in butadiene weight fractions across the different fuels. Increases in olefin content in unburned fuel may increase butadiene emissions in vehicle exhaust (e.g., Table 3 of Gorse et al., 1991). Therefore, ARB staff should consider whether converting 80% of butane content to butene to construct profile 650 would lead to increased butadiene in the exhaust profiles for gasoline without oxygenate.

Response:

We have no information on the effects of specific olefins on butadiene emissions. However, as shown in Table 12, the Predicted Model predicts that the total olefinic content of the oxygen-free CaRFG (modeled by MathPro) would not cause higher butadiene emissions. The butane content in profile 650 was incorrect and has been dropped.

Comment 8: ACETALDEHYDE. Profiles 673-676 correspond to exhaust emissions for gasoline with 3.5% oxygen as ethanol. Given the higher fuel ethanol levels, emissions of acetaldehyde should increase compared to profiles 663-666 where ethanol is present at only 2% oxygen, yet the profiles are virtually identical in terms of acetaldehyde content.

Response:

We have changed the acetaldehyde contents to reflect the ethanol content of the fuels.

The dataset used to generate the species adjustments (ARB's MTBE-EtOH study) does not include multiple ethanol contents in the fuels; so other than the assumed linearity in the ethanol content of emissions, there has been no distinction in emission strengths of particular species according to the ethanol content of the fuel. However, ARB has developed oxygenate-specific aldehyde emission models (whereas the Predictive Model uses only oxygen content as an input). These new models produce the following emission predictions versus oxygen and oxygenate. In the final document, the emissions relative to emissions for 11% MTBE are combined with changes between fuels in hydrocarbon emissions to yield new values of the aldehyde contents of the profiles.

Aldehyde Emission Predictions

	11% MTBE	***No Oxygen***	***EtOH, 3.9% O_2***	***EtOH, 3.5% O_2***	***EtOH, 2.0% O_2***
Formaldehyde					
rel. to 11% MTBE	*1.00*	*.90*	*.90*	*.91*	*.95*
rel. to 3.9% O_2	*xx*	*xx*	*1.00*	*1.01*	*1.05*
Acetaldehyde					
rel. to 11% MTBE	*1.00*	*.96*	*2.74*	*2.33*	*1.28*
rel. to 3.9% O_2	*xx*	*xx*	*1.00*	*.85*	*.47*

Comment 9: OTHER. There are errors in the molecular weights assigned to some of the chemical species in the speciation profiles that were sent to me. Recommended corrections are listed in the attached Table 1. Depending on the chemical mechanism and emission processing procedures used in air quality modeling, these errors in molecular weights could affect conversion of emission rates from mass to molar units. Also, in estimating headspace vapor composition from liquid fuel composition, accurate molecular weights are needed to convert between mass fractions and mol fractions. The most important change is likely methylcyclohexane (43261) where the molecular weight should be 98.2 rather than 85.2 g mol^{-1}.

Response:

We agree with the molecular weight changes and have changed our database.

D-2. Response to Public Comments

These are responses to comments on AARB Work Plan for Conducting an Airborne Environmental Fate and Transport Analysis Of Ethanol-Containing Gasoline@ dated July 8, 1999 and ADevelopment of Emission Profiles for CARFG W/o MTBE@ dated July 12, 1999.

Comments were received from Dennis Hoagland of Shell, David A. Smith of ARCO, Gary Z. Whitten of ICF Consulting, and Gina Grey of the Western States Petroleum Association (WSPA). The comments are paraphrased and responded to below.

Emission Inventory Component

1. Comment: No consistent, comprehensive data set exists from which to derive the speciation profiles for all the fuels -- and emissions from these fuels -- which will be used by ARB. Given this lack of data, ARB is compelled to adjust existing profiles, using many assumptions,

comparisons, arbitrary additions and deletions, etc. ARB's approach is described in a document entitled ADevelopment of Emission Profiles for CaRFG w/o MTBE.@ While far from satisfying, this approach is probably the best that can be done, given the time constraints of the Governor's Executive Order. Nevertheless, we are concerned about the precedent this methodology setsCspecifically that many tasks are fraught with subjective engineering judgement. We are also concerned that future policy could be made using results from this work. To address these concerns, we urge ARB to generate more experimental data in the future, using appropriate fuels and vehicle sets. (WSPA)

Response: California Air Resources Board (ARB) staff agree that in the absence of the availability of production fuels, the airborne environmental fate and transport analysis of ethanol-containing gasoline relies on engineering judgement and should not be viewed as definitive. However, the approach should provide adequate information to allow evaluation of the use of reformulated gasoline with ethanol and non-oxygenated reformulated gasolines. It is preferable to use experimental data where possible, however, even in the best of circumstances engineering judgment must be exercised.

2. Comment: Assuming ethanol-blended fuels are precluded from pipeline distribution, surface transport of this gasoline component between manufacturing/refining locations to the distribution network will need to increase substantially. My estimate is a potential increase of tank truck traffic (depending upon locations rail cars do not work) by as much as 30%. Is the extent to which traffic accident and spills have been addressed in risk analyses? At present, and for our facility, this exposure would be minor. (Inasmuch as our receipts are by ship/pipeline and bulk of outgoing transportation is pipe). What steps would be necessary to assure this impact is addressed in an Environmental Impact Report for an ethanol fuels requirement? (Hoagland)

   What about the diesel emissions from trucks delivering all the ethanol to the terminals for blending into the gasoline? (Smith)

   Response: Emissions from diesel trucks are not pertinent to comparing the environmental transport and environmental fate of ethanol versus MTBE in gasoline. Any issues about extra diesel emissions and other risks will be considered by permitting authorities and California Environmental Quality Act (CEQA) lead-agencies when new facilities would under go CEQA and permit reviews.

   Spilled ethanol is pertinent to the current analysis in that it would become air emissions. However, the amount of ethanol would be trivial compared to the ambient burden of ethanol from vehicular emissions.

3. Comment: First we must all realize that the future is uncertain regarding just how the refineries will blend fuels to meet the emissions requirements of CaRFG without using MTBE. Given such uncertainty, the development of emissions profiles might best require that some attention first be given to some likely scenarios before heading off to analyze exiting data on emissions from vehicles using non-oxygenated or ethanol-containing gasolines.

For example, it is the understanding of this reviewer that a scenario with a high probability would have premium gasoline using ethanol and a large fraction of regular grade made without oxygen. The approach described in this draft ARB document appears to be based on some single average fuel containing either ethanol (at either 2 or 3.5% oxygen) or no oxygenate. Perhaps the final assessment of the air quality impact of removing MTBE can very readily incorporate some mixture of ethanol and neat gasolines using the fuels described in this document, but the present text and fuels chosen don=t appear to have addressed such a possibility.

Some reasons supporting a mixture of oxygenated and non-oxygenated are as follows:

- MTBE in the present CaRFG market supplies about one grade of octane, 11% volume, between 10 and 20 points to T50, and about 11% dilution for sulfur, aromatics, benzene, and olefins. MTBE also adds a couple of tenths to RVP and it contains enough oxygen to meet the federal Clean Air Act requirement for reformulated gasoline, and this oxygen is known to reduce carbon monoxide which is known to be a significant ozone precursor.
- Ethanol blended to the 10% volume level essentially replaces MTBE except that the oxygen content exceeds the federal oxygen requirement, RVP increases nearly an additional psi and, according to the Predictive Model, NO_X emissions will increase unacceptably.
- Using only 10% ethanol to replace MTBE would require refinery adjustments mainly to reduce RVP and predicted NO_X emissions. A current draft Predictive Model (Beta 1) suggests that RVP levels above 7 psi will be possible if further refinery adjustments are made to reduce exhaust THC emissions. However, a full psi does not appear possible, and the Beta 1 Predictive Model appears to require extra refinery adjustments to bring predicted NO_X emissions into conformity.
- If pentanes are removed to reduce RVP for the ethanol blends, then these refinery streams might be used to replace MTBE (for dilution and T50) in the lower octane grades of gasoline.

The above points suggest that the regular-grade oxygen-free gasoline might be similar to current CaRFG with paraffins roughly replacing MTBE. At the same time the higher octane grades would contain ethanol in place of MTBE, but multiple adjustments may be necessary to meet the NO_X requirements of the Predictive Model. The sensitive parameters seem to be sulfur and T90 with some additional effects possible from minor adjustments in aromatics, olefins and T50. In the end, such adjustments may not significantly alter the balance of reactive components (i.e., olefins and higher aromatics) to render the profiles inappropriate for use in assessing the ozone chemistry of using ethanol blends. However, the ARB documentation should address the use of their proposed profiles in light of a mixed market of regular grade non-oxygenated gasoline with premium and some mid-grade fuels using ethanol. (Whitten)

Response: Given the very small differences in the results for single gasolines, there is no need to analyze a situation with multiple gasolines.

4. Comment: Are you trying to estimate the incremental emissions associated from using ethanol that might come from increased vapor emissions when Cleaner-Burning Gasoline with and without ethanol are mixed together in a car's tank? (Smith)

Response: *The effect is probably real, but there are not now enough data on consumers' habits to allow an estimate of the increased emissions. Some analyses may be forthcoming in the future. As long as the federal oxygen mandate remains for federal RFG areas, the point is moot. If a waiver from the federal oxygen regiment is provided, the situation will have to be monitored and appropriate recommendations developed.*

5. Comment: On page iv of the summary of the draft report it is clear that more paraffins are expected in the non-oxygenated fuel and that MTBE-related exhaust products (i.e., isobutylene and formaldehyde) would be reduced, but the reasons for less benzene are not clear. (Whitten)

   Response: *The adjustments for each of the four toxic species have been made via the Predictive Model.*

6. Comment: On page 2 of the report (in Table 2) the difference in octane of the Auto/Oil fuels is noted, but the text does not comment on this. Then on page 20 (Table 9) the proposed non-oxygen fuel is shown to have less aromatics than the MTBE-related fuels. And on the next page (page 21) that the proposed profile is then to be further reduced by a factor of 21.7/27.1. In light of the above discussion, the octane of the proposed profile may be too low to be representative of the California market. (Whitten)

   Response: *The non-oxygenated A/O fuel described in Table 2 is not one of the fuels that are described in Table 9. The speciated emissions from the A/O fuel (in comparison to its baseline MTBE fuel) were used to make certain adjustments to the ARB's exhaust and evaporative profiles to create profiles for oxygen-free fuel. The fuels described Table 9 are those predicted by MathPro for CEC. Within that table, there is a decrease in the aromatic content between the MTBE-blended and oxygen-free fuels. That decrease was transferred to the ARB's profile for whole gasoline.*

7. Comment: In light of the discussions on page 22, it is surprising that the EPA Complex Model was not used to test the impact of removing MTBE on benzene exhaust emissions. The EPA Complex Model actually predicts that benzene exhaust will increase by about 12% rather than the decrease of 12% shown in the unnumbered table on page 24. In fact the Complex Model also suggests that 1,3 butadiene will increase by 7% and acetaldehyde will increase 7.6% going from CaRFG flatline specifications to the same with 11% volume MTBE substituted by paraffins giving the same boiling and T50 specifications (i.e., all parameters at flatline except oxygen). (Whitten)

   Response: *The ARB's regulation for RFG does not allow toxics to increase. In changing one fuel parameter, other parameters must be adjusted using the Predictive Model to preserve the emission benefits. The EPA program is not designed to do this.*

8. Comment: As explained by ARB, each experimental study they used in deriving their speciation profiles has "imperfections that complicate its use." (These studies were conducted by ATL, the Auto/Oil Program, and internal ARB work.) The problems included the use of small and inconsistent sets of vehicles, non-representative fuels, failure to measure all emissions

of interest, and incomplete characterization of the test fuels. Another problem--not mentioned by ARB--is that each study used different analytical techniques for determining the speciated emissions profiles. Lab-to-lab differences for speciation analyses are significant -- even when using identical procedures -- and are even more substantial when using different analytical procedures. (WSPA)

Response: For each of the ethanol-blended and oxygen-free fuels, the emission profiles were based on the ARB study for ethanol and the A/O study for oxygen-free. This should minimize the problem.

The incompleteness of data and the non-representativeness of the non-MTBE fuels in the studies is recognized. However, no alternatives were available when the inputs to the original model were being developed. For that reason, we recognize uncertainty in the quality of the inputs to UAS modeling, and we think that the slight differences in predicted ozone among fuel types may be well within the effects of that uncertainty.

9. Comment: The differences in analytical methodologies and reporting procedures make it very difficult to compare results from one experimental study to another for many individual species. A simple illustration of this is shown in ARB's Figure 5: "Hot Soak Profiles -- MTBE-Blended CaRFG." Here we see that ARB reported about 1% of 2,3-dimethylbutane, while ATL reported none. On the other hand, ATL reported about 1% of 2,3,3-trimethylpentane, while ARB reported none. It is likely that these differences are not real, but arise from the unique ways in which the two labs chromatographically distinguish and report these compounds. Under some chromatographic conditions, 2,3,3-trimethylpentane cannot be resolved from toluene. It is possible that ARB could not make this distinction, while ATL could (or ATL used some other method to estimate the split between toluene and 2,3,3-trimethylpentane). A similar resolution problem exists between 2,3-dimethylbutane and MTBE, and between numerous other pairs of compounds. The point here is that simply comparing lists of numbers, without an understanding of the chromatographic analyses that generate the numbers, may lead to incorrect conclusions. (WSPA)

   Response: See response to Comment 8.

10. Comment: Professor Rob Harley provided a good assessment of ARB's proposed speciation profiles, and identified a number of problems that should be corrected. We agree with the points made by Prof. Harley. In most cases, however, it is not clear how these problems have been addressed. It appears that some of Harley's suggestions have been followed. For instance, the ethanol fractions in ARB's updated catalyst exhaust profiles for the ethanol-blended fuels (dated 7/9/99) are now 2-3% as compared to <1% in the profiles Harley reviewed. On the other hand, the acetylene levels in ARB's updated profiles are still higher in catalyst stabilized emissions than in non-catalyst stabilized emissions. As pointed out by Harley, this seems incorrect. ARB should clearly explain how each of the issues raised by Harley has been addressed. (WSPA)

    Response: The responses to the comments by Prof. Harley on June 23, 1999, are in Section D-1 above.

The acetylene content of ARB's MTBE profiles were not adjusted in "turning" those profiles into ethanol-blended or oxygen-free profiles

11. Comment: ARB's work plan indicates that Prof. Harley will 'Ycalculate headspace vapors from the liquid fuel speciation profiles as a check on the ones developed in-house." It is not clear from Harley's letter of June 23 whether he has done this. However, he did point out that 'Yan equilibrium headspace vapor composition profile may not represent all diurnal evaporative emissions correctly." What is ARB planning to do to address this concern? (WSPA)

    Response: The main issue in the evaporative profiles is whether or not the ethanol content is linear with the ethanol in the fuel. We acknowledge that it probably is not linear and that the ethanol contents of the evaps from the 10% ethanol fuel are too high. However, the close similarity of photo-chemical modeling results among the fuels indicates no need to revise the ethanol contents downward.

Air Quality Modeling Component

12. Comment: The August SCAQS episode is an ozone episodeCnot CO, and consequently there was no previous need to develop CO model performance. Before spatial and temporal behavior of toxics emissions dispersion and reaction can be used and related to CO concentrations, acceptable model performance must be demonstrated. (WSPA)

    Response: The CO model performance was calculated for the August 26-28 SCAQS episode using the updated SAPRC97 mechanism and the Carbon Bond IV mechanism. We found that both photochemical mechanisms have similar CO model performance. As expected, the CO model performance exhibits underestimation. This is generally true for all primary emitted compounds (like CO and NO) which are volume averaged in the model. However, it is important to note that model estimated CO concentrations were not used to adjust concentrations of other compounds to the future year or to estimate the impact of alternate fuels on other compounds.

13. Comment: The UAM-FCM is a grid model that does not incorporate subgrid-scale treatmentCconsequently UAM is known to predict neighborhood scale concentrationsCnot microscale concentrations as measured by CO monitors. In other words, the grid resolution is not fine enough to adequately portray changing CO concentration gradients. This has been known and is one of the reasons the CAL3QHC model has been used to characterize subgrid-scale Ahot-spot@ CO concentrations, which are overlayed on UAM regional predictions. ARB's work plan describes using interpolation techniques with ambient measured CO concentrations to characterize annual exposure to the compounds of interest supplemented by UAM predictions. Critical uncertainties are how quickly CO hot-spot concentration gradients fall off with distance from a monitor, and how well UAM portrays these concentration gradients and population exposures. (WSPA)

    Response: The problem of comparing measured concentrations at a monitoring site against volume-average concentrations predicted by air quality models (the "incommensurability"

problem) has been recognized in the past. The use of a finer grid resolution in the model could partially address this problem. However, it is important to note that the model is being used for this study in a relative sense, i.e., to estimate changes in species concentrations, not absolute values. While the use of predicted CO concentrations will not yield "hot spots" exposures, the study results provide an indication of the directional change in CO concentrations. As indicated in the previous response, it is also important to note that model estimated CO concentrations were not used to adjust concentrations of other compounds to the future year or to estimate the impact of alternate fuels on other compounds.

Data Analysis Component

14. Comment: Another concern arises about consistency of the relationship between CO and the toxic compound of concern between August episode temperatures and more moderate (e.g., wintertime temperatures). Both atmospheric reaction rates and primary emission rates differ as a function of temperature. (WSPA)

    Response: We agree that atmospheric reaction rates and primary emission rates differ as a function of temperature. Although this comment seems to arise from a concern that a relationship between modeled CO and modeled toxic compound levels would be used in estimating future toxics levels, such was not the case. While these relationships were used to establish base year concentrations, only ratios of model predicted toxic compound levels were used to estimate future year toxics levels from base year toxics levels.

15. Comment: It is not clear how the 1-hour peak and the 24-hour average concentrations will be used to develop baseline concentrations. How well do the spatial and temporal relationships of these metrics represent annual average conditions? (WSPA)

    Response: Ratios of 2003 to 1997 model predicted one-hour maximum concentrations were multiplied by the maximum 1997 (measured or estimated) one-hour concentrations to estimate a maximum one-hour concentration in 2003, as described in Appendix 5 of the report. Similarly, the ratio of 2003 to 1997 modeled daily (24-hour average) concentrations was multiplied by the 1997 maximum daily average to calculate a maximum 2003 daily average.

    To estimate changes in population weighted annual average concentrations between 1997 and 2003 the ratio of the 2003 to 1997 modeled region population weighted daily average results were used. For formaldehyde and acetaldehyde, the ratio was applied separately to primary and secondary aldehyde components so as to better represent annual average conditions. When used in this way, the metrics are believed reasonably appropriate for the specific application.

16. Comment: Population exposure developed solely on spatial interpolative techniques assumes linear concentration gradients between monitoring sites. In fact, mobile source emissions occur between sites and change the gradients. Therefore, population exposure may be incorrect. (WSPA)

Response: The current method for calculating population exposure has been in use for a long time and has been used extensively. It is the best technique available at this time. ARB will modify the technique, as a better method becomes available and data are available to drive the method.

17. Comment: Assuming a consistent emissions relationship of toxics species to CO for all vehicle types (light-duty autos, light-, medium- and heavy-duty gasoline trucks, and motorcycles) is erroneous--albeit necessary. We don't know the true effects of fuel changes on emissions from most of these vehicle types, and can only speculate whether the bias this assumption introduces is high or low. (WSPA)

    Response: The analysis approach only used a correlation between toxic compounds and CO to estimate 1997 toxics levels. This approach was only done where there was good correlation. Correlation was not used for estimating future concentrations for the various fuel scenarios.

General

18. Comment: With the layers of uncertainty in ARB's planned analyses, it is unclear whether the results can provide even directional guidance. Further work is necessary to bolster the credibility of any results to be released in December. (WSPA)

    Response: As mentioned in the report, the air quality impact study of ethanol-containing fuel relies on engineering judgement. Deliberate effort was made to solicit comments and improvements and investigate specific alternatives suggested. The approach to uncertainty generally encompassed the consideration and evaluation of such alternatives. Ranges of estimates are provided where the results are different using different approaches. It is believed that the open process and evaluation of alternative methods provides an adequate foundation to establish the credibility of results. We agree that additional work is beneficial and have outlined such work in our report. A fuel and vehicle testing program has been conducted (results still being gathered) and a field measurement program is planned to confirm that actual impacts are consistent with impacts estimated in this study.

D-3. Response to Public Comments on CO Reactivity

D-3.1. Recent UAM Simulations On The "Reactivity" Of Carbon Monoxide

Gary Z. Whitten of ICF Consulting submitted this in a personal communication forwarded from Tom Koehler to Steve Brisby on September 23, 1999.

Previous evaluations of the "reactivity" of carbon monoxide (CO) have focused on the use of Maximum Incremental Reactivity (MIR) factors developed by W. Carter of the University of California at Riverside. These factors were developed using a 1-day moving box model. However, the rate of atmospheric decay for CO is an order of magnitude slower than the average hydrocarbon decay rate. While a 1-day model might be considered appropriate to evaluate the relative reactivities of various volatile organic compounds (VOC) to each other, the same 1-day model would not reflect the multi-day impact of CO. The Urban Airshed Model (UAM), on the other hand, is a far more appropriate tool for comparing the relative reactivity of CO to VOC.

Recent simulations for the year 2000 of the South Coast Air Basin, the Chicago area, and New York all point to a reactivity of CO that is about 65 percent greater than the 1-day approach used to develop the MIR factor for CO. That is, the Carter MIR for CO is 0.07 grams ozone per gram of CO, but using the UAM implies a value closer to 0.12 instead.

The base UAM simulations for the three cities have all been used in other projects. For the South Coast Air Basin the inputs were developed by the South Coast Air Quality Management District (SCAQMD). The Chicago and New York base simulations were originally developed for the Auto/Oil program (Guthrie et al, 1997, SYSAPP-96/31). In each case the on-road mobile CO emissions were set to zero and compared to one or more simulations where mobile-related VOC emissions were reduced. Also, simulations were performed where the initial and boundary conditions for CO were reduced according to the mobile-related emissions percentages (48 percent in Chicago and 35 percent in New York). Even for the Chicago case, which used the newer UAM-V version with a five-day simulation covering a large region of the Lake Michigan area, the boundary conditions for CO proved to play a significant role. Tables 1, 2, and 3 list many of the detailed results, which show considerable variation. Nevertheless, the impact of on-road CO emissions are clearly significant compared to VOC emissions.

The base simulation for the South Coast Air Basin comes from the 1997 Air Quality Management Plan (AQMP). The main information on the use of the UAM in the AQMP can be found in Appendix 5, Chapter 3 of the AQMP documentation. The simulations reported here use the same input files (or input file preparation software) as were used in the AQMP for the control simulations for the year 2000 based on the meteorological episode on the 26th, 27th and 28th of August 1987.

The sensitivity simulations shown below illustrate the relative importance of the various parts of the gasoline-related mobile emissions inventory. For the most part these simulation scenarios involve setting a particular part of the gasoline-related inventory to zero. For carbon monoxide

(CO), two sensitivity simulations were performed to bracket the impact of gasoline-related CO emissions. For one CO scenario the chemistry of CO was totally eliminated and for the other the gasoline-related emissions were set to zero. . Gasoline-related CO emissions are only 60 percent of the total CO emissions as seen in the AQMP emissions inventory. For convenience, 60 percent of eliminating CO chemistry from the UAM are represented in parenthesis in Table 1 for the peak impact values.

The CO chemistry was eliminated by setting the chemical reaction rate of CO with the hydroxyl radical to zero. Such a sensitivity test includes non-gasoline related emissions, off-road engines, secondary CO from VOC, carry-over from previous days, plus initial and boundary conditions. In the other test only the on-road gasoline-related emissions were set to zero; carry-over effects from first day emissions into the second and third days would still be included. The actual impact of the CO emissions would be expected to fall somewhere between these simulations because emissions both in the basin and in surrounding areas would affect initial and boundary conditions over a period of several days due to the month-long atmospheric lifetime of CO compared to the day-long lifetimes of urban VOC.

A potential update to the AQMP is included as a sensitivity scenario that uses a newer running-exhaust profile (#882) supplied by P. Allen of the ARB. The original AQMP profile had 57 percent methane; the new profile has 18 percent methane, and for reference the Caldecott tunnel data show 9.9 percent methane. The newer profile (#882) resulted from a special ARB workshop in the summer of 1998.

Table 1. 1-Hour Max Ozone (ppb) UAM Results, South Coast Air Basin, 2000

Scenario	August 27th	Peak Impact	August 28th	Peak Impact
Base	**129.0**		**148.3**	
CO Chem	**114.1**	**-14.9(-8.9)**	**132.4**	**-15.9(-9.5)**
CO Emiss.	**126.4**	**-2.6**	**143.3**	**-5.0**
Run Evap	**127.8**	**-1.2**	**146.9**	**-1.4**
Hot Soak	**128.1**	**-0.9**	**147.7**	**-0.6**
Diurnal	**125.4**	**-3.6**	**145.4**	**-2.9**
VOC Strt	**121.6**	**-7.4**	**143.9**	**-4.4**
VOC Rn	**125.3**	**-3.7**	**144.7**	**-3.6**
Rn Spec.	**132.0**	**+3.0**	**150.9**	**+2.6**

Table 2. 1-Hour Maximum Ozone (ppb) UAM-V Results for Chicago, 2000

Scenario	June 26	Peak D	June 27	Peak D	June 28	Peak D
Base	124.6		122.1		116.7	
CO emis	123.0	1.55	120.6	1.53	115.6	1.11
CO w.bc	120.7	3.85	117.6	4.53	113.3	3.41
VOC 4.7%road	124.3	0.28	121.9	0.24	116.6	0.16

Table 3. 1-Hour Maximum Ozone (ppb) UAM Results for New York, 2000

Scenario	July 9	Peak D	July 10	Peak D	July 11	Peak D
Base	184.4		179.7		174.9	
CO emis	183.3	1.08	175.8	3.89	172.9	1.97
CO w.bc	182.1	2.28	174.0	5.69	170.9	3.97
VOC 6.9%road	184.3	0.12	178.9	0.79	174.5	0.33

Carbon Monoxide Contribution to Ozone

The National Research Council (NRC) recently (National Academy Press, 1999, "Ozone-Forming Potential of Reformulated Gasoline") stated that "CO in exhaust emissions from motor vehicles contributes about 20% to the overall reactivity [i.e., ozone-forming potential] of motor-vehicle emissions." However, this statement is based on the use of Carter MIR factors. For comparison, the UAM sensitivity tests reported here can be expressed as overall contribution to ozone formation.

For the South Coast simulations the ozone sum of all mobile VOC tests shown in Table 1 is 19.8 ppb for the August 27th day and 15.5 ppb for the August 28th day. For the scenario eliminating CO chemistry the 60 percent ozone impacts (reduced to account for the on-road percentage of emissions) are 8.9 ppb and 9.5 ppb, respectively. These results indicate an upper limit contribution of CO to the combined VOC and CO ozone formation appears to be 31 percent on the August 27th day and 38 percent on the August 28th day. An increase from one day to the next is consistent with some carry-over of emissions. For the lower-limit estimate cutting just the emissions shows an even stronger apparent carry-over effect by going from an 11.6 percent impact on the 27th to a 24.4 percent impact on the August 28th day. Taking the average of the second of these days a contribution of 31 percent is estimated for CO to the total CO and VOC ozone formation.

For the Chicago simulations VOC emissions were reduced by 14.2 tons, which were 4.7 percent of the total 301 gasoline-related mobile inventory. The changes in ozone listed in Table 2 would be expected to increase to 6.0, 5.1, and 3.4 ppb, respectively for the three days if the full 301 tons were reduced. For the emissions only CO scenarios the percent contribution to total ozone for the three days would then be 20, 23, and 25 percent, respectively. Again these results are consistent with an

accumulation due to day-to-day carry-over. For the upper-limit estimates with the boundary and initial conditions reduced by 32 percent CO to account for the on-road contribution (off-road would decrease this further), the estimated ozone contributions would be 39, 47, and 50 percent, respectively for the three days. The average of the two last day contributions is a 38 percent ozone conrtibution for CO.

For the New York simulations were reduced by 41.9 tons, which were 6.9 percent of the total 607 gasoline-related mobile inventory. The changes in ozone listed in Table 3 would be expected to increase to 1.7, 11.4, and 4.8 ppb, respectively for the three days if the full 607 tons were reduced. For the emissions-only CO scenario the percent contribution to total ozone for the three days would then be 38, 25, and 29 percent, respectively. For the upper-limit estimates with the boundary and initial conditions reduced by 50 percent CO to account for the on-road contribution (off-road would decrease this further), the estimated ozone contributions would be 57, 33, and 45 percent, respectively for the three days. The average of the two last day contributions is a 37 percent ozone contribution for CO.

In summary, when the UAM is used to estimate the carbon monoxide contribution to mobile VOC and CO ozone formation in three cities (Los Angeles, Chicago, and New York) for the year 2000, the average is 35 percent on the last day of the simulations. With the exception of the first day of simulation in New York, the estimated CO contribution appears to increase each day, which is consistent with the slow decay of CO leading to carry-over effects. In each of the cities the results were highly sensitive to adjustments in the boundary conditions assumed for CO, which is also consistent with the importance of carry-over effects resulting from the long atmospheric lifetime of carbon monoxide. The analyses used by the California Air Resources Board and the NRC have used the 1-day Carter MIR factor of 0.065 to 0.07 grams ozone per gram CO. The NRC used such a value to derive an overall CO contribution to urban VOC and CO ozone of 20 percent. Since the percent derived here is 35 percent, this implies that a UAM-derived MIR factor for CO would then be 1.75 (i.e., 35/20) times 0.07 or 0.12 grams ozone per gram CO. It might also be added that off-road CO emissions were not included in the present study, but these emissions could enhance the importance of CO to overall ozone formations. These multi-day UAM grid-model simulations all tend to show a considerably higher contribution to ozone formation from on-road mobile CO emissions than the one-day simulations used in the MIR factors which formed the basis of the NRC estimate.

D-3.2. Why Carbon Monoxide Grows in Importance on Multi-Day Smog Episodes

Received on November 12, 1999 from Gary Z. Whitten of ICF Consulting

Recent sensitivity results from photochemical grid modeling show a day-to-day progression in the contribution that carbon monoxide (CO) makes to urban ozone formation. Moreover, the contribution of CO exceeded that expected from Maximum Incremental Reactivity (MIR) factors. An explanation for such a progression and the appropriateness of using a higher factor for CO relative to organic emissions is discussed here.

The Urban Airshed Model was used with base case simulations that had been prepared for State Implementation Plans (SIP). The sensitivity simulations compared mobile CO emissions reductions

with and without boundary condition adjustments against volatile organic compound (VOC) emissions reductions for three cities: Los Angeles, Chicago, and New York. In one simulation the chemistry of CO was deleted to provide an upper bound estimate to the overall importance of CO (this is more than the contribution from emissions of CO because CO is an intermediate product of many VOC). Using an average of the emissions-only and emissions plus boundary adjustment simulations it was found that over two or three days the contribution to ozone relative to VOC tended to increase.

The causes of this observation appear to relate to the fundamental characteristics of how carbon monoxide contributes to ozone formation. The most frequent pathway for either CO or VOC to begin the atmospheric chemistry leading to urban ozone formation is through reaction with the hydroxyl radical (OH). However, carbon monoxide yields only one intermediate peroxy radical, namely the hydroperoxyl radical (HO2) and no other products that might contribute to ozone formation. On the other hand, VOC usually yield not only two intermediate peroxy radicals (RO2 and HO2), but secondary organic products that can either react as a VOC themselves or can contribute new free radicals to the overall process through photolysis. These new free radicals and secondary VOC products can be especially important under VOC-limited conditions like those used by W.P.L Carter in the development of the MIR factors.

Even under conditions that lead to peak ozone formation under NOx-limited conditions, the mixture of smog-forming precursors can be VOC-limited during the morning and mid-day hours. Because the decay of NOx tends to be faster than VOC decay on average, this progression from early VOC-limited chemistry (that is enhanced by new free radicals) can occur not only over a single day, but over a multi-day episode as well. At the time when ozone might be peaking under NOx-limited conditions the addition of new free radicals can actually reduce ozone because these new radicals tend to remove NOx even faster. Because CO contributes neither secondary VOC nor new free radicals, the importance of CO relative to VOC will become greater under such conditions relative to the strongly VOC-limited conditions used to develop the MIR factors.

Although previous airshed studies have tended to show that the MIR factors correlated well with exposure estimates, exposure estimates emphasize the period of the day when ozone is rapidly forming (still during the VOC-limited part of the day) in highly populated areas. Peak ozone (by definition, slowly forming) often tends to form further downwind in less populated regions later in the day under more NOx-limited conditions. However, as an airshed becomes closer to attainment the only exposures to high ozone will be near the downwind peaks and, further, it is these peaks which drive the SIP strategies. Hence, it is appropriate to consider a higher reactivity factor for CO relative to other VOC.

Carter in 1994 (published in the *Journal of Air and Waste Management*), developed a series of reactivity factors. This series of three reactivity sets (MIR, MOIR for maximum ozone, and EBIR for equal benefit) were developed by reducing the NOx inputs to progress towards more NOx-limited conditions. Others, including Carter, have noted that the three sets of factors in this series show surprisingly similar relative reactivities between the various VOC. A notable exception, of course has been toluene which has secondary chemistry that removes NOx so that “reactivity” can actually become <u>negative</u> under NOx-limited conditions. However, a new look at this series of factors is presented here which shows that the reactivity of CO consistently increases relative to VOC as the series (with reduced NOx) progresses. Hence, the progressive series published by

Carter is consistent with the progressive trended observed in the recent UAM sensitivity simulations using SIP-like conditions.

Table 1 compares the reactivity factors published by Carter (1994) in their original form relative to the base VOC mixture. A group of VOC were chosen to be representative of various types. In the last two columns the percent increase of CO reactivity to each VOC is given relative to the MIR factor of CO relative to each VOC. It is seen that the relative reactivity of CO consistently increases relative to all VOC as the series progresses toward more NOx-limited conditions. Also it is noteworthy that for VOC which are known to supply significant secondary new free radicals (e.g., formaldehyde and methyl glyoxal) the relative increase of CO reactivity is especially large as would be expected from the fundamental explanation given above. Finally, it is perhaps coincidental but the average increase in CO reactivity seen in the UAM simulations is consistent with the average seen in Table 1. That is, the reactivity of CO appears to be approximately 65 percent more, on average, than the MIR estimate relative to other VOC under multi-day airshed episodes and in the Carter progressive series of reactivity factors.

Table 1. Reactivity Relationships from Carter (1994)

Compound	MIR	MOIR	EBIR	% MIR to MOIR	to EBIR
CO	0.018	0.032	0.044		
Methane	0.005	0.008	0.01	11.1	22.2
Ethane	0.079	0.14	0.18	0.3	7.3
Propane	0.16	0.27	0.33	5.3	18.5
n-Butane	0.33	0.57	0.7	2.9	15.2
n-Pentane	0.33	0.58	0.71	1.1	13.6
i-Pentane	0.39	0.63	0.8	10.1	19.2
3-M-Pentane	0.48	0.8	0.99	6.7	18.5
2,2,4-TM-Pe	0.51	0.78	0.94	16.2	32.6
Cyclopentan	0.76	1.19	1.46	13.5	27.2
Ethene	2.4	2.8	3.2	52.4	83.3
Propene	3	3.2	3.7	66.7	98.2
1-Butene	2.9	3	3.4	71.9	108.5
Isobutene	1.7	1.6	1.9	88.9	118.7
trans-2-but	3.2	3.2	3.6	77.8	117.3
2-Heptene	1.8	1.8	1.9	77.8	131.6
1,3-Butadie	3.5	3.5	4.1	77.8	108.7
Benzene	0.135	0.114	0.051	110.5	547.1
Toluene	0.88	0.53	-0.023	195.2	

m-Xylene	2.6	2.1	1.7	120.1	273.9
1,3,5-TM-Be	3.2	2.6	2.4	118.8	225.9
Methanol	0.18	0.23	0.28	39.1	57.1
Ethanol	0.43	0.61	0.72	25.3	46.0
t-Butyl Alc	0.132	0.21	0.27	11.7	19.5
Formaldehyd	2.3	1.8	1.7	127.2	230.7
Acetaldehyd	1.8	1.8	2.2	77.8	100.0
Methyl Glox	4.7	4	3.9	108.9	194.6
Acetone	0.18	0.17	0.18	88.2	144.4
			Average % increase from MIR -->	**59.4**	**106.9**

D-3.3. ARB Response

The proposed regulations for Phase 3 reformulated gasoline (ARB, 1999) allow increased evaportive hydrocarbon emissions as the oxygen content of the fuel increases above 2 wt%, reducing CO emissions. This adjustment compensates for the ozone-forming potential of CO. The proposed Phase 3 reformulated gasoline regulations uses the MIR scale to make the adjustment. A recent modeling analysis (Whitten, 1999) suggests the reactivity should be raised by 65%.

Our review of the literature indicates the reactivity of CO is well established. Additionally, changes to the MIR scale on which California's reactivity regulations are based should only be undertaken after careful analysis and only when the scientific evidence and the advice of ARB's Reactivity Scientific Advisory Committee warrant such a change. We believe the Whitten (1999) analysis of the reactivity of CO focuses on an inappropriate metric for the comparison of three-dimensional airshed models with MIR values. In addition, the approach by Whitten (1999) to eliminate CO chemistry creates a bias in the modeling analysis as CO produced by reactions of VOCs will also artificially contribute to a pervived decrease in the reactivity of CO. Our conclusion is that an increase in the reactivity of CO is not justified.

On a per-mole basis, the atmospheric reactions of CO create a minimal amount of ozone. Literature values for the incremental reactivity of CO are given in Table 3.1. The latest version of SAPRC (Carter, 1999) calculates the MIR for CO as 0.066 g O_3/g CO. Earlier work by Carter (1994) reports a slightly lower values of 0.054 g O_3/g CO. Bowman and Seinfeld (1994) report incremental reactivities in units of ppb O_3/ppbC but a comparison of CO and CH_4 in the two scale allows an estimate of relative reactivity of CO. The stability of the MIR for CO is consistent with Carter's estimate of the uncertainty of the value. In both the 1994 and 1999 work, Dr. Carter lists the uncertainty of CO's reactivity in the least uncertain category. The peer review of SAPRC99 (Stockwell, 1999) found that the relative rank of CO in terms of reactivity for the compounds common to both works did not change at all between 1994 and 1999.

Table 3.1. Comparison of Incremental Reactivities for CO and CH_4

Compound	Carter (1994)	Carter (1999)	Bowman (1994)
CO	0.054	0.066	0.005
CH_4	0.015	0.0153	0.001

[a]Units of gO_3/g CO.

[b]Units of ppb O_3/ppbC with VOC to NO_X ratio of 8.2.

Dr. Whitten's analysis of the reactivity of CO using the Urban Airshed Model (UAM) focuses on the changes in the maximum ozone concentration. Maximum ozone concentration is the reactivity metric used in the MIR scale; however, the model used to calculate MIR values is a simple zero-dimensional box model. The UAM is a more complex, three-dimensional, Eulerian model. As such, it allows the calculation of ozone concentrations as a function of spatial distribution. Using the spatial distribution and population data, the UAM can generate three ozone metrics; peak ozone, population-weighted ozone exposure, and spatial exposure. Peak ozone corresponds to the maximum ozone concentration used in the MIR values. Population-weighted exposure multiplies the ozone concentrations greater than a selected threshold by the population in that grid cell and sums over all the grid cells. The spatial exposure weights the ozone concentration by the grid cell area and, again, sums over all the grid cells. The three reactivity metrics can provide significantly different estimates of reactivity. An analysis (Bergin *et al.*,1998) of the effects of uncertainties in the rate parameters used in the chemical mechanism found that the use of different metrics in determining compounds reactivities as well as the differences between single-cell and airshed model predictions have a larger impact on relative reactivity predictions than do rate constant uncertainties for the compounds and reactions examined. For this reason, care should be taken to select the most appropriate metric to compare with MIR values.

Several comparisons of reactivity calculated with a three-dimensional airshed model and Dr. Carter's MIR scale have been published (Bergin et al., 1998; Bergin et al., 1995; Russell et al., 1995). Bergin et al. (1998) calculated composite normalized reactivities for CO. The results for the three-dimensional model are peak ozone = 0.05, population exposure = 0.02, spatial exposure = 0.03. The MIR value for CO in the same normalized scale = 0.02, (Bergin, 1995). The peak ozone value which is most similar to the metric used in Dr. Whitten's analysis is significantly higher than the values for population and spatial exposures. The agreement between the three metrics calculated with the three-dimensional model and the MIRs for 25 compounds was quantified by calculating the normalized bias. The normalized bias was greatest for MIR to peak ozone, 0.26, while MIR to population exposure and MIR to spatial exposure had smaller biases of –0.16 and 0.05 respectively (Bergin, 1998).

California's reactivity regulations (LEV/CF, CLEAR) are based on the MIR scale. The choice of this particular reactivity scale was made for several reasons. Carter suggested it as the single scale most appropriate for regulations due to the robustness of its response to variations in NO_X concentrations (Carter, 1994). Additionally ARB determined it to be the most appropriate reactivity scale to complement California's NO_X control program. As the choice of reactivity scale was made for specific reasons and is codified in the California Code of Regulations, it is inadvisable to change scales or metrics without serious consideration. Of the three reactivity metrics calculated with a

three-dimensional airshed model, peak ozone shows the greatest bias when compared with the MIR scale; while population and spatial exposure demonstrate better correlation. This supports the choice of one of the latter metrics as the appropriate metric to evaluate three-dimensional simulations. Health-based concerns support the population exposure metric. Both the Federal and State ozone standards were designed with the goal of protecting public health. The population exposure metric more clearly evaluates the public health effects by providing an estimate of public exposure to ozone concentrations above a threshold value.

The conclusion of Dr. Whitten's analysis based on peak ozone values suggests that the reactivity of CO, as measured by MIR, should be multiplied by 1.65. The values of the population and spatial metrics cited above can not be directly compared to MIRs. "The absolute reactivities calculated with box models (g of O_3/g of VOC) are not directly comparable to the more complex metric used here." (Bergin, 1995). However, a comparison within the three metrics suggests that peak ozone reactivity is significantly higher than population exposure. The population exposure result of 0.02 is identical to the composite normalized MIR. This suggests three-dimensional models do not justify a significant increase in the reactivity of CO.

Use of a different chemical mechanism within a 5-day trajectory model actually calculates CO's reactivity as less than that of CH_4. Derwent et al. (Derwent, 1996) used a predecessor to the Master Chemical Mechanism and a trajectory model to calculate photochemical ozone creation potentials (POCP). A POCP is defined as the change in ozone caused by a compounds relative to the change in ozone caused by ethene. In this study, the POCP of CO = 2.7, CH_4 = 3.4, and C_2H_6 = 14.0 (Derwent, 1999). The most recent MIRs values are CO = 0.066, CH_4 = 0.0153, and C_2H_6 = 0.35.

In summary, California's reactivity regulations are based on the MIR scale. Changes to the scale should only be undertaken after careful analysis and only when the scientific evidence warrants a change. Dr. Whitten's suggestion that the reactivity of CO is underestimated is based on his analysis of three-dimensional airshed simulations. However his analysis is based on the peak ozone metric. Other works indicate poor agreement between peak ozone values as calculated with a 3D airshed model and MIRs values. A comparison of population exposure and MIR indicate identical reactivities. Additionally, the MIR of CO is well established and regarding as having a low uncertainty. Taken together, these recommend against any increase in the reactivity of CO.

D-4. Response to Public Comments on CO Emission

D-4.1. The Impact of Fuel Oxygen on Carbon Monoxide in California Cleaner Burning Gasoline

Gary Z. Whitten of. ICF Consulting submitted this in a personal communication forwarded from Tom Koehler to Bart Croes on October 26, 1999.

The California Air Resources Board (CARB) is considering a credit for reducing carbon monoxide (CO) in the cleaner burning gasoline (CBG) regulations. The ozone forming chemistry of CO has been known for many years, but due to its low reactivity relative to hydrocarbons and due to its own health hazards, carbon monoxide has been regulated only for the latter. Also CO is reduced by the same vehicle emissions control technology used to meet regulatory requirements for hydrocarbons (some recent on-board computer chips can "fine tune" between more hydrocarbon

control relative to CO control). However, fuel oxygen is widely known to provide additional CO reductions, and during winter months when CO levels can still exceed air quality standards, fuel oxygen is often required. In the California CBG summer ozone program fuel oxygen is not required except in areas such as the South Coast Air Basin and Sacramento where the Federal requirements of the 1990 Amendments to the Clean Air Act mandate a minimum average level of 2 weight percent.

Although fuel oxygen can reduce hydrocarbon emissions in parallel with its ability to reduce CO, the amount of hydrocarbon reduction is typically less than the CO reductions that are possible from this fuel effect. Other fuel effects appear to be parallel as well, but some, like T90 can be opposite when comparing the emissions impacts on hydrocarbons relative to CO impacts. For sulfur and T50 the impacts appear to be parallel, but the relative magnitudes are revered compared to fuel oxygen. That is, fuel sulfur and T50 tend to reduce hydrocarbon emissions more that they can reduce CO emissions. Hence, for neither vehicle control technology impacts nor for fuel parameter effects does it appear that hydrocarbon impacts might serve as an accurate surrogate for predicting carbon monoxide impacts. Nevertheless, the California Air Resources Board has indeed suggested that other fuel parameters that might be adjusted to reduce hydrocarbon emissions would similarly impact CO emissions. In particular the ARB has suggested that the CO debit between 2 percent oxygen and zero oxygen would be less in magnitude (per percent fuel oxygen) than the credit for increasing fuel oxygen from 2 percent up to the cap limit of 3.5 percent oxygen.

The ARB has currently suggested that a credit for increasing fuel oxygen to 3.5 from the standard CBG level of 2 percent be based on a CO reduction of 7.5 percent. This is close to the approximately 5 percent <u>linear</u> CO reduction per percent fuel oxygen recommended by the OSTP study (1997). For reducing fuel oxygen from 2 percent to zero the ARB has suggested that a debit be based on only a 5 percent CO increase, which is less than half the OSTP recommendation. While it can be argued that even the OSTP recommendation is low (which is another issue not discussed here), the "non-linear" relationship suggested by the ARB between reducing fuel oxygen and increasing it, is the issue to be discussed here.

The ARB has suggested that, according to the Predictive Model, reducing fuel oxygen will increase hydrocarbon emissions, and to restore hydrocarbons to their original level other fuel parameters will have to be adjusted which will, in turn, reduce CO also. The ARB then concludes that the actual CO increase will be less (by half) than the 10 percent expected from a linear application of their recommended impact for increasing fuel oxygen. Unfortunately, there is only one study where a non-oxygenated fuel intended to meet the CBG regulations was tested against an oxygenated CBG gasoline (see Auto/Oil Technical Bulletin No. 17). Nevertheless, even in this widely quoted study the CO emissions difference in Tech 4 vehicles (actually model year 1989 and known as "current fleet" in the Auto/Oil program) turned out to be 11 percent, close to what was predicted from the OSTP (1997) recommendation[1]. However, the fuel made without oxygen did not quite meet CBG requirements and it was a full grade in octane lower than the oxgenated fuel. The hydrocarbons for the non-oxygen fuel (according to the Predictive Model) were too high by

[1] Ironically, the Auto/Oil study reported in Technical Bulletin No. 21 does recommend a difference of about 5 percent between these fuels for the Los Angeles emissions inventory for the years 2000 and 2010. However, this recommendation is based on future fleet assumptions that weight new technologies that might have low to zero impact from fuel oxygen. That is, the 5 percent impact is derived, not from fuel adjustments as the ARB claims, but from fleet-weighting assumptions.

2.12 percent compared to flatline requirements in the CBG program. As noted above the Auto/Oil data for the non-oxgenated fuel indicated an 11 percent carbon monoxide increase; it is not known what the CO changes might have been had the octane been increased to match that of the oxygenated fuel and had it been further changed to fully meet the CBG requirements. Furthermore, as noted above and discussed in more detail below, there are other parameters (like T90) that might have been adjusted instead of those used to reduced hydrocarbons when oxygen is absent and some of these (especially) T90 might conceivably have increased CO beyond the observed 11 percent.

A review of Auto/Oil studies and an earlier version of the California Predictive Model indicate a variety of responses between fuel parameters and CO emissions that seems quite different that the responses for hydrocarbons, NOx, and toxics. A summary of this review is presented in Table 1.

The earlier version of the Predictive Model did contain CO estimates, but the final version of 1994 did not. Both model predictions are included for reference. While the earlier version provides a relative reference between CO and THC, the final version provides a relative reference between the two model versions for THC. The database (even with the latest additions) does contain CO along with THC and NOx, so it would be possible to construct and updated Predictive Model that includes CO.

In summary it has been shown that several fuel parameters might be adjusted to compensate for the loss of oxygen in California CBG and there is little if any evidence to support the ARB claim that these compensating adjustments would consistently reduce the expected increase in CO. Therefore, it is recommended that a linear relationship be used to estimate the CO impacts associated with fuel oxygen content.

Table 1. Summary of Auto/Oil and Predictive Model impacts on CO and hydrocarbons from various fuel parameters.

	Sulfur[2]		**Aromatics[3]**		**Olefins**		**T90**		**T50**	
	CO	**HC**	**CO**	**HC**	**CO**	**HC**	**CO**	**HC**	**CO**	**HC**
Auto/Oil # 2	**-13**	**-16**								
Auto/Oil # 1			**-13.6**	**-6.3**	**+1.5**	**+6.1**	**+0.8**	**-21.6**		
Pred Mdl # 6	**-0.88**	**-0.82**	**-2.6**	**+0.2**	**0.0**	**+0.6**	**+2.5**	**-1.1**	**-0.9**	**-3.2**
Pred Mdl fnl	**----**	**-1.44**	**----**	**0**	**----**	**-0.74**	**----**	**-0.1**	**----**	**-5.9**

[2] In this Auto/Oil study (#2) sulfur was reduced from 466 ppm to 49 ppm. For the Predictive Model results sulfur was reduced from 40 ppm to 20 ppm with the other parameter set at current flatline.

[3] In the Auto/Oil study (#1) aromatics were reduced from 45 to 20 percent, olefins from 20 to 5 percent, and T90 from 360 to 280 degrees F. For the Predictive model results aromatics were reduced from 30 to 25 percent, olefins from 10 to 6 percent, T90 from 300 to 280 degrees F, and T50 from 210 to 190 degrees F, with the base parameters set to 7 RVP, 20 ppm S, 0.8 benz, 25 aromatics, 6 olefins, 210 T50, 300 T90, and zero oxygen.

D-4.2. ARB Response

The 7.5% increase for the higher oxygen content has been derived from data taken by ARB under the REPO5 test cycle (ARB, 1998b). According to FTP testing, the decrease in the CO inventory would be about 2.5% if oxygen were increased from 2.0 to 3.5 wt% of gasoline. However, the REPO5 data indicate that under "off-cycle" (non-FTP) operation, CO emissions are reduced much more. The staff has estimated the actual CO inventory reduction as 2.8 times the value calculated from FTP data. In contrast, available data do not show a difference between FTP and off-cycle testing in the effect of eliminating oxygen from gasoline. Therefore, the increase in the CO inventory estimated from FTP data, 5%, has been applied for the oxygen-free fuel.

We are not simply taking oxygen out of gasoline. The linearity assumption is generally based on the addition of oxygen to gasoline without significantly changing other parameters. This is not the case here. A CaRFG without oxygen has to make up the hydrocarbon loss from the removal of the oxygen. In reducing hydrocarbons, there is also a reduction in CO due to the other changes in the CaRFG. Adding oxygen results in increases in NO_X which need to be mitigated by adjusting other fuel parameters. Offsetting NO_X does not result in decreases in CO.

D-5. References

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