

California Environmental Protection Agency



Air Resources Board

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

Appendix D

**Scientific Peer Review
and Public Comments**

December 1999

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D-1. University of California Scientific Peer Review

This section contains comments received from a scientific peer review conducted by four reviewers approved by the University of California Office of the President under a process defined by Health and Safety Code section 57004. The reviewers commented on the November 18, 1999 version of the main report and versions of Appendix A through Appendix D dated November 10, 1999. This is the version of the report presented at the December 9, 1999 hearing of the Air Resources Board (ARB). Each reviewer was asked to comment on the Executive Summary and sections of the report related to their particular area of expertise. The reviewers were selected by the University of California Office of the President to complement one another, so each section of the report was reviewed by at least one individual. Each comment is presented as received in normal font and is followed by the ARB staff response inserted in italics.

D-1.1. Professor Roger Atkinson of the University of California at Riverside

Attached are my comments on selected portions of the above report and its appendices

Summary

The findings of this report are supported by the evidence presented, and indicate that vehicle exhaust emissions and their impact on ozone formation will not be significantly affected by replacing one oxygenate for another, or by eliminating the oxygenate, in reformulated gasoline. In addition, the findings are consistent with previous, more restricted, investigations and/or reviews of the impacts of oxygenated (containing methyl tert-butyl ether (MTBE) or ethanol) and non-oxygenated reformulated gasolines on air quality. The report presents the results of a rather complete assessment in a logical manner, and does point out areas of uncertainty (especially in the mobile source emissions inventory).

Detailed comments are as follows:

Appendix B: Photochemical Modeling

1. Page B-6, Section B-3.1. Based on the text, I conclude that the meteorology of the August 26-28, 1987 episode was used in conjunction with the VOC and NO_x emissions appropriate for 1997 with present MTBE-containing gasoline and for 2003 with three gasolines (2.0 wt% O₂ ethanol-containing, 3.5 wt% O₂ ethanol-containing, and a non-oxygenated gasoline). This needs to be stated more explicitly than presently done. The use of "August 26-28, 1987" further on in this Appendix makes for potential confusion on the part of the reader. One specific example of this confusion is on page B-12, 13-18 lines from bottom, where the sentences state that "Figure 4.1 through 4.5 show hourly O₃, NO, and NO₂ for August 26-28, 1987, . . . The time plots clearly show that the 1997 and 2003 scenarios . ." I suggest that it is made clear on page B-6 that all of the scenarios are for the August 26-28, 1987, meteorology and that "August 26-28, 1987" not be referred to again except on page B-32 (which deals with sensitivity studies).

Response: We have added a paragraph in Section B-3.1 explaining that the meteorology of August 26-28, 1987 will be used in all simulations, in conjunction with the appropriate

VOC and NO_x emissions for the 1997 and 2003 scenarios. We have deleted reference to August 26-28, 1987 in other parts of the report, except in the section of the report that discusses model performance (instead of sensitivity studies as stated in the comment).

2. Pages B-8 (Table 3.3) and B-9 (Table 3.4). The "baseline boundary" and "region top" concentrations assumed for N₂O₅ (1.0 ppb) and NO₃ radicals (1.0 ppb) are unrealistically high. While the assumed NO₂, N₂O₅ and NO₃ radical concentrations are close to equilibrium (from the NO₂ + NO₃ ⇌ N₂O₅ reactions), the NO₃ radical concentration is a factor of 2 higher than ever observed and a factor of 10 higher than previously observed "high" concentrations. These boundary layer and upper level concentrations need to be more realistic.

Response: A subsequent conversation with Professor Atkinson determined that 20 ppt is a more appropriate boundary and region top concentration for both N₂O₅ and NO₃ radicals. We do not expect any impact on the simulation results and overall conclusions as MTBE and ethanol do not have significant atmospheric reaction pathways with NO₃ radicals (see Section 2.1 of the main report) and the effect of lowering the NO₃ radical concentration by a factor of 50 will decrease the ozone formation potential of the alkylates, further supporting the overall conclusions of the report. However, we made the suggested changes for upper-bound model simulations now described in the main report and Appendix B.

3. Page B-13, line 6. The concentrations of radical species such as OH, HO₂, organic peroxy radicals, etc., are neither tabulated nor graphically shown in this report. I therefore suggest that "radical flux" be replaced by "O₃, NO and NO₂".

Response: The suggested change has been incorporated into the report.

4. Page B-29, line 10 of text, and page B-30, line 1. Surely the emissions inventory used allows a definitive assessment of whether or not the non-motor vehicle source(s) of ethanol dominate over vehicle sources. The use of "also appears" gives the impression that no one bothered to look into it.

Response: Please note that the word "appears" was also used on page B-11, line 2 from the bottom, and on page B-12, line 2 of the text, in the same context. The emission inventory clearly shows that ethanol emissions are dominated by non-motor vehicle sources for each of the scenarios (see Appendix A, Table 4.1 through Table 4.5). To avoid any potential confusion on this matter by our choice of words, we have omitted the use of the word "appears" in the text, where appropriate.

5. Page B-29, lines 4 and 5 from bottom. I believe that "2003 3.5%" should be replaced by "2003 Et3.5%".

Response: The label has been corrected.

6. Page B-30 on. The fact that VOC emissions from vehicles using EMFAC2000 are a factor of 2-3 higher than predicted using EMPAC7G casts some doubt on the analysis carried out in the previous 30 pages of this Appendix. The use of EMFAC7G appears to be necessitated because of time-constraints, and the sensitivity analysis supports the analysis using the EMFAC7G emissions inventory in that replacing MTBE in gasoline by ethanol (or removing the oxygenates altogether) will have no significant impact on air quality. However, the uncertainties in the mobile source emissions inventory (or the use of an

outdated emissions inventory) is troubling and leads to uncertainties in the 2003 (and 1997!) predicted air quality contained in this report. A number of questions arise:

Is the 1987 inventory (and hence the comparison of predicted vs observed 1987 ambient concentrations) subject to changes in the mobile source VOC and NO_x emissions ?

Is the 1997 inventory, multiplied by the factor of 3, realistic - and if so then the LA Basin maximum O₃ levels could have been (if the meteorology had been conducive to it) almost as high as 1970's values (400 ppb). Since 1997 has come and gone (with a large-scale field study for ozone having been conducted), what does modeling the 1997-SCOS data tell us about the mobile source inventory ?

If the 2003 inventories used in Tables 5.1 and 5.2 are close to reality then O₃ levels in the basin may well increase significantly over the next few years.

Why weren't the NO_x emissions increased as indicated by EMFAC2000, and what is the impact of increasing vehicle NO_x emissions by a factor of 1.8 ?

This rather casual mention of (in essence) "and by the way the real VOC and NO_x emissions from vehicles are believed to be higher than used by factors of around 2.3 and 1.8, respectively" subtracts from the credibility of this report. Significantly more discussion needs to be given concerning the "real" 1987, 1997 and 2003 inventories (or at least CARB's best opinion of them) and the implications for maximum (and 8-hr) O₃ levels. As mentioned above, surely the 2003 inventories should use VOCs increased by a factor of 2.3 and NO_x by a factor of 1.8 in addition to, or instead of, those used in Table 5.1.

Response: The new California on-road motor vehicle emission factor model, EMFAC2000, is still under development and we are reluctant to use it until it receives public scrutiny and possible Board approval in March 2000. We are conducting a detailed in-house comparison of EMFAC2000 against "top-down" studies (i.e., tunnel, ambient ratio, fuel-based). The Singer and Harley (2000) fuel-based inventory discussed in the report is for stabilized exhaust emissions and does not include cold start or evaporative emissions, so it is not necessarily inconsistent with draft versions of EMFAC2000. We also have some concerns with Singer and Harley's methodology (primarily lack of freeway measurements where gm/gallon emission rates are likely to be lower) and view it as an upper-bound estimate. We share your concern that EMFAC2000 will increase the 1987 inventory and significantly erode model performance, and may predict 1997 ozone levels well above those observed in July 1998 (0.244 ppm maximum) when meteorology was more conducive to high ozone than in August 1987. Unfortunately, SCOS97-NARSTO modeling results will not be available until sometime late in 2000. Because of these concerns, we tripled the gasoline-related VOC emissions to bracket the effect of EMFAC2000. Increasing the VOC emissions without a concurrent increase in NO_x maximizes the effect on photochemically generated pollutants and is consistent with producing upper-bound model simulations. More complete results and discussion are now included in the main report and Appendix B.

7. Page B-31, first paragraph of text. Reaction with O₃ will not be the dominant loss process for 1,3-butadiene during daylight hours. Even assuming 200 ppb of O₃ and

1.0×10^6 molecule cm^{-3} of OH (a low daytime value), the OH radical reaction is a factor of 2 faster than the O_3 reaction.

Response: We agree with the comment that during daylight hours the OH radical reaction is the dominant loss process, with the OH radical reaction a factor of 2 faster than the O_3 reaction (when using the O_3 and OH radical concentrations in the comment). However, we neglected to mention in the report that the model predicted that the peak 1,3-butadiene was at 0400 hours, when nighttime reactions with O_3 and NO_3 radicals are the important loss processes. Assuming a nighttime O_3 concentration of 100 ppb, and a NO_3 radical concentration of 0.02 ppb, the NO_3 radical reaction is a factor of 3 faster than the O_3 reaction. The lack of sensitivity of the 1,3-butadiene domain peak to emission changes in the sensitivity scenarios was incorrectly attributed to an increase in its reaction with ozone. The domain peak 1,3-butadiene also happens at the same location in Ventura County for all sensitivity scenarios because a local source is influencing the domain peak. We modified the text to reflect this finding.

8. Page B-40, line 4. Replace "under predict PAN" by "underpredicts PAN".

Response: The text has been corrected.

9. Page B-43, line 1. Replace "compared" by "compare".

Response: The text has been corrected.

10. Page B-46, Table 7-1. The rate parameters given in this table for PAN formation and decomposition use the Troe fall-off expression. Somewhere (here or in Attachment B.1) the Troe fall-off expression needs to be given and the parameters used therein defined. Otherwise Table 7.1 is useless.

Response: We have included expressions for the rate constant parameters used in the SAPRC97 mechanism at the bottom of Table 7-1, and also at the beginning of Attachment B1.

11. Page B-49. For essentially all of the individual compounds shown in Figures, the O_3 formation potentials vary significantly. Some discussion of why this variation occurs (different VOC/ NO_x ratio, etc. ?) needs to be given. The O_3 formation potentials should be compared on a relative basis to see if the variations of the absolute numbers diminish. In my opinion, this complete section (B-7) dealing with O_3 , PAN and PPN formation potentials could be deleted with no adverse impact on the report.

Response: Ozone formation potentials are dependent on local ambient conditions, such as the VOC/ NO_x ratio and the chemical composition (Carter and Atkinson, 1989; Derwent and Jenkin, 1991). Additional variability is introduced from the lack of complete VOC speciation for some of the historical episodes and differences in lumped reaction rates. This explanation is now contained in the text. We believe the box modeling complements the airshed model's finding that ethanol and directly emitted acetaldehyde are not major contributors to ozone and PAN formation and is a necessary part of the analysis.

12. Page B-49, PPN formation potentials. A minor point: because PPN is a "lumped" higher peroxyacyl nitrate, the data cannot indicate which specific higher PAN is involved.

Response: Elsewhere in the report we have noted that PPN represents peroxypropionyl nitrate and higher molecular weight acyl peroxy nitrates. We have modified the text for the PPN formation potentials to reflect the lumped nature of PPN.

13. Page B-56, Table 7.5. The heading for this table caused me some confusion (because of the words "total" and "individual"), and may be better given as "Contribution from individual VOCs to ozone formation", since $(\text{OFP})_i(\text{VOC})_i$ is the amount of ozone predicted to be formed because of the presence of VOC_i .

Response: Similar headings are used in Table 7.6 through Table 7.10 and can also be a potential source of confusion for the reader. We have used the suggested text in the headings for Table 7.5 through Table 7.10.

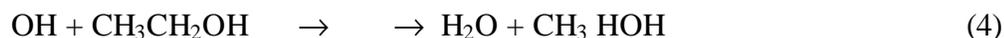
14. Page B-61, last sentence. I am surprised that acetaldehyde does not have a significant contribution to PAN formation, because PAN formation arises from the OH radical-initiated reaction of acetaldehyde and from the production of acetyl radicals arising from alkoxy radical decomposition reactions. I suspect that this "acetaldehyde" is that directly-emitted (or initially present) and does not include acetaldehyde formed *in situ* in the atmosphere from VOCs (including from ethanol) [this would then be consistent with the data in Table 7.11]. If so, this needs to be stated.

Response: You correctly inferred that the ozone, PAN, and PPN (including higher molecular weights acyl peroxy nitrates) formation potentials of a given VOC were estimated from the initial VOC concentration. This is the same methodology used by Bowman and Seinfeld (1994b). This was made clear only for the ozone formation potential on page B-44, where it says "the ozone forming potential can be estimated as the local sensitivity of the predicted ozone concentration to the initial concentrations of each organic compound in the mixture". We have added this clarification in Section B-7 where appropriate.

15. Attachment B1, page B-66. See Comment #10. Also a legend for the kinetic parameters should be given at the beginning of this section. After looking at the OH + ethanol and OH + MTBE rate constants, I figured out that the parameters are A ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$), E (kcal mol^{-1}) and n in $k = A(T/300)^n e^{-E/RT}$.

Response: We have added a description of the kinetic parameters used in the SAPRC97 chemical mechanism at the beginning of Appendix B1.

16. Attachment B3, page B-74, and also Executive Summary, section 2.1.2. The most recent (1997 and 1999) IUPAC evaluations and that of Atkinson (*J. Phys. Chem. Ref. Data, Monograph 2*, 1-216, 1994) recommend that the OH + ethanol reaction proceeds by (reaction channels numbered as in the Executive Summary):



with channels (3) and (5) each accounting for 5^{+10}_{-5} % of the overall reaction at 298 K. The relative importance of reaction (5) in the IUPAC evaluations and in Atkinson (1994) is based on the assumption that H-atom abstraction from the O-H group in ethanol occurs with a rate constant equal to that for the corresponding reaction in methanol. The rate constant

for reaction (3) is based on an estimation and on the elevated temperature data of Hess and Tully (see the above references). In the atmosphere, reactions (4) and (5) give rise to the same products (acetaldehyde plus HO₂) and are hence indistinguishable.

Response: The suggestion will have a slight impact on the product yield parameters currently used in the SAPRC97 chemical mechanism currently implemented in the UAM-FCM. We defer to Dr. Carter to provide us with a representation of the OH + ethanol reaction appropriate for the airshed model simulation and will use the updated reaction in any future simulations. In addition, based on a follow-up discussion with Professor Atkinson, we will also use an updated OH + ethanol reaction rate constant according to the most recent IUPAC recommendation of $k=5.56 \cdot 10^{-13} (T/300)^2 \exp(532/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 1999) which results in a 0.03% increase at 298 K. We included this correction in upper-bound model simulations.

17. Attachment B3, page B-74, and also Executive Summary. The OH + MTBE mechanism is "lumped" in that the specific products are not represented as such. However, this is not going to make any difference for ozone predictions. The rate parameters used for OH + MTBE are from Atkinson (*J. Phys. Chem. Ref. Data*, **Monograph 1**, 1-246, 1989) and have been superseded by a very slightly different rate constant in Atkinson (1994).

Response: The OH + MTBE reaction in the SAPRC97 chemical mechanism uses a lumped representation of the reaction products, which is deemed appropriate for airshed model simulations. A detailed mechanism with inclusion of all the potential reaction channels is not possible, since it will be very computer resource intensive. Hence, to save time, and at the same time have a good representation of the overall effect of a reaction (including the reactions of the products), a lumped representation is appropriate. Please note that the same approach is used for the other "explicit" mechanisms used in the model. These representations of explicit mechanisms are available by Dr. W.P.L. Carter at his web page (<ftp://cert.ucr.edu/pub/carter/mech/saprc97>). The OH + MTBE reaction rate constant was updated to $5.89 \cdot 10^{-13} (T/300)^2 \exp(483/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which results in a 3.8% increase at 298 K. We included this correction in upper-bound model simulations.

Staff Report

18. Page 2, Executive Summary. Two typographical errors.

On line 20, sentence starting "Prior studies". "greater" should be "greater than".

10 lines from bottom, "decreases" should be "decrease".

Response: The text has been corrected.

19. Page 3, Executive Summary. The discussion concerning the increased VOC emissions predicted using EMFAC2000 glosses over the fact that (at least with the emissions scenarios used in the sensitivity studies and using the August 26-28, 1987 meteorology) the predicted maximum ozone levels are 300 ppb for 2003 and the peak 1-hr PAN concentrations are increased by a factor of 3. As noted above in Comment #6, the use of the "correct" emissions (or the most up-to-date estimates) for both VOCs and NO_x would have been optimum. For the scenarios given in Table 1, the basin may be NO_x-limited and relatively

small changes in VOC emissions and/or profiles would then have little or no effect on ozone.

Response: See response to Comment #6 above.

20. Page 6, Section 2.1.1. The rate constant cited is from Atkinson (1994) [IUPAC (Atkinson *et al.* 1999a) did not evaluate OH + MTBE]; see also Comment #17 above. The product data cited are correct; however, it should be noted that these data are for NO being present and are therefore applicable to urban areas but possibly not to downwind areas with low NO_x concentrations. Based on the same studies used by Koshland *et al.* (1998), the reaction mechanism in the presence of NO has been discussed in more detail by Atkinson (1994) and a product profile of *tert*-butyl formate (76%), formaldehyde (48%), methyl acetate (18%) and acetone (6%) recommended [formation of *tert*-butyl nitrite was observed in one of the laboratory studies due to the (CH₃)₃CO + NO → (CH₃)₃CONO reaction competing with the (CH₃)₃CO → CH₃C(O)CH₃ + CH₃ decomposition reaction; under atmospheric conditions the decomposition reaction will totally dominate]. No comment is made concerning the products expected to be formed at low NO_x concentrations from the reactions of (CH₃)₃COCH₂OO and CH₃OC(CH₃)₂CH₂OO radicals with HO₂ and RO₂ radicals, namely (CH₃)₃COCH₂OOH, (CH₃)₃COCHO (also formed in the presence of NO as noted above and in the Executive Summary), (CH₃)₃COCH₂OH, CH₃OC(CH₃)₂CH₂OOH, CH₃OC(CH₃)₂CH₂OH and CH₃OC(CH₃)₂CHO (plus HCHO, methyl acetate and acetone formed from the CH₃OC(CH₃)₂CH₂O and (CH₃)₃COCH₂O radicals). Some mention should be made that *tert*-butyl formate is less reactive in the atmosphere than is MTBE (by about a factor of 4).

Response: The suggested changes have been incorporated into the report.

21. Page 6, Section 2.1.2. See Comment #16 above. Reaction pathway (5) has not been shown experimentally to be negligible under atmospheric conditions, and the only experimental data concerning the importance of the three possible reaction channels are a branching ratio of $k_4/(k_3 + k_4 + k_5) = 0.75 \pm 0.15$ at room temperature (Meier *et al.*, *Chem. Phys. Lett.*, **115**, 221-225, 1985; *Ber. Bunsenges. Phys. Chem.*, **89**, 325-327, 1985) and an acetaldehyde yield under atmospheric conditions of $80 \pm 15\%$ (Carter *et al.*, *J. Phys. Chem.*, **83**, 2305-2311, 1979). The formation of CH₃CHOH and CH₃CH₂O radicals from reactions (4) and (5) lead to the formation of acetaldehyde plus HO₂, independent of the presence or absence of NO, and hence the data of Carter *et al.* (1979) indicate that $(k_4 + k_5)/(k_3 + k_4 + k_5) = 0.80 \pm 0.15$. Formation of HOCH₂CH₂ radicals leads to the formation of glycolaldehyde [HOCH₂CHO] (22%) and HCHO + HCHO (78%) in the presence of NO (yields are for 298 K and atmospheric pressure of air), and to HOCH₂CH₂OOH, HOCH₂CH₂OH, HOCH₂CHO and HCHO in the absence of NO. The atmospheric reactions of the HOCH₂CH₂ radical have been reviewed by Atkinson (*J. Phys. Chem. Ref. Data*, **26**, 215-290, 1997). Formation of methyl nitrate is not expected to be of any significance; rather the formation of ethyl nitrate in very small overall yield (<0.1%) could occur from the reaction of the ethyl peroxy radical with NO.

Response: The suggested changes have been incorporated into the report.

22. Page 7, Section 2.1.3. The atmospheric chemistry of the "alkylates" was most recently reviewed and evaluated by Atkinson (1997). The rate constants for NO₃ + C₄ alkanes at

298 K range from $5 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ to $4 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson, 1997); the rate constants ascribed to Aschmann and Atkinson (1995) are incorrect by 4 orders of magnitude. The products observed and expected in the presence of NO include carbonyls, alkyl nitrates, hydroxycarbonyls and hydroxynitrates, and at low NO_x concentrations will include hydroperoxides, alcohols, hydroxycarbonyls, diols, and hydroxyhydroperoxides (Atkinson, 1997).

Response: The suggested changes have been incorporated into the report.

23. Page 8, Table 2.1. The use of a 12-hr daytime OH radical concentration of $1.6 \times 10^6 \text{ molecule cm}^{-3}$ seems low, because the global tropospheric 24-hr (annual) average OH radical concentration is $1.0 \times 10^6 \text{ molecule cm}^{-3}$ (Prinn *et al.*, *Science*, **269**, 197-192, 1995).

Response: Table 2.1 has been updated with a 12-hour daytime OH radical concentration of $3 \times 10^6 \text{ molecule cm}^{-3}$, as suggested by Professor Atkinson in a subsequent conversation.

24. Page 8, Section 2.1.5. Should include the formation of hydroxycarbonyls and hydroxynitrates from alkylates.

Response: The suggested change has been incorporated into the report.

25. Page 16, footnote 5. I suspect that on line 7 of this footnote, the "RVP of about 8.5" should be "RVP of about 7.5" [further on it is stated that there will be a 1.0 psi increase (from the 6.5 psi of the gasoline mixture)].

Response: The text has been corrected.

Appendix B: Emissions

26. Page A-17, 9 lines from bottom. Why was the SAPRC97 mechanism not used for these reactivity calculations? The NRC (1999) report shows that the absolute MIRs change significantly from SAPRC90 to SAPRC97, although on a relative basis the changes are much less. On line 12 from bottom, the units of specific reactivity ($\text{gO}_3/\text{g organic}$) should be given.

Response: The suggested changes have been incorporated into the report.

27. Page A-19. Units need to be given for the data in Tables 3.7 and 3.8.

Response: Table 3.7 now clarifies that the units are gram ozone/gram NMOG. Table 3.8 is a listing of profile codes used for the alternate scenarios so there are no units.

28. Page A-24 states that vegetative emissions were incorporated into the source inventory, yet Table 4.1, under "natural sources", has only "wildfires". Some comment is needed.

Response: The text on this page now states that the total vegetative emissions from the SCAQS August episode are 103.5, 128.8, and 139.8 tons/day for August 26, 27, and 28, respectively. Since these vegetative emissions are constant for all scenarios they do not affect the anthropogenic emission comparisons.

29. Page A-47. The units at the head of this table (kilogram moles/day) appear incorrect; either kilograms/day or moles/day.

Response: The correct units of kilomoles/day are now noted on Table 4.9.

D-1.2. Professor Barbara J. Finlayson-Pitts of the University of California at Irvine

As per your request, I have reviewed the Staff Report, “Air Quality Impacts of the Use of Ethanol in California Reformulated Gasoline”, and my comments are attached. Overall, the ARB staff have done a good job in this initial examination of the potential effects of the use of ethanol in fuels, especially given the time constraints.

As you can see from the first part of my comments, my major concern is that historically, emissions from vehicles have been underestimated both in California and nationally. As a result, what might have been thought in the past to be unrealistic “worst case” scenarios have turned out to be closer to reality. Because of this, I think that it would be important for the ARB to treat some “worst case” scenarios for ethanol use (e.g. in which the RVP is assumed to be higher than 7, the canisters are assumed to malfunction etc.).

I think this is particularly important in that despite all the caveats in the report, this initial assessment will likely end up being used extensively both inside and outside California. I fear that the preliminary assessment may give a misleadingly positive impression which may not ultimately be representative of the “real world” effects.

Response: We now more fully discuss the results of the ARB (1998) analysis of a non-complying ethanol-blended fuel (which shows significant air quality impacts) in the main report and Executive Summary. This serves both as a caution that it is important to meet the RVP requirements (including addressing the commingling and permeation issues) and to not extend our findings to the parts of the country (non-Federal RFG areas) that the U.S. EPA allows an RVP exemption for ethanol.

COMMENTS ON DRAFT REPORT:

AIR QUALITY IMPACTS OF THE USE OF ETHANOL IN CALIFORNIA REFORMULATED GASOLINE

This report is a good initial approach to addressing air quality impacts from the potential future use of ethanol in reformulated gasoline. Appropriately, it includes a number of caveats and areas of uncertainty which will be the subject of ongoing work by the ARB on this problem.

My major concern is that this report will be taken by many, both inside and outside California, as a final assessment. As such, the initial conclusions regarding potential impacts on air quality being minimal are likely to be cited in a widespread manner. However, as detailed in the following comments, I believe that this may change significantly as new data become available, and hence the initial impression left by this assessment may be overly optimistic. In this regard, I have two major concerns, one regarding the emissions estimates and one regarding the use of population-weighted exposures.

Major Overall Concerns:

Emissions: The history of air pollution both in California and the U.S. shows that emissions, particularly from motor vehicles, have been significantly underestimated. This was pointed out, for example, in the 1991 National Research Council Report *Rethinking the Ozone Problem in Urban*

and Regional Air Pollution. Adjustments were subsequently made to motor vehicle emission models, but as this current draft report on ethanol points out, the EMFAC2000 model is expected to include additional new multiplication factors of 2.3 for VOC and 1.8 for NO_x. These very large adjustments were not foreseen by the scientific community, and it is not clear to me that the reasons for the underestimations are thoroughly understood even today.

Response: We agree and that is why our study included a review of ambient air quality studies for areas that have already introduced large amounts of ethanol into their fuel supply and why we have already implemented an ambient air quality measurement program to provide a “real-world” check on our analysis. This is now discussed more thoroughly in the main report and Executive Summary.

This history suggests to me that what are often taken as “worst cases” end up being more typical cases. In the particular case of ethanol, there are some areas of uncertainty discussed in the report which are already known to possibly contribute to underestimates of emissions:

1. The Executive Summary states that “Our analysis did not include the possibility of increased evaporative emissions due to reduced canister function or commingling”. The issue of impacts on canister function is discussed in detail on page 15, where it is pointed out that “Oxygenates such as ethanol and MTBE bind more tightly to the activated carbon than hydrocarbons such as butane..... may have the effect of reducing the canister’s working capacity. Additionally, ethanol is hygroscopic (i.e. attracts water) and water is clearly known to reduce working capacity...”.

Response: These issues are prominent in the California Phase 3 Reformulated Gasoline Regulations and the report now includes additional discussion on steps being taken to address these issues.

2. Throughout the report, it appears to be assumed that the RVP will not increase with the use of ethanol because of the California RVP requirements. In the Executive Summary, it is stated that the “impact on acetaldehyde concentrations is substantial only in Brazil, where the fuels contain either neat ethanol or 22 vol% ethanol. Due to the lack of RVP requirements for gasolines in Brazil, this acetaldehyde increase could be due to the addition of substantial evaporative emission, rather than strictly the results of an ethanol-for-MTBE substitution”.

The summary of recent assessments in Section 2.2 cites many studies where ethanol has been stated to significantly increase species such as acetaldehyde and PAN, but these are dismissed as not being germane. For example, in Section 2.2.1 in the discussion of the University of California MTBE report, it is stated: “However, these findings are not applicable to fully complying CaRFG2 fuels that have the same Reid vapor pressure (RVP) requirement and are constrained by the ARB Predictive Model .. to meet the same limits on exhaust emissions of VOC, NO_x and cancer risk-weighted toxic air contaminants.” On page 19, with regard to the predicted emissions, it is stated that “For the three fully complying non-MTBE gasolines, the ARB Predictive Model (ARB, 1995) constrains the total mass emissions of VOC and NO_x, so emissions of these pollutants were held constant for all the 2003 scenarios”.

These assumptions may indeed be the case but it seems to me that given the history of underpredicting emissions, the possibility of increased emissions in the “real-world” should not

be discounted. This may be particularly important since as pointed out on page 15, “Hot soak emissions from a test program conducted by the ARB (1998b) using a blend of 10 vol% ethanol with an RVP of 7.8 psi confirmed that the proportion of ethanol in the vapor was higher than in the fuel. In this case, the proportion of ethanol in the vapor was on the order of 25 to 50 wt%..”.

Response: We now more fully discuss the results of the ARB (1998) analysis of a non-complying ethanol-blended fuel (which shows significant air quality impacts) in the main report. This serves both as a caution that it is important to meet the RVP requirements (including addressing the commingling and permeation issues) and to not extend our findings to the parts of the country (non-Federal RFG areas) that the U.S. EPA allows an RVP exemption for ethanol.

3. On page 5, it states that “We also did not consider the possible mileage penalty from increasing the oxygen content of the ethanol-containing gasoline to 3.5 wt %”. I do not know what sort of penalty this would be or the effects on emissions, but again, this is an example of a potential source of underestimation.

Response: Relative to typical current CaRFG2 made with MTBE, CaRFG2 containing 2 wt% oxygen as ethanol would only provide a slightly different fuel economy (change of 0.6% or less). CaRFG2 with 3.5 wt% oxygen would likely provide less fuel economy (by ~2%) than current gasoline, while a non-oxygenated CARFG2 would improve fuel economy by ~2%. However, mass emissions rate should not change in proportion to the change in fuel economy. The Predictive Model tends to force emissions to meet constant standards regardless of the oxygen content. The model is built from data on emissions versus oxygen content of gasoline with emissions measured in mass per mile, not in mass per volume of fuel. This discussion is now included in the main report.

4. It is not clear to me whether evaporative emissions during refueling were considered in the air quality analysis?

Response: All sources with either gasoline evaporative or gasoline exhaust emissions reflect gasoline reformulation. Evaporative losses from refueling or storage evaporation were assigned the headspace vapor organic gas species profile.

The report does point out that many of these issues are being examined, but again, my fear is that this *initial* assessment, which indicates there will be little impact on air quality due to the use of ethanol, will tend to be the one which will be generally used.

I would recommend that some “worst case” scenario’s be treated in which it is assumed that the mandated requirements are not met, e.g. the RVP is higher than 7.0, the evaporative emissions are greater and have relatively more ethanol etc. These could provide some idea of what could happen in an less-than-ideal control scenario.

Response: See response to Comment #2 above.

Use of Population-Weighted Exposures: The results of the photochemical modeling are summarized in Tables 4.4 – 4.6 for four scenarios. While Table 4.6 shows population-weighted exposure, maximum daily average and maximum 1-hour average for a variety of pollutants, Tables 4.4 and 3.5 show only the population-weighted averages for the organics of major concern, acetaldehyde, ethanol and formaldehyde. Air quality standards both in California and the U.S. are expressed in terms of maxima for a given time span, not as population-weighted values. There are

clearly many potential problems with the use of population-weighted values. While it appears that the ARB was asked by OEHAA to express the modeling results in part in this form (page 26), I am particularly concerned to see only the population weighted data cited in Tables 4.4 and 4.5. The same is true of the air quality numbers in Tables 4.8 and 4.9. I recommend that the 1-hour, and where appropriate the 8-hour, maxima be cited first and the emphasis put on these values since they represent estimates of the effects expected on the ambient concentrations due to the introduction of ethanol.

Response: We agree that the averaging times presented in Table 4.4 and Table 4.5 were not as comprehensive as the information presented in Table 4.6 and this has now been corrected. The purpose of Table 4.8 and Table 4.9 is to present a reality check between the changes in estimated emissions and modeled air quality. Since the emissions estimates are a daily total for the entire modeling domain, it is more appropriate to compare these results with the 24-hour population-weighted modeled air quality results.

Comments and Questions on Modeling:

1. There is an increasing recognition [e.g. De Haan *et al. Int. Rev. Phys. Chem.* **18**, 343 (1999)] that chlorine atoms may play a role in the oxidation of organics in coastal areas, which includes such major California cities as Los Angeles, San Francisco and San Diego. Specific measurements of Cl_2 [Spicer *et al., Nature* **394**, 353 (1998)] and non-specific measurements of photolyzable chlorine compounds in coastal areas in the eastern U.S. [e.g. Keene *et al., Environ. Sci. Technol.*, **27**, 866 (1993)] find nighttime concentrations of Cl_2 (and perhaps other species) of ~ 150 ppt. At dawn, photolysis generates highly reactive chlorine atoms at concentrations up to $\sim 1 \times 10^5$ atoms cm^{-3} . There is also evidence for a continuous daytime source of Cl atoms, giving a steady-state Cl atom concentration of as much as mid- 10^4 Cl atoms cm^{-3} at noon over the somewhat polluted North Atlantic Ocean [Wingenter *et al.*, **101**, 4331 (1996)]. The rate constants for oxidation of ethanol and MTBE by OH are similar ($\sim 3 \times 10^{-12}$ cm^3 molecules $^{-1}$ s $^{-1}$), giving estimated atmospheric lifetimes of 53-59 hours for OH at 1.6×10^6 cm^{-3} , or 530-590 hours at 1.6×10^5 cm^{-3} which might be typical of early morning hours. The Cl + ethanol rate constant is 9.4×10^{-11} cm^3 molecules $^{-1}$ s $^{-1}$ and that for Cl + MTBE is 1.66×10^{-10} cm^3 molecules $^{-1}$ s $^{-1}$, corresponding to lifetimes of about 30 and 17 hours respectively at a Cl atom concentration of 1×10^5 cm^{-3} which appears to be reasonable for the early morning hours. That is, if indeed chlorine atom chemistry is important in coastal regions, the oxidations of these oxygenates may be speeded up significantly. It might therefore be worthwhile considering doing some modeling runs with a concentration of Cl_2 of about 10^5 cm^{-3} at dawn (each day, not just the first day which is not used in the modeling results) and a steady-state daytime concentration at the coast of $\sim 10^4$ cm^{-3} to see the effect, if any, on the formation of formaldehyde, acetaldehyde and PAN.

Response: There is a limited chlorine chemistry module available in the SAPRC97 mechanism and, hence, it could be added to our atmospheric chemical mechanism (W.P.L. Carter, personal communication, 1999). However, chlorine chemistry was not included in our simulations since we were unaware of the potential significance of the chlorine radical reaction with hydrocarbons, such as ethanol and MTBE. Note that chlorine chemistry is not included in the more recent SAPRC99 (Carter, 1999). There are significant uncertainties in the reliability

of models on chlorine chemistry because there are limited smog chamber data to test mechanisms for chlorine radical reactions (Carter, personal communication, 1999). We conducted a simulation to bound the effect of chlorine chemistry by adding the Cl + ethanol rate constant suggested above and an upper-bound chlorine atom concentration of 10^4 Cl atoms cm^{-3} throughout the entire modeling domain for all hours, not just coastal areas during daylight hours. We will add the relevant chlorine radical reactions to any future air quality modeling.

2. Some of the model predictions do not seem to make sense intuitively. For example, Table 4.4 shows that the 1-hour PAN maximum will be lower for the 2003 Et2.0% scenario compared to the 2003 MTBE scenario. Similarly, Table 4.6 shows that although the maximum 1-hour average and maximum daily average ethanol concentrations are expected to be about 50% greater for the 2003 Et2.0% scenario compared to the 2003 MTBE scenario, acetaldehyde and PAN concentrations are predicted either not to be affected at all, or in the case of the 1-hour maximum PAN levels, even decrease. There should be some discussion of the reasons for these surprising results.

Response: The differences in predicted PAN concentrations for each scenario are due to differences in the emissions of various VOCs with higher PAN formation potentials than ethanol. From Table 4.9 in Appendix A, it is clear that the 2003 Et2.0% scenario has higher ethanol emissions than the 2003 MTBE. However, the 2003 MTBE has higher emissions of alkanes, aromatics, and olefins compared to the 2003 Et2.0%. Figure 7.3 and Figure 7.4 in Appendix B suggest that the lumped species ALK2, ARO2, OLE1, OLE2, and OLE3 can have (depending on the environmental conditions) higher PAN formation potentials than ethanol. Another factor is that although ethanol emissions are higher in the 2003 Et2.0% scenario, they only represent 8% of the nonmethane VOC emissions. For comparison, ALK2, ARO2, OLE1, OLE2, and OLE3 comprise about 31% of the nonmethane VOC emissions in 2003 Et2.0%. Hence, PAN formation is primarily governed by the differences in alkane, aromatic, and olefinic emissions between scenarios, rather than the emissions of ethanol. This discussion is now highlighted in the report.

3. The concentration of CO_2 in Tables 3.3, 3.4 and 3.5 should be 358 ppm, not 1 ppm (no difference to chemistry, I assume, since condensed phase chemistry where CO_2 would act as a buffer is not included). The boundary, top and initial species HONO concentrations also seem low for the Los Angeles region, where something of the order of 1 ppb might be more applicable [e.g. Winer and Biermann, *Res. Chem. Inter.* **20**, 423 (1994)]. In Table 7.4, the methane concentration must be about 1.7 ppm, since this is a global average; smaller values as shown in the table don't seem reasonable.

Response: CO_2 concentrations do not have an effect on the photochemistry and the major source of HONO is direct emissions (assumed to be 2% of the NO_x) and in situ formation. We revised the boundary, top, and initial conditions that we use for CO_2 and HONO to the suggested values for the upper-bound modeling simulations. The methane concentration used in the Brazilian box model simulations was a mistake that has now been corrected.

4. In Appendix B on pages B-11 and B-12, it is stated that "Although domain ethanol emissions have increased from 1997 to 2003, reflecting changes to the motor vehicle cleaner burning gasoline used, the emissions from non-motor vehicle sources (which appear to dominate the magnitude of the maximum ethanol concentrations) have decreased". The data in Table 4.1

accompanying this statement show a decrease of about 10% in predicted ethanol concentrations. I have two questions:

- a. What are the non-motor vehicle sources? It seems surprising that there are sufficient stationary sources of ethanol that they would dominate those associated with motor vehicles.

Response: Ethanol is a commonly used as a solvent, especially in consumer products. Everyday products from mouthwash to air fresheners, and many household-cleaning products contain ethanol. The 2003 baseline inventory for a non-ethanol fuel contains about 32 tons/day of ethanol, of which 24 tons/day comes from consumer products.

- b. What is the difference between the data cited in Table 4.1 of Appendix B and Table 4.6 of the report? The former cites concentrations of ethanol, for example, of 41-45 ppb while the latter cite 78-165 ppb for the maximum 1-hour average.

Response: The data in Table 4.1 of Appendix B represent model results for an August (summertime) ozone episode day. The data in Table 4.6 are estimated annual maximum or populated-weighted concentration values. The latter tables (which is reported to OEHHA) may have higher values, particularly for primary pollutants where the maximum value typically occurs under stagnant wintertime conditions.

On page B-43, it is stated that there are large discrepancies between predicted and observed 3-hour average concentrations for the Los Angeles site but that others are of the same order of magnitude. This might be strictly correct but the differences are still factors of two or more at some non-Los Angeles sites. Rewording of these sentences might be appropriate.

Response: There is insufficient discussion of the results presented in Table 6.4. Model results and measured data also differ significantly at other sites. For example, at Anaheim, the 1,3-butadiene 3-hour average concentration was measured at 0.3 ppb, while the model predicted an extremely lower concentration, measured formaldehyde is almost twice the predicted values, and measured acetaldehyde is about three times higher than what the model predicts. At Riverside, measured benzene is almost twice the predicted value at 0600, but at 1100 the measured benzene 3-hour-average concentration is three times the predicted value. This section now included the revised discussion.

Minor Comments:

1. In the fifth paragraph of the Executive Summary (starting “It is possible that ethanol’s propensity..”), it should be made clear that this discussion refers to the charcoal canister used for vapor control on automobiles.

Response: The suggested change has been incorporated into the report.

2. The ethanol concentration in fuel is sometimes given in % by weight and sometimes in % by volume. It would be very helpful to the reader to give it in both units throughout.

Response: The suggested change has been incorporated into the main report.

3. On page 32, line 6 of Section 4.2.3.3, the end of the sentence “The results are reported in....” is missing.

Response: The text has been corrected.

4. It is not clear to me what “Upper Baseline” and “Lower Baseline” mean in Table 4.6.

Response: Upper baseline and lower baseline refer to baseline 1997 concentrations estimated under a variety of methods are discussed in Section C-3 of Appendix C. The highest estimated 1997 concentration became the "Upper Baseline" and the lowest estimated 1997 concentration became the "Lower Baseline." The estimated future year concentrations were generally made starting with the upper and lower baselines and then applying model results to account for changes from the 1997 "baseline". The procedure for estimating future year concentrations is described in Section C-4 of Appendix C.

5. In Table 6.4, the predicted acetaldehyde concentrations are given to 4 significant figures in some cases; 2 significant figures is probably more appropriate.

Response: The model results in Table 6.4 have been revised to duplicate the number of significant figures of the measurements.

D-1.3. Dr. Donald Lucas of Lawrence Berkeley National Laboratory and the University of California at Berkeley

This letter contains my review of the California Air Resources Board document titled “Air Quality Impact of the Use of Ethanol in California Reformulated Gasoline.” This reviews covers the following parts of this document and several other documents, including the following:

1. Air Quality Impact of the Use of Ethanol in California Reformulated Gasoline – Staff Report (Nov. 18, 1999).
2. Appendix A - Emissions (Nov. 10, 1998).
3. Appendix D – Responses to Scientific Peer Review and Public Comments (Nov. 10, 1999).
4. Attachment A1 – Peer Review of Organic Gas Emission Profiles.
5. Other documents mentioned and/or cited in the above reports.

My review focused on the Executive Summary and Section 3 of the main document, Appendix A, and Sections D-1, D-2 and D-4 of Appendix D.

The purpose of the study was to analyze the environmental fate and transport of ethanol in air, surface water, and groundwater (Executive Order D – 5 – 99). The analysis estimates the changes in ambient air concentrations of potentially detrimental contaminants of the exhaust and evaporative emissions components and subsequent reaction products that would result from substituting ethanol-blended gasolines for gasoline blended with MTBE.

There were few conclusions drawn directly from the part of the work reviewed here. The emissions predicted were used in modeling to calculate how the atmosphere would change as a result of increased use of ethanol in gasoline. The atmospheric results themselves are only part of environmental impact.

The predicted changes in emissions expected from using ethanol in gasoline appear reasonable, both in the direction and magnitude of the changes. With no MTBE in the gasoline, MTBE emissions should decrease to approximately zero (there may be a trace amount of MTBE in future fuels, but its concentration will be capped at 0.05% by the proposed CaRFG3 regulations). Compared with emissions expected for a 2003 fuel with MTBE, ethanol emissions will increase, with the value depending on the level of ethanol in the fuel. Ethanol containing fuels will have higher acetaldehyde emissions and could have lower levels of CO, depending on the amount of oxygenate used. Fuels without oxygen will produce more CO, but no ethanol or MTBE emissions. The predicted levels of NOx and reactive organic gases (ROG) are unchanged.

The calculations presented in this study appear to be consistent and reasonable, and are well documented. The calculations are complicated, and there are many assumptions made regarding emissions. These include the need to predict what fuel will be used in 2003, what the vehicle fleet will be, and what other emissions are significant. In this regard, it is difficult to determine exactly what the best set of assumptions should be, and how significant the results are from a statistical viewpoint. This is not to say that the results are incorrect, but that the uncertainties are large, and additional work needs to be done. The ARB recognized that the results rely on engineering judgement, and that the results need to be confirmed by the planned field measurements.

In developing the emission estimates for 1997 and 2003, the ARB made many adjustments to the profiles developed for MTBE-based CaRFG2. Changes were made for several compounds to be consistent with the fuel. Prof. Robert Harley of UC Berkeley reviewed the emission factors previously, and suggested several changes that were adopted by the ARB. I have no further suggestions. It is important to continue the early review process, as it allowed corrections to be made earlier in the process, probably saving considerable time and resources.

Response: The ARB staff agree.

Future gasoline compositions used in this study are predicted. Even though they may not be the exact formulations that will be sold in California in 2003, they are not unreasonable. The calculations in this study were performed as the new proposed Phase 3 Reformulated Gasoline (CaRFG3) regulations were being written, and both studies have similar deadlines. Since the CaRFG3 regulations may be adopted soon, the follow-up study suggested here should incorporate these changes. The timing of these two related studies made it difficult to use the information generated in the CaRFG3 regulation process, which was ongoing during the same period as this study. While better results could have been obtained by better coordinating the studies, time constraints placed on the ARB prevented this. While I do not think that the results from this study would change significantly if more time were allowed, care must be taken in balancing the need for a timely decision with the effort and time needed to produce sound scientific results.

Response: The ARB staff agree.

The effect of changing CO emissions when oxygenated fuels are used is accounted for in this study. Since CO acts as an organic compound in terms of ozone formation, it must be combined with other emissions. CO is treated here as other compounds, using the well-established and

reviewed reactivity. The ARB is consistent in their approach. Whitten (1999) suggested a higher value for the reactivity of CO, and the ARB responded in detail. While the calculations presented by Whitten appear correct, it is difficult to justify using different models and scenarios for a single species. The value of examining issues such as these should not be underestimated, and the continued input from outside experts such as Whitten should be encouraged.

Response: The ARB staff agree.

The effect of consumer commingling, where ethanol-containing and ethanol-free gasolines are mixed, produces a fuel with a higher Reid Vapor Pressure (RVP). The mixed fuel would increase non-exhaust emissions. Under current federal law, where most of the gasoline in California is required to have an oxygenate, it is likely that commingling would not be a significant problem, since all gasolines would probably contain ethanol. However, Governor Davis has requested a waiver (April 12, 1999) from the EPA, and the ARB has supported this request. If granted, commingling could be more common. The effect of a waiver on commingling should be researched in a timely fashion, and potential solutions should be examined.

Response: The ARB staff agree.

The mileage penalty that occurs when using oxygenated fuels was not considered in this study. The mileage penalty is well known from previous research, and could be added as a simple factor. The small change will probably not effect these results, but they should be included in future work.

Response: Relative to typical current CaRFG2 made with MTBE, CaRFG2 containing 2wt% oxygen as ethanol would only provide a slightly different fuel economy (change of 0.6% or less). CaRFG2 with 3.5 wt% oxygen would likely provide less fuel economy (by ~2%) than current gasoline, while a non-oxygenated CARFG2 would improve fuel economy by ~2%. However, mass emissions rate should not change in proportion to the change in fuel economy. The Predictive Model tends to force emissions to meet constant standards regardless of the oxygen content. The model is built from data on emissions versus oxygen content of gasoline with emissions measured in mass per mile, not in mass per volume of fuel. This discussion is now included in the main report.

A small number of vehicles were tested at the ARB laboratory in El Monte. Three different commercially available fuels were used, including an ethanol-blend. However, the fuels are not representative of the fuels expected to be sold in 2003, and the ethanol-blended fuel had a very low sulfur level of approximately 1ppm (the sulfur level in the fuel is known to have a significant effect on exhaust emissions). The vehicles are not representative of the fleet either in terms of vehicle number, miles driven, or fraction of emissions. Given the high cost and difficulty of this type of vehicle testing, this is a disappointing part of the study. It is not clear how the criteria for vehicle selection were made. Half of the vehicles were required to have mid-range emissions of hydrocarbons. The average model year was 1981, and only one car was Japanese. While it is important to learn how the mid- and high-emitters will perform on any new fuels, the ARB has previously reported that it is nearly impossible to test these types of cars under current testing protocols because of their non-reproducible behavior.

Response: We planned to test vehicles that contribute the most to emissions. This is not the same group of vehicles that have the highest vehicle miles traveled (VMT). While the average emission rates and test variability were higher than desired, the results are not a crucial part of our conclusions.

Running and evaporative losses were not measured directly. The composition of emissions expected was estimated in part by measuring vapor in equilibrium with the liquid fuel. Since these emissions are becoming a larger fraction of the total vehicle emissions, it is important to know these emissions, especially since material permeability and canister performance is not well understood for fuels with varying ethanol levels. The ARB has noted the limitations of their testing in this study. Their conclusions are qualitative, and they claim that they do not contradict the model profiles. Given the uncertainties the claim is probably true, but of little value.

Response: The lack of evaporative emission measurements taken on commercial fuels did not directly bear on evaluating the profiles used to represent evaporative emissions in the photochemical modeling. The modeling input profiles are gasoline composition profiles and their corresponding headspace compositions, rather than actual hot-soak and diurnal/running compositions. This was the type of data taken in the commercial fuel study. While the substitution of gasoline and headspace compositions for actual evaporative emissions introduces uncertainty, that uncertainty could not have been reduced by comparison to speciated evaporative emissions from the commercial fuels. As noted by the reviewer, those fuels cannot be viewed as typical of future MTBE-free CaRFGs.

In summary, the ARB has produced a set of emissions expected in the 2003 if ethanol replaced MTBE in California gasolines. The results are a good starting point for evaluating the environmental impact of ethanol in fuels, and provide the necessary data for further analysis. This type of modeling effort should continue, especially as the composition of the new fuels becomes more certain.

Response: The ARB staff agree.

D-1.4. Professor John Seinfeld of the California Institute of Technology

I am reporting to you on Appendix B Photochemical Modeling. (I looked at the other reports but did not read them closely.) I have reviewed the model application protocol reported in Appendix B and find it to be not inconsistent with standard practice in South Coast Air Basin photochemical modeling. Replacement of the CBM with SAPRC-97 was an important feature. The use of the model simulations in a relative sense enhances their value in looking for differences between scenarios. I have not reviewed the emissions profiles for the MTBE and ETOH cases; I assume they accurately reflect those profiles. The predicted direction of differences in O₃ and other pollutants between the scenarios can be considered to be accurate. It is noteworthy that the predicted differences in O₃ between the MTBE and ETOH cases are small. (Interestingly, this was also the case a number of years ago when comparisons between gasoline and reformulated gasoline were being made.) Assuming that the MTBE and ETOH emissions profiles and amounts are accurate, this says that other factors are governing the overall concentration of O₃, not these ingredients. One can gauge if this makes sense from the change in magnitude of emissions of gaseous products associated with MTBE and ETOH. Presumably this is the case.

Response: The ARB staff agree.

In summary, the photochemical modeling is consistent with current practice. There are no evident danger signals associated with the results. Model performance in an absolute sense could be better, but the use of simulations in a relative sense should bypass these difficulties.

As you have requested, I have read Section D-3 of the report. Gary Whitten's analysis of the effect of CO on ozone formation, as simulated in a three-dimensional model, is correct. The question, though, is not whether Whitten is correct, but what scale is being used to judge reactivity. The ARB has utilized Carter's MIR scale, which is not based on three-dimensional, multiday simulations. Most would agree that three-dimensional, multiday simulations are preferable to trajectory box simulations in assessing reactivity. This point was made by the ARB's Reactivity Advisory Committee at its last meeting. Moreover, the fact that peak ozone reactivities differ between the MIR scale and those predicted on the basis of a 3D model points not to a weakness of 3D models, but to a weakness of the trajectory model MIR simulation. That having been said, however, it is recognized that the ARB has invested in the Carter MIR scale for judging reactivity and changing lock stock and barrel over to a 3D airshed model scale is a nontrivial undertaking. The question is whether the reactivity of CO should be increased by 1.65 in the current application. The ARB response argues that in the interests of consistency they do not wish to alter the scale that has been used and that population exposure correlates better with that predicted by the MIR scale than peak ozone anyway. Short of basing all reactivities on 3D model simulations, I cannot recommend that the ARB make this one single adjustment.

Response: The ARB staff agree.

D-2. Response to Scientific Peer Review of Emission Profiles

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 similar 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 Raoult's 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 0.67 and 0.80 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.

Table 2.1. Aldehyde Emission Predictions

	<i>11% MTBE</i>	<i>No Oxygen</i>	<i>EtOH, 3.9% O₂</i>	<i>EtOH, 3.5% O₂</i>	<i>EtOH, 2.0% O₂</i>
<i>Formaldehyde</i>					
<i>rel. to 11%</i>	<i>1.00</i>	<i>.90</i>	<i>.90</i>	<i>.91</i>	<i>.95</i>
<i>MTBE</i>					
<i>rel. to 3.9% O₂</i>	<i>xx</i>	<i>xx</i>	<i>1.00</i>	<i>1.01</i>	<i>1.05</i>
<i>Acetaldehyde</i>					
<i>rel. to 11%</i>	<i>1.00</i>	<i>.96</i>	<i>2.74</i>	<i>2.33</i>	<i>1.28</i>
<i>MTBE</i>					
<i>rel. to 3.9% O₂</i>	<i>xx</i>	<i>xx</i>	<i>1.00</i>	<i>.85</i>	<i>.47</i>

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-3. Response to Public Comments

D-3.1. Public Comments on Work Plan

This section contains public comments and ARB staff responses on "ARB Work Plan for Conducting an Airborne Environmental Fate and Transport Analysis of Ethanol-Containing Gasoline" dated July 8, 1999 and "Development 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, Jim White of White Environmental Associates, Gary Z. Whitten of ICF Consulting, and Gina Grey of the Western States Petroleum Association (WSPA). The comments are paraphrased below with the ARB staff responses in italics.

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 "Development 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 sets--specifically 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)

I cannot remember hearing or seeing any mention of the CARB portion of the EtOH fate and transport analysis evaluating the impacts stemming from the consumer mixing of non-oxygenated gasoline with gasoline containing EtOH. As you know, this will create an increase in vapor pressure as the EtOH blends mix with the non-oxygenated gasoline. This phenomena is happening right now and will continue as refiners are making both non-oxygenated and EtOH

blended gasolines. This should most certainly be a part of your analysis. (White)

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 requirement 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-2. 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 "...calculate 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 "...an 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 evaporative emissions from the 10% ethanol fuel are too high. However, the close similarity of photochemical 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 episode--not 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 treatment--consequently UAM is known to predict neighborhood scale concentrations--not 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 "hot-spot" CO concentrations, which are overlaid 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-3.2. Public Comments on Reactivity of Carbon Monoxide

D-3.2.1. 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 of Parallel Products, Inc. to Steve Brisby of ARB 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 27 th	Peak Impact	August 28 th	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 contribution 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-3.2.2. Why Carbon Monoxide Grows in Importance on Multi-Day Smog Episodes

Gary Z. Whitten of ICF Consulting submitted this in a personal communication to Bart Croes of ARB on November 12, 1999.

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 NO_x-limited conditions, the mixture of smog-forming precursors can be VOC-limited during the morning and mid-day hours. Because the decay of NO_x 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 NO_x-limited conditions the addition of new free radicals can actually reduce ozone because these new radicals tend to remove NO_x 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 NO_x-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 NO_x inputs to progress towards more NO_x-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 NO_x so that “reactivity” can actually become negative under NO_x-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 NO_x) 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 NO_x-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-3.2.3. Response

The proposed regulations for Phase 3 reformulated gasoline (ARB, 1999) allow increased evaporative 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 perceived 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 O₃/g CO. Earlier work by Carter (1994) reports a slightly lower value of 0.054 g O₃/g CO. Bowman and Seinfeld (1994a) report incremental reactivities in units of ppb O₃/ppbC but a comparison of CO and CH₄ 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 CH₄

Compound	Carter (1994)	Carter (1999)	Bowman (1994a)
CO	0.054	0.066	0.005
CH ₄	0.015	0.0153	0.001

^aUnits of gO₃/g CO.

^bUnits of ppb O₃/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 O₃/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 CH₄. 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, CH₄ = 3.4, and C₂H₆ = 14.0 (Derwent, 1999). The most recent MIRs values are CO = 0.066, CH₄ = 0.0153, and C₂H₆ = 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 regarded as having a low uncertainty. Taken together, these recommend against any increase in the reactivity of CO.

D-3.3. Public Comments on Carbon Monoxide Emissions

D-3.3.1. 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 of Parallel Products, Inc. to Bart Croes of ARB 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 reversed 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 linear 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) recommendation¹. However, the fuel made without oxygen did not quite meet CBG requirements and it was a full grade in octane lower than the oxygenated fuel. The hydrocarbons for the non-oxygen fuel (according to the Predictive Model) were too high by 2.12 percent compared to flatline requirements in the CBG program. As noted above the Auto/Oil data for the non-oxygenated 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 than 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.

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.

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

D-3.3.2. 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-3.4. Public Comments on Peer Review Draft Report at ARB Hearing

This section contains the written comments and oral testimony at the public hearing of the Air Resources Board on December 9, 1999 to consider the November 18, 1999 version of the main report and versions of Appendix A through Appendix D dated November 10, 1999. The written comments are included with the ARB staff responses in italics. A transcript of the oral testimony is

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.

included in full as ARB staff addressed all public comments at the hearing. The transcript has been slightly modified to remove banter and to correct obvious transcription errors.

D-3.4.1. Written Comments

Letter from Larry Pearce of the Governors' Ethanol Coalition

On behalf of the coalition, I am pleased to submit the enclosed study, entitled *The Fate and Transport of Ethanol-Blended Gasoline in the Environment: A Literature Review and Transport Modeling*. We hope the study is helpful in your deliberations under Governor Davis's Executive Order D-5-99 and ask that the study be made part of the hearing record. The study is also available on the coalition's home page at <http://www.ethanol-gec.org/publicat.htm>

Response: This study is summarized in the main report. It focused primarily on the impact on subsurface and surface water quality and placed only cursory attention on air quality issues. The report recommended that additional information on air quality issues should be considered, including whether PAN concentrations increased with ethanol-blended gasolines. Our analysis addresses this recommendation. We have provided the report to the Lawrence Livermore National Laboratory, who is performing the water quality analysis for the State Water Resources Control Board.

Letter from Gina D. Grey of the Western States Petroleum Association

The Western States Petroleum Association (WSPA) has reviewed ARB's revised Staff Report (dated November 18, 1999) on the "Air Quality Impacts of the Use of Ethanol in California Reformulated Gasoline," and was pleased to find that several of our criticisms from earlier this year have been addressed. Our comments initially delineate the areas where revisions by staff have improved the results, and then we outline several areas where corrections and clarifications are still needed.

Most significantly, ARB has developed more realistic speciated profiles for the fuels and emissions used in the air quality modeling assessments. The striking inconsistencies observed earlier between the fuel and emissions profiles for the 2003 non-oxy fuel case are no longer evident. As a consequence of these profile changes, identical ozone results are now obtained from modeling of all four fuel cases in 2003. Previously, the non-oxy fuel case had shown slightly higher ozone levels. More reasonable benzene results are also evident, with the non-oxy fuel now showing slightly lower ambient benzene concentrations compared to the other three fuels, as would be expected based upon the gasoline benzene levels.

The emissions profiles for the ethanol fuels now include higher levels of ethanol itself, and the modeled ambient concentrations seem more believable, showing 40-60 ppb increases in ethanol compared to the baseline case. This change is now similar in magnitude to the approximate 50 ppb reduction in ambient MTBE resulting from removal of 15% MTBE from the base case fuel.

The CO emissions impacts of the four fuels considered in 2003 are also modified. Previously, staff assumed a 5% CO increase for the non-oxy fuel compared to baseline, and a 15% CO decrease for the high ethanol fuel (3.5% oxygen). In the revised assessment, ARB still uses a 5% CO increase for the non-oxy fuel, but the CO decrease from the ethanol fuel has been reduced from 15% to 7.5%. This smaller CO benefit is more consistent with our expectations.

The modified emissions profiles have also led to more reasonable specific reactivity values. Previously, emissions from the non-oxy fuel (hot-soak, headspace, and exhaust) had higher specific reactivity than did emissions from the other three fuels, although when considering the liquid fuels themselves, the non-oxy gasoline had the lowest reactivity. Now, emissions from the non-oxy fuel have reactivity as low, or lower than emissions from the other fuels.

Finally, WSPA would agree with ARB's proposal to redo certain analyses once the new mobile source emissions model, EMFAC2000, is officially released, and the Phase 3 gasoline specifications are finalized. Also, we encourage ARB to conduct a robust vehicle emissions testing program using authentic Phase 3 gasoline formulations, to eliminate certain assumptions and obtain more reliable emissions profiles.

Response: The new upper-bound modeling simulations bracket the effect of EMFAC2000. The Phase 3 regulations preserve the air quality benefits of Phase 2 gasoline, and apply equally to ethanol-blended and non-oxygenated gasolines, consideration of Phase 3 will not affect our overall conclusions. We will consider further vehicle testing as warranted.

Despite all these improvements, there are still a few minor corrections, clarifications, and other considerations:

- In describing the development of emissions inventories for modeling (page 19 of ARB's revised report) it is stated that "Stationary source emissions were assumed to be the same for all scenarios." Does this mean that no changes in stationary source emissions were applied between the 1997 and 2003 scenarios? If so, this clearly is an erroneous assumption, which would affect the air quality modeling results.

Response: Stationary source emissions were different for 1997 and 2003. The main report now clarifies that stationary source emissions were assumed to be the same for all 2003 scenarios.

- It is not clear how the annual average exposure estimates were derived for specific pollutant species. On page 26 it is stated that "For the population-weighted annual-average exposure estimates, we normally used the region-wide population-weighted average of the daily-average model results." Does this mean that only concentrations from the modeled August 26-28, 1987 episode were used? If so, wouldn't this overestimate the annual averages for many species, since this period represents a high pollution episode, rather than an average situation?

Response: The population weighted concentrations predicted by the model were not the only basis for the estimated 2003 air quality concentrations for the various fuel scenarios. The method for calculating future year air quality concentrations used both model results and 1997 base year concentrations. Basically, the relative change in the model results between 1997 and the various 2003 fuel scenarios was used to scale the 1997 baseline concentrations to the future. Details of the procedures are contained in Section C-4 of Appendix C. Regarding the question of overestimate, the procedures protect against this. For secondary dominated pollutants (e.g. acetaldehyde and formaldehyde) which may have their highest concentrations in summer or fall, annual concentrations are lower than summer concentrations, as suggested. However, for primary pollutants (e.g. CO, benzene, 1,3-butadiene, MTBE, ethanol) which have their highest concentrations in winter, annual concentrations are higher than summer concentrations.

- The approach used to estimate future-year air pollutant concentrations is unclear, and should be explained in more detail. The ARB report indicates that photochemical modeling results were used to scale the 1997 baseline results to 2003 (page 26). What is the justification for this scaling approach? How was this scaling done?

Response: The details on the procedures for estimating future year concentrations are in Section C-4 of Appendix C. The scaling approach combines model results for 1997 and 2003 with 1997 base year concentrations for the various averaging times of interest to estimate future year air quality concentrations. This scaling procedure was done for all pollutants. Special adjustments are made for primary pollutants (whose highest base year value occurred at Lynwood) and annual exposure estimates for the aldehydes (which required separate treatment of primary and secondary components). The scaling approach is justified because it provides better concentration estimates (particularly for times of the year not represented by the modeled episode), than is provided directly by the modeling results.

- As shown in Table 4.1 (page 21), NO_x emissions were assumed to be identical for all four fuel cases considered in 2003. This is inconsistent with experience and Predictive Model projections showing that NO_x emissions increase with increasing oxygen level.

Response: The Phase 2 and Phase 3 regulations require that any NO_x emission increases due to increasing oxygen content be offset by adjusting other fuel parameters in the Predictive Model.

D-3.4.2. Oral Testimony

CHAIRMAN LLOYD: Good to have a professor here. First we have Dr. Don Lucas from the Lawrence Berkeley National Lab, who was one of our peer reviewers.

DR. LUCAS: Morning, Mr. Chairman. My name is Donald Lucas. I'm a staff scientist at the Lawrence Berkeley National Laboratories. I'm a researcher in the School of Public Health at UC Berkeley. I have a Ph.D. in physical chemical from UC Berkeley. My research interests include combustion-generated air pollutants, and developing new diagnostic methods. I was an investigator on the UC MTBE report requested by Senate Bill SB 521. We reviewed previous data on the combustion byproducts of MTBE in laboratory and vehicle studies, and performed laboratory experiments and flow reactivity. I also reviewed last year's ARB report on the RVP waiver for ten percent ethanol fuels. I've also read previous studies relating to this subject and comments and reviews made by other interested parties and the subsequent responses of ARB staff. I also served as a reviewer for the reformulated gasoline regulations that will be discussed later today. The review of this work was done by four individuals, Professor John Seinfeld, Cal Tech; Professor Barbara Finlayson-Pitts of UC Irvine; Professor Roger Atkinson of UC Riverside; and myself. Each of us reviewed the executive summary and the sections relating to our areas of expertise.

My comments today are a short summary based on all the reviews and some communications we have had. However, my comments have not been reviewed or approved by the other reviewers. The predicted changes in the emissions expected from using ethanol in gasoline appear reasonable, both in the direction and magnitude of the changes. The calculations presented appear to be consistent and are well documented.

Professor Atkinson states that the findings of the report are supported by the evidence presented, indicate that vehicle exhaust emissions and their impact on ozone formation will not be

significantly affected by replacing MTBE with ethanol. The results are also consistent with previous studies, the reviews regarding the impacts of oxygenated and reformulated fuels.

Professor Seinfeld states that the photochemical modeling is consistent with current practices and there are no evident danger signals associated with the results. The model performance could be better in an absolute sense, but using the simulations in a relative sense should bypass many of the problems. It is noteworthy that the predicted differences in ozone between MTBE and ethanol cases are small.

Professor Finlayson-Pitts used the report as a good initial approach to addressing air quality impacts from the use of ethanol in reformulated fuels. Her major concern is that this report will be taken by many as the final assessment and could be cited as such in a widespread manner.

The calculations presented in the report are very complicated and there are many assumptions made regarding the emissions. The reviewers and the ARB staff recognize that the results rely on engineering judgments and that additional modeling and testing needs to be done.

There were concerns expressed about several issues. There was a large, complex report that was conducted at the same time as the Phase 3 reformulated gasoline and the EMFAC 2000 studies. They're all related and all have time constraints. The timing of these studies make it difficult to use information generated in the other reports. While I do not think the results from this study would change significantly if more time were allowed, care must be taken in balancing the need for timeliness issues with the effort and time needed to produce sound scientific results.

Professor Finlayson-Pitts and I are concerned about the potential for increased evaporative emissions. The increase could be from an increase in the RVP allowed, from commingling of fuels, decreased canister performance and/or increased permeability of the fuels. I was disappointed that the vehicle testing done in this study did not include testing of the evaporative emissions from vehicles. These issues need to be clarified as they could have significant impact on real-world emissions.

Professor Seinfeld and I agree that the ARB should not change the way it calculates the importance of CO in ozone formation. The value of examining issues such as these should not be underestimated and continued input from outside experts such as Gary Whitten and others should be encouraged. They are also a number of changes and corrections suggested by the reviewers, such as adding additional chlorine chemistry, revised rate constants and also boundary conditions. As mentioned, ARB staff has responded to these and made many changes in the report.

In summary, conclusions reached by the ARB staff appear correct and are justified by the data and analysis performed. The emissions are calculated in a consistent and defensible manner and the assumptions made in reaching the conclusion are reasonable.

Thank you.

CHAIRMAN LLOYD: Thank you very much. Questions from the board? Thank you very much also for responding, and I realize on a very short time frame on a lot of information to assimilate. Thank you very much.

By the way, the witness list is growing, so I guess somebody heard that I'm not going to keep it to five minutes, so I guess we have two more, so now we have four people.

The next one is Dr. Gary Whitten, from ICF Consulting.

DR. WHITTEN: Good morning. My name is Gary Whitten. I'm the chief scientist with ICF Consulting in San Rafael, California, here to talk about the assessment in terms of airshed modeling that was done. And I want to applaud the staff for the work that they did in the past year or even less than that. It was a lot of work and I think it was quite well done.

I agree with most of the peer review comments that the urban airshed model that was used is a good tool for assessing things on a relative basis and that the overall main conclusion that was the beginning of this was the impact of use of ethanol fuels on PAN and acetaldehyde. I believe that the comments and suggestions that I have today will not appreciably affect that in any way whatsoever. But I do believe that the results that one gets from a model such as the urban airshed model depend very strongly on the inputs that are used and the quality of those inputs. And the peer review did not comment on the fact that the initial modeling efforts were quite a bit different than the final modeling efforts. And it was not clear to me from our interactions with the staff what was done to the inputs to make these changes.

And I also agree with the peer reviewers that the impending inputs from EMFAC2000, which have now been postponed to March for full approval, could change some of the results substantially.

The main things that I wish to bring in at this point that are new are, first of all, that the speciation profiles, the representation of the gasoline components needs to, I think some more work in terms of, especially in terms of the area of aromatics. And then also wish to comment on some of the formaldehyde importance as you've been hearing already. I can talk without slides, I think.

The point I'd like to make is that the results of this modeling study have changed dramatically during the one-month period between October and November. The initial results showed a spread in ozone formation between the 3.5 or full 10 percent volume ethanol fuel and the non-oxygenated fuel, a difference of six ppb in ozone. Now, this is a phenomenal large difference. The newest results show a difference of only three-tenths of a 22 ppb between these two fields. So the fact that this change from a six ppb spread to three-tenths of a ppb spread is something that I think it needs some explanation and would like to hear what that is. A six ppb spread between these two fuels is comparable from other modeling that we've done at ICF, is comparable to removing all of the evaporative emissions from the model. So this is a large difference, six ppb. And the fact that it's diminished to only three-tenths is something that's not clear.

The next thing I'd like to talk about is higher aromatics that may be possible from non-oxygenated fuels. In 1994 there was a introduction of oxygen, the MTBE that was the beginning of the use of MTBE in the fall of 1994, and Professor Harley and his group did, I think, a seminal measurement in the Caldecott Tunnel where there was enough -- no regulations towards performance of these fuels except that they must have oxygen. And what the oil companies did was add this oxygen at about the two percent level where it was required at, the same time they reduced aromatics.

So now we're at the, if you will, the flip side of that situation where we're talking about not making appreciable changes to the regulations, but removing MTBE and in some case removing the oxygenate, and so without --it seems to me that you would expect aromatics then to go back up, because both MTBE and ethanol are very powerful octane enhancers, and this sensitivity to

aromatics and various toxins and things like that that might be involved, especially ozone, has not been addressed, I believe, in the study to date.

On the carbon monoxide issue, the point I'd like to make here is that it is a very important part of the overall ozone-forming process. The ARB staff did do a sensitivity analysis when they were looking at the three times the emissions to take into account the EMFAC 2000, and the six ppb spread then spread to 22 ppb between full ethanol fuel and the non-oxygenated fuel. And the sensitivity that they did for CO was, I think, was very good and that they set the CO the same between these two and they found that a seven ppb of the 22 ppb was accounted for by the CO. That's one-third of the difference between these fuels. And seven ppb, just a CO adjustment to make them the same, I think attests to the fact how important CO is towards the ozone-formation process.

I would add that in the analysis that we have done and commented on earlier this morning, that we also had changed boundary conditions and found that boundary condition for CO could also play a factor, and I suggest a sensitivity analysis of that be done as well. So one of the things that did occur between the six ppb spread that I told you about and the three-tenths of a ppb in the new staff analysis was a reduction in the amount of CO.

And later today in the reformulated gasoline regulations I will talk more about the amount of CO that might be adjusted. But that was one of the things that was reduced in the final analysis.

So thank you. That's my comments at this time.

CHAIRMAN LLOYD: Thank you very much, Gary. Maybe we could ask staff to respond.

MR. SIMEROTH: Chairman Lloyd, maybe I can start. The tunnel study in 1994 was done before implementation of Phase 2 gasoline vapor recovery. With that the aromatic content with gas control for 1994, premium gasolines could be found that added up to 60 percent aromatics. So putting something in to give the aromatic --or the octane and reducing aromatics is fairly logical. The Phase 2 aromatics were capped at 30 percent and the average has been around 24 or 25, so there are two entirely different situations, so the logic that oxygenates are going to cause a significant decrease in aromatics by our program doesn't hold because of the way our program is structured. There will be some shifts that it's going to be relatively minor, one or two percent.

In terms of the changes of what happened from the first draft to the second draft, at the workshop I indicated that there was some errors in the analysis and we were working on correcting. Subsequent to that statement we found what the errors were, we found that staff had simply taken the oxygenate out and grown the remaining compounds there to fill the void, so to speak, so you saw an increase in aromatics and olefins and everything else. In real life, it won't happen that way. Something will replace the oxygenate, whether it be ethanol or alkylates, and they have different characteristics than what staff assumed. Staff corrected that assumption and published the corrections. We think we're now correct and the previous one was simply incorrect.

We also corrected -- we made the same mistake on the two percent ethanol fuel as well and we corrected that one as well.

CHAIRMAN LLOYD: I think on the speciation profiles, we probably all agree that we can do better there and get those as time goes on. And again, with all due respect to Dr. Whitten, I don't think there's anybody, by the way, who's probably done more modeling runs than Gary throughout the years. He started this, pioneered a lot of the work. But I don't think probably, Gary, you would

admit it's unusual for some of the air modeling results to change, not only by the month, but probably by the day, depending on what's done there. So I think again I think we understand the issue in this case that staff has changed some of the results, but I think we understand that part of it. But clearly we will continue to refine the modeling. But I'm not sure the bottom line here is that we don't see a major show stopper for ethanol from an air quality perspective, and that's what we were trying to do in terms of the Governor's Executive Order.

DR. WHITTEN: My comments were more directed to the non-oxy fuel and that the direction of aromatics was down rather than up, and that's contrary to what we would expect.

CHAIRMAN LLOYD: Dean, I'm sure you can respond.

MR. SIMEROTH: Dr. Lloyd, I think the direction was correct and it was wrong initially, and we spent a lot of time working on that correction. We also found that we made a similar error on the two percent ethanol or 5.7 percent ethanol fuel and corrected that one as well.

DR. WHITTEN: We'll have more comments later.

CHAIRMAN LLOYD: I'm sure. Dee Dee, sorry. Ms. D'Adamo. Sorry.

BOARD MEMBER D'ADAMO: Yes. Just one other question then of staff. So initially a non-complying fuel was used and then you made a change so that you used a fuel that would comply with the proposal?

MR. SIMEROTH: It was an error made on how we were assessing what the exhaust emissions would be. And also it would have been a non-complying if we simply had done it that way, backing it back up in the liquid gasoline. I think the corrections were necessary and appropriate and are consistent with what we expect in the future under Phase 3 reformulated gasoline.

BOARD MEMBER D'ADAMO: And the problems that you saw with the first set of data disappeared once you did the run a second time with fuels that would comply?

MR. SIMEROTH: Yes. We found all the mistakes, corrected them and gave the results that you see in the report today that's been peer reviewed, and we've listed every single assumption that we've made and referenced what the source of those assumptions was.

BOARD MEMBER D'ADAMO: Great.

MR. SCHEIBLE: I just want to note that we actually identified the problem with the emissions input prior to putting out the draft report, judged that since the major results in the report about how ethanol substitution affected toxics and PAN needed as much time as possible for review, so we put that advisory in the report when it went out, noticing people that we would be revisiting that particular section.

CHAIRMAN LLOYD: Thank you. Thank you very much, Gary. Look forward to seeing you later. Next witness is Janet Hathaway from NRDC.

MS. HATHAWAY: I'm Janet Hathaway from Natural Resources Defense Council. I did want to make one just brief comment about this segment of the proceedings today. First of all, I recognize that this is an extraordinarily complex issue that the board and the staff have had to deal with in a very short time because of the Governor's order. But I do think that it's important to just pay attention to a couple of possible concerns that need further addressing, and although I know that the Water Resources Board is chiefly designated to be looking at some of these questions, I think

part of the problem that happened in our last round with RFG is having two segmented and segregated series of reviews, so I just want to draw attention to these issues and hopefully they will get resolved fully as we move forward.

One is the fact that we still don't really understand enough, I think, about the effect of ethanol blends on the environmental persistence of the other toxic compounds in gasoline. That is very problematic, precisely because we know that many of the contamination places that are most likely to see ethanol spills, places around refineries, around distribution centers, near gas delivery systems, already are contaminated with BTEX compounds, with the benzene, toluene, xylene, ethylene compounds. And because there is reason to believe that there is an effect on making those compounds more soluble, making them migrate more through soil, I just think we need to be very concerned to have those answers before we actually do wide-scale introduction of an ethylene -- I mean of an ethanol-blended gasoline in this state.

Now, many people will say, oh, well, there's no reason to worry, because other states have already done this. But there is reason to worry, because this is from the peer reviewed report. None of the states require ethanol concentrations to be measured in groundwater. So we wouldn't know, even if there were indeed problems going on. We do know from laboratory scale experimentation that ethanol can change the structure of clay lenses, which are known or at least believed to help protect our groundwater sources by sort of capping them and providing a barrier that is usually impenetrable to the usual gasoline compounds, the BTEX compounds. That can be affected by ethanol, so that's a reason for concern, in addition to the co-solvency effect, the effect of -- not melting -- the solvency that occurs that allows the BTEX compounds to move more rapidly through soil. And then finally some of the studies that have been done to date show that the hydraulic activity or the moving of the water through soils that have ethanol blends in them is increased by an order of magnitude or in some cases even two. So, again, reason just to flag that, make sure we have the answers and that we know how to respond if indeed there are changes in how gasoline and ethanol would move through soil.

Now, this is not to say at all that ethanol is something more problematic than MTBE. It is widely and, I think, probably universally acknowledged that ethanol itself will break down in soils pretty rapidly. And that is very reassuring. Whether there's air in the soil or not, ethanol is very likely to break down. The only concern here that I'm raising is the transport of other possibly even more toxic substances through our soil systems into groundwater and that we have to be very careful about. And keep in mind that we already have thousands and thousands of MTBE-contaminated sites. The effects should be looked at not just in terms of BTEX, these benzene, toluene, xylene compounds, but also in terms of the co-solvency effect that might move more of the MTBE already in the soil. Not wanting to rain on any parades or anything, I just wanted to make sure that we are very careful about this approach. I do think that the staff has been extraordinarily conscientious at looking at all the air quality impacts. But this board and I think every agency has to keep in mind the cross-media issues, because it's easy for them to sort of slide into somebody else's domain and not get fully addressed.

Any questions?

CHAIRMAN LLOYD: Thank you very much, Janet. And I think we take your comments to heart. And I hope that you passed those on to the State Water Resource Control Board, and also make comments at the October 18th first meeting of the Environmental Council. And, as you

know, Senator Bowen has made sure that we will not in the future forget cross-media, inter or intramedia interactions, as well as the Governor and Secretary Hickox.

MS. HATHAWAY: Absolutely. I'll be attending those.

CHAIRMAN LLOYD: And that's an issue. See if any board members have any comments or questions.

BOARD MEMBER C.H. FRIEDMAN: I have a quick question. Does our report explicitly raise this issue?

MR. CROES: Our report does not raise any issues on surface or groundwater impact.

BOARD MEMBER C.H. FRIEDMAN: I know we didn't investigate it, I take it, but do we point out that we -- that we raised this concern and so that it --

MR. CROES: Our report is one chapter of a three-chapter report that is going to the Environmental Policy Council. The chapter being written by the State Water Resources Control Board and their contractor, Lawrence Livermore National Lab, will completely address these issues.

BOARD MEMBER C.H. FRIEDMAN: So we say at the end, if not the beginning of our report, that this is one in three chapters?

MR. CROES: Yes.

BOARD MEMBER C.H. FRIEDMAN: And be sure to read the others?

MR. CROES: Yes.

CHAIRMAN LLOYD: Last witness on this particular item is Tom Koehler, representing the ethanol industry.

MR. KOEHLER: Good morning. Thank you. My name is Tom Koehler. I'm here today representing Parallel Products, the only current ethanol producer in the State of California. And hopefully after these and other proceedings are over, we will be joined by many others.

I'd like to just briefly touch on Janet's comments. I mean, her questions are absolutely appropriate, and I believe that that discussion has been reviewed extensively by the Water Board and a study with Lawrence Livermore Lab and perhaps, I notice there are people from the Water Board here today, they may want to just clarify issues. My understanding is that ethanol biodegrades at warp speed and in fact the water issue is not an issue.

I would like to thank staff for their work on the urban airshed modeling. I think it was a very good piece of work. Staff was extremely responsive. And I think, Dr. Lloyd, you're correct when you look at the analysis, both the previous analysis and the current analysis, what it says is that the fate and transport of ethanol gives you air quality benefits as good, if not better, than what we currently receive from the California reformulated gasoline program, which in itself is very good air quality benefits. I guess I would encourage if there's other runs to be done to include some ancillary benefits of the use of ethanol here in California, like the reduction of rice straw burning that affect on air pollution, the reduction of other potential wildfire burning that can be all turned into and will be turned into ethanol. I think that would be appropriate to include in further analysis.

I think you'll find that the use of ethanol on an air quality issue alone will provide multi benefits for the environment. Just one comment, there has been talk about the aromatic level of the

non-oxygenated gasoline versus ethanol, and I agree, Dr. Lloyd, and with Bart that these are assumptions and over time they change. I would like to point out that the non-oxygenated fuel that was actually measured by the ARB staff in the field versus the actual ethanol fuel that was measured in the field, the non-oxy had twice the amount of aromatics. So just wanted to point that out.

And lastly wanted to follow up on the peer review by Dr. Seinfeld. And in his analysis, I'll quote, Dr. Whitten's analysis of the effect of carbon monoxide on ozone formation is correct. And essentially what Dr. Whitten has been saying is the carbon monoxide is extremely important to the formation of ozone, and is in fact underrepresented by the MIR scale. Now, Dr. Seinfeld goes on to say it's not appropriate to change the MIR for CO alone, but that it would be appropriate to go back, and in fact I believe he is recommending to go back and revisit this issue, and change all of the species based upon the more accurate 3D modeling. And I would encourage the board possibly to direct staff in that direction, and that would be appropriate, would be appropriate action. I believe that's all I have.

CHAIRMAN LLOYD: Thank you very much, Tom. Any questions from the board? Mr. Calhoun.

BOARD MEMBER CALHOUN: I think Dr. Lucas made some remark, I'd like to get staff's reaction to the suggestion about changing the reactivity scale, in particular as it pertains to CO.

MR. CROES: The comments from both Donald Lucas or Dr. Lucas and Professor Seinfeld were that the -- that it would be desirable to base the reactivity scales on state-of-the-science airshed models. MIRs are currently based on models with simple physics with complex chemistry. And the reason that was done a number of years ago was because those were the models that best represented a range of conditions that you would expect around California and throughout the country.

We recognize when we adopted the reactivity scales that as we developed better information with more complex models that we would eventually go to using those as the basis for the reactivity scales. And there's been a long-term research program that has begun since the early '90s to eventually go toward that objective.

The staff feels that we aren't there yet, and I believe that the Reactivity Scientific Advisory Committee would agree with that as well, but it's something that we're going towards.

BOARD MEMBER CALHOUN: Thank you.

CHAIRMAN LLOYD: Dean.

MR. SIMEROTH: Chairman Lloyd, I'd like to indicate the liquid fuels used in the test program that ARB conducted, the total aromatics ranged from 24 percent to 28 percent in liquid fuels.

CHAIRMAN LLOYD: Okay. That range. I'd like to make two comments. One I think that Bart is correct, I think in heading towards the urban airshed model to look up the reactivity, but on the other hand, I think that's a huge exercise when you look at the fact that we still have tremendous degrees of freedom outside the chemistry when we do that. So I understand staff and the scientific community's concerns, but on the other hand I think the -- you should be congratulated for supporting a lot of Dr. Whitten's work which actually has consistently actually pushed the issue that we have to look at CO as an ozone precursor. And I think that significant strides have been made in that, and I've seen that evolve over the last ten years, and clearly as we've pushed the hydrocarbons

down in the atmosphere, then CO acting as a hydrocarbon has been recognized. So I think the investment you've made on that, we're reacting and putting that in there, so I congratulate you for supporting that work.

MR. KOEHLER: I think the environment is the winner, and the peer reviews essentially note that CO is an essential component of ozone, and I think that's an important issue to remember as we go into the next board item as well. Thank you.

CHAIRMAN LLOYD: Thank you. I think that's the last witness we have. Mr. Kenny, are there any written comments on that item?

MR. CROES: Yes. We received three letters in response to this item. The first two letters were from the Western States Petroleum Association. There's a letter dated December 3rd, which actually was addressed to Dr. Bill Vance from the California Environmental Protection Agency. And I clarified this letter with WSPA, but apparently he was commenting on the earlier draft of the report from late September. And then it's superseded by a letter dated December 7th, which is actually fairly complimentary that several of our criticisms from early this year have been addressed. And the letter primarily describes the revisions that WSPA agrees have improved the results. And then they outline four areas of minor corrections, clarifications, and we will certainly address those in the final version of the report and feel these are fairly minor issues and just explains what we did.

We also got a letter from the Governor's Ethanol Coalition signed by Larry Pearce, and it just wanted to submit a report that they funded, titled, "The Fate and Transport of Ethanol-Blended Gasoline in the Environment: A Literature Review and Transport Modeling." We had actually included a review of this report. It was one of the seven reports that we reviewed in our assessment of prior work. And the report is almost completely focused on groundwater impacts, so we have passed this report on to the State Water Resources Control Board.

D-4. References

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