APPENDIX E
REACTIVITY CALCULATIONS

Reactivity Calculations

Contents:

E.1) SUMMARY

E-1.1) Hydrocarbon Reactivity and Ozone Forming Potential

This section details reactivity assessments by staff for fuel-based emission processes for use in the 2006 Predictive Model staff report. The 1999 staff report[1] for Phase 3 RFG amendments allowed trade-offs between exhaust hydrocarbons, evaporative hydrocarbons and carbon monoxide on an ozone forming potential basis using reactivity adjustment factors. Since that report, new data from the Vehicle Surveillance Program[2] using ethanol blends have become available to staff. Maximum Incremental Reactivity (MIR) values used in calculating reactivities were also updated at the Board Hearing in 2003[3]. This section presents information on efforts on how staff calculated new reactivity adjustment factors using the updated information.

E-1.2) Maximum Incremental Reactivity (MIR)

Reactivity of an individual Volatile Organic Compound (VOC) is a measure of its potential to enhance ozone formation in the air once emitted. The effect of a VOC on ozone formation in a particular environment can be measured by its “incremental reactivity”, which is defined as the amount of additional ozone formed when a small amount of the VOC is added to the environment, divided by the amount added. A research program developed by Dr. William Carter used this concept to ‘rank’ VOCs by their incremental reactivities by assigning unique values to each VOC emitted. This scale constituted the Maximum Incremental Reactivity scale[4]. This scale was adopted by the ARB because it was determined to be the most appropriate reactivity scale to complement California's NOx control program.

The 1999 staff report developed reactivity assessments using the MIR values adopted by the Board in 1998. An update to the reactivity factors was required in response to the requirement of Resolution 00-22, which approved the 2000 rulemaking action and states that MIR values should be reviewed 18 months after the effective date of amendments and every 18 months thereafter to determine if modifications to the MIR values are warranted. This is because the chemical mechanism used to calculate the MIR values is evolving and improving as new chemical information becomes available. The updating process is meant to ensure that the ARB’s reactivity-based VOC regulations are based on the most up-to-date science.

Staff incorporated the updated MIR values approved by the Board at a public hearing on December 3, 2003. The Board approved amendments to the section 94700 of title 17, California Code of Regulations (i.e., Tables of Maximum Incremental Reactivity Values) by adding 102 new compounds with associated MIR values and updating the MIR values for 14 existing reactive organic compounds whose values had changed by at

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[1] Proposed California Phase 3 Reformulated Gasoline Regulations, Release Date: October 22, 1999

[2] Conducted by the ARB, El Monte, CA location. Additional details follow later in this section.

[3] Air Resources Board, “Initial Statement of Reasons for Proposed Amendments to the Tables of Maximum Incremental Reactivity (MIR) Values,” October 17, 2003.

[4] Carter, W. P.L., "Development of Ozone Reactivity Scales for Volatile Organic Compounds," Journal of the Air and Waste Management Association, 44, 881-899, 1994.

least 5 percent from the previous values. The 2003 updated MIR Table consists of approximately 800 chemicals or mixtures and their associated MIR values and was intended to be a comprehensive list for reactivity-based rulemakings for different source categories such as consumer products and mobile sources in California. The adopted MIR values were originally provided by Dr. William Carter at the University of California, Riverside, and peer-reviewed and approved by the ARB's Reactivity Scientific Advisory Committee.

Staff however noted that the 2003 MIR list did not contain unique MIR values for 66 compounds that were in the speciated evaporative and exhaust emissions data (total compounds ~ 190) from the Vehicle Surveillance Program. Staff consulted Research Division of the ARB which serves as the gatekeeper on all matters related to reactivity. Research Division indicated that the use of surrogates in the 2003 list would allow for 61 compounds to be assigned unique MIR values. Staff in that division also obtained values for the remaining five conjugated alkenes and alkynes (1,2-butadiene, 1,2-propadiene, 1,3-butadiyne, 2-buten-3-yne, and trans-1,3-pentadiene) directly from Dr. Carter[5] at UC Riverside. The composite updated list is referred to as the 2006 MIR list and was used to calculate average reactivities for all data sets in this report. This composite list labeled the 2006 MIR list has been provided in Appendix B and is available for review on the ARB website at:

http://www.arb.ca.gov/fuels/gasoline/premodel/pmdevelop.htm

E-1.3) Stakeholder Review

A reactivity working group with participants from the ARB, air districts and industry experts was formed to review the application of the updated MIR values to the reactivity assessments for the various emission processes impacting air quality in CA. The members of this group included:

a) Anil Prabhu from ARB
b) Dongmin Luo from ARB
c) Steve Brisby from ARB
d) Winardi Setiawan from ARB
e) Adrian Cayabyab from ARB
f) Jim Uihlein from British Petroleum
g) Cynthia Williams from Ford Motor Company
h) Gary Whitten from Smog Reyes Inc.,
i) Rory Macarthur from Chevron
j) Paul Webben from the South Coast Air Quality Management District.

Recommendations and comments from the working group members was incorporated during the whole process of computing average reactivity calculations detailed later in this section.

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[5] Personal communication with Dr. Carter, August 2006.

E-1.4) Reactivity of Emission Process from Light Duty Vehicles (LDVs)

Emissions from vehicles can be generally classified into:

1) Exhaust emissions
2) Diurnal/Resting Loss
3) Hot Soak
4) Running Loss
5) Permeation

Exhaust Emissions

Exhaust emissions include emissions generated by combustion of fuel in the engine and exhausted through the tailpipe of a vehicle. Data for use in this report was obtained from the ARB's Vehicle Surveillance Program. The purpose of the Vehicle Surveillance Programs has been to take periodic measurements of a representative sample of California fleet of in-use vehicles. Data are used to support the mobile source emissions inventory, to measure the effectiveness of the inspection and maintenance program procedures, and to monitor the life and effectiveness of emissions control equipment, among other uses. A typical Vehicle Surveillance Program lasts about two years, and tests about 300 vehicles. Vehicles are chosen randomly from registered owners living within a 25-mile radius of the Air Resources Board's test facility in El Monte, CA. Vehicles are tested using the laboratory chassis dynamometer tests used to certify new vehicles (the Enhanced CVS Test) and a test designed to more closely simulate driving in urban areas (the Unified Cycle Test). The Unified Cycle test data was chosen for use here because it is the cycle used to estimate emissions in the EMFAC mobile source emissions inventory model. Speciated data from 25 vehicles was used to calculate specific reactivities by vehicle and then averaged to obtain a fleet average reactivity. During data processing, staff noticed the presence of methanol in the speciated data and noted that the likely source of methanol was from the antifreeze and not the fuel. Staff in consultation with the reactivity work group removed this compound from each data set before calculating the specific reactivity for each data set. Details of calculating reactivities are described later in this Appendix.

Evaporative Emissions

Evaporative emissions are non-tailpipe hydrocarbon emissions and include:

a) Hot soak emissions comprised of fuel vapors emitted from a vehicle after the engine is turned off. The elevated engine and body temperature causes fuel vaporization from fuel delivery lines, purge line to the canister, gas cap, etc.
b) Diurnal emissions comprised of fuel vapors that are given off when the vehicle is at rest excluding the short periods of time which comprises the "hot soak" regime.
c) Running Loss Emissions includes emissions produced by a vehicle while it is in operation (includes vehicle at rest if engine is running).

Hot Soak and Diurnal/Resting Loss

Data for the Hot Soak and Diurnal emissions was also obtained from the Vehicle Surveillance Program at El Monte, CA. The set included speciated data sets from 25 vehicles. Specific reactivities were calculated as detailed above. As with the exhaust data set, staff removed methanol from the calculation process. Methane which was present was also removed from the process. This was because reformulated fuel does not contain any methane and the presence in the data set was attributed to contamination in the collection chamber. This step was also performed in consultation with the reactivity working group. Details of the calculations are provided in sections that follow in this Appendix.

Running Loss

The running loss reactivity used was a calculated value. This was because there is lack of testing data available on running loss emissions due to the complexity of the measurement. The running loss calculation was split into three portions: liquid, vapor, and permeation. The liquid, vapor, and permeation portions were then calculated using the speciated ethanol blended gasoline (E6) fuel from CRC E-65[6] permeation study.. Using the E6 fuel speciation, the weight percents of each compound were multiplied by the appropriate MIR value. The MIR values for each compound were then summed and a total MIR value was determined for the liquid portion of the running loss emissions. Details of the calculations are provided later in this section.

Permeation Loss

Elastomeric materials (rubber and plastic parts) allow fuel molecules to migrate via diffusion from the vehicle's fuel storage and transfer systems and constitute permeation emissions. In this report, permeation, though an evaporative process has been treated separately when used as an input in the predictive model. Average reactivity was calculated using the speciated data sets available from the CRC E-65 study and this data is available from www.crcao.org.

Table 1 below provides a summary of the average reactivities from the various emissions process detailed above. Carbon Monoxide reactivity adopted by the Board in 2003 is also provided in the table. Detailed calculations for all the various emission processes is provided later in this Appendix.

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[6] http://www.crcao.org/, "Permeation from Automotive Fuel Systems", CRC Project No. E-65, September 2004.

Table 1. Average Reactivity of Emissions from EtOH Blends

	Average Specific Reactivity (g O_3/g TOG)	Number of Observations
Diurnal Emissions	2.74	25
Hot Soak Emissions	3.12	25
Running Losses	2.73	calculated
Permeation Emissions	3.29	22
Exhaust Emissions	4.01	25
CO	0.06	Board approved value

To ascertain differences in reactivity between EtOH and the MTBE blends it replaced, staff also obtained MTBE fuel data sets from the Vehicle Surveillance Program at El Monte, CA. Appendix A provides details on the specific reactivity calculations. It was observed that differences in average reactivities between MTBE and EtOH blends for the experimentally measured diurnal, hot soak, and exhaust emissions were small, within limits of confidence for such data sets. This and the fact that the MTBE fleet tested was generally older and not representative of current fleet make-up, staff has chosen to use only the EtOH specific reactivities for use in the predictive model.

E-1.5) Applicability of Incremental Reactivity to Carbon Monoxide (CO)

As described before, the MIR scale, was first developed in 1994 by Dr. Carter and was deemed the most appropriate scale for use in regulations for California. It is calculated using a single-cell trajectory (box) model, which allows more detailed chemistry to be included in the model, a wide range of conditions to be investigated, and the reactivity of hundreds of VOCs to be calculated. However, this model lacks physical details (e.g., wind shear) as well as spatial and temporal details of emissions. In addition, the model does not include pollutant transport and mixing that may affect reactivity. For instance, the model does not take into account multi-day effects, the box model tends to under predict reactivities for the slower-reacting chemicals such as carbon monoxide (CO), ethane, and some alkanes. To address these concerns, the MIR scale was compared with 3-dimensional airshed reactivities calculated for the South Coast Air Basin and Central California and was found to correlate well with reactivities predicted through these models for selected VOCs (Martien et al., 2002[7]). Good correlation was also found in other regions of the Eastern United States (Carter, 2003[8]; Hakami et al., 2003[9]).

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[7] Martien, P.T., R.A. Harley, J.B. Milford, A. Hakami, & A.G. Russell, “Development of Reactivity Scales via 3-D Grid Modeling of California Ozone Episodes,” Final Report to Air Resources Board, May, 2002.

[8] Carter, W. P. L., “Investigation of VOC Reactivity Effects Using Existing Regional Air Quality Models,” Final Report to American Chemical Council, April, 2003.

[9] Hakami A., M.S. Bergin, and A.G. Russell, “Assessment of the Ozone and Aerosol Formation Potentials (Reactivities) of Organic Compounds over the Eastern United States,” May, 2003.

The ARB adopted a value of 0.06 for CO in the 1999 staff report. During the process leading up to this report presentation at the Board hearing in 1999 as well as after the hearing, it was suggested by some stakeholders that a different (higher) reactivity value, instead of the ARB adopted MIR value of 0.06 be used for CO, a major component of motor vehicle exhaust. The justification was that CO is a slower-reacting chemical whose reactivity is under predicted by the box model. Ideally, an airshed model should be used to calculate reactivities for all the VOC in the atmosphere so multi-day effects can be better addressed. However, it is not practical at the present time to calculate reactivities for the approximately 800 chemicals or mixtures in ARB's list of MIR values using a 3-D airshed model due to the tremendous computing resources necessary to accomplish this for all chemicals. A staff review (Luo, 2004[10]) indicated that while the MIR value of 0.06 for CO may be lower compared to those derived from 3-D airshed models for different regions, its reactivity relative to the selected chemicals studied using 3-D models is reasonably consistent in terms of rankings. Thus, the use of a different reactivity scale than MIR for CO and all other VOCs would not be expected to significantly change the relative impact of CO on ozone formation. It would therefore be inappropriate to use different reactivity scales for CO and VOCs (i.e., 3-D airshed model derived reactivity for CO and MIR for other VOCs) in the same reactivity applications such as the predictive model for fuel based emissions. At present, the MIR scale remains the best one available for scientific and regulatory applications. Thus, the MIR value of 0.06 for carbon monoxide is appropriate for the predictive model and is the one approved by the ARB Board. Additional information related to CO reactivity and correspondence between ARB staff and stakeholders on CO reactivity is provided later in this section.

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[10] Luo D.M., "Comments on 'CO Reactivity'", September 2, 2004.

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E-2) DETAILS OF REACTIVITY CALCULATIONS

Details of various emission processes

E-2.1) Permeation emissions

The data set was obtained from the CRC E-65 project and details and data sets are available from the CRC website at www.crccao.org. The study conducted tests with 10 vehicles and used one EtOH and one MTBE blend in all the 10 vehicles tested. Each data set was used to calculate a specific reactivity for that set. It included multiplying the mass of a compound with its corresponding MIR value. This was performed for all the compounds in the data set. The products were then summed and divided by the total mass of compounds in that data set. A sample calculation is shown in the Table 1 below. The first column provides species name, the second is the CAS number for that compound, the third is the experimentally measured mass of that compound in mg, the fourth is the MIR value and the fifth column is the product of the mass times its MIR. The average reactivity for this speciated data set is calculated by summing all the entries in column 5 and dividing this sum by the sum of the masses (as given at the bottom of column 3).

Table 1. Calculating Specific Reactivity from the Speciated Data Set

Column 1	Column 2	Column 3	Column 4	Column 5
Species Name	CAS #	VOC (mg)	MIR	O_3 (mg)
Benzene	00071-43-2	6.424	0.81	5.20
Methane	00074-82-8	0.549	0.01	0.01
2-Methylpropane	00075-28-5	0.694	1.34	0.93
2,2-Dimethylbutane	00075-83-2	1.199	1.33	1.59
2-Methylbutane (Isopentane)	00078-78-4	32.940	1.67	55.01
2,3-Dimethylbutane	00079-29-8	4.089	1.13	4.62
ortho-Xylene	00095-47-6	1.690	7.48	12.64
3-Methylpentane	00096-14-0	5.285	2.06	10.89
Methylcyclopentane	00096-37-7	5.738	2.40	13.77
Ethylbenzene	00100-41-4	3.575	2.79	9.97
Styrene	00100-42-5	0.061	1.94	0.12
n-Propylbenzene	00103-65-1	0.534	2.20	1.17
1,4-Diethylbenzene	00105-05-5	0.449	3.36	1.51
p-Xylene	00106-42-3	3.600	4.24	15.26
n-Butane	00106-97-8	6.863	1.32	9.06
1-Butene	00106-98-9	0.130	10.22	1.33
1-Butyne	00107-00-6	0.682	6.18	4.21
2,4,4-Trimethyl-2-Pentene	00107-40-4	0.207	8.52	1.77
2-MePentane	00107-83-5	9.176	1.78	16.33

2,4-Dimethylpentane	00108-08-7	1.321	1.63	2.15
m-Xylene	00108-38-3	11.739	10.61	124.55
1,3,5-Trimethylbenzene	00108-67-8	1.144	11.22	12.84
Methylcyclohexane	00108-87-2	1.614	1.97	3.18
Toluene	00108-88-3	47.503	3.97	188.59
n-Pentane	00109-66-0	10.984	1.53	16.81
1-Pentene	00109-67-1	0.217	7.73	1.68
n-Hexane	00110-54-3	5.789	1.43	8.28
Cyclohexane	00110-82-7	2.459	1.44	3.54
n-Octane	00111-65-9	0.391	1.09	0.43
2-Methylpropene	00115-11-7	0.246	6.31	1.55
1,3-Diethylbenzene	00141-93-5	0.278	8.39	2.33
Cyclopentene	00142-29-0	0.446	7.32	3.27
n-Heptane	00142-82-5	1.771	1.26	2.23
2,2,3-Trimethylbutane	00464-06-2	0.408	1.32	0.54
Indan	00496-11-7	0.403	3.16	1.27
2-Methyl-2-butene	00513-35-9	2.808	14.44	40.55
2,2,4-TriMePentane (IsoOctane)	00540-84-1	3.976	1.43	5.69
3,3-Dimethylpentane	00562-49-2	0.232	1.32	0.31
3-Methyl-1-butene	00563-45-1	0.639	6.95	4.44
2-Methyl-1-butene	00563-46-2	0.672	6.47	4.35
2,3-Dimethylpentane	00565-59-3	1.456	1.53	2.23
2,3,4-Trimethylpentane	00565-75-3	1.140	1.22	1.39
3-Methylhexane	00589-34-4	2.495	1.84	4.59
2,4-Dimethylhexane	00589-43-5	1.093	1.79	1.96
4-MeHeptane	00589-53-7	0.411	1.46	0.60
3-Methylheptane	00589-81-1	0.554	1.33	0.74
c-2-Butene	00590-18-1	0.180	13.22	2.38
2,2-Dimethylpentane	00590-35-2	0.457	1.21	0.55
2-Methylhexane	00591-76-4	2.488	1.36	3.38
2,5-DiMeHexane	00592-13-2	0.208	1.66	0.35
2-Methylheptane	00592-27-8	0.737	1.18	0.87
1-Hexene	00592-41-6	0.147	6.12	0.90
1-Ethyl-2-Methylbenzene	00611-14-3	0.513	6.61	3.39
1-Methyl-3-Ethylbenzene	00620-14-4	1.853	9.37	17.36
1-Methyl-4-Ethylbenzene	00622-96-8	0.908	3.75	3.41
t-2-Butene	00624-64-6	0.432	13.90	6.00
2-Methyl-2-pentene	00625-27-4	0.585	11.87	6.95
c-2-Pentene	00627-20-3	0.637	10.23	6.51
t-2-Pentene	00646-04-8	1.558	10.23	15.94

1-Methylcyclopentene	00693-89-0	0.239	13.44	3.21
2-Methyl-1-pentene	00763-29-1	0.335	5.15	1.72
2,3,5-Trimethylhexane	01069-53-0	0.301	1.31	0.39
MTBE	01634-04-4	33.333	0.78	26.00
EtCyPentane	01640-89-7	0.200	2.25	0.45
Ethylcyclohexane	01678-91-7	0.719	1.72	1.24
2,4-Dimethylheptane	02213-23-2	0.192	1.46	0.28
4-Methyloctane	02216-34-4	0.542	1.05	0.57
2,2,5-Trimethylhexane	03522-94-9	0.547	1.31	0.72
t-2-Hexene	04050-45-7	0.465	8.35	3.89
c-2-Hexene	07688-21-3	0.232	8.35	1.94
	SUM	233.879		713.86
			MIR	3.05

The above calculation procedure was used on all data sets and these were used to calculate an arithmetic average of all data sets. The average reactivity of the EtOH and MTBE blends are provided in Table 2 below.

Table 2. Average Reactivity of Permeation Emissions from EtOH and MTBE Blends

	Average Specific Reactivity (g O_3/g TOG)
EtOH Blend	3.29
MTBE Blend	3.47

E-2.2) Evaporative Emissions

Ethanol Blends

The evaporative emissions (diurnal and hot soak) data sets were from the Vehicle Surveillance Program described earlier. This facility routinely conducts evaporative and exhaust tests on available LDVs with fuel blends approved for use in CA. The data sets from El Monte were checked to ensure available data sets used EtOH summertime blends only. This provided 25 data sets that were used to calculate average reactivities for the fleet. The original raw data sets are available from the link below:

http://www.arb.ca.gov/fuels/gasoline/premodel/pmdevelop.htm

Specific reactivities was calculated for each speciated data set using a combination of the masses of each compound and its MIR value. This procedure has been described earlier in the section on permeation emissions. Any presence of methanol (a contaminant from windshield wiper fluid) in the speciated data was removed from the calculation with masses normalized after eliminating methanol. Methane, if present was also removed from the data set. This is because fuel contains only trace amounts of methane and larger amounts may be attributed to contamination from the test shed. The reactivities for each data set was then used to calculate an arithmetic average for the fleet and is given in Table 3 below.

MTBE Blends

The evaporative emissions (diurnal and hot soak) data sets for MTBE blends was also obtained from the Vehicle Surveillance Program in El Monte, CA. There were 17 data sets from vehicles with summertime blends that were used to calculate average reactivities for the fleet. The data sets are available from the link below:

http://www.arb.ca.gov/fuels/gasoline/premodel/pmdevelop.htm

Specific reactivities was calculated for each speciated data set as discussed for the EtOH blends above. As with the EtOH blends, methanol and methane if present in the speciated data set, were not considered when calculating specific reactivities for the individual data sets. The reactivities for each data set was then used to calculate an arithmetic average for the fleet and is given in the Table 3 below.

Table 3. Average Specific Reactivity of Evaporative Emissions from EtOH and MTBE Blends

	Average Specific Reactivity (g O_3/g TOG)	
	EtOH	MTBE
Diurnal Emissions	2.74	2.60
Hot Soak Emissions	3.12	3.12

Note:

For some data sets, meta and para isomers of xylene were summed together since they elute concurrently in a GC column. The relative abundances were obtained from the liquid fuel speciation data which indicated the ratio to be 80% meta to 20% para. Differences between the physical properties of the two isomers that govern their evaporation rates are small The Table below provides information for calculating a unique MIR value when the two isomers are summed together. Staff used an average MIR of 9.34 to calculate the OFP for a mixture that contains these compounds in the above indicated abundance.

CAS #	Compound	Relative abundance	MIR
00108-38-3	m-xylene	4/5	10.61
00106-42-3	p-xylene	1/5	4.25
	Composite weighted MIR		9.34

E-2.3) Running Loss Emissions

The running loss reactivity used in the Predictive Model is a calculated value. There is a lack of data available on running loss emissions due to the complexity of the measurement. The running loss calculation is split into three portions: liquid, vapor, and permeation. These portions are weighted based on EMFAC. The permeation portion does not have to be calculated because staff is using the permeation reactivity result from CRC E-67. The permeation reactivity value from the CRC E-67 was 3.29 as calculated in the earlier description on permeation emissions. Table 4 shows the running loss weightings.

Table 4. Running Loss Weightings

Emission Type	Relative Weighting
Liquid	0.5
Vapor	0.5
Permeation	0

The liquid, vapor, and permeation portions were then calculated using the speciated ethanol blended gasoline (E6) fuel from CRC E-65. Using the E6 fuel speciation, the weight percents of each compound were multiplied by the appropriate MIR value. The MIR values for each compound were then summed and a total MIR value was determined for the liquid portion of the running loss emissions.

The vapor portion of the running loss calculation was based on headspace calculations performed by Dr. Robert Harley[11] of the University of California Berkeley. Using the same E6 fuel and Dr. Harley's calculations, staff was able to determine the weight fraction of the E6 compounds found in the vapor headspace. These calculated weight fractions were then multiplied by the appropriate MIR. The compound MIR values were summed and a total MIR value was determined for the vapor potion of the running loss emissions.

The basic formula for the vapor and liquid portion of the running loss calculation is show below:

$$\text{Compound Wt\%} * \text{Compound MIR} = \text{Compound MIR Contribution}$$

and

$$\Sigma_i(\text{Compound MIR Contribution})_i = \text{Total MIR}$$

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[11] Harley, Robert A., and Coulter-Burke, Shannon C. "Relating Liquid Fuel and Headspace Vapor Composition for California Reformulated Gasoline Samples Containing Ethanol." Environmental Science and Technology Vol. 34 Nov 2000: 4088-4093

The permeation portion of the running loss uses the permeation reactivity value determined in the CRC E-65 study. The vapor, liquid, and permeation MIR values are shown in Table 5.

Table 5. Running Loss MIRs

Emission Type	MIR
Liquid	3.40
Vapor	2.06
Permeation	3.27

The final step is to multiply the liquid portion MIR, the vapor portion MIR, and the permeation portion MIR by their weightings show in Table 4 and then sum all three portions. The overall reactivity for running loss was therefore calculated to be 2.73. Specific details of the calculations are presented below.

Liquid Portion Reactivity:

Step 1: Obtain E6 speciation data from CRC E-65.
Step 2: Obtain ARB Board approved MIR list
Step 3: Merge the two lists based on CAS numbers
Step 4: Normalize compound weight percents
Step 5: Multiply normalized weight percents with MIRs
Step 6: Sum all the MIRs for a total MIR
Step 7: Liquid Portion MIR is 3.40

Vapor Portion Reactivity:

Step 1: Obtain E6 speciation data from CRC E-65.
Step 2: Obtain ARB Board approved MIR list
Step 3: Merge the two lists based on CAS numbers
Step 4: Normalize compound weight percents
Step 5: Determine molecular weights of all compounds
Step 6: Determine saturation pressure for each compound using the Wagner equation

$$\ln p_r^o = (a\,\tau + b\,\tau^{1.5} + c\,\tau^3 + d\,\tau^6) / T_r$$

where $p_r^o = p_i^o/p_c$ is reduced vapor pressure
$T_r = T/T_c$ is reduced temperature
p_c is critical pressure
T_c is critical temperature
p_i^o is the vapor pressure of the compound
$\tau = (1 - T_r)$

Values of p_c, T_c, a, b, c, and d are tabulated for numerous individual organic compounds in Appendix A of Reid et. Al (1).

Step 7: Determine the activity coefficients for each compound. Staff used the mid-grade activity coefficients for alkanes, cycloalkanes, alkenes, and aromatics in Table 2 of Harley et. al.[12] Values used are shown in Table 6.

Table 6. Activity Co-efficients for VOCs from Harley et. al.

	Activity Coefficients
Alkanes	1.7
Cycloalkanes	1.6
Alkenes	1.5
Aromatics	1.7

Step 8: Calculate ethanol activity coefficient using the following equation from Figure 3 of Harley et. Al. (2).

$$\gamma = 0.65x^{-0..87}$$

where γ = activity coefficient of ethanol
x = mol fraction of ethanol

Step 9: Determine the partial pressure of each compound using the following formula

$$p_i = \gamma_i x_i p_i^o$$

where p_i = the partial pressure
Step 10: Determine the mole fraction headspace of each compound by dividing the partial pressure of the compound by the sum of all the partial pressures.
Step 11: Multiply the mole fraction headspace of each compound by their molecular weight. This will be defined as “weightings” for explanatory ease.
Step 12: The weight fraction of the headspace is determined by dividing the “weightings” for each compound by the sum of all the “weightings”.
Step 13: Normalize the weight fraction of the headspace
Step 14: Multiply normalized weight fractions with MIRs
Step 15: Sum all the MIRs for a total MIR
Step 16: Vapor Portion MIR is 2.06

Final Running Loss calculation:

Each of the three portions of running loss are weighted based on EMFAC. Table 7 shows how each portion of running loss is weighted and is based on the CRC E-35[13] study.

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[12] Harley, Robert A., and Coulter-Burke, Shannon C. "Relating Liquid Fuel and Headspace Vapor Composition for California Reformulated Gasoline Samples Containing Ethanol." Environmental Science and Technology Vol. 34 Nov 2000: 4088-4093

Table 7. Running Loss Weightings

Emission Type	Weighting
Liquid	0.5
Vapor	0.5
Permeation	0

The final step is to multiply the liquid MIR, the vapor MIR, and the permeation MIR by the appropriate weighting as indicated in Table 7 and sum the results. This gives a running loss reactivity of 2.73.

E-2.4) Exhaust Emissions

The data sets for EtOH and MTBE were obtained from in-use testing at the laboratory in El Monte, CA. It included 25 data sets for the EtOH blends and 17 for the MTBE fuel. The data sets are available online at the site listed below:

http://www.arb.ca.gov/fuels/gasoline/premodel/pmdevelop.htm

As with evaporative emissions, average reactivities were calculated for each data set. For exhaust emissions, the actual emissions are collected per the Unified Cycle (UC) which is a dynamometer driving schedule for light-duty vehicles developed by the Air Resources Board. The UC test has a three-bag structure similar to the federal FTP-75 driving cycle but is more aggressive; it has higher speed and acceleration, fewer stops per mile, and less idle time. The test includes: Bags 1 and 2 are run consecutively, followed then by a ten minute hot soak, then Bag 3 is utilized which is a duplicate of Bag 1. Overall cycle emissions are calculated by taking actual mileage from the UC into account. Figure 1 below shows a schematic of this driving cycle.

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[13] Running Loss Emissions from In-Use Vehicles CRC Project No. E-35-2, www.crccao.org

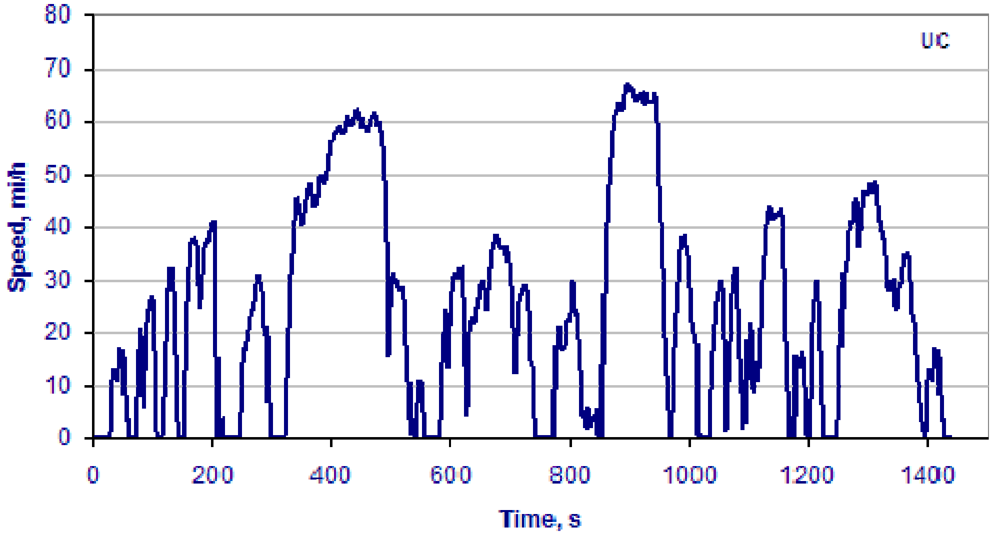

Figure 1. Schematic of the Unified Cycle for Exhaust Emissions Testing

Details of the cycle include:

Duration: 1435 seconds, Total distance: 9.8 miles (15.7 km), Average Speed: 24.6 mi/h (39.6 km/h)

Bag 1: Duration: 300 seconds, Total distance: 1.2 miles (1.9 km)

Bag 2: Duration: 1135 seconds, Total distance: 8.6 miles (13.8 km)

Based on this, average reactivities for the data sets for each set was weighted by 1.2/9.8 for bag 1 and by 8.6/9.8 for bag 2 to calculate an average specific reactivity for that data set. This was done for all data sets for a given fuel blend and the arithmetic average of the individual data sets is given in Table 8 below.

Table 8. Average Reactivity of Exhaust Emissions from EtOH and MTBE Blends

	Specific Reactivity (g O_3/g TOG)
EtOH Blend	4.01
MTBE Blend	3.93

E-2.5) Maximum Incremental Reactivities used for this report

(Updated 2006 MIR LIST)

Name	Other Names (if any)	2006 MIR	CAS number
Benzaldehyde	Phenylmethanal	0.00	00100-52-7
m-Tolualdehyde	m-Tolualdehyde	0.00	00620-23-5
Methane	Methane	0.01	00074-82-8
Ethane	Ethane	0.31	00074-84-0
Acetone	Acetone	0.43	00067-64-1
Propane	Propane	0.56	00074-98-6
N-dodecane	n-Dodecan	0.66	00112-40-3
Neopentane	2,2 dimethyl propane	0.69	00463-82-1
Methanol	Methanol	0.71	00067-56-1
N-undecane	Undecane	0.74	01120-21-4
Methyl t-Butyl Ether	Methyl t-Butyl Ether	0.78	01634-04-4
Benzene	Benzene	0.81	00071-43-2
N-decane	decane	0.83	00124-18-5
2-Methyl Nonane	2-Methyl Nonane	0.86	00871-83-0
N-nonane	nonane	0.95	00111-84-2
2-Methyl Octane	2-Methyl Octane	0.96	03221-61-2
2,2,5-trimethylheptane	2,2,5-trimethylheptane	1.09	20291-95-6
4-Methyl Octane	4-Methyl Octane	1.08	02216-34-4
2,4-Dimethyl Octane	2,4-Dimethyl Octane	1.09	04032-94-4
2,2,4-trimethylheptane	2,2,4-trimethylheptane	1.09	14720-74-2
3,3-dimethyloctane	3,3-dimethyloctane	1.09	04110-44-5
2,3-dimethyloctane	2,3-dimethyloctane	1.09	07146-60-3
2,2-dimethyloctane	2,2-dimethyloctane	1.09	15869-87-1
2,5-dimethyloctane	2,5-dimethyloctane	1.09	15869-89-3
n-Octane	octane	1.11	00111-65-9
2,2-Dimethyl Hexane	2,2-Dimethyl Hexane	1.13	00590-73-8
2,3-Dimethyl Butane	diisopropyl	1.14	00079-29-8
2-Methyl Heptane	2-Methyl Heptane	1.20	00592-27-8
3,4-dimethylhexane	3,4-dimethylhexane	1.57	00583-48-2
2,2-Dimethyl Pentane	2,2-Dimethyl Pentane	1.22	00590-35-2
2,3,4-Trimethyl Pentane	2,3,4-Trimethyl Pentane	1.23	00565-75-3
ethyne	Acetylene	1.25	00074-86-2
2,4,4-trimethylhexane	2,4,4-trimethylhexane	1.25	16747-30-1
2,6-dimethylheptane	2,6-dimethylheptane	1.25	01072-05-5
2,3-dimethylheptane	2,3-dimethylheptane	1.25	03074-71-3
3-methyloctane	3-methyloctane	1.25	02216-33-3
2,6-Dimethyl Octane	2,6-Dimethyl Octane	1.27	02051-30-1
n-Heptane	Heptane	1.28	00142-82-5
2,2,3-Trimethyl Butane	2,2,3-Trimethyl Butane	1.32	00464-06-2
3,3-Dimethyl Pentane	3,3-Dimethyl Pentane	1.32	00562-49-2
2,2-Dimethyl Butane	2,2-Dimethyl Butane	1.33	00075-83-2
2,3,5-Trimethyl Hexane	2,3,5-Trimethyl Hexane	1.33	01069-53-0
2,2,5-Trimethyl Hexane	2,2,5-Trimethyl Hexane	1.33	03522-94-9

n-Butane	n-Butane	1.33	00106-97-8
2,3-Dimethyl Hexane	2,3-Dimethyl Hexane	1.34	00584-94-1
3-Methyl Heptane	3-Methyl Heptane	1.35	00589-81-1
Isobutane	2-Methyl propane	1.35	00075-28-5
2-Methyl Hexane	2-Methyl Hexane	1.37	00591-76-4
2,2,4-Trimethyl Pentane	2,2,4-Trimethyl Pentane (Isooctane)	1.44	00540-84-1
2,2,4-trimethylhexane	2,2,4-trimethylhexane	1.25	16747-26-5
n-Hexane	Hexane	1.45	00110-54-3
Cyclohexane	Hexamethylene	1.46	00110-82-7
Propyl Cyclohexane	n-Propyl Cyclohexane	1.47	01678-92-8
4-Methyl Heptane	4-Methyl Heptane	1.48	00589-53-7
2,4-Dimethyl Heptane	2,4-Dimethyl Heptane	1.48	02213-23-2
Methyl Ethyl Ketone	Methyl Ethyl Ketone (2-Butanone)	1.49	00078-93-3
n-Pentane	n-Pentane	1.54	00109-66-0
2,3-Dimethyl Pentane	2,3-Dimethyl Pentane	1.55	00565-59-3
1,3,5-trimethylcyclohexane	1,3,5-trimethylcyclohexane	1.55	01839-63-0
3,3-dimethylhexane	3,3-dimethylhexane	1.57	00563-16-6
2,3,3-trimethylpentane	2,3,3-trimethylpentane	1.57	00560-21-4
Indan	indane	3.17	00496-11-7
1-methyl-4-ethylcyclohexane	trans 1-methyl-4-ethylcyclohexane	1.62	06236-88-0
3,5-Dimethyl Heptane	3,5-Dimethyl Heptane	1.63	00926-82-9
3-ethylpentane	3-ethylpentane	1.63	00617-78-7
2,4-Dimethyl Pentane	2,4-Dimethyl Pentane	1.65	00108-08-7
2,5-Dimethyl Hexane	2,5-Dimethyl Hexane	1.68	00592-13-2
Iso-Pentane	2-methyl butane	1.68	00078-78-4
Ethanol	Ethanol	1.69	00064-17-5
1-Dodecene	dodec-1-ene	1.72	00112-41-4
cis-1,3-dimethylcyclohexane	cis-1,3-dimethylcyclohexane	1.72	00638-04-0
trans-1,3-dimethylcyclohexane	trans-1,3-dimethylcyclohexane	1.72	02207-03-6
cis-1-methyl-3-ethylcyclopentane	cis-1-ethyl-3-methylcyclopentane	1.75	02613-66-3
Ethylcyclohexane	Ethylcyclohexane	1.75	01678-91-7
(1a,2a,3b)-1,2,3-trimethylcyclopentane	(1a,2a,3b)-1,2,3-trimethylcyclopentane	1.75	15890-40-1
trans-1,4-dimethylcyclohexane	trans-1,4-dimethylcyclohexane	1.75	02207-04-7
trans-1-methyl-3-ethylcyclopentane	trans-1-methyl-3-ethylcyclopentane	1.75	02613-65-2
cis-1,2-dimethylcyclohexane	cis-1,2-dimethylcyclohexane	1.75	02207-01-4
n-pentylbenzene	n-pentylbenzene	1.78	00538-68-1

2-Methyl Pentane	isohexane	1.80	00107-83-5
2,4-Dimethyl Hexane	2,4-Dimethyl Hexane	1.80	00589-43-5
3-Methyl Hexane	3-Methyl Hexane	1.86	00589-34-4
1-ethyl-1-methyl-cyclopentane	1-ethyl-1-methyl-cyclopentane	1.75	16747-50-5
1-Undecene	1-Undecene	1.95	00821-95-4
Styrene	vinyl benzene	1.95	00100-42-5
n-Butyl Benzene	n-Butyl Benzene	1.97	00104-51-8
trans-1,2-dimethylcyclopentane	trans-1,2-dimethylcyclopentane	1.99	00822-50-4
(2-methylpropyl)benzene	(2-methylpropyl)benzene	1.97	00538-93-2
(1-methylpropyl)benzene	(1-methylpropyl)benzene	1.97	00135-98-8
Methylcyclohexane	hexahydrotoluene	1.99	00108-87-2
3-Methylpentane	3-Methyl Pentane	2.07	00096-14-0
Ethyl t-Butyl Ether	Ethyl t-Butyl Ether	2.11	00637-92-3
trans-1,3-dimethylcyclopentane	trans-1,3-dimethylcyclopentane	2.15	01759-58-6
cis-1,3-dimethylcyclopentane	cis-1,3-dimethylcyclopentane	2.15	02532-58-3
n-Propyl Benzene	n-Propyl Benzene	2.20	00103-65-1
Ethyl Cyclopentane	Ethyl Cyclopentane	2.27	01640-89-7
Isopropyl Benzene (cumene)	Cumene (Isopropyl Benzene)	2.32	00098-82-8
Methylcyclopentane	Methylcyclopentane	2.42	00096-37-7
Cyclopentane	Cyclopentane	2.69	00287-92-3
1-Nonene	1-Nonene	2.76	00124-11-8
Ethyl Benzene	Ethyl Benzene	2.79	00100-41-4
5-methylindan	5-methylindan	2.83	00874-35-1
4-methylindan	4-methylindan	2.83	00824-22-6
2-methylindan	2-methylindan	2.83	00824-63-5
Di-n-butyl Ether	Di-n-butyl Ether	3.14	00142-96-1
Naphthalene	Naphthalene	3.26	00091-20-3
1,4-diethylbenzene	1,4-diethylbenzene	3.36	00105-05-5
1-Octene	1-Octene	3.45	00111-66-0
2,4,4-trimethyl-1-pentene	2,4,4-trimethyl-1-pentene	3.45	00107-39-1
Toluene	methyl benzene	3.97	00108-88-3
1-Heptene	Hept -1-ene	4.20	00592-76-7
p-Xylene	1,4-dimethyl benzene	4.25	00106-42-3
3,4-dimethyl-1-pentene	3,4-dimethyl-1-pentene	4.20	07385-78-6
2,4-dimethyl-1-pentene	2,4-dimethyl-1-pentene	4.20	02213-32-3
3-methyl-1-hexene	3-methyl-1-hexene	4.20	03404-61-3
2,3-Dimethyl-1-Butene	2,3-Dimethyl-1-Butene	4.77	00563-78-0
Hexanal	hexaldehyde	4.98	00066-25-1
2-Methyl-1-Pentene	2-Methyl-1-Pentene	5.18	00763-29-1
1-(1,1-dimethylethyl)-2-methylbenzene	1-(1,1-dimethylethyl)-2-methylbenzene	5.35	01074-92-6

1-ethyl-2-n-propylbenzene	1-ethyl-2-n-propylbenzene	5.35	16021-20-8
1-butyl-2-methylbenzene	1-butyl-2-methylbenzene	5.35	01595-11-5
Cyclohexene	tetrahydrobenzene	5.45	00110-83-8
Pentanal	Pentanal (Valeraldehyde)	5.76	00110-62-3
Trans-4-Octene	trans -oct-4-ene	5.90	14850-23-8
cis-2-octene	cis-2-octene	5.90	07642-04-8
2,4,4-trimethyl-2-Pentene	2,2,4-Trimethyl-3-Pentene	8.52	00107-40-4
trans-2-octene	trans-2-octene	5.90	13389-42-9
1-methyl-3-(1-methylethyl)benzene	1-methyl-3-(1-methylethyl)benzene	5.92	00535-77-3
1-methyl-4-(1-methylethyl)benzene	1-methyl-4-(1-methylethyl)benzene	5.92	00099-87-6
1-methyl-2-(1-methylethyl)benzene	1-methyl-2-(1-methylethyl)benzene	5.92	00527-84-4
1-methyl-3-n-propylbenzene	1-methyl-3-n-propylbenzene	5.92	01074-43-7
1-methyl-4-n-propylbenzene	1-methyl-4-n-propylbenzene	5.92	01074-55-1
1,3-diethylbenzene	1,3-diethylbenzene	5.92	00141-93-5
1-methyl-2-n-propylbenzene	1-methyl-2-n-propylbenzene	5.92	01074-17-5
1,2-diethylbenzene	1,2-diethylbenzene	5.92	00135-01-3
1,2,4-trimethylcyclopentane	1,2,4-trimethylcyclopentane	1.75	16883-48-0
3,3-Dimethyl-1-Butene	3,3-Dimethyl-1-Butene	6.06	00558-37-2
1-Hexene	1-Hexene	6.17	00592-41-6
Ethyl Acetylene	1-Butyne	6.20	00107-00-6
3-Methyl-1-Pentene	3-Methyl-1-Pentene	6.22	00760-20-3
2 methyl 2-propenal	Methacrolein	6.23	00078-85-3
4-Methyl-1-Pentene	4-Methyl-1-Pentene	6.26	00691-37-2
2-methylpropene	2-methylpropene	6.35	00115-11-7
Methyl Acetylene	1-propyne	6.45	00074-99-7
2-Methyl-1-Butene	2-Methyl-1-Butene	6.51	00563-46-2
1-methyl-3-ethylbenzene	m-ethyl toluene	9.37	00620-14-4
1-methyl-4-ethylbenzene	p ethyl toluene	3.75	00622-96-8
1-methyl-2-ethylbenzene	o ethyl toluene	6.61	00611-14-3
Butanal	Butanal	6.74	00123-72-8
Ethanal	Acetaldehyde	6.84	00075-07-0
Trans 2-Methyl-3-Hexene	Trans 2-Methyl-3-Hexene	6.96	00692-24-0
Trans-3-Heptene	Trans-3-Heptene	6.96	14686-14-7
Trans 4-Methyl-2-Hexene	Trans 4-Methyl-2-Hexene	7.88	03683-22-5
2,4-dimethyl-2-pentene	2,4-dimethyl-2-pentene	6.96	00625-65-0

3-methyl-trans-3-hexene	3-methyl-trans-3-hexene	6.96	03899-36-3
2-methyl-2-hexene	2-methyl-2-hexene	6.96	02738-19-4
3-ethyl-2-pentene	3-ethyl-2-pentene	6.96	00816-79-5
2,3-dimethyl-2-pentene	2,3-dimethyl-2-pentene	6.96	10574-37-5
cis-2-heptene	cis-2-heptene	6.96	06443-92-1
3-Methyl-1-Butene	3-Methyl-1-Butene	6.99	00563-45-1
1,2,4-Trimethyl Benzene	1,2,4-Trimethyl Benzene	7.18	00095-63-6
1-(1,1-dimethylethyl)-3,5-DMbenzene	1-(1,1-dimethylethyl)-3,5-DMbenzene	7.33	00098-19-1
Trans-2-Heptene	Trans-2-Heptene	7.33	14686-13-6
1,3-di-n-propylbenzene	1,3-di-n-propylbenzene	4.90	17171-72-1
Cyclopentene	Cyclopentene	7.38	00142-29-0
o-Xylene	1,2 dimethyl benzene	7.49	00095-47-6
2-propenal	Acrolein	7.60	00107-02-8
Cyclopentadiene	Cyclopentadiene	7.61	00542-92-7
1-Pentene	1-Pentene	7.79	00109-67-1
propanal	Propionaldehyde	7.89	00123-38-6
Trans-3-Hexene	Trans-3-Hexene	8.16	13269-52-8
Cis-3-Hexene	Cis-3-Hexene	8.22	07642-09-3
1,2,3,5-tetramethylbenzene	1,2,3,5-tetramethylbenzene	8.25	00527-53-7
Cis-2-Hexene	Cis-2-Hexene	8.44	07688-21-3
Trans-2-Hexene	Trans-2-Hexene	8.44	04050-45-7
4-methyl-cis-2-pentene	cis 4-methyl-2-pentene	8.44	00691-38-3
4-methyl-trans-2-pentene	trans 4-methyl-2-pentene	8.44	00674-76-0
3-methyl-trans-2-pentene	trans 3-methyl-2-pentene	8.44	00616-12-6
cis-3-methyl-2-pentene	cis-3-methyl-2-pentene	8.44	00922-62-3
3-methylcyclopentene	3-methylcyclopentene	8.65	01120-62-3
1,3-dimethyl-5-ethylbenzene	1,3-dimethyl-5-ethylbenzene	8.86	00934-74-7
1,4-dimethyl-2-ethylbenzene	1,4-dimethyl-2-ethylbenzene	8.86	01758-88-9
1,3-dimethyl-4-ethylbenzene	1,3-dimethyl-4-ethylbenzene	8.86	00874-41-9
1,2-dimethyl-4-ethylbenzene	1,2-dimethyl-4-ethylbenzene	8.86	00934-80-5
1,3-dimethyl-2-ethylbenzene	1,3-dimethyl-2-ethylbenzene	8.86	02870-04-4
1,2-dimethyl-3-ethylbenzene	1,2-dimethyl-3-ethylbenzene	8.86	00933-98-2
1,2,4,5-tetramethylbenzene	1,2,4,5-tetramethylbenzene	8.86	00095-93-2
1,2,3,4-tetramethylbenzene	1,2,3,4-tetramethylbenzene	8.86	00488-23-3
Formaldehyde	Formaldehyde	8.97	00050-00-0

Ethene	Ethene	9.08	00074-85-1
Crotonaldehyde	2-butenal	10.07	04170-30-3
trans-2-Pentene	trans-2-Pentene	10.23	00646-04-8
cis-2-Pentene	cis-2-Pentene	10.24	00627-20-3
1-Butene	1-Butene	10.29	00106-98-9
m-Xylene	1,3 dimethyl benzene	10.61	00108-38-3
1,2-butadiene	1,2-butadiene	11.53	00590-19-2
Isoprene	2-methyl 1,3 Butadiene	10.69	00078-79-5
trans-1,3-pentadiene	trans-1,3-pentadiene	10.69	02004-70-8
1-buten-3-yne	1-buten-3-yne	11.09	00689-97-4
1,3,5-Trimethyl Benzene	1,3,5-Trimethyl Benzene	11.22	00108-67-8
1,2,3-Trimethyl Benzene	1,2,3-Trimethyl Benzene	11.26	00526-73-8
1,3-butadiyne	1,3-butadiyne	10.67	00460-12-8
Propene	Propene (Propylene)	11.58	00115-07-1
1,2-propadiene	1,2-propadiene	12.16	00463-49-0
2-Methyl-2-Pentene	2-Methyl-2-Pentene	12.28	00625-27-4
cis-2-Butene	cis-2-Butene	13.22	00590-18-1
cis 3-methyl-2-hexene	cis 3-methyl-2-hexene	13.38	10574-36-4
1,3-Butadiene	1,3-Butadiene	13.58	00106-99-0
trans-2-Butene	trans-2-Butene	13.91	00624-64-6
1-Methyl cyclopentene	1-Methyl Cyclopentene	13.95	00693-89-0
2-Methyl-2-Butene	2-Methyl-2-Butene	14.45	00513-35-9
2-Butyne	2-Butyne	16.33	00503-17-3
1,4 diisopropyl benzene	1,4 diisopropyl benzene	4.90	00100-18-5
1-Methylcyclohexane	1-Methylcyclohexane	1.99	00591-49-1
4-Nonene	4-Nonene	5.23	02198-23-4
(1,2 Dimethylethyl) Benzene	(1,2 Dimethylethyl) Benzene	4.90	00098-06-6
1,3 Dimethyl Benzene	1,3 Dimethyl Benzene	10.61	00108-38-3
trans 1,2 Dimethylcyclohexane	trans 1,2 Dimethylcyclohexane	1.75	06876-23-9
Trans 2-Nonene	Trans 2-Nonene	5.31	06434-78-2
Indan	Indan	3.17	00496-11-7
3-Ethyl 2-Methyl Pentane	3-Ethyl 2-Methyl Pentane	1.57	00609-26-7
3-Isopropyl Cumene	3-Isopropyl Cumene	4.90	00099-62-7
p-Isobutyleme	p-Isobutyleme	5.35	05161-04-6
1,1-Dimethyl Cyclohexane	1,1-Dimethyl Cyclohexane	1.75	00590-66-9
cis-3-Heptene	cis-3-Heptene	6.98	07642-10-6
Methylindan	Methylindan	2.83	27133-93-3
cis-1,4 Dimethyl Cyclohexane	cis-1,4 Dimethyl Cyclohexane	1.75	00624-29-3
Allylbenzene	Allylbenzene	1.72	00300-57-2
2,2,5 trimethyl heptane	2,2,5 trimethyl heptane	1.27	02091-95-6
1,2,4 trimethyl cyclopentane	1,2,4 trimethyl cyclopentane	1.75	02815-58-9

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E-3) CORRESPONDENCE BETWEEN ARB AND STAKEHOLDERS ON CO REACTIVITY

This section presents stakeholder comments/recommendations related to CO reactivity. It also presents ARB staff response related to the issues raised by stakeholders.

Bart Croes,
ARB, Research Division Chief
P.O. Box 2815
Sacramento, CA 95812
3/3/05

Dear Bart,

CalEPA Secretary Alan Lloyd has asked us to frame a question for consideration by the Reactivity Scientific Advisory Committee. The question is this:

> Given California's combined fuel and vehicle regulations are designed to have the maximum impact at reducing the new eight hour peak ozone episodes in order to meet Federal and State ozone standards, what is the appropriate CO reactivity to use in the fuel regulation for such peak episodes or "SIP Conditions"?

Dr Whitten has undertaken a review that suggests current MIR factors are appropriate for the new Federal eight hour standard or similar SIP conditions but there exists a few exceptions with the most notable being CO.

California's CARFG3 regulations were revised in 2000 and for the first time incorporated CO as an important element in fighting ozone. The regulation will be revised over the next eight months and having the correct CO reactivity factor for maximum ozone reduction control is an essential element in assuring that the combined fuel and vehicle regulations are designed for maximum impact at reducing peak ozone periods.

Dr Whitten has written two documents, the first is an attempt at a policy framework that could accommodate exceptions to the current MIR policy. This piece is meant as only a suggestion of possible policy revisions. The second documents is a technical document highlighting CO's impact on ozone and its relative discounting in the Box Model approach compared to a Multi Day Grid approach.

The new federal ozone standards have increased the difficultly of obtaining attainment. It is critical California has all the tools necessary to help meet attainment. CO reduction is a part of the tool box and can play an important role in helping California meet the standards.

We appreciate very much your consideration of this important issue and helping determine the best CO reactivity factor under peak ozone or SIP conditions.

Sincerely,

Tom Koehler
California Renewable Fuels Partnership

CC: Dr, Alan Lloyd, Secretary CALEPA
Dr John Seinfeld, Chair RSAC

Ozone Formation Policy Concept Framework

by

Gary Z. Whitten, Ph.D.

03 March, 2005

The policy of the California Air Resources Board (ARB) for the ozone formation potential (or reactivity) of many volatile organic compounds (VOC) and carbon monoxide (CO) was established about ten years ago. During this ten year period several developments are discussed below that support a new consideration of reactivity policy. The policy changes proposed here would, for the most part, leave the present set of reactivity factors unchanged, but two fundamental changes are proposed: first it is proposed that the ideal conditions to determine reactivity would be those conditions found to be those most important to attain the ozone air quality standard, such conditions would be those used in the demonstration simulation for a State Implementation Plan (SIP); second it is proposed that a procedure be set up to accommodate exceptions to existing reactivity factors based on using a SIP demonstration simulation.

The existing policy focuses on the maximum incremental reactivity (MIR) scale developed by W.P.L Carter based on single-day photochemical simulations with a box model. A recent study by Carter et al. (2003) showed that for the most part, single-day box-model MIR factors compared well on a relative basis to reactivity factors determined for most of the important VOC using a regional multi-day grid model. Nevertheless, the Carter et al. (2003) study did show that there could be some exceptions, notably slow reacting molecules such as ethane and CO, that appeared to be more reactive in their multi-day grid-model compared to the single-day box-model-based MIR factors. Also a study by Whitten et al. (2003) showed that using a SIP demonstration simulation, the slow-reacting molecule n-bromopropane could be much less (if not negative) in reactivity compared ethane from what was predicted by the MIR-type box-model method.

Precedence for starting with MIR factors, but making final “reactivity based” rulings based on episodic grid-model simulations, is found in both U.S. EPA decisions (e.g. 66 FR 37156, 17 July, 2001) and California ARB decisions such as the Reactivity Adjustment Factor (RAF) for methanol-based fuel (i.e. M85). In the U.S. EPA case, a 0.3 psi RVP volatility wavier was granted for the Chicago area for using 10 volume percent ethanol blends in Federal reformulated gasoline. Initially, at the suggestion of ARB, the EPA considered granting only a 0.2 psi RVP waiver based on MIR factors used in the California Predictive Model. After studying several grid-model studies of the relationship of CO to mobile VOC towards the formation of ozone under episodic conditions used for SIP consideration, the EPA concluded that on a per ton basis, mobile VOC was only 15 times more effective than mobile CO emissions towards making ozone. The MIR relationship implies a ratio of 46 to 1 rather than 15 to 1. The higher reactivity for CO implied by the grid-model studies then led the EPA to increase the waiver to 0.3 psi RVP in their final decision.

The ozone precursor conditions for the existing MIR scale involve high nitrogen oxide (NOx) concentrations to establish what is commonly referred to as a strongly VOC-limited condition. The NOx levels are adjusted in Carter’s box model simulations to produce the largest change in ozone for an incremental change in the model's base urban-like mixture of VOC. Under such conditions, an incremental VOC reduction can be most effective towards reducing the simulated ozone concentrations in the box model. These conditions could also be characterized as free radical-limited, because VOC are rated high in reactivity if they decay rapidly to secondary products that, in turn, photolyze to give free radicals. CO has a low reactivity relative to typical VOC under such conditions partially because CO decay does not lead to secondary free radical production. Conversely, n-bromopropane decay leads to some bromine radicals that under high NOx/low ozone conditions act similarly to the free radicals from VOC, but under high ozone/low NOx conditions bromine destroys ozone.

At the other end of ozone formation spectrum the very lowest NOx concentrations can lead to NOx-limited conditions, where reductions in NOx become the most effective towards further reducing ozone concentrations. Under such conditions the production of secondary free radicals contributes to NOx loss. Hence, CO becomes more important <u>relative</u> to typical VOC because the lack of secondary free radicals from CO decay becomes an asset rather than a liability to higher reactivity when making comparisons between typical VOC and CO. Although both VOC and CO do become less important than NOx at the limit where NOx levels are too low to sustain further ozone formation, there exists a large range of intermediate conditions where both VOC (including CO) and NOx controls can be effective for reducing ozone. Ozone episodes, such as those used in SIP attainment demonstrations typically fall into this intermediate range where both VOC (including CO) and NOx control are effective.

Ten years ago it was shown that the MIR box-model scale was close to a VOC reactivity scale developed using a photochemical grid model measuring population exposure to ozone concentrations above an air quality standard. Thus, the policy to use the MIR scale was justified first because it related to population exposure to high ozone concentrations and second because this scale, by definition, related to conditions where VOC was most effective towards reducing ozone. In reality, the typical regions that had high NOx concentrations were close to where most ozone precursors were emitted and where population densities were likewise the highest. That is, the high NOx conditions in the box model coincided with the high population density areas seeing the onset of problematically high ozone concentrations.

A complementary part of the ARB policy for VOC reactivity was to also control NOx so that ozone could be reduced in regions far downwind, which typically become NOx-limited. That is, the full policy covered VOC reductions at the point where ozone was beginning to be problematically high and it covered NOx reductions where ozone had stopped forming due to lack of NOx.

During the last ten years several things have happened that now pose a rationale to consider revisions to the policy . First of all, the U.S. EPA has changed the national air quality standard for ozone from a 1-hour at 125 ppb to an 8-hour standard at 85 ppb. This level of ozone is near the California 1-hour ozone standard and is consistent with the level of ozone previously used to determine the onset of ozone exposure. Part of the reasoning the U.S. EPA has used for this new 8-hour standard is to make the new standard relate more to population exposure than was possible under the older 1-hour standard. A second thing that has happened in the last ten years is that the 1-hour ozone peaks seen in urban areas have come down significantly in concentration and these peaks are now seen further downwind from the urban core areas of high emissions and high population density. That is, the coincidence has been perhaps lost where high population density and high NOx concentrations more closely matched the MIR condition of the Carter box model.

Thirdly, it can be argued that the cost and inconvenience of using multi-day grid models has greatly diminished such that single-day box models are rarely in use today. Moreover, the focus of VOC and NOx controls has become much more directed towards the demonstration of ozone attainment for a State Implementation Plan (SIP). That is, a VOC reactivity policy could now more easily account for how it may help or hinder ozone attainment and this accounting would be accomplished by evaluating VOC reactivity using a grid model as set up to show attainment in a SIP. The conditions set up in the old box model simulations may no longer relate to the conditions found in a SIP attainment demonstration simulation using a grid model.

A fourth thing that has happened in the last ten years is that photochemical grid models have begun to show that peak ozone concentrations are neither VOC-limited nor NOx-limited, but respond significantly to either pollutant type. Thus, the problematic concentrations of ozone neither begin near high population densities under high-NOx conditions nor end far downwind under low-NOx conditions. The problematic ozone concentrations are reached under intermediate conditions which are neither fully VOC-limited nor fully NOx-limited. As hinted above CO becomes a more important ozone precursor relative to VOC under these intermediate conditions where peak ozone concentrations respond significantly to both VOC (including CO) and NOx emissions.

Ironically, some information that show this progression of CO reactivity increase relative to typical VOC has actually been around for ten years. Carter (1994) published a progressive series of reactivity factors. This series of three reactivity sets (MIR, MOIR for maximum ozone, and EBIR for equal molar benefit) were developed by reducing the NOx inputs in his box model to progress towards more NOx-limited conditions. Others, including Carter, have noted that the three sets of factors in this series show surprisingly similar relative reactivities between the various typical VOC. This series shows that the reactivity of CO consistently increases relative to typical VOC as the series (with reduced NOx) progresses.

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 for this table to be representative of various types. In the last two columns the percent increase of CO reactivity ratio to each individual VOC is given relative to the original MIR ratio of CO relative to each VOC. It is seen that the individual relative reactivity of CO consistently increases relative to each VOC as the series progresses toward more NOx-limited conditions. It is perhaps coincidental, but the average increase in CO reactivity seen in UAM simulations (Carter et al., 2003, and Whitten, 1999 and 2001) 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 of CO relative to average VOC in both multi-day airshed episodes and in the Carter progressive series of relative reactivity factors.

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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

Ozone Formation Potential of Carbon Monoxide

by

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03 March, 2005

While not a volatile organic compound (VOC), carbon monoxide (CO) does react similarly to VOC with hydroxyl radicals (OH) to produce peroxy radicals leading to ozone build-up under smog-like condition. Therefore, CO is a VOC-like compound that is a smog precursor. The National Academy (NRC, 1999) estimated that

"CO in exhaust emissions from motor vehicles contributes about 20% to the overall [VOC plus CO] reactivity of motor-vehicle emissions."

In the latest version of its Predictive Model, the California Air Resources Board (ARB) has incorporated a VOC-equivalence credit for the ability of high oxygen-containing fuels to reduce CO emissions. Both the NRC estimate of 20 percent contribution and the VOC-equivalence credit used by the ARB utilize MIR (maximum incremental reactivity) factors developed by W.P.L Carter (1994). However, the U.S. EPA (2001) has also provided a VOC-equivalence credit for CO reduction using ethanol blends in Federal reformulated gasoline (RFG) for the Chicago-Milwaukee area. In this case the EPA rejected its initial intension to use the MIR-based approach, which had been suggested by the California ARB. Instead the EPA decided on adapting grid-model results that led to a 15 to 1 ozone-forming equivalence between mobile VOC and CO emissions on a weight basis. The MIR-based factors used in the ARB's Predictive Model lead to a 47 to 1 ratio between exhaust VOC and CO. Combined exhaust and non-exhaust mobile emissions as used in the Predictive Model[14] would lead to a ration of 40 to 1. Even accounting for the possibility that the EPA's 15 to 1 ratio might have included some methane (EPA's MOBILE model estimates total VOC, not reactive VOC) while the Predictive Model does not, it is clear that there is a significant difference in the

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[14] The relative mass emissions used in the Predictive Model are 0.896, 0.07, and 0.034 for CO, exhaust VOC, and evaporative VOC, respectively. These mass emissions fractions can be found in the Predictive Model at cells X80 to X84 of worksheet B. They are consistent with the mass fractions of 0.899, 0.066, and 0.035 for CO, exhaust and evaporative VOC, respectively, obtained from the total tons per day values of 4995, 365.9, and 195.05, respectively given in Table 3 of ARB (1999).

Ozone forming potential or VOC reactivity values used in the Predictive Model are 0.021, 1.0, and 0.676 for CO, exhaust VOC, and evaporative VOC, respectively. The reactivity value for CO is located in the Predictive Model at cell E21of worksheet D. The exhaust reactivity used is defined as 1.0 The average evaporative reactivity of 0.676 is found by combining the relative mass emissions and reactivities from diurnal resting losses (0.0101mass fraction, 0.65 reactivity), hot soak emissions (0.0082 mass fraction, 0.86 reactivity), and running losses (0.0157 mass fraction, 0.6 reactivity). These evaporative-related quantities are located between cells D15 to E17 on worksheet C of the Predictive Model.

importance of CO emissions between these two approaches relative to mobile-VOC emissions.

Recent studies of CO reactivity --- Whitten (1999, 2001) used grid-modeling for three major cities (South Coast, Chicago, and New York) that concludes the maximum increment reactivity (MIR) approach appears to under-predict the importance of CO relative to mobile VOC emissions.

The reactivity of CO has also recently been studied by Carter et al. (2003). Their results for the southern seaboard part of the United States appear to be higher the modeling results for Chicago, Los Angeles and New York results discussed here from Whitten (2001). In particular, the Carter et al. (2003) study clearly shows that their regional grid-model approach showed higher apparent CO reactivity relative to MIR-like EKMA box-model estimates. Such was not the case for most of the typical urban VOC studied by Carter et al. (2003). This is verified by the following quote from page 56 of Carter et al. (2003), under the topic heading “Comparison of Regional and EKMA Relative Reactivities”:

> “For most model species the EKMA results are surprisingly close to the comparable regional relative reactivity metrics given the significant differences in the types of models and scenarios employed.…. However, there are some consistent differences in EKMA vs. regional relative reactivities for certain model species. Perhaps the most significant is the consistent bias for the EKMA scales towards predicting lower relative reactivities for the slower reacting species, specifically CO, ethane and to a lesser extent PAR.”

Moreover, the report of Carter et al (2003) shows that the Carbon Bond mechanism used in their study gives a lower value (i.e. 0.051) using the box-model approach, than the SAPRC mechanism used to get the 0.07 value used in the Predictive Model.

Another study by Martiens et al. (2002) also has places were multi-day or other conditions such as going from VOC-limited to NOx-limited conditions do show higher reactivity for CO relative to other VOC. For example, in Figure 5.5 of Martiens et al. (2002) the reactivity of CO is seen to jump much closer to those of other VOC when changing from NOx to VOC-limited conditions. However, there may be a misprint in the Martiens et al. (2002) report which reverses the labels for its Figure 5.5, since it is the opposite of what would be expected from Table 1 here (see below). In the South Coast Martiens et al. (2002) also show results in their Table B.1 of Regional MIR from 8 sites. The average of these 8 sites can be computed to be 0.0412, which is 38 percent higher than the box-model value they show for comparison. Further, the average for an important VOC, say m-xylene for example, is some 6.6 percent less than the referenced box-model MIR value. Hence, other studies (e.g. Martiens et al., 2002, used here) apparently do show an enhanced CO reactivity relative to typical VOC for episode conditions. However, these other studies appear to not have focused on such results like Carter et al. (2003) or Whitten (1999 and 2001) and extracting the information on the relative reactivity of CO to other VOC is not often as easy or so clearly evident.

Another point is that the reactivity of CO can be seen to dramatically increase relative to other VOC as NOx is reduced. Carter (1994) developed a series of reactivity factors. The series of three reactivity sets (MIR, MOIR for maximum ozone, and EBIR for equal benefit) were developed by reducing the NOx inputs to progress in the direction of more NOx-limited conditions. Others, including Carter, have noted that the three sets of factors in this series show surprisingly similar relative reactivities between the various VOC or the base ROG mixture. However it may not be well known that this series of three reactivity scales shows that the reactivity of CO consistently increases relative to average VOC as the series (with reduced NOx) progresses.

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 commonly seen in urban atmospheres. In the last two columns the percent increase of CO reactivity to each VOC is given relative to the MIR factor of CO relative to each VOC. It is seen that the relative reactivity of CO consistently increases relative to all VOC as the series progresses toward more NOx-limited conditions. It is perhaps coincidental, but the average increase in CO reactivity seen in UAM simulations (Carter et al., 2003, and Whitten, 1999 and 2001) 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 <u>relative</u> to other VOC under multi-day airshed episodes and in the Carter progressive series of reactivity factors.

It should also be noted that the EBIR scale of Carter (1994) for "equal benefit" between NOx and VOC is for moles not weight. On a weight basis the base VOC is still seen to be about 3 times more effective than NOx. Hence, the EBIR scale is still not out of the VOC-limited condition that the South Coast is famous for. Whitten (1999) reports that the SIP condition used to study mobile source reactivity showed that mobile VOC was 8 times as effective on a weight basis as NOx for generating peak ozone. That is, the condition used the 1997 SIP was apparently not far from that of the Carter EBIR scale.

Table 1. Reactivity Relationships from Carter (1994a) and Percent of CO Reactivity Increases Relative to Each VOC Reactivity.

Compound	MIR	MOIR	EBIR	% MIR <u>to MOIR</u>	to <u>EBIR</u>
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

Finally, there is also a fundamental scientific reason to explain a higher ozone-forming potential for CO relative to common VOC as NOx is reduced and becoming scarce during the afternoon of an episode day (a typical condition as ozone is peaking). The reason is that CO can become more reactive (relative to typical VOC) is that its chemistry does not lead to net new radicals at a time when radials are also driving NOx to lower and lower levels. Conversely, in the mornings of urban areas when more than enough NOx is present (which is also consistent with the Carter MIR scale conditions), the generation of new net radicals (e.g. from typical VOC decay products) helps accelerate the rate of ozone formation, which is why CO (without those extra radicals) is then less reactive than typical VOC.

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Predicitive Model issues on CO

by

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Data clearly show that fuel oxygen does indeed reduce tailpipe carbon monoxide (CO) emissions from tech 5 vehicles. This new data combined with a proposal to update CO reacitivity factor should give confidence in adjusting the models to reflect oxygen's role in reducing CO emissions from Tech 5 vehicles. Thus, there will be significant CO reductions available to offset the impact of permeation emissions associated with the use of ethanol fuel.

CO reductions as an offset to permeation emissions

A trade-off of CO emissions for permeation is built into the California Reformulated Gasoline (CaRFG) regulations. This "trade-off" was implemented to encourage the use of non-oxygenated RFG fuels. The implied "trade-off" was for on-road emissions, but obviously there would be a non-road impact as well because fuel oxygen is the only fuel property known to reduce exhaust CO (EPA, 2002).

At the time the regulations were finalized there were uncertain estimates of permeation emissions associated with the use of ethanol. California RFG uses the Predictive Model, a statistically based model similar to the Federal Complex Model. However, in the California Predictive Model the base fuel is a so-called flat-line reformulated fuel with 2 weight percent oxygen. To be a certified CaRFG fuel the Predictive Model must show that the candidate fuel performs as well as the flat-line fuel for reactivity-weighted VOC, NOx, and toxics. If the candidate fuel has more oxygen than the flat-line 2 weight percent a reactivity-weighted VOC credit is added based on CO. However, for fuels with less oxygen than 2 weight percent there is no debit assigned. This inconsistency in approach was explained primarily due to the projected increases in permeation emissions associated with ethanol.

For non-oxy fuels an on-road increase due to CO increases in equivalent volatile organic compound (VOC) emissions of 18 tons per day can be computed using the assumptions built into the Predictive Model (details are given below). This on-road estimate uses the latest summer statewide tons of (gasoline-related) mobile carbon monoxide CO emissions of 7227 tons per day projected for 2005 that are available from the ARB website: http://www.arb.ca.gov/app/emsinv/ccos/fcemssumcat_query.php.

The latest gasoline non-road CO inventory for summer 2005 is 2823 tons per day. The U.S. EPA recommends (EPA, 2002) that 2-weight percent oxygen gasoline fuel can reduce non-road CO emission by 13 percent, which would be 367 tons of CO reduced. The non-road exhaust VOC-equivalent to this amount of CO reduction would then be about 7.7 tons per day (using reactivity values in the Predictive Model).   The combined on and non-road total “trade-off” would then be nearly 26 tons per day of exhaust VOC equivalent for 2005.

Details of trade-off calculation

The reduction of carbon monoxide from fuel oxygen is only partially recognized in the existing CaRFG regulations. For fuels containing oxygen greater than 2 percent by weight, a credit is given in the Predictive Model for volatile organic compound (VOC) emissions. This credit is derived from an assumed 5.93333 percent reduction of carbon monoxide emissions per weight percent of fuel oxygen[15]. For fuels with oxygen less that 2 percent, no debit is assessed for potential CO increases over the baseline fuel (which contains 2 percent oxygen by weight). This disparity is, therefore, a recognized trade-off between a potential VOC-like increase from the non-oxygenated fuels against uncertain permeation increases from the use of ethanol.

As discussed by the National Academy (NRC, 1999) CO is an ozone precursor similar in effect to volatile organic compounds (VOC). In their report the National Academy estimated that

“CO in exhaust emissions from motor vehicles contributes about 20% to the overall [VOC plus CO] reactivity of motor-vehicle emissions.”

The Predictive Model uses built-in reactivity and relative emissions estimates that give a CO contribution of 16.8 percent, which is a little lower than this NRC estimate of 20 percent. The relative mass emissions used in the Predictive Model are 0.896, 0.07, and 0.034 for CO, exhaust VOC, and evaporative VOC, respectively[16]. Ozone forming potential or VOC reactivity values used in the Predictive Model are 0.021, 1.0, and 0.676 for CO, exhaust VOC, and evaporative VOC, respectively[17]. When the weight fractions and reactivity terms are combined it is seen that 16.8 percent of the total ozone comes from CO, 20.6 percent comes from evaporative VOC, and the rest or 62.6 percent comes from exhaust VOC. Thus, the CO contribution is nearly as much (82 percent) as the evaporative VOC contribution to ozone formation.

The “trade-off” VOC estimate of 18 tons per day exhaust VOC equivalents is based on the latest total summer CO emissions for 2005 of 7227 tons per day taken from ARB website (see above). As noted above the Predictive Model uses 5.9333 percent CO reduction per percent oxygen in the fuel. A non-oxygenated fuel would then have 11.87

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[15] This value of 5.93333 can be found in the final version of the Predictive Model (16 June, 2000) at cell D21 of worksheet D.

[16] These mass emissions fractions can be found in the Predictive Model at cells X80 to X84 of worksheet B. They are consistent with the mass fractions of 0.899, 0.066, and 0.035 for CO, exhaust and evaporative VOC, respectively, obtained from the total tons per day values of 4995, 365.9, and 195.05, respectively given in Table 3 of ARB (1999).

[17] The reactivity value for CO is located in the Predictive Model at cell E21of worksheet D. The exhaust reactivity used is defined as 1.0 The average evaporative reactivity of 0.676 is found by combining the relative mass emissions and reactivities from diurnal resting losses (0.0101mass fraction, 0.65 reactivity), hot soak emissions (0.0082 mass fraction, 0.86 reactivity), and running losses (0.0157 mass fraction, 0.6 reactivity). These evaporative-related quantities are located between cells D15 to E17 on worksheet C of the Predictive Model.

percent more CO emissions than the 2-weight percent oxygen baseline fuel. If this baseline fuel lead to 7227 tons CO per day in 2005, the non-oxygenated fuel, would then lead to 858 more tons CO emissions per day. The Predictive Model uses a reactivity value of 0.021 for the weight of VOC that would produce the same amount of ozone as an equivalent weight of exhaust VOC. Thus, 18 tons (i.e. 0.021 X 858 = 18) is the equivalent exhaust VOC that should produce the same amount of ozone as the 858 tons of CO that a non-oxygenated fuel would cause to be increased over the baseline fuel (using 2 percent oxygen).

Consideration of New Data

Since the formulation of the Predictive Model new data and information has become available in three areas relevant to the estimation of the VOC "trade-off" given to encourage non-oxygenated CaRFG over the fear of permeation emissions from the use of ethanol: (1) the reduction of CO from new (Tech 5) vehicles has been measured to higher than the value of zero used in the Predictive Model; and (2) the reactivity of CO has been estimated to be higher than used in the Predictive Model.

(1) New Tech 5 data In the existing Predictive Model the newest vehicles (Tech 5) are assumed to have zero CO reduction from fuel oxygen. This statement is based on the apparent derivation of the overall fleet CO reduction of 5.9333 per percent fuel oxygen noted above. Such a derivation is given in Table 5 of ARB (1999). In that Table 5 the reduction from 1 percent change in fuel oxygen is estimated to be 296.44 tons per day CO. In Table 3 of ARB (1999), it is shown that the emissions of CO for 2005 are estimated to be 4995 tons per day in California, which implies a 5.93 percent reduction of CO from a 1 percent change in fuel oxygen. In Table 5 of ARB (1999) the CO reduction from model years 1996 to 2005 (Tech 5) is shown to be zero from a 1 percent increase in fuel oxygen.

A new study shows that Tech 5 vehicles appear to reduce the CO emissions by 7.5 percent per fuel oxygen percent (Alliance, AIAM, Honda, 2001). The new study was "performed at the request of CARB in conjunction with the MTBE-ban and new CBF3 [CaRFG] regulations." However, the results were not available in time to be codified in the new Predictive Model. Also there appears some to be some confusion on how these new results might be incorporated because the database for the Predictive Model used the older federal test procedure (FTP) while the new study used the newer USO6 procedure. In Table 5 of ARB (1999), an attempt is made to relate FTP data to newer tests that involve aggressive driving; a factor of 2.8 was incorporated into the CO reduction on top of the FTP results. For the present case the reductions for Tech 5 will be used without this extra 2.8 factor.

Table 3 of ARB (1999) shows CO emissions in 2005 to be 2071 tons per day from Tech 5. A 7.5 percent reduction of these would be 155.3 tons per day. When added to the old Table 5, ARB (1999), total of 396.44 tons, the new total would be 451.8 tons, which compared to the total emissions of 4995 given in Table 3 then implies a new CO reduction rate of 9.04 percent per fuel oxygen percent. This new estimate for CO reduction leads directly to an on-road "trade-off" tonnage of 27.4 tons equivalent exhaust reactivity-weighted VOC (i.e. 18 X 9.04 / 5.93 = 27.4). The non-road would still add an additional 7.7 tons VOC to give 35 tons total VOC "trade-off."

(2) New reactivity of CO --- Whitten (2001) used grid-modeling for three major cities (South Coast, Chicago, and New York) that concludes the maximum increment reactivity (MIR) value for CO should be 0.12 tons ozone per ton of CO emitted instead of the 0.07 value used by the California Air Resources Board in developing the Predictive Model. The MIR of 0.07 value was also used by the National Academy noted above to estimate the 20 percent contribution of CO to the total ozone formed from mobile VOC and CO. A higher MIR for CO also leads by itself directly to a higher VOC "trade-off" tonnage of 30.9 tons per day of reactivity-weighted VOC (i.e. 18 X 0.12 / 0.07 = 30.9). Combining the new Tech 5 reduction data just discussed above with this new MIR for CO leads to an on-road "trade-off" estimate as high as 47 tons per day of reactivity-weighted (as exhaust) VOC. Using the 2005 non-road impact with the new reactivity factor of 0.12, brings the non-road estimate up to 13.2 tons per day extra "trade-off," giving a combined on- and non-road total VOC "trade-off" of over 60 tons per day.

Additionally, the use of the higher MIR estimate for CO raises the base ozone contribution of CO from the 16.8 percent noted above using the old MIR for CO up to 25.6 percent of the total combined VOC and CO related ozone using the newer MIR for CO. It is also interesting to note here that the evaporative contribution is then reduced to only 18.4 percent. That is, the CO contribution to ozone appears to be greater (by 40 percent) than from evaporative VOC emissions.

The reactivity of CO has also recently been studied by Carter et al. (2003). Their results for the southern seaboard part of the United States are even higher the modeling results for Chicago, Los Angeles and New York results discussed here from Whitten (2001). Carter's study shows on a regional scale the highest ozone concentrations (on both the 1-hour and 8-hour) are formed from CO at the rate of 0.17 to 0.25 tons ozone per ton CO and clearly well above the previous box-model estimate of 0.07 tons ozone per ton CO used in the Predictive Model. Moreover, the report of Carter et al (2003) shows that the Carbon Bond mechanism used in their study gives a lower value (i.e. 0.051) using the box-model approach, than the mechanism used to get the 0.07 value used in the Predictive Model. Thus, the use of the 0.12 reactivity value here (and described in Whitten, 2001) is considered conservative.

All of the above estimates compare non-oxygenated fuel with 2.0 weight percent oxygen. However, ethanol can be blended up to 3.5-weight percent oxygen (or 10 volume percent ethanol). At these higher levels permeation impacts[18] and volatility impacts of ethanol are not significantly increased over the impacts from using ethanol at the 2.0 weight percent oxygen level. Yet the benefits of ethanol continue to increase. Hence, the "trade-off" in equivalent exhaust VOC tons per day for the CO reduction lost by using non-oxygenated fuel will rise accordingly. That is, for 10 volume percent ethanol blends compared to non-oxygenated fuel in 2005, the on-road CO effect could range from 31.5 tons VOC using the existing Predictive Model assumptions up to over

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[18] For example the EPA notes "the permeation rate of fuel through HDPE is fairly insensitive to the amount of alcohol in the fuel." EPA420-R-02-022, September 2002.

82 tons VOC per day using the new Alliance data for recent and future vehicles and the conservative (i.e. Whitten, 2001)[6] estimate for the increased reactivity of CO. For 10 percent ethanol blends the non-road "trade-off" could be as high as 23 tons for a combined on- and non-road estimate over 100 tons VOC per day.

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On 2 September, 2004, Dr. Dongmin Luo of the Research Division of the California Air Resources Board, prepared a brief critique of a document entitled “CO Reactivity”, prepared by Whitten dated 24 March, 2004. Three issues raised in the Whitten document were responded to by Dr. Luo. Listed below are comments on the ARB responses.

1. The CO reactivity of 0.07 grams ozone per gram CO used in the Predictive Model for the CaRFG3 Regulations is very low and is in contradiction to the most up-to-date science.

   The ARB response to this issue correctly notes that the general set of MIR factors has recently been updated. However, these updates have focused on improved chemical representation of individual compounds within the context of continuing with a single methodology to determine the factors, namely the single-day EKMA model and the procedures developed by W.P.L. Carter of U.C Riverside. Apparently, a special focus on low-reactivity compounds like CO and ethane, especially in the context of SIP grid modeling, is needed for the ARB Reactivity Scientific Advisory Committee to revue.

   Dr. Luo notes that “Several recent studies … have investigated multi-day effects on the reactivity of CO and slowly reacting VOCs. Their results indicate that reactivities derived from multi-day episodes are well correlated with the single-day MIR values.” This statement appears to be inconsistent with the following quote from page 56 of Carter et al. (2003), under the topic heading “Comparison of Regional and EKMA Relative Reactivities”:

   “For most model species the EKMA results are surprisingly close to the comparable regional relative reactivity metrics given the significant differences in the types of models and scenarios employed.…. However, there are some consistent differences in EKMA vs. regional relative reactivities for certain model species. Perhaps the most significant is the consistent bias for the EKMA scales towards predicting lower relative reactivities for the slower reacting species, specifically CO, ethane and to a lesser extent PAR.”

   Nevertheless, studies such as Martiens et al. (2002) do have places were multi-day or other conditions such as going from VOC-limited to NOx-limited conditions do show higher reactivity for CO relative to other VOC. For example, in Figure 5.5 of Martiens et al. (2002) the reactivity of CO is seen to jump much closer to those of other VOC when changing from NOx to VOC-limited conditions. However, there may be a misprint in the Martiens et al. (2002) report which reverses the labels for its Figure 5.5, since it is the opposite of what would be expected from Table 1 here (see below). In the South Coast Martiens et al. (2002) also show results in their Table B.1 of Regional MIR from 8 sites. The average of these 8 sites can be computed to be 0.0412, which is 38 percent higher than the box-model value they show for comparison. Further, the average for an important VOC, say m-xylene for example, is some 6.6 percent less than the referenced box-model MIR value.

> Hence, other studies (e.g. Martiens et al., 2002, used here) apparently do show an enhanced CO reactivity relative to typical VOC for episode conditions. However, these other studies appear to not have focused on such results like Carter et al. (2003) or Whitten (1999 and 2001) and extracting the information on the relative reactivity of CO to other VOC is not often as easy or so clearly evident.

2. The MIR value for carbon monoxide should be higher (0.12) based on grid-modeling for three major cities (South Coast Air Basin, Chicago, and New York) conducted by Whitten (1999, 2001), than the MIR value of 0.07 used by the ARB. A copy of Whitten (1999) is attached.

The ARB claims that using the MIR values of 0.07 and 0.12 "misrepresents the incremental reactivity concept." In the original Whitten (2004) and the supporting document, Whitten (2001) it was perhaps not written clearly enough that the derivation of the suggested higher MIR came about from the study of relative reactivities of VOC and CO in a multi-day SIP-related grid model versus the single-day EKMA box model used to develop the Carter scales. The use of a single number such as the MIR of 0.07 for CO was meant to be an example. The MIR scale was chosen as an example because the relative numbers used in the Predictive Model for CaRFG3 use the MIR numbers.

The ARB also claims that it is "fundamentally incorrect to use a scaling factor" between grid model and single-day box model derived incremental reactivity values. The intent by Whitten (2004) was to adjust a regulatory tool such as the Predictive Model to account for the bias towards CO that studies such as Whitten (2001) and Carter et al. (2003) have now shown. As noted above in the quote from Carter et al. (2003), the relationship between box and grid models is quite good for the relative reactivities seen between most VOCs. Carbon monoxide is an important exception. In other words, the use of the MIR scale derived from box-model simulations is probably okay in the Predictive Model, except for CO, which seems to need an adjustment.

The ARB claims "The CB4 mechanism is deemed to be inappropriate for reactivity estimates due to its simplifying assumptions for VOC chemistry." However, the work of Liang and Jacobson (2000) involved comparing the organic part of CB4 against a 4,000-reaction mechanism used in European modeling (Jenkin et al., 1997). They found that for the most part, both mechanisms gave similar results when used to simulate urban smog episodes. Thus, the simplifying assumptions used in CB4 seem to stand up quite well, at least in this one test. To study the reactivity of individual VOCs in a grid model the CB4 like SAPRC99 in Martien et al. (2002) has been "expanded" to include explicit reactions for specific individual VOCs under study. A recent example is the peer-reviewed paper by Whitten et al. (2003) where the reactivity of n-bromo-propane was studied using a grid model and nearly 60 reactions specific to the chemistry of n-bromo-propane were added to CB4.

Also it is noteworthy that as shown by Figure 5.1 of Martiens et al. (2002) the SAPRC99 and CB4 give quite similar overall results in the MAQSIP grid model. Additionally, the work of Carter (1994b) showed that MIR values for nearly 300 individual VOC derived using CB4 where, by and large, quite similar to MIR values derived by the more detailed SAPRC90 mechanism.

Dr. Luo states there is a “major problem” with bounding the problem of CO reactivity by turning “off” the CO chemistry. In the South Coast grid modeling done by Whitten (2001, also reported by Whitten, 1999) two CO sensitivity simulations were performed, the lower bound was found by varying only the CO emissions without changing the initial or boundary values (which would to some extent be less if CO were reduced everywhere). The text of Whitten (2001) was meant to make it clear that turning “off” the CO chemistry would only be an upper limit because of several factors that included secondary CO from VOC. The final CO estimate was based on an average of the upper and lower bounding simulations specifically to eliminate taking credit for secondary CO from VOC (and other factors such as non-gasoline related emissions mentioned in the text of Whitten, 2001).

3. The reactivity of CO has also recently been studied by Carter et al. (2003). Their results for the Eastern United States are even higher than the Whitten (2001) results.

The ARB claims that Whitten (2004) has misinterpreted the results of Carter’s report. So does Dr. Carter (personal communication to Whitten circa May, 2004). However, the statements given by Whitten (2004) had actually taken into account the mole-carbon units and relative relationship to base ROG considerations in the Carter et al. (2003) study. Although not clear in the text, the units were converted by Whitten (2004) for the convenience of the reader. In Carter (1994a) the mass-based MIR of the base ROG mixture is given as 3.1. To convert to mole-carbon units one uses the ratio of the ozone molecular weight (48) to VOC per carbon (14 to 15) which gives a conversion factor of approximately 3.2 to 3.4, depending on the per carbon molecular weight of the average ROG mixture. Hence, the mole-carbon base tends to have a mole carbon base MIR between 0.9 and 1.0. When considering the range of results reported by Carter et al. (2003) the ROG mixture carbon base MIR was considered close enough to unity by Whitten (2004) to not require further conversion. Nevertheless, the EKMA MIR reported by Carter et al. (2003) was 0.03, and the grid-based numbers of Carter et al. (2003) were seen to be consistently higher as reported by Whitten (2004). In the text of Carter et al. (2003) it is also noted that “the EKMA as well as the regional relative reactivities are all given on a carbon basis, so the units are constistent.”

Dr. Luo states that “another issue is that the objective or the Carter’s study was to assess the validity of different reactivity metrics so a condensed mechanism, CB4, was used in the project due to its computational efficiency. The reactivity estimates derived from each metric are less valuable than the metric itself. To obtain more reasonable reactivity estimates, a more detailed chemical mechanism such as

> SAPRC99 is necessary." First of all, the Carter et al. (2003) report specifically states (on page 56) that "Although, the major focus of this project is to derive relative reactivities using the regional model, it is also of interest to determine the extent to which regional model relative reactivities differ from those derived using the 1-day EKMA scenarios employed to drive the reactivity scales of Carter." Second, the CB4 is and has been used in more SIP modeling than any other chemical mechanism. Reactivities of VOC categories like mobile exhaust or CO itself become the central focus of control strategies so it is important to ascertain how these VOC categories are to be treated in the SIP itself. Individual VOC reactivities are more of a research goal, one of which could be to test the CB4 treatment against explicit chemistry (such a research project has been proposed to the ARB by Whitten). Third, there are essentially two SAPRC99 mechanisms, one is the detailed version used to study individual VOC chemistries in smog chamber experiments. In special grid studies such as reported by Martiens et al. (2002) some detailed reactions for individual VOC from the larger SAPRC99 mechanism were apparently added to the more condensed grid-model version of SAPRC99. The other SAPRC99 mechanism that is normally used in grid models is much smaller and comparable to the CB4 or CB5. CB4 is a condensed version of CBM-EX, which was developed to simulate smog chamber data by Gery et al. (1989). However, it can be argued that in many instances the CB4 still can provide more details in chemistry than the grid version of SAPRC99; for example, the grid version of SAPRC99 treats styrene in the inventory as a propene-like olefin, while CB4 treats styrene as a combination of TOL and OLE which represents both the aromatic and olefinic types of bonds found in styrene.
>
> Dr. Luo states that "Although our focus is the applicability of reactivity estimates to California urban areas, Whitten (2004) should not cite only one East Coast and ignore the other studies." Whitten (2004) and especially Whitten (2001) and Whitten (1999) first discusses SIP-like grid-modeling studies for the South Coast, then it is noted that other areas (Chicago, New York, and East Coast) all are consistent with the finding that CO reactivity is higher than expected compared to other VOC from existing MIR factors.

Another point is that the reactivity of CO can be seen to dramatically increase relative to other VOC as NOx is reduced. Carter (1994a) developed a series of reactivity factors. The series of three reactivity sets (MIR, MOIR for maximum ozone, and EBIR for equal benefit) were developed by reducing the NOx inputs to progress in the direction of more NOx-limited conditions. Others, including Carter, have noted that the three sets of factors in this series show surprisingly similar relative reactivities between the various VOC or the base ROG mixture. However it may not be well known that this series of three reactivity scales shows that the reactivity of CO consistently increases relative to average VOC as the series (with reduced NOx) progresses.

Table 1 compares the reactivity factors published by Carter (1994a) in their original form relative to the base VOC mixture. A group of VOC were chosen to be representative of various types commonly seen in urban atmospheres. In the last two columns the percent increase of CO reactivity to each VOC is given relative to the MIR factor of CO relative to each VOC. It is seen that the relative reactivity of CO consistently increases relative to all VOC as the series progresses toward more NOx-limited conditions. It is perhaps coincidental, but the average increase in CO reactivity seen in UAM simulations (Carter et al., 2003, and Whitten, 1999 and 2001) 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.

It should also be noted that the EBIR scale of Carter (1994a) for "equal benefit" between NOx and VOC is for moles not weight. On a weight basis the base VOC is still seen to be about 3 times more effective than NOx. Hence, the EBIR scale is still not out of the VOC-limited condition that the South Coast is famous for. Whitten (1999) reports that the SIP condition used to study mobile source reactivity showed that mobile VOC was 8 times as effective on a weight basis as NOx for generating peak ozone. That is, the condition used the 1997 SIP was apparently not far from that of the Carter EBIR scale.

Table 1. Reactivity Relationships from Carter (1994a) and Percent of CO Reactivity Increases Relative to Each VOC Reactivity.

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

> There is also a fundamental scientific reason to explain a higher ozone-forming potential for CO relative to common VOC as NOx is reduced and becoming scarce during the afternoon of an episode day (a typical condition as ozone is peaking). The reason is that CO can become more reactive (relative to typical VOC) is that its chemistry does not lead to net new radicals at a time when radials are also driving NOx to lower and lower levels. Conversely, in the mornings of urban areas when more than enough NOx is present (which is also consistent with the Carter MIR scale conditions), the generation of new net radicals (e.g. from typical VOC decay products) helps accelerate the rate of ozone formation, which is why CO (without those extra radicals) is then less reactive than typical VOC.

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Abstract

There has been a debate over the need for oxygenates in reformulated gasoline (RFG). Recent photochemical air-quality modeling shows that carbon monoxide plays a significant, and perhaps growing, role in urban ozone formation relative to regulated volatile organic compounds (VOC). Oxygenates like MTBE and ethanol are well-known for reducing carbon monoxide and, therefore, can help reduce ozone more than non-oxygenated fuels meeting the same VOC emissions standards. Systems Applications International has performed several sensitivity simulations based on the Urban Airshed Model (UAM) simulations used in the 1997 Air Quality Management Plan (AQMP) reported by the South Coast Air Quality Management District. For the year 2000, using a meteorological episode from August 1987, the new UAM simulations indicate that exhaust CO emissions from gasoline vehicles make about as much ozone as do the exhaust VOC emissions. That is, these UAM simulations suggest that a 10 percent reduction in CO (as would be expected if oxygen is used in RFG) appears to be as important as a 10 percent exhaust VOC reduction and these two effects would be additive. New emissions data and regulations indicate that future vehicles will have even higher CO-to-VOC ratios than the current on-road fleet.

In addition to the CO effects on ozone there may be more air quality benefits that can be associated with the use of oxygenates, especially when they are used to maintain octane by substitution for aromatic hydrocarbons. Aromatic hydrocarbons have been implicated with a growing list of air quality problems such as the toxic compound benzene, hazardous air pollutants like nitro-cresols and nitro-phenols, long-term emissions increases through combustion chamber deposits, both primary and secondary fine particulates, and other pollutants like peroxyacetyl nitrates (e.g., PAN). Finally, there is uncertainty about the potential for olefin impacts if non-oxygenated RFG formulations replace oxygenated formulations: more aromatics to replace lost octane may bring olefins from catalytic cracker streams or the use of more paraffins may lead to increased exhaust olefin emissions.

Introduction

A recent report by UC Davis (1998) states that "there is no significant additional air quality benefit to the use of oxygenates such as MTBE in reformulated gasoline, relative to alternative CaRFG2 non-oxygenated formulations." The air-quality focus of the UC Davis study is closely aligned with the regulatory emphasis on short-term impacts of RFG on hydrocarbon, NOx and toxic emissions: long-term air quality impacts are not considered in the RFG specifications. Moreover, the UC Davis evaluation relies heavily on some tests with a single non-oxygenated fuel that actually fails to meet the CaRFG2 standards and did not match the octane level of the MTBE-containing fuel it was compared to. Air quality modeling shows that carbon monoxide plays a greater role in urban ozone formation than predicted by reactivity factors such as those developed by Carter (1994). Oxygenates like MTBE and ethanol are well-known for reducing carbon monoxide (OSTP, 1997, and Whitten et al, 1997) and, therefore, can help reduce ozone more than non-oxygenated fuels meeting the same hydrocarbon standards. Besides ignoring the ozone impact of oxygenates through carbon monoxide reduction, the UC Davis study did not report potential air quality benefits that might be associated with the use of oxygenates to maintain octane when they are substituted for aromatic hydrocarbons. Aromatic hydrocarbons have been associated with long-term emissions increases of CO, VOC, and NOx through combustion chamber deposits. Aromatics are also associated with the emissions of other pollutants such as primary and secondary fine particulates, toxics like benzene, nitro-phenols, and peroxyacetal nitrate or PAN.

Background

Oxygenates like MTBE and ethanol are not adequately described as additives, they are key components of reformulated gasoline. Using the word “additive” often implies that adding it to gasoline improves that gasoline. Adding 11 percent MTBE or 10 percent ethanol to gasoline gives a product that is significantly different in four ways from the original gasoline: the product is about a full grade higher in octane, it has 10 to 11 percent more volume, it has 2 to 3.5 percent by weight oxygen, and virtually all the undesirable properties have been reduced (e.g., T_{50}, see below) or diluted compared to the original gasoline. The correct comparison to judge the “improvement” attributable to an oxygenate is not so much the original gasoline that existed before the oxygenate was added, but what might be the oxygenate-free gasoline which would have the same octane, the same total market volume, and can reduce all air pollution as well. Traditionally, refineries have on average added aromatic compounds to gain a full grade in octane. However, all aromatics lead to some exhaust benzene and aromatics (as discussed below) have been associated with other undesirable environmental effects. Hence, one way of describing use of oxygenates to replace aromatics would be more in a “subtractive” sense than in an “additive” one.

There appear to be uncertainties in comparing oxygenate-free gasoline with oxygen-containing blends because the stringent specifications in the California cleaner burning gasoline (CBG) program were designed around an example recipe containing MTBE. On one hand, the new recipe demonstrated reduced emissions compared to conventional gasoline, while on the other hand, the CBG recipe could be supplied (after some refinery modifications) to fully meet the huge California market for both octane and volume. Even though an oxygenate-free recipe has shown similar emissions to the original CBG recipe, it remains unclear what the average oxygenate-free formulation would be that the refineries (even after additional modifications) could make with sufficient octane and volume to fill the California market. Moreover, there is evidence discussed below that oxygenates may actually be helping to improve air quality more than merely meeting the original CBG specifications. Any such extra improvements might be lost without the use of oxygenates.

The Federal reformulated gasoline program and the California CBG program are both mass-based approaches to ozone abatement. Even though CBG can be defined to 0.05 percent using the Predictive Model test, it should be noted that Auto/Oil Technical Bulletin No. 3 (1991) clearly shows that mass reductions do not necessarily reduce ozone if the mass reduction is accompanied by changes in fuel formulation. For the fuels tested, this Auto/Oil report shows that the best fuel formulation for reducing ozone did not necessarily reduce mass emissions and the best fuel for reducing mass emissions did not necessarily reduce (and may actually increase) ozone. Thus, there is evidence to suggest that the apparent success of gasoline reformulation programs to date, based on ambient ozone observations, may be fortuitous and may not continue should oxygenates be removed from the program. The UC Davis (1998) report relies heavily on Auto/Oil research (Technical Bulletin No. 17), based on a single non-MTBE batch of gasoline that almost meets CBG specifications, to conclude that the same air quality can be attained without MTBE.

The data on non-oxygenated CBG

Auto/Oil Technical Bulletin No. 17 reports comparative emissions in three vehicle fleets between a 92.4 octane [(R+M)/2] premium grade CBG made with MTBE and a 90 octane mid-grade gasoline without any oxygenates. This mid-grade fuel fails to meet a key CBG requirement known as the Predictive Model test. An oxygenate-free CBG must show predicted emissions within 0.05 percent of emissions from a “flat limit” reference CBG by using a sophisticated statistical model known as the Predictive Model. This model is designed to give a statistically optimized representation of 20 studies having about 7000 individual emissions tests from about 800 vehicles using a wide range of fuel formulations. The mid-range oxygenate-free fuel used in the Auto/Oil study passes the Predictive Model tests for nitrogen oxides (NO_X) and toxic emissions by showing decreases compared to the standard flat-limit recipe for CBG, but the hydrocarbon emissions are predicted to be 2.12 percent above the CBG standard. According to the Predictive Model, the fuel with MTBE that was used in the Auto/Oil study does pass for all three of the emissions tests. In fact, the hydrocarbons for the conforming premium fuel (with MTBE) are predicted to be nearly 7 percent less than the non-oxygenated mid-range gasoline. In the actual tests for this Auto/Oil study the hydrocarbon emissions were, in fact reported to be about 6 percent higher for the fuel without MTBE in a fleet of 1989 vehicles.

Although the emissions between the two fuels of this Auto/Oil study rarely showed statistically significant differences, the reported average hydrocarbon increase of about 6 percent and a reported carbon monoxide (CO) increase of 10 percent are both close to expected impacts for a non-oxygenated fuel compared to one with 11 percent MTBE in vehicles similar to the 1989 model year. As noted above the Predictive Model predicts a 7 percent hydrocarbon increase. For carbon monoxide the OSTP (1997) report concludes that the 2 percent oxygen in a 11 percent MTBE blend should reduce CO by about 10 percent. Whitten et al. (1997) also show that reductions in ambient CO levels are statistically consistent with oxyfuel programs. Carbon monoxide reduction can be important to urban ozone abatement.

Carbon monoxide as an ozone precursor

For more than thirty years carbon monoxide (CO) has been known to be a precursor to smog (urban ozone) formation. However, the focus of smog abatement strategies for the past 45 years has been only on the emissions of volatile organic compounds (VOC) and nitrogen oxides NO_x. Carbon monoxide, of course, is recognized on its own as a ubiquitous criteria pollutant with harmful effects on human health. It has been regulated quite successfully until the CO air quality standards, set up to protect the public, are now approaching compliance nationwide. Nevertheless, as discussed below, CO can be considered as a growing fraction of the urban ozone problem relative to VOC. On the one hand, success in controlling CO for its direct health effects may be leading to complacency, while on the other hand the new and more stringent 8-hour ozone standard might be expected to warrant more stringent standards on all smog precursors.

Carbon monoxide abatement programs have often been directed towards mobile sources through increasingly stringent certification standards and by requiring the use of oxygenated fuels. However, mobile sources continue to dominate overall carbon monoxide emissions. Figure 1 is reproduced from Figure 19 in EPA's 1970-1997 Emissions Trends Report (available at http://www.epa.gov/ttn/chief/trends97). This figure shows that while total CO emissions have been reduced substantially since 1970, on-road vehicles remain as the dominant source. In spite of increasing vehicle-miles-traveled (VMT) such overall decreases can be largely attributed to ever more stringent certification standards for both CO and VOC. Figure 2 shows the certification standards for CO in California since 1970. Figure 3 shows the comparable standards for VOC in California during this period.

Until the present set of low emitting vehicle (LEV) standards in California became applicable, only a slight trend towards more stringent control of VOC than CO is evident in Figure 4, where the ratio of CO to VOC certification standards are plotted. However, Figure 4 shows that these California LEV standards indicate a new trend towards VOC control over CO control. As seen in Figure 4 the new super-ultra-low-emitting vehicle (SULEV) standard implies a ratio of 100 to 1 for the tailpipe emissions of CO to VOC, while this CO to VOC emissions ratio was only 10 to 1 for 1970 vehicles.

On-road exhaust emissions inventory information for 1998 obtained from the California Air Resources Board (private communication, 1998) is consistent with a modest upward trend in the CO to VOC emissions as is shown in Figure 5. Emissions inventories reflect estimates of all vehicles on the road in a given calendar year, which would include high mileage effects from older vehicles and other causes of emissions levels being above the certification standards shown in Figure 4.

The U.S. EPA also provides estimates of projected emissions trends in the same 1970-1997 Emissions Trends Report. Figure 6 based on that report, shows the EPA projection for CO emissions to the year 2010. A projected leveling in emissions is evident in Figure 6 from 2005 and 2010. Figure 7 shows the EPA projection for road

VOC emissions and no leveling is seen for the years 2005 to 2010. Hence, the EPA projects that the ratio of CO-to-VOC emissions will increase.

Another form of input to the carbon monoxide issue is an apparent trend in ambient observations towards a slower rate of improvement. Figure 8 shows the trend in average daily maximum (1-hour) concentrations at the same Burbank site from 1963 to 1997. A least-squares fit with a 6 percent per year decline fits well until 1980, but the last 17 years are fit best with only a 3.8 percent decline rate.

The chemistry of how carbon monoxide forms ozone is very straightforword. In fact, it is often used as an example to help explain how urban ozone is formed (e.g., Whitten, 1983, and Johnston, 1992). Carbon monoxide reacts with the hydroxyl radical (OH) in air leading to the hydroperoxy radical (HO_2). These are the same reactant and product radicals associated with VOC that lead to urban ozone formation. The rate constant for the CO reaction with OH is essentially the same as the OH reaction with ethane (De More et al., 1997). Ethane has been the hydrocarbon the U.S. EPA has used as the “bright line” test between reactive VOC and molecules that can be considered as non-reactive. On a weight basis CO would actually be slightly more reactive than ethane so even though CO is technically not an organic compound, it would be classified as reactive according to this EPA “bright line” test. In terms of showing CO to be growing in importance as an urban ozone precursor, it is also noteworthy that the rate constant for the reaction of CO with OH has recently been evaluated upward by about 10 percent (see De More et al., 1997) compared to the value used in the Urban Airshed Model (see Gery et al., 1989).

Systems Applications International has performed new sensitivity simulations based on the use of the Urban Airshed Model (UAM) in the 1997 Air Quality Management Plan (AQMP) reported by the South Coast Air Quality Management District. For the year 2000, using a meteorological episode from August 1987, the new UAM simulations indicate that exhaust hydrocarbon emissions from gasoline vehicles make about as much ozone as do the exhaust CO emissions. That is, these UAM simulations suggest that a 10 percent reduction in CO (as would be expected from the oxygen in MTBE) appears to be as important as a 10 percent hydrocarbon reduction and these two effects would be additive. Tables 1, 2, and 3 show the results of these simulations.

A potential update to the AQMP is included as a sensitivity scenario (labeled “Rn Spec” in the tables) 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 contains 18 percent as methane, and for reference the Caldecott tunnel data (Kirchstetter et al, 1996), show 9.9 percent methane. The newer profile (#882) resulted from a special ARB workshop in the summer of 1998.

The results of the UAM sensitivity runs are given in Tables 1 and 2. No 8-hour results were part of the AQMP, but they are included here to be used as a guide for potential impacts to the new ozone standard[19]. All results in Table 1 come from the highest

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[19] Because some concern has been expressed over the use of the standard UAM-IV for 8-hour ozone concentrations that include darkness, the 8-hour period between noon and 8 pm PDT has been used here. Comparisons with

simulated concentration in the UAM for each day. Impacts are given for single cells and in general such cells do not correspond to the cells that have the highest total ozone concentration. To obtain impacts at the highest ozone concentration one must subtract the appropriate base case value shown; for convenience Table 3 presents the impacts for the 28 August day peak concentrations.

These tables show the results from two types of sensitivity tests on the importance of CO. In one type of test (labeled “Chem” in the tables) the chemical reaction of OH with CO was deleted from the chemical mechanism. This is intended to be an upper limit to the importance of CO from exhaust emissions in the ozone chemistry, first because some CO is formed from the decay of VOC, and second because gasoline-related exhaust emissions are only about 60 percent of the total CO emissions inventory. The second CO test (labeled “Emiss” in the tables) involves setting gasoline-related CO emissions to zero. This would be a lower limit to the importance of these CO emissions because much of the CO in the initial and boundary conditions plus that carried over from day to day within the model would come from vehicle exhaust emissions (even if from other cities). The atmospheric lifetime of CO is approximately 20 days (using an average daytime OH concentration of 0.2 ppt).

For comparisons with the CO emissions, three other sensitivity tests were performed involving exhaust VOC from gasoline-fueled vehicles. In the first test (labeled “VOC Strt” in the tables) all starting exhaust VOC emissions were set to zero. In the second test (labeled “VOC Run” in the tables) all running exhaust VOC emissions were set to zero. As can be seen in Table 3, the sum of the exhaust VOC impacts (without the new profile) fall within the limits of the CO sensitivity tests. Even with the updated profile the CO impact on ozone is seen to be at least comparable to exhaust VOC emissions.

Although the reported Auto/Oil study (Technical Bulletin No. 21, 1995) results do not show a statistically significant combined impact of CO and hydrocarbons, part of the reason would be due to a much larger ratio of CO to hydrocarbon emissions found in the AQMP emissions inventory.

During the discussions leading to the Clean Air Act revisons of 1990, it was known that mandating oxygenates was one way of ensuring that CO reductions would enhance the ozone-reduction of the reformulated gasoline program without the complications of trying to revise hydrocarbon-based control stragegies to give credit to the well-known ozone-forming potential of CO (Whitten, 1988).

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maximum values at any hour show that for the 28 August day there are very small differences. A more recent version of the UAM (UAM-V as used in OTAG) includes a special layer at ground level and improved surface effects that combine to enhance the accuracy of simulated ozone concentrations during darkness.

Table 1. 1-Hour Maximum Ozone (ppb) Results of UAM Simulations.

Scenario	August 27th	Highest Impact	Lowest Impact	August 28th	Highest Impact	Lowest Impact
Base	129.0			148.3		
CO Chem	114.1	-0.1	-16.1	132.4	-0.2	-33.3
CO Emiss.	126.4	+0.7	-4.5	143.3	+0.5	-9.1
VOC Strt	121.6	+1.3	-12.6	143.9	+1.0	-22.8
VOC Rn	125.3	+0.5	-6.2	144.7	+0.4	-11.9
Rn Spec.	132.0	+5.5	-0.3	150.9	+10.6	-0.4

Table 2. 8-Hour Maximum Ozone (ppb) Results of UAM Simulations. Because there have been questions about the UAM-IV evening ozone values, the 8-hour values used here are all noon to 1800 PDT.

Scenario	August 27th	Highest Impact	Lowest Impact	August 28th	Highest Impact	Lowest Impact
Base	93.6			132.1		
CO Chem	86.1	-0.1	-11.7	117.4	-0.2	-20.6
CO Emiss	92.3	+0.3	-3.1	127.7	+0.3	-6.1
VOC Strt	92.2	+0.5	-8.3	127.0	+0.7	-16.4
VOC Rn	92.6	+0.3	-4.7	128.1	+0.3	-9.2
Rn Spec.	95.8	+3.9	-0.3	135.0	+7.6	-0.2

Table 3. The peak impacts for the 28 August day. These are obtained in each case by subtracting the appropriate base simulation values (148.3 ppb for the 1-hour and 132.1 ppb for the 8-hour, respectively) shown in Tables 1 and 2.

Scenario	August 28th 1-hour	August 28th 8-hour
CO Chem	-15.9 (-9.5 for 60%)	-14.7 (-8.8 for 60%)
CO Emiss	-5.0	-4.4
VOC Strt	-4.4	-5.1
VOC Rn	-3.6	-4.0
Rn Spec.	+2.6	+2.9

The importance of octane and aromatics

Another part of comparing CBG related emissions with and without MTBE involves the average response of the oil industry to maintain octane. Since the Auto/Oil study discussed above compared a mid-grade fuel to a premium, an illustrative example can also be based on these two fuels. In recent decades the oil industry often relies on aromatic hydrocarbons to boost octane. Important evidence of this was seen in the Caldecott tunnel data of 1994 where emissions from 8000 vehicles could be compared just prior and just after the introduction of a mandated oxygenate program. The main oxygenate used was 11 percent MTBE and there were no other requirements as the California CBG program had not yet started.

The tunnel data (see Kirstetter et al., 1996) clearly show that the refineries maintained octane by reducing aromatics by about 17 percent on average. Hence, if MTBE were not in gasoline there is reason to believe that some octane would instead come from aromatics and 11 percent MTBE can be estimated to be worth a 17 percent reduction in aromatics on average. A 17 percent reduction corresponds to a 20 percent increase going from MTBE to a fuel without it. Also since 11 percent MTBE can increase octane about 1 level, an octane boost from mid-grade to premium can be estimated to result in a 20 percent increase in aromatics. Since the mid-grade MTBE-free fuel used in the Auto/Oil study had 22.7 percent aromatics a premium version of such a fuel might have 27.3 percent aromatics (which is still below the 30 percent aromatics cap in the CBG program). The Predictive Model indicates that increasing the aromatics from 22.7 to 27.3 percent would have little impact on the predicted hydrocarbon emissions, but the predicted NO_X and toxic emissions would increase. That is, the new fuel, which might now match the premium octane level of the MTBE-containing fuel, would still fail the hydrocarbon test, but just pass the NO_X and toxic tests. The predicted NO_X and toxic emissions increases are about 0.6 percent and 3.8 percent, respectively compared to the MTBE-free fuel used in the Auto/Oil study. One of many ways to bring the hydrocarbon emissions into conformity for this fuel using the Predicted Model would be a small reduction in T_{50} (the temperature where half the fuel can be distilled). Reducing T_{50} is one of the attributes of MTBE referred to above.

Another comparison of the two fuels used the Auto/Oil study is the paraffinic content. The MTBE-free fuel had 18 percent more paraffins than the CBG fuel with 11 percent MTBE. The example MTBE-free fuel just discussed that might match octane by using more aromatics would need about 15 percent more paraffins. If the oil industry were to make MTBE-free CBG similar to the fuel used in the Auto/Oil study and maintain total gasoline volume and total octane, it is apparent that an increased supply of high-octane paraffins would be required. Additionally, these paraffins would need to have low enough boiling points to maintain a favorable T_{50} value (e.g., the Auto/Oil fuel that failed the hydrocarbon Predictive Model test had a T_{50} value of 208 F). This T_{50} requirement restricts the size of such paraffins to no larger than 7 carbon atoms, while the low volatility specifications of CBG essentially limit the range to no smaller than 5 carbon atoms. Thus, there would be an apparent demand for high-octane paraffins with a narrow range of carbon content.

More data on the use of higher paraffin fuels in modern vehicles are needed, especially when holding octane to the levels found in comparable fuels containing MTBE. Paraffin content was not specifically addressed in the Auto/Oil program, but it may be possible to analyze the data for paraffin impacts because fuels made without MTBE generally increased paraffins to replace the MTBE while keeping aromatics and olefin content the same. However, replacing MTBE with paraffins can dramatically alter octane, which was not held constant in the Auto/Oil program. Paraffins have long been known to be associated with combustion-generated olefins (Wigg et al., 1972).

It should also be noted that if aromatics were used to fill the octane “gap” left by removing MTBE, there are other potential problems that will need further investigation: (1) toluene is the lowest-boiling aromatic above toxic benzene, but even toluene would increase the T_{50} value; (2) even though toluene has low ozone-forming potential it leads to the formation of hazardous air pollutants (HAP) known as nitrocresols (Killus and Whitten, 1982 and 1983); (3) increased aromatics can lead to more peroxyactyl nitrates (e.g., PAN, see Altshuller, 1993); (4) as shown in both the EPA Complex Model and the California Predictive Model, increases in any aromatics lead to more exhaust benzene emissions, the major toxic compound in exhaust; and (5) if the added aromatics came from those in the fluid catalytic cracker units, olefins would increase as well. As shown in both the Federal Complex Model and the California Predictive Model, olefin increases tend to help reduce mass emissions, but Auto/Oil studies indicate that ozone increases with olefin content in mass emissions decreases (see Schleyer et al., 1992).

Finally, there is the uncertainty caused by the fact that few (if any) MTBE-free fuels have been tested that actually meet the full stringent CBG requirements imposed by the Predictive Model. A wide range of fuel formulations with MTBE have been tested, and several do meet the CBG requirements. The Auto/Oil study reported in Technical Bulletin No. 17 apparently confirms that at least one gasoline formulation made without oxygenates can produce emissions similar to a typical CBG made with MTBE. However, close inspection of even this Auto/Oil study reveals that in this highly quoted study a MTBE-free mid-grade gasoline was tested against a premium grade CBG made with MTBE, and the MTBE-free fuel actually did not quite meet the CBG Predictive Model test for hydrocarbons. Also there is UAM evidence that suggests that the extra carbon monoxide reduction offered by MTBE might reduce ozone by an amount equivalent to a 10 percent reduction in hydrocarbons. If the octane lost by removing MTBE is replaced to any significant amount by aromatics there are other air quality impacts besides ozone to consider (i.e., toxics, long-term impacts, PAN, and $PM_{2.5}$).

Long Term Impacts

First, Bitting et al (1994) noted that combustion chamber deposits (CCD) are associated with long term emissions increases of CO, NO_X, and hydrocarbons. Bitting et al. showed that removal of CCD build at high mileage can restore emissions to low-mileage levels. Second, Choate and Edwards (1993) and Price et al (1995) have shown that these CCD’s are strongly associated with high-boiling aromatic compounds in gasoline. Hence, it now appears that reformulated gasoline containing oxygenates in place of aromatics may be preventing some CCD build-up and, in turn, leading to long term de facto emissions reductions previously not accounted for in the more or less instantaneous effects of reformulated gasoline tested to date such as used in the Predictive Model.

$PM_{2.5}$

Fine particulate matter ($PM_{2.5}$) can be emitted directly from vehicles (primary $PM_{2.5}$) or formed in the atmosphere (secondary $PM_{2.5}$). A Colorado (1987) study showed that gasolines containing oxygenates significantly reduced the emissions of primary particulates. Other studies have shown that aromatic compounds in gasoline contribute significantly to exhaust particulates (See Graskow et al, 1998). Thus, using oxygenates in place of aromatics for octane would reduce primary $PM_{2.5}$ emissions even more than had been seen in the Colorado (1987) study.

The formation of secondary $PM_{2.5}$ is a very complicated process currently being studied by several scientists. One notable recent result published in Science by Odum et al (1997) from Caltech, showed that the organic fraction of secondary $PM_{2.5}$, attributable to gasoline in the atmosphere could be completely accounted for by the aromatics content of the gasoline. Hence, the use of oxygenates in place of aromatics can be expected to reduce secondary $PM_{2.5}$ as well.

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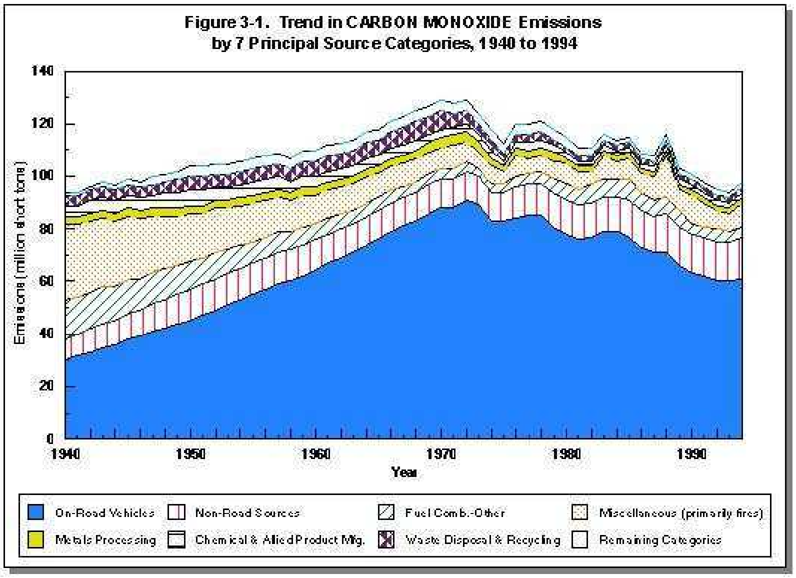
Figure 3-1. Trend in CARBON MONOXIDE Emissions by 7 Principal Source Categories, 1940 to 1994

Figure 1

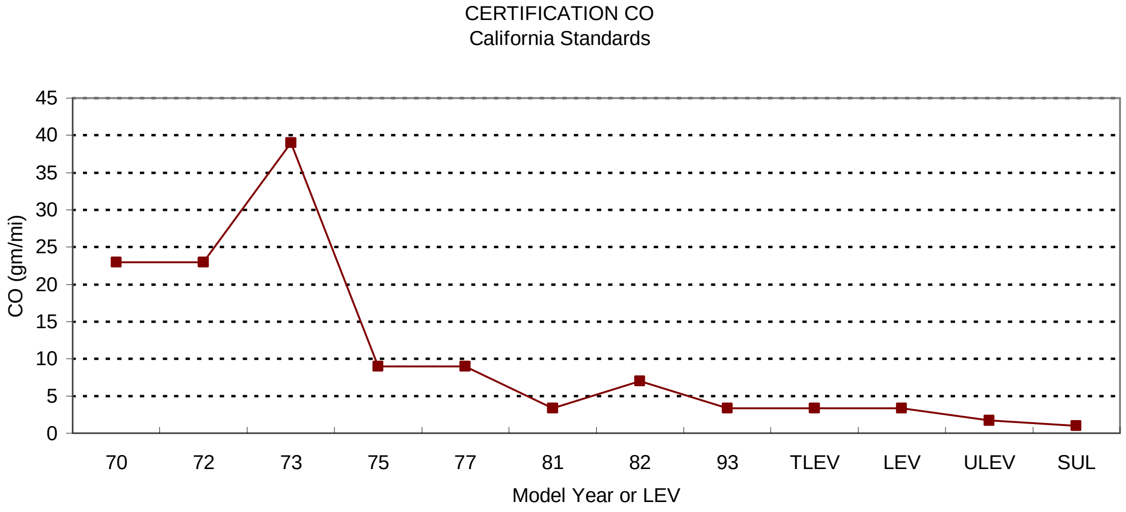

Figure 2

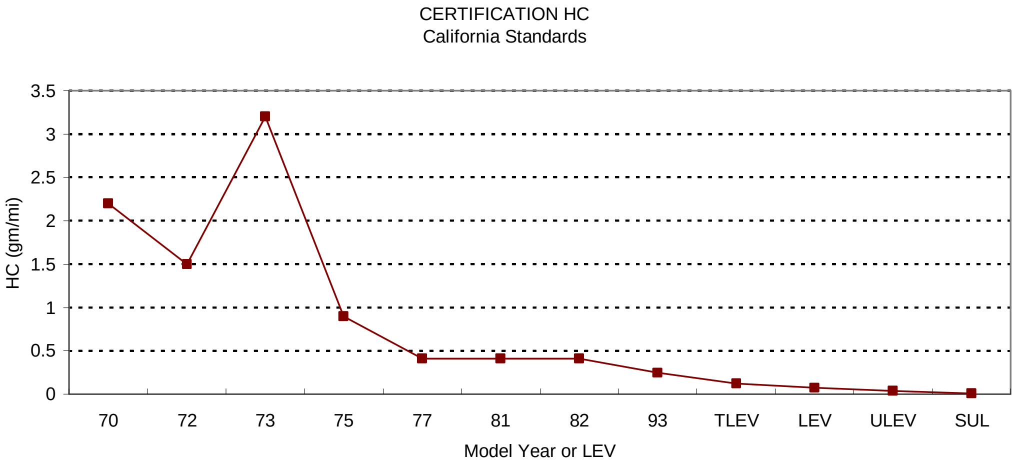

Figure 3

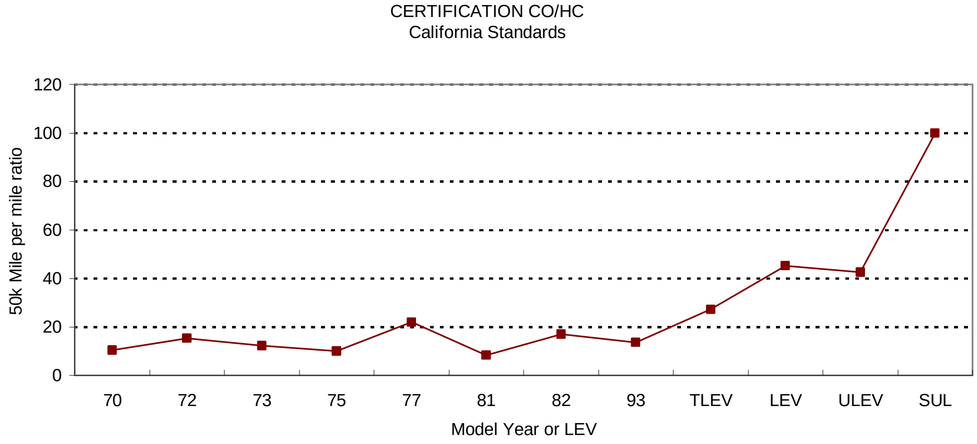

Figure 4

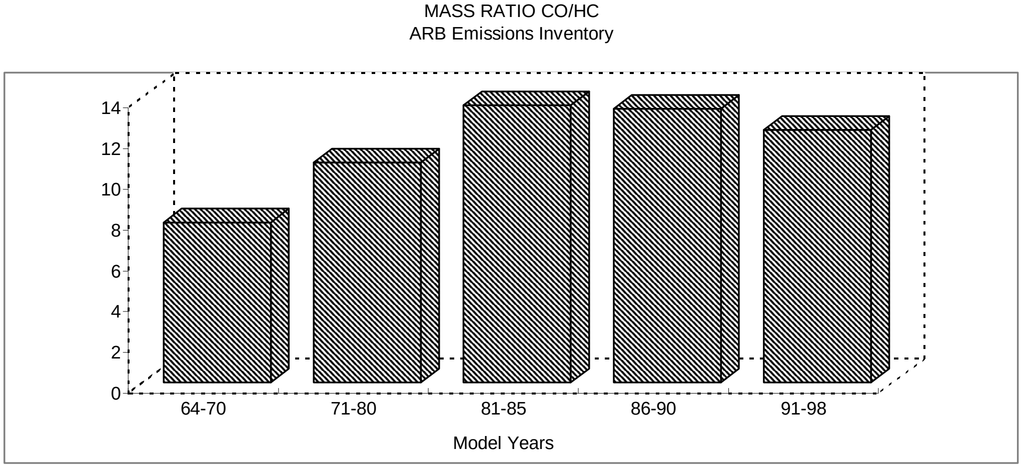

Figure 5

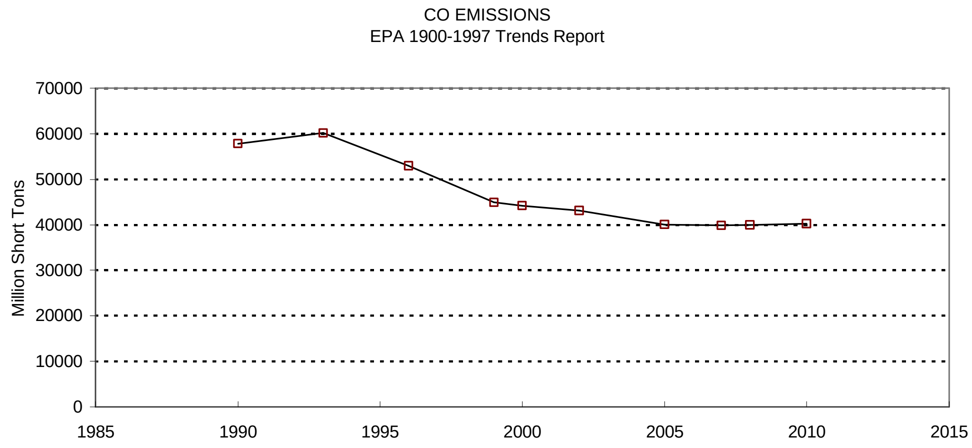

Figure 6

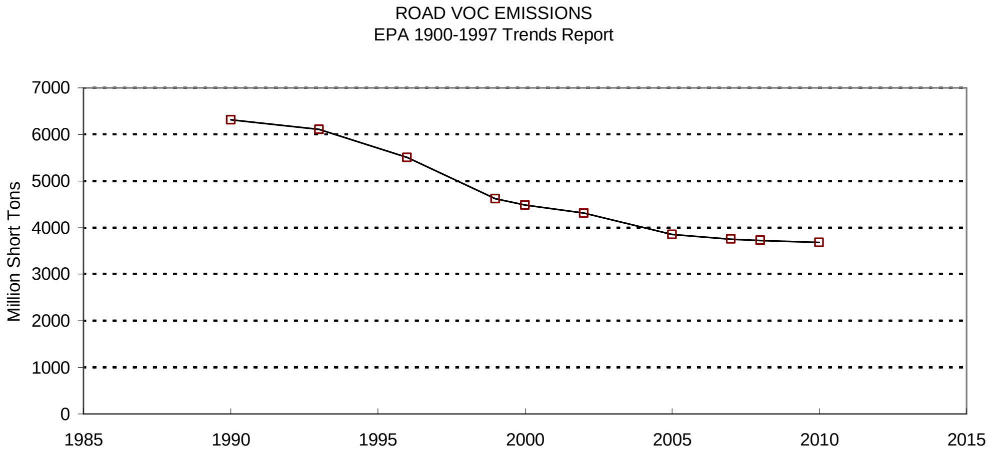

Figure 7

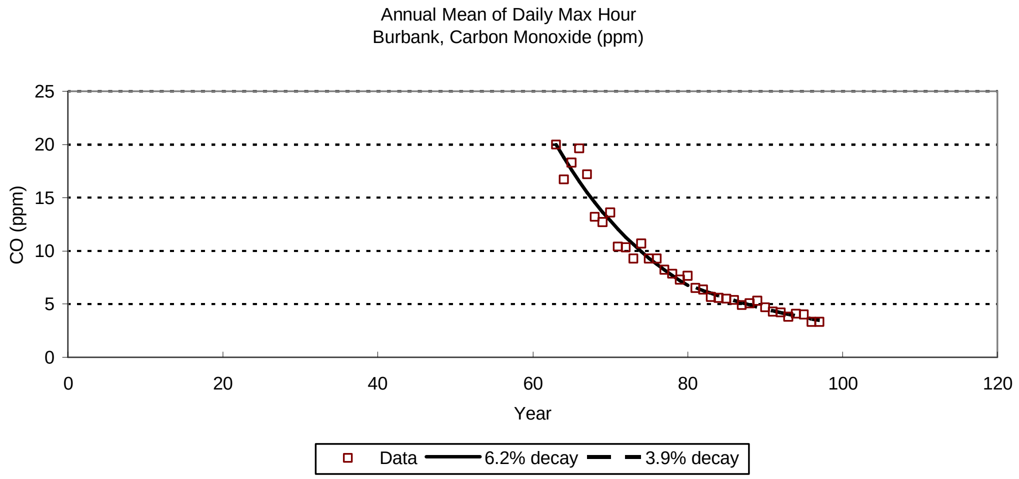
Annual Mean of Daily Max Hour
Burbank, Carbon Monoxide (ppm)
CO (ppm)
25
20
15
10
5
0
0
20
40
60
80
100
120
Year
Data
6.2% decay
3.9% decay

Figure 8

Comments on “CO Reactivity”

September 2, 2004
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In July 2004, Tom Koehler of the Renewable Fuels Association submitted a report entitled “CO Reactivity”, prepared by Whitten (March 24, 2004), to ARB for comment. Listed below is a brief summary of several issues raised by Whitten, followed by our response inserted in italics.

1. The value of CO reactivity (0.07) used in the Predictive Model for the CaRFG Regulations is very low. This is in contradiction to the most up-to-date science.

   Response: The Maximum Incremental Reactivity (MIR) scale, used in two California regulations (i.e., Low Emission Vehicle & Clean Fuel regulation and aerosol coatings regulation) and other applications, has been recently updated (ARB, 2003). The requirement for periodic updates was included in resolution 00-22 that approved the aerosol coatings regulation, which directed the Executive Officer to review the MIR values 18 months after the effective date of amendments and every 18 months thereafter to determine if modifications to the MIR values are warranted (ARB, 2000). This is because the chemical mechanism used to calculate the MIR values is evolving and improving, as new chemical mechanism information becomes available. Updating the MIR scale ensures that our regulations and applications are based on the use of the most up-to-date reactivity science.

   The most recent update began in early 2003 and was approved at a Public Hearing in December 2003 (ARB, 2003). At the Hearing, staff proposed to add 102 new compounds with their associated MIR values and to update the MIR values for 14 compounds in the existing MIR tables (section 94700, title 17, California Code of Regulation). The MIR values for the other approximately 500 compounds, including carbon monoxide, remain unchanged based on our review and public comments. The proposed changes are based on updated values provided by Dr. Carter, which were peer reviewed and approved by the ARB’s Reactivity Scientific Advisory Committee. The committee was established to make recommendations to the ARB on the science related to volatile organic compound (VOC) reactivity and is made up of six independent, respected scientists:

   Professor John Seinfeld, California Institute of Technology (Chairman)
   Professor Roger Atkinson, University of California at Riverside
   Dr. Jack Calvert, National Center for Atmospheric Research
   Professor Harvey Jeffries, University of North Carolina at Chapel Hill
   Professor Jana Milford, University of Colorado at Boulder
   Professor Ted Russell, Georgia Institute of Technology

ARB has supported reactivity research since early 1990. The focus of earlier research was on the dependence of reactivity measures on the level of chemical and physical detail and uncertainty in the models used for quantifying reactivity. Several studies using multi-day photochemical air quality simulation models were employed to derive reactivity estimates in South Coast and Central California (Russell et al. 1995, Bergin et al. 1995, and Kaduwela et al. 1999) and the results were well correlated with those derived from Carter's single-day box model. It was concluded, with Reactivity Scientific Advisory Committee concurrence, that in locations of California where VOC control is important, the use of the MIR scale is appropriate.

Most recently, ARB funded Professor Robert Harley of the University of California at Berkeley and Professor Ted Russell of the Georgia Institute of Technology to develop reactivity scales for the South Coast Air Basin and Central California using multi-day photochemical air quality simulation models (Martien et al. 2002, 2003). Currently, the ARB is supporting several reactivity projects to improve reactivity estimates by computer simulations and smog chamber experiments (Carter 2001, 2003a). More information about ARB's reactivity program is available at http://www.arb.ca.gov/research/reactivity/reactivity.htm.

All of the research findings that ARB has relied on for its reactivity-based have either been reported in the peer-reviewed literature or reviewed by the Reactivity Scientific Advisory Committee.

At the national level, the U.S. EPA is leading the Reactivity Research Working Group (RRWG), consisting of representatives from government, academic institutions, and industry, to coordinate and prioritize VOC reactivity research. ARB is actively participating in the RRWG and has co-sponsored several reactivity research projects with respect to improvement of reactivity metrics. More information about the RRWG can be found at http://www.cgenv.com/Narsto/.

In summary, ARB has and is continuing to support reactivity research and is using the most up-to-date peer-reviewed reactivity science in our reactivity-related applications.

2. The MIR value for carbon monoxide should be higher (0.12) based on grid-modeling for three major cities (South Coast Air Basin, Chicago, and New York) conducted by Whitten (2004), than the MIR value (0.07) used by ARB.

Response: Whitten (2004) misrepresents the incremental reactivity concept originally developed by Carter. The purpose of a reactivity scale is to compare the relative importance of ozone-forming potentials between different VOCs. To date, dozens of reactivity scales (such as MIR) have been developed but these values are only useful to compare reactivities between VOCs (and CO) under the same scale. In other words, It is misleading if the reactivity value for CO derived from one metric is compared to reactivity values for CO or VOCs derived from a different metric. Hence, it is fundamentally incorrect to use a scaling factor (1.75) derived from Urban Airshed Model (UAM) simulations of CO to adjust the MIR for CO (0.07) derived from Carter's single-day box model simulations, and then applying the "new" MIR factor (0.12) to CO emissions for comparison with VOC reactivity-weighted emissions based on the single-day box model. For a consistent comparison, Whitten (2004) should use an appropriate photochemical air quality simulation model for California for CO and the VOCs – as has already been done by the Russell et al. 1995, Bergin et al. 1995, Kaduwela et al. 1999, Martien et al. 2002, 2003 – to assess multi-day effects. Whitten (2004) ignores these peer-reviewed studies.

Whether the CO MIR underestimates the ozone impact of CO depends on the scenario and the quantification method used. Several recent studies (Carter et al. 2003b, Martien et al. 2002, 2003, Hakami et al. 2003) for California and the East Coast have investigated multi-day effects on the reactivity of CO and slowly reacting VOCs. Their results indicate that reactivities derived from multi-day episodes are well correlated with the single-day MIR values. In addition, a more advanced sensitivity analysis technique, i.e., the decoupled direct method (DDM), has proved to be a superior method for reactivity estimates (e.g., Hakami et al., 2003) than other techniques such as the scaling method used by Whitten (2004).

In addition, several assumptions were inappropriate based on the limited information provided by Whitten (2004). The CB4 mechanism is deemed to be inappropriate for reactivity estimates due to its simplifying assumptions for VOC chemistry. The CO mechanism may be the same or not very different from the explicit SAPRC99 mechanism but the mechanisms for other VOCs are quite different. As explained earlier, the CO reactivity derived from the Whitten (2004) analysis is only valid if reactivity estimates for other VOCs were obtained in the same manner. The same lack of consistency exists for boundary and initial conditions (changed for CO but not VOCs). Another major problem is that CO chemistry was turned off to "bound" the problem; thus, the elimination of secondary CO from VOCs is improperly credited to CO emission reactivity. The studies on other two cities (Chicago and New York) should be disregarded due to their irrelevance to California conditions although it is useful to see if the reactivity scale can still apply to non-Californian urban areas.

3. The reactivity of CO has also recently been studied by Carter et al. (2003). Their results for the Eastern United States are even higher than the Whitten (2004) results.

   Response: Whitten (2004) misinterpreted the results in Carter's report (Carter, 2003b). The RRWG study reported values as relative reactivities, not mass-based absolute reactivity that can be compared to MIR. Therefore, the comparison is invalid. Dr. Carter (personal communication, 2004) concurred with our assessment and indicated that the ratios of reactivities do not seem to correspond with the numbers cited by Whitten (2004).

Another issue is that the objective of Carter's project was to assess the validity of different reactivity metrics so a condensed mechanism, CB4, was used in the project due to its computational efficiency. The reactivity estimates derived from each metric are less valuable than the metric itself. To obtain more reasonable reactivity estimates, a more detailed chemical mechanism such as SAPRC99 is necessary.

CO reactivity has been studied in a number of different regions with different mechanisms and models (e.g., Russell et al. 1998 and references therein, Hakami et al. 2003). Although our focus is the applicability of reactivity estimates to California urban areas, Whitten (2004) should not cite only one East Coast and ignore other studies.

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The Ozone Impact of Permeation VOC Relative to Carbon Monoxide

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March 2006

The purpose of this document is to summarize ARB's draft modeling analysis for assessing the potential air quality impacts of increased permeation VOC emissions relative to reduced CO emissions for California vehicles using ethanol gasolines. This document describes the problem to be addressed, previous related work, and the air quality modeling results. It is not intended to estimate the air quality impact of ethanol vs. MTBE gasolines.

PROBLEM

A recent study sponsored by Coordinating Research Council, Inc. indicates that, on average, the increase in permeation VOC emissions of ethanol gasoline (5.7% ethanol by volume) is about 1.1 g/vehicle/day relative to non-oxygenate fuel (Haskew et al., 2004). Based on EMFAC2002 (ver. 2.2, April 23, 2003), CO exhaust emissions of ethanol gasoline are about 7.8 g/vehicle/day less than those of non-oxygenate fuel statewide in 2004. In other words, the CO mass reduction is approximately 7 times the VOC mass increase from permeation. It is therefore argued that, on a mass basis, ozone reductions could be achieved by adding ethanol to gasoline because of the significant reduction of CO emissions.

REACTIVITY ANALYSIS

A preliminary analysis based on VOC reactivity was conducted to assess the ozone impact of permeation VOC relative to CO. Several reactivity scales derived from box models (e.g., MIR and MOIR) and 3-D models (e.g., regional-MIR) for both 1-hr and 8-hr episodes were used to characterize the ozone impact of ethanol fuel. In addition to California areas, the 3-D model-derived scales include those conducted for other areas such as the Eastern U. S. region. For this analysis, we compared the reactivity of CO with the reactivity of the top seven species of VOC (i.e., ethanol, toluene, 1-methylbutane, m-xylene, 2-methylpentane, o-xylene, and 1-methyl-2-butene) that represent over 60 percent of the total permeation VOC in terms of mass and MIR reactivity.

Table 1 presents the ozone impact assessment of permeation VOC relative to CO under different reactivity scales. A total of ten reactivity scales were chosen for this analysis based on recent publications and recommendations by several reactivity experts. Following is a summary of our key findings.

Table 1. Ozone impacts of permeation VOC relative to carbon monoxide under different reactivity scenarios

			MIR-1h[1]		MOIR-1h[2]		EBIR-1h[3]		MIR-8h[4]		MOIR-8h[5]		South Coast[6]		Central Cali.[7]		Eastern US-1h[8]		Eastern US-8h[9]		Eastern US-1h[10]	
Species Name	VOC (mg)	Mass Fraction	A[11]	B[12]	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B
Carbon Monoxide			0.06		0.04		0.03		0.03		0.03		0.04		0.03		0.07		0.08		0.05	
Permeation VOCs																						
Ethanol	657.23	28.25%	1.69	0.48	0.93	0.26	0.65	0.18	0.77	0.22	0.61	0.17	0.31	0.09	1.52	0.43	1.02	0.29	1.15	0.33	0.64	0.18
Toluene	507.01	14.35%	3.97	0.57	1.17	0.17	0.36	0.05	2.00	0.29	1.31	0.19	1.33	0.19	1.10	0.16	1.25	0.18	1.17	0.17	0.40	0.06
2-Methylbutane	249.82	7.66%	1.67	0.13	1.01	0.08	0.71	0.05	0.79	0.06	0.67	0.05	0.74	0.06	0.70	0.05	0.74	0.06	0.85	0.07	0.51	0.04
m-Xylene	234.12	6.29%	10.61	0.67	3.19	0.20	1.55	0.10	6.24	0.39	4.17	0.26	4.99	0.31	3.75	0.24	2.79	0.18	2.43	0.15	2.42	0.15
2-Methylpentane[13]	141.68	3.83%	1.78	0.07	1.02	0.04	0.68	0.03	0.79	0.03	0.67	0.03	0.74	0.03	0.70	0.03	0.74	0.03	0.85	0.03	0.51	0.02
o-Xylene[14]	64.22	1.76%	7.48	0.13	1.36	0.02	1.22	0.02	2.20	0.04	1.45	0.03	1.62	0.03	1.32	0.02	1.31	0.02	1.23	0.02	2.42	0.04
2-Methyl-2-butene	34.63	0.94%	14.44	0.14	4.65	0.04	2.63	0.02	9.61	0.09	7.04	0.07	15.77	0.15	9.26	0.09	3.39	0.03	3.37	0.03	5.51	0.05
sum	1888.69	63.08%		2.18		0.82		0.46		1.12		0.79		0.85		1.01		0.78		0.80		0.54
Conversion (sum/0.63)				3.45		1.29		0.73		1.77		1.26		1.36		1.61		1.24		1.27		0.86
Reactivity Ratio of VOC to CO				58		32		24		59		42		34		54		17		15		17

1: Maximum Incremental Reactivity (1-hr) (Carter, 2003). 2: Maximum Ozone Incremental Reactivity (1-hr) (Carter, 2003). 3: Equal Benefit Incremental Reactivity (1-hr) (Carter, 2003). 4: Maximum Incremental Reactivity (8-hr) (Carter, 2003). 5: Maximum Ozone Incremental Reactivity (8-hr) (Carter, 2003). 6: Average 3-D reactivity in South Coast (Martien et al., 2002). 7: MIR-3D (1-hr) in Central California (Martinez et al., 2002). 8: MIR-3D (1-hr) in Eastern US (Hakami et al., 2003). 9: MIR-3D (8-hr) in Eastern US (Hakami et al., 2003). 10: MIR-3D (1-hr) in Eastern US (Carter et al., 2003). 11: reactivity in unit of (gram ozone/gram VOC). 12: ozone formed in unit of gram = A x mass fraction. 13: No 3-D reactivity is available for 2-methylpentane so a surrogate isopentane reactivity is used instead. 14: No 3-D reactivity is available for *o*-xylene so a surrogate *p*-xylene or *m*-xylene reactivity is used instead.

- CO has an MIR of 0.06 while the permeation VOC emissions derived from ethanol fuel have a composite MIR of 3.27 (Haskew et al., 2004). This difference indicates that one ton of permeation VOC is about 55 times as effective as one ton of CO emissions (3.27/0.06) in terms of ozone formation. The composite MIR of the top seven chemicals is 2.18. The composite MIR of the permeation VOC using the top seven chemicals as a surrogate can be calculated to be 3.45 after taking the mass fraction into consideration (2.18/0.63). The estimated reactivity ratio of permeation VOC to CO is about 58 (3.45/0.06), which is in good agreement with the aforementioned value (55). This indicates that the top seven chemicals can represent the permeation VOC well in terms of reactivity analysis.

- Reactivity analysis using reactivity scales other than MIR indicates that one ton of permeation VOC is in the range of 24 (EBIR-1h) to 59 (MIR-8h) times as effective at ozone formation as one ton of CO emissions using metrics for California and is about 15-17 times as effective at ozone formation using metrics derived for the Eastern U. S.. The difference is expected since California urban areas tend to be more sensitive to VOC emissions and thus have conditions more similar to MIR-like conditions than the Eastern U. S. regions. It is also the case for the box model-derived reactivity scales that the reactivity ratios of permeation VOC to CO are the highest for MIR-like conditions (MIR-1hr and MIR-8hr) and the lowest for the less MIR-like condition (EBIR-1h).

MODELING ANALYSIS

An urban airshed air quality model was employed to characterize the ozone impact of permeation VOC relative to CO emissions, as defined in the ARB modeling protocol, posted at http://www.arb.ca.gov/research/reactivity/reactivity.htm. Note that the total model domain covers a much larger area than the South Coast Air Basin (SoCAB) and includes areas such as San Diego and Imperial Counties. The gridded, hourly, 2010 baseline emission inventory used for the 2003 South Coast SIP update (SCAQMD, 2006) was employed to investigate the effect on peak ozone concentration (both 1-hr and 8-hr episodes) due to CO and VOC emissions from on-road vehicles in the SoCAB. On-road CO emissions for the SoCAB were reduced by 10 percent (all hours and grid cells) to see the impact on peak ozone while in a separate simulation, the emissions of on-road vehicle exhaust VOC for the basin were increased by 10 percent (all hours and grid cells). On-road VOC exhaust emissions were used as a surrogate for permeation VOC because they have a similar composite reactivity and because permeation VOC emissions are not readily available in the ARB's vehicle emission inventory model. The 10 percent increase in VOC include both diesel and gasoline exhaust and would not significantly affect the results since the diesel fuel share of CO and VOC is small. Table 2 shows the 2010 SoCAB on-road exhaust emissions.

Thus, a total of three scenarios (baseline, 10% CO reduction, and 10% VOC increase) were simulated in this analysis. All the simulations were conducted for a multiple-day ozone episode (August 3-7, 1997) using the CALGRID photochemical model with the SAPRC99 photochemical mechanism.

Table 2. 2010 SoCAB On-road Vehicle Exhaust Emissions (Tons/Day)*

Compounds	Total on-Road	Gasoline	Diesel
CO	2,017	1,970	47
NO_X	409	181	228
VOC	93	85	8

* Many significant figures are included to calculate more precise differences.

The 2010 baseline 1-hr and 8-hr peak ozone modeling was conducted first. Modeling simulations with CO reduction and permeation VOC increase were then conducted and the resulting ozone difference from the baseline was calculated. The effective 1-hr and 8-hr ozone impacts of VOC relative to that of CO per ton of emission change can then be obtained and compared to those derived from the reactivity analysis. Population exposures for 1-hr ozone above a threshold of 125 ppb and 8-hr ozone above a threshold of 85 ppb were also analyzed, respectively, for the same three scenarios.

Table 3 summarizes the results of the modeling simulations for both 1-hr and 8-hr peak ozone. As shown in the table, the 2010 baseline one-hour peak ozone is 135.96 ppb. The CO reduction resulted in 0.36 ppb ozone reduction and the VOC increase resulted in a 0.79 ppb ozone increase. The resulting difference in ozone (ppb) per ton of CO change is 0.0018 while the ozone difference per ton of VOC change is 0.085. Therefore, the effective 1-hour ozone impact of VOC is 47 times that of CO per ton of emission change. The 8-hour peak ozone VOC ozone impact is 39 times that of CO.

Table 3. Peak Ozone Model Simulation Results*

Scenario	1-Hr Peak ozone		8-Hr Peak ozone	
	(ppb)	(ppb/ton)	(ppb)	(ppb/ton)
Baseline	135.96		119.58	
CO Reduction	135.60	0.0018	119.35	0.0011
VOC Increase	136.75	0.085	119.98	0.043
Ratio (VOC/CO)		47		39

* Many significant figures are included to calculate more precise differences.

Population exposure results for 1-hr ozone above a threshold of 125 ppb and 8-hour ozone above a threshold of 85 ppb are shown in Table 4 for the same three scenarios. The ratios of VOC/CO 1-hr and 8-hr population-weighted exposure impacts were estimated to be 51 and 38, respectively.

Table 4. Population Exposure Model Simulation Results*

Scenario	1-Hr Population Exposure		8-Hr Population Exposure	
	(people·ppb)	(exposure/ton)	(people·ppb)	(exposure/ton)
Baseline	3,274,314		137,630,480	
CO Reduction	3,043,314	1,145	136,714,928	4,539
VOC Increase	3,817,849	58,444	139,231,248	172,126
Ratio (VOC/CO)		51		38

* Many significant figures are included to calculate more precise differences.

DISCUSSION

Based on the four metrics (1-hr and 8-hr peak ozone and 1-hr and 8-hr ozone population exposure) estimated for the three scenarios, the modeling results indicate that the ozone impacts of permeation VOC relative to CO emissions range from 38 to 51, which are reasonably consistent with those derived from the reactivity analysis for California (i.e., 24-59). In other words, the modeling simulations resulted in a similar conclusion as observed from the reactivity analysis. Thus, it can be concluded that the ozone impacts of permeation VOC relative to CO in California using different metrics are reasonably consistent. In this case, it appears that simple reactivity-scale based data analyses can be a useful tool for assessing the ozone impact of permeation VOC relative to CO emissions. Because of the high impact of VOC relative to CO, it is expected that the addition of ethanol into gasoline would result in increased ozone formation in the atmosphere although a reduction of CO emissions on a mass basis is about 7 times that of permeation VOC increase. However, assessing the net ozone effect of an increase in VOC permeation emissions and a reduction in CO resulting from the use of ethanol is beyond the scope of this analysis.

Several comments were received after the release of the modeling protocol and are summarized below, along with our response.

1. The three scenarios are not well defined.
2. All impacts (permeation and tailpipe) should be evaluated simultaneously. Other scenarios such as with and without ethanol should be included.
3. The base case should be MTBE gasoline since most ARB gasoline contained MTBE before ethanol was introduced
4. Emission inventory should be well developed since it is the most important input to this exercise.
5. The timing and location of the emissions should be accounted for in the modeling efforts.

6. Change in NO_X emissions due to the addition of ethanol to gasoline should be assessed as part of the modeling efforts.

Comments (1 to 5) can be categorized as a request for a broader modeling analysis. As indicated in the protocol, this is a scoping analysis and was intended to determine how sensitive the simulations are in terms of ozone formation by varying CO and VOC emissions, respectively (i.e., the ozone impact of permeation VOC relative to CO). If deemed appropriate and necessary, refined modeling simulations, including attainment conditions and the aforementioned comments, would be conducted. The preliminary results indicate that the ozone impacts of permeation relative to CO emissions are overwhelming and consistent. The results are not expected to change substantially if refined simulations with other variables such as those raised above were considered in the simulations. In other words, other variables may contribute to the impact of ozone formation to a certain degree but are not expected to alter the overall disparity.

A change in NO_X emissions due to the addition of ethanol to gasoline (comment 6) was not assessed as part of the modeling efforts since the emission data of NO_X associated with the ethanol addition was not readily available. In addition, the focus of the exercise was to compare the ozone impact of permeation VOC relative to CO emissions. Emission changes in other pollutants such as NO_X and PM are beyond the scope of this work.

CONCLUSIONS

Our preliminary analysis indicates that the model simulation results are consistent with the previous reactivity-based findings in assessing the ozone impact of permeation VOC relative to CO emissions. Overall, the results tend to support that the ozone impact of permeation VOC relative to CO is overwhelming and significant.

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