

# The Ozone Impact of Permeation VOC Relative to Carbon Monoxide

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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**

Species Name	VOC (mg)	Mass Fraction	MIR-1h <sup>1</sup>		MOIR-1h <sup>2</sup>		EBIR-1h <sup>3</sup>		MIR-8h <sup>4</sup>		MOIR-8h <sup>5</sup>		South Coast <sup>6</sup>		Central Cali. <sup>7</sup>		Eastern US-1h <sup>8</sup>		Eastern US-8h <sup>9</sup>		Eastern US-1h <sup>10</sup>		
			A <sup>11</sup>	B <sup>12</sup>	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A
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	
<i>m</i> -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 <sup>13</sup>	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	
<i>o</i> -Xylene <sup>14</sup>	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 <sub>x</sub>	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<sub>x</sub> 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<sub>x</sub> 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<sub>x</sub> 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<sub>x</sub> 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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