

# Development And Application Of An Advanced Air Toxics Hybrid Photochemical Grid Modeling System

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## ABSTRACT

An air toxics modeling capability has been implemented in the Comprehensive Air-quality Model with extensions (CAMx) photochemical grid model that includes full chemistry of organic air toxic compounds, the treatment of both gas and particulate phase air toxics and the treatment of the near-source impacts of air toxics using a subgrid-scale plume model. The CAMx air toxics modeling system was demonstrated using the April 1998 through March 1999 annual database from the Multiple Air Toxics Exposure Study (MATES-II) in the South Coast Air Basin (SoCAB). The MATES-II mobile source emissions were updated from EMFAC7G to EMFAC2000. The CAMx estimated air toxics concentrations using the EMFAC7G and EMFAC2000 emissions were compared against 24-hour observations at the 10 MATES-II monitoring sites in the SoCAB. The performance of the MATES-II UAM-Tox modeling application was also evaluated. The subgrid-scale treatment of point sources was demonstrated using air toxics point source emissions from the MATES-II database. The CAMx air toxics modeling system was also demonstrated using the August 3-7, 1997 Southern California Ozone Study (SCOS) episode using both the CB-IV and SAPRC99 chemical mechanisms. Finally, risk and exposure estimates were made both accounting for and not accounting for indoor/outdoor effects and using both gridded and basin-wide population estimates. This paper presents the innovative procedures used to simulate the near-source and far-field impacts of inert and reactive air toxics and the evaluation of the hybrid air toxics modeling system for benzene, 1,3-butadiene, formaldehyde, acetaldehyde, chromium, hexavalent chromium and diesel particulate.

## INTRODUCTION

Exposure to air toxics and associated risk is an increasing concern in urban areas across the United States (US) as well as regionally for some compounds. Urban air toxics include compounds that have been traditionally associated with gasoline and diesel combustion (mobile sources), such as diesel particles, benzene, 1,3-butadiene, formaldehyde, and acetaldehyde, as well as compounds associated with other industrial activities, such as carbon tetrachloride and hexavalent chromium and heavy metals (e.g., mercury and cadmium). The US Environmental Protection Agency (EPA) has several programs underway to assess exposure to air toxics and to develop mitigation strategies. The evaluation of alternative control strategies for air toxics is performed using air quality modeling.

Currently EPA recommends the use of the ISC air quality model to assess the impacts of urban air toxic compounds<sup>1</sup>. ISC is a steady-state Gaussian plume model that treats transport and dispersion assuming instantaneous transport of pollutants from the source to the receptor and treats chemistry through a constant half-life decay rate. However, such a modeling approach has several limitations for simulating air toxics:

- The steady-state Gaussian plume model formulation is not valid for downwind distances longer than a few kilometers;
- The chemical decay of organic air toxic compounds (e.g., benzene and 1,3-butadiene) depends on atmospheric photochemistry so varies spatially (both horizontally and vertically) and temporally and can not be accurately treated using a single half-life decay;
- The secondary formation of air toxics (e.g., formaldehyde and acetaldehyde) cannot be adequately treated by plume models; and
- Plume models also cannot address regional-scale and mesoscale (e.g., urban airshed) air toxics issues.

More recently there have been significant advances in regional/mesoscale photochemical and particulate matter (PM) models. Multi-scale photochemical grid models have been developed that can treat many scales and pollutants addressing both urban and regional-scale ozone, PM and visibility issues all within a one-atmosphere modeling framework. When combined with a near-source treatment such modeling platforms would be ideal for simulating air toxic compounds.

The Coordinating Research Council (CRC) and the Department of Energy (DOE) are interested in advancing the state-of-science for air toxics modeling. CRC/DOE funded Project A-42-1 to review air toxics modeling techniques and make recommendations for improvements<sup>2</sup>. This was followed by CRC/DOE Project A-42-2 to implement air toxics modeling capability into a state-of-science multi-scale photochemical grid model<sup>3</sup>, which is the subject of this paper.

## **APPROACH**

The development and testing of the advanced air toxics modeling system involved the following activities:

- Implementation of the reactive tracer (RTRAC) modeling capability in the CAMx “Probing Tools” infrastructure including an air toxics chemistry module to treat the formation and destruction of reactive air toxic compounds;
- Implementation of code to extract CAMx-estimated hourly air toxic compound decay rates at each vertical layer for user selected receptor locations for use with a near-source model;
- Modification of an existing near-source plume model to accept the hourly air toxic compound decay rates generated by the CAMx air toxics module;
- Development of a three-dimensional hourly air toxics modeling database for the SoCAB and the MATES-II annual (April 1998 – March 1999) sampling period;
- Application and evaluation of the CAMx air toxics modeling system for the SoCAB and the April 1998-March 1999 year using the MATES-II monitoring database and comparison of model performance with the MATES-II UAM-Tox application;
- Development of air toxics modeling inputs for the August 3-7, 1997 SCOS episode and application and evaluation of the CAMx air toxics modeling system, including the testing of the air toxics modeling capability using both the CB-IV and SAPRC99 photochemical mechanisms and comparison against measurements from the photochemical assessment monitoring sites (PAMS);

- Calculation of risk and exposure using both outdoor exposures as well as a simplified approach for accounting for indoor/outdoor effects; and
- Documentation of the results in a final report<sup>3</sup> and delivery of the publicly available hybrid air toxics modeling system and database to CRC/DOE.

### **Multiple Air Toxics Exposure Study (MATES-II)**

During April 1998 to March 1999, an air toxics sampling field study was conducted for the SoCAB as part of the Multiple Air Toxics Exposure Study (MATES-II)<sup>5</sup>. The South Coast Air Quality Management District (SCAQMD) applied the UAM-Tox photochemical air toxics grid model for the MATES-II annual period. Air toxic concentration estimates were obtained across the SoCAB at 10 fixed sites for approximately 50 air toxic compounds. The UAM-Tox model was applied on a 210-km by 120-km modeling domain covering the SoCAB using a horizontal resolution of 2-km and five vertical layers up to a region top of 2-km above ground level (AGL). The UAM-Tox emissions inventory inputs were generated by the SCAQMD for the expanded CB-IV chemical mechanism (the TOX mechanism). The TOX mechanism explicitly treats several organic air toxics including benzene, 1,3-butadiene, acetaldehyde, and formaldehyde. The UAM-Tox model was then applied and evaluated against the MATES-II air toxics observations and modeled and observed risk and exposure calculations were made<sup>5</sup>. The MATES-II study calculated outdoor or “front yard” exposure and risk. That is, the population was assumed to be stationary outdoors at their place of residence and no indoor effects on exposure was accounted for nor any effects due to changes in the spatial distribution of the population due to their movement throughout the day.

### **Development of CAMx Air Toxics Modeling Inputs for the MATES-II Year**

The surface and upper-air meteorological observations, air toxics observations, and emissions data for the April 1, 1998 through March 31, 1999 period were acquired from the SCAQMD. Three-dimensional meteorological fields were generated for CAMx using the CALMET diagnostic wind model. CAMx was configured on the same 210-km by 120-km 2-km horizontal resolution modeling domain as used by the UAM-Tox in MATES-II. CAMx was set up with 6 vertical layers of spatially and temporally constant thickness up to a region top of 2,000-m AGL. The CAMx reactive tracer (RTRAC) modeling approach was configured to treat Benzene, 1,3-Butadiene, Acetaldehyde, Formaldehyde, Chromium, Hexavalent chromium [Cr(VI)], Diesel Particulate Matter, Elemental Carbon “air toxic” compounds. Note that elemental carbon (EC) and chromium are not actually air toxic compounds, however they are carried as a separate species to provide insight into the model performance evaluation.

The MATES-II mobile source emissions were updated from EMFAC7G to EMFAC2000. For the 1997/1998 year and the SoCAB, EMFAC2000 estimates approximately 50%, 32%, and 8% more VOC, NO<sub>x</sub> and PM emissions, respectively, than EMFAC7G. The resultant total air toxics emissions for the EMFAC7G and EMFAC2000 emissions databases are shown in Table 1. The total primary air toxics emissions for the organic species (i.e., benzene, 1,3-butadiene, acetaldehyde and formaldehyde) are 20% to 35% higher using EMFAC2000 than EMFAC7G due to the ~50% increase in VOC emissions from on-road mobile sources, whereas the increase in total PM air toxics species (e.g., diesel PM, Cr(VI), etc.) is less than 5%.

**Table 1.** Summary of annual air toxics emission totals (lb/day) for the South Coast Air Basin (SoCAB) from MATES-II using EMFAC7G and updated using EMFAC2000.

<b>Pollutant</b>	<b>On-Road</b>	<b>Off-Road</b>	<b>Point</b>	<b>AB2588</b>	<b>Area</b>	<b>Total</b>
<i><b>MATES-II Emissions Based on EMFAC7G</b></i>						
Benzene	21308.8	6338.1	245.7	267.4	2379.9	30540.0
1,3-Butadiene	3852.8	1557.0	9.7	2.0	369.9	5791.5
Acetaldehyde	5242.4	5403.1	45.8	57.1	185.2	10933.6
Formaldehyde	16270.2	15780.1	581.2	674.4	1075.4	34381.2
Chromium	2.3	2.6	5.0	2.2	291.1	303.3
Hexavalent Chromium	0.4	0.4	0.5	1.0	0.0	2.3
Diesel PM	23042.1	18249.6	0.0	5.4	806.0	42103.2
Elemental Carbon	26669.5	5586.6	762.9	0.0	25326.7	58345.6
<i><b>Updated Emissions Using EMFAC2000</b></i>						
Benzene	31547.7	6338.1	245.7	267.4	2379.9	40778.9
1,3-Butadiene	5704.1	1557.0	9.7	2.0	369.9	7642.8
Acetaldehyde	7761.4	5403.1	45.8	57.1	185.2	13452.6
Formaldehyde	24088.0	15780.1	581.2	674.4	1075.4	42199.1
Chromium	2.5	2.6	5.0	2.2	291.1	303.5
Hexavalent Chromium	0.4	0.4	0.5	1.0	0.0	2.3
Diesel PM	24908.5	18249.6	0.0	5.4	806.0	43969.6
Elemental Carbon	28829.7	5586.6	762.9	0.0	25326.7	60505.8

## Hybrid CAMx Air Toxics Modeling System

The hybrid CAMx air toxics modeling system consists of two main components:

- The CAMx photochemical grid model with the reactive tracer (RTRAC) treatment of air toxics accounting for full photochemistry effects on air toxics within the grid modeling framework; and
- A near-source air quality model to treat the local subgrid-scale (e.g., < 2-km) impacts of air toxics due to local point, area, volume and line sources using the CAMx estimated hourly chemical decay rates for reactive air toxics.

The CAMx photochemical grid model is first used to obtain the mesoscale/regional impacts of air toxics. The near-source model is then applied for user-selected emission complexes to obtain the near-source air toxics impacts within a few km of the source. The results of the near-source and mesoscale/regional impact of air toxics are then combined using procedures that are mass consistent and avoid double counting.

## Implementation of Reactive Tracers in CAMx

The CAMx model was modified to treat reactive tracers (RTRAC). Reactive tracers operate in parallel to the host photochemical grid model extracting information on chemical transformation and deposition from the host model that are applied to the air toxic reactive tracers. There were several objectives in the implementation of an air toxics modeling capability into CAMx:

- Implement state-of-science (SOS) treatment of air toxic compounds including full atmospheric chemistry of reactive air toxics and species-dependent and size resolved deposition;
- Ability to treat both the regional and urban-scale impacts of air toxics using a flexible two-way nested-grid modeling framework;
- Ability to treat the near-source impacts of air toxic fence-line or hot-spot impacts using a subgrid-scale near-source model;
- Ease of use and ease of extension to treat additional air toxics; and
- Demonstrate the advanced air toxics modeling system using the 1998/1999 annual MATES-II<sup>5</sup> and the August 1997 SCOS episode<sup>6</sup> databases for the South Coast Air Basin (SoCAB).

The extension of the CAMx modeling system to treat air toxics included the following activities:

- Implementation of the reactive tracer (RTRAC) approach in CAMx that carries air toxic compounds in parallel to the host photochemical grid model, extracts information on chemical formation and decay of air toxics from the host model chemistry module and deposits the air toxics using gaseous or particle deposition rules.
- Extraction of a vertical array of hourly air toxics decay rates from the CAMx chemical mechanism at selected locations that can be used with a near-source model.
- Modification of a near-source model to use the CAMx generated hourly air toxic decay rates.
- Develop pre- and post-processing software to combine air toxics estimates for different families of tracers, compare the results with observations and combine the grid model and near-source model air toxics estimates in a mass consistent fashion.

## **APPLICATION AND EVALUATION USING THE MATES-II ANNUAL DATABASE**

Model estimated air toxics concentrations for the April 1998-March 1999 period and the SoCAB region were evaluated against the MATES-II 24-hour air toxics observations for three photochemical grid model configurations:

- The MATES-II UAM-Tox results provided by the SCAQMD using EMFAC7G emissions (UAM-Tox/7G)
- CAMx/RTRAC results using EMFAC7G emissions (CAMx/7G); and
- CAMx/RTRAC results using EMFAC2000 emissions (CAMx/2000).

### **Statistical Performance Evaluation**

There are no recommended performance goals for air toxic compounds. EPA has published performance goals for ozone modeling<sup>7</sup>, however the ozone performance goals and measures are inappropriate for air toxics. Seigneur, Lohman, and Pun<sup>2</sup> have noted that the accuracy of the emissions for organic air toxics compounds is around a factor of 2 or 3.

Table 2 provides summary model performance evaluation measures for the seven “air toxic” species measured in MATES-II and modeled using the CAMx/RTRAC and the UAM-Tox. Scatter plots of the predicted and observed 24-hour benzene, formaldehyde, and hexavalent chromium concentrations and the UAM-Tox/7G and CAMx/7G model configurations are shown in Figure 1. All three model configurations estimate the average observed benzene concentration to within a factor of 2, with UAM-Tox/7G exhibiting a near zero bias and CAMx/7G and CAMx/2000 exhibiting an overestimation tendency of approximately 20 and 55 percent, respectively.

All three model configurations underestimate the average observed 1,3-butadiene concentrations by 40% to 55%, with the UAM-Tox/7G and CAMx/2000 exhibiting an approximate 40% underprediction bias that is slightly better than the CAMx/7G bias (55%). However, all three models underestimate the average observed 1,3-butadiene concentrations by approximately a factor of 2.

The UAM-Tox/7G and CAMx (7G and 2000) exhibit very different performance for carbonyls. UAM-Tox/7G underestimates acetaldehyde and formaldehyde by 65% and 30%, respectively. Whereas CAMx/7G exhibits an overprediction tendency of approximately 50%-60%. The higher mobile source VOC emissions from EMFAC2000 (Table 1) exacerbate the CAMx carbonyl overestimation tendency. Figure 1b displays the UAM-Tox/7G and CAMx/7G scatter plots of predicted and observed formaldehyde concentrations that illustrate the different tendencies of the two models toward under- and over-prediction, respectively. UAM-Tox/7G never estimates 24-hour formaldehyde concentrations greater than 10 ppb, although there are numerous (~30) observed values, whereas CAMx/7G estimates several (~10) 24-hour formaldehyde concentrations greater than 20 ppb, although no such observations ever occur. Formaldehyde and acetaldehyde in the CB-IV chemical mechanism are lumped species so they contain mass associated with other species than pure formaldehyde or acetaldehyde which the measurements represents, thus one would expect the model to overestimate the observed carbonyl concentrations.

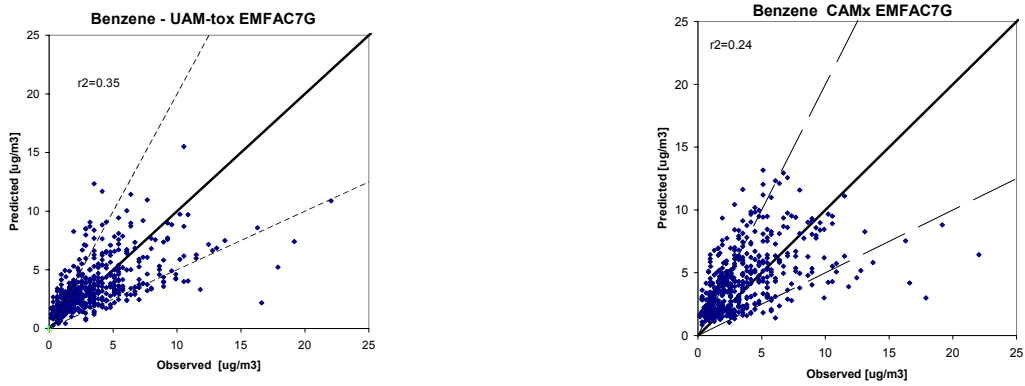
Chromium and hexavalent chromium [Cr(VI)] in the fine mode (PM<sub>2.5</sub>) are severely overestimated by all three model configurations. UAM-Tox/7G overestimates the average chromium and Cr(VI) concentrations by approximately a factor of 4, whereas the CAMx overprediction tendency is a factor of 2-2.5 on average. The scatter plot of predicted and observed 24-hour Cr(VI) concentrations (Figure 1c) reveals that many of the observed values are reproduced within a factor of 2, but there are several observed values that are overestimated by over a factor of 10.

Much better model performance is seen for the three model’s ability to predict the observed elemental carbon (EC) concentrations (Table 2). On average the models reproduce EC to within 20% and most of the 24-hour average EC observations are estimated to within a factor of 2.

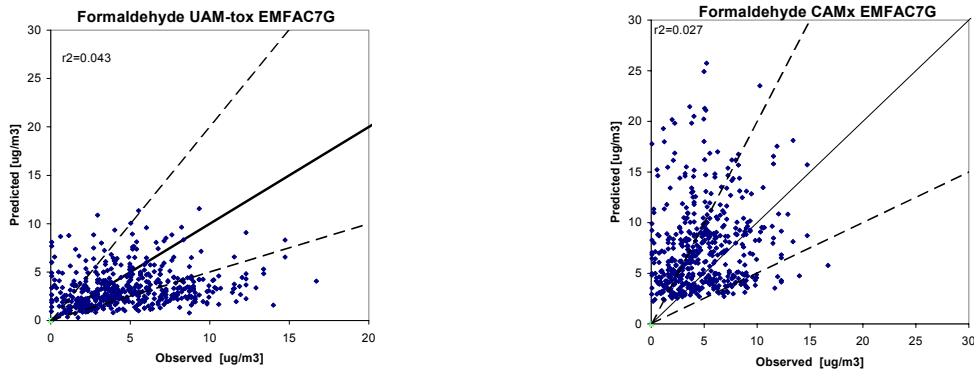
**Table 2.** Summary air toxics model performance statistics using the MATES-II database.

	<b>UAM-Tox/7G</b>	<b>CAMx/7G</b>	<b>CAMx/2000</b>
<b><i>Benzene Concentrations</i></b>			
Number of Parts	499	499	499
Average Observed (: g/m <sup>3</sup> )	3.58	3.58	3.58
Average Predicted (: g/m <sup>3</sup> )	3.57	4.33	5.55
Bias (: g/m <sup>3</sup> )	-0.01	0.75	1.97
Gross Error (: g/m <sup>3</sup> )	1.65	2.09	2.85
Ratio Avg Pred/Avg Obs	1.00	1.21	1.55
<b><i>1,3-Butadiene Concentrations</i></b>			
Number of Parts	499	499	499
Average Observed (: g/m <sup>3</sup> )	1.00	1.00	1.00
Average Predicted (: g/m <sup>3</sup> )	0.62	0.45	0.61
Bias (: g/m <sup>3</sup> )	-0.37	-0.55	-0.39
Gross Error (: g/m <sup>3</sup> )	0.56	0.64	0.60
Ratio Avg Pred/Avg Obs	0.63	0.45	0.61
<b><i>Acetaldehyde Concentrations</i></b>			
Number of Parts	490	490	490
Average Observed (: g/m <sup>3</sup> )	3.05	3.05	3.05
Average Predicted (: g/m <sup>3</sup> )	1.08	4.92	5.58
Bias (: g/m <sup>3</sup> )	-1.97	1.88	2.53
Gross Error (: g/m <sup>3</sup> )	2.15	2.47	2.96
Ratio Avg Pred/Avg Obs	0.35	1.62	1.83
<b><i>Formaldehyde Concentrations</i></b>			
Number of Parts	502	502	502
Average Observed (: g/m <sup>3</sup> )	4.84	4.84	4.84
Average Predicted (: g/m <sup>3</sup> )	3.35	7.43	9.11
Bias (: g/m <sup>3</sup> )	-1.49	2.59	4.26
Gross Error (: g/m <sup>3</sup> )	2.70	4.06	5.26
Ratio Avg Pred/Avg Obs	0.69	1.54	1.88
<b><i>Chromium Concentrations PM<sub>2.5</sub></i></b>			
Number of Parts	429	429	429
Average Observed (: g/m <sup>3</sup> )	4.82	4.82	4.82
Average Predicted (: g/m <sup>3</sup> )	18.19	12.54	12.55
Bias (: g/m <sup>3</sup> )	13.38	7.73	7.73
Gross Error (: g/m <sup>3</sup> )	13.86	9.75	9.75
Ratio Avg Pred/Avg Obs	3.78	2.60	2.61
<b><i>Hexavalent Chromium Concentrations PM<sub>2.5</sub></i></b>			
Number of Parts	486	486	486
Average Observed (: g/m <sup>3</sup> )	0.18	0.18	0.18
Average Predicted (: g/m <sup>3</sup> )	0.73	0.38	0.39
Bias (: g/m <sup>3</sup> )	0.55	0.20	0.21
Gross Error (: g/m <sup>3</sup> )	0.62	0.29	0.29
Ratio Avg Pred/Avg Obs	4.06	2.11	2.14
<b><i>Elemental Carbon Concentrations PM<sub>2.5</sub></i></b>			
Number of Parts	426	426	426
Average Observed (: g/m <sup>3</sup> )	3.39	3.39	3.39
Average Predicted (: g/m <sup>3</sup> )	3.91	3.92	3.95
Bias (: g/m <sup>3</sup> )	0.52	0.53	0.56
Gross Error (: g/m <sup>3</sup> )	1.52	1.72	1.73
Ratio Avg Pred/Avg Obs	1.15	1.16	1.17

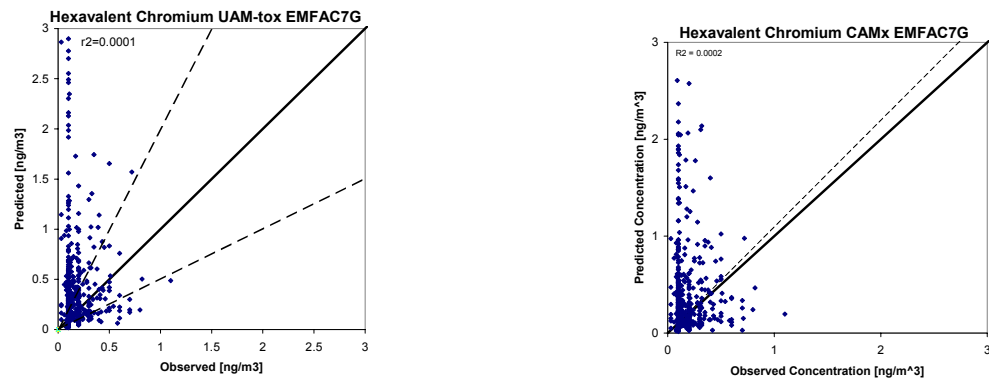
**Figure 1a.** Scatter plots of predicted and observed 24-hour benzene concentrations ( $\mu\text{g}/\text{m}^3$ ) for the SoCAB and MATES-II April 1998 – March 1999 period and the UAM-Tox/7G (left) and CAMx/7G (right) models.



**Figure 1b.** Scatter plots of predicted and observed 24-hour formaldehyde concentrations ( $\mu\text{g}/\text{m}^3$ ) for the SoCAB and MATES-II April 1998 – March 1999 period and the UAM-Tox/7G (left) and CAMx/7G (right) models



**Figure 1c.** Scatter plots of predicted and observed 24-hour hexavalent chromium concentrations ( $\mu\text{g}/\text{m}^3$ ) for the SoCAB and MATES-II April 1998 – March 1999 period and the UAM-Tox/7G (left) and CAMx/7G (right) models.



## Spatial Distribution of Air Toxic Compound Estimates

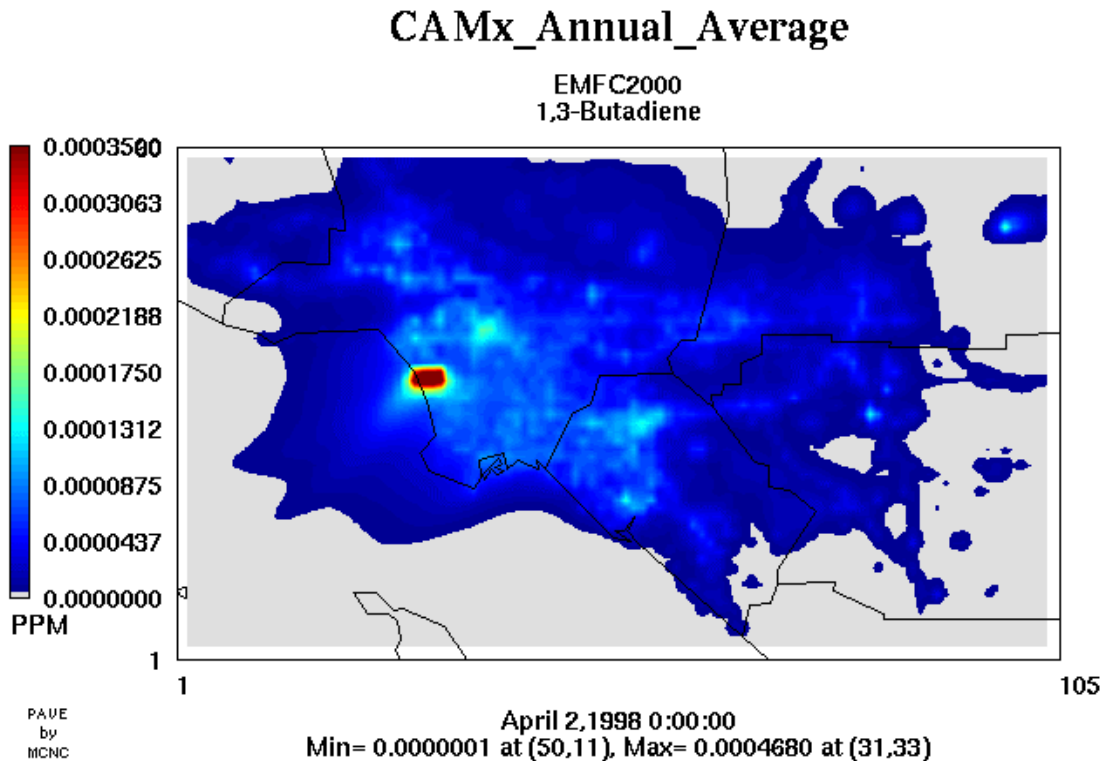
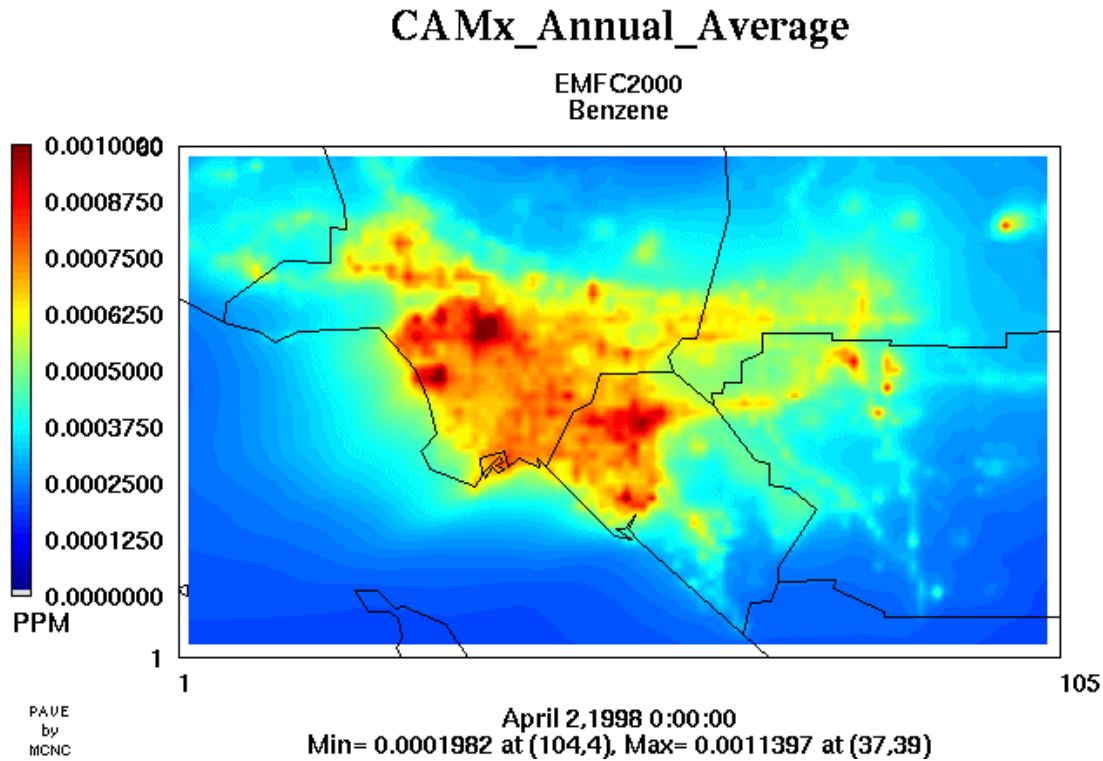
Figure 2a displays the spatial distribution of the annual average CAMx/2000 estimated benzene and 1,3-butadiene concentrations. The footprint of the major roadways is clearly evident in the spatial distribution of the benzene concentrations. The highest estimated benzene concentrations occur in downtown Los Angeles and Anaheim, as well as at the LAX airport near the coast (Figure 2a, top). This is in contrast to the spatial distribution of 1,3-butadiene where by far the largest concentration occurs at the LAX airport (Figure 2a, bottom).

Figures 2b and 2c (top) display the spatial distribution of primary formaldehyde, secondary formaldehyde, and the ratio of primary to secondary formaldehyde concentrations. There are two major hot spots (>3 ppb) of primary formaldehyde concentrations that occur at the LAX airport (maximum of 7.7 ppb) on the coast near El Segundo and at the port area near Long Beach. Lower hot spots of primary formaldehyde, in the 1-3 ppb range, occur over the downtown areas of Los Angeles and Anaheim. Over most of the rest of the domain, primary formaldehyde concentrations are much less than 1 ppb. Except for the two hot spot locations, secondary formaldehyde has a higher contribution to the total formaldehyde concentrations, with a maximum concentration of 8.8 ppb occurring over the San Bernardino Mountains. It should be noted that the spatial distribution of primary and secondary formaldehyde are very different (Figure 2b). Thus, the EPA Urban Air Toxics Modeling Guidance (UATMG)<sup>1</sup> procedures to account for secondary formaldehyde by scaling the primary formaldehyde concentrations is clearly incorrect.

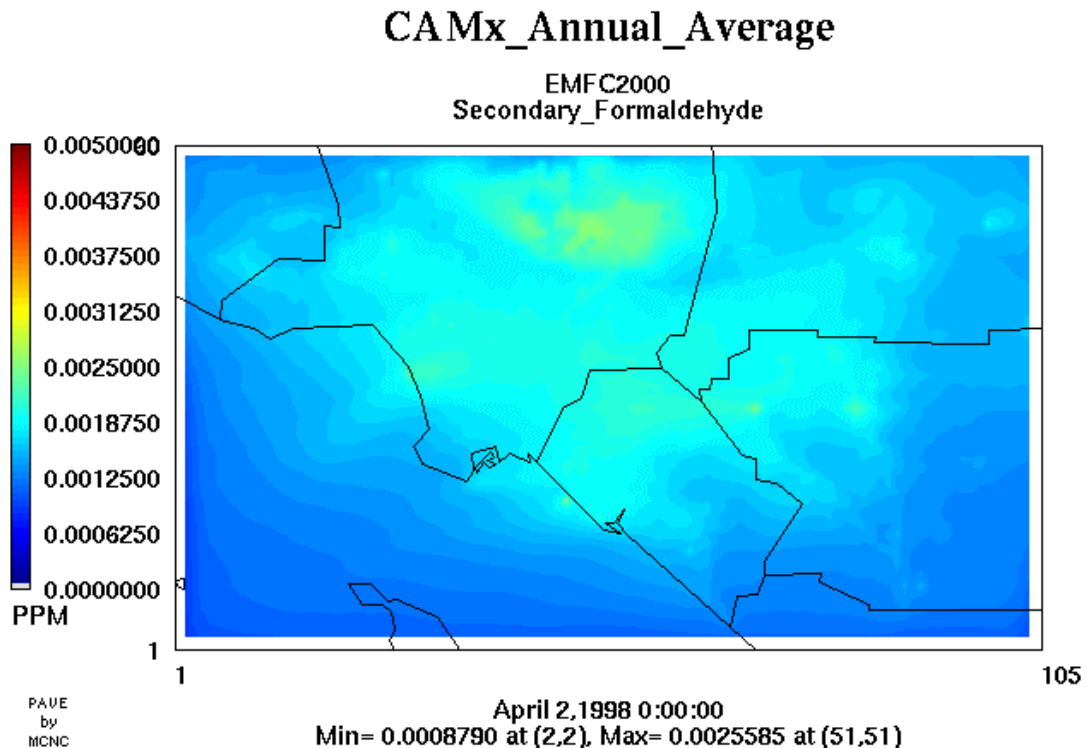
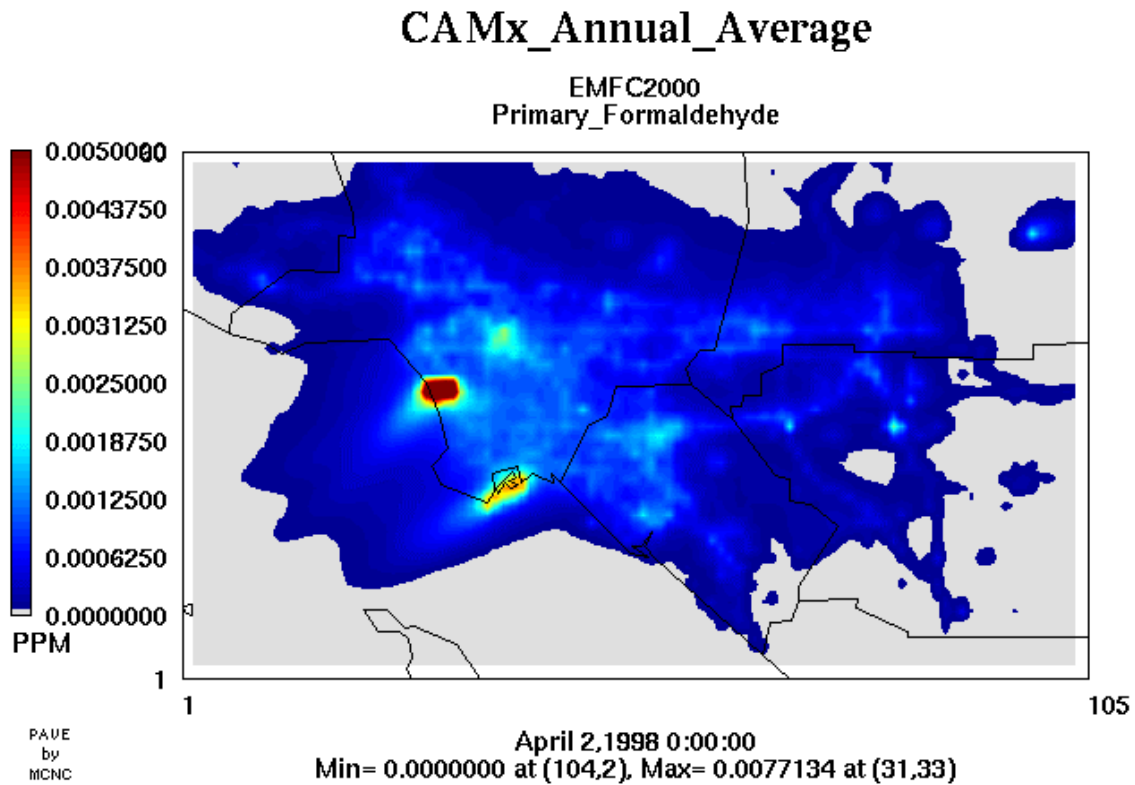
The spatial distribution of the roadways are clearly evident in the annual average diesel fine particulate matter concentrations (Figure 2c, bottom). However, by far the largest diesel PM<sub>2.5</sub> source area is the port area near Long Beach. Diesel PM emissions from marine vessels are believed to be the largest contributor to diesel PM at this location, although trucks, cranes and other sources associated with the port operations also contribute.

Finally, Figure 2d displays the spatial distribution of Cr(VI) concentrations in the fine (top) and coarse (bottom) PM modes. Unlike the other air toxics, whose spatial distributions followed roadways and or were associated with the airport or port areas, the spatial distribution of Cr(VI) concentrations are highly localized spikes that are likely associated with local chrome plating or other industrial operations. The coarse mode Cr(VI) concentrations are much higher than the fine mode Cr(VI) concentrations and the coarse mode Cr(VI) spikes are more prevalent than the fine mode Cr(VI) spikes (Figure 2d). As the MATES-II monitoring study only measured fine mode Cr(VI) and the fine mode is much lower than the coarse mode Cr(VI), this raises questions about the adequacy of the MATES-II fine model only Cr(VI) observation database for model evaluation and risk assessment.

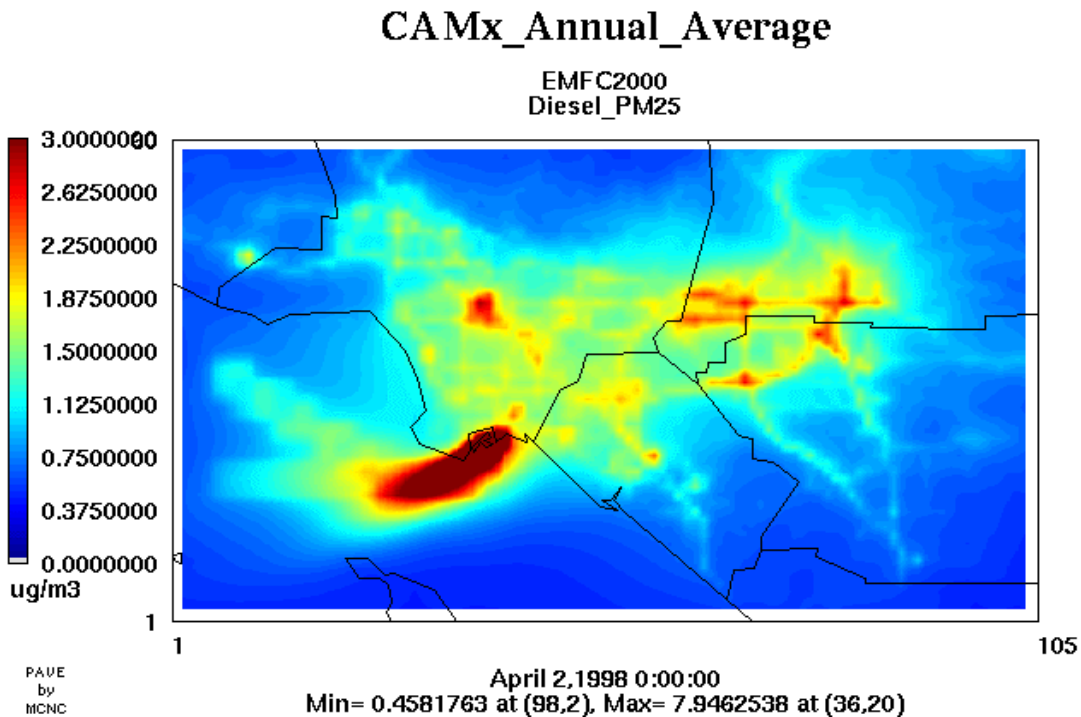
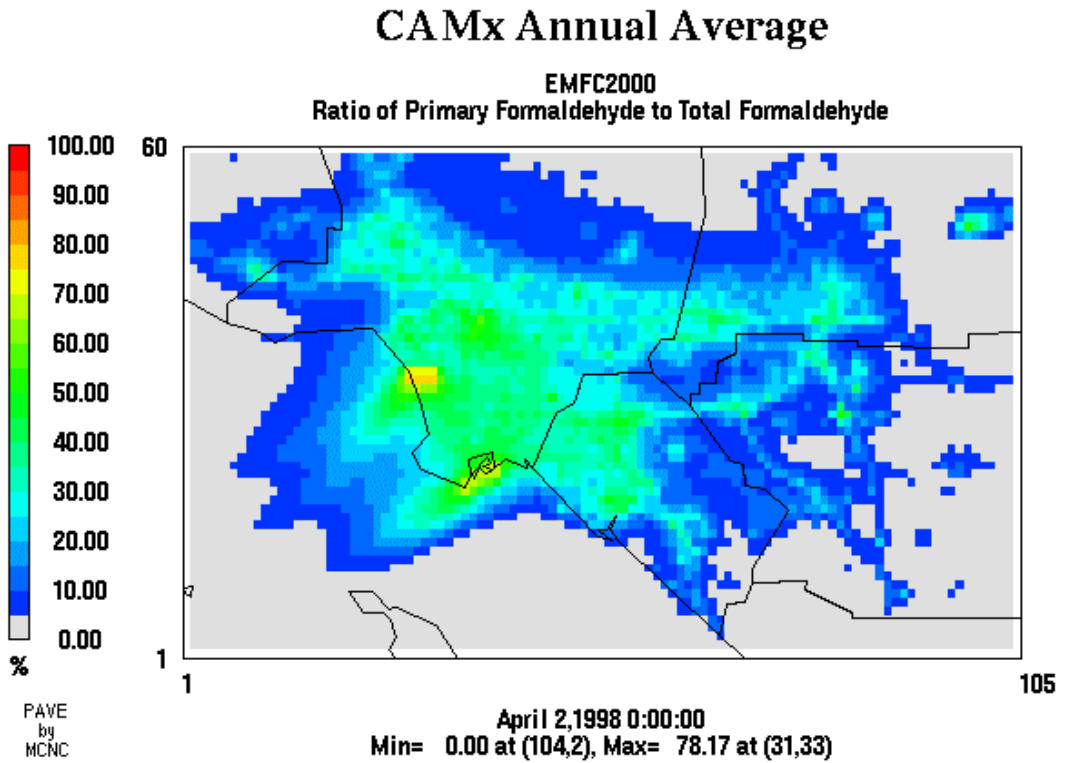
**Figure 2a.** Annual average benzene (top) and 1,3-butadiene (bottom) concentrations (ppm) in the SoCAB estimated by the CAMx/EMFAC2000.



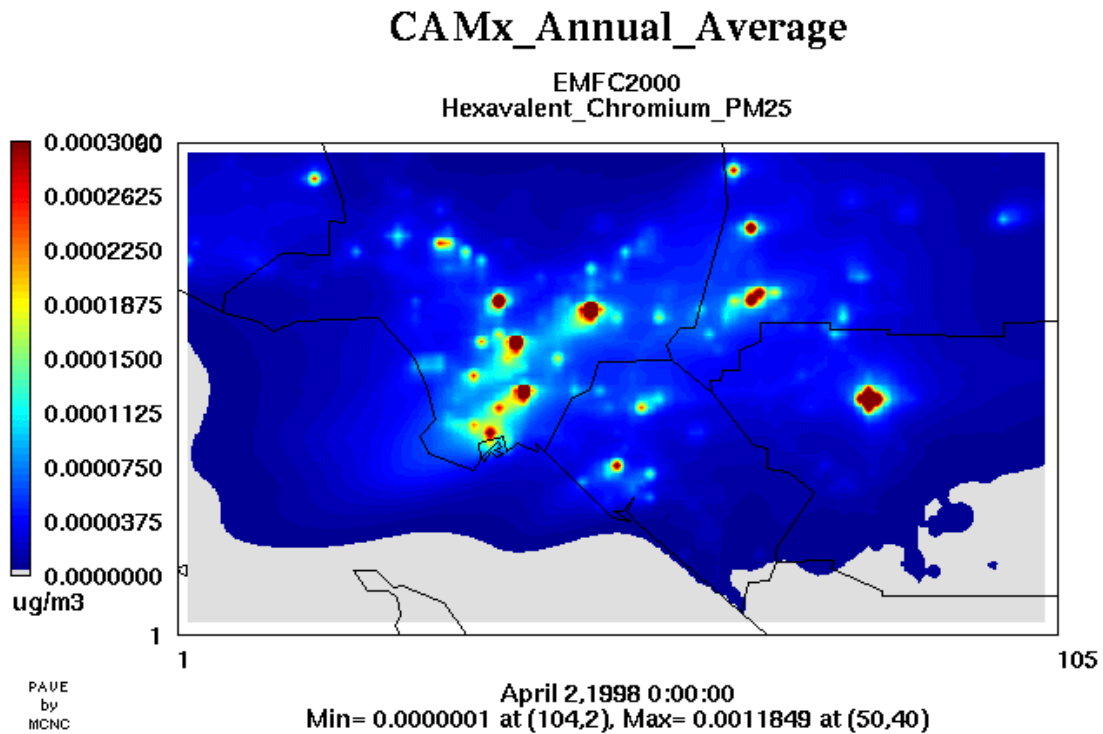
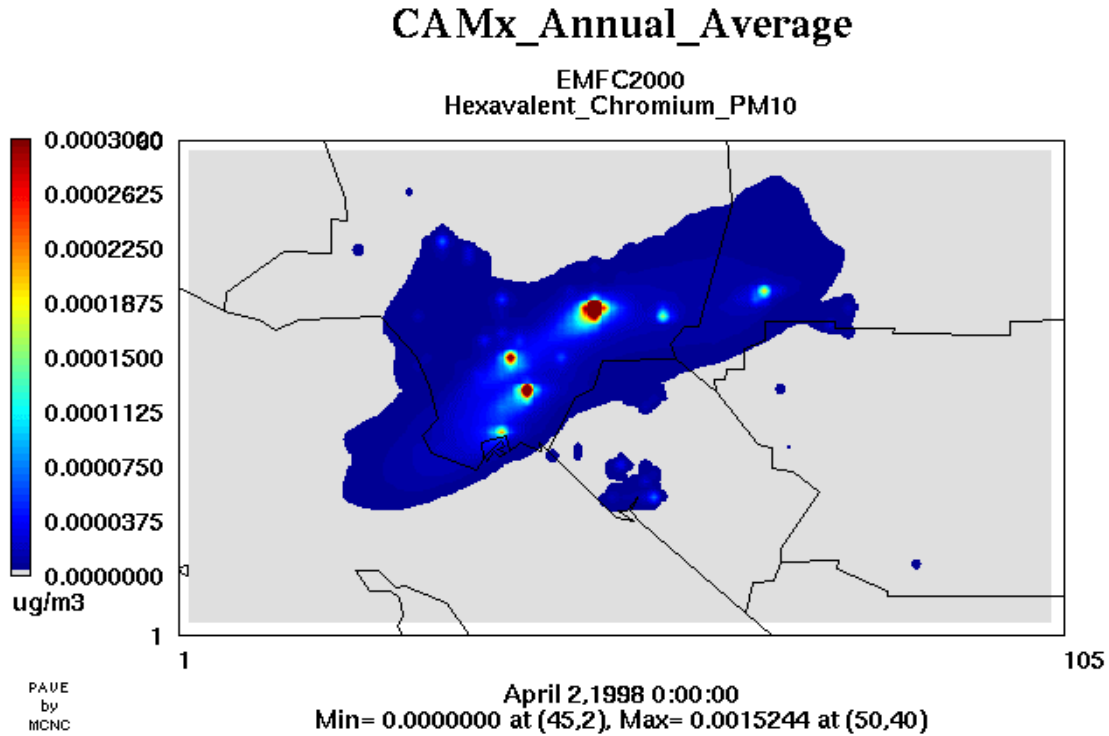
**Figure 2b.** Annual average primary formaldehyde (top) and secondary formaldehyde (bottom) concentrations (ppm) in the SoCAB estimated by the CAMx/EMFAC2000.



**Figure 2c.** Ratio (%) of annual average primary to total formaldehyde concentrations (top) and annual average diesel PM<sub>2.5</sub> concentrations (µg/m<sub>3</sub>) (bottom) concentrations (ppm) in the SoCAB estimated by the CAMx/EMFAC2000.



**Figure 2d.** Annual average Cr(VI) (hexavalent chromium) PM2.5 (top) and Cr(VI) PM<sub>2.5-10</sub> (bottom) concentrations ( $\mu\text{g}/\text{m}^3$ ) in the SoCAB estimated by the CAMx/EMFAC2000.



## Risk and Exposure Calculations using the CAMx MATES-II Results

The MATES-II study used species-dependent unit risk factors (URFs) that are applied to the annual average air toxics concentrations and summed to estimate the one in a million risk of premature death due to exposure to air toxics. In MATES-II, risk was calculated in terms of outdoor exposures. That is, the long-term rate of cancer incidence due to exposure to air toxics assumed that the population was outdoors 24 hours/day 365 days/year using a basin-wide average concentration and population. In this study we accounted for indoor/outdoor effects on risk and exposure several different ways:

- 10 site average using annual average concentrations and no indoor/outdoor ratio (i.e., the method used in MATES-II study <sup>5</sup>);
- 10 site average using annual average concentrations and constant (0.59) indoor/outdoor ratio; and
- 10 site average using hourly concentrations and hourly indoor/outdoor ratio.

These approaches are very simplistic ways of accounting for indoor/outdoor effects on risk and exposure, but do represent an improvement over the MATES-II “outdoor” exposure approach. The results of these risk calculations using the CAMx air toxics modeling results are displayed in Table 3, where the risk results from the MATES-II modeling and monitoring are also listed<sup>5</sup>. The estimated risk calculated in this study is actually greater than the risk calculated in MATES-II even though this study did not simulate all of the air toxic compounds that MATES-II did (according to MATES-II the air toxic compounds not considered in this study accounted for approximately 10% of the MATES-II risk estimates). This study’s risk, without accounting for indoor/outdoor effects, is 35%-60% higher than the average risks reported in MATES-II. The higher aldehyde and benzene concentrations estimated by CAMx/RTRAC than UAM-Tox (see Table 2) account for most of these differences (although diesel particles also plays a role). When accounting for indoor/outdoor effects on diesel particles only, the estimated risk due to air toxics is reduced by approximately one-third. Note that there is little difference (within 2%) in the calculated risk whether a composite annual average indoor/outdoor factor is used or if hourly indoor/outdoor values are used that account for population activity and are applied to the hourly air toxics concentrations.

**Table 3.** Average risk across the 10 MATES-II sites calculated in MATES-II (all toxic compounds with no indoor/outdoor effect) and by this study (missing some MATES-II air toxic compounds that accounted for approximately 10% of the risk) with no indoor/outdoor (I/O) effects and accounting for indoor/outdoor effects on an annual average and hourly basis.

Scenario	Risk (Number in a million)	Percent different from no indoor/outdoor ratio.
<i>MATES-II Study UAM-Tox/7G Results No Indoor/Outdoor Effects<sup>1</sup></i>		
Modeled Average, no I/O	1,230	--
Monitored Average, no I/O	1,414	--
<i>This Study’s CAMx/7G Modeling Risk w/ and w/o Accounting for Indoor/Outdoor Effects</i>		
No Indoor/Outdoor Effects	1,950	--
Annual Indoor/Outdoor Ratio	1,284	-34.1
Hourly Indoor/Outdoor Ratios	1,257	-35.5

## Subgrid-Scale Near-Source Impact Assessment

The implementation of air toxics modeling capability into the CAMx modeling system contained provisions for interfacing with a subgrid-scale near-source model. It is recognized that photochemical grid models, such as CAMx, have limitations in estimating the near-source impacts of sources (e.g., fence-line impacts). The MATES-II emissions databases were analyzed and all point sources that contained emissions for any one of the seven air toxics being analyzed were extracted for use with the subgrid scale near-source algorithm. Note that the hybrid CAMx/RTRAC air toxics modeling system near-source treatment is not limited to just point sources, but could also be applied to area, volume and line sources. However, the model-ready MATES-II emissions already combines the low-level emissions into the 2-km grid cells so only point source emissions could be isolated for this demonstration study. There were five different point source complex locations with emissions for benzene, acetaldehyde and formaldehyde that were modeled using the subgrid-scale plume model. These point source emissions were treated as a separate family of reactive air toxics tracer emissions in the CAMx/RTRAC tracer run. This results in the model tracking air toxic concentrations for six separate families of tracers, the five point source complex emissions and the remainder of the emissions. The CAMx/RTRAC simulation generated gridded hourly air toxic concentration impacts for each of the six families of tracers, as well as a vertical profile of hourly air toxic compound decay rates extracted from the CAMx chemistry module at the location of each of the five point source complexes to be used with the near-source model.

The ISC steady-state Gaussian plume model was selected for the subgrid-scale near-source model as it is the current recommended model in EPA's UATMG<sup>1</sup>. ISC treats the chemical decay of pollutants through input of a constant half-life decay factor. The ISC model was modified to read in the CAMx/RTRAC vertical sounding of hourly decay rates for the April 1998 through March 1999 year. Different air toxic compound decay rates were used for each hour of each day of the year and potentially for each point source in the point source complex being modeled depending on the point source's plume rise (i.e., vertical height).

The ISC model was used to estimate the subgrid-scale near-source impacts of the 5 point source complexes at receptor rings around the point source complex at distances of 100-m, 200-m, etc. out to 1-km. Beyond 1-km, the CAMx grid model estimates are used (i.e., ISC is just used to estimate the near-source impacts of air toxics within  $\leq 1$ -km of the source). Note that beyond a few km the steady-state Gaussian plume model (ISC) estimates are not reliable.

Table 4 summarizes the results of the subgrid-scale point source modeling using the MATES-II database whose main features are as follows:

- The point sources that included air toxics emissions in the MATES-II emissions input file generally have small impacts compared to the regional "background" concentration estimated by the grid model;
- With one exception, the ISC maximum estimated near-source air toxic concentration is greater than the CAMx/RTRAC grid cell volume average value;
- The ISC estimated maximum value with decay is either the same or less than the maximum estimated value without decay; and

- The ISC estimated maximum near-source benzene and formaldehyde concentrations due to a point source complex are as much as, respectively, 20 and 10 times higher than the corresponding CAMx grid cell volume estimate.

These results demonstrate the need to depict both the near-source (e.g., fence-line) impact of local sources as well as the regional contribution of more distant sources to accurately simulate urban air toxics impacts.

**Table 4.** Summary of CAMx/RTRAC subgrid-scale near-source modeling annual results for the MATES-II air toxics point sources.

IX	IY	Species	CAMx Total (: g/m <sup>-3</sup> )	CAMx Point (: g/m <sup>-3</sup> )	ISC Point W/ Decay (: g/m <sup>-3</sup> )	ISC Point No Decay (: g/m <sup>-3</sup> )	CAMx Total – Point (Backgrnd) (: g/m <sup>-3</sup> )	ISC Point w/ Decay + Backgrnd (: g/m <sup>-3</sup> )	ISC Point No Decay + Backgrnd (: g/m <sup>-3</sup> )
34	48	BENZ	3.879316	0.000063	0.000090	0.000090	3.879253	3.879343	3.879343
39	36	BENZ	5.282383	0.001360	0.001710	0.001720	5.281023	5.282733	5.282743
41	36	BENZ	5.799652	0.002099	0.003900	0.003900	5.797553	5.801453	5.801453
42	44	BENZ	5.865131	0.001506	0.007010	0.007010	5.863625	5.870635	5.870635
50	43	BENZ	5.978545	0.000071	0.001360	0.001360	5.978474	5.979834	5.979834
34	48	FORM	3.502453	0.000107	0.000170	0.000180	3.502346	3.502516	3.502526
39	36	FORM	5.617651	0.002453	0.003260	0.003430	5.615198	5.618458	5.618628
41	36	FORM	5.655835	0.003790	0.007130	0.007800	5.652045	5.659175	5.659845
42	44	FORM	5.001340	0.002465	0.013410	0.014020	4.998875	5.012285	5.012895
50	43	FORM	4.982802	0.000270	0.002730	0.002730	4.982532	4.985262	4.985262
42	44	ACET	1.277799	0.000000	0.000000	0.000000	1.277799	1.277799	1.277799

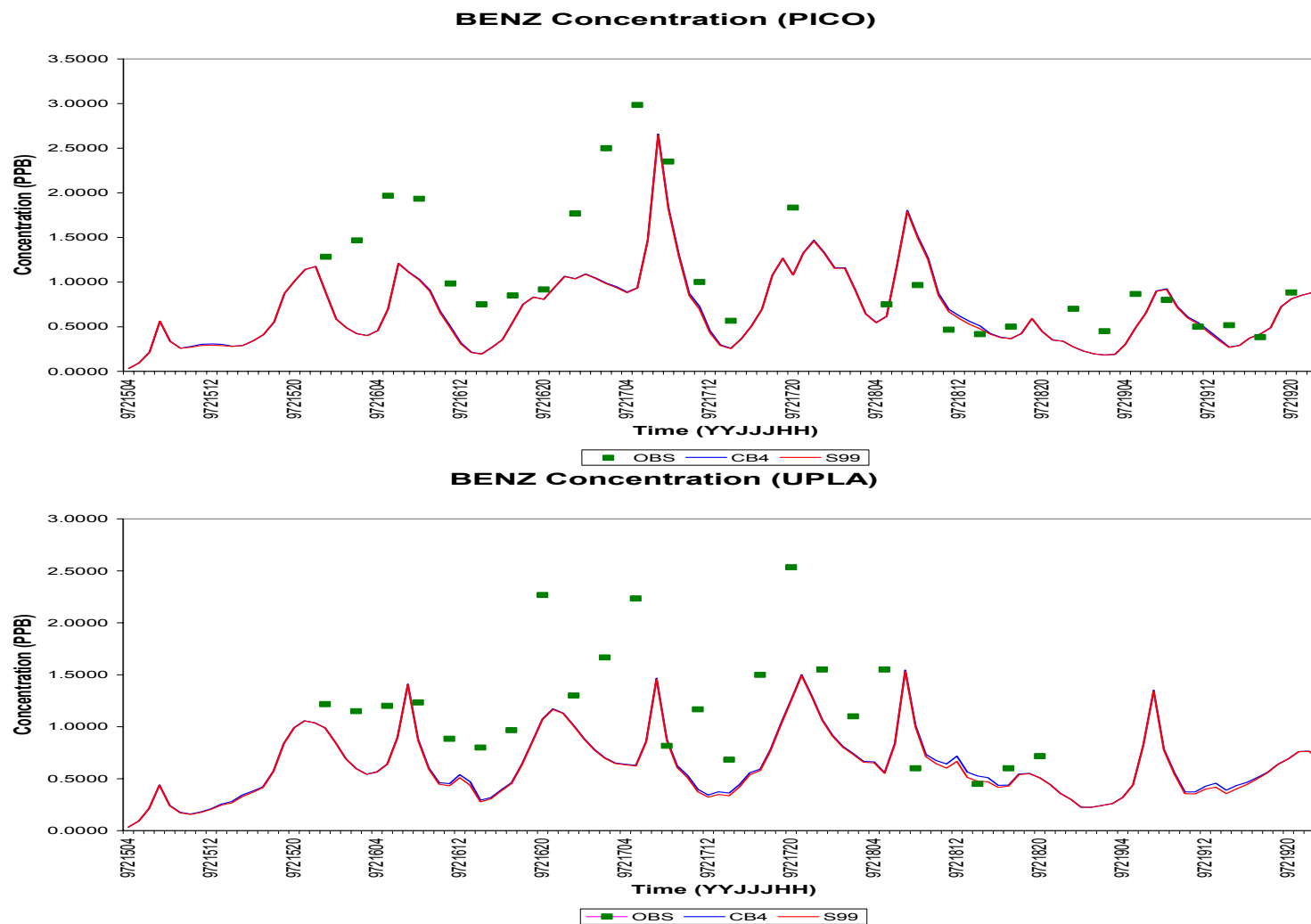
## APPLICATION AND EVALUATION USING THE AUGUST 1997 SCOS DATABASE

To provide an additional test of the new CAMx/RTRAC air toxics capability, the modeling system was also applied for the August 3-7, 1997 Southern California Ozone Study (SCOS) episode and the air toxics modeling results were compared against data from the PAMS network. In this application, CAMx air toxics simulations were performed using both the CB-IV and SAPRC99 chemical mechanisms to assure that the air toxics capability worked with both chemical mechanism and to provide an estimate of the sensitivity of the reactive air toxics impacts to the choice of chemical mechanism.

### Model Performance Evaluation

Six Photochemical Assessment Monitoring Stations (PAMS) sites were in operation during the August 1997 SCOS episode that collected hourly concentrations of benzene. In addition, one PAMS site also collected hourly formaldehyde and acetaldehyde concentrations. Figure 3a displays example predicted and observed time series of hourly benzene concentrations at two of the PAMS sites (Upland and Pico Rivera).

**Figure 3a.** Time series of observed and estimated hourly benzene concentrations during August 3-7, 1997 at the Pico Rivera (top) and Upland (bottom) PAMS sites using the CAMx air toxics modeling system with the CB-IV (CB4) and SAPRC99 (S99) chemistry mechanisms.



**Figure 3b.** Time series of observed and estimated hourly acetaldehyde (top) and formaldehyde (bottom) concentrations during August 3-7, 1997 at the Pico Rivera PAMS site using the CAMx air toxics modeling systems with the CB-IV (CB4) and SAPRC99 (S99) chemistry mechanisms.

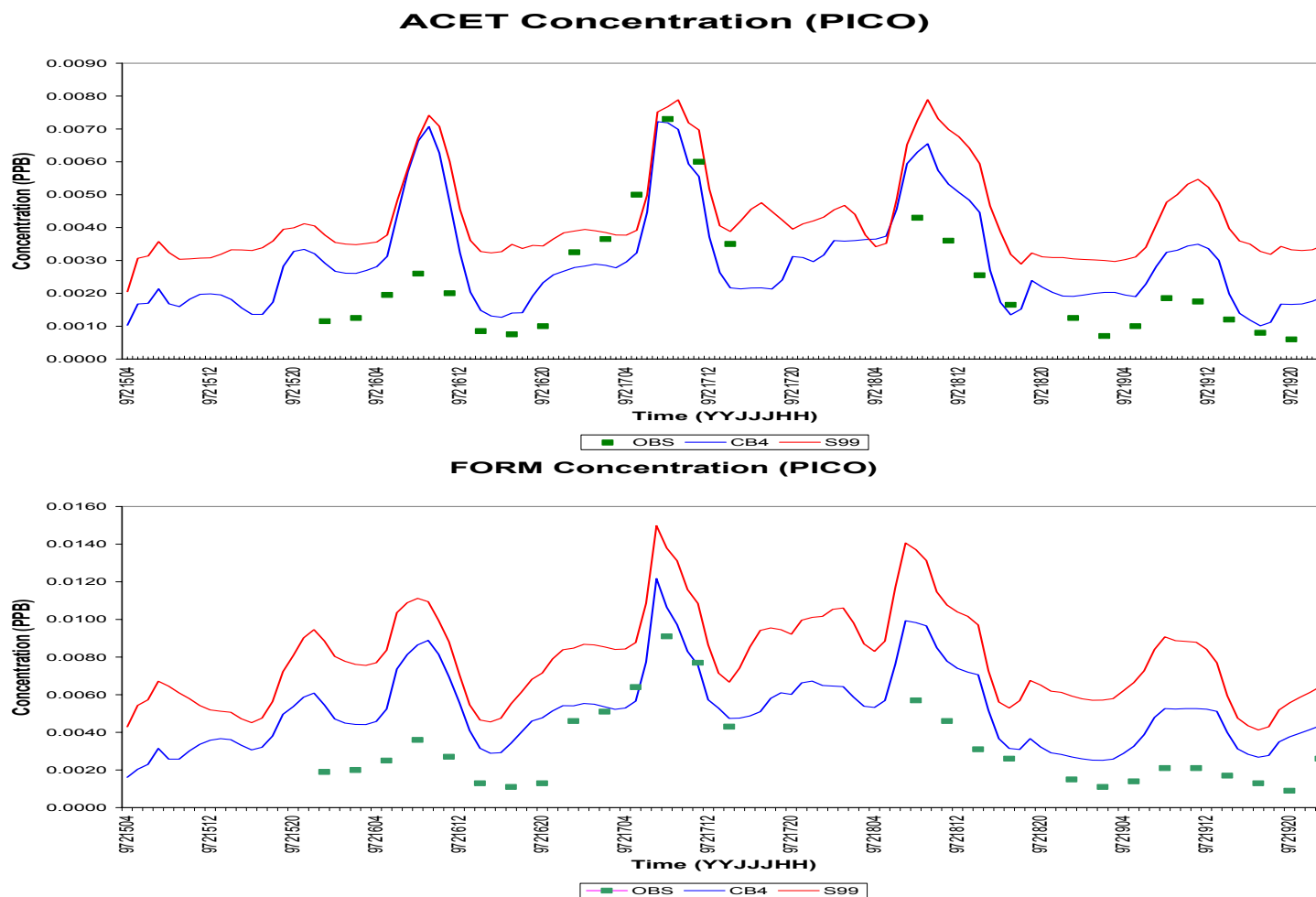


Figure 3b displays hourly time series of hourly formaldehyde and acetaldehyde concentrations at Pico Rivera. CAMx air toxics modeling results are presented using both the CB-IV and SAPRC99 chemical mechanisms. The estimated benzene concentrations are generally lower than the observed values but agree reasonably well, including reproducing the peak morning observed benzene concentration on August 5 (Julian day 217) at Pico Rivera as well as the observed values during the last two days of the episode (August 6-7). The CAMx/CB-IV and CAMx/SAPRC99 estimated benzene concentrations are nearly identical, with the CAMx/CB-IV estimates being slightly higher in the afternoons at Upland due to the higher photochemical activity in the SAPRC99 chemistry that decays the benzene slightly faster.

There are larger differences in the CAMx/CB-IV and CAMx/SAPRC99 acetaldehyde and formaldehyde concentration estimates. The CAMx/SAPRC99 carbonyl concentrations are greater than observed, whereas there is better agreement using CAMx/CB-IV. The hotter chemistry in SAPRC99 generates more secondary acetaldehyde and formaldehyde than the CB-IV chemistry.

For the August 1997 CAMx/RTRAC application, the model was configured to obtain air toxics source apportionment for on-road mobile, point and other anthropogenic emissions sources, as well as secondarily formed air toxics. On-road mobile sources were estimated to contribute 44% (SAPRC99) to 55% (CB-IV) of the risk due to air toxic in the SoCAB. They were followed by secondarily formed air toxic compounds (31% and 46% using the CB-IV and SAPRC chemistries), point sources (~10%) and other anthropogenic emissions (1-2%).

## CONCLUSIONS

There are several conclusions from the study related to the MATES-II database, the new hybrid CAMx air toxics modeling system, and air toxics model evaluation, risk, and exposure calculations.

### MATES-II Databases

- The MATES-II emissions inventories are suspect and have over-allocated point source air toxics emissions to the low-level gridded emissions rather than leaving them in the point source files.
- The CALMET generated hourly meteorological fields for the SoCAB are highly suspect and likely introduce spurious vertical velocities.
- For several species (e.g., chromium and hexavalent chromium  $PM_{2.5}$ ) the MATES-II measured concentrations were frequently below the detection limit so were set to half of the detection limit which affected the model performance evaluation.
- In MATES-II chromium and hexavalent chromium were measured only in the fine PM mode ( $PM_{2.5}$ ), yet the emissions inventory suggest a majority of these compounds are in the coarse mode so the model performance evaluation for these species is limited and incomplete.

### CAMx Air Toxics Modeling System

- The CAMx reactive tracer (RTRAC) treatment of air toxics has been demonstrated to be an effective, accurate, flexible and efficient methodology for treating both inert

and reactive, gaseous and particulate, and primary and secondary air toxic compounds as well as a valuable air toxics source apportionment tool.

- The near-source subgrid-scale plume treatment, that is coupled with CAMx through the CAMx chemistry and RTRAC reactive tracers as background concentrations, has proven to be an efficient and flexible approach for estimating maximum fence-line or hot-spot air toxics impacts in a mass consistent fashion with a grid model.
- The CAMx air toxics modeling system is applicable to many scales, from local plume impacts using the subgrid-scale near-source plume models, to the urban-scale, to the regional-scale using the CAMx two-way nested-grid formulation.
- The update of the MATES-II emissions from EMFAC7G to EMFAC2000 results in substantial increases (approximately 50%) in on-road mobile source organic air toxics emissions (e.g., benzene, 1,3-butadiene, and aldehydes) and lesser increases in the mobile source PM air toxics (<5%).
- The use of the subgrid-scale near-source model produced maximum concentrations due to point sources that were as much as 10-20 times greater than the CAMx/RTRAC estimated 2-km by 2-km grid cell average concentration.

### **Model Performance Evaluation using the MATES-II Annual Database**

- The UAM-Tox and CAMx models both exhibit some skill in estimating the MATES-II observed benzene concentrations reproducing the observed benzene concentrations to within the uncertainties of the emissions inventory that is believed to be approximately a factor of 2<sup>2</sup>. The spatial distribution of the estimated benzene concentrations in the SoCAB follow the major roadways in the region.
- CAMx and UAM-Tox both underestimate the observed 1,3-butadiene by approximately a factor of 2 on average. The very highest annual average estimated 1,3-butadiene concentrations occur over the LAX airport, with lower 1,3-butadiene concentrations in the remainder of the domain that follow the roadways in the SoCAB.
- The UAM-Tox underestimates the observed acetaldehyde concentrations by approximately a factor of 3, whereas CAMx is within a factor of 2 with an average overestimation bias of 60% (EMFAC7G) and 80% (EMFAC2000).
- Both UAM-Tox and CAMx estimate the average observed formaldehyde concentrations within a factor of 2, with UAM-Tox exhibiting a 30% underprediction tendency and CAMx exhibiting a 50% (EMFAC7G) and 90% (EMFAC2000) overprediction tendency
- Both models overestimate the observed chromium and hexavalent chromium concentrations with the UAM-Tox overestimation bias quite severe (factor of 4 to 5), whereas the CAMx overestimation tendency is not as severe (factor of 2 to 2.5). The spatial distribution of chromium follows the roadways with the coarse mode chromium being much higher than the fine mode chromium. The spatial distribution of the hexavalent chromium is very spotty. The coarse mode hexavalent chromium concentrations are greater than their fine mode counterparts. As the MATES-II monitoring only measured fine mode chromium and hexavalent chromium and a majority of these species are in the coarse mode, the evaluation for these two species is incomplete.

## **Model Evaluation Using the August 1997 SCOS Episode Database**

- The observed benzene concentrations during the August 3-7, 1997 SCOS episode are reproduced by the CAMx model fairly well using both the CB-IV and SAPRC99 chemical mechanisms.
- The observed formaldehyde and acetaldehyde concentrations are also replicated fairly well by the CAMx model, with much better model performance being exhibited by the CAMx using the CB-IV chemistry than using the SAPRC99 chemistry.
- The SAPRC99 chemistry is more reactive than the CB-IV chemistry, so it decays primary emitted organic air toxic species much faster (e.g., 1,3-butadiene) and forms more secondary air toxic compounds (e.g., formaldehyde and acetaldehyde) than CB-IV.

## **Risk and Exposure Calculations**

- The CAMx air toxics modeling in this study estimated higher risk than estimated by UAM-Tox in the MATES-II even though less air toxic species were considered (which accounted for ~10% of the risk in MATES-II. This was due to both increased concentration estimates of primary air toxics, which was partly due to the EMFAC2000 update, and increased concentrations in the secondary air toxics due to higher aldehyde estimates.
- Accounting for indoor/outdoor effects on the risk and exposure calculations reduced the risk and exposure by approximately one-third.
- Very similar risk and exposure estimates were obtained whether an annual composite indoor/outdoor factor was used with annual average air toxics concentrations or whether hourly indoor/outdoor factors were applied to hourly air toxics concentrations.
- Use of the SAPRC99 chemistry decreases the risk due to primary air toxics and increases the risk due to secondary air toxics for a net increase in total toxic risk of approximately 10% over using the CB-IV chemistry.
- The two highest areas of risk are first the port area near Long Beach and then downtown Los Angeles, whereas downtown Los Angeles has much higher exposure due to the higher population.

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## **REFERENCES**

1. EPA. Air Dispersion Modeling of Toxic Pollutants in Urban Areas – Guidance, Methodology, and Example Applications. Office of Air Quality Planning and Standards.

U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. (EPA-454/R-99-021) July. 1999.

2. Seigneur, C., Lohman, K., Pun, B. Critical Review of Air Toxics Modeling Current Status and Key Issues; CRC A-42-Phase I. Prepared for Coordinating Research Council, Inc., Alpharetta, GA. September. (Available at [www.crao.com](http://www.crao.com) under Project A-42-1). 2001.
3. ENVIRON. Development, Application, and Evaluation of an Advanced Photochemical Air Toxics Modeling System; A-42-2. Prepared for Coordinating Research Council, Inc., Alpharetta, GA. September. (Available at [www.crao.com](http://www.crao.com) under Project A-42-2). 2002.
4. ENVIRON. User's Guide - Comprehensive Air Quality Model with Extensions (CAMx). Version 3.1. April. (Available at [www.camx.com](http://www.camx.com)). 2002.
5. SCAQMD. Multiple Air Toxics Exposure Study in the South Coast Air Basin-MATES-II. South Coast Air Quality Management District, Diamond Bar, CA. November. (Available at [www.aqmd.gov](http://www.aqmd.gov)). 2000.
6. Yarwood, G., et al. Proximate Modeling of Weekday/Weekend Ozone Differences for Los Angeles. Draft. Prepared for Coordinating Research Council, Alpharetta, GA. May. (Available at [www.crao.com](http://www.crao.com) under Project A-36). 2002.
7. EPA. "Guidelines for the Regulatory Application of the Urban Airshed Model". U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. 1991.

## **KEYWORDS**

Air Toxics  
Photochemical Grid Model  
Hybrid Model  
Diesel Particulate  
MATES-II