

Final Report**DEMONSTRATION TOXICS MODELING
FOR THE BAY AREA USING CAMx**

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1. INTRODUCTION

Toxic air pollutants are a concern because of their acute and/or chronic health impacts. Emissions in densely populated urban areas may particularly impact low income neighborhoods, thereby raising environmental justice issues. The BAAQMD (District) has developed emission inventories for toxic air pollutants and is developing air quality modeling tools specifically for toxics. Traditional Gaussian plume and puff dispersion models are applicable to primary pollutants (e.g., diesel particulate matter [DPM], benzene) at neighborhood to urban spatial scales, but have limitations for chemically reactive pollutants (e.g., 1,3-butadiene, acrolein) and secondary pollutants (e.g., acrolein, formaldehyde). Photochemical grid models are better suited to treat chemically reactive toxics at urban- to regional scales because they can address complex non-linear interactions and simulate three-dimensional dispersion patterns over wide areas. The purpose of this project is to further develop and demonstrate air toxic modeling methods in the CAMx photochemical grid model.

We performed three simulations to demonstrate how CAMx can be used for modeling air toxics over the Bay Area. Additionally, these runs can be used to quantitatively evaluate the District's annual toxics inventory. In one run, CAMx simulated the dispersion of DPM over most of the Bay Area for the entire year of 2000. A second run examined dispersion and a basic chemical decay mechanism for butadiene and acrolein during the July 29 to August 2, 2000 CCOS episode. A third run incorporated a much more detailed chemical mechanism for butadiene decay to acrolein and formaldehyde, and also included benzene.

The District provided the current annual 9-county Bay Area toxic emissions inventory to ENVIRON. Note that this inventory is split by on-road, area, and point sources; the former two are gridded, and none of the components include any seasonal, monthly, or diurnal profiles. The gridded components are at 2 km resolution in a Lambert Conformal Projection (LCP) (center at 37.0N, 120.5W with true latitudes of 30N and 60N). This projection aligns with the central California emissions modeling grid developed by the ARB during CCOS. This is important because it facilitates the use of existing photochemical inventories to be used in conjunction with the toxics inventory for chemical modeling. The District's toxics inventory includes emissions for many gas-phase toxic species and includes DPM.

2. ANNUAL CAMx DPM SIMULATION

2.1 INPUT DATASETS

The DPM run used meteorological fields extracted from an annual CALMET simulation performed by the ARB for the year 2000. The District provided a copy of the CALMET output to ENVIRON. The ARB ran CALMET version 6.209 for a 200 by 200 grid cell domain with 0.5 km grid spacing on a UTM zone 10 map projection; 10 vertical layers resolved the vertical grid up to 3 km AGL. Note that this domain was designed for CALPUFF DPM modeling of the Oakland area, and thus does not cover the entire nine-county Bay Area, as shown by the blue box in Figure 2-1. Therefore, the meteorological fields were remapped to conform to the projection of the emissions grid. The red box in Figure 2-1 shows the largest feasible domain – 46 by 47 grid cells at 2 km resolution.

ENVIRON developed a FORTRAN program (“calmet2camx”) to convert CALMET output into CAMx meteorological input formats. The program converts the meteorological fields from UTM to LCP and interpolates data fields from 0.5 km to the 2 km grid point array to match the resolution and projection of the gridded emissions. Due to the limited three-dimensional outputs from CALMET, the following assumptions were made:

- Water vapor (ppm) is constant with height until the air mass becomes saturated;
- CAMx layer-interface heights are defined by the CALMET vertical grid, while pressure is computed using the hypsometric equation;
- Wind components are not staggered (i.e., both u and v components are co-located at cell centers);
- Vertical diffusivity is based on the O’Brien profile scheme, as available in the “mm5camx” program, with a minimum value set to 0.1 m²/s;
- No cloud/rain file could be generated due to lack of proper information carried by CALMET.

The Bay Area DPM emissions were windowed to fit inside the CALMET domain and then separated into 12 species – DPM from six source regions and two emission groups (on-road and area) – for the purposes of a source apportionment demonstration. There were no DPM emissions from point sources. According to the emission inventory files provided, DPM emissions were held constant each day and throughout the entire year.

The six source regions were defined mostly along county lines (San Francisco, San Mateo, Alameda, Contra Costa, North Bay, and offshore). The northern portion of Santa Clara County was grouped with San Mateo County. Marin, Sonoma, Napa, and Solano Counties were grouped together because DPM emissions were relatively small. Figure 2-2 displays a spatial plot of all DPM emissions with the source region boundaries. The DPM emission rates by source region and emission group are listed in Table 2-1. In most source regions, area DPM emissions were much larger than on-road mobile emissions; Alameda County was the exception as on-road DPM was almost as large as the area source DPM. As a whole, area sources accounted for almost 70% of the 19,000 lb/day DPM emitted within the Bay Area domain. According to the District, the bulk of area sources are comprised of non-road sources, including marine vessels and

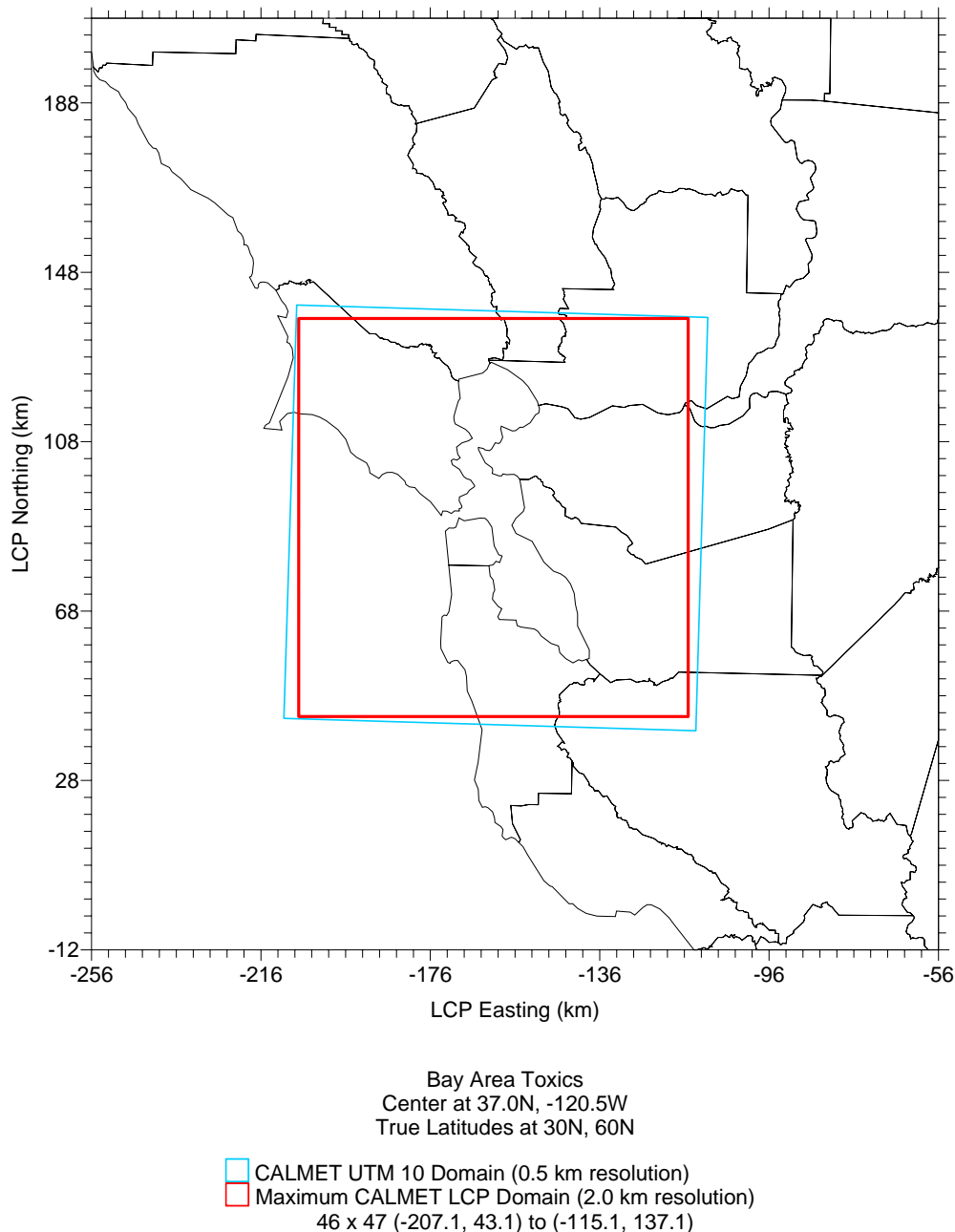


Figure 2-1. DPM modeling domain (red inset). The ARB CALMET domain is shown as blue inset, while entire map shows the approximate coverage of the BAAQMD toxics emission inventory.

Table 2-1. DPM emissions by source region and emission group (lb/day).

Region	Area	Onroad
1. San Francisco Co.	2380	290
2. San Mateo Co.	2647	835
3. Alameda Co.	3371	2812
4. Contra Costa Co.	2254	1065
5. North Bay	1434	843
6. Offshore	1186	3
Total	13272	5848

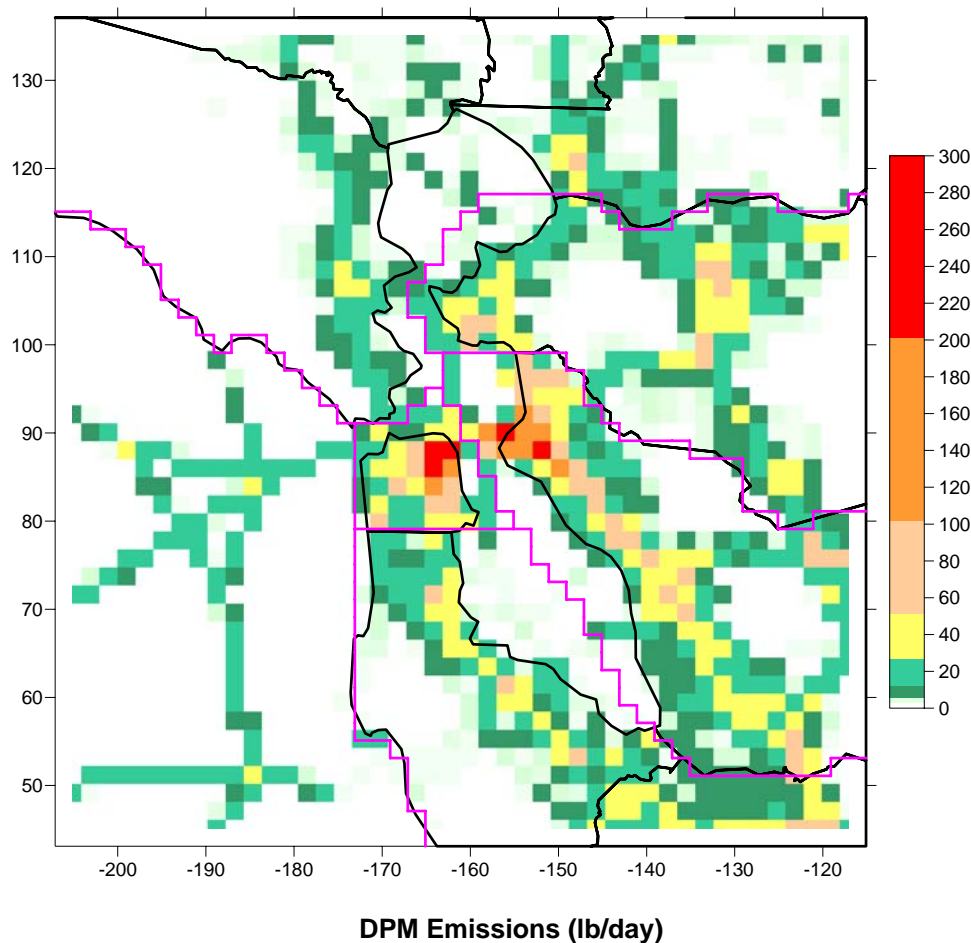


Figure 2-2. Spatial plot of DPM emissions in the six Bay Area regions.

construction equipment. The District staff considers the construction estimates to be too high, especially in San Francisco.

ENVIRON used CAMx version 4.50 for the annual DPM simulation. The domain consisted of 46 by 47 grid cells at 2 km resolution. The same 10 vertical layers used in CALMET were applied to CAMx, up to 3 km. For simplicity, DPM was treated as a fine particulate with a density of 2 g/cm^3 (consistent with elemental carbon) for dry deposition calculations. DPM was the only species modeled, but it was apportioned into six regions and two emission sources as described above. Chemistry, wet deposition, and point sources were all turned off. Initial and boundary conditions were set to uniformly clean values ($0.001 \text{ } \mu\text{g/m}^3$), although we recognize that this is not appropriate for most boundaries other than the west. Thus, this demonstration focuses on source apportionment of only those sources within this limited domain.

2.2 MODEL RESULTS

Figure 2-3 shows the annual average DPM from all sources in the Bay Area. Northeast San Francisco County, where emissions were highest, had the highest annual concentration of DPM at $18.3 \text{ } \mu\text{g/m}^3$; West Oakland was second highest at $10.7 \text{ } \mu\text{g/m}^3$. Figure 2-4, which separated the

area source contributions from the on-road mobile source contributions, shows that area source DPM was the dominant contributor to most parts of the Bay Area, including up to $17 \mu\text{g}/\text{m}^3$ in San Francisco. The largest annual DPM contribution from on-road mobile sources was $3.5 \mu\text{g}/\text{m}^3$ near Emeryville, and 1 to $2 \mu\text{g}/\text{m}^3$ along most of 880 in Alameda County. These concentrations are much higher than expected, perhaps by a factor of 3; while the location of the West Oakland peak agrees conceptually with the known local source mix in that area (multiple freeways, port and rail activity), the magnitude and location of the peak in northeastern San Francisco remains highly suspect. We have identified three major reasons for the high concentrations, in order of likely importance:

1. According to the District, reported DPM emissions from construction activities, especially in downtown San Francisco, are probably too high;
2. Lack of any diurnal activity profiles applied to the annual DPM emissions database is probably contributing to the high concentrations as emissions during nighttime hours are over stated and are trapped in the stable surface layer at night;
3. Lack of wet deposition and enhanced dry deposition in fog.

Annual contributions from each source region and emission group are shown in Figure 2-5. Area source DPM contributions are on the left and on-road contributions are on the right. Each row shows contributions from the six source regions from top to bottom: San Francisco County, Southwest Bay (San Mateo and northern Santa Clara Counties), Alameda County, Contra Costa County, North Bay, and offshore waters.

In all source regions except Alameda County, area source DPM contributions were higher than on-road mobile sources, following their respective emissions densities. San Francisco County area sources contributed up to $16.6 \mu\text{g}/\text{m}^3$ within the county and were an order of magnitude greater than on-road mobile source contributions. In most of Alameda County, area and on-road mobile source DPM contributions were comparable in magnitude. Contra Costa County contributions were localized to the major urban centers. Annual DPM contributions from both area and on-road sources were relatively small in the North Bay and offshore.

Figure 2-6 shows daily stacked bar charts of the 24-hour DPM contributions from each of the 12 DPM components for a grid cell in West Oakland that had the highest 24-hour average DPM concentration. Plots are separated into four quarters. DPM concentrations were highest in the first and fourth quarters. As expected, local area and on-road mobile source contributions from Alameda County dominated. In the spring and summer, DPM concentrations were lower due to windier conditions, and contributions from San Francisco County area sources increased as the sea breeze transported DPM across the bay. A histogram of daily DPM concentrations in West Oakland is shown in Figure 2-7 using $5 \mu\text{g}/\text{m}^3$ bin widths. Almost half of the dates in the year fell in the 5 to $10 \mu\text{g}/\text{m}^3$ bin.

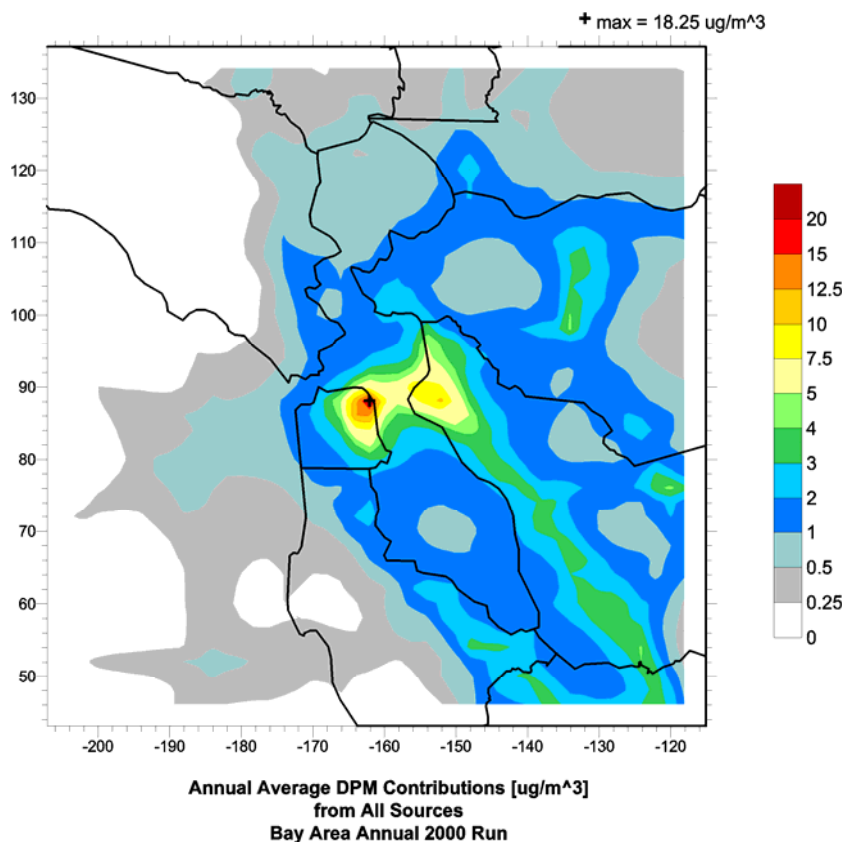


Figure 2-3. Annual average DPM concentrations from all sources.

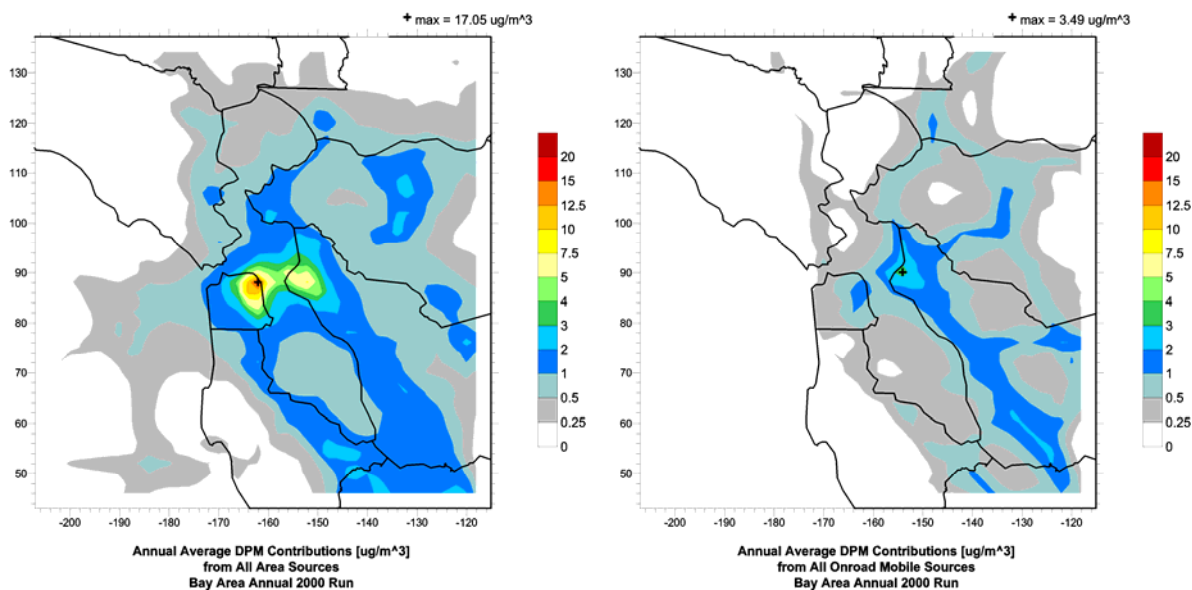


Figure 2-4. DPM contributions from all area sources (left) and from all on-road mobile sources (right).

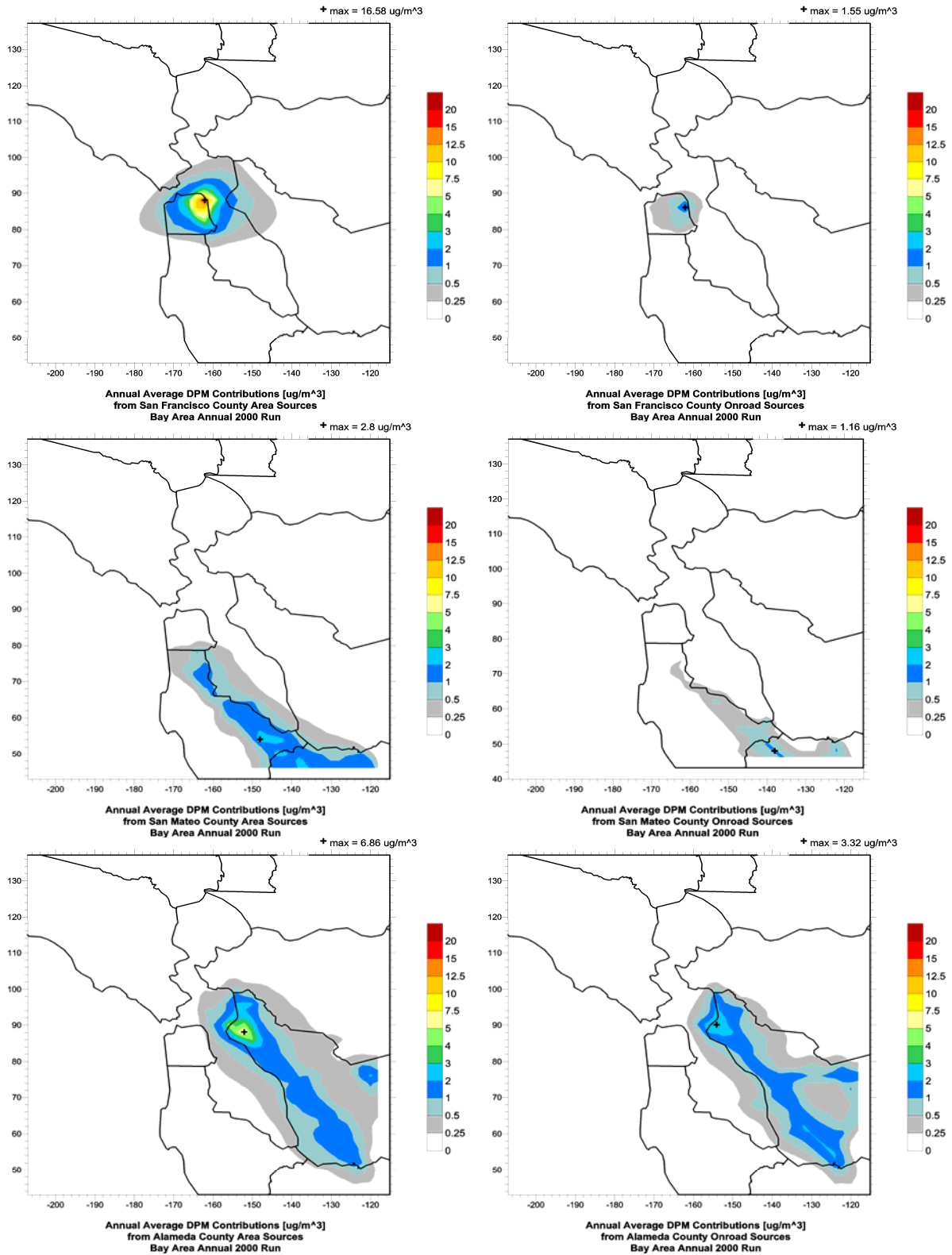


Figure 2-5. Annual average DPM contributions from area (left) and on-road mobile sources (right), and from six source regions from top to bottom: San Francisco County, Southwest Bay, Alameda County, Contra Costa County, North Bay, and Offshore.

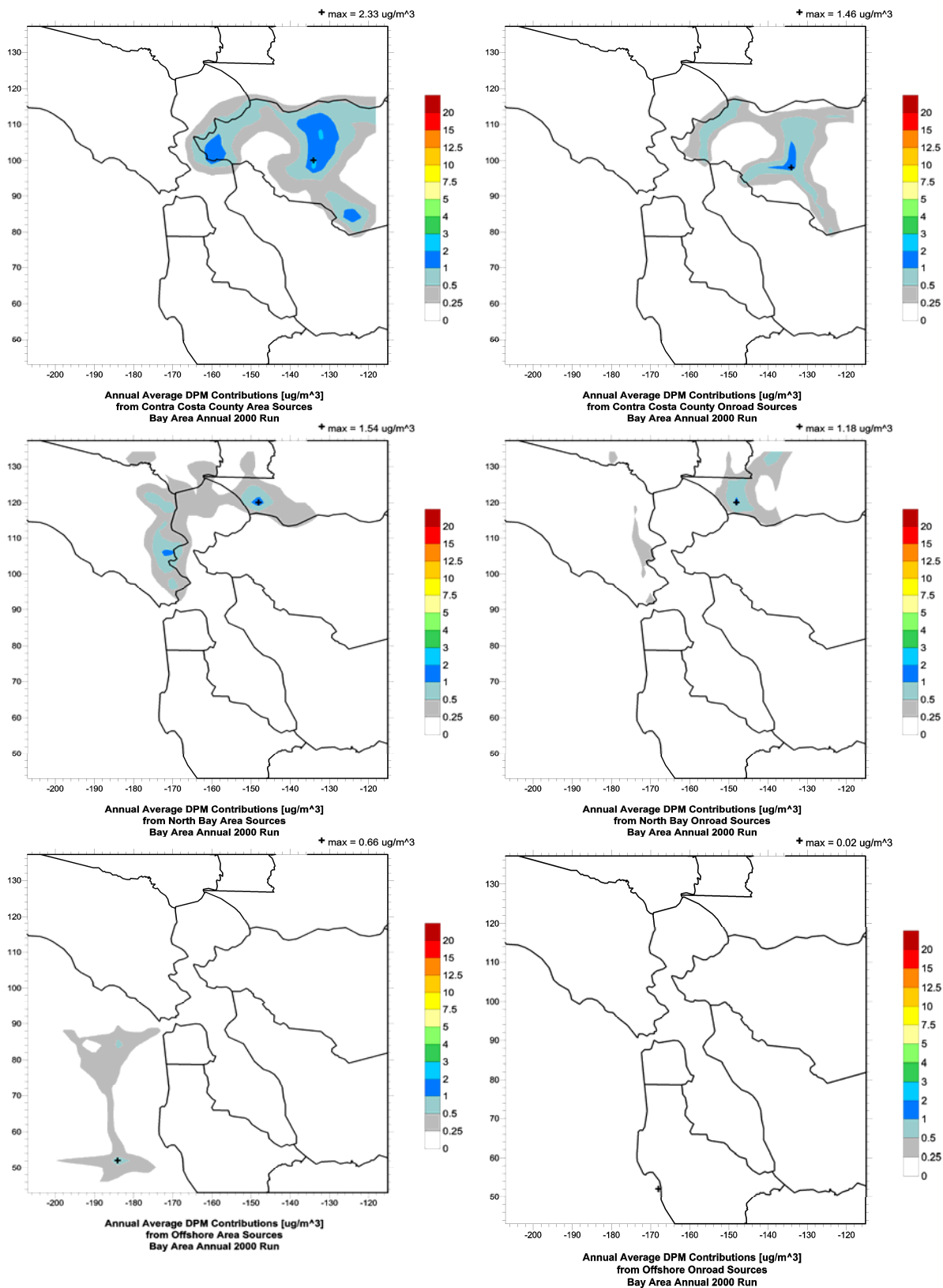


Figure 2-5 (concluded).

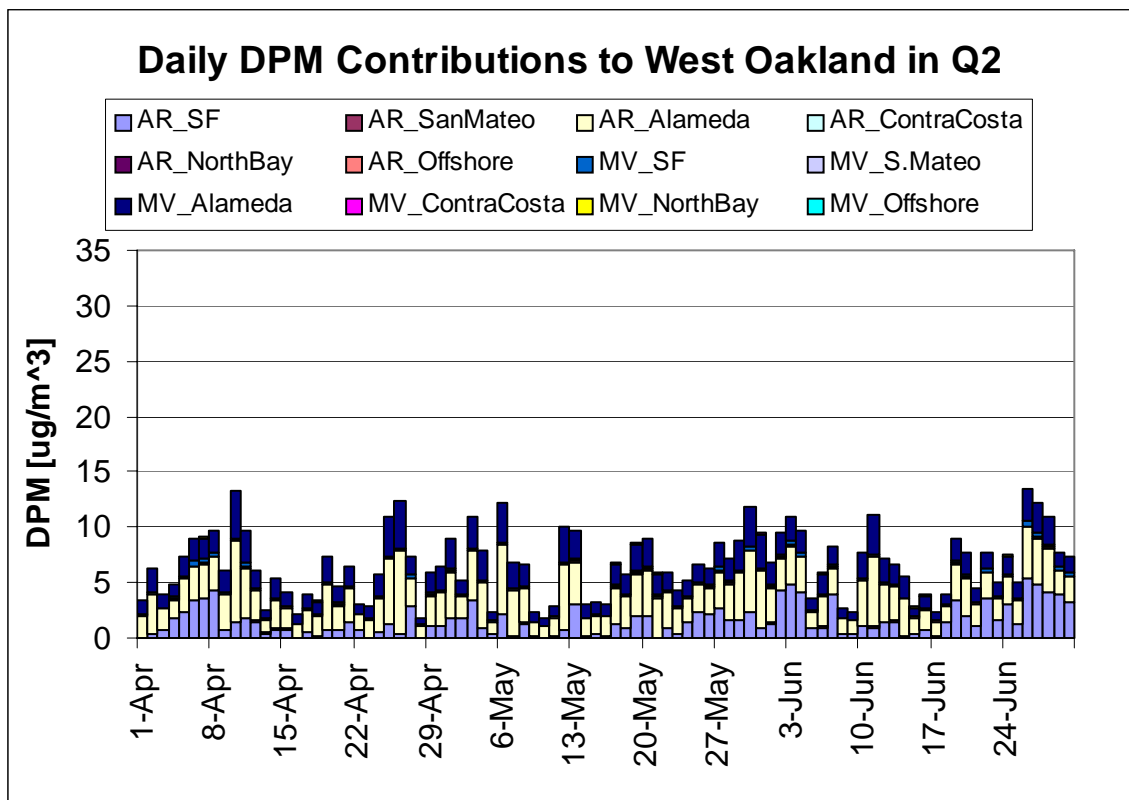
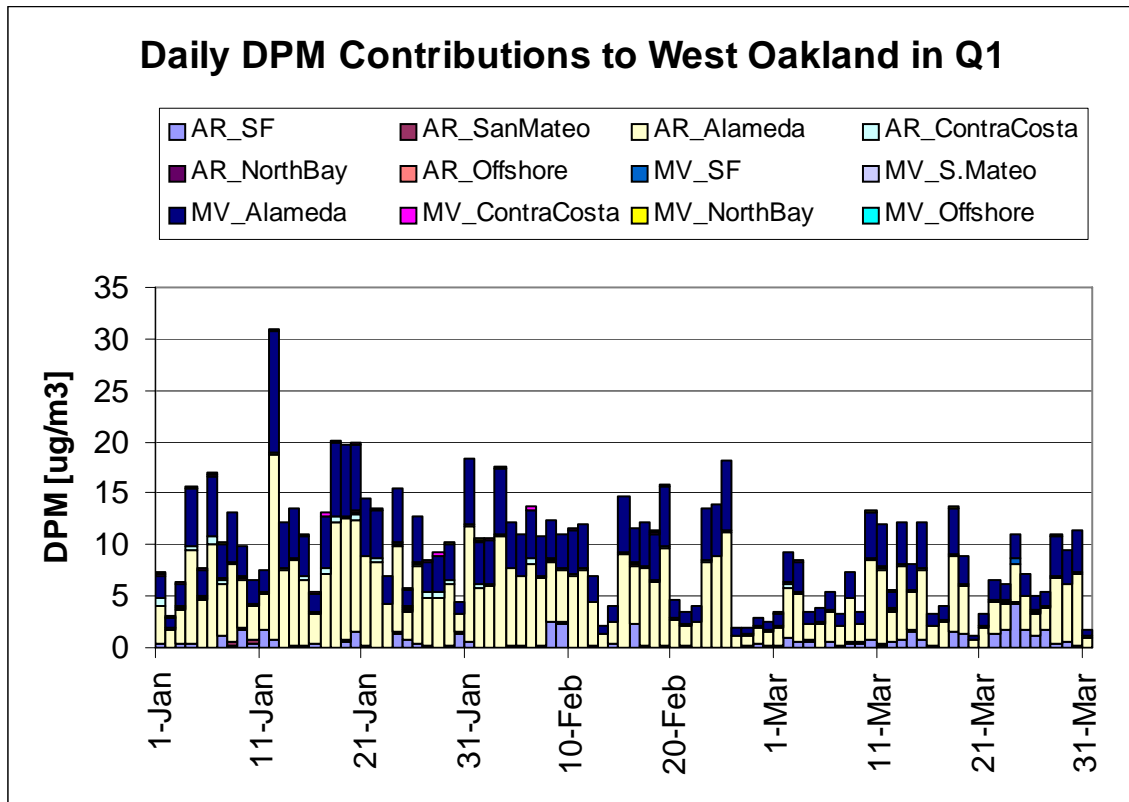


Figure 2-6. Stacked bar chart of the daily DPM contributions to West Oakland during the four quarters of simulated year.

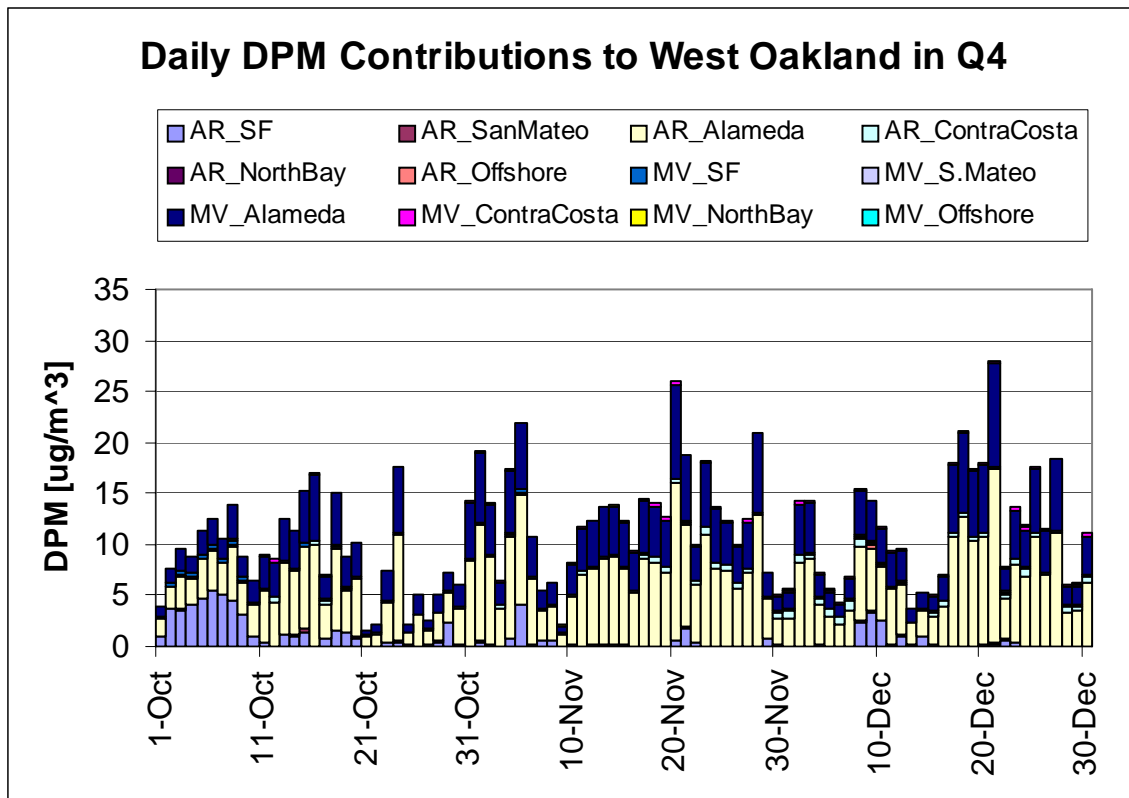
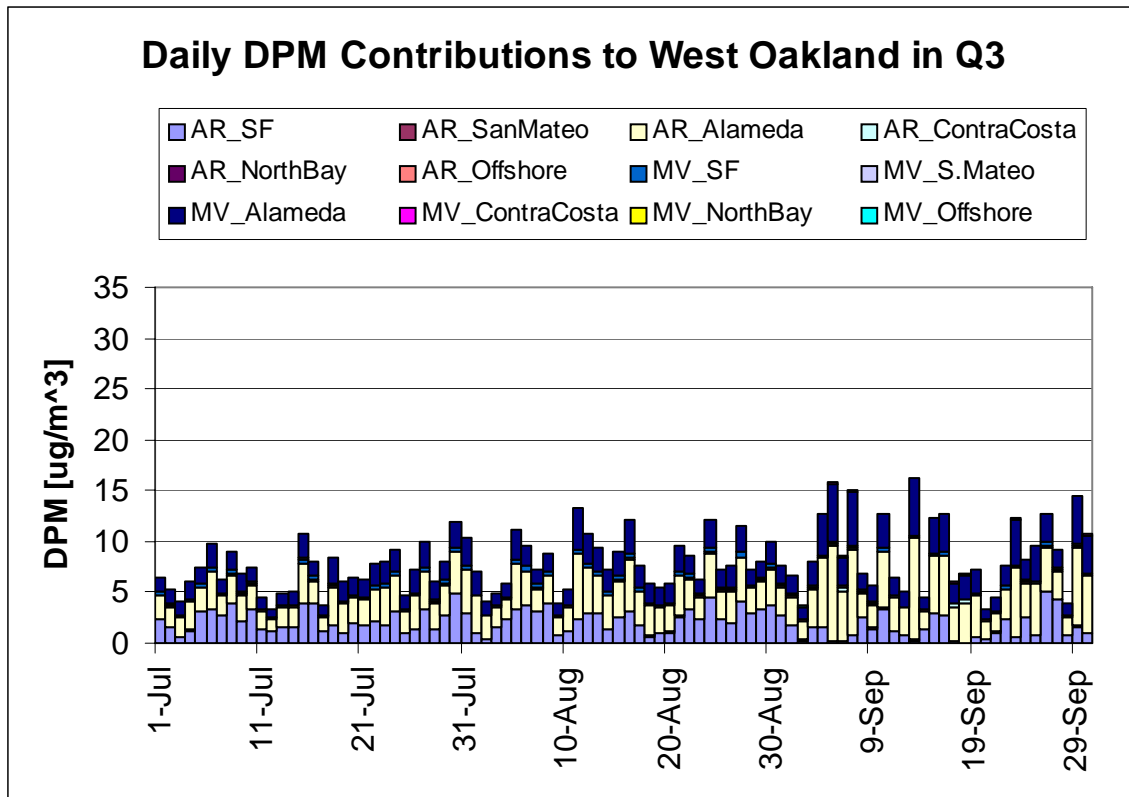


Figure 2-6 (concluded).

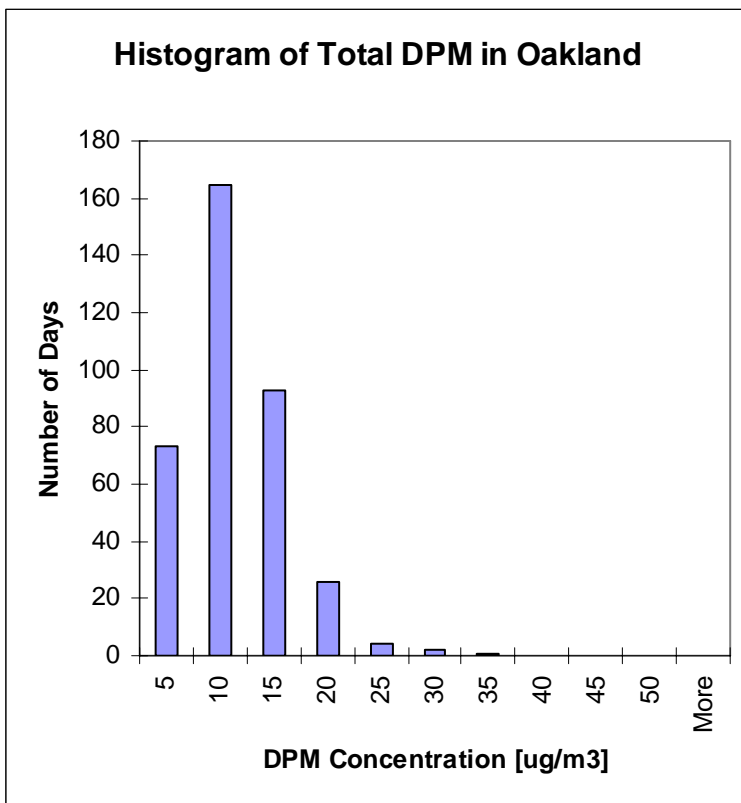


Figure 2-7. Histogram of daily DPM concentrations in West Oakland during the entire annual simulation.

3. BUTADIENE/ACROLEIN SIMULATIONS

Many toxic gases undergo chemical decay and transformation as they are dispersed in the atmosphere. ENVIRON conducted two CAMx demonstrations of the Reactive Tracer Chemical Mechanism Compiler (RTCMC) to show how the chemical decay and secondary production for two common toxic species (butadiene and acrolein) can be tracked as their emissions are dispersed downwind. Since oxidant concentrations (ozone, hydroxyl radical, etc.) are needed to decay these compounds, a full photochemical simulation was needed. Thus, ENVIRON ran the July 29 to August 2, 2000 CCOS episode using the SAPRC99 emissions inventory and MM5 meteorological fields obtained from the District in late spring of 2007.

The RTCMC allows users to input, in a text-based (ASCII) format, a set of chemical reactions (mechanism) for certain target species to be treated by the CAMx Reactive Tracer (RTRAC) Probing Tool. RTRAC is the CAMx tool for simulating reactive tracers, whereas RTCMC is the front-end to RTRAC that reads (and solves) a user-defined chemical mechanism for reactive tracers. The core model's photochemical mechanisms (CB4, CB05, and SAPRC99) remain intact and separate from the reactive tracer chemistry. A suitable application for RTCMC is simulating air toxic species that are photolyzed and/or decay according to ambient concentrations of ozone, OH, NO, etc.

The user defines a complete toxics chemical mechanism in an ASCII format (examples are provided below). Upon startup, CAMx/RTCMC compiles the information and configures the reactive tracer chemistry solver to numerically solve the toxics mechanism. During the model simulation, the toxics chemistry receives ambient pollutant information from the core photochemical mechanism and uses this to calculate the concentrations of toxic species. The current implementation of RTCMC is for gas-phase reactions, i.e., gas-phase tracers reacting with each other and/or gas-phase host model species. The text input file format is described in Appendix A and will be documented in an updated CAMx User's Guide.

3.1 DEMONSTRATIONS OF A BASIC TOXIC CHEMICAL MECHANISM

The first CAMx RTCMC simulation demonstrated a basic chemical mechanism among certain toxic species and oxidants. Three new species were introduced in a separate RTCMC chemistry definition file: butadiene, acrolein, and secondary acrolein formed from the decay of butadiene. This chemical mechanism was developed for EPA as part of the project to develop the CB05 chemical mechanism¹. This chemical mechanism is listed in Figure 3-1 illustrating the RTCMC input format, and showing each species' properties, photolysis rates, and reactions. CAMx version 4.50_RTCMC was run on the full CCOS 185 by 185 grid domain at 4 km resolution with 20 vertical layers.

ENVIRON extracted acrolein and butadiene emissions from the BAAQMD toxics inventory; emissions were available for the Bay Area 9-county region only. Area and on-road mobile toxics were processed into CAMx gridded emission files similar to DPM. Point sources were processed into CAMx format using a separate program. Since stack parameters were not

¹ Yarwood, G., S. Rao, M. Yocke, and G.Z. Whitten. 2005. Updates to the Carbon Bond chemical mechanism: CB05. Final Report prepared for US EPA. Available at http://www.camx.com/publ/pdfs/CB05_Final_Report_120805.pdf.

```

#Control
  rate_species_units = 'molecules/cm3'
  rate_time_units = 'sec'
  solver = 'dlsode'
  Jacobian = 'numeric'
#Species,Type,Ambient,Tolerance,deposition vel,wet scav,mw,ldep
O3      A      1.0      1.0E-12      0.0      0.0  1.0
OH      A      1.0      1.0E-12      0.0      0.0  1.0
NO3     A      1.0      1.0E-12      0.0      0.0  1.0
O       A      1.0      1.0E-12      0.0      0.0  1.0
BUTADIENE F      1.0      1.0E-12      0.0      0.0  54.09
ACROLEIN F      1.0      1.0E-12      0.0      0.0  56.06
SEC_ACRO F      1.0      1.0E-12      0.0      0.0  56.06
#Table
  0      0.      10.      20.      30.      40.      50.
60.     70.     78.     86.
  8  5.158E-04  5.105E-04  4.937E-04  4.648E-04  4.223E-04  3.633E-04
2.843E-04  1.830E-04  9.297E-05  2.472E-05
 12  5.158E-04  5.105E-04  4.937E-04  4.648E-04  4.223E-04  3.633E-04
2.843E-04  1.830E-04  9.297E-05  2.472E-05
#Equations
  1 [BUTADIENE] + [OH] -> [SEC_ACRO] ; 2 1.400E-11 424. 0.
  2 [BUTADIENE] + [O3] -> [SEC_ACRO] ; 2 8.200E-15 -2070. 0.
  3 [BUTADIENE] + [NO3] -> [SEC_ACRO] ; 1 1.790E-13
  4 [BUTADIENE] + [O] -> [SEC_ACRO] ; 2 1.030E-15 0. -1.45
  5 [ACROLEIN] + [OH] -> ; 1 2.000E-11
  6 [ACROLEIN] + [O3] -> ; 1 2.610E-19
  7 [ACROLEIN] + [NO3] -> ; 2 1.700E-11 -3131. 0.
  8 [ACROLEIN] -> ; 0
  9 [SEC_ACRO] + [OH] -> ; 1 2.000E-11
 10 [SEC_ACRO] + [O3] -> ; 1 2.610E-19
 11 [SEC_ACRO] + [NO3] -> ; 2 1.700E-11 -3131. 0.
 12 [SEC_ACRO] -> ; 0

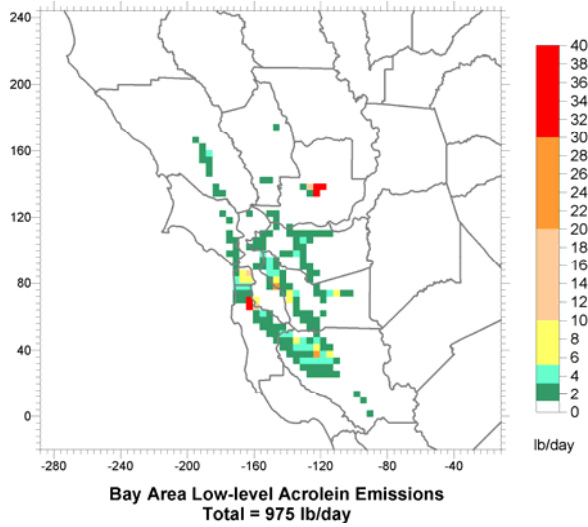
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Figure 3-1. Chemical mechanism applied in the basic RTCMC run.

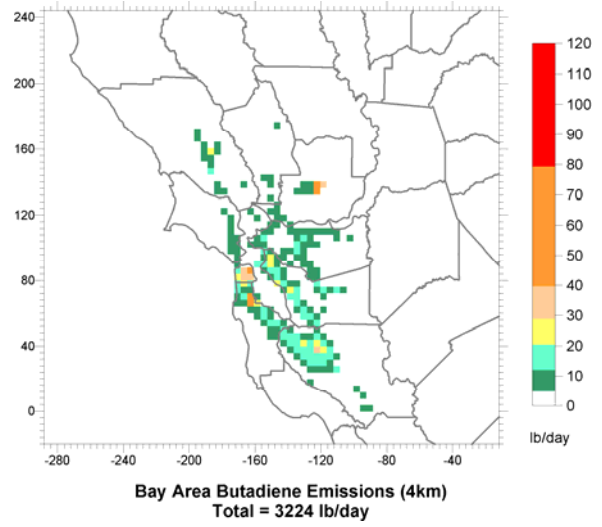
provided in the raw inventory, defaults were used. All emissions were assumed to be constant for all hours and dates.

Figure 3-2 shows the acrolein and butadiene emissions on the left and right, respectively. The top row shows emissions from area and on-road sources; the bottom row shows point source emissions. Total Bay Area emissions were 976 lb/day for acrolein and 3257 lb/day for butadiene; the majority of both came from low-level sources. The largest emissions of both toxics were associated with major airports in the area (SFO, OAK, SJO, and Travis Air Force Base in Fairfield). Jet aircraft operations are especially known to be sources of acrolein.

Spatial plots of 24-hour average primary butadiene and primary and secondary acrolein on July 31 are shown in Figure 3-3. Plots focus on the Bay Area. Acrolein and butadiene concentrations were highest near Fairfield, where emissions were greatest; other hot spots of acrolein were located near the three major Bay Area airports. Very little butadiene was found outside the Bay Area as it reacted to form secondary acrolein. From a quality assurance standpoint, this modeling indicates that aircraft emissions of organic compounds at Travis are larger than at SFO, the Bay Area's most busy airport. This is probably not related to activity, but more likely a



ACROLEIN Emissions



BUTADIENE

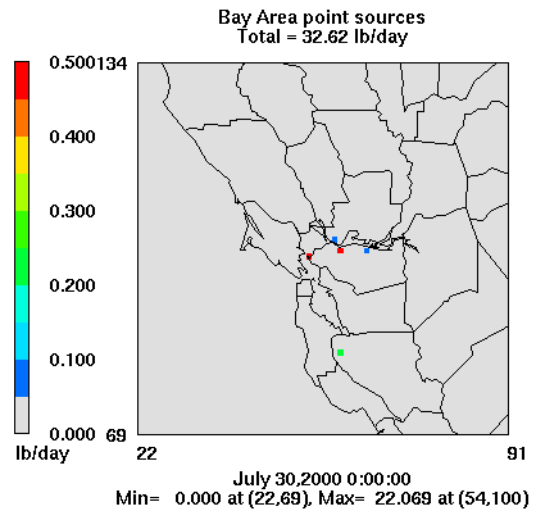
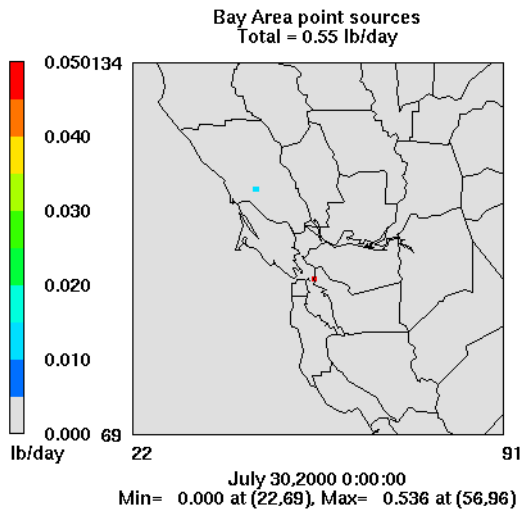


Figure 3-2. Bay Area acrolein (left) and butadiene (right) emissions from gridded (top) and point sources (bottom).

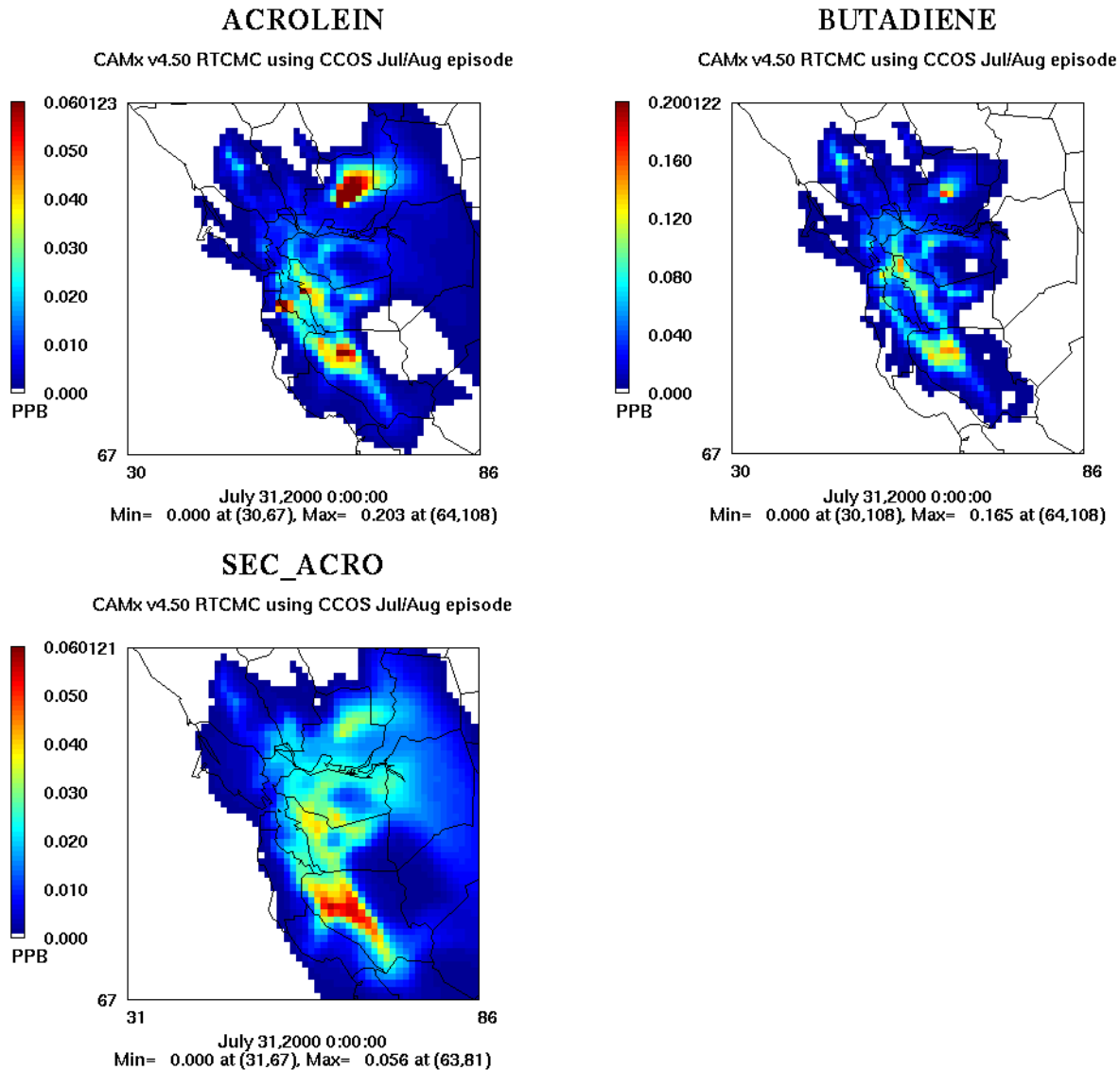


Figure 3-3. Spatial plots of 24-hour average acrolein (top left), secondary acrolein (bottom left), and butadiene (top right) on July 31, 2000 windowed over the Bay Area.

result of the much higher emission factors assigned to military jet aircraft relative to more modern passenger aircraft. The military routinely replaces and upgrades jet engines on older airframes, so emission factors may be over stated. Some of the aircraft activity and emission factors for Travis should be re-evaluated.

Secondary acrolein concentrations were highest downwind of the local butadiene peaks. The highest was in Santa Clara County, south of San Jose. Plumes were also found downwind of Fairfield, spreading into the Sacramento Valley, and downwind of Oakland, whose plume meandered into the Livermore Valley and toward the northern San Joaquin Valley.

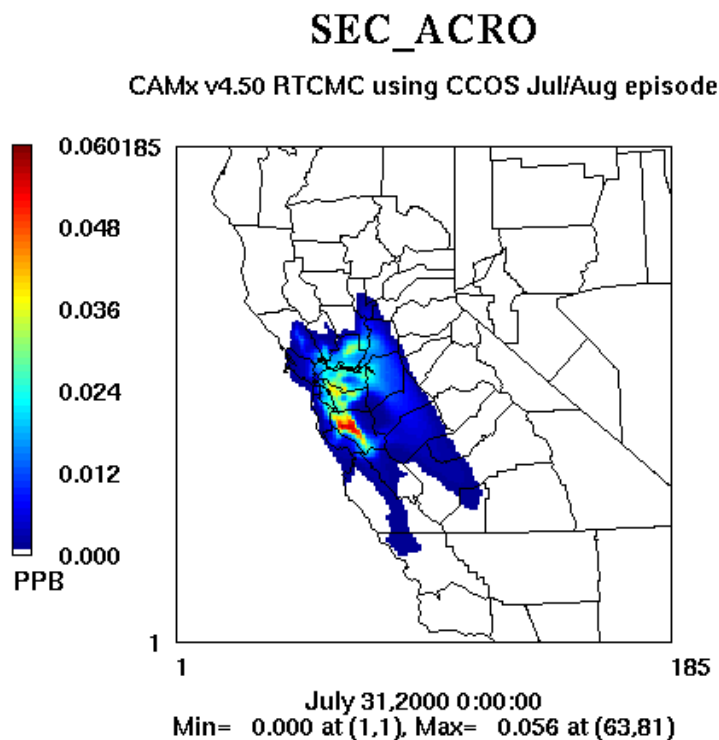


Figure 3-4. Spatial plot of 24-hour average secondary acrolein (from butadiene) on July 31 in the full CCOS domain.

Figure 3-4 shows a spatial plot of secondary acrolein over the full CCOS domain. The longer-range extent of this product species is apparent, as a summertime transport pattern extended trace concentrations of secondary acrolein into the Sacramento, San Joaquin, and Salinas Valleys.

3.2 DEMONSTRATION OF A DETAILED BUTADIENE MECHANISM

The second CAMx RTCMC simulation demonstrated a detailed chemical mechanism for the decay of butadiene to acrolein to formaldehyde. The detailed mechanism simulates 34 species (including 7 “ambient” species such as ozone, which come from the core model SAPRC99 results) in 59 reactions, and is condensed from the Master Chemical Mechanism (MCM) v3.1 for butadiene with 397 reactions and 123 organic species.² The chemistry parameters for the detailed mechanism are listed in Figure 3-5, a schematic diagram of all reactions is shown in Figure 3-6, and the chemical definition for each species is listed in Table 3-1.

The detailed butadiene/acrolein mechanism for this study focuses on toxics and includes only species that are needed to track decay of butadiene through acrolein to formaldehyde. Note that formaldehyde treated in the toxics mechanism (named H2CO) is distinct from formaldehyde in the core model’s SAPRC99 photochemical mechanism (named HCHO). Three species were added to track the amount of reacted butadiene (BUTD_R), acrolein (ACR_R) and benzene (BENZ_R). The seven key species names are as follows:

² <http://chmlin9.leeds.ac.uk/MCM/>

```

#Control
  rate_species_units = 'molecules/cm3'
  rate_time_units = 'sec'
  solver = 'dlsode'
  Jacobian = 'numeric'
#Species,Type,Ambient,Tolerance,deposition vel,wet scav,mw,l dos,ldep
O3      A      0.0      1.0E-12      0.0      0.0      1.0
NO      A      0.0      1.0E-12      0.0      0.0      1.0
NO2     A      0.0      1.0E-12      0.0      0.0      1.0
OH      A      0.0      1.0E-12      0.0      0.0      1.0
HO2     A      0.0      1.0E-12      0.0      0.0      1.0
NO3     A      0.0      1.0E-12      0.0      0.0      1.0
CXO2    A      0.0      1.0E-12      0.0      0.0      1.0
BUTD    F      0.0      1.0E-12      0.0      0.0      1.0
BUTD_R  F      0.0      1.0E-12      0.0      0.0      1.0
BUO2_A  F      0.0      1.0E-12      0.0      0.0      1.0
BUO2_B  F      0.0      1.0E-12      0.0      0.0      1.0
ACR     F      0.0      1.0E-12      0.0      0.0      1.0
ACR_R   F      0.0      1.0E-12      0.0      0.0      1.0
H2CO    F      0.0      1.0E-12      0.0      0.0      1.0
C2H4    F      0.0      1.0E-12      0.0      0.0      1.0
NPRD    F      0.0      1.0E-12      0.0      0.0      1.0
DIOL    F      0.0      1.0E-12      0.0      0.0      1.0
BUPX_A  F      0.0      1.0E-12      0.0      0.0      1.0
HBAL    F      0.0      1.0E-12      0.0      0.0      1.0
HBO2    F      0.0      1.0E-12      0.0      0.0      1.0
HBPX    F      0.0      1.0E-12      0.0      0.0      1.0
BUPX_B  F      0.0      1.0E-12      0.0      0.0      1.0
GLAL    F      0.0      1.0E-12      0.0      0.0      1.0
GXAL    F      0.0      1.0E-12      0.0      0.0      1.0
ACO3    F      0.0      1.0E-12      0.0      0.0      1.0
ACPN    F      0.0      1.0E-12      0.0      0.0      1.0
ACCA    F      0.0      1.0E-12      0.0      0.0      1.0
ACPA    F      0.0      1.0E-12      0.0      0.0      1.0
HBO3    F      0.0      1.0E-12      0.0      0.0      1.0
HBPN    F      0.0      1.0E-12      0.0      0.0      1.0
HBCA    F      0.0      1.0E-12      0.0      0.0      1.0
HBPA    F      0.0      1.0E-12      0.0      0.0      1.0
BENZ    F      0.0      1.0E-12      0.0      0.0      1.0
BENZ_R  F      0.0      1.0E-12      0.0      0.0      1.0
#Table
      0      0.      10.      20.      30.      40.      50.      60.
70.      78.      86.
12 4.125E-04 4.071E-04 3.899E-04 3.615E-04 3.195E-04 2.629E-04 1.920E-04 1.101E-
04 4.903E-05 1.112E-05
15 4.125E-04 4.071E-04 3.899E-04 3.615E-04 3.195E-04 2.629E-04 1.920E-04 1.101E-
04 4.903E-05 1.112E-05
19 3.313E-02 3.284E-02 3.189E-02 3.025E-02 2.768E-02 2.392E-02 1.870E-02 1.176E-
02 5.688E-03 1.384E-03
30 1.527E-03 1.497E-03 1.404E-03 1.254E-03 1.046E-03 7.885E-04 5.053E-04 2.373E-
04 8.485E-05 1.484E-05
43 1.527E-03 1.497E-03 1.404E-03 1.254E-03 1.046E-03 7.885E-04 5.053E-04 2.373E-
04 8.485E-05 1.484E-05
46 1.527E-03 1.497E-03 1.404E-03 1.254E-03 1.046E-03 7.885E-04 5.053E-04 2.373E-
04 8.485E-05 1.484E-05
49 8.344E-03 8.267E-03 8.019E-03 7.597E-03 6.953E-03 6.035E-03 4.787E-03 3.124E-
03 1.583E-03 3.598E-04
55 3.333E-03 3.297E-03 3.185E-03 2.993E-03 2.697E-03 2.278E-03 1.718E-03 1.021E-
03 4.670E-04 1.095E-04
56 2.502E-03 2.463E-03 2.341E-03 2.141E-03 1.850E-03 1.468E-03 1.011E-03 5.247E-
04 2.074E-04 4.005E-05
#Equations
1 [BUTD] + [OH] ->(0.78)[BUO2_A] +(0.22)[BUO2_B] + [BUTD_R] ; 2 1.48E-11 448. 0.
2 [BUTD] + [O3] ->(0.62)[ACR] +(0.83)[H2CO] +(0.17)[C2H4] + [BUTD_R] ; 2 1.34E-14 -
2283. 0.
3 [BUTD] + [NO3] -> [NPRD] + [BUTD_R] ; 1 1.03E-13
4 [BUO2_A] + [NO] ->(0.95)[ACR] +(0.95)[H2CO] +(0.05)[NPRD] ; 2 2.54E-12 360. 0.
5 [BUO2_A] + [CXO2] ->(0.8 ) [ACR] +(0.8 ) [H2CO] +(0.2 ) [DIOL] ; 1 2.0E-12
6 [BUO2_A] + [HO2] -> [BUPX_A] ; 2 1.8E-13 1300. 0.
7 [BUO2_B] + [NO] ->(0.95)[HBAL] +(0.05)[NPRD] ; 2 2.54E-12 360. 0.
8 [BUO2_B] + [CXO2] ->(0.8 ) [HBAL] +(0.2 ) [DIOL] ; 1 2.0E-12
9 [BUO2_B] + [HO2] -> [BUPX_B] ; 2 1.8E-13 1300. 0.
10 [BUPX_A] + [OH] -> [ACR] + [H2CO] ; 1 8.0E-11
11 [BUPX_A] + [O3] -> [GLAL] + [H2CO] ; 1 8.0E-18

```


Table 3-1. Model species included in the detailed mechanism for decomposition of 1,3-butadiene and acrolein.

Model Species	Name/description	Chemical formula
BUTD	1,3-butadiene	CH ₂ =CH-CH=CH ₂
BUO2_A	peroxy radical from butadiene	CH ₂ =CH-CH(OH)-CH ₂ (OO)
BUO2_B	peroxy radical from butadiene	CH ₂ (OO)-CH=CH-CH ₂ OH
BUPX_A	hydroperoxide from butadiene	CH ₂ =CH-CH(OH)-CH ₂ OOH
BUPX_B	hydroperoxide from butadiene	CH ₂ (OOH)-CH=CH-CH ₂ OH
ACR	acrolein	CH ₂ =CH-CHO
ACO3	peroxyacyl radical from acrolein	CH ₂ =CH(OH)-C(O)OO
ACCA	carboxylic acid from acrolein	CH ₂ =CH(OH)-C(O)OH
ACPA	percarboxylic acid from acrolein	CH ₂ =CH(OH)-C(O)OOH
ACPN	peroxyacyl nitrate from acrolein	CH ₂ =CH(OH)-C(O)OONO ₂
HBAL	hydroxybutenal	CH ₂ (OH)CH=CH-CHO
HBO3	peroxyacyl radical from hydroxybutenal	CH ₂ (OH)CH=CH-C(O)OO
HBCA	carboxylic acid from hydroxybutenal	CH ₂ (OH)CH=CH-C(O)OH
HBPA	percarboxylic acid from hydroxybutenal	CH ₂ (OH)CH=CH-C(O)OOH
HBPX	peroxyacyl nitrate from hydroxybutenal	CH ₂ (OH)CH=CH-C(O)OONO ₂
HBO2	peroxy radical from hydroxybutenal	CH ₂ (OH)CH(OO)-CH(OH)-CHO
HBPX	hydroperoxide from hydroxybutenal	CH ₂ (OH)CH(OOH)-CH(OH)-CHO
GLAL	glycolaldehyde	CH ₂ (OH)-CHO
GXAL	glyoxal	CHO-CHO
ETHE	ethene	CH ₂ =CH ₂
H2CO	formaldehyde	HCHO
NPRD	lumped organic nitrate	
DIOL	lumped dialcohol	
OH ^A	hydroxyl radical	OH
HO2 ^A	hydroperoxy radical	HO ₂
RO2 ^A	organic peroxy radical	
NO ^A	nitric oxide	NO
NO2 ^A	nitrogen dioxide	NO ₂

Note:

^A The concentration of this species is determined by the core model mechanism (SAPRC99).

1. BUTD: emitted butadiene
2. BUTD_R: butadiene that has reacted to form secondary products
3. ACR: acrolein formed from butadiene
4. ACR_R: acrolein that has reacted to form secondary products
5. H2CO: formaldehyde formed from butadiene and acrolein
6. BENZ: emitted benzene
7. BENZ_R: benzene that has decayed due to reactions with hydroxyl and nitrate radicals

Acrolein and formaldehyde emissions were not included in this run, so that acrolein and formaldehyde (i.e., the toxic species H₂CO) were solely from decay of butadiene. This simulation also included benzene, which decays slowly in the atmosphere via reaction with the hydroxyl radical³. All other aspects of this simulation were similar to the previous RTCMC run.

Figures 3-7 and 3-8 display the 24-hour average concentrations of butadiene and benzene on July 31, 2000. Again, the patterns echo the emissions distribution of these primary species, but note

³ Calvert, J.G. R. Atkinson, K.H. Becker, R.M. Kamens, J.H. Seinfeld, T.H. Wallington, G. Yarwood. 2002. *The mechanisms of atmospheric oxidation of aromatic hydrocarbons*. Oxford University Press.

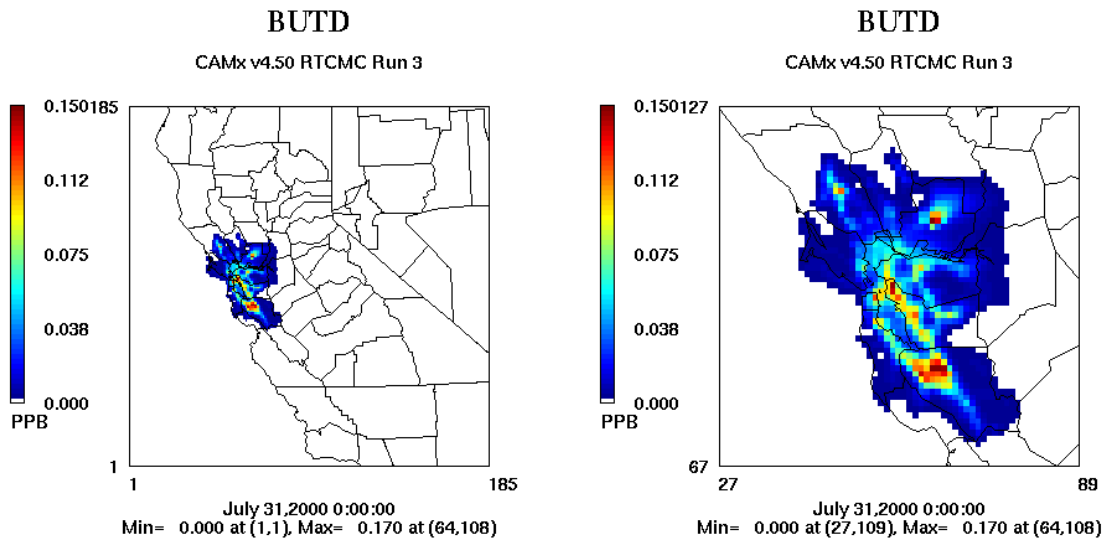


Figure 3-7. Spatial plots of 24-hour average emitted butadiene on July 31, 2000. The entire CCOS domain is shown on the left; the Bay Area is shown on the right.

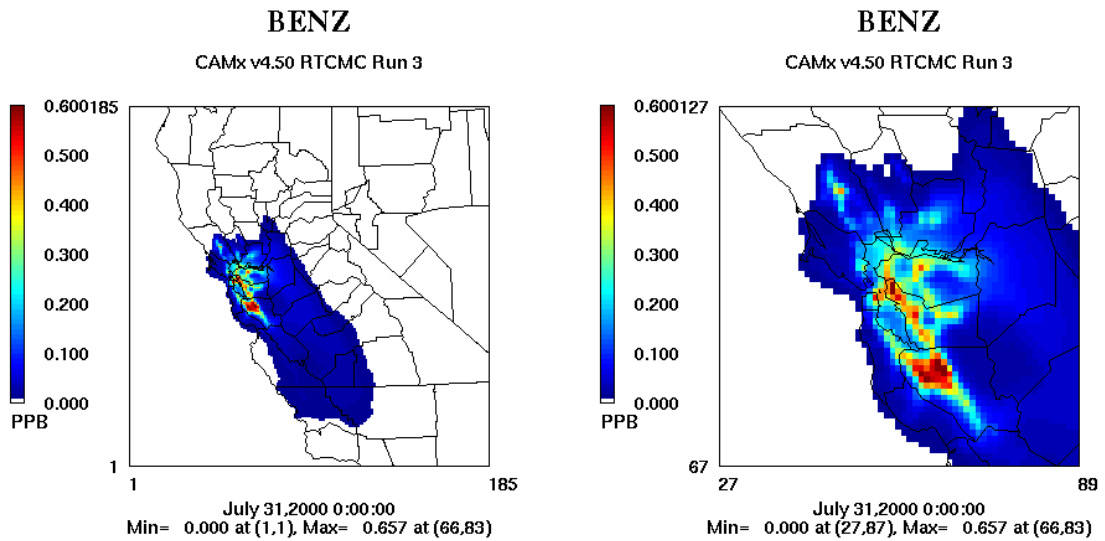


Figure 3-8. Spatial plots of 24-hour average emitted benzene on July 31, 2000. The entire CCOS domain is shown on the left; the Bay Area is shown on the right.

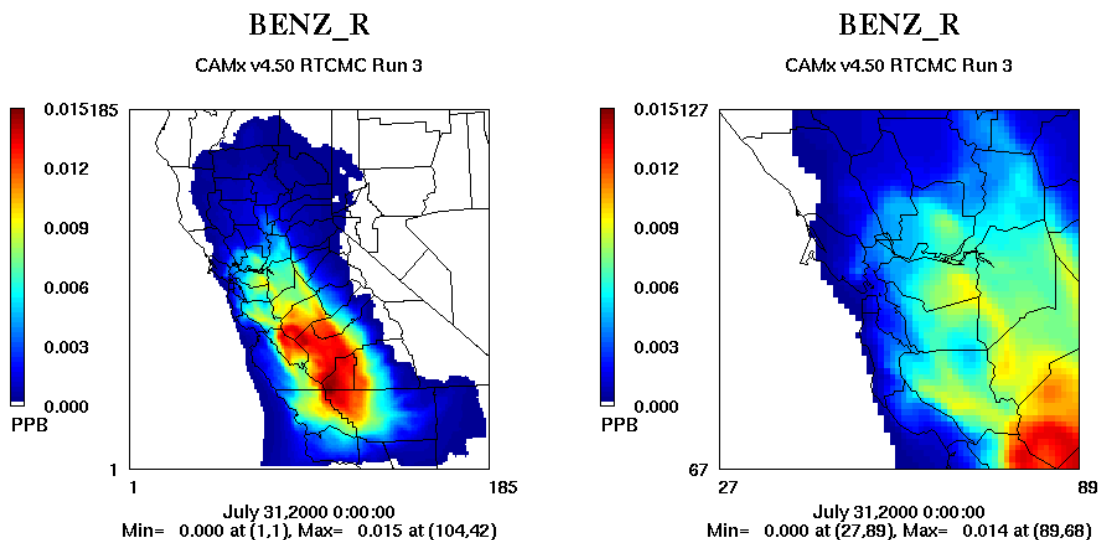


Figure 3-9. Spatial plots of 24-hour average reacted benzene on July 31, 2000. The entire CCOS domain is shown on the left; the Bay Area is shown on the right.

that benzene extends further downwind than butadiene given the former compound's much lower decay rate. Figure 3-9 shows the pattern for reacted benzene due to oxidation with hydroxyl and confirms that BENZ_R is formed (i.e., benzene decays) far downwind of where benzene is emitted.

Figures 3-10 and 3-11 show 24-hour average concentrations of secondary acrolein and secondary formaldehyde from butadiene, respectively. The prompt formation of acrolein from butadiene, along with its own decay, result in peak secondary acrolein concentrations anchored to areas of high butadiene emissions within the Bay Area. However, the peak acrolein concentrations are an order of magnitude lower than for butadiene, and the secondary nature of this compound results in a more diffuse spatial distribution than for primary butadiene. These characteristics extend to formaldehyde as well. Given that formaldehyde forms from butadiene, acrolein and their decay products (Figure 3-6), peak formaldehyde concentrations are also anchored to areas of high butadiene emissions areas, but extend even farther downwind with the acrolein.

For comparative purposes, we show in Figure 3-12 the differences in butadiene and secondary acrolein between the two RTCMC runs. Butadiene concentrations are slightly higher in the more detailed simulation (by ~1%) due to slightly different reaction rate constants for butadiene removal. Concentration differences for secondary acrolein are relatively large (25-50%) and negative, meaning less acrolein is generated by the detailed mechanism. Secondary acrolein is higher with the basic mechanism because the mechanism assumes 100% yield of acrolein from butadiene (i.e., one acrolein molecule formed from each butadiene molecule reacting).

The fractional yields of acrolein and formaldehyde from butadiene within the detailed mechanism is investigated in Figures 3-13 through 3-15. Since we tracked the amount of butadiene reacted (i.e., BUTD_R) it is possible to determine the yields as follows:

- $[ACR + ACR_R] / [BUTD_R]$ is the total yield of acrolein formed from butadiene (accounting for the fact that acrolein also decays once it is formed);

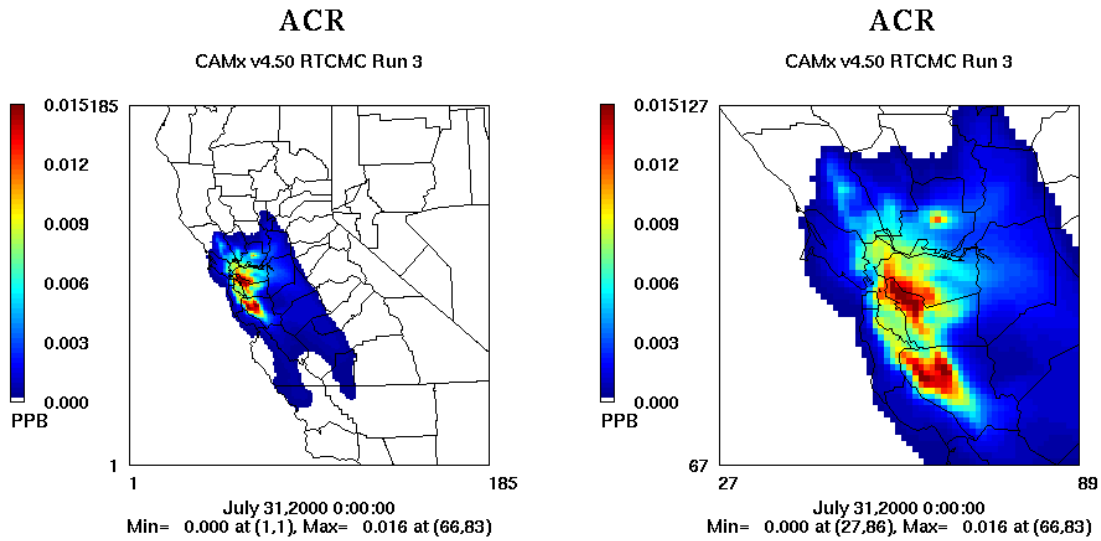


Figure 3-10. Spatial plots of 24-hour average acrolein on July 31, 2000. The entire CCOS domain is shown on the left; the Bay Area is shown on the right.

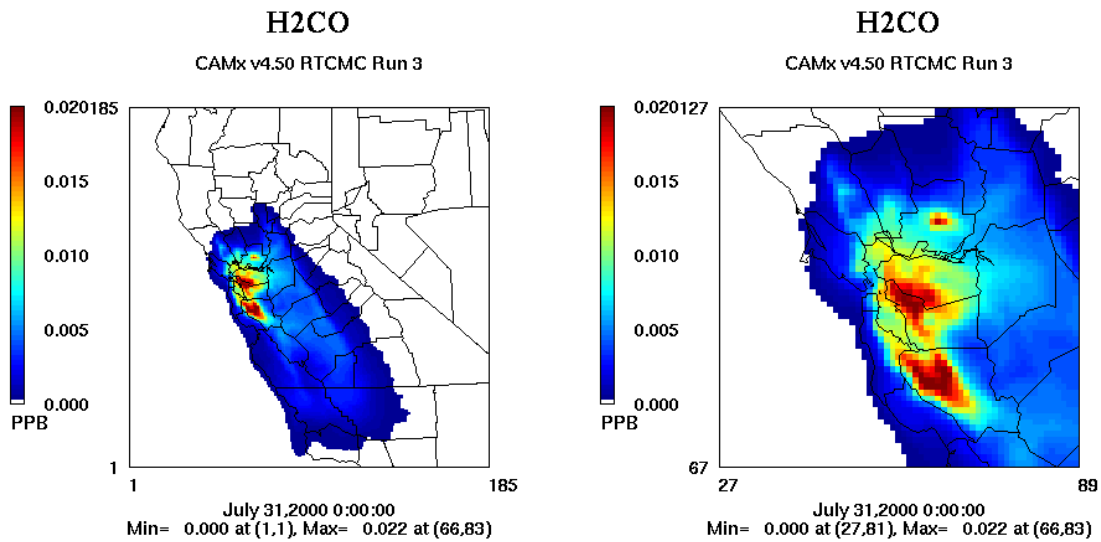


Figure 3-11. Spatial plots of 24-hour average formaldehyde on July 31, 2000. The entire CCOS domain is shown on the left; the Bay Area is shown on the right.

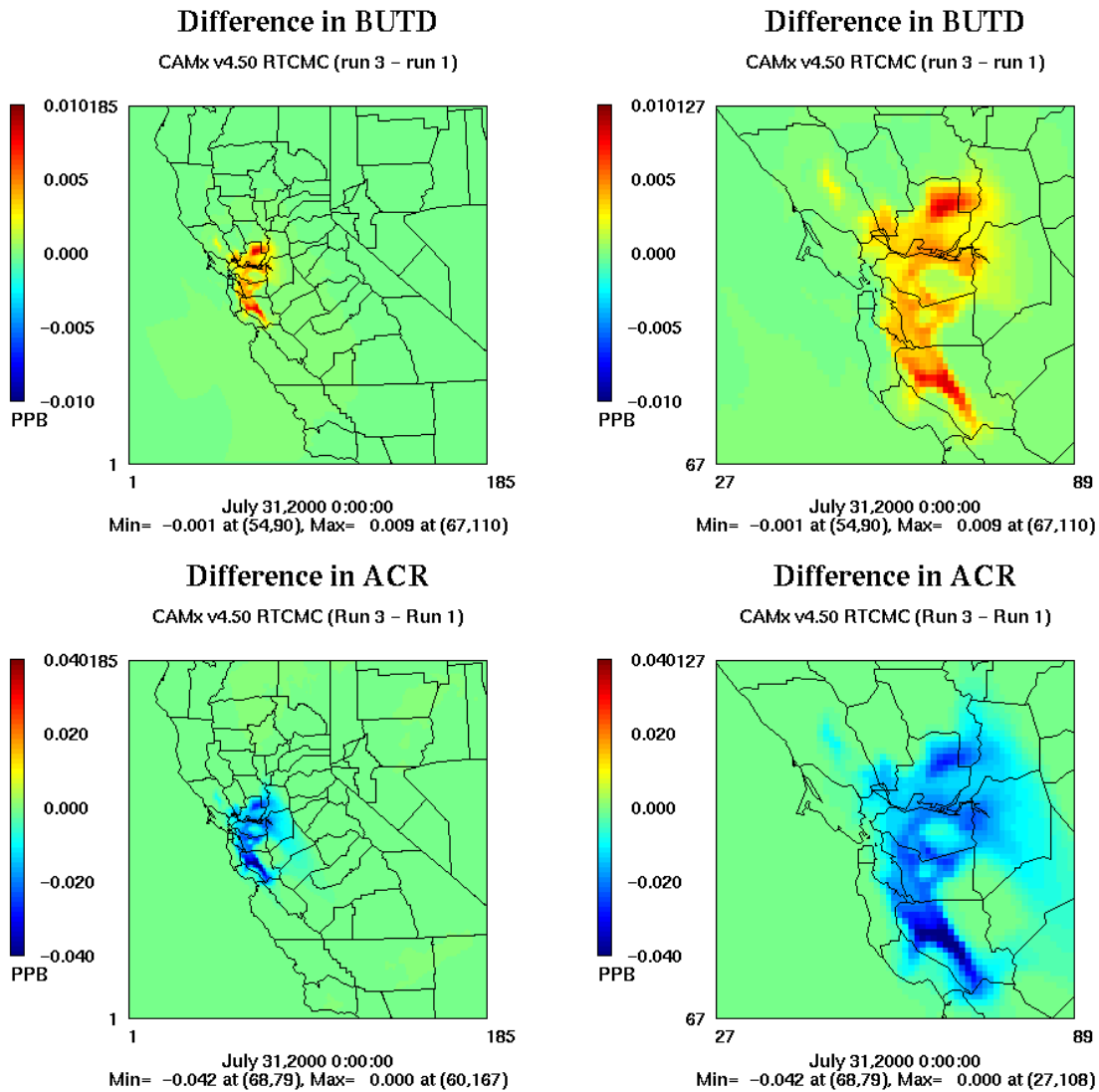


Figure 3-12. Differences in 24-hour average butadiene (top row) and secondary acrolein (bottom row) on July 31, 2000 between the basic and detailed RTCMC simulations. The entire CCOS domain is shown on the left, the Bay Area is shown on the right.

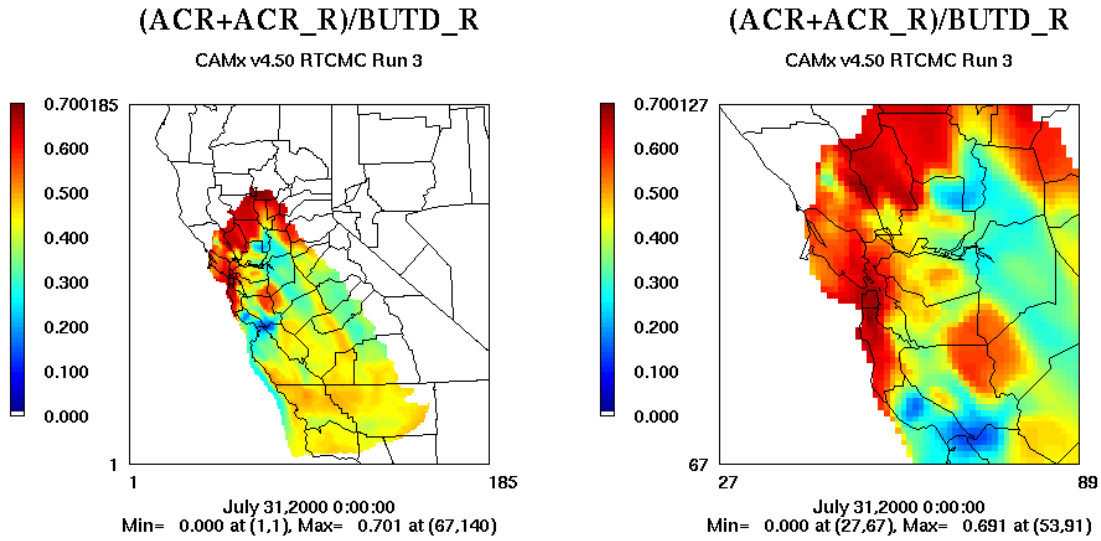


Figure 3-13. Spatial plots of 24-hour average total acrolein yield from butadiene on July 31, 2000. The entire CCOS domain is shown on the left; the Bay Area is shown on the right.

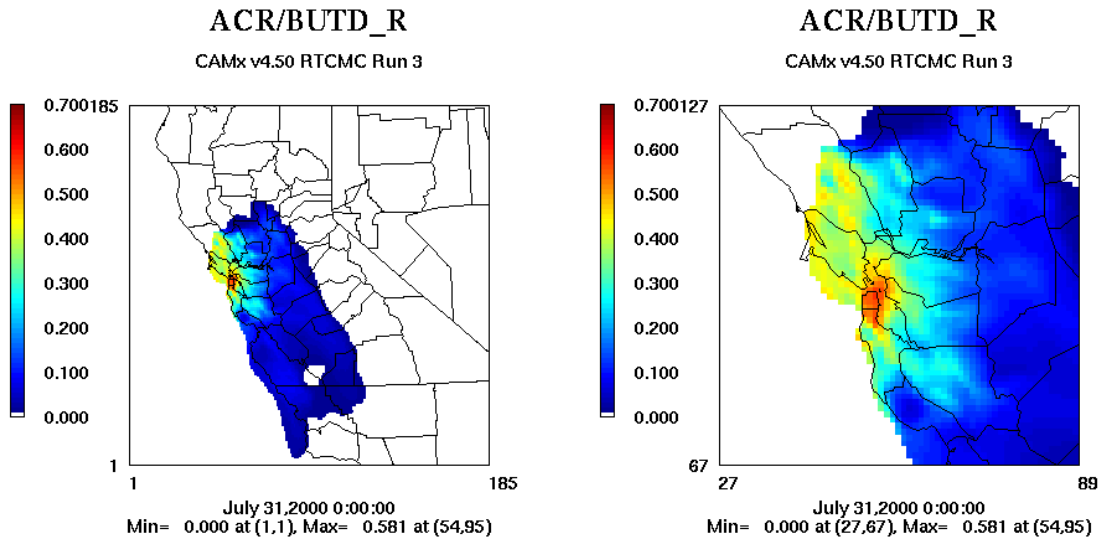


Figure 3-14. Spatial plots of 24-hour average net acrolein yield from butadiene on July 31, 2000. The entire CCOS domain is shown on the left; the Bay Area is shown on the right.

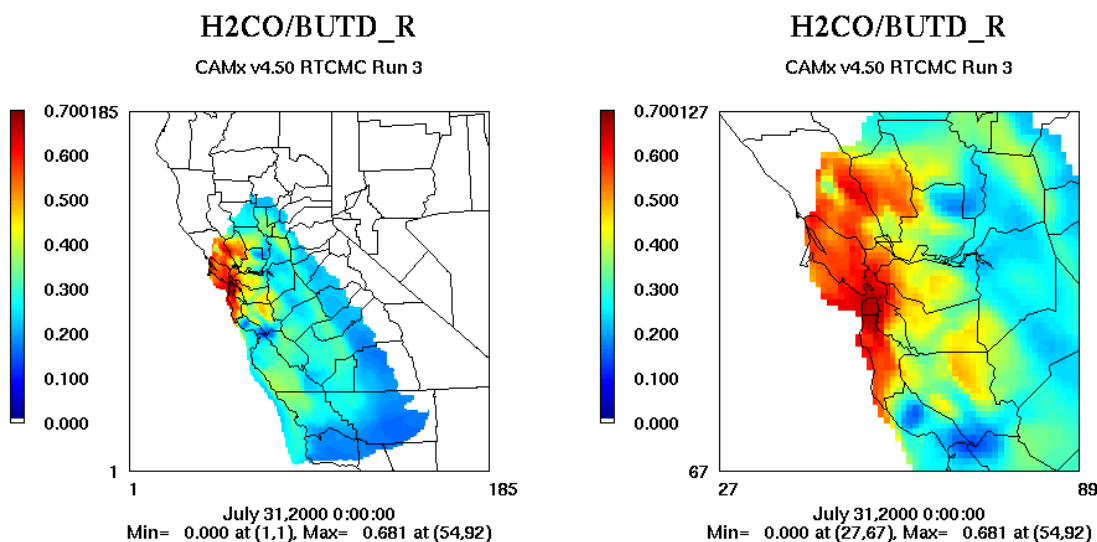


Figure 3-15. Spatial plots of 24-hour average net formaldehyde yield from butadiene on July 31, 2000. The entire CCOS domain is shown on the left; the Bay Area is shown on the right.

- $[ACR] / [BUTD_R]$ is the net yield of acrolein from butadiene (accounting for only the acrolein that is present);
- $[H2CO] / [BUTD_R]$ is the net yield of formaldehyde from butadiene (the mechanism did not track H2CO reacted).

In developing these figures, we generated 24-hour average ratios only for areas of the grid in which BUTD_R exceeds 1 part per trillion ($\text{ppt} = 10^{-6} \text{ ppm}$). The total yield of acrolein from butadiene can be as high as 0.7 close to San Francisco. The maximum possible yield of acrolein from OH radical initiated reaction of butadiene is 74% ($0.78 \times 0.95 = 0.74$) under high NO_x conditions where RO₂ radicals react predominantly with NO (Figure 3-6). The acrolein yield is 30 to 50% in areas where air is exiting the Bay Area toward the East and South. Note that this yield increases to 40-50% well downwind to the south. The net yields of acrolein are always lower than the total yields due to acrolein decay. The net yield is much lower far downwind (below 20%) due to the continuing decay of acrolein to formaldehyde and other products. The net yield of formaldehyde relative to butadiene is similar to the total yield of acrolein around the Bay Area (30 to 60%). The net yield of formaldehyde well downwind is consistently 20 to 40%.

4. CONCLUSION

The District has developed emission inventories for toxic air pollutants and is developing air quality modeling tools specifically for toxics. The purpose of this project is to further develop and demonstrate air toxic modeling methods in the CAMx photochemical grid model.

ENVIRON performed three simulations to demonstrate how CAMx can be used for modeling air toxics over the Bay Area. In one run, CAMx simulated the dispersion of DPM for the entire year of 2000 using CALMET meteorological fields developed by the ARB. Given the extent of the CALMET meteorological fields, the modeling domain was limited to the central Bay Area. CAMx simulated DPM in a source apportionment configuration by tracking DPM emissions split by region, and by on-road and area sources.

ENVIRON then conducted two CAMx demonstrations of the Reactive Tracer Chemical Mechanism Compiler (RTC MC) to show how the chemical decay and secondary production for two common toxic species (butadiene and acrolein) can be tracked as their emissions are dispersed downwind. Since oxidant concentrations (ozone, hydroxyl radical, etc.) are needed to decay these compounds, a full photochemical simulation was needed. Thus, ENVIRON ran these simulations for the July/August 2000 CCOS episode using the SAPRC99 emissions inventory and MM5 meteorological fields obtained from the District. The first CAMx RTC MC simulation demonstrated a basic chemical mechanism that included emitted butadiene, emitted acrolein, and secondary acrolein formed from the decay of butadiene. The second CAMx RTC MC simulation demonstrated a detailed chemical mechanism for the decay of butadiene to acrolein to formaldehyde. The detailed mechanism simulates 34 species in 59 reactions and includes benzene and its decay.

While considered preliminary, these CAMx demonstrations have provided useful information. First, we have shown that differences in the detail of chemical mechanisms can have important ramifications. For example, the basic butadiene/acrolein simulation resulted in an over estimate of the secondary acrolein yield. When implementing additional toxics chemistry into existing solvers for SAPRC99 or CB05, for example, more basic toxic mechanisms (such as our first case) would be typically considered for inclusion given their straightforward approach and low number of reactions. The effort required to code, check, and test additional toxics reactions into an existing chemistry solver quickly compounds with the complexity of the additional reactions. However, we have shown through the automation of RTC MC that once a mechanism is defined, significant detail can be added to the model very quickly and easily with commensurate improvements in mechanism accuracy.

Modeling is an effective means to evaluate the emission inventory; this is clearly valuable for all types of applications, ranging from photochemical ozone, to PM, to reactive toxics. The DPM results reported herein suggest that area source emissions in the current District inventory are probably over stated, especially construction-related emissions. The over predictions exhibited in the DPM simulation are also caused by a lack of diurnal activity profiles, which distribute too much emissions into overnight hours. Our modeling with RTC MC further indicates higher acrolein emissions from Travis Air Base relative to the other major civil airports in the Bay Area.

We offer the following recommendations toward further expanding and improving the District's toxics modeling capabilities:

- Refine the toxics inventory (emission rates, speciation, temporal and spatial distributions) – develop detailed point source inventories in CAMx format;
- Develop annual photochemical simulations that support toxics – consider utilizing annual/regional datasets from WRAP and add detail in Bay Area through the use of grid nesting (e.g., higher resolution meteorological modeling developed in-house);
- Test CAMx using the PiG sub-model for fence-line and neighborhood scale evaluations within Bay Area model;
- Develop chemical mechanisms for other toxics.

APPENDIX A
DESCRIPTION AND FORMAT OF THE
RTCMC MECHANISM INPUT FILE

DESCRIPTION AND FORMAT OF THE RTCMC MECHANISM INPUT FILE

The purpose of RTCMC is to add tracer species to a CAMx “core model” simulation and have the tracers undergo chemical changes that depend upon the evolution of CAMx core model species. A suitable application for RTCMC is simulating air toxic species that are oxidized by hydroxyl radical (OH), ozone (O₃) or nitrate radical (NO₃). The RTCMC approach differs from the existing RTRAC approach by allowing more complex chemical reaction schemes. The current implementation of RTCMC is for gas-phase reactions, i.e., gas-phase tracers reacting with each other and/or gas-phase host model species.

CAMx RTCMC User Interface

- Activated by keyword in the CAMx control namelist: `Probing_Tool = "RTCMC"`
- All other control file options are the same as for RTRAC
- RTCMC chemistry (species and reactions) is defined in a single text (ASCII) input file and specified as the RTRAC “chemistry parameters file” in the control namelist

The RTCMC IMC Format Input File

The format of the RTCMC input file is essentially the same as the “IMC” input file format of the SCICHEM Lagrangian puff model. An example IMC format file is shown in Figure 1.

```
#Control
  rate_species_units = 'ppm'
  rate_time_units = 'min'
  solver = 'dlsode'
  Jacobian = 'numeric'
#Species, Type, Ambient, Tolerance, deposition vel, wet scav
O3      A      1.0      1.0E-12   0.0      0.0
OH      A      1.0      1.0E-12   0.0      0.0
ATRAC   F      1.0      1.0E-12   0.010    0.0
BTRAC   F      1.0      1.0E-12   0.001    0.0
CTRAC   F      1.0      1.0E-12   0.020    0.0
DTRAC   F      1.0      1.0E-12   0.001    0.0
ETRAC   F      1.0      1.0E-12   0.030    0.0
FTRAC   F      1.0      1.0E-12   0.001    0.0
#Table
  0          0.          15.          30.          45.          60.          75.
    80.          86.          87.          88.
  1 4.1590E-04 4.0600E-04 3.7540E-04 3.27E-04 2.6040E-04 9.4990E-05
  2.9930E-05 4.8590E-06 8.3030E-08 1.0000E-09
#Equations
  1 [ATRAC]                -> (2.0)[BTRAC] ; 0 0.000E-00
  2 (1.5)[CTRAC] + [OH]   -> (0.5)[DTRAC] ; 1 4.2000E+04
  3 [ETRAC] + [O3]        -> [FTRAC]       ; 1 1.8000E-02
```

Figure 1. Example RTCMC chemistry input file.

There are four sections in an IMC file that are identified by a keyword at the start of each section, as follows:

#Control	Configuration information identified by keywords
#Species	Names of chemical species and associated data
#Table	Photolysis rate data for any photolytic reactions
#Equations	Chemical reactions and thermal rate constants

The IMC file uses space delimited ASCII format. Leading white space at the start of any line will be ignored. CAMx reads the IMC file as *case insensitive*.

The hash symbol (#) before each section keyword marks the start of a section and should be reserved for this purpose. The four sections should appear in the order shown above. The only section that may be unnecessary in some cases (i.e., if there are no photolytic reactions) is the #Table section and guidance on handling this case is provided below.

The Control Section

According to the SCICHEM documentation, the #Control section of the IMC file must always have at least three lines, as follows:

```
#CONTROL
  &CONTROL
  &END
```

The first line is the keyword identifying the control section. The second and third lines are additional keywords denoting the start and end of the control section. Note, however, that CAMx ignores the &CONTROL and &END lines.

One or more control options may be specified using keywords inserted one per line ahead of the closing &END line, like this:

```
#CONTROL
  &CONTROL
    Keyword = 'option'
    Keyword = 'option'
  &END
```

The keywords used by CAMx and SCICHEM are listed in Table 1 and are case insensitive. Not all keywords are used by both models, and CAMx will ignore any non-recognized keyword. A “=” symbol must separate each keyword and option. The option must be enclosed within single quotes. In practice, only the first six letters of each keyword and the first three letters of each option are considered and you may abbreviate accordingly (i.e., `keywor = 'opt'`). All CAMx recognized keywords have a default option that will be used if the keyword is omitted, meaning that the CAMx RTCMC may be run without specifying any keywords provided that that all other input data (e.g., rate constants) are consistent with the defaults.

Table 1. Keywords, options and default values for the Control section of the IMC file.

Keyword	Used by SCICHEM	Used by CAMx	Options Allowed by CAMx
Ambient_file	•		n/a
Species_units	•		n/a
Emission_units			n/a
Rate_species_units	•	•	molecules/cm3 (<i>default</i>) ppm
Rate_time_units	•	•	seconds (<i>default</i>) minutes hours
Solver		•	DLSODE (<i>default</i>) SLSODE Rosenbrock
Rtol	•	•	Real number (<i>default</i> = 1.0E-5)
Atol		•	Real number (<i>default</i> = 1.0E-18)
Jacobian		•	Numeric (<i>default</i>) Algebraic

The allowed keyword options in Table 1 are discussed below:

Rate_species_units – The concentration units for thermal rate constant expressions.

Rate_time_units – The time units for photolysis and thermal rate constant expressions.

Solver – The name of the numerical integrator to be used as the chemistry solver. SLSODE and DLSODE are, respectively, the single and double precision versions of the Livermore Solver for Ordinary Differential Equations (Hindmarsh 1980). The Rosenbrock solver is the double precision RODAS solver (Hairer and Wanner, 1991).

Rtol – The relative error tolerance (convergence criterion) employed for all chemical species by the chemistry solver.

Atol – The absolute error tolerance (convergence criterion) employed for all chemical species by the chemistry solver. CAMx does not use species specific Atol values that may appear in the species section, as discussed below.

Jacobian – The chemistry solvers employ a Jacobian matrix of first-order derivatives of each chemical species with respect to all species. The Jacobian matrix is constructed automatically by the RTCMC. This option controls whether the Jacobian is constructed algebraically or numerically. Both options may be used with the double precision solvers and numeric may be more efficient. The algebraic option is strongly recommended for the single precision SLSODE solver (because single precision may be inadequate for constructing a numeric Jacobian by finite difference).

Concentration Units

CAMx does not use the *Species_units* or *Emission_units* keywords and will ignore them if they are present. CAMx will output RTCMC species average concentrations in ppm units. Emissions of RTCMC species must be provided in moles/hour.

Setting Error Tolerances

All three RTCMC chemistry solvers use the `Rtol` and `Atol` parameters specified in the control section to manage errors in predicted concentrations. CAMx does not use the species specific `Atol` values that may appear in the species section because it is difficult to select reliable `Atol` values for each species. The error (`err`) in the predicted concentration (`con`) for species `I` should be roughly less than:

$$err(i) = rtol \times con(i) + atol$$

The combined `Rtol` and `Atol` determine accuracy. Setting `Atol` to zero will result in pure relative error control. Relative error control has the advantage of being easily understood (the errors should be smaller than X percent) but suffers the disadvantage of excessive computational resources may be expended to manage errors in species concentrations that are essentially zero. Note that RTCMC sets a concentration floor of 1.0E-16 ppm.

The default settings for `Rtol` and `Atol` listed in Table 1 should be generally applicable because they are conservative and effectively result in pure relative error control. We recommend against setting `Rtol` greater than 0.001. Appropriate settings for `Atol` depend upon the magnitude of concentration predictions and the need for accurate predictions in high vs. low concentration areas (e.g., plume centerline vs. out of plume).

Do not request infeasible accuracy from single precision SLSODE by setting `Rtol` and `Atol` smaller than about 1.0E-7.

The Species Section

The species section of the IMC file lists chemical species that and associated data. All chemical species referred to in the equation section must appear in the species section. Extra species may appear in the species section, but including numerous extra species may cause a run-time error by exceeding the memory available for storing species information (if this happens, delete some of the unused species from the species section).

The first line is the keyword identifying the species section. The following information must be provided for each listed species:

- Name – Species names may be up to 8 characters and must start with a letter. They are case insensitive. Accurate names are important because other CAMx input data (e.g., emissions, boundary conditions) will be matched to RTRAC species by name.
- Type – There are four permissible species types identified by first letter: Ambient (A), Fast (F), Slow (S), Equilibrium (E). Setting the species type is discussed in more detail below.
- Ambient – The ambient value is not used by CAMx, but is used by SCICHEM. Provide a real number (e.g., 0.0).

- Atol** – Species specific error tolerances are not used by CAMx, but are used by SCICHEM. Provide a real number (e.g., 0.0).
- Dep** – The species deposition velocity in m/s. This deposition velocity will be used for all land surface types which is a simplification compared to the CAMx dry deposition scheme. Provide a real number (e.g., 0.0).
- Wet Scav** – The wet scavenging coefficient is not used by CAMx. For SCICHEM, this is a washout ratio. CAMx does not use the washout ratio because this approach is incompatible with the CAMx wet deposition algorithms. Provide a real number (e.g., 0.0).
- MW** – The molecular weight is not needed by CAMx. Provide a real number (e.g., 1.0).

Choosing the Species Type

The **Type** for each RTCMC species should be set according to (a) whether the species concentration should be obtained from the core model or modeled using the RTCMC, and (b) the most accurate and efficient numerical method for performing chemistry within RTCMC.

All species to be obtained from the core model (e.g., O₃, OH, NO, NO₂, H₂O, M, O₂) must be set to type **Ambient**. This rule will be enforced by CAMx and, for example, the species O₃ must be set to type **A**, because it is part of all the core chemical mechanisms (CB4, CB05, SAPRC99).

Species that are solved by the RTCMC may be type **F**, **S** or **E**. The recommended default type is **F** (fast) in which case chemistry will be performed using the selected chemistry solver (e.g., DLSODE). Species that undergo slow chemical change (lifetime of hours or longer) may be set to type **S** (slow) with potential gain in efficiency but some loss in accuracy. Species that undergo extremely rapid chemical change (lifetime smaller than a second) may be set to type **E** (equilibrium) and solved using a steady-state approximation with some gain in efficiency but some loss in accuracy. The Rosenbrock solver does not work well with species types **S** or **E**. Equilibrium species may be used effectively with the single precision SLSODE solver to avoid the need for double precision. You should use types **S** or **E** with caution and evaluate both computational speed and concentration accuracy by comparing against results with using type **F**.

The Table Section

The table section of the IMC file provides photolysis rates for any photolytic reactions in the RTCMC mechanism. It must contain at least two lines

```
#Table
0 zenith1, zenith2, zenith3, ...
```

The first line is the keyword identifying the table section. The second line must begin with 0 (zero) followed by a list of space delimited zenith angles (in degrees) starting with zero degrees and ascending to the largest angle. If the largest zenith angle specified is less than 90 degrees a value of 90 degrees is implicitly added to the list. By default, up to 15 zenith angles are allowed

(this may be changed as described under adjustable parameters, below). If the final zenith angle is not 90 degrees, no more than 14 angles should be listed to allow the 15th angle to be implicitly set to 90 degrees.

If the reaction mechanism has no photolytic reactions include just the first two lines (keyword followed by zenith angles) in the table section. If the reaction mechanism includes photolytic reactions, list them one reaction per space delimited line after the zenith angles:

```
reaction, rate1, rate2, rate3, ...
```

Reaction must be the integer number of the photolytic reaction followed by the photolysis rate at each zenith angle, from zero to the largest angle. Photolysis reactions are first order and have rate units of reciprocal time to be provided in the `Rate_time_units` specified in the control section of the IMC file. A photolysis rate of zero is implicitly assumed at 90 degrees unless you specify otherwise.

The Equations Section

The equations section of the IMC file lists the chemical reactions and rate constants for the RTCMC reaction mechanism and must contain at least two lines:

```
#Equations  
Number [Reactant] > (Stoichiometry) [Product] ; Rate Constant
```

The first line is the keyword identifying the equations section and must be followed by at least one reaction line. Reaction lines list reactions and rate constants and are delimited by white space and separators. The reaction `Number` and the `Reactants` must be separated by white space. The `Reactants` and `Products` must be separated by a right arrow symbol (the right arrow may be preceded by characters, e.g., `=>` or `->`). The `Products` and the `Rate Constant` must be separated by a semi-colon.

The reaction `Number` must be an integer value that uniquely identifies each reaction. Reaction numbers need not be in order or continuous.

`Reactant` and `Product` names must be enclosed within square brackets, begin with a letter, and not exceed 8 characters in length. All species name used in the equations section must also appear in the species section. Zero to three reactants are allowed. Zero to 20 products are allowed (the maximum is a user adjustable parameter). Product names may be preceded by a stoichiometric coefficient enclosed within round brackets. If the stoichiometric coefficient is omitted it is assumed to be unity.

Rate constants are specified using SCICHEM conventions and must be in the units specified by the keywords `Rate_species_units` and `Rate_time_units` in the control section (the defaults are molecules cm⁻³ and seconds). SCICHEM supports numerous rate constant expression types and CAMx should interpret all of them correctly, although not all have been

thoroughly tested. Table 2 defines a sub-set of the SCICHEM rate constant expression types that are recommended for use with CAMx. The format for specifying rate expressions is the integer expression type followed by a list of the numerical values required by that expression type. It is important that rate expressions are defined in units that are consistent with the reaction order and Table 3 defines how the reaction order and rate constant unit dimensions may be determined.

The CAMx *.diag file lists diagnostic information on the mechanism and rate constant expressions read by from the IMC file.

User Adjustable Parameters

User adjustable parameters for RTRAC are set in two CAMx include files, `tracer.com` and `rtcmc.com`. The maximum number of RTCMC species set by parameter `MXTRSP` in the `tracer.com` include file (as for all other CAMx probing tools). Other parameters that may need adjustment are defined in `rtcmc.com` and are listed in Table 4. If an error is encountered at model start up because one of these RTCMC parameter has been exceeded, consult the list of parameters in Table 4 and then change the parameter appropriately in the `rtcmc.com` include file. Rebuild the CAMx executable (we recommend performing a “`make clean`”) after changing any RTCMC parameter.

Table 2a. Recommended SCICHEM rate constant expression types for use in CAMx.

Expression Type	Description	Expression
0	Photolysis	$k = 0$
1	Constant	$k = k_0$
2	General temperature dependence	$k = AT^{-c} e^{(B/T)}$
16	Troe-type temperature and pressure dependence	$k = \left[\frac{k^0[M]}{1 + k^0[M]/k^\infty} \right] F^G$ $k^0 = AT^B$ $k^\infty = CT^D$ $F = 0.6$ $G = \left\{ 1 + \left[\log(k^0[M]/k^\infty) \right]^2 \right\}^{-1}$
8	Equilibrium with a previously defined reaction (k_{ref})	$k = k_{ref} A e^{(B/T)}$
13	Lindemann - Hinshelwood as used for OH + HNO ₃	$k = k_0 + \frac{k_3[M]}{1 + k_3[M]/k_2}$ $k_0 = A e^{(B/T)}$ $k_2 = C e^{(D/T)}$ $k_3 = E e^{(F/T)}$
7	Simple pressure dependence used for OH + CO	$k = k_0(1 + 0.6P)$

Table 2b. Parameters required by SCICHEM rate constant expression types.

Expression Type	Parameters					
	1	2	3	4	5	6
0	k_o					
1	k_o					
2	A	B	C			
16	A	B	C	D		
8	k_{ref}	A	B			
13	A	B	C	D	E	F
7	k_o					

Table 3. Determining the reaction order and consequent unit dimensions for rate constants.

Number of Reactants	Reaction Order	Concentration Unit Dimension	Time Unit Dimension
0	Zero	None	Time ⁻¹
1	First	None	Time ⁻¹
2	Second	Concentration ⁻¹	Time ⁻¹
3	Third	Concentration ⁻²	Time ⁻¹

Table 4. RTCMC parameters default settings in the rctmc.com include file.

Name	Description	Default
MXRX	maximum number of RTCMC reactions	200
MXPHOT	maximum number of photolysis reactions	30
MXZEN	maximum number of photolysis reaction zenith angles	15
MXPRD	maximum number of products in each reaction	20
MXEQM	maximum number of equilibrium species	5
MXSLO	maximum number of slow species	25

References

- Hindmarsh, A.C. (1980). "LSODE and LSODI, two new initial value ordinary differential equation solvers." ACM SIGNUM Newsletter, Volume 15, Issue 4 (December).
- E. Hairer and G. Wanner. (1991). "Solving ordinary differential equations II Stiff and differential-algebraic problems." Springer-Verlag, Berlin.