

## MODELING CHEMICALLY REACTIVE AIR TOXICS IN THE SAN FRANCISCO BAY AREA USING CAMx

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### INTRODUCTION

Toxic air pollutants are of concern because they cause acute and/or chronic health impacts. Toxic emissions in densely populated urban areas—with high numbers of youth, seniors, and in low-income families—add to the pollution burden of sensitive populations. The Bay Area Air Quality Management District (BAAQMD) has developed an emissions inventory for toxic air pollutants over the San Francisco Bay Area and is developing air quality modeling tools to specifically address air toxics. Traditional Gaussian plume and puff dispersion models are applicable for simulating primary pollutants (e.g., diesel particulate matter [DPM]). Such dispersion models are not suitable, however, for simulating chemically reactive pollutants (e.g., formaldehyde, 1,3-butadiene, acrolein) and secondary pollutants (e.g., acrolein, formaldehyde). Photochemical grid models can address chemical transformation pathways for toxics, and simulate their three-dimensional dispersion over wide areas.

We performed several simulations to demonstrate how the Comprehensive Air quality Model with extensions (CAMx) can be used for modeling air toxics over the Bay Area. The BAAQMD provided an annual toxic emissions inventory of benzene, formaldehyde, 1,3-butadiene, acrolein and DPM on a 2 km grid for the 9-county Bay Area. ENVIRON then used a newly developed highly flexible Reactive Tracer Chemical Mechanism Compiler (RTCMC) for CAMx. This module allows a user-defined toxic chemistry mechanism to run in parallel with, and to draw oxidant information from, a standard gas-phase photochemical simulation (i.e., CB05 or SAPRC99). In one preliminary simulation, CAMx modeled inert DPM dispersion over the Bay Area for the entire year of

2000. Two chemistry simulations modeled the decay of butadiene to acrolein and formaldehyde with different levels of chemical detail during a July 29 to August 2, 2000 ozone episode. The more detailed mechanism for butadiene/acrolein/formaldehyde uses 58 reactions and 32 species to represent chemistry initiated by hydroxyl radical, nitrate radical, ozone and photolysis. In this paper, we describe the CAMx RTCMC and present results from the two chemistry simulations.

The RTCMC allows users to input, in a text-based format, a set of chemical reactions (mechanism) for certain target species to be treated by the CAMx Reactive Tracer (RTRAC) Probing Tool. RTRAC simulates reactive tracers, whereas RTCMC is the front-end to RTRAC that reads (and solves) the user-defined chemical mechanism for reactive tracers. The core model's photochemical mechanisms (CB4, CB05, or SAPRC99) remain intact and separate from the reactive tracer chemistry.

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. 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. When implementing toxics chemistry into existing solvers, the effort required to code, check, and test the additional reactions quickly compounds with the complexity of the reactions. We show through the automation of RTCMC that significant detail can be added to the model very quickly and easily with commensurate improvements in mechanism accuracy.

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#Control
  rate_species_units = 'molecules/cm3'
  rate_time_units = 'sec'
  solver = 'dlsode'
  Jacobian = 'numeric'
#Species,Type,Ambient,Tolerance,deposition vel,wet scav,mw,ldos,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

```

Figure 1. Chemical mechanism input file applied in the basic RTCMC run.

## 2. CHEMICAL SIMULATIONS

ENVIRON conducted two CAMx applications with the RTCMC to show how the chemical decay and secondary production of several common toxic species (butadiene, acrolein, and formaldehyde) 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 Central California Ozone Study (CCOS) episode using the California Air Resources Board's (CARB) SAPRC99 emissions inventory and MM5 meteorological fields. CAMx/RTCMC was run on the full CCOS modeling domain (185 by 185 grid cells at 4 km resolution with 20 vertical layers).

### 2.1 A Basic Butadiene/Acrolein Chemical Mechanism

The first CAMx RTCMC simulation demonstrated a basic chemical mechanism among a limited

number of 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 (Figure 1). This chemical mechanism was developed for the U.S. Environmental Protection Agency (EPA) as part of a project to develop the Carbon Bond 2005 (CB05) chemical mechanism (Yarwood, 2005).

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, while point sources were processed into CAMx point source format. Since stack parameters were not provided in the raw inventory, defaults were used. All emissions were assumed to be constant for all hours and dates. Total Bay Area emissions were 976 lb/day for acrolein and 3257 lb/day for butadiene; the majority of both came from mobile sources. The largest emissions of both toxics were associated

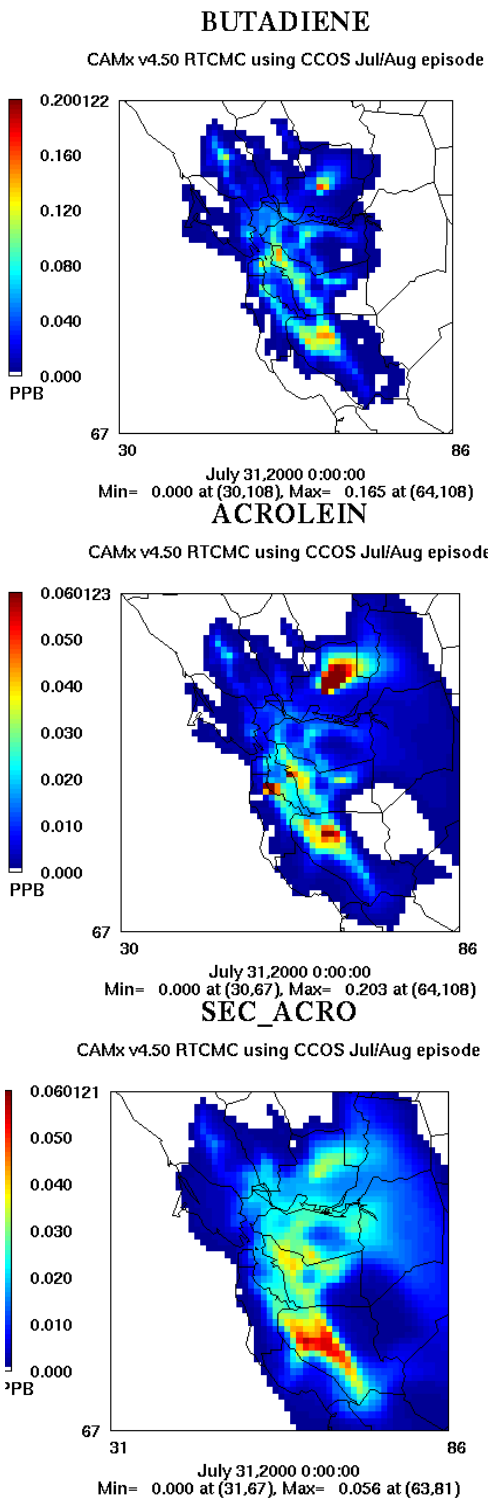


Figure 2. Spatial plots of 24-hour average butadiene (top), primary acrolein (middle), and secondary acrolein (bottom) on July 31, 2000 over the Bay Area.

with major airports in the area (jet aircraft operations are especially known to be sources of acrolein).

Spatial plots focusing on the Bay Area are shown in Figure 2 for 24-hour average primary butadiene and primary and secondary acrolein on July 31. Primary acrolein and butadiene concentrations are highest where emissions are greatest. Very little butadiene was found outside the Bay Area as it reacted quickly to form secondary acrolein. Secondary acrolein concentrations were highest downwind of the local butadiene peaks, and far more diffuse than the primary species.

## 2.2 A Detailed Butadiene Mechanism

The second CAMx RTCMC simulation demonstrated a detailed chemical mechanism for the decay of butadiene to acrolein and ultimately to formaldehyde. This simulation also included benzene, which decays slowly in the atmosphere via reaction with the hydroxyl radical (Calvert, 2002). 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 (Leeds, 2004). A schematic diagram of all reactions is shown in Figure 3. 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 are defined as follows:

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., H2CO) resulted solely from

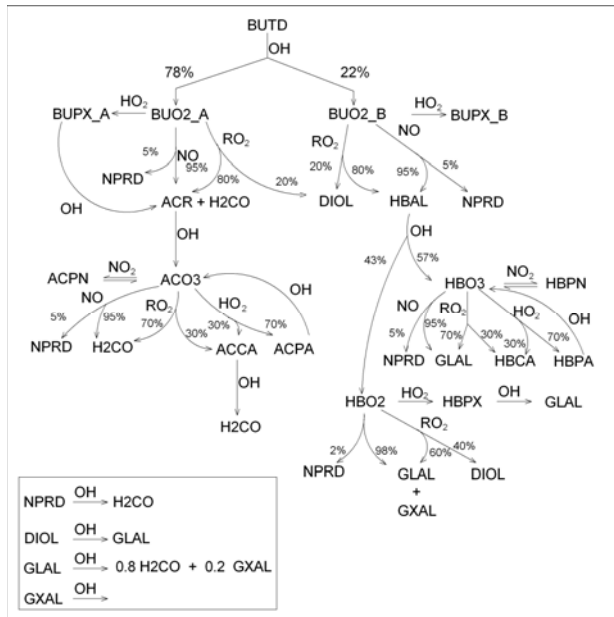


Figure 3. Schematic of the detailed mechanism for the OH radical initiated reactions of butadiene/acrolein/formaldehyde included in the RTCMC chemical mechanism.

decay of butadiene. All other aspects of this simulation were similar to the previous RTCMC run.

Figure 4 shows 24-hour average concentrations of secondary acrolein and secondary formaldehyde from butadiene, respectively. As seen in the first simulation, 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, 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. These characteristics extend to formaldehyde as well. Given that formaldehyde forms from butadiene, acrolein and their decay products (Figure 3), peak formaldehyde concentrations are also anchored to areas of high butadiene emissions areas, but extend even farther downwind with the acrolein.

Butadiene concentrations were slightly higher in the more detailed simulation (by ~1%) due to slightly different reaction rate constants for butadiene removal. Secondary acrolein was much lower in the detailed mechanism (25-50%). Secondary acrolein was higher with the basic mechanism because that mechanism assumes

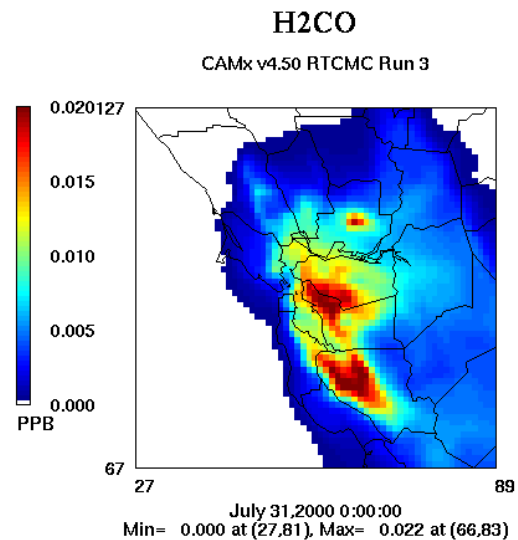
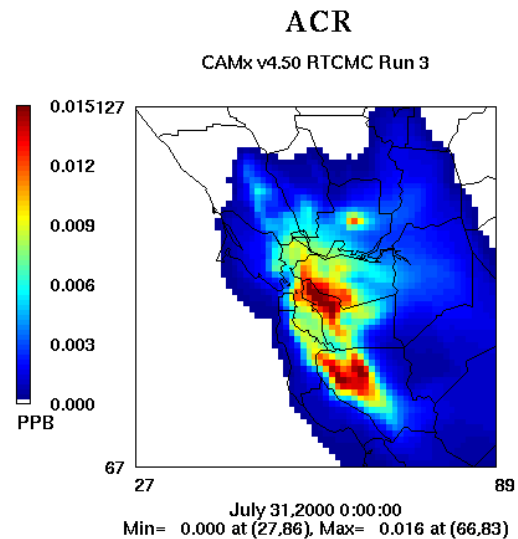


Figure 4. Spatial plots of 24-hour average butadiene (top), primary acrolein (middle), and secondary acrolein (bottom) on July 31, 2000 over the Bay Area.

100% yield of acrolein from butadiene (i.e., one acrolein molecule formed from each butadiene molecule reacting).

Figure 5 displays the 24-hour average concentrations of benzene on July 31, 2000. Again, the pattern of emitted benzene echoes the emissions distribution of this species, but note that primary benzene extends further downwind than butadiene given the former compound's much lower decay rate. Figure 5 confirms that benzene decays far downwind of where benzene is emitted.

The fractional yields of acrolein and formaldehyde from butadiene within the detailed mechanism

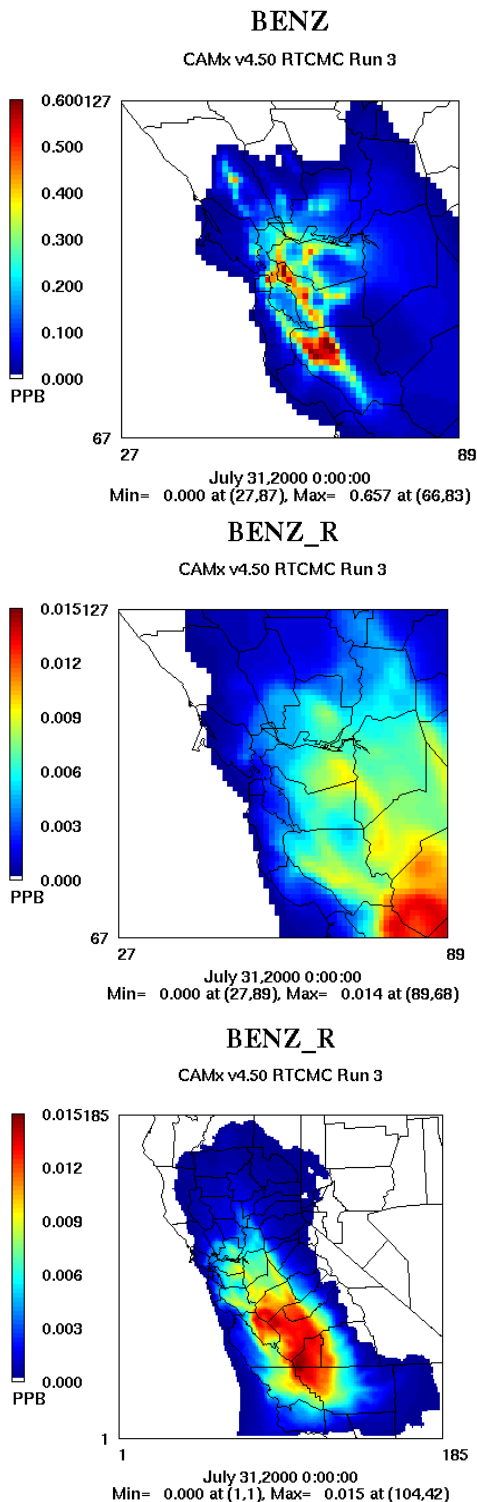


Figure 5. Spatial plots of 24-hour average emitted and reacted benzene on July 31, 2000 over the Bay Area (top 2 panels) and reacted benzene over the entire modeling domain (bottom panel).

were determined from the following ratios as displayed in Figure 6:

- $[ACR + ACR\_R] / [BUTD\_R]$  is the total yield of acrolein formed from butadiene (accounting for the fact that acrolein also decays once it is formed);
- $[ACR] / [BUTD\_R]$  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 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<sub>x</sub> conditions where RO<sub>2</sub> radicals react predominantly with NO. 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%.

### 3. CONCLUSION

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 RTCMC that once a mechanism is defined, significant detail can be added to the model very quickly and easily with commensurate improvements in mechanism accuracy.

### 3. REFERENCES

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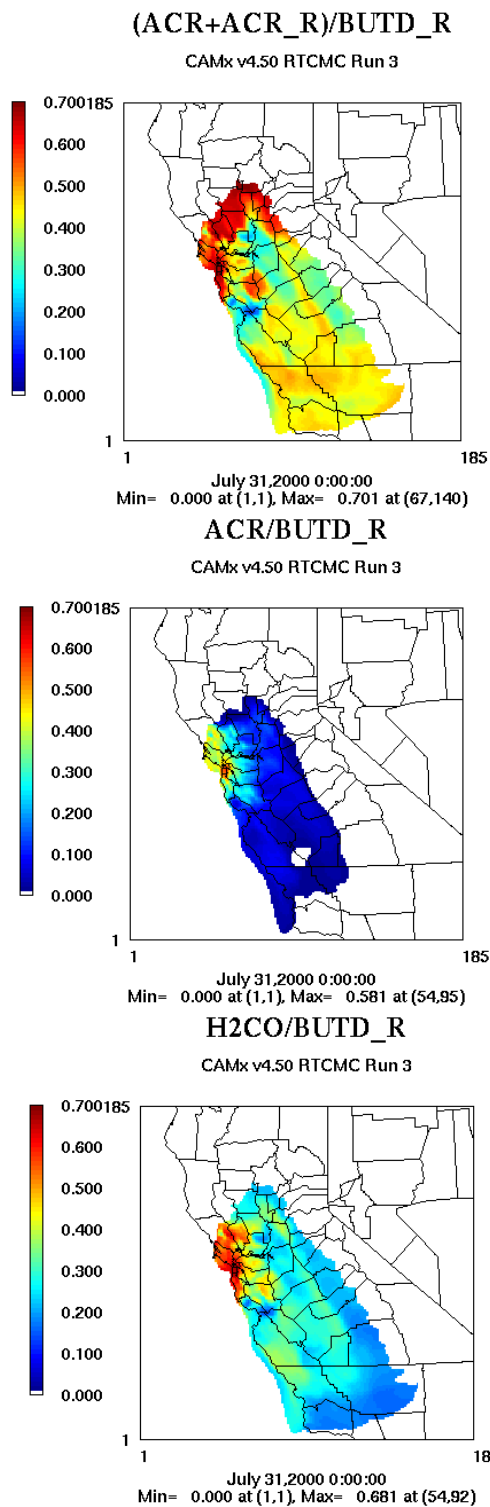


Figure 6. Spatial plot of 24-hour average total acrolein yield from butadiene, net acrolein yield from butadiene, and net formaldehyde yield from butadiene on July 31, 2000 over the entire CCOS domain.