Changes to the Chemical Mechanisms for Hazardous Air Pollutants in CMAQ version 4.6

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1. INTRODUCTION

In the Community Multiscale Air Quality (CMAQ) model version 4.5, atmospheric chemistry included options for two different mechanisms to predict the transport and fate for several Hazardous Air Pollutants (HAPs). They were derived from either the Carbon Bond IV (Gery et. al 1989) or State Air Pollution Research Center (SAPRC99, Carter 2000) mechanisms. Each mechanism treated HAPs that were identified by National Air Toxic Assessments (NATAs) to produce large risks to human health over urban areas (USEPA, 2002). These toxics compounds were also treated based on their high volatility and can be simulated as gas phase compounds. Because of the criteria, version 4.5 HAP mechanisms omitted toxic components found in atmospheric Particulate Matter (PM).

Version 4.6 of CMAQ introduces two new mechanisms that attempt to remove this shortcoming. The model can now simulate the atmospheric concentration and deposition of several toxic metals and diesel components in PM. In addition to these aerosol species, the new mechanisms simulate a greater number of gas phase HAPs. One new mechanism extends the version 4.5 of SAPRC99 for HAPs and is labeled SAPRC99TX3. The other adapts the Carbon Bond 05 (CB05) mechanism released in version 4.6 (Sarwar et al. 2006 and Yarwood et al. 2005) and is labeled CB05CLTX.

This paper describes the new mechanisms. The following section lists the HAPs simulated by both mechanism and describes how the standard versions of CB05 and SAPRC99 were adapted. Descriptions include how the CMAQ

chemical transport model treats the HAPs in gas and aerosol phases. The last two sections present simulations that use these mechanisms. The latter of these two sections compares results between mechanisms for several HAPs and proposes possible causes.

2. Description of New HAP Mechanisms.

The following section describes how the chemical transport model treats HAPs based on its phase. Each description focuses on the chemical and physical processes. Note that all pollutants undergo transport and deposition based on their phase. Wet deposition is determined by the Henry's Law Constant or scavenging rate of the aerosol mode. Aerosol mode determines dry deposition velocity for aerosol phase pollutants. For the gas phase HAPS, dry deposition has a nonzero velocity if the EPI Suite™ program (USEPA, 2005) and the SPECTRUM Laboratory database (http://www.speclab.com/price.htm) indicate dry deposition as a fate determining process.

Chemical transformation of gas phase HAPs (Table 1) is calculated with two methods. The first is accomplished in standard numerical solver for ozone and radical chemistry within CMAQ such as the Euler Backward Iterative solver (Hertel et al., 1993). The method may affect the solution for ozone and radical concentrations if the pollutant has high enough concentrations. The second method estimates loss from chemical reactions based on the solution from ozone and radical chemistry. It does not alter the solution. Luecken et al (2006) describes the approach. The second method is justified because either the compounds are already accounted in lumped model species or their low emissions rates have an insignificant effect on ozone and radical chemistry.

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The first method treats two types of model species. Type one participates in photochemistry by destroying and producing model species controlling ozone and radical concentrations. In CB05CLTX, formaldehyde and acetaldehyde belong to type one. In SAPRC99TX3, acrolein and 1,3-butadiene also belong to type one. Type two does not alter ozone and radical concentrations. The treatment is used because their emissions are already accounted in explicit or lumped species within the mechanisms. Type two serves as tracers of emitted pollutants. Tracers for formaldehyde, acetaldehyde, and acrolein allow determining photochemical production of the given pollutant.

Table 1. HAP Gas Species

HAP	CAS#
Acrylonitrile	107-13-1
Carbon Tetrachloride	56-23-5
Propylene Dichloride	78-87-5
1,3-Dichloride Propene	542-75-6
1,1,2,2-Tetrachloride Ethane	79-34-5
Benzene	71-41-2
Chloroform	67-66-3
1,2-Dibromomethane	106-93-4
1,2-Dichloromethane	107-06-2
Ethylene Oxide	75-21-8
Methylene Chloride	75-09-2
Perchloroethylene	127-18-4
Trichloroethylene	79-01-6
Vinyl Chloride	7501-4
Naphthalene	91-20-3
Quinoline	91-22-5
Hydrazine	302-01-2
2,4-Toluene Diisocyanate	584-84-9
Hexamethylene 1,6-Diisocyanate	822-06-0
Maleic Anhydride	108-31-6
Triethylamine	121-44-8
1,4-Dichlorobenzene	106-46-7
Total Formaldehyde	50-00-0
Total Acetaldehyde	75-07-0
Total Acrolein	107-02-8
1, 3-Butadiene	106-99-0
Formaldehyde Emissions Tracer	50-00-0
Acetaldehyde Emissions Tracer	75-07-0
Acrolein Emissions Tracer	107-02-8

Aerosol phase HAPs (Table 2) use a modeling approach analogous to tracers in the gas phase. They track emissions of toxic components within PM and undergo microphysical processes and deposition similar to elemental carbon and unidentified coarse mode matter. However, the HAP species do not affect rates of microphysical processes and deposition based on their tracking function. They also do not participate in cloud chemistry. The approach is not valid for two toxic components in

PM. Research (Kotas and Stasicka 2000, Zhang 2000 and Seigneur and Constantinou 1995) indicates that hexavalent and trivalent states of chromium exchange mass through chemistry within cloud droplets. Removing the shortcoming is an avenue for model developers within CMAS.

3. Simulations

To demonstrate each mechanism, applications were conducted over January and July 2001, excluding the spin-up period. The modeling domain covered the continental United States with grid cells that had horizontal dimensions of 36X36 km^2. The vertical structure spanned from the surface to 100 mbar with 14 layers in sigma pressure coordinates. The SMOKE modeling system (CEMPD, 2005) produced emission files based on the 1999 National Emissions Inventory (USEPA, 2004) for criteria and toxic air pollutants.

Table 2. HAP Aerosol Species

HAP
Beryllium Compounds
Nickel Compounds
Chromium (III) Compounds
Chromium (VI) Compounds
Lead Compounds
Manganese Compounds
Cadmium Compounds
Diesel Emissions Tracer

4. Results

For gas phase HAPs, we compare predications from each mechanism by examining 1,3-butadiene, benzene, photochemically produced formaldehyde and acetaldehyde. The comparison uses these pollutants because emissions are the only sources for 1,3-butadiene and benzene while the last two pollutants have sources based on how each mechanism represents the chemistry of organic compounds. Figure 1 shows that CB05CLTX tends to produce higher concentrations for benzene and 1,3-butadiene. The cause seems to be that CB05CLTX produces lower hydroxyl and oxidant concentrations. Our results imply that CB05CLTX predicts longer photochemical lifetimes and generally higher HAP concentrations than SAPRC99TX3.

Differences between mechanisms become complex for photochemically produced pollutants (Figure 2). For formaldehyde, neither mechanism shows a net difference. For

acetaldehyde, CB05CLTX produces higher concentrations than SAPRC99TX3 especially during the summer period. A possible cause is how CB05CLTX treat and represents olefins or alkenes excluding ethene and isoprene. In CB05CLTX, olefins have higher acetaldehyde yields in their reactions. CB05CLTX also lumps greater amounts of emitted compounds into fast reacting olefins based on what olefins represent in CB05CLTX versus SAPRC99TX3. The net effect is that CB05CLTX produces more photochemical acetaldehyde. Our conclusion is supported because larger differences occur during the July period when biogenic sources emit large amounts of olefins.
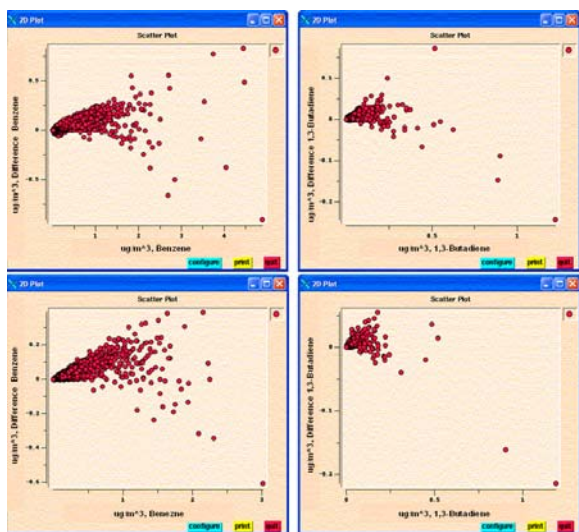
Figure 1. Benzene (left) and 1,3-butadiene (right) differences from CB05CLTX to SAPRC99TX3 mechanisms plotted against the SAPRC99TX3 predictions. Top and bottom panels show results from the January and July simulations, respectively.

For aerosol phase HAPs, the comparison between mechanisms examine an accumulation mode species, trivalent chromium, and a coarse mode species, diesel emissions. For both species, CB05CLTX generally produce greater concentrations than SAPR99TX3 (Figure 3). The difference results because SAPRC99TX3 causes larger removal rates of bulk PM through either wet or dry deposition.

In closing, the developed mechanisms have not been evaluated against observations. Each does give results consistent to the mechanisms from that they were derived, i.e., CB05 or SAPRC99. The HAP mechanisms then allow users to simultaneously study criteria and numerous toxic pollutants.
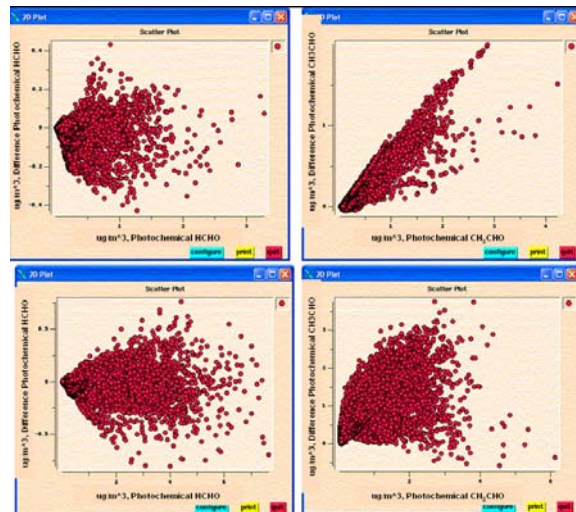

Figure 2. Photochemically produced formaldehyde (left) and acetaldehyde (right) differences between CB05CLTX to SAPRC99TX3 plotted against CB05CLTX predictions. Top panels show CB05CLTX minus SAPRC99TX3 results plotted from the January simulations. Bottom panels show results from the July simulations.
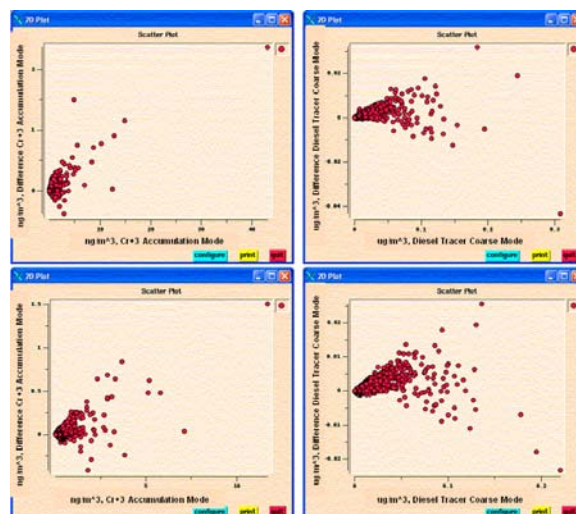

Figure 3. Trivalent chromium in the accumulation mode (left) and Diesel emissions tracer in the coarse mode (right) differences from CB05CLTX to SAPRC99TX3 mechanisms plotted against the SAPRC99TX3 predictions. Top and bottom panels show results from the January and July simulations, respectively.

it does not necessarily reflect their policies or views.

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