IMPROVEMENT OF THE AROMATIC HYDROCARBON REPRESENTATION IN THE SAPRC99 CHEMICAL MECHANISM OF THE COMMUNITY MULTISCALE AIR QUALITY (CMAQ) SYSTEM

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1. INTRODUCTION

Aromatic hydrocarbons represent a significant fraction of the reactive hydrocarbon classes in urban areas, and are rated among the most important classes of compounds with regard to the formation of photo-oxidants in the lower atmosphere.

Theoretical studies using the trajectory model approach estimated the aromatic hydrocarbons to be responsible for about 35% of the anthropogenic ozone formation; their contribution to the total non-methane hydrocarbon (NMHC) emissions was calculated to be 30%, being the second major contributor to the NMHCs. (Calvert, 2002)
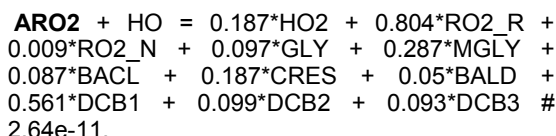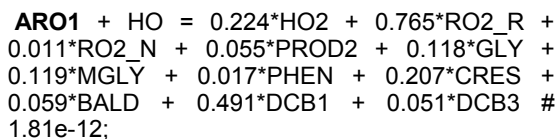
2. BACKGROUND

For our work we used the EPA's air toxics version of the Community Multiscale Air Quality (CMAQ) system, which accepts meteorology inputs from the Mesoscale Model 5 (MM5) (Grell et al. 1994) and includes both Carbon Bond (CBIV) (Gery, 1989) and State-wide Air Pollution Research Center (SAPRC99) (Carter, 2000) mechanisms. We focused on the SAPRC99 mechanism, which is chemically up-to-date and has been tested extensively against environmental chamber data.

Currently, in the SAPRC99 chemical mechanism, the aromatic hydrocarbons are represented by two lumped species, ARO1 and ARO2, based on their reactivity with OH radicals:

(a) ARO1: $K_{OH} < 2x10^4 ppm^{-1}min^{-1}$;
(b) ARO2: $K_{OH} > 2x10^4 ppm^{-1}min^{-1}$

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The ARO1 and ARO2 SAPRC99 mechanism reactions are:

ARO1 + HO = 0.224*HO2 + 0.765*RO2_R + 0.011*RO2_N + 0.055*PROD2 + 0.118*GLY + 0.119*MGLY + 0.017*PHEN + 0.207*CRES + 0.059*BALD + 0.491*DCB1 + 0.051*DCB3 # 1.81e-12;

ARO2 + HO = 0.187*HO2 + 0.804*RO2_R + 0.009*RO2_N + 0.097*GLY + 0.287*MGLY + 0.087*BACL + 0.187*CRES + 0.05*BALD + 0.561*DCB1 + 0.099*DCB2 + 0.093*DCB3 # 2.64e-11.

We have performed an aromatic hydrocarbon study on the observational data of Clinton site (Houston, TX) for the whole year 2000, and used the study conclusions to modify the SAPRC99 mechanism. We analyzed and compared 16 aromatic compounds: trimethyl isomers (3 isomers), benzene, ethylbenzene, isopropyl benzene, styrene, toluene, diethyl-benzene (m-, p- isomers), ethyl-toluene (m-, o-, p- isomers) and xylene isomers (o and m, p-isomers). According to the study, the most important aromatic species are toluene, benzene and xylene isomers, as shown in Figure 1.
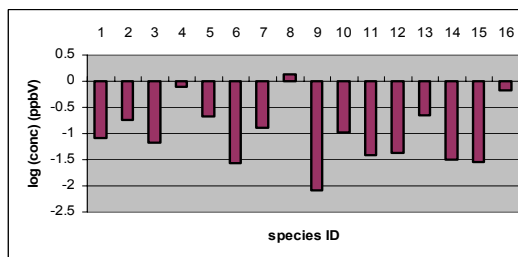
1	1,2,3-TMB	9	m-diethyl-benzene
2	1,2,4-TMB	10	m-ethyl-toluene
3	1,3,5-TMB	11	m-propyl-benzene
4	benzene	12	o-ethyl-toluene
5	ethyl-benzene	13	o-xylene
6	isopropyl-benzene	14	p-diethyl-benzene
7	styrene	15	p-ethyl-toluene
8	toluene	16	p,m-xylenes

Fig. 1 Annual average concentration of aromatic hydrocarbons at Clinton site (2000)

Figures 2, 3, and 4 show the monthly and daily (for February and July) concentration profiles of the toluene, benzene and m,p-xylenes, with respect to the other aromatic hydrocarbons.
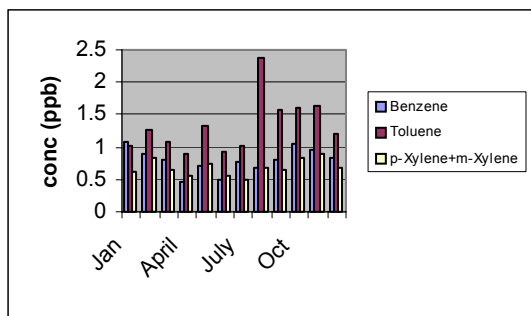

Fig. 2 Monthly variation of toluene, benzene and m,p-xylene concentrations at Clinton site (2000)
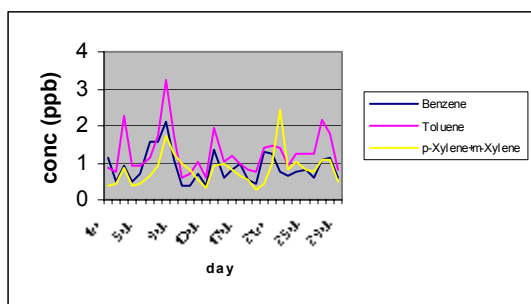

Fig. 3 Daily variation of toluene, benzene and m, p-xylene concentrations at Clinton site for February 2000
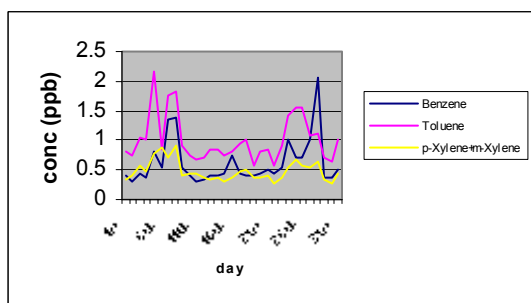

Fig. 4 Daily variation of toluene, benzene and m, p-xylene concentrations at Clinton site for July 2000

Analysis of the Clinton site data shows that toluene, m, p-xylenes and benzene are the most important aromatic species that should be considered in modelling, due to their high concentration with respect to the other species. Toluene has also been measured to be the most abundant aromatic component in urban air (Jeffries, 1995).

In order to more accurately analyze the impact of such hydrocarbons on ozone formation, we modified the SAPRC99 mechanism so that it explicitly represents several aromatic hydrocarbon species that are emitted in significant amounts in the atmosphere. The new species added to the mechanism are toluene and xylene isomers. Benzene was already included in the SAPRC99 mechanism of the air toxic version of CMAQ system.

In our simulations we used the National Emissions Inventory 1999 (NEI99) for the Houston-Galveston area; according to this inventory, mobile sources are responsible for the high emissions of the species of our interest.
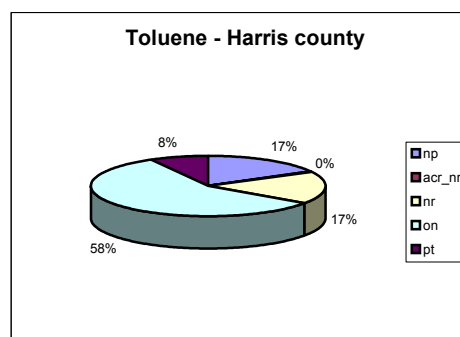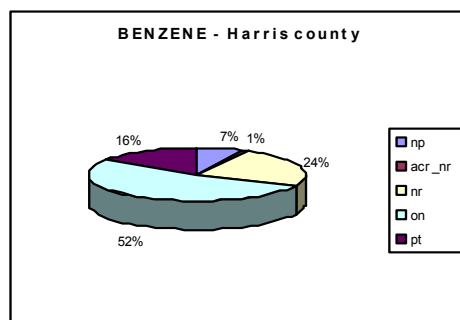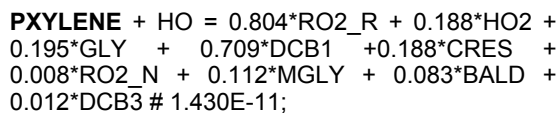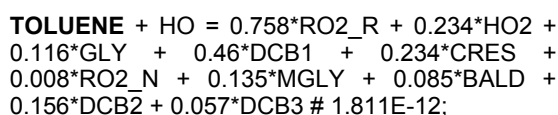

Fig. 5 The benzene and toluene emissions for Harris county -Houston (NEI99): np - nonpoint sources, acr_nr – aircraft nonroad sources, nr – nonroad sources, on – onroad sources, pt – point sources

3. IMPROVEMENTS OF THE AROMATIC REPRESENTATION IN SAPRC99 MECHANISM

The SAPRC99 chemical mechanism was modified to account for new aromatic species, such as toluene and xylene isomers. New reactions were added to the mechanism:

TOLUENE + HO = 0.758*RO2_R + 0.234*HO2 + 0.116*GLY + 0.46*DCB1 + 0.234*CRES + 0.008*RO2_N + 0.135*MGLY + 0.085*BALD + 0.156*DCB2 + 0.057*DCB3 # 1.811E-12;

PXYLENE + HO = 0.804*RO2_R + 0.188*HO2 + 0.195*GLY + 0.709*DCB1 +0.188*CRES + 0.008*RO2_N + 0.112*MGLY + 0.083*BALD + 0.012*DCB3 # 1.430E-11;

MXYLENE + HO = 0.782*RO2_R + 0.21*HO2 + 0.107*GLY + 0.347*DCB1 + 0.21*CRES + 0.008*RO2_N + 0.335*MGLY + 0.037*BALD + 0.29*DCB2 + 0.108*DCB3 # 2.360E-11;

OXYLENE + HO = 0.831*RO2_R + 0.161*HO2 + 0.084*GLY + 0.572*DCB1 + 0.161*CRES + 0.008*RO2_N + 0.238*MGLY + 0.054*BALD + 0.06*DCB2 + 0.145*DCB3 + 0.139*BACL # 1.370E-11.

The kinetic parameters for the lumped species ARO1 and ARO2 were updated using software developed by William P.L. Carter (Carter, 2004).

ARO1 + HO = 0.214*HO2 + 0.775*RO2_R + 0.012*RO2_N + 0.116*PROD2 + 0.152*GLY + 0.053*MGLY + 0.121*PHEN + 0.092*CRES + 0.635*DCB1 + 0.024*DCB3 # 3.38e-12;

ARO2 + HO = 0.236*HO2 + 0.203*RO2_R + 0.07*RO2_N + 0.084*GLY + 0.008*MGLY + 0.024*CRES + 0.212*PHEN + 0.105*DCB1+ 0.054*DCB2 + 0.053*DCB3 + 0.491*RCO_O2 # 5.15e-13^1.85.

The modified Euler backward interative solver (MEBI) (Hertel et al, 1993) has been extended to consider the new species; to validate our modifications, we compared the results of the new MEBI solver with those obtained by using the more general but slower sparse-matrix, vectorized Gear solver (SMVGEAR) (Jacobson and Turco, 1994).

4. PRELIMINARY RESULTS

We performed simulations using the NEI99 inventory for the modelling episode Aug, 21 -Aug, 31, 2000. The modelling domain was set up at the 4km resolution (83x65 cells) that covers the southeastern part of Texas, the Gulf of Mexico and a part of Louisiana. The inventory emissions were pre-processed through Sparse Matrix Operator Kernel Emissions (SMOKE) system for temporal allocation and spatial distribution.
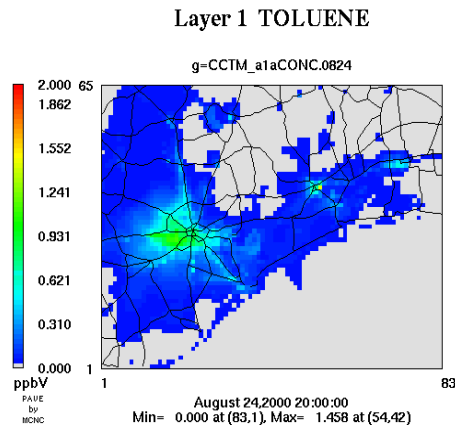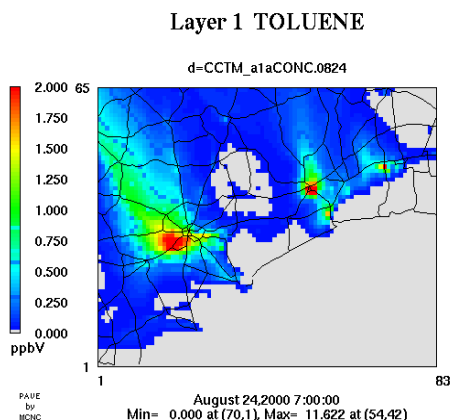

Layer 1 TOLUENE

Fig. 6 The toluene morning and afternoon concentration values for August 24.

We compared our simulation results against the surface observational data of Clinton and La Porte sites for the same time frame, in order to check the accuracy of the new mechanism implementations.
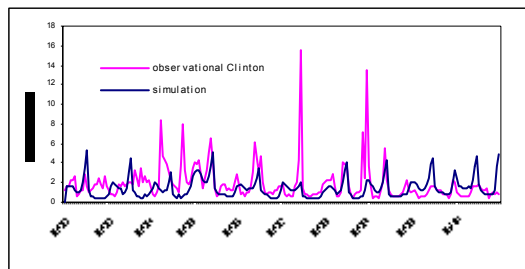

Fig. 7 Comparison of the simulation results for toluene with the observational Clinton data.
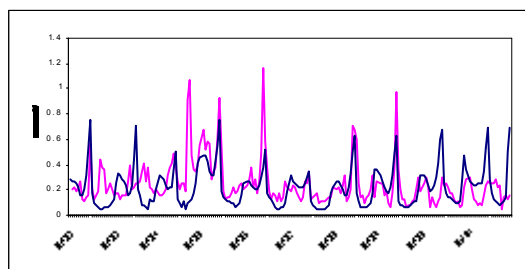

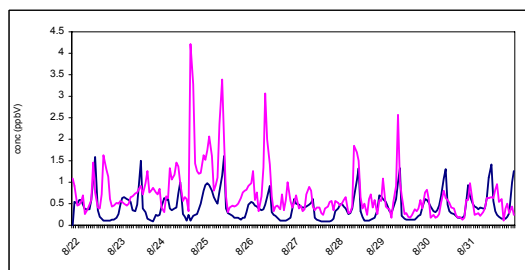Fig. 8 Comparison of the simulation results for o-xylene with the observational Clinton data.

Fig. 8 Comparison of the simulation results for meta and para xylene isomers with the observational Clinton data.
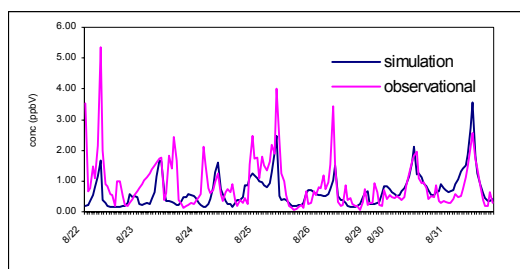
Fig. 9 Comparison of the simulation results for toluene with the observational La Porte data.

5. CONCLUSIONS

Aromatic compounds represent a significant fraction of the reactive hydrocarbon concentration in urban areas. Model calculations indicate that they might contribute more than 30% of the photo-oxidant formation in urban areas (Le Bras, 1997).

In order to more accurately analyze the impact of the aromatic hydrocarbons on the ozone formation, we have modified the SAPRC99 mechanism so that it explicitly represents several aromatic species emitted in large amounts in the atmosphere. The new mechanism will also enable us to use modelling tools to identify the spots with high aromatic hydrocarbon concentration (hot spots).

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