Modelling Toxic Air Contaminants from Ethanol Blend Fuels using a Modified SAPRC-99 Chemical Mechanism

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1. INTRODUCTION

To model gasoline toxic air pollution and its health impacts, a study was undertaken to modify the SAPRC-99 condensed chemical mechanism with explicit 1,3-butadiene and benzene chemical species and implement the new mechanism into the Models-3 modelling system. The upgrades to the Models-3 system included: the creation of a new set of SAPRC-99 speciation programs and speciation database; the integration of the new speciation database into SMOKE (v1.3); and the modification of the SAPRC-99 chemical mechanism in CMAQ (v4.3).

The study included the application of the new SMOKE/CMAQ system to model the effects of on-road vehicles operating on 10% ethanol blend gasoline (E10) on toxic and photochemical pollutants in two distinct regions in Canada. The results from this work are currently being integrated into comprehensive health impact studies being performed by Health Canada.

2. MODIFICATION OF SAPRC-99

The model simulations discussed here used a modified version of the SAPRC-99 mechanism developed by Carter (2000a), with 1,3-butadiene and benzene represented explicitly. The starting point was the currently implemented version of SAPRC-99 in CMAQ, as described by Carter (2000b) and the CMAQ model documentation (Byun and Ching, 1999), which does not represent these compounds explicitly. Rather, it groups 1,3-butadiene into the lumped higher alkene species OLE2, and benzene into the lower reactivity aromatic model species ARO1 (used primarily for toluene). The latter is given a reactivity weighting factor of 0.295 to account for its lower reactivity compared to toluene and the other monoalkylbenzenes that are represented in ARO1.

In the modified mechanism used for this work, separate model species were used to represent 1,3-butadiene and benzene. The modified mechanism employed the detailed version of SAPRC-99 described in Carter (2000a), where they are represented explicitly for the purpose of reactivity calculations. OLE2 and ARO1 were used to represent all the other compounds they typically represent in the standard CMAQ version of SAPRC-99. The representations of other compounds in the lumped SAPRC-99 mechanism for CMAQ were not modified.

The rate constants and product yield coefficients for OLE2, ARO1 and other lumped model species in SAPRC-99 used in CMAQ were derived based on the mechanistic parameters for the individual compounds they represent based on a representative mixture of anthropogenic VOCs measured in urban atmospheres (Carter, 2000b). The specific mixture is the same as that used to represent the base case total reactive organic gas (ROG) emissions in the Carter (1994, 2000a) reactivity scales.

The mixture of compounds represented by OLE2 and ARO1 are based on ambient measurements made by Lonneman (1986) and summarized by Jeffries *et al.* (1989). Because these mixtures contained 1,3-butadiene and benzene, the parameters for OLE2 and ARO1 used in the modified mechanism were re-derived for the same mixture, but with these two compounds removed using emissions speciation processing software developed for this purpose by Carter (2005; see also Adelman *et al.*, 2005).

The modifications to SAPRC-99 for this study also required re-processing the emissions input data so that the emissions of 1,3-butadiene and benzene were represented explicitly instead of by the lumped species. The emissions speciation software developed by Carter (2005; see also Adelman *et al.*, 2005) was used to produce the modified emissions speciation assignment files used by GSPRO to determine model species that represent the various emissions sources with these two compounds represented explicitly. This software also computes the mechanistic parameters for consistency with the alternative lumping approach (as indicated above) and outputs source files for the modified SAPRC-99 mechanism with the modified parameters for the lumped OLE2 and ARO1 species and new explicit species for 1,3-butadiene and benzene.

The emissions processing software, and SAPRC-99 assignment and mechanistic parameter input files needed to run it with these or other compounds represented explicitly were then integrated into the SMOKE emissions processing system, as described by Adelman *et al.* (2005).

3. MODIFICATION OF MODELS-3 WITH THE NEW SAPRC-99 MECHANISM

Modifications to CMAQ (v.4.3) are required to accommodate 1,3-butadiene and benzene as they are not included explicitly in the original model formulation. Changes were made primarily to the gas-phase modules to address the chemical properties of 1,3-butadiene and benzene in the atmosphere. While both species are volatile organic compounds, benzene (BENZ) has relatively low reactivity and is oxidized mainly by hydroxyl (OH) radicals in the atmosphere. On the other hand, 1,3-butadiene (13BD) is extremely reactive, and its chemical degradation in the gas phase includes reactions with several important oxidants, the hydroxyl radical, ozone, O(3P) and NO_3 radical.

Gas-phase reactions (Atkinson *et al.* 1997), were added exclusively to the current SAPRC99 mechanism as shown, where: k is the rate constant (molecules^{-1} cm^3 second^{-1}), R is the gas constant; and, T is temperature (Kelvin). The only new species added to the modified mechanism were 13BD and BENZ. The resulting products from these reactions are used elsewhere and are being 'recycled'.

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13BD + HO = (0.961 x RO_2_R) + (0.039 x RO_2_N) + (0.48 x HCHO) + (0.48 x MACR) + (0.48 x IPRD)
where: $k = 1.480 \times 10^{-11} \times e^{-448/RT}$

13BD + O_3 = (0.06 x HO_2) + (0.06 x HO) + (0.25 x CO) + (0.50 x HCHO) + (0.185 x HCOOH) + (0.125 x PRD2) + (0.50 x MACR) + (0.375 x MVK)
where: $k = 1.340 \times 10^{-14} \times e^{2283/RT}$

13BD + O_3P = (0.75 x PRD2) + (0.25 x HO_2) + (0.23 x RO_2_R) + (0.02 x RO_2_N) + (0.23 x CO) + (0.23 x MACR)
where: $k = 1.980 \times 10^{-11}$

13BD + NO_3 = (0.92 x RO_2_R) + (0.08 x RO_2_N) + (0.92 x MVK)
where: $k = 1.000 \times 10^{-13}$

BENZ + HO = (0.764 x RO_2_R) + (0.207 x GLY) + (0.236 x HO_2) + (0.236 x PHEN) + (0.764 x DCB1)
where: $k = 2.471 \times 10^{-12} \times e^{207/RT}$

MODIFICATION OF MODELS-3 WITH THE NEW SAPRC-99 MECHANISM (Cont'd)

This implementation of a new chemical mechanism into CMAQ involved creating and formatting several chemical species "include files" (e.g., *.EXT), which provide cross linkages to CMAQ's main chemical-transport model processor (CCTM) as per Byun and Ching (1999). Model species "include files" were edited to reflect the naming and reaction order changes made to the mechanism. Changes made in association with 13BD and BENZ also included several physical processes handled by the model.

While 13BD is not involved in aerosol chemistry, BENZ is assumed to participate in the gas-to-particle processes in a manner similar to toluene. Both species are involved in advection and diffusion processes, and assumed to undergo wet scavenging, with 13BD being similar to isoprene and BENZ similar to toluene. Dry and wet deposition were not simulated for either species, under the assumption that these processes are relatively negligible for them.

4. MODEL RUN CONFIGURATIONS

Two meteorological 'Episodes' covering two geographic regions ('Domains'), and two 'Base Year' emission inventories were assessed as part of this project. The table below provides a summary of the meteorological Episode dates, model Domains, grid cell resolutions, and emission inventory Base Years used. A figure is also provided depicting graphical representations of the Pacific Northwest (PNW) and Eastern North America (EAST) Domains (top right).

Domain	Resolution	Episode	Emission Inventory Base Year
Pacific Northwest (PNW)	12 km	Aug. 09 to 20, 2001	Canada: 2000 US: 1999 / 2000 Canada: 2010 (grown from 2000) US: 2010 (grown from 1999 / 2000)
Eastern North America (EAST)	36 km	July 10 to 19, 1999	Canada: 1995 (grown to 2000) US: 1999

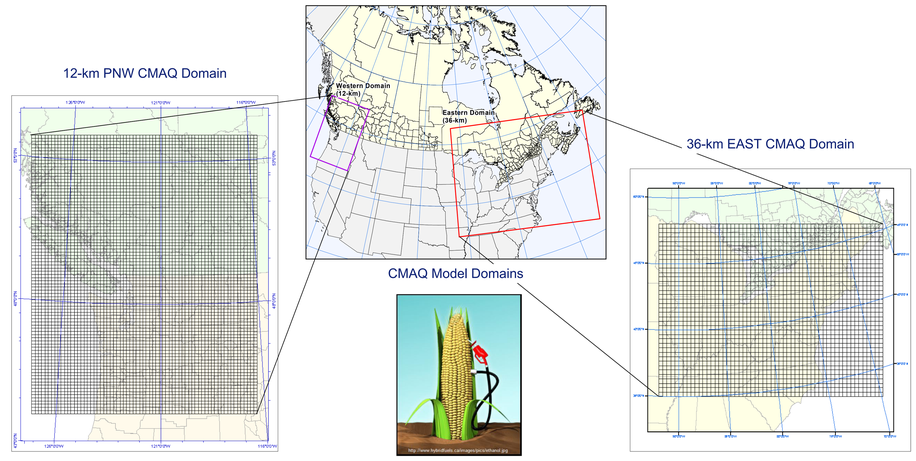
The modelling framework (configuration, meteorological modelling and domain designs, etc.) was based on a series of meteorological and CMAQ air quality modeling studies performed over the past several years (Boulton, *et. al*, 2004; Qiu, *et. al*, 2004; Snyder, 2003).

Emissions associated with gasoline vehicles operating on 10% ethanol fuel (E10) were generated using the modified Canadianized MOBILE6.2C+$_{TOX}$ model as described in Vitale *et al.* (2004). Emissions modelling indicated that on average, a 10% tailor blend results in a 23% reduction in both Benzene and 1,3-butadiene emissions from vehicles. Other effects include: CO decreases by 19%, total VOCs decrease by 7%, Formaldeyhde increases by about 4%, and Acetaldehyde increases on the order of 137%. These numbers are quoted for the for the PNW domain; results for the EAST domain were similar.

5. CMAQ MODEL RESULTS

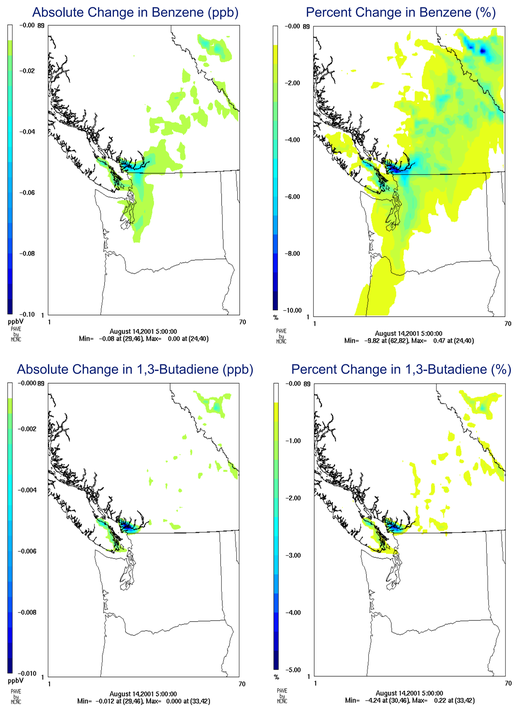
CMAQ results for the PNW model domain are presented in the bullets below and further illustrated in the graphics to right.

- CMAQ modelling results show that ground level concentrations of BENZ and 13BD are reduced by the introduction of E10 fuel in on-road gasoline vehicles.
- Reductions in BENZ and 13BD occur mostly along highways and other heavy-traffic areas. The figures to right show one-hour snapshots of changes in BENZ and 13BD associated with the E10 Tailor scenario relative to the Base Case (I.e., regular gasoline fuel).
- Peak reductions of BENZ and 13BD are located in the more heavily-trafficked areas. For the specific hour and day shown in the figures to right, maximum hourly BENZ concentrations in downtown Vancouver were reduced by about 0.2 ppbV, or -18%. Reductions of 13BD were on the order of 0.06 ppbV or -10%.
- The use of ethanol blended fuel will cause an increase in acetaldehyde emissions. This increase in emissions cause maximum hourly acetaldehyde concentrations to increase by about 0.2 ppb, or +30% in downtown Vancouver (graphic not shown).



CMAQ MODEL RESULTS (Cont'd)

- Decreases in ground level concentrations of CO and NO_X are relatively insignificant.
- CMAQ modelling results for the EAST domain show similar distribution patterns and concentration levels of reductions in BENZ and 13BD associated with the use of E10 fuels (results not shown).
- The E10 scenarios are designed for fuel type changes in Canada only. However, BENZ and 13BD reductions are seen to occur in the U.S. (Puget Sound and coastal areas in the State of Washington).
- Future year simulations (2010) also indicate slightly more BENZ and 13BD reductions due to the composition of fuel changes (not shown).



6. CONCLUSIONS

A modified SAPRC99 chemical mechanism with explicit BENZ and 13BD was developed for integration with both SMOKE and CMAQ.

- SMOKE and CMAQ, with modification, were successfully used to model explicit toxic compounds (benzene and 1,3-butadiene).
- The methodology of modifying SAPRC99 is expandable to model other toxic species that are usually lumped in CMAQ chemical mechanisms.
- The wide-spread integration of 10% ethanol blend gasoline fuel could reduce benzene levels by up to 20%, and 10% for 1,3-butadiene. Other effects (I.e., increases in acetaldehyde) may counter some of these benefits.
- A rigorous model evaluation is required to better understand the overall performance of SMOKE and CAMQ for modelling toxic species explicitly.

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