ADAPTING THE SAPRC CHEMISTRY MECHANISM FOR LOW TEMPERATURE CONDITIONS

Scope of Work for a project submitted to the Utah Division of Air Quality.

Principal Investigators: Marc Mansfield[1] and Jaron Hansen[2]

[1]Commercialization and Regional Development, Bingham Research Center, Utah State University, Vernal, Utah, marc.mansfield@usu.edu

[2]Department of Chemistry, Brigham Young University, Provo, Utah, jhansen@chem.byu.edu

July 3, 2014

Project Background

Gas-phase chemistry mechanisms (e.g.; Carbon Bond 2005 with updated toluene chemistry, CB05-TU [Yarwood, et al. 2005; Whitten et al., 2010]; version 2 of the Regional Atmospheric Chemistry Mechanism, RACM2 [Goliff et al., 2013]; and the Statewide Air Pollution Research Center-2007, SAPRC-07 [Carter, 2010a]) have been primarily developed and tested for tropospheric ozone pollution in urban areas during summer time. They are based on smog chamber experiments conducted at a reference temperature of 300 K. Winter ozone in the rural Uintah Basin is a newer area of research that is notably different from summer ozone because of different meteorological conditions (winter versus summer) and different ozone precursor emission conditions (urban versus high oil and gas-activity). The appropriate temperature range for winter ozone in the Uintah Basin is around 265 K to 270 K. Photochemical grid models need to account for the fundamental differences between winter and summer ozone.

The SAPRC-07 mechanism is one of three that has been incorporated into the Community Multi-scale Air Quality (CMAQ) photochemical grid model. SAPRC-07 is more chemically detailed than CB05, and therefore is usually more computationally expensive. However, it is still a good candidate for studying winter ozone pollution in the Uintah Basin where chemical accuracy is a priority. SAPRC-07 was used in a box model study of winter ozone in the Upper Green River Basin of Wyoming [Carter and Seinfeld, 2012] but has not been applied in winter ozone studies using a comprehensive air quality model like CMAQ.

SAPRC-07 is an updated version of SAPRC-99 [Carter, 2000]. The general structure of SAPRC-99 is maintained in SAPRC-07: 17 inorganic species, four inorganic short-lived species, and lumped organic model species based on the similarity of reactivity toward OH. Important updates include addition of more volatile organic compounds (VOCs) and a reformulation of the reactions of aromatics.

All of the reactions in CB05 or SAPRC-07 are temperature dependent, but all have not been studied extensively at lower T. There are two general approaches for such low-T studies. Dr. Hansen's lab at BYU has one of the few low-temperature smog chambers in the country, and one approach would be to use that apparatus to study ozone formation at low T. However, such experiments are beyond the scope of the present project. The second is a computer modeling approach using transition-state theory based on ab initio quantum chemistry calculations. Such calculations will be included in the present study.

Another problem is that not all available temperature dependencies have been programmed into the models. For example, the overall rate of a photolysis reaction depends on three properties: the actinic flux which measures the intensity of available light, the absorption cross section which measures the efficiency with which the molecule absorbs and gets excited by that light, and the quantum yield of the reaction, which measures the probability that the excited molecule decays in the specified manner. The latter two properties depend on the rotational and vibrational state of the molecule, and therefore are temperature dependent. For obvious reasons, these properties have been studied most extensively at 300 K, but low temperature data have been taken for a few of the more important reactions. Preliminary calculations based on five different photolysis reactions indicate as a rule of thumb that a photolysis rate drops about 1% for every 5 K drop in the temperature. [Martin, et al, 2011, Ch. 5]. However, to the best of our knowledge, the photolysis reactions in the various chemistry mechanisms are all parameterized at 300 K, with no option for lower temperatures.

The current version of SAPRC-07 in CMAQ already carries temperature-dependent rate constants for all inorganic and explicitly represented organic gas-phase reactions. However, most non-aromatic VOCs are parameterized at 300K [Carter and Seinfeld, 2012]. Carter and Seinfeld [2012] developed a specific version of SAPRC-07 for a box model in which non-aromatic VOC reaction rates were derived at 265K to examine ozone formation in the Upper Green River Basin. These adjustments produced a decrease in NO to NO_2 conversions, and an increase in overall nitrate formation, see Figure 1. A similar modification should be implemented into the SAPRC-07 mechanism incorporated in CMAQ and other photochemical grid models.

This research represents a collaboration between Dr. Jaron Hansen's group in the Chemistry Department at Brigham Young University, and the air quality modeling team under Dr. Marc Mansfield at the Bingham Research Center at Utah State University in Vernal. Although our work will focus on air quality issues in the Uintah Basin, these results are expected to be directly applicable to wintertime air quality issues in other regions, including the Wasatch Front and Cache Valley.

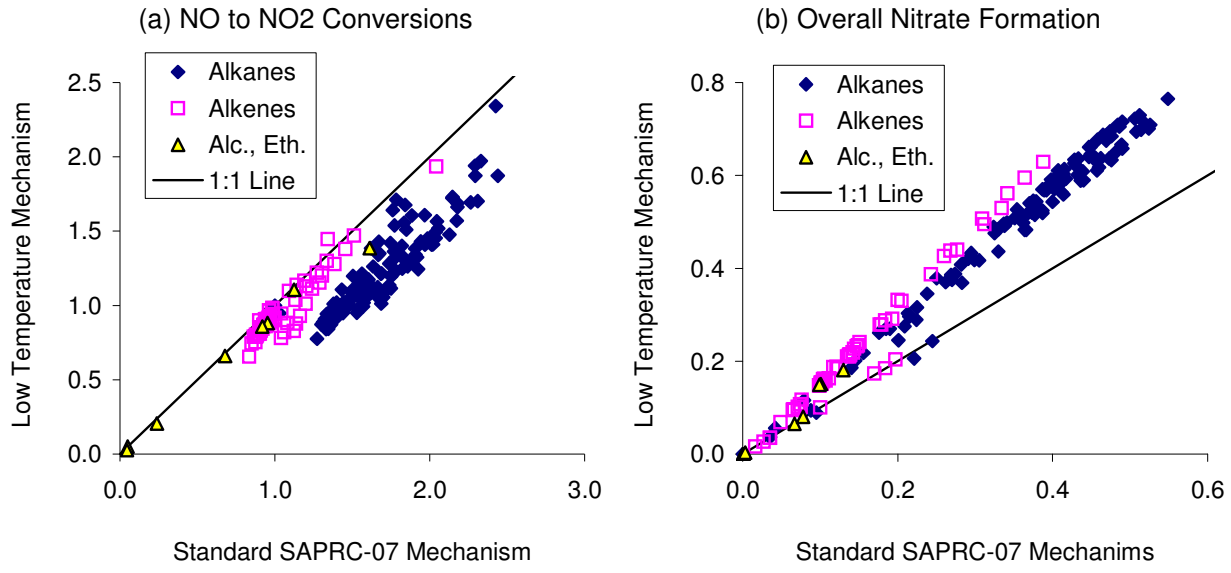

Figure 1. Plots of low vs. standard temperature numbers of NO to NO_2 conversions and overall organic nitrate yields in the mechanisms derived for the reactions of OH radicals with alkanes, alkenes, and alcohols and ethers (Taken from Figure A-1, Supplementary Materials, Carter and Sienfeld, 2013)

Task Descriptions

This research will consist of four major tasks. Task (a) consists of quantifying the low temperature behavior of reactions in the SAPRC mechanism, gathering available data from the literature and performing computer calculations to cover gaps in the literature. Task (b) consists of developing emissions speciation profiles that will be compatible with CMAQ. Tasks (c) and (d) involve incorporating and testing, respectively, the newly developed low-temperature SAPRC mechanism into CMAQ. More detailed descriptions of these tasks are as follows:

a. Improving the SAPRC-07 Chemical Mechanism

BYU will take the lead in quantifying the cold temperature behavior of the photolysis, bimolecular, and trimolecular reaction rates in the SAPRC07 chemical mechanism. This is necessary because many of the reactions included in the SAPRC07 mechanism are temperature-dependent but are currently only implemented at their 300 K value. The necessary low-temperature data will be harvested from the scientific literature where available. For thermally activated reactions that have not been adequately

measured at low temperature but are deemed to be important for modeling in the Uintah Basin and Wasatch Front, we will determine the temperature dependence of both the Arrhenius law pre-factor (A) and the activation barrier (E_a) by performing high level ab initio quantum chemistry calculations. Slices of the potential energy curve for these reactions will be computed. This will include identifying the lowest energy structures for reactants and products and then connecting these species by finding the transition state. Analyzing the potential energy surface with Transition State Theory will allow for calculation of the temperature dependence over the relevant range of temperatures. Detailed documentation describing the reference or method for determining the temperature dependence of each reaction will be included in the final technical report submitted to the Utah DAQ.

b. Developing SAPRC-07 speciation profiles and a cross-reference file for the SMOKE emission model

Default SMOKE speciation profiles are not available for the SAPRC-07T mechanism. Fortunately, a few speciation profiles for SAPRC-07T have been shared among CMAQ users on the Model-3 Technical Support Forum (m3user@listserv.unc.edu). The USU research group has obtained these shared profiles, and will modify them for simulation in the Uintah Basin as needed. Alternatively, the EPA's Speciation Tool (Jimenez et al., 2013) can be employed to create the required profiles. The developed speciation profiles and cross-reference file will be submitted to Utah DAQ as a deliverable of the project.

c. Incorporating the Improved SAPRC-07 Chemical Mechanism to CMAQ

Beginning with the release of CMAQ version 5.0, a Chemical mechanism compiler (CHEMMECH) has been made available to users to facilitate the process of modification of the chemical mechanism and species used in the CMAQ Chemistry-Transport Model, CCTM (CMAS, 2012). A mechanism definition file (mech.def) that lists the stoichiometry and kinetics of a photochemical reaction mechanism is input to CHEMMECH to generate two include files, RXDT.EXT and RXCM.EXT. These two include files are required for the compilation of the CCTM model. Gaseous and aerosol chemical species for the selected mechanism can be added or removed through the modification of the namelist files (*.nml).

The USU group will incorporate the results of the BYU group on quantifying the cold temperature dependence (Task a) into the SAPRC-07T mech.def file. Modifications to the chemical species namelist files will also be made as needed. The mech.def file and the modified species namelist files (if any) will be submitted to Utah DAQ as a deliverable of the project. If any CMAQ Fortran code has to be modified in order to support the improved SAPRC-07T mechanism, the modified code and its documentation will also be submitted as a deliverable.

The USU group will perform a one-day benchmark CMAQ simulation to QA/QC the modifications made to the mechanism.

d. Evaluation of a CMAQ simulation with improved SAPRC-07 mechanism

We will perform CMAQ simulations with both the unmodified and the modified SAPRC-07T mechanisms covering an episode extending from January 20 to February 6, 2013. During this episode, at several monitoring sites, high ozone (>75ppb) was observed during January 21-27 and Feb 1-6; whereas low ozone (< 75ppb) was observed during Jan 28-31. Ambient temperature varied from –20^{o}C to 0^{o}C during the episode. This selection will allow us to evaluate effects of the modifications made to SAPRC-07 under different ozone and temperature conditions. WRF and CMAQ model setups for this episode will be adopted from the setup that is being developed by collaboration between University of Utah and USU research groups for studying ozone in the Uintah Basin.

Deliverables

- SAPRC-07T speciation cross-reference and profile files for processing emission files with the SMOKE emission model.
- A modified chemical mechanism definition file (mech.def) of SAPRC07TB, and species namelist files (if any) that is ready for use with CHEMMECH and CCTM.
- Modifications to CMAQ Fortran code, if any, and any necessary documentation.
- A technical report containing: (1) detailed documentation of the reference or method used to determine the temperature dependence of each modification made to a reaction in SAPRC-07, (2) a description of the development of SAPRC-07T speciation cross-reference and profile files for processing emission files, (3) a snippet on each modification made in SAPRC-07TB mech.def and chemical species namelist files, (4) evaluation of the effect of the improved SAPRC-07 mechanism on the simulation results for the selected episode, and (5) recommendations on how to perform model simulations with the improved SAPRC-07 in CMAQ.

Project Schedule

Tasks	Schedule (month)											
	01	02	03	04	05	06	07	08	09	10	11	12
Reviews of current chemical reactions implemented in SAPRC-07 (which is the current SAPRC mechanism supported in photochemical model such as CMAQ)												
Literature reviews of most current findings on temperature-dependence of gas-phase chemical reactions; review updates in SAPRC-11 (not yet supported in photochemical models); identify reactions in SAPRC-07 that could be improved												
Ab initio quantum chemistry calculations on important reactions												
Modify SAPRC-07 mechanism for identified reactions; perform a benchmark simulation using CMAQ for QA/QC the modified mechanism												
Perform CMAQ simulations using original and improved SAPRC-07 mechanism for high ozone episode in January 2013												
Compare and evaluate effects of the improvements												
Documentations and reports												

Proposed Budget

USU

Salary & Fringes	Mansfield (PI) H. Tran (post-doc) T. Tran (post-doc)	$ 8045 $10500 $10500	$29045	
Travel			$ 500	
Subcontract to BYU			$25000	
Subtotal		$54545		
Indirect costs (10%)			$ 5455	
TOTAL				$60000

Other related funded projects

Recipient(s)	Title	Description
BYU	The Role of Radical-Water Complexes in the Atmosphere, National Science Foundation, $547,782, Aug. 2013-Aug. 2016	The goal of this project is to measure the influence of water vapor at cold temperatures on reactions that produce tropospheric ozone. The results of this project will aid in the understanding of the ozone forming reactions in both the Uintah Basin and Wasatch Front during winter time conditions.
BYU	A Semi-Continuous Monitor for the 1-hr Determination of Organic Matter Compounds, Sunset Laboratories, $46,741, Sept. 2013-Aug. 2014	The goal of this project is to build an instrument that will allow for determination of the sources of particulate matter. This instrument will aid the State of Utah in understanding the relative importance of biological and anthropogenic emissions on particulate matter formation along the Wasatch Front.
USU	Bonanza Power Plant Emissions Model, Deseret Power Electric Cooperative, $27,798, Jan 2014 – Dec 2014	Establish emissions model for the Bonanza Power Plant to simulate air quality conditions under various ozone precursor control scenarios.
USU, UU, BYU	Computer Modeling of Winter Ozone in the Uintah Basin, Utah Energy Research Triangle, $128,331, Mar 2014 – Feb 2015	Development of meteorological, emissions, and photochemical models appropriate to winter ozone formation in the Uintah Basin.
USU	Research in support of BLM-Utah's Air Resource Management Strategy (ARMS).	MOU is in place since May 2014. Other terms of project are being negotiated.

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