AQRP Monthly Technical Report

PROJECT TITLE	The Influence of Alkyl Nitrates from Anthropogenic and Biogenic Precursors on Regional Air Quality in Eastern Texas	**PROJECT #**	16-019
PROJECT PARTICIPANTS	University of Texas at Austin (Drs. McDonald-Buller and Hildebrandt Ruiz) Ramboll Environ (Dr. Yarwood)	**DATE SUBMITTED**	4//2017
REPORTING PERIOD	**From:** 3/1/2017 **To:** 3/31/2017	**REPORT #**	6

A Financial Status Report (FSR) and Invoice will be submitted separately from each of the Project Participants reflecting charges for this Reporting Period. I understand that the FSR and Invoice are due to the AQRP by the 15th of the month following the reporting period shown above.

Detailed Accomplishments by Task

Task 1: Refinements to the CB6r4 Mechanism in CAMx

Initial CAMx v.6.40 base case simulations were completed at the Texas Advanced Computing Center (TACC) at the University of Texas at Austin using the hybrid 1.5-dimensional (1.5-D) Volatility Basis Set (VBS) or Secondary Organic Aerosol Partitioning (SOAP2) schemes. The team evaluated model performance using surface and aircraft observations for the DISCOVER-AQ time period in southeastern Texas. Both simulations exhibited a high bias in hourly average $PM_{2.5}$, organic aerosol, and organic carbon concentrations relative to surface observations, in particular with the SOAP2 scheme. Sodium and nitrate indicative of sea salt emissions also exhibited a high bias. Predictions of contemporary carbon contributions were biased low relative to radiocarbon source apportionment analysis at Conroe. The Particulate Source Apportionment Technology (PSAT) tool was enabled in runs with SOAP2 for diagnostic purposes. The results have been guiding refinements in SOA yields and removal processes in the CAMx simulations with SOAP2 with the aim of improving model performance.

Modifications to the CB6r4 chemical mechanism have been made to differentiate terpenes into two classes, α-pinene represented by new model species APIN and other terpenes represented by existing model species TERP. Reactions of APIN and TERP with oxidants OH, O_3 and NO_3 were developed by updating the reactions for TERP in CB6r4 using published laboratory studies and analyses of ambient data. In particular, yields of alkyl nitrate from APIN and TERP reactions have been defined that are consistent both with laboratory studies and ambient data. In CB6r4 volatile alkanes containing 4 or more carbon atoms (C4+ alkanes) are represented by the model species PAR. Consequently, the alkane reaction rate with OH (k_{OH}) is proportional to the number of carbons and the yield of organic nitrates under high-NOx conditions is constant at 12%. Modifications to CB6r4 have been made to differentiate alkanes into two classes called PAR and PARH. Lighter C4+ alkanes (e.g., butanes) are now represented solely by PAR whereas heavier alkanes are now represented by a combination of PAR and PARH, with the assignment to PARH equal to the number of secondary carbon atoms (i.e., CH_2 groups) minus 2 minus the number of rings (e.g., to represent cyclohexane, PARH = 6−2−1 = 3 and PAR = 6−3 = 3). The PAR/PARH scheme can better represent k_{OH} and organic nitrate yields for C4+ alkanes. Based alkane composition data typical urban areas will have higher PARH/PAR ratios than oil and gas producing areas and, consequently, higher tendency to form alkyl nitrates. Another mechanism update is increasing the rate of heterogeneous hydrolysis of alkyl nitrates consistent with recent analyses of ambient data. The SOA scheme in CAMx is being revised to be consistent with the APIN/TERP update to by fitting of SOA yields from oxidation reactions associated with the new species. The CAMx emission inventory will be updated to split TERP into APIN and TERP, and PAR into PAR and PARH. The PAR/PARH split will be lower for oil and gas emissions than for mobile source emissions.

Task 2. Evaluating CB6r4 Updates in CAMx Modeling for DISCOVER-AQ
Not yet initiated.

Task 3. Project Reporting and Presentation
On-going per requirements.

Preliminary Analysis

Figure 1 compares rate constants for gas-phase OH-initiated oxidation reactions for C4 to C12 alkanes and nitrate yields in the original and revised CB6r4 PAR schemes relative to those for alkanes in the near-explicit Master Chemical Mechanism (MCM). The new PAR/PARH scheme exhibits better performance than the original PAR scheme in both plots. Figure 2 shows overall nitrate yields from the original and new PAR/PARH schemes with VOC mixtures of differing composition.

(a) (b)

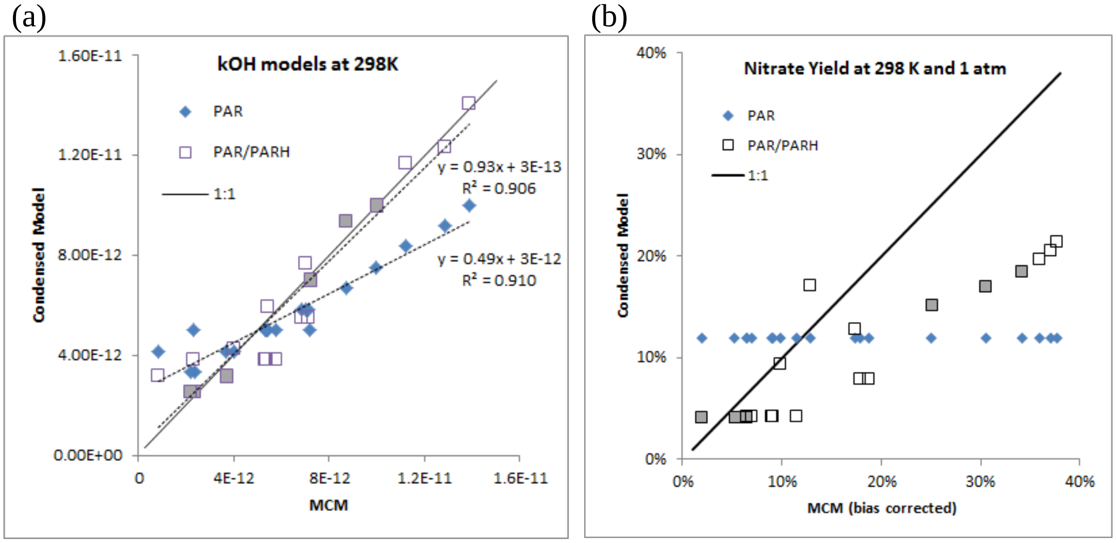

Figure 1. kOH models at 298K (left) and nitrate yields at 298 K and 1 atmosphere pressure (right) for the original CB6r4 PAR scheme (blue diamonds) and revised PAR/PARH scheme (squares). Alkanes used in the development of the revisions are shown as gray squares. Note that MCM nitrate yields were corrected for a known ~30% high bias.

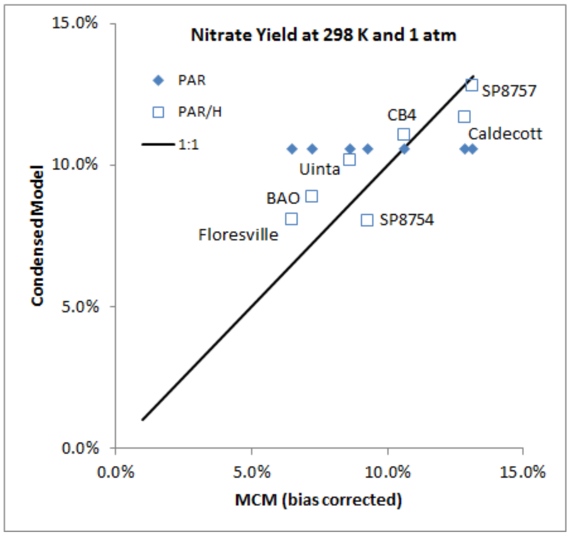

Figure 2. Nitrate yields for the original CB6r4 PAR scheme (blue diamonds) and revised PAR/PARH scheme (squares) in the CAMx CB6r4 mechanism for VOC mixtures of different composition: Floresville, Texas (oil and gas production region), Boulder Atmospheric Observatory (oil and gas production region), Uinta Basin (oil and gas production region), SPECIATE profile 8754 (gasoline evaporative emissions), SPECIATE profile 8757 (gasoline exhaust emissions), CB4 urban mixture as used to derive PAR, and the Caldecott Tunnel (gasoline exhaust and running evaporative emissions). Note that MCM nitrate yields were corrected for a known ~30% high bias.

Data Collected
None.

Identify Problems or Issues Encountered and Proposed Solutions or Adjustments
None.

Goals and Anticipated Issues for the Succeeding Reporting Period
Goals for the next reporting period include establishing the configuration and completing the evaluation of the base case CAMx simulation with the SOAP2 scheme, and conducting CAMx simulations with updates in the representations of alkanes and terpenes in the CB6r4 mechanism.

Detailed Analysis of the Progress of the Task Order to Date
The project is proceeding as planned.

Do you have any publications related to this project currently under development? If so, please provide a working title, and the journals you plan to submit to.

___Yes __X_No

Do you have any publications related to this project currently under review by a journal? If so, what is the working title and the journal name? Have you sent a copy of the article to your AQRP Project Manager and your TCEQ Liaison?

___Yes _X__No

Do you have any bibliographic publications related to this project that have been published? If so, please list the reference information. List all items for the lifetime of the project.

___Yes __X_No

Do you have any presentations related to this project currently under development? If so, please provide working title, and the conference you plan to present it (this does not include presentations for the AQRP Workshop).
___Yes _X__No

Do you have any presentations related to this project that have been published? If so, please list reference information. List all items for the lifetime of the project.

___Yes _X__No

Submitted to AQRP by

Elena McDonald-Buller