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	5/8//2017
REPORTING PERIOD	**From:** 4/1/2017 **To:** 4/30/2017	REPORT #	7

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 completed using the Secondary Organic Aerosol Partitioning (SOAP2) scheme exhibited a high bias in hourly average $PM_{2.5}$, organic aerosol, and organic carbon concentrations relative to surface observations for the DISCOVER-AQ time period in southeastern Texas. Predictions of contemporary carbon contributions were biased low relative to radiocarbon source apportionment analysis at Conroe. A primary aim this month was to refine the SOAP2 scheme to improve CAMx model performance.

The current SOAP2 scheme in CAMx v.6.40 implicitly accounts for functionalization (and fragmentation) by chemical aging of secondary organic aerosol (SOA) components in the gas phase as they are based on a parameterization that describes multiple generations of oxidation of SOA precursors (Hodzic et al., 2016). However, it doesn't include SOA loss by photolysis, which can be competitive with other aging mechanisms of atmospheric SOA (Henry and Donahue, 2012; Hodzic et al., 2016). To account for this removal process in the particle phase, the photolytic loss of SOA, as a first-order decay reaction with a photolysis rate derived by scaling the NO_2 photolysis rate, was implemented in a new version of SOAP identified as SOAP2r3:

$$\frac{d[SOA]}{dt} = -J_{SOA}\,[SOA] = -s\,J_{NO_2}\,[SOA]$$

There remain significant uncertainties in the SOA photolysis rate with estimates varying by orders of magnitudes (Henry and Donahue, 2012; Hodzic et al., 2016). For this work, the rate was estimated as 0.4% of J_{NO2} assuming a photolysis lifetime of approximately one day as suggested by Henry and Donahue (2012).

The performance of CAMx v.6.40 with the SOAP2r3 scheme was evaluated against observations at CAMS sites throughout eastern Texas and surface and aircraft observations in southeastern Texas, with a focus on aerosol measurements at the Conroe surface site. CAMx predictions were generally comparable to those using the hybrid 1.5-dimensional (1.5-D) Volatility Basis Set (VBS) approach for organic gas- aerosol partitioning and oxidation. CAMx v6.40 with the SOAP2r3 scheme will serve as the base case for future simulations that evaluate updates to the CB6r4 mechanism. The team is currently writing the results of the CAMx performance evaluation with SOAP2r3 and comparisons with SOAP2 and the 1.5-D VBS schemes that will be incorporated into the final project report.

Updates to the CB6r4 mechanism began last month and are on-going. Terpenes have been differentiated into two classes, α-pinene represented by the new model species APIN and other terpenes represented by the 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.

The CB species, NTR2, represents organic nitrates that can partition significantly to organic aerosol. NTR2 is assumed to undergo reaction with OH or hydrolysis within aerosols. The gas-particle partitioning of NTR2 and subsequent hydrolysis of NTR2 in the particle phase are implemented as a pseudo gas-phase reaction in CAMx v.6.40. The particle-phase NTR2 hydrolysis lifetime was set to 6-hours according to Liu et al. (2012). Recent laboratory experiments as well as findings from the Southeast Atmosphere Studies (SAS) (e.g., Rindelaub et al., 2016; Fisher et al., 2016) have indicated much shorter atmospheric lifetimes are appropriate for acidic aerosols. In this study, aerosol pH, derived by the inorganic thermodynamic model ISORROPIA in CAMx and obtained via the Chemical Process Analysis (CPA) tool, was investigated in the 4-km eastern Texas domain. Daily mean aerosol pH was generally acidic in nature throughout the region. Instead of implementing pH-dependent hydrolysis rates in CAMx as described in previous monthly technical reports, a decision was made to reduce the particle-phase NTR2 hydrolysis lifetime in the CB6 mechanism to 1-hour.

Collectively the changes to the terpene chemistry and the NTR2 hydrolysis lifetime were implemented in a new version of the CB mechanism identified as CB6r6T.

The planned approach for updating alkane chemistry (i.e., the CB6 model species PAR) to differentiate lighter from heavier alkanes is being revised because of results obtained in another project. We will not develop a revised PAR mechanism from previous work using the Master Chemical Mechanism (MCM) because this MCM-derived PAR scheme is not performing well. Instead, we will develop a revised PAR mechanism for use in this study by making reference to SAPRC condensed chemical mechanisms for alkanes.

Task 2. Evaluating CB6r4 Updates in CAMx Modeling for DISCOVER-AQ

The CAMx emission inventory was updated to split TERP into APIN and TERP. A CAMx simulation that replaced the CB6r4 mechanism with CB6r6T but was otherwise identical to the base case (i.e., with the SOAP2r3 scheme) was completed. Analysis of the results of this simulation relative to the base case is on-going.

Task 3. Project Reporting and Presentation

On-going per requirements.

Preliminary Analysis
As above.

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 completing documentation of the base case model performance with the SOAP2r3 scheme and evaluating the CAMx simulation with the CB6r6T mechanism implemented. The team will continue to work on revisions to the alkane chemistry.

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

References

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Henry, K. M. and Donahue, N. M., 2012, Photochemical Aging of α-Pinene Secondary Organic Aerosol: Effects of OH Radical Sources and Photolysis, J. Phys. Chem. A, 116, 5932-5940.

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Rindelaub, J.D., Borca, C.H., Hostetler, M.A., Lipton, M.A., Slipchenko, L.V., 2016, The acid-catalyzed hydrolysis of an α-pinene-derived organic nitrate: kinetics, products, reaction mechanisms, and atmospheric impact, Atmos. Chem. Phys. Discuss., 16, 15425–15432.