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**	2/8/2017
REPORTING PERIOD	**From:** 1/1/2017 **To:** 1/31/2017	**REPORT #**	4

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

Our work for this task during January 2017 has had focal points that are described below.

(i) CAMx Base Case Development
Our team from the University of Texas at Austin and Ramboll Environ has been working to establish and run the CAMx base case. The project leverages a CAMx episode for the DISCOVER-AQ time period (August 18-September 30, 2013) developed for AQRP Project #14-024, but will have several important updates. The 4-km domain for the project now includes all of eastern Texas (Fig. 1) instead of only the Houston area. Land use/land cover and leaf area index (LAI) have been updated based on 2012 data. The CAMx and Carbon Bond chemical mechanism versions have been updated to 6.40 and CB6r4, respectively. We applied Ramboll Environ's "watermask" tool to distinguish between ocean and fresh water bodies, which is required to use in-line oceanic inorganic emissions for the new halogen chemistry mechanism (CB6r4).

CAMx 6.40 includes two algorithms for organic gas- aerosol partitioning and oxidation: the hybrid 1.5-dimensional (1.5-D) Volatility Basis Set (VBS) or Secondary Organic Aerosol Partitioning (SOAP) schemes. SOAP has been recently updated for the latest information on SOA yields, saturation concentrations, and water solubility. The latest version of SOAP is known as SOAP2 and is available in CAMx 6.40. In our workplan, we proposed to use the 1.5-D VBS approach in the evaluation of the chemical mechanism updates for the project. However, with the TCEQ's approval, we would like to apply the SOAP2 scheme instead, as we expect it to be more widely used. We would compare results with VBS to those with SOAP2 as a sensitivity study. However, all other CAMx sensitivity studies with the mechanism updates (Task 2) will use the SOAP2 scheme. Emissions estimates for intermediate volatile organic compounds (IVOCs) will be prepared for the VBS scheme and then mapped to species for SOAP2.

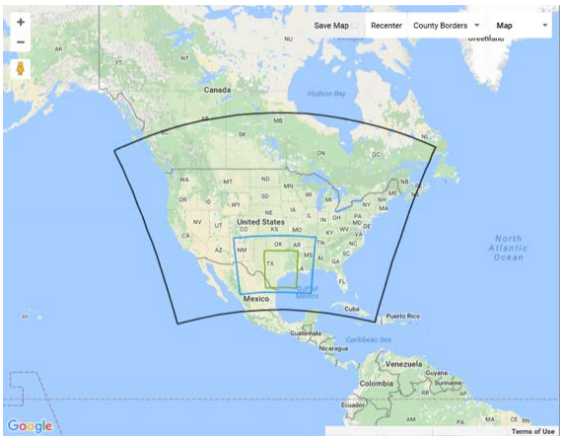

Fig. 1 36-km (black)/12-km (blue)/4-km (green) nested grid domain to be used for the project.

(ii) Chemical Mechanism Updates
On-going experiments by Dr. Lea Hildebradt-Ruiz under a project sponsored by the Texas Air Research Center (TARC) and a literature review conducted for the project are informing the planning for updates to the CB6r4 mechanism. We have three major areas of focus:

(a) Organic Nitrates from Anthropogenic Alkane and Alkene Precursors
Dr. Hildebrandt-Ruiz's on-going chamber experiments are examining the gas-particle partitioning and particle-phase hydrolysis of organic nitrates from alkane and alkene precursors that typically originate from anthropogenic emission sources. This work is being sponsored by the Texas Air Research Center (TARC) but is informing our AQRP project. Alkane and alkene precursors of differing sizes and structures are being considered for chamber experiments. Experiments are characterizing the dependence of particle-phase hydrolysis loss rates of organic nitrates on relative humidity and aerosol pH. We plan to modify the CB6r4 surrogate species for C4+ alkanes (named PAR) into two species to better differentiate organic nitrate yields and their tendency to partition to the aerosol phase where they can be hydrolyzed.

(b) Organic Nitrates from the Nitrate-Radical Initiated Oxidation of Monoterpenes
Recent environmental chamber experiments and measurements in the southeastern U.S. as part of the Southern Oxidant and Aerosol Study (SOAS) and Southeastern Center for Air Pollution and Epidemiology (SCAPE) studies have provided new insights on the effects of nitrate radical-initiated oxidation of monoterpenes on organic nitrate and secondary organic aerosol (SOA) formation and fate. Characterizations of organic aerosol species in the southeastern U.S., as well as during DISCOVER-AQ in southeastern Texas, have indicated that less-oxygenated organic aerosol (LO-OOA), which peaks at night, is correlated with the nitrate functionality from organic nitrates. Its prevalence indicates the important contribution of monoterpene organic nitrates to total organic aerosol in both regions. SOA yields and the ability of organic nitrates formed from NO_3+monoterpene chemistry to serve as permanent or temporary NO_x sinks vary with monoterpene precursors. For example, nitrate radical oxidation of α-pinene has been found to produce lower SOA mass loadings than β-pinene and other monoterpenes. Particle-phase organic nitrates have been found to evaporate from α-pinene SOA during photochemical aging, serving as a temporary NO_x sink, in contrast to β-pinene SOA that retains reactive nitrogen and serves as permanent NO_x sink. We plan to modify the CB6r4 mechanism to differentiate the single

surrogate species for all terpenes (named TERP) into two species based on α-pinene and β-pinene as surrogates.

(3) pH-Dependent Hydrolysis of Organic Nitrates
Hydrolysis of organic nitrates in the aerosol phase at elevated relative humidity can act as a NO_x sink, influencing NO_x and O_3 transport. Recent experimental work has examined the effects of solution acidity on hydrolysis rates of simple alkyl nitrates and an organic nitrate derived from α-pinene oxidation by hydroxyl radical. Hydrolysis rate constants increased with solution acidity for all organic nitrates studied, with shorter hydrolysis lifetimes for α-pinene-derived organic nitrate than the simple alkyl nitrates. Hydrolysis of the tertiary α-pinene-derived organic nitrate at low pH was found to be a unimolecular specific acid-catalyzed mechanism forming pinol. We expect to implement pH-dependent hydrolysis rates using aerosol pH derived by the inorganic thermodynamic model ISORROPIA in CAMx.

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
Examination of aerosol pH across the 4-km eastern Texas domain from an initial CAMx 6.40 simulation with the 1.5-D VBS scheme and CB6r4 gas-base mechanism has been on-going.

Data Collected
Not yet initiated.

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 comparing CAMx simulations with the 1.5-D VBS and SOAP2 schemes as a sensitivity study, compiling surface and relevant aircraft observations during the DISCOVER-AQ time period and preparing for the model performance evaluation, and on-going development of CB6r4 mechanism changes.

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