

Scope of Work For

Project #16-019

The Influence of Alkyl Nitrates from Anthropogenic and Biogenic Precursors on Regional Air  
Quality in Eastern Texas

Prepared for

Air Quality Research Program (AQRP)  
The University of Texas at Austin

By

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## **Approvals**

This Scope of Work was approved electronically on **9/9/2016** by David Sullivan, The University of Texas at Austin

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Project Manager, Texas Air Quality Research Program

This Scope of Work was recommended electronically on **9/29/2016** by Jim Smith, Texas Commission on Environmental Quality

Jim Smith  
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## 1.0 Abstract

Mono and multifunctional alkyl nitrates (ANs) are formed from the oxidation of biogenic or anthropogenic volatile organic compound (VOC) precursors and serve as a reservoir or sink of nitrogen oxides ( $\text{NO}_x$ ). Alkyl nitrates have sufficiently long atmospheric chemical lifetimes (hours to days), such that they can influence tropospheric ozone and secondary organic aerosol (SOA) formation over regional to global spatial scales. Their functionalities, yields, and fates are known to depend upon the size and structure of the VOC. Depending on their structure, ANs can be transported, chemically processed, removed by deposition to vegetation and other surfaces, or undergo partitioning to and from the aerosol phase where hydrolysis is thought to be a loss mechanism. Although knowledge gaps still exist, recent laboratory and field studies have provided new insights on these processes for ANs formed from biogenic and anthropogenic hydrocarbon precursors. An ongoing need will be to incorporate these findings into the chemical mechanisms of photochemical models used to assess regional air quality. The objectives of this work are to apply the findings of ongoing experimental studies examining alkyl nitrates formed from the OH-initiated oxidation of C8-C11 alkanes at the University of Texas at Austin in addition to those of new publications that have focused on other hydrocarbon precursor classes relevant to Texas emissions inventories to improve how ANs are represented in the version 6 of the Carbon Bond mechanism (CB6). Revision 4 of CB6 (CB6r4) will soon be available in version 6.32 of the Comprehensive Air quality Model with extensions (CAMx v6.32). Sensitivity tests with CAMx will evaluate the formation and fate of ANs in central and southeastern Texas, the influence of ANs on regional ozone by recycling  $\text{NO}_x$ , and dependencies on organic aerosol concentrations.

## 2.0 Background

Although major metropolitan areas in eastern Texas have experienced significant declines in ozone design values over the past decade, more stringent federal standards present new challenges. Understanding anthropogenic and biogenic emissions sources and chemical and physical processes which influence regional ozone concentrations is essential for future air quality planning and management efforts. Mono and multifunctional ANs serve as a reservoir or sink of  $\text{NO}_x$  (Lee et al., 2016). The effects of ANs on air quality and climate over regional to global scales (Perring et al., 2013) have received increasing attention associated with advances in measurement capabilities, controlled laboratory studies, and ambient observations. Campaigns such as SEAC<sup>4</sup>RS (Studies of Emissions and Atmospheric Composition, Clouds and Climate Coupling by Regional Surveys) and SOAS (Southern Oxidants and Aerosols Study) and coordinated modeling studies have provided new insights on AN chemistry and the influences on  $\text{NO}_x$  budgets and ozone and SOA production in the southeastern United States, a region with both anthropogenic  $\text{NO}_x$  sources and high biogenic emissions (Fisher et al., 2016).

Two pathways for the formation of ANs are OH-initiated or  $\text{NO}_3$ -initiated oxidation of anthropogenic or biogenic VOC precursors (Perring et al., 2013; Hildebrandt Ruiz and Yarwood, 2013). Although information for many compounds is not complete, AN functionalities, yields,

and fates are known to depend upon the size and structure of the organic backbone (R), as well as the location of the organic nitrate functional group on the backbone. Precursors to alkyl nitrates vary by location with anthropogenic or biogenic emission source regions (Perring et al., 2013). Alkyl nitrates only form in the presence of  $\text{NO}_x$  or  $\text{NO}_3$  that are of anthropogenic origin; thus the formation of ANs from biogenic hydrocarbon precursors is a main mechanism through which biogenic and anthropogenic emissions interact and affect air quality.

Depending on their structure, ANs can be transported, chemically processed, removed by deposition to vegetation and other surfaces, or undergo partitioning into the aerosol phase where hydrolysis is thought to be a loss mechanism (Bean and Hildebrandt Ruiz, 2016; Boyd et al., 2015; Liu et al., 2012). Alkyl nitrates have sufficiently long atmospheric chemical lifetimes (hours to days), such that they can be affected by regional or longer-range transport and influence air quality over extended spatial scales. Photolysis of small ANs (C1- C4) has been shown to liberate  $\text{NO}_2$ , such that  $\text{NO}_x$  is “recycled” and is available to participate in ozone production. Alkyl nitrates from large precursors (aromatics, terpenes, large alkanes) or chemically aged ANs from smaller precursors (anthropogenic alkenes, isoprene, and smaller alkanes) are expected to partition into the aerosol phase or be subject to removal by deposition. Gas-particle partitioning and hydrolysis of ANs in the condensed phase influence their roles as sources and sinks of  $\text{NO}_x$ . Controlled experimental chamber studies focusing on these processes have been limited to date. The particle-phase hydrolysis rate has only been determined for ANs from trimethylbenzene (Liu et al., 2012),  $\alpha$ -pinene (Bean and Hildebrandt Ruiz, 2016), and  $\beta$ -pinene (Boyd et al., 2015). Experiments currently being conducted at the University of Texas at Austin, sponsored by the Texas Air Research Center (TARC), are examining the gas-particle partitioning and particle phase hydrolysis rates of organic nitrates formed from the OH-initiated oxidation of C8-C11 alkanes typically associated with oil and gas production activity. An ongoing need will be to incorporate the findings from recent laboratory and field studies into the chemical mechanisms of photochemical models used to assess regional air quality.

### **3.0 Objectives**

The objectives of the work are to apply the findings of ongoing experimental studies involving alkanes at the University of Texas at Austin and those of new publications that have focused on other biogenic and anthropogenic hydrocarbon precursor classes relevant to Texas emissions inventories, including isoprene, monoterpenes, and aromatics, to guide refinements to Revision 4 of the CB6 chemical mechanism (CB6r4) in version 6.32 of the Comprehensive Air quality Model with extensions (CAMx v6.32; Ramboll Environ, 2016). Sensitivity tests with CAMx will evaluate the formation and fate of ANs in central and southeastern Texas, the influence of ANs on regional ozone by recycling  $\text{NO}_x$ , and dependencies on organic aerosol concentrations.

## 4.0 Task Descriptions

### 4.1 Refinements to the CB6r4 Mechanism in CAMx

The CB6r2 mechanism was developed in AQRP project 12-012 to improve the level of detail regarding the formation and fate of organic nitrates (Hildebrandt Ruiz and Yarwood, 2013). Subsequently, CB6r3 implemented temperature and pressure dependent yields of organic nitrates for alkanes larger than ethane (Emery et al., 2015). CB6r4 adds reactions of iodine species that deplete ozone (e.g., in the marine boundary layer over the Gulf of Mexico), removes oxygen-atom ( $O^3P$ ) reactions with VOCs that are important in smog chambers but not in the atmosphere, and makes no changes to gas-phase reactions of organic nitrates (Emery et al., 2016). CB6r4 represents 1<sup>st</sup> generation isoprene hydroxynitrates as INTR, nitrocresols as CRON, and other ANs using two species: (1) NTR1 representing simple alkyl and hydroxyalkyl nitrates that remain in the gas-phase and undergo degradation by photolysis or oxidation by OH and (2) NTR2 representing multi-functional ANs that can partition into OA (Hildebrandt Ruiz and Yarwood, 2013). The NTR2 species undergoes hydrolysis to nitric acid within aerosols, which is implemented in CAMx with a hydrolysis lifetime that depends upon NTR2 partitioning into OA and defaults to 6 hours if OA is not modeled explicitly (Hildebrandt Ruiz and Yarwood, 2013). Other models are also implementing pseudohydrolysis schemes for ANs, for example, Pye et al. (2015) convert particle-phase semivolatile ANs to nitric acid and non-volatile SOA assuming  $\tau = 3$  h in CMAQ. Fisher et al. (2016) apply a bulk lifetime of 1 h in GEOS-Chem for modeling of the southeastern United States during the SOAS and SEAC<sup>4</sup>RS time period. Considerable uncertainties remain in current representations of the fate of ANs in the chemical mechanisms of CAMx and other models.

This task will interpret the most recent information about gas-particle partitioning and hydrolysis of ANs, propose strategies for improved differentiation of ANs in CB6r4, and test potential new strategies in CAMx. The findings will guide refinements to the CB6r4 chemical mechanism. The hydrolysis lifetime currently implemented in CAMx is based largely on the work of Liu et al. (2012), which measured the hydrolysis of condensed ANs from the precursor, trimethylbenzene, under varying relative humidity. Recent and ongoing observational studies at the University of Texas at Austin and elsewhere will be evaluated with attention on those that quantify hydrolysis rates of ANs from a range of precursors and/or parameterize gas-particle partitioning of organic nitrates under varying environmental conditions. A focus will be on straight-chained and branched C8-C11 alkanes that are the subject of ongoing studies by Dr. Hildebrandt Ruiz and other biogenic and anthropogenic hydrocarbon precursor classes relevant to Texas emissions inventories, including isoprene, monoterpenes, and aromatics. As organic nitrate yields and atmospheric chemical reactions depend on the size and structure of the organic backbone, the team will also evaluate whether improved resolution of AN precursors is appropriate; for example, CB6r4 represents all alkanes larger than propane as PAR but they could be differentiated, as SAPRC mechanisms do, if this sufficiently improves model performance related to ANs.

Drs. McDonald-Buller and Hildebrandt Ruiz of the University of Texas at Austin and Drs. Greg Yarwood and Bonyoung Koo of Ramboll Environ will collaborate to lead and accomplish the efforts for this task. The task will result in the development of refined version(s) of the CB6r4 mechanism reflecting the current understanding of the chemistry and fate of ANs for application in CAMx. The timeline for this task is shown in Table 1 of Section 6.0.

#### 4.2 Evaluating CB6r4 Updates in CAMx Modeling for DISCOVER-AQ

Updates to the representation of ANs in the CB6r4 gas-phase mechanism will be evaluated in a model with OA so that partitioning of ANs to OA is included in the evaluation. The team expects to use CAMx model inputs for the Houston DISCOVER-AQ period (September 2013) and modeled OA using the 1.5-D volatility basis set (VBS) approach that were developed in AQRP Project 14-024 (Hildebrandt Ruiz et al., 2015). The 1.5-D VBS scheme uses four basis sets to model OA with different oxidation states: two sets for chemically aged oxygenated OA (OOA: anthropogenic and biogenic) and two for freshly emitted OA (hydrocarbon-like OA [HOA] from anthropogenic sources and biomass burning OA [BBOA]). Each basis set has five volatility bins ranging from  $10^{-1}$  to  $10^3$   $\mu\text{g m}^{-3}$  in saturation concentration ( $C^*$ ), approximately the range of semi-volatile organic compounds (SVOCs). The 1.5-D VBS scheme accounts for systematic variations in both volatility and oxidation state (O:C ratio) to model the magnitude and chemical aging of organic aerosol (OA), but with greater computational efficiency and suitability for 3-D chemical transport modeling than the 2-D VBS formulation originally described by Donahue et al. (2011, 2012) and Jimenez et al. (2009).

Figure 1 shows the model domain, which consists of a 36-km continental-scale grid, a nested 12-km grid covering Texas, and a 4-km nested grid covering the Houston area. Meteorological inputs were developed using version 3.6.1 of the Weather Research Forecast (WRF) model. Anthropogenic emissions were obtained from the Texas Commission on Environmental Quality (TCEQ) for the 36/12/4 km domains compatible with the CB6 mechanism. Biogenic emissions estimates were developed for the time period using version 2.1 of the Model of Emissions of Gases and Aerosols from Nature (MEGAN; Guenther et al., 2012). Fire emissions were based on the Fire Inventory from NCAR (FINN) version 1 dataset (<http://bai.acd.ucar.edu/Data/fire>). In this work, modifications to CB6r4 identified in the previous task may require changes in emitted species (e.g., differentiation of PAR), which would be made directly to the CAMx-ready emission files. CAMx-ready emission files are available for several broad categories (on-road mobile, area, biogenic, point sources) such that changes can be adapted to the source sector. This approach is efficient for sensitivity testing and will provide sufficient information to guide and evaluate mechanism changes.

**Figure 1.** CAMx modeling domain with outer 36 km grid and nest 12 km (blue) and 4 km (green) grids.



In this task, CB6r4 mechanism refinements will be applied within the revised CAMx model developed in AQRP Project 14-024 to evaluate the effects on regional air quality in central and southeastern Texas. Sensitivity tests with CAMx will evaluate the formation and fate of ANs in central and southeastern Texas, the influence of ANs on regional ozone by recycling  $\text{NO}_x$ , and dependencies on organic aerosol concentrations. A particular focus will be on regional changes in maximum daily averaged 8-hour (MDA8) ozone concentrations.

Model performance evaluation will make use of monitoring data for ozone and  $\text{NO}_x$  collected at TCEQ Continuous Ambient Monitoring Stations (CAMS). All CAMS within the 4-km grid will be used to evaluate how mechanism changes influence ozone in and around Houston. Within the 12-km grid covering Texas and neighboring states, regionally representative monitoring sites (i.e., rural and suburban locations) will be selected from the TCEQ and U.S. Environmental Protection Agency (EPA) monitoring networks to evaluate how mechanism changes influence regional ozone. Because ANs effectively redistribute  $\text{NO}_x$  at regional scales, this regional ozone evaluation is expected to be informative. Routine  $\text{NO}_x$  monitoring may be less useful because monitors tend to be located in urban areas where they are influenced most strongly by nearby emission sources. Ozone model performance will be used to assess the impact of mechanism changes, but changes will neither be selected nor rejected based simply on whether they improve ozone model performance because many other factors influence model ozone predictions. The numerical performance evaluation will be supplemented by comparing model predictions for nitrogen-containing secondary species, including ANs and PANs, to recent measurement campaigns (e.g., Fisher et al., 2016). Alkyl nitrate concentrations in the particle phase and OA concentrations measured at Conroe during DISCOVER-AQ will also be used in the performance evaluation.



Dr. McDonald-Buller and Dr. Greg Yarwood will collaborate to lead the efforts for this task. Dr. Nopmongcol and Dr. Kimura will coordinate the transfer of the CAMx modeling database and associated model post-processing software from Ramboll Environ to the University of Texas at Austin and conduct, evaluate, and interpret the results of the CAMx simulations. This task will result in CAMx predictions of regional air quality that have applied the refinements to the CB6r4 mechanism and evaluations of model performance against available observations. The timeline for this task is shown in Table 1 of Section 6.0.

#### 4.3. Project Reporting and Presentation

As required, monthly technical, monthly financial status, and quarterly reports as well as an abstract at project initiation and, near the end of the project, the draft final and final reports will be submitted according to the schedule shown in Section 7.0. Dr. McDonald-Buller or her designee will electronically submit each report to both the AQRP and TCEQ liaisons and will follow the State of Texas accessibility requirements as set forth by the Texas State Department of Information Resources (<http://aqrp.ceer.utexas.edu/>). Dr. McDonald-Buller and Dr. Yarwood anticipate attending and presenting at the AQRP data workshop. Draft copies of any planned presentations (such as at technical conferences) or manuscripts to be submitted for publication resulting from this project will be provided to both the AQRP and TCEQ liaisons per the Publication/Publicity Guidelines included in Attachment G of the subaward. Final project data and associated metadata will be prepared and submitted to the AQRP archive.

Dr. McDonald-Buller will lead this task with Dr. Yarwood and with assistance from team members from the University of Texas at Austin and Ramboll Environ. Deliverables include the abstract, monthly technical reports, monthly financial status reports, quarterly reports, draft final report, final report, attendance and presentation at AQRP data workshop, submissions of presentations and manuscripts, project data and associated metadata. The schedule for Task 4.3 deliverables is shown in Section 7.0.

#### 5.0 Project Participants and Responsibilities

Project roles and responsibilities for the University of Texas at Austin and Ramboll Environ teams are described in this section.

##### The University of Texas at Austin

- **Dr. Elena McDonald-Buller** will provide overall guidance, integration, and supervision of the air quality modeling work and will be responsible for the preparation and submission of the monthly progress, quarterly progress, and final reports.
- **Dr. Yosuke Kimura** will work on the coordination of the transfer of the CAMx modeling database and associated model post-processing software from Ramboll Environ to the

University of Texas at Austin and conduct, evaluate, and interpret the results of the CAMx simulations.

- **Dr. Lea Hildebrandt Ruiz** will assist in the interpretation of experimental and observational data used to guide the CB6r4 mechanism refinements.

#### Ramboll Environ

- **Dr. Greg Yarwood** will update how ANs are represented in the CB6r4 gas-phase chemical mechanism.
- **Dr. Bonyoung Koo** will implement in CAMx updates to the AN chemistry in the CB6r4 mechanism and to the pseudohydrolysis of ANs.
- **Dr. Ou Nopmongcol** will transfer the CAMx modeling database and associated model post-processing software and participate in the evaluation and interpretation of CAMx simulations performed at the University of Texas at Austin. Dr. Nopmongcol also will perform CAMx simulations at Ramboll Environ to test and quality assure model updates.
- Ramboll Environ Associates, **Andy Wentland** and **Tasko Olevski**, will assist with these efforts.

## 6.0 Timeline

A schedule of project activities including a timeline for each task defined in Section 4.0 is shown in Table 1.

**Table 1.** Project schedule by task.

ID	Task	Sep.- Oct. 2016	Nov.- Dec. 2016	Jan.- Feb. 2017	Mar.- Apr. 2017	May- Jun. 2017	Jul.- Aug. 2017
4.1	<b>Refinements to the CB6r4 Mechanism in CAMx</b>	X	X	X			
4.2	<b>Evaluating Updates to CB6r4 in CAMx Modeling for DISCOVER-AQ</b>		X	X	X	X	
4.3	<b>Project Reporting and Presentation</b>	X	X	X	X	X	X

## 7.0 Deliverables

Project reporting and presentation requirements are described in Section 4.3. Each deliverable and required deadline for submission are presented below.

**Abstract:** At the beginning of the project, an Abstract will be submitted to the Project Manager for use on the AQRP website. The Abstract will provide a brief description of the planned project activities, and will be written for a non-technical audience.

**Abstract Due Date:** Wednesday, August 31, 2016

**Quarterly Reports:** Each Quarterly Report will provide a summary of the project status for each reporting period. It will be submitted to the Project Manager as a Microsoft Word file. It will not exceed 2 pages and will be text only. No cover page is required. This document will be inserted into an AQRP compiled report to the TCEQ.

### Quarterly Report Due Dates:

Report	Period Covered	Due Date
Aug2016 Quarterly Report	June, July, August 2016	Wednesday, August 31, 2016
Nov2016 Quarterly Report	September, October, November 2016	Wednesday, November 30, 2016
Feb2017 Quarterly Report	December 2016, January & February 2017	Tuesday, February 28, 2017
May2017 Quarterly Report	March, April, May 2017	Friday, May 31, 2017
Aug2017 Quarterly Report	June, July, August 2017	Thursday, August 31, 2017
Nov2017 Quarterly Report	September, October, November 2017	Thursday, November 30, 2017

**Monthly Technical Reports (MTRs):** Technical Reports will be submitted monthly to the Project Manager and TCEQ Liaison in Microsoft Word format using the AQRP FY16-17 MTR Template found on the AQRP website.

### MTR Due Dates:

Report	Period Covered	Due Date
Aug2016 MTR	Project Start - August 31, 2016	Thursday, September 8, 2016
Sep2016 MTR	September 1 - 30, 2016	Monday, October 10, 2016
Oct2016 MTR	October 1 - 31, 2016	Tuesday, November 8, 2016

Nov2016 MTR	November 1 - 30 2016	Thursday, December 8, 2016
Dec2016 MTR	December 1 - 31, 2016	Monday, January 9, 2017
Jan2017 MTR	January 1 - 31, 2017	Wednesday, February 8, 2017
Feb2017 MTR	February 1 - 28, 2017	Wednesday, March 8, 2017
Mar2017 MTR	March 1 - 31, 2017	Monday, April 10, 2017
Apr2017 MTR	April 1 - 28, 2017	Monday, May 8, 2017
May2017 MTR	May 1 - 31, 2017	Thursday, June 8, 2017
Jun2017 MTR	June 1 - 30, 2017	Monday, July 10, 2017
Jul2017 MTR	July 1 - 31, 2017	Tuesday, August 8, 2017

**Financial Status Reports (FSRs):** Financial Status Reports will be submitted monthly to the AQR Grant Manager (Maria Stanzione) by each institution on the project using the AQR FY16-17 FSR Template found on the AQR website.

**FSR Due Dates:**

Report	Period Covered	Due Date
Aug2016 FSR	Project Start - August 31	Thursday, September 15, 2016
Sep2016 FSR	September 1 - 30, 2016	Monday, October 17, 2016
Oct2016 FSR	October 1 - 31, 2016	Tuesday, November 15, 2016
Nov2016 FSR	November 1 - 30 2016	Thursday, December 15, 2016
Dec2016 FSR	December 1 - 31, 2016	Tuesday, January 17, 2017
Jan2017 FSR	January 1 - 31, 2017	Wednesday, February 15, 2017
Feb2017 FSR	February 1 - 28, 2017	Wednesday, March 15, 2017
Mar2017 FSR	March 1 - 31, 2017	Monday, April 17, 2017
Apr2017 FSR	April 1 - 28, 2017	Monday, May 15, 2017
May2017 FSR	May 1 - 31, 2017	Thursday, June 15, 2017
Jun2017 FSR	June 1 - 30, 2017	Monday, July 17, 2017
Jul2017 FSR	July 1 - 31, 2017	Tuesday, August 15, 2017
Aug2017 FSR	August 1 - 31, 2017	Friday, September 15, 2017
FINAL FSR	Final FSR	Monday, October 16, 2017

**Draft Final Report:** A Draft Final Report will be submitted to the Project Manager and the TCEQ Liaison. It will include an Executive Summary. It will be written in third person and will follow the State of Texas accessibility requirements as set forth by the Texas State Department of Information Resources. It will also include a report of the QA findings.

**Draft Final Report Due Date:** Tuesday, August 1, 2017

**Final Report:** A Final Report incorporating comments from the AQR and TCEQ review of the Draft Final Report will be submitted to the Project Manager and the TCEQ Liaison. It will be

written in third person and will follow the State of Texas accessibility requirements as set forth by the Texas State Department of Information Resources.

**Final Report Due Date:** Thursday, August 31, 2017

**Project Data:** All project data including but not limited to QA/QC measurement data, metadata, databases, modeling inputs and outputs, etc., will be submitted to the AQRP Project Manager within 30 days of project completion (September 29, 2017). The data will be submitted in a format that will allow AQRP or TCEQ or other outside parties to utilize the information. It will also include a report of the QA findings.

**AQRP Workshop:** A representative from the project will present at the AQRP Workshop in the first half of August 2017.

**Presentations and Publications/Posters:** All data and other information developed under this project which is included in published papers, symposia, presentations, press releases, websites and/or other publications shall be submitted to the AQRP Project Manager and the TCEQ Liaison per the Publication/Publicity Guidelines included in Attachment G of the Subaward.

## 8.0 References

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