Quality Assurance Project Plan

Project 14-016
Improved Land Cover and Emission Factor Inputs for Estimating Biogenic Isoprene and Monoterpene Emissions for Texas Air Quality Simulations

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Summary of Project

QAPP Category Number: III
Type of Project: Secondary Data Project and Research or Development (Modeling)

QAPP Requirements: This QAPP includes descriptions of the project and objectives; organization and responsibilities; scientific approach; modeling procedures; quality metrics; data analysis, interpretation, and management; reporting; and references.

QAPP Requirements:
Audits of Data Quality: 10% Required
Report of QA Findings: Required in final report

May 29, 2014

DISTRIBUTION LIST

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1. PROJECT DESCRIPTION AND OBJECTIVES

1.1 Problem Statement

The exchange of gases and aerosols between the earth's surface and the atmosphere is an important factor in determining the atmospheric composition and regional air quality. Accurate quantification and simulation of these fluxes is a necessary step towards developing air pollution control strategies and for attributing observed changes to their causes. Emissions of some compounds, including sulfur dioxide and nitric oxide emitted from electric utilities, are either directly measured or can be estimated with reasonable confidence in the U.S. In contrast, large uncertainties are associated with area source emission estimates including biogenic terpenoid emissions. Current flux estimates are typically based on a few indirect measurements that may not be representative and so could be of limited use for informing regional air quality models. The need for accurate emission estimates requires a transformation of the approaches used to characterize the emissions needed as inputs for air quality models.

1.2 Project Objectives

The objective of this project is to improve quantitative estimates of terpenoid (isoprene and monoterpene) emissions from Texas and the Southeast United States. An opportunity exists to substantially improve these estimates using recent airborne measurements. During the Southeast Atmosphere Study (SAS) 2013 summer field campaign, the National Center for Atmospheric Research (NCAR) C-130 aircraft and the National Oceanic and Atmospheric Administration (NOAA) P-3 aircraft measured terpenoid (isoprene and total monoterpenes) concentrations over Texas and surrounding states using proton transfer reaction spectrometer (PTR-MS) systems and speciated monoterpenes using gas chromatograph mass spectrometry (GC-MS) (in-situ fast-response GC-MS on the NCAR C-130 and canister sampling with laboratory GC-MS analysis for the NOAA P-3). Both aircraft have fast response vertical wind measurements suitable for applying the eddy covariance (EC) technique which provides a direct measurement of fluxes as described below. Approximately a third of the NCAR C-130 flights were designed to optimize terpenoid EC flux measurements. Measurement protocols and flight patterns of other NCAR C-130 flights and some NOAA flights were not specifically designed for terpenoid EC flux measurements, but we will investigate the possibility of estimating EC fluxes with these measurements. In addition, the availability of direct EC flux measurements and estimates of terpenoid lifetimes (based on measured ozone and hydroxyl radical [OH] concentrations) provide an opportunity to examine the utility of using concentration measurements (both mean values and variance measured with fast response PTR-MS) to estimate fluxes in different regimes of nitrogen oxides (NOx). This has the potential to greatly expand the observations available for relating terpenoid emissions to land cover distributions because of the large database of NOAA P-3 aircraft measurements. These emission estimates will be used to evaluate and improve the Model of Emissions of Gases and Aerosols from Nature (MEGAN) (Guenther et al., 2012). In addition, high-resolution land cover inputs for MEGAN will be generated and described in detail. The new and old land cover and emission factor inputs will be used to examine the sensitivity of emission and air quality model estimates to uncertainties in these inputs.

Our specific objectives are:

1. Use the eddy covariance technique to directly quantify terpenoid emission fluxes for all suitable NCAR C-130 observations during the 2013 SAS study.
2. Using the relationship between terpenoid fluxes and concentrations derived from the NCAR C-130 data, estimate terpenoid fluxes in the southeastern U.S. and Texas using NOAA P-3 aircraft observations from the 2013 SAS research program and the 2006 Texas Air Quality Study.
3. Develop high-resolution (30-m) land cover inputs for MEGAN 2.1 (Leaf Area Index, plant functional type and emission factors) for Texas and southeastern U.S. using best available satellite imagery and ground measurements. Provide a clear description of methods to ensure reproducibility and future modifications.
4. Use aircraft flux measurements and improved landcover data to a) determine average emission factors for various emission types and investigate variability within emission types, b) identify land cover types with unexpectedly high or low emissions that should be targeted by future studies, c) investigate relationships between foliage density (satellite based Leaf Area Index) and emissions across a given emission type, d) revise emission factors as needed based on aircraft observations.
5. Develop MEGAN biogenic emissions for regional photochemical modeling using updated land cover and emission factors for Texas and the Southeastern U.S. and compare with MEGAN emissions developed using default land cover and emission factors. Evaluate both MEGAN inventories against aircraft flux data.
6. Perform air quality modeling with the MEGAN emission inventory prepared with default inputs and the improved MEGAN emission inventories and evaluate modeled concentrations against measurements in high and low isoprene and NOx regimes.
7. Prepare recommendation as to whether MEGAN inputs developed in 3 and 4 above should be used in future Texas Commission on Environmental Quality (TCEQ) modeling.

2. ORGANIZATION AND RESPONSIBILITIES

2.1 Personnel and Responsibilities

This project is being conducted by ENVIRON, PNNL and NOAA under a grant from the Texas Air Quality Research Program. The project Co-Principal Investigators (Co-PIs) are Dr. Greg Yarwood of ENVIRON, Dr. Alex Guenther of Pacific Northwest National Laboratory (PNNL), and Dr. David Parrish and Dr. Joost de Gouw of NOAA's Earth System Research Laboratory. The Co-PIs will assume overall responsibility for the research and associated quality assurance. Dr. Guenther and Dr. de Gouw will lead the estimation of terpenoid emission fluxes from aircraft data. Dr. Guenther will direct the development of high resolution land cover data for biogenic emissions modeling in Texas and the Southeastern U.S. as well as the development of an emission factor database. Dr. Yarwood will lead development of biogenic emission inventories and will evaluate the inventories using a regional photochemical model. Dr. Parrish will provide scientific oversight and will review the final report.

The project will be overseen by AQRP Project Manager Dr. Elena McDonald-Buller and TCEQ Project Liaison Mr. Mark Estes. The scientists working on this project and their specific responsibilities are listed in Table 1 below.

Table 1. Project participants and their affiliations and key responsibilities.

Participant	Project Responsibility
Dr. Greg Yarwood (ENVIRON)	Co-Principal Investigator: Project oversight; responsible for development of biogenic emission inventories, photochemical modeling and reporting
Dr. Alex Guenther (PNNL)	Co-Principal Investigator: Lead researcher; responsible for estimation of terpenoid emission fluxes from aircraft data, development of high resolution land cover data for biogenic emissions modeling, emission factor database, and contributions to final report
Dr. David Parrish (NOAA)	Co-Principal Investigator: Responsible for scientific oversight and compliance with reporting requirements
Dr. Joost de Gouw (NOAA)	Co-Principal Investigator: Lead NOAA researcher; responsible for estimation of terpenoid emission fluxes from aircraft data and contributions to final report
Dr. Susan Kemball-Cook (ENVIRON)	Lead day-to-day modeling activities and evaluation of biogenic and air quality model results against aircraft and surface data and carry out project management and report preparation
Dr. Tanarit Sakulyanontvittaya (ENVIRON)	Conduct modeling with the Weather Research and Forecasting (WRF) model, the Comprehensive Air Quality Model with Extensions (CAMx) model, and the MEGAN model and evaluate biogenic and air quality model results
Mr. Jeremiah Johnson (ENVIRON)	Assist Dr. Sakulyanontvittaya with WRF and CAMx modeling

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2.2 Schedule

The schedule for specific tasks is listed in Table 2.

Table 2. Schedule of project activities.

Task	2014									2015							
	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Aug	Nov
Task 1: Emission Flux Estimation		→	→	→	→												
WP/QAPP	●																
Executive Summary		#															
Task 2: Land Cover Development		→	→	→	→												
Task 3: Emission Factor Development						→	→	→							X		
Task 4: Emission Inventories and CAMx Modeling								→	→	→	→						
Task 5: Reporting											→	→	→	→			
Draft Report													●				
Final Report															●		
Project Presentation																●	
Progress Reports		■▲	▲	▲	▲	■▲	▲	▲	■▲	▲	▲	■▲	▲	▲	■▲	■	■

Project Report Material ●
Monthly Progress Report ▲
Quarterly Progress Report ■
Journal Article X
Executive Summary #

2.3

Deliverables
A description of the specific reports to be submitted and their due dates are outlined below. All reports 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. Report templates and accessibility guidelines found on the AQRP website at http://aqrp.ceer.utexas.edu/ will be followed.

Executive Summary
At the beginning of the project, an Executive Summary will be submitted to the Project Manager for use on the AQRP website. The Executive Summary will provide a brief description of the planned project activities, and will be written for a non-technical audience.
Due Date: Friday, May 30, 2014

Quarterly Reports
The Quarterly Report will provide a summary of the project status for each reporting period. It will be submitted to the Project Manager as a Word doc file. It will not exceed 2 pages and will be text only. No cover page will be attached.

Due Dates:

Report	Period Covered	Due Date
Quarterly Report #1	June, July, August 2014	Friday, August 30, 2014
Quarterly Report #2	September, October, November 2014	Monday, December 1, 2014
Quarterly Report #3	December 2015, January & February 2015	Friday, February 27, 2015
Quarterly Report #4	March, April, May 2015	Friday, May 29, 2015
Quarterly Report #5	June, July, August 2015	Monday, August 31, 2015
Quarterly Report #6	September, October, November 2015	Monday, November 30, 2015

Technical Reports
Technical Reports will be submitted monthly to the Project Manager and TCEQ Liaison as a Word doc using the AQRP FY14-15 MTR Template found on the AQRP website.

Due Dates:

Report	Period Covered	Due Date
Technical Report #1	Project Start – June 30, 2014	Tuesday, July 8, 2014
Technical Report #2	July 1 - 31, 2014	Friday, August 8, 2014
Technical Report #3	August 1 - 31, 2014	Monday, September 8, 2014
Technical Report #4	September 1 - 30, 2014	Wednesday, October 8, 2014
Technical Report #5	October 1 - 31, 2014	Monday, November 10, 2014
Technical Report #6	November 1 - 30 2014	Monday, December 8, 2014
Technical Report #7	December 1 - 31, 2014	Thursday, January 8, 2015
Technical Report #8	January 1 - 31, 2015	Monday, February 9, 2015
Technical Report #9	February 1 - 28, 2015	Monday, March 9, 2015
Technical Report #10	March 1 - 31, 2015	Wednesday, April 8, 2015
Technical Report #11	April 1 - 28, 2015	Friday, May 8, 2015
Technical Report #12	May 1 - 31, 2015	Monday, June 8, 2015

Financial Status Reports
Financial Status Reports will be submitted monthly to the AQRP Grant Manager (Maria Stanzione) by each institution on the project using the AQRP FY14-15 FSR Template found on the AQRP website.
Due Dates:

Report	Period Covered	Due Date
FSR #1	Project Start – June 30, 2014	Tuesday, July 15, 2014
FSR #2	July 1 - 31, 2014	Friday, August 15, 2014
FSR #3	August 1 - 31, 2014	Monday, September 15, 2014
FSR #4	September 1 - 30, 2014	Wednesday, October 15, 2014
FSR #5	October 1 - 31, 2014	Monday, November 17, 2014
FSR #6	November 1 - 30 2014	Monday, December 15, 2014
FSR #7	December 1 - 31, 2014	Thursday, January 15, 2015
FSR #8	January 1 - 31, 2015	Monday, February 16, 2015
FSR #9	February 1 - 28, 2015	Monday, March 16, 2015
FSR #10	March 1 - 31, 2015	Wednesday, April 15, 2015
FSR #11	April 1 - 28, 2015	Friday, May 15, 2015
FSR #12	May 1 - 31, 2015	Monday, June 15, 2015
FSR #13	June 1 - 30, 2015	Wednesday, July 15, 2015
FSR #14	Final FSR	Wednesday, August 15, 2015

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.
Due Date: Thursday, April 30, 2015

Final Report
A Final Report incorporating comments from the AQRP 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.
Due Date: Tuesday, June 30, 2015

Project Data
All project data including but not limited to QA/QC measurement data, databases, modeling inputs and outputs, etc., will be submitted to the AQRP Project Manager within 30 days of project completion. The data will be submitted in a format that will allow AQRP or TCEQ or other outside parties to utilize the information.

AQRP Workshop
A representative from the project will present at the AQRP Workshop in June 2015.

3. SCIENTIFIC APPROACH

3.1 Data Required to Meet Project Objectives and Data Sources

In the following sections, we describe the data required to meet the project objectives as well as the sources and the application of the data.

3.1.1 Terpenoid Emission Fluxes from Aircraft Data

Airborne Eddy Covariance Measurements of Biogenic Volatile Organic Compound (VOC) Emissions

The preferred micrometeorological method for measuring trace gas fluxes in the turbulent boundary layer is eddy covariance. This approach is a direct measurement of the fluctuating vertical wind velocity and trace gas concentration. The flux is determined from the mean covariance between vertical wind velocity (w) and concentration (c) fluctuations. The successful demonstration of airborne eddy covariance techniques for measuring fluxes of anthropogenic VOC (Karl et al., 2009), biogenic VOC (Karl et al., 2013), nitrogen oxide (NO) (Hasel et al., 2005) and ozone (Lenschow et al., 1980) provides a promising approach for characterizing chemical fluxes on scales relevant for regional air quality modeling. The major components of an airborne eddy covariance flux system are 1) a system that measures vertical wind speed with a fast (typically <100 ms) response time, 2) an instrument that measures the targeted atmospheric constituent with a fast response time, and 3) a system to receive and store the data (e.g., datalogger or computer). The main challenge of the EC technique is the requirement of sampling rates on the order of 10 Hz (<100 ms response times). This is especially the case with a quadrupole PTR-MS because in order to sample more than one mass, the detector does not continuously monitor a given compound. However, Lenschow et al. (1994) demonstrated that this can be accomplished by the introduction of disjunct sampling. The random and systematic error for disjunct EC flux measurements relative to EC flux measurements can be obtained following Lenschow et al. (1994) and is typically <5%. Both the C-130 and P-3 have the components needed for EC measurements but the P-3 was used to look at a large number of masses and so this disjunct data may not be suitable for calculating EC fluxes. We will determine if this is an acceptable error by using the C-130 data to compare the original signal with one that results if a digital filter is used to the P-3 sampling routine.

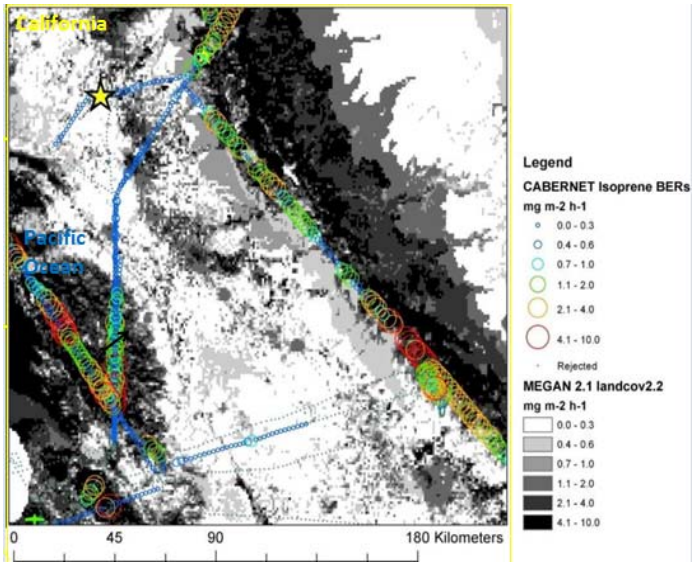

Figure 1. Example of isoprene emission factors estimated using aircraft eddy covariance flux measurements (Misztal et al. in preparation). The spatial resolution of each flux measurement is ~2 km. MEGAN model estimates are shown for comparison.

Spatially resolved eddy covariance fluxes will be obtained from wavelet analysis (Mauder et al., 2007, Karl et al., 2009, Karl et al., 2013) along flight tracks flown in the mixed layer. As shown in Figure 1, the horizontal spatial resolution of these measurements will be about 2 km (Karl et al., 2009; Misztal et al., in preparation), which provides sufficient resolution for quantifying fluxes even in heterogeneous landscapes such as oak savannas.

Karl et al. (2013) recently showed that vertical profiles of isoprene fluxes in the daytime mixed layer can be used to estimate OH concentrations. The vertical divergence in measured isoprene flux is directly related to OH concentration. These observations provide an opportunity for assessing the relationships between fluxes and concentrations under different chemical regimes (e.g., NOx levels). Figure 2A shows the flight plan used for vertical profiling and Figure 2B illustrates an example of vertical flux profiling over a site in east Texas. Preliminary observations shown in Figure 2C demonstrate that there are detectable fluxes of isoprene and total monoterpenes.

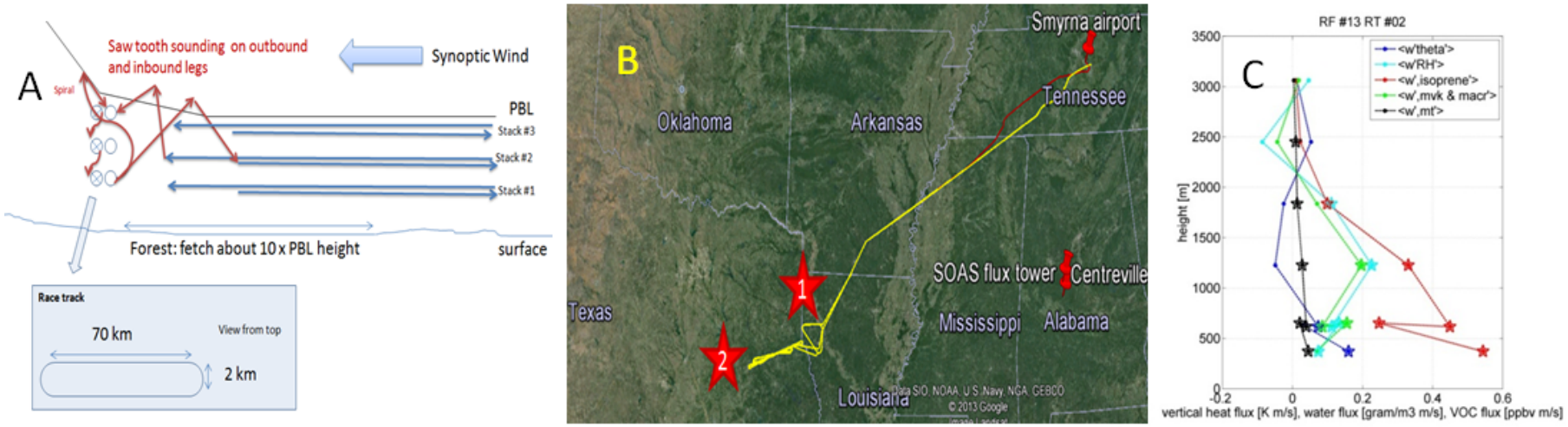

Figure 2. Panel A: Flux profiling flight pattern with stacked racetrack patterns (3 to 5 levels) with a sawtooth sounding on the inbound and outbound legs. Panel B: Example of C-130 flight track with stacked racetracks over Texas. Panel C: Vertical profiles of fluxes of water (w'RH'), sensible heat (w'theta'), isoprene (w'isoprene'), total monoterpenes (w'mt'), and isoprene oxidation products (w'mvk&macr') over Texas site #2

NCAR C-130 Aircraft VOC Measurements

Fast response VOC measurements were made on the NCAR C-130 using a custom-designed airborne PTR-MS developed at NCAR using some components manufactured by IONICON Analytik (Innsbruck, Austria) and described by Karl et al. (2013). During flights focused on biogenic volatile organic compound (BVOC) fluxes, a limited suite of VOC measurements were targeted in order to increase sensitivity. Measurements typically included isoprene, total terpene, methanol, and methacrolein plus methyl vinyl ketone). A fast GC-MS measured isoprene, methyl butenol, a-pinene and other speciated monoterpenes, methanol, and many other VOC with a time resolution of about 5 minutes.

NOAA P-3 Aircraft VOC Measurements

Onboard the NOAA P-3, measurements of VOCs were made both by a custom-built PTR-MS instrument as well as from GC-MS analyses of whole air samples. While the PTR-MS measurements onboard the C-130 were focused on determining terpenoid fluxes, the PTR-MS measurements onboard the P-3 included a much broader suite of compounds to characterize anthropogenic, biogenic and biomass burning emissions as well as their oxidation products. The P-3 measurements by themselves are therefore less suitable for direct EC determination of terpenoid fluxes. We will use observations from the C-130 to assess the accuracy of flux estimates using the NOAA P-3 data. The C-130 data will be subsampled to simulate the P-3 data, which has less data for each mass to enable sampling of a greater range of masses, in order to determine the impact on the accuracy of the fluxes. We will examine potential approaches for correcting the P-3 flux estimates and to estimate the higher level of uncertainty. This will be applied to the P-3 measurements during the 2006 Texas Air Quality Study as well as the 2013 Southeast Atmosphere Study, to give information about biogenic fluxes over large parts of Texas and the Southeastern U.S.

3.1.2 High Resolution Land Cover Data for MEGAN Modeling in Texas and the Southeastern U.S.

MEGANv2.1 land cover driving variables include 1) Leaf Area Index of vegetation-covered fraction of each grid cell (LAIv), 2) Fraction of each grid cell covered by each plant functional type (PFT) (e.g., broadleaf trees, shrubs), and 3) Emission factor for isoprene and monoterpene categories for each grid cell (EF).

LAIv is an input for the MEGANv2.1 canopy environment model that simulates increases in terpenoid emissions with increasing foliage. Emissions of some compounds, such as isoprene, are emitted primarily from sunlit leaves and so emissions become saturated at high LAI levels. In addition, changes in LAIv are used as inputs to the MEGANv2.1 model to estimate leaf age which is also a driver of biogenic VOC emission variations. A database of LAIv values at 1-km spatial resolution and 8-day temporal resolution will be compiled for April to September of 2013 using Moderate Resolution Imaging Spectrometer (MODIS) satellite data.

3.1.3 Emission Factor Database

MEGANv2.1 uses a plant functional type (PFT) scheme with 16 categories. We will develop a high-resolution (30-m) PFT database for Texas and the surrounding region by integrating the existing 30-m MEGANv2.1 PFT database and landcover data currently used by

TCEQ for biogenic emission modeling. A detailed description of the approach will be included in the final report and python scripts which show each step in the process will be also provided.

Isoprene and monoterpene emission factor maps for Texas and the surrounding region will be calculated by modifying the existing 30-m MEGANv2.1 EF maps using the aircraft data described above, where available. Average values based on the aircraft flux measurements will be used to calibrate the landcover scale emission factors for PFT types within different ecoregions.

3.1.4 MEGAN Biogenic Emission Inventories and Inventory Evaluation Developed using Regional Photochemical Modeling

We will prepare model-ready MEGAN biogenic emissions based on improved landcover and emission factor databases and evaluate the biogenic emission inventories using a photochemical grid model. Two or more emission inventories will be developed for this project. The first inventory is a base-case biogenic emission inventory, which will be developed using the MEGAN default landcover database and default emission factors. Then, one or more improved biogenic emission inventories will be derived from the new high-resolution landcover database and Texas and Southeastern U.S. emission factor database. The default and improved biogenic emission inventories will be compared against aircraft flux data and then evaluated using a photochemical model.

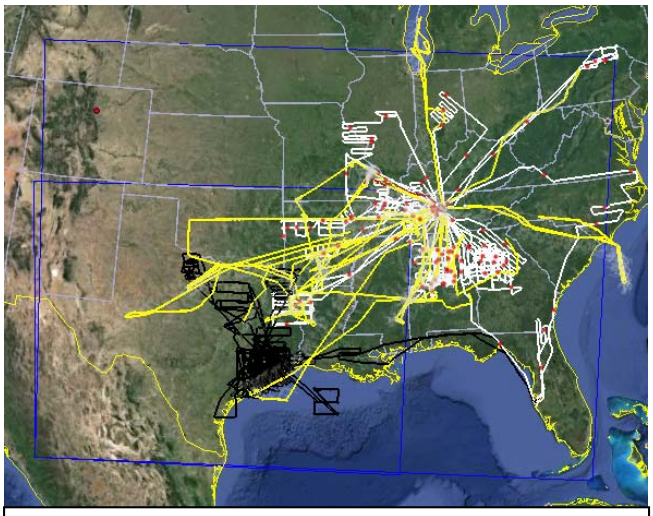

Figure 3. Proposed 12 km modeling grid and aircraft flight paths. Aircraft flight paths: SAS C-130 (yellow), SAS P-3 (white), and TEXAQS 2006 (black). TCEQ 12 km grid extent (smaller blue domain), and expanded 12 km grid (larger blue domain).

The Comprehensive Air quality Model with Extensions v6.1 (CAMx; ENVIRON, 2013) will be used to model fluxes and atmospheric concentrations of BVOCs. The modeling platform is adapted from a 2013 Texas ozone forecast modeling application developed by ENVIRON for the TCEQ (Johnson et al., 2013). The modeling domain consists of a 36 km continental-scale grid and a nested 12 km grid. The regional 12 km grid used in the forecasting project to cover Texas and surrounding states will be expanded so that it encompasses nearly all of the overland flight tracks of the C-130 and P-3 made during June-July 2013 (Figure 3). CAMx will be run from June 1-July 15, 2013 to simulate the period when C-130 and P-3 aircraft data are available. CAMx will be run with Revision 2 of the Carbon Bond 6 chemical mechanism (CB6r2) (Yarwood et al., 2013). The Weather Research and Forecasting (WRF) (Skamarock et al., 2008) meteorological model will be used in hindcast mode to develop the June-July 2013 meteorological fields required for input to CAMx.

For both the base-case MEGAN emission inventory using default inputs and the improved MEGAN emission inventories, we will compare modeled and measured isoprene fluxes along the aircraft flight tracks. We will evaluate CAMx modeled concentrations against

aircraft measurements for the following species: OH, isoprene, 1st generation isoprene products, isoprene nitrates, terpenes, methanol, acetone, ozone and NOx. Model performance will be stratified with respect to high and low isoprene and NOx regimes. Modeled NOx and ozone will be also evaluated against surface measurements. Changes in the CAMx chemical mechanism will be tested if the model performance evaluation indicates that this is needed.

4. QUALITY METRICS

4.1 Quality Metrics for observations

4.1.1 Eddy covariance fluxes

The preferred micrometeorological method for measuring surface exchange of trace gases in the turbulent boundary layer is eddy covariance (EC). This technique is based on the 3-dimensional mass balance of a species within a hypothetical volume. If the landscape is relatively flat with homogeneous vegetation, horizontal and vertical advection can be ignored and the flux can be determined simply from the covariance between the vertical wind velocity (w) and trace gas density (c) expressed as:

$$Flux = \overline{w'c'} \qquad (1)$$

The overbar on w′c′ represents the time average of the product of w′ and c′. Primed values are defined as the difference between the mean value ($\overline{x}$) and the instantaneous value (*x(t)*): $x' = \overline{x}$ - *x(t)*. The averaging time used for aircraft micrometeorological flux measurements is typically around 5 minutes.

This technique provides the most direct measurement method of determining surface exchange on the scale of a few kilometers. As such, this method has been used extensively over the past decades to measure surface energy exchanges (sensible and latent heat fluxes) and has been the technique of choice of current flux networks (i.e, FLUXNET) dedicated to quantifying net ecosystem exchange (via CO_2 flux) from various landscapes (Baldocchi et al. 1996).

The major components of a PTR-MS eddy covariance flux system are:

(1) A measurement of 3-dimensional wind velocities with a fast sampling rate (typically ≥ 10 Hz).

(2) Measurements of the trace gas of interest at a similarly high sample rate. Since the PTRMS is not co-located with the wind measurement, flow is pulled through a co-located inlet to the measuring instrument. High frequency flux loss due to axial diffusion in the tube is characterized and minimized as described by Lenschow and Raupach (1991).

(3) A system to receive and store the data (e.g., datalogger or computer).

Before computation of the covariance one must: (1) apply a tilt correction to the wind velocities and (2) align the two time series (*w* and *c*) in time. The tilt correction is necessary since it is difficult to physically align the sonic anemometer to the main wind streamlines, thus some of the vertical wind velocity can be "contaminated" by the horizontal components. The time lag between the wind and concentration time series will be calculated via flow rates and distance (for an inlet tube) and also via the use of cross-correlation. Cross-correlation calculates the correct lag by determining a correlation coefficient (as a function of lag time) between the two time series – *w* and *c*. When a maximum (or minimum, depending on the sign of the flux) correlation coefficient is observed, the proper lag has been determined.

We will use a variation of the EC method called disjunct eddy covariance (DEC) (Lenschow et al., 1994). This technique involves measuring the trace gas concentration very rapidly (0.1 to 0.2

sec) at discrete time intervals (between 1 to 20 seconds, denoted as Δt). Over a 30 minute flux averaging period, this creates a statistically valid subsample of concentrations that can be aligned in time with the corresponding wind velocities (as in EC). The covariance of this subsample can be shown to be equivalent to the flux (equation 1, conventional EC). Less sampling does lead to a larger statistical uncertainty. This has been shown to be a function of Δt (Lenschow et al., 1994, Turnipseed et al., 2009) and is less than 20% at $\Delta t \leq 5$ seconds. We have used this approach extensively (Karl et al., (2002), the fluxes of a larger number of chemical compounds can be measured by sequentially monitoring a different ion with the PTR-MS for ~ 0.1 seconds. A suite of up to about different 15 ions (i.e., different chemical compounds) can be sensitively measured in about ~5 seconds and then repeated. This technique has come to be known as *virtual* Disjunct Eddy Covariance (*v*DEC).

Mass spectrometric techniques have proven to be extremely valuable for the measurement of common atmospheric chemical species due to their high data acquisition rates. In particular, chemical ionization mass spectrometers used to detect atmospheric trace gases have found a wide application to the study of many atmospheric processes. In the last 15 years, PTR-MS has been widely-used for quantifying the VOC composition during various ground and airborne field campaigns. Instrumental details on the technique including sensitivity and specificity can be found in Lindinger et al. (1998) and de Gouw et al. (2003). The basic operation principle involves the mixing of an air sample with water vapor flowing in a drift tube under high voltage (~750 V) that creates H_3O^+ ions. H_3O^+ does not react with any of the main components of air (i.e. nitrogen (N_2), oxygen (O_2), carbon dioxide (CO_2)), as they all have lower proton affinities than water (H_2O), but H_3O^+ performs proton transfer to many VOCs in non-dissociative reactions,

$$H_3O^+ + VOC \xrightarrow{k} VOC \cdot H^+ + H_2O \qquad (2)$$

The proton transfer rate constants (k) are large, corresponding to the collisional limiting values (10^{-9} cm^3 s^{-1}). The value for E/N (E being the electric field strength and N the buffer gas density) in the drift tube is kept at about 123 Townsend (Td). This value helps to minimize H_2O-H_3O^+ clustering. From equation (2) it is apparent that in theory the quantification of concentrations in an organic mixture can be calculated from first principles according to:

$$[VOC] = \frac{1}{k \cdot t} \cdot \frac{cps\left(VOC \cdot H^+\right)}{cps\left(H_3O^+\right)} \qquad (3)$$

Where [*VOC*] is the concentration of the particular VOC of interest, $VOC{\cdot}H^+$ is the protonated VOC, t is the reaction time in the drift tube, and *cps* indicates the counts per second read by the electron multiplier. Rate constants k have been published in the literature [e.g. Lindinger et al., 1998] and can be calculated if polarizability and dipole moments of the species are known. The drift (reaction) time t can be measured by gating the ion signal and measuring the arrival spectrum of the ions. The random bias of the instrument (σ) is dependent on the sensitivity S (cps/ppbv – counts per second per ppbv) of the instrument, the ambient concentration (ppbv) and integration time (t_i) per mass unit: $\sigma = \sqrt{S \cdot C \cdot t_i}$. Further information on determining background and instrument sensitivity are discussed below in the QA/QC (section 6.4) below. The PTR-MS

technique can detect concentrations of individual species in complex mixtures at mixing ratios as low as 10 ppt.

We have designed our screening procedures for time series after the protocol prescribed by the Euroflux network (Aubinet et al. 2000). Data are initially screened for electronic "spikes" and basic statistical parameters. Spikes are detected using a simple filter based on the standard Q-test. Those values that fall between 4-5 standard deviations of the mean are replaced by the median value (which will not contribute to the calculated flux). When the percentage of replaced data is greater than a threshold of 7%, data from that particular time period are discarded. If the offset of a sensor is known to predictably drift in time from repeated calibrations, the time series for that sensor is also linearly de-trended before fluxes are calculated. The following screening tests that are based on turbulence (derived from the sonic anemometer) are also performed and data are discarded if these criteria are not met:

(a) Friction velocities (denoted as u*) greater than 0.25 m s-1 are typically required to insure adequate turbulent mixing for the EC technique.

(b) Monin-Obuhkov similarity functions are used to compare turbulence parameters. Under neutral atmospheric stability, it is observed that $\sigma_w = 1.25u*$ (Kaimal and Finnigan, 1994). For different atmospheric stability regimes, other turbulence models have been derived (Foken and Wichura, 1996, Panofsky et al., 1977). If observed data disagree with these models by more than 25%, the data is deemed questionable.

(c) Statistical stationarity of the time series. The test for flux stationarity, which is based on the work of Foken and Wichura (1996), consists of dividing each flux period into six sub-intervals. The flux for each sub-interval is then calculated and the mean of these 5-min. fluxes is then compared to the total flux. If these differ by more than 25%, this period would then be deemed "non-stationary" and flagged.

Time periods with unacceptable turbulence statistics, excessive spikes and invalid turbulence tests will be flagged (series of flags, one for each test, 0=OK, 1=non-stationary, etc) and included with the final data set.

Additional checks:

(d) Time lags between the concentration and the wind measurements induced by the inlet lines are accounted for by measuring the cross correlation between w (vertical wind velocity) and the concentration, c. It can also be calculated using flow rates and the length of the inlet tube. These should agree to within ± 10%.

(e) The coordinate frame of the wind velocities is rotated such that the mean vertical wind velocity over the averaging period is zero (Kaimal and Finnigan, 1994; Wilczak et al., 2001).

(f) Corrections due to flux loss in sample tubing and density corrections are applied.

Covariances (fluxes) are calculated and archived with a set of flags to indicate potential issues with the measurements or calculations.

The NCAR PTR-MS system is calibrated using a dynamic dilution system where a multi-component ppm level NIST-certified standard is mixed with zero (VOC free) air at different concentrations using mass flow controllers. All flows are verified using a volumetric flow meter (e.g. DryCal or Gilibrator). The resulting sensitivity (in counts per second per ppb compound) is compared with theoretical calculations for compounds where the rate constants (k) have been

published (see equation 3 above). This quality control measure is performed before, during and after every laboratory experiment and field deployment. PTR-MS interferences have been assessed with a GC-PTR-MS coupling in the laboratory prior to the study and will be assessed by comparison with a GC-MS flown on the NCAR C130 during the campaign.

In addition to the calibration mentioned above, additional checks are performed to ensure data quality. The instrument sensitivity is exactly defined by equation (3) and is directly influenced by the primary ion density (H_3O^+) and the buffer gas density (N), which in turn is directly related to drift tube pressure. Four additional cases that contribute to instrument performance are:

(a) internal background (IB)
(b) losses in inlet system
(c) aging secondary electron multiplier (SEM)
(d) quadrupole mass spectrometer (QMS) transmission

(a) IB is checked routinely every 10-30 minutes by passing the ambient air stream over a heated catalyst (a custom-built heating tube containing platinum wool and held at 440 ºC) that converts all VOCs of interest to CO_2, which is not detected by the PTR-MS. This technique has the additional advantage of avoiding any change in humidity downstream when switching from ambient measurement mode to reference mode. All inlet lines are conditioned at the same humidity, which is important when measuring polar compounds. (Note: we avoid the use of de-activated charcoal (DC), which is often used for internal background measurements. DC tends to remove water, and tests have shown that IB measurements are subsequently underestimated if DC is used. Once the IB has been determined the detection limit (DL) can be calculated according to:

$$DL = \frac{2 \cdot \sigma_{blank}}{S} \qquad (4)$$

Note that we typically define the DL as twice the standard deviation of the blank. If higher precision is needed then longer dwell times at each mass can be implemented.

(b) Losses in inlet lines are minimized by using perfluoroalkoxy alkane (PFA) Teflon and silica coated stainless steel tubing. The inlet sampling lines can be heated up to 100 ºC, which minimizes condensing volatile species on the inlet surfaces. Multi-component NIST-certified standards are used for assessing any potential losses.

(c) SEM aging is determined by monitoring the primary ion (mass to charge ratio m/z=19) count rates under constant conditions (e.g. during a blank) while increasing the voltage on the multiplier from 2500 to 3500V. The primary ion (H_3O^+) is actually calculated by monitoring m/z=21 and multiplying this value by 500. This is based on the natural isotopic abundance of ^{18}O in water (0.002 mole fraction). By monitoring m/z=19 instead of m/z=21, the number of ions actually reaching the SEM is reduced by nearly 500x, and thus prolongs its useful life. 3500V is the SEM's maximum operating voltage and when it becomes necessary to use that voltage to

achieve the maximum primary ion count, sensitivity starts to be degraded. At that point, the multiplier is replaced. This sensitivity is routinely checked during each experiment.

(d) QMS transmission is checked by spiking a high concentration VOC standard and monitoring the decrease of the primary ions (H_3O^+). By using different high purity VOCs the transmission is plotted as a function of m/z (mass to charge ratio).

4.1.2 Quality Metrics for Terpenoid Data

Calibration procedures that were used for the terpenoid data onboard the NCAR C-130 and NOAA P-3 aircraft will be documented and the uncertainties quantified. An inter-comparison flight between the C-130 and P-3 was conducted during the SAS study and the terpenoid data will be compared to further evaluate data quality and quantify measurement uncertainties. If needed, a comparison of calibration standards that were used by the NCAR and NOAA teams will be conducted.

Uncertainties in the eddy-flux terpenoid emissions measurements from the C-130 and P-3 aircraft will be documented and uncertainties quantified. The procedures to calculate fluxes from the P-3 data using flux-concentration relationships from the C-130 measurements will be documented and the uncertainties quantified.

The measurements of other parameters that are needed to calculate emissions fluxes along flight tracks (temperature, photoactive radiation) will be documented and the uncertainties quantified.

4.2 Quality Metrics for Modeling Data

The models that will be used in this project are the WRF meteorological model and the CAMx photochemical grid model. The models were selected for use in this project to ensure consistency with TCEQ's State Implementation Plan (SIP) modeling, which uses both WRF and CAMx. The WRF model will be run first in order to provide required meteorological inputs for the MEGAN biogenic emissions model and the CAMx photochemical model.

WRF is a primitive equation model that has been used extensively for regional air quality modeling applications. WRF is the successor to the MM5 model (Dudhia et al., 1993), which the TCEQ has used in previous SIP modeling. NCAR and NOAA led the development of WRF in collaboration with universities and other government agencies within the U.S. and overseas. WRF is a public-domain model that is freely available. Documentation of the model may be found at http://www.wrf-model.org/index.php. WRF allows the user to choose from a set of parameterizations for boundary layer processes, cloud and precipitation physics, heat budgets for multiple soil layers, the kinematic effects of terrain, and cumulus convection. The physics parameterizations selected by the TCEQ in their SIP ozone modeling will be used for the initial model run in this project. WRF contains a four-dimensional data assimilation (FDDA) capability that allows the "nudging" of the model solution toward gridded analyses and individual observations either separately or in combination. This nudging capability will be employed in the WRF run for this project.

ENVIRON will run the WRF model for the TCEQ's continental-scale 36 km RPO grid shown in Figure 4 and a nested 12 km grid which is slightly larger than the expanded CAMx 12 km grid shown in Figure 3. The vertical layer structure developed by the TCEQ for its SIP modeling will be used; this layer structure may be found at

http://www.tceq.texas.gov/airquality/airmod/rider8/modeling/domain. WRF will be run for the June 1-July, 2013 period of interest with an additional period of model spinup before June 1.

ENVIRON will evaluate the performance of the WRF model in reproducing observed winds, temperature, humidity, cloudiness and precipitation. Output from WRF will be compared against meteorological observations from the TCEQ's Continuous Air Monitoring Stations (CAMS) and airport meteorological monitoring sites throughout the 12 km WRF modeling domain. A graphical and statistical evaluation of model performance will be carried out for winds, temperatures, and the placement, intensity, and evolution of key weather phenomena.

WRF surface performance will be assessed using the METSTAT program to generate statistics and hourly graphical model-observation comparisons for winds, temperature and humidity. We will calculate bias and error statistics for wind speed, direction, temperature, and humidity (Table 3). Each statistical metric will be compared to performance benchmarks to evaluate how well the model performed.

Table 3. Definition of performance metrics for meteorological and photochemical modeling.

Metric	**Definition**[1]
Mean Bias (MB)	$\frac{1}{N}\sum_{i=1}^{N}(P_i - O_i)$
Mean Error (ME)	$\frac{1}{N}\sum_{i=1}^{N}\lvert P_i - O_i\rvert$
Mean Normalized Bias (MNB) (-100% to +∞)	$\frac{1}{N}\sum_{i=1}^{N}\left(\frac{P_i - O_i}{O_i}\right)$
Mean Normalized Error (MNE) (0% to +∞)	$\frac{1}{N}\sum_{i=1}^{N}\left\lvert\frac{P_i - O_i}{O_i}\right\rvert$
Normalized Mean Bias (NMB) (-100% to +∞)	$\frac{\sum_{i=1}^{N}(P_i - O_i)}{\sum_{i=1}^{N} O_i}$
Normalized Mean Error (NME) (0% to +∞)	$\frac{\sum_{i=1}^{N}\lvert P_i - O_i\rvert}{\sum_{i=1}^{N} O_i}$
Fractional Bias (FB) (-200% to +200%)	$\frac{2}{N}\sum_{i=1}^{N}\left(\frac{P_i - O_i}{P_i + O_i}\right)$
Fractional Error (FE) (0% to +200%)	$\frac{2}{N}\sum_{i=1}^{N}\left\lvert\frac{P_i - O_i}{P_i + O_i}\right\rvert$
Coefficient of Determination (r^2) (0 to 1)	$\left(\frac{\sum_{i=1}^{N}(P_i - \overline{P})(O_i - \overline{O})}{\sqrt{\sum_{i=1}^{N}(P_i - \overline{P})^2 \sum_{i=1}^{N}(O_i - \overline{O})^2}}\right)^2$

[1] P_i and O_i are prediction and observation at the *i*-th site, respectively; $\overline{P}$ and $\overline{O}$ are mean prediction and observation, respectively.

Emery et al. (2001) derived and proposed a set of daily performance benchmarks for typical meteorological model performance. These standards were based upon the evaluation of about 30 meteorological simulations (using a variety of regional meteorological models) since 1993 in support of air quality applications as reported by Tesche et al. (2001) and other studies. The purpose of these benchmarks was not to give a passing or failing grade to any one particular meteorological model application, but rather to put its results into the proper context of other models and meteorological data sets. Since 2001, the benchmarks have been promoted by the EPA-sponsored National Ad Hoc Meteorological Modeling Group and have been consistently relied upon to evaluate Pennsylvania State University / National Center for Atmospheric Research (MM5) and WRF model performance in many regulatory modeling projects throughout Texas and the U.S. As part of the Western Regional Air Partnership (WRAP) meteorological modeling of the western United States, including complex conditions in the Rocky Mountain Region and in Alaska, Kemball-Cook et al., (2005) proposed model performance benchmarks for complex conditions. McNally (2009) performed a reassessment of these benchmarks using WRF runs, and suggested a revision to the humidity benchmark. The determination to use simple or complex benchmarks will be made on a site-by-site basis depending on the presence of significant terrain or local circulations (e.g. Houston sea breeze).

The benchmarks for each variable are shown in Table 4. Being outside one or more of these ranges does not mean the meteorological data fields for a particular parameter are unacceptable. However, such a result indicates that caution should be exercised in the use of such variables, and in interpreting subsequent air quality modeling based on those meteorological fields. If wind, temperature and humidity bias and error statistics are reasonably near their respective benchmarks, WRF model performance will be considered acceptable.

Table 4. WRF Performance Benchmarks.

Parameter	Emery et al. (2001)	Kemball-Cook et al. (2005)	McNally (2009)
Conditions	Simple	Complex	Complex
Temperature Bias	≤ ±0.5 K	≤ ±2.0 K	≤ ±1.0 K
Temperature Error	≤ 2.0 K	≤ 3.5 K	≤ 3.0 K
Temperature IOA	≥ 0.8	(not addressed)	(not addressed)
Humidity Bias	≤ ±1.0 g/kg	≤ ±0.8 g/kg	≤ ±1.0 g/kg
Humidity Error	≤ 2.0 g/kg	≤ 2.0 g/kg	≤ 2.0 g/kg
Humidity IOA	≥ 0.6	(not addressed)	(not addressed)
Wind Speed Bias	≤ ±0.5 m/s	≤ ±1.5 m/s	(not addressed)
Wind Speed RMSE	≤ 2.0 m/s	≤ 2.5 m/s	(not addressed)
Wind Speed IOA	≥ 0.6	(not addressed)	(not addressed)
Wind Dir. Bias	≤ ±10 degrees	(not addressed)	(not addressed)
Wind Dir. Error	≤ 30 degrees	≤ 55 degrees	(not addressed)

ENVIRON will evaluate upper-air WRF meteorological estimates through comparison with available upper-air observations and satellite images. The focus of this evaluation will be on performance in the 12 km grid. High resolution satellite data will be employed to evaluate cloud locations and depth. Precipitation measurement analyses will be compared to WRF results to evaluate location, timing, and intensity of rainfall in the 12 km domain.

To place the WRF performance in context of other Texas air quality modeling efforts, the performance of the June-July, 2013 WRF run will be compared with that of previous Texas

meteorological modeling applications. Depending on the outcome of the evaluation, ENVIRON may elect to refine the WRF model physics and/or nudging options in order to improve model performance over the 12 km grid.

Figure 4. 36 km WRF (red) and CAMx (blue) modeling domains. Figure from http://www.tceq.texas.gov/airquality/airmod/rider8/modeling/domain.

Once model performance has been evaluated and determined to be satisfactory, the WRF model output data will be used in the development of biogenic emission inventories for the June 1-July 15, 2013 period. The MEGAN model requires information about temperature, soil moisture and solar radiation from the meteorological model. WRF model output will be formatted for use by MEGAN through application of the MCIP processor. Photosynthetically active radiation (PAR) data, an important input driving the MEGAN light dependency algorithm, can be derived from satellite observation or from predicted solar radiation from WRF/MCIP. However, the satellite PAR observations are not available for year 2013. This study will use solar radiation from WRF/MCIP with a solar radiation-to-PAR conversion factor of 0.45 (Sakulyanontvittaya et al., 2012).

Besides the meteorological data, MEGANv2.10 inputs include plant functional type fraction (PFTf), emission factors, and leaf area index (LAI). This study will develop two or more emission inventories to be used in CAMx modeling. The first inventory is a base-case biogenic emission inventory, which will be developed using the MEGAN default PFTf, emission factors, and LAI. Then, one or more improved biogenic emission inventories will be derived from the new high-resolution landcover database and Texas and Southeastern U.S. emission factor database. ENVIRON will run the MEGAN model for the CAMx 36/12 km nested modeling domains for the June 1-July, 2013 period of interest. ENVIRON will conduct a quantitative comparison of the biogenic emissions inventories developed from new improved landcover and emission factors to the default inventory for quality assurance and to understand the potential impact to air quality modeling. MEGAN modeling will be performed with the improved inputs and the default inputs to generate CAMx-ready emission inventories for both 36 km and 12 km grids. The extraction of

the emission inventories will summarize the quantities of the important pollutants, such as isoprene, monoterpene, and nitrogen oxide. The summary will be provided in table format and will include the domain-wide total emissions and annual Texas county level emissions. The temporal resolutions for the summary will be annual total and monthly total. The comparison will be performed on both 36 km and 12km grids.

The CAMx photochemical model was developed by ENVIRON and is publicly available at www.camx.com. CAMx is a "one-atmosphere" model for ozone, particulates, visibility, and air toxics. CAMx has been used by the State of Texas for the recent Houston-Galveston, Beaumont-Port Arthur, and Dallas-Fort Worth ozone attainment demonstration modeling for the Texas SIP. CAMx has also been used by other states for their 8-hour ozone planning and by the EPA for the NOx SIP Call, Clean Air Transport Rule, and other rulemakings. The CAMx 36/12 km nested modeling domains are shown in Figures 3 and 4, and the vertical structure is shown in http://www.tceq.texas.gov/airquality/airmod/rider8/modeling/domain.

Before CAMx is run, input data such as model-ready emissions and meteorological input files will be reviewed using visualization software such as PAVE or VERDI to ensure that each field has the expected spatial patterns and range of values. Where visualization is not useful or impractical (e.g. in inspection of the chemistry parameters file or model run script), comparison with similar files used in comparable applications will be performed.

5. DATA ANALYSIS, INTERPRETATION, AND MANAGEMENT

5.1 Analysis of Aircraft Observations

Fast response VOC measurements were made on the NCAR C130 during the 2013 Nitrogen, Oxidants, Mercury, and Aerosol Distributions, Sources, and Sinks (NOMADSS) study using a custom-designed airborne PTR-MS developed at NCAR and described by Karl et al. (2013). During flights focused on BVOC fluxes, a limited suite of VOC measurements were targeted in order to increase sensitivity. Measurements typically included isoprene, total terpene, methanol, and methacrolein plus methyl vinyl ketone). A fast GC-MS measured isoprene, methyl butenol, a-pinene and other speciated monoterpenes, methanol, and many other VOC with a time resolution of about 5 minutes. Measurements on the NOAA P-3 PTRMS data for concurrent Southeast Nexus (SENEX) study will also be analyzed to estimate fluxes. However, since the NOAA PTRMS was monitoring a larger number of masses, this disjunct data may not be suitable for calculating EC fluxes. We will determine if these data are suitable for estimating fluxes by using the C-130 data to compare the original signal with one that results if a digital filter is used to the P-3 and DC-8 sampling routines.

Spatially resolved eddy covariance fluxes will be obtained from wavelet analysis (Mauder et al., 2007, Karl et al., 2009, Karl et al., 2013) along flight tracks flown in the mixed layer. The horizontal spatial resolution of these measurements will be about 2 km (Karl et al., 2009), which provides sufficient resolution for quantifying fluxes even in heterogeneous landscapes such as oak savannas.

Karl et al. (2013) recently showed that vertical profiles of isoprene fluxes in the daytime mixed layer can be used to estimate OH concentrations. The vertical divergence in measured isoprene flux is directly related to OH concentration. These observations provide an opportunity for assessing the relationships between fluxes and concentrations under different chemical regimes (e.g., NOx levels).

5.2 Analysis of CAMx Model Output Data

We will carry out two types of model performance evaluation during this project. The first type of evaluation assesses CAMx model performance in simulating observed ground level ozone and NOx throughout the 12 km grid during the 2013 episode. The purpose of this evaluation is to ensure that the model is functioning as expected and that the meteorological and other inputs are of good quality and have been properly prepared. Within Texas, monitoring data used for the model performance evaluation will come from the TCEQ's Continuous Air Monitoring Station (CAMS) sites. Outside Texas, we will use data from rural EPA Air Quality Station (AQS) network sites, the Clean Air Status Trends Network (CASTNet) monitoring networks and SouthEastern Aerosol Research and Characterization (SEARCH) monitoring sites, which are located in the southeastern U.S. We will focus on evaluation at rural sites, since the model's 12 km resolution may make it difficult to simulate ozone formation in urban areas with sufficient accuracy. CASTNet sites are located in rural areas and only AQS sites that are determined to be rural based on their site description will be used. The SEARCH network contains urban, suburban, and rural sites, but only the suburban and rural sites will used in this study.

The second type of evaluation will compare CAMx modeled concentrations and fluxes with C-130 and P-3 aircraft data. The aircraft flight paths will be mapped to grid cells within the CAMx 12 km modeling domain. For the grid cells containing aircraft transects, we will

document the model's performance in simulating measured isoprene fluxes as well as measured concentrations of OH, isoprene, 1st generation isoprene products, isoprene nitrates, terpenes, methanol, acetone, ozone and NOx. Model performance will be stratified with respect to high and low isoprene and NOx regimes where the regime is defined by the observed values. A CAMx run that uses the base-case MEGAN emission inventory prepared with default inputs will be evaluated in this manner, as will CAMx runs that used the improved MEGAN emission inventories. The performance of the CAMx runs will be compared and the effect of the MEGAN inventories on the CAMx model's ability to simulate the aircraft measurements will be determined.

In both the first and second types of evaluation, model performance will be reviewed using both graphical and statistical methods. Graphical methods will include spatial maps and time-series comparing model predictions to observations. Graphics may be developed using a mix of several plotting applications, including GIS, PAVE, Surfer, and NCAR/NCL. Statistical methods will include computation of metrics for bias and error between predictions and observations for the species listed above. Standard statistical metrics as described in EPA air quality modeling guidance (EPA, 2007) will be calculated. These include normalized mean and fractional bias (NMB and FB), and normalized mean and fractional absolute error (NME and FE) (Table 3). Use of mean normalized bias (MNB) and error (MNE) is not encouraged due to the propensity for misinterpretation and lack of symmetry around zero (they tend to be skewed by low observed concentrations with the bias skewed towards large positive numbers). Linear regression analysis (e.g., coefficient of determination, r^2) will be used to examine the model's ability to capture observed variability.

5.3 Audits of Data Quality

Aircraft Data: A member of the team who did not develop the aircraft data will review at least 10% of the data for quality assurance purposes.

Biogenic Emissions Modeling: A member of the research team who did not conduct the MEGAN modeling or MEGAN input data processing and model simulations will review at least 10% of the input data and model output for quality assurance purposes.

WRF Meteorological Modeling: A member of the research team who did not conduct the WRF modeling or the input data processing and model simulations will review at least 10% of the input data and model output for quality assurance purposes.

CAMx Modeling: A member of the research team who did not conduct the modeling or air quality model input data processing and model simulations will review at least 10% of the input data and model output for quality assurance purposes.

5.4 Data Management

Data generated for this project, including model inputs, final model outputs and various air quality observational data and statistical performance calculations, will be securely archived during the project on portable hard drives and stored for a period of at least three years following the completion of the project. All data obtained for this project will be stored in electronic format. Our teams' experience has been that 100+ GB hard drives provide an accessible and portable

system for storing data files of the size routinely encountered in the type of modeling activities for this effort. If data are provided on paper, the paper documents will be scanned to electronic PDF files for storage. The University of Texas will receive an electronic copy of all data sets.

The aircraft data used in this project is archived in data repositories at NCAR and NOAA, respectively. A master list of data from SAS is posted at http://data.eol.ucar.edu/master_list/?project=SAS and contains the C-130 terpenoid data used in this project. The data manager for the NCAR C-130 data is Steve Williams (sfw@ucar.edu). The C-130 data are currently password protected (available upon request), and will be publicly available on January 15, 2015. Data from the NOAA P-3 are posted at http://esrl.noaa.gov/csd/groups/csd7/measurements/2013senex/P3/DataDownload/ and are managed by Ken Aikin (kenneth.c.aikin@noaa.gov). These data are also password protected (available upon request), and will be publicly available on July 31, 2015.

6. REPORTING

ENVIRON will prepare monthly financial and technical reports which document the status of monthly project progress. Additionally, a quarterly report will be submitted at the end of each quarter. Interim reports/presentations may be provided upon request. A draft final report summarizing our analyses, findings, and recommendations will be prepared by April 30, 2015. Following receipt of comments from AQRP and TCEQ, a final report will be produced at the end of the project. The final report will meet State of Texas Accessibility requirements in 1 TAC 213. Electronic copies of all text, graphic, spreadsheet files and models used in the preparation of any documents related to the project reports, to document results and conclusions (e.g. sampling data, work files, etc.) or developed as work products under this Contract, will be supplied the conclusion of the project. All copies of deliverable documents and other work products will be provided in Microsoft Word and PDF format. Dr. Yarwood will supervise the completion of all reports and other deliverables.

7. REFERENCES

Dudhia, J. 1993. "A Non-hydrostatic Version of the Penn State/NCAR Mesoscale Model: Validation Tests and Simulation of an Atlantic Cyclone and Cold Front", Mon. Wea. Rev., Vol. 121. pp. 1493-1513.

Emery, C., E. Tai, and G. Yarwood (2001). "Enhanced Meteorological Modeling and Performance Evaluation for Two Texas Episodes." Prepared for the Texas Natural Resources Conservation Commission, by ENVIRON, International Corp, Novato, CA.

ENVIRON, 2013. The Comprehensive Air quality Model with extensions (CAMx) homepage, http://www.CAMx.com.

EPA, 2007. Guidance on the Use of Models and Other Analyses for Demonstrating Attainment of Air Quality Goals for Ozone, PM2.5 and Regional Haze. US Environmental Protection Agency, Research Triangle Park, NC. EPA-454/B-07-002. April. (http://www.epa.gov/ttn/scram/guidance/guide/final-03-pm-rh-guidance.pdf).

Guenther, A. (2013), Biological and Chemical Diversity of Biogenic Volatile Organic Emissions into the Atmosphere, ISRN Atmospheric Sciences, 2013(doi: 10.1155/2013/786290).

Guenther, A. B., X. Jiang, C. L. Heald, T. Sakulyanontvittaya, T. Duhl, L. K. Emmons, and X. Wang (2012), The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2.1): an extended and updated framework for modeling biogenic emissions, Geosci. Model Dev., 5(6), 1471-1492.

Hasel, M., C. Kottmeier, U. Corsmeier, and A. Wieser. 2005. Airborne measurements of turbulent trace gas fluxes and analysis of eddy structure in the convective boundary layer over complex terrain. Atmospheric Research 74 (1-4):381-402.

Hildebrandt-Ruiz, L. and G. Yarwood 2013. Interactions between Organic Aerosol and NOy: Influence on Oxidant Production. Final report for AQRP project 12-012.

Johnson, J., P. Karamchandani, G. Wilson, and G. Yarwood, 2013. TCEQ Ozone Forecasting System. Prepared for Mark Esters, TCEQ. November.

Karl, T., E. Apel, A. Hodzic, D. D. Riemer, D. R. Blake, and C. Wiedinmyer 2009. Emissions of volatile organic compounds inferred from airborne flux measurements over a megacity, Atmos. Chem. Phys., 9(1), 271-285.

Karl, T., P. K. Misztal, H. H. Jonsson, S. Shertz, A. H. Goldstein, and A. B. Guenther. 2013. Airborne flux measurements of BVOCs above Californian oak forests: Experimental investigation of surface and entrainment fluxes, OH densities and Dahmköhler numbers. J. Atmos. Sci., 70, 3277–3287.

Kemball-Cook, S.R., Y. Jia, R. C. Emery, R. Morris, 2005. "Alaska MM5 Modeling for the 2002 Annual Period to Support Visibility Modeling." Prepared for the Western Regional Air Partnership, Denver CO. September.

Lenschow, D. H., J. Mann, and L. Kristensen. 1994. How Long Is Long Enough When Measuring Fluxes and Other Turbulence Statistics. Journal of Atmospheric and Oceanic Technology 11 (3):661-673.

Mauder, M., R. L. Desjardins, and I. MacPherson. 2007. Scale analysis of airborne flux measurements over heterogeneous terrain in a boreal ecosystem. Journal of Geophysical Research-Atmospheres 112 (D13).

McNally, D. E., 2009. 12 km MM5 Performance Goals. Presentation to the Ad-Hoc Meteorology Group. June 25, 2009. Available at: http://www.epa.gov/scram001/adhoc/mcnally2009.pdf

Sakulyanontvittaya, T., G. Yarwood and A. Guenther. 2012. Improved Biogenic Emission Inventories Across the West. Final Report. Prepared for: Western Governors' Association, 1600 Broadway, Suite 1700, Denver, CO 80202. http://www.wrapair2.org/pdf/WGA_BiogEmisInv_FinalReport_March20_2012.pdf.

Skamarock, W. C., J. B. Klemp, J. Dudhia, D. O. Gill, D. M. Barker, W. Wang, and J. G. Powers, 2008. A description of the Advanced Research WRF Version 3. NCAR Tech Notes-475+STR. http://www.mmm.ucar.edu/wrf/users/docs/arw_v3.pdf.

Tesche, T.W., D.E. McNally, C.A. Emery, E. Tai (2001). "Evaluation of the MM5 Model Over the Midwestern U.S. for Three Oxidant Episodes." Prepared for the Kansas City Ozone Technical Workgroup, by Alpine Geophysics, LLC, Ft. Wright, KY, and ENVIRON International Corp, Novato, CA.