Quality Assurance Project Plan

Project 14-030
Improving Modeled Biogenic Isoprene Emissions under Drought Conditions and Evaluating Their Impact on Ozone Formation

Dr. Qi Ying
Texas A&M University

Dr. Gunnar W. Schade
Texas A&M University

Dr. John Nielsen-Gammon
Texas A&M University

Dr. Huilin Gao
Texas A&M University

Summary of Project

QAPP Category Number: III
Type of Project: Measurement

QAPP Requirements: This QAPP requires descriptions of project description and objectives; organization and responsibilities; scientific approach; sampling procedures; measurement 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

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DISTRIBUTION LIST

Elena McDonald-Buller, Project Manager, Texas Air Quality Research Program

Cyril Durrenberger, Quality Assurance Project Plan Officer, Texas Air Quality Research Program

Maria Stanzione, Program Manager, Texas Air Quality Research Program

Mark Estes, Project Liaison, Texas Commission on Environmental Quality

To be announced, Quality Assurance Project Plan Officer, Texas Commission on Environmental Quality

Table of Contents

1. Project Description and Objectives

1.1 Processes and Environmental Systems to be Evaluated

A number of studies have shown that drought will affect emissions of biogenic volatile organic compounds (BVOCs) due to its impact on plant physiological processes [e.g., 1, 2-17], triggering responses such as reduction in stomatal conductance and photosynthesis rates. However, treatment of drought effect in biogenic emissions models were derived based on limited observations and the appropriateness of these simple, linear parameterizations has not been extensively field tested yet. In Global Biosphere Emissions and Interactions System (GloBEIS) version 3, the influence of drought on isoprene emission is accounted for using a simple linear parameterization that scales the emission rates based on the widely used Palmer Drought Severity Index (PDSI). In Model of Emissions of Gases and Aerosols from Nature (MEGAN) version 2.1, isoprene emission rate is scaled by the difference between soil moisture (volumetric water content) and the wilting point. The most recent version of the Biogenic Emissions Inventory System version 3 (BEIS3) model (version 3.14) does not consider drought impacts on biogenic emissions. In addition to limitations in the parameterization of drought effects in emission models, field and laboratory measurements have shown that different tree species respond differently to drought conditions. While most plants are generally drought sensitive, some Texas grown oak species appear to be drought adapted. More data need to be collected on the drought adaptiveness and biogenic emissions from the trees in Texas. The current emission models do not treat the drought effect differently for different types of oak trees.

Predicting the drought effect on biogenic emissions requires accurate description of regional soil moisture. The capability of regional meteorological models in simulating the spatial and temporal variation of soil moisture and other meteorological parameters under Texas drought conditions has not been evaluated. The uncertainties in BVOC emissions and meteorological modeling will affect the capability of regional air quality models in reproducing or forecasting the air quality. The capability of air quality models in reproducing observed concentrations of criteria pollutants, especially ozone, under drought conditions needs to be evaluated.

1.2 Project Purpose and Objectives

Our project's objectives are: (1) to evaluate the MEGAN emission model (MEGAN 2.1), with a focus on isoprene predictions under drought conditions. The default drought parameterization in MEGAN and two new drought parameterizations, one to be provided by Dr. Alex Guenther and one based on new data to be collected in this study. (2) to evaluate the capability of the Weather Research and Forecasting (WRF) model in predicting meteorological conditions for air quality simulations under drought conditions; and (3) to evaluate the sensitivity of Community Multi-scale Air Quality (CMAQ) model ozone predictions in Southeast Texas when using different drought parameterizations for isoprene emissions. The following shows a list of tasks to be conducted in this study:

Task 1: Perform regional meteorology simulations using the Weather Research and Forecast (WRF) model.
Task 2: Perform field and laboratory measurements on common Texas tree species.
Task 3: Evaluate drought parameterizations for isoprene emissions.
Task 4: Perform regional BVOC modeling using MEGAN 2.1.
Task 5: Perform air quality simulations to evaluate the different BVOC drought parameterizations on ozone and isoprene concentrations
Task 6: Project Report and Presentation

2. Organization and Responsibilities

2.1 Project Organization

The project will be carried out by the Texas A&M University (TAMU) under a grant from the Texas Air Quality Research Program (AQRP) of the University of Texas, Austin. Dr. Qi Ying at TAMU serves as the Principal Investor (PI) with overall responsibility of the research and associated quality assurance. The TAMU team also includes co-Principal Investigators Dr. Gunnar W. Schade, Dr. John Nielsen-Gammon and Dr. Huilin Gao. The PI and Co-PIs will be supported by a postdoc and two PhD students, as well as a couple of undergraduate students to carry out the research. This project will be overseen by AQRP Project Manager Dr. Elena C. McDonald-Buller and TCEQ Project Liaison Mark Estes. The scientists working on this project and their specific responsibilities are listed in Table 1.

Table 1 A list of project participants and their responsibilities

Participant	**Project Responsibility**
Dr. Qi Ying	Principal Investigator (PI). Overseeing all aspects of this project, guiding a PhD graduate student to work on Task 1 (WRF modeling), Task 4 (BVOC emission modeling) and Task 5 (Air Quality Modeling), participating and coordinating in Task 2 and 3, and writing draft and final report.
Peng Wang	Ph.D. student. Working with Dr. Ying. Performing WRF, BVOC and air quality simulations.
Dr. Gunnar W. Schade	Co-PI. Leading Task 2 and 3. Responsible for guiding and assisting with the field and laboratory measurements, including selection of tree species and field locations, and smooth operation of the laboratory setup. Writing draft and final report
Dr. Monica Madronich	Postdoc research associate (PRA) working with Dr. Schade. Conducting field and laboratory measurements.
Undergraduate student (to be named)	Assist Dr. Schade and the PRA on field operation and data analysis.
Dr. John Nielsen-Gammon	Co-PI. Performing initial WRF modeling and provide suitable configurations for WRF modeling under drought conditions. Writing draft and final report.
Dr. Huilin Gao	Co-PI. Responsible for guiding and assisting with preparing satellite products needed for the project. Writing draft and final report.
Ph.D. student (to be named)	Ph.D. student working with Dr. Gao. Preparing satellite products needed for the project.

2.2 Project Schedule and Milestones

The overall timeline of the project is shown in the following table.

Table 1: Project Timetable

TASK (lead PI, co-PI) *month*	06/14	07/14	08/14	09/14	10/14	11/14	12/14	01/15	02/15	03/15	04/15	05/15	06/15
	5	6	7	8	9	10	11	12	13	14	15	16	17
1. Perform WRF simulations (Ying, Nielsen-Gammon)	🟩	🟩	🟩	🟩									
2. Perform additional field and laboratory measurements (Schade)	🟪	🟪	🟪	🟪	🟪	🟪							
3. Evaluate drought parameterizations for isoprene emissions (Schade, Guenther)				🟧	🟧	🟧	🟧	🟧	🟧	🟧			
4. Perform regional BVOC models using MEGAN (Ying, Gao)					🟦	🟦	🟦	🟦	🟦	🟦	🟦		
5. Perform regional air quality simualtions (Ying)		🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	
6. Project report and presentation (Ying, Schade)												🟪	🟪

Detailed timelines for the task 2 and 3 are available in Part II of this QAPP.

The following are considered milestones of the project:

1) 30 September 2014: All WRF simulations completed.
    a. 15 July 2014: Preliminary WRF simulation completed; optimal configuration provided.
2) 30 November 2014: All field and laboratory completed. (see detailed milestone in Part II of the QAPP)
3) 31 March 2015: Drought parameterizations evaluation completed. (see detailed milestone in Part II of the QAPP)
    a. October 2014: A new parameterization will be provided by Dr. Guenther and incorporated in MEGAN.
4) 15 April 2015: BVOC modeling completed.
    a. October 2014: 2007, 2011 emission without drought effect
    b. November 2014: 2011 emission with original MEGAN parameterization
    c. December 2014: 2011 emission with updated parameterization from Dr. Guenther
    d. April 2014: 2011 emission with parameterization developed in this study
5) 30 May 2015: All CMAQ modeling completed
    a. November 2014: Simulation for 2007 and 2011 using base case emission (without drought effect)
    b. December 2014: Simulation for 2011 with original MEGAN parameterization
    c. January 2014: Simulation for 2011 with the updated parameterization from Dr. Guenther
    d. April 2014: Simulation for 2011 with the parameterization developed in this study

3. Scientific Approach

3.1 Secondary Data Needed

The secondary data needed for each Task is listed below:

Task 1: Modeling input data for the WRF meteorological model to simulate two seven-month episodes (April to October, during which isoprene emissions from trees are most significant), one dry episode in 2011 and one wet episode in 2007. Observation data, including surface wind speed, wind direction, temperature, relative humidity, and soil moisture, and upper air wind and temperature profiles, are needed to compare model predictions with observations.

Task 2: Satellite derived photosynthetically active radiation (PAR) in case measured PAR is not available.

Task 3: No secondary data is needed other than satellite derived PAR in case measured PAR is not available.

Task 4: Modeling input data for the MEGAN biogenic emissions model to simulate two seven-month episodes, one dry episode in 2011 and one wet episode in 2007.

Task 5: Modeling input data for the CMAQ air quality model to simulate two seven-month episodes, one dry episode in 2011 and one wet episode in 2007. Observation data , including isoprene from TCEQ sites equipped with automatic gas chromatography (AutoGC) and ozone, nitrogen oxides (NOx) and carbon monoxide (CO) from all available TCEQ's continuous air monitoring stations (CAMS), are needed to compare model predictions with observations.

3.2 Field and Laboratory experiments

Field and laboratory experiments will be performed to measure isoprene emissions flux from common Texas trees during Task 2. A separate QAPP (QAPP: Part II) accompanies this QAPP.

4. Quality Metrics

4.1 Quality Requirements

Reasonably accurate input data for WRF, MEGAN and CMAQ modeling, such as the initial and boundary conditions and the land use/land cover data, are needed for the project. However, the required accuracy for these data is not straightforward

4.2 Procedure to Determine the Quality of Secondary Data

4.2.1. Procedure for WRF modeling

WRF Input data: The WRF model domain for this study follows the Regional Planning Organization (RPO) WRF domains used by the TCEQ for ozone air quality modeling. Three nested domains will be used (na_36km, sus_12km, tx_4km). Lambert Conformal Conic projection parameters, and other details such as vertical domain structures, can be found on the TCEQ website: http://www.tceq.texas.gov/airquality/airmod/rider8/modeling/domain. Initial and boundary conditions for WRF modeling will mostly be taken from the North American Regional Reanalysis (NARR) data (available from National Oceanic and Atmospheric Administration (NOAA), http://www.esrl.noaa.gov/psd/data/gridded/data.narr.html) with 32-km horizontal resolution and 3-h time resolution. Figure 1 shows an example of the spatial coverage of the data. Land use/land cover data for WRF/CMAQ modeling will be based on the 30-m-resolution National Land Cover Database 2011 (NLCD 2011).

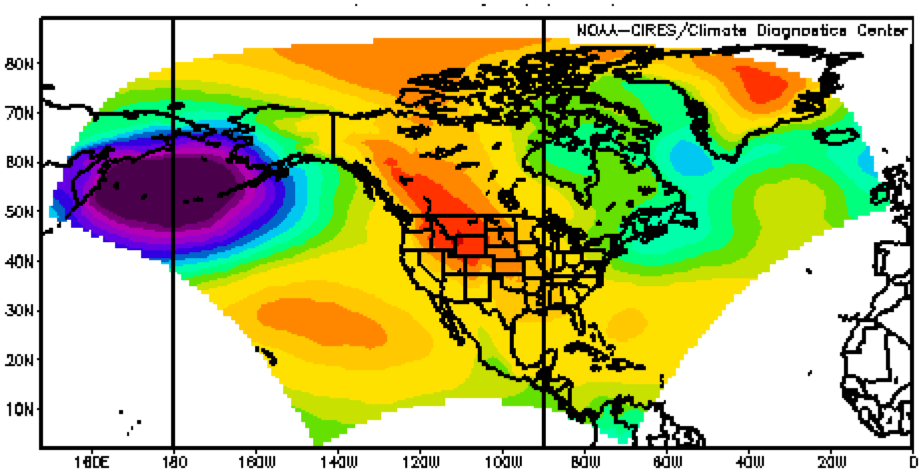

Figure 1: Spatial coverage of the NARR reanalysis data (figure source: NOAA). The native data are in a Lambert Conformal Conic grid, with corners at 12.2N;133.5W, 54.5N; 152.9W, 57.3N; 49.4W , and 14.3N;65.1W (essentially, North America). The grid resolution is 349x277 which is approximately 0.3 degrees (32km) resolution at the lowest latitude.

The quality of these data has been checked by the data developers and no additional QA will be conducted other than making sure the correct files are being used for the modeling. The land use and land cover data will be updated to match those used by the TCEQ.

The quality of these land use and land cover data is quality checked by TCEQ so no additional check is necessary other than making sure that they are correctly merged into the WRF input files. Initial land surface conditions interpolated from the North American Land Data Assimilation System (NLDAS) archive. Again, the quality of the archived data is checked independently so no additional check will be performed other than making sure they are inserted into the WRF initial files correctly.

WRF modeling: Log files and run scripts will be independently checked to ensure that correct model configurations and input files are used for the simulation. The log files will be checked to ensure that all simulations are completed successfully. As with the input files, the output files will also be stored in directories that correctly reflect the nature of the simulation.

WRF output: Model simulated wind speed, wind direction, surface temperature, relative humidity, and soil moisture content will be evaluated against all available observations using statistical measures to examine model performance. Soil moisture predictions will also be compared with the 25-km gridded surface soil moisture data from the Advanced Microwave Scanning Radiometer (AMSR-E) onboard NASA's Earth Observing System (EOS) Aqua satellite. Necessary adjustments to the WRF code and configurations will be made by Dr. Nielsen-Gammon based on the model performance, and an additional set of simulations will be made and evaluated by Dr. Ying. Model performance statistics to evaluate WRF model results will be based on Emery et al.[18], including mean fractional bias (MB), gross error (GE) and root mean square error (RMSE) (See Table 2 for the definition of these statistical measures).

4.2.2 Procedure for MEGAN modeling

MEGAN input files: The leaf area index (LAI) will be from the Moderate Resolution Imaging Spectroradiometer (MODIS) 1-km resolution products [19] by Dr. Gao's group. The MODIS products are also quality checked so no additional QA is necessary. The LAI in urban areas will be replaced with values recommended by TCEQ staff. Urban mask file will be acquired from TCEQ and no additional QA is needed other than making sure that it is applied correctly. We will also consult Dr. Sorin Popescu in the Ecosystem Science and Management Department at TAMU for recommendations about appropriate LAI for Texas urban areas. Plant functional type (PFT) will be taken from Dr. Guenther directly and no additional QA will be performed. Other meteorology input files are based on WRF output and will be quality checked as described in section 4.2.1. Per discussion with TCEQ, several other land use/land cover databases might also be available for the project. Including the 30-m resolution data developed by ENVIRON/Pacific Northwest National Laboratory (PNNL) and the Texas Parks and Wildlife Department (TPWD) 10-m resolution data for Texas ecosystems (might be useful to update base MEGAN emission rates). Depending on TCEQ's initial evaluation of the datasets and their model-readiness, they can be adopted for this project.

MEGAN output files: Simulated biogenic emissions will be visualized hour by hour. Monthly averaged emissions will be calculated and compared with historical data to ensure the results are in reasonable ranges.

4.2.3 Procedure for CMAQ modeling

CMAQ Input data: The CMAQ model domain for this study follows the Regional Planning Organization (RPO) Comprehensive Air Model with Extensions (CAMx) domains used by the

TCEQ for ozone air quality modeling. Three nested domains will be used (rpo_36km, tx_12km, tx_4km, see Figure 2 below). Lambert Conformal Conic projection parameters, and other details such as vertical domain structures, can be found on the TCEQ website: http://www.tceq.texas.gov/airquality/airmod/rider8/modeling/domain.

Figure 2: CMAQ modeling domains. The largest to the smallest domains are rpo_36km, tx_12km and tx_4km, as discussed in the text above.

Input data for CMAQ modeling includes meteorology, emissions and initial/boundary conditions. Meteorology input files will be quality checked as described in section 4.2.1. Biogenic emissions are quality checked, as described in section 4.2.2. Emission inventory for the CMAQ simulations will be developed based on the National Emission Inventory (NEI) 2008 and 2010, and TCEQ's own inventory for those years if they are available. All anthropogenic emissions for 2007 will be based on NEI 2008, and 2011 emissions will be based on NEI 2012. Emissions will be adjusted to represent 2007 and 2012 emissions using the NEI Air Pollutant Emissions Trends Data (http://www.epa.gov/ttn/chief/trends/). Biogenic emissions will be generated for the 2007 and 2011 episodes directly, driven by WRF simulated meteorology for these two years. The VOC emissions will be speciated for the Carbon Bond mechanism version 2005 (CB05). The speciation profiles provided with the NEI will be used directly. As these speciation profiles are quality checked by EPA, no additional quality checks will be conducted. Speciated emissions from TCEQ, if available, will be used directly. Emission totals of the species will be checked with totals calculated from the raw inventory to ensure that no emissions are neglected or double counted. Initial condition/boundary condition (IC/BC) based on

CMAQ's default IC/BC files will be used for 36-km simulations. For 12 and 4-km simulations, IC and BC will be based on simulation results of the parent domain. The impact of initial conditions decrease as simulation goes on. First five days of simulation results will not be used in subsequent analysis to avoid initial condition impact. Likewise, 36-km boundary conditions only impact areas near the boundaries of the 36 km domain. The quality of IC/BC will be indirectly checked through model performance evaluation, although they are not expected to affect evaluation of isoprene emissions in this study. Emissions using different drought parameterizations will be stored in different subdirectory with clear names to ensure that no confusion about these files in future simulations.

CMAQ Modeling: For each CMAQ model simulation, run scripts and log files will be kept in a permanent location. The run scripts will be independently checked to ensure that correct mechanisms and input files are used for the simulation. The log files will be checked to ensure that all simulations are completed successfully. As with the input files, the output files will also be stored in directories that correctly reflect the nature of the simulation.

CMAQ Model Performance: The performance of the CMAQ model with different drought parameterizations will be evaluated extensively with available surface observation data measured at the Continuous Air Monitoring Station (CAMS) operated by TCEQ and other surface observation available in the Air Quality System (AQS) from United States Environmental Protection Agency (US EPA) (available from http://www.epa.gov/ttn/airs/airsaqs/detaildata/downloadaqsdata.htm) throughout this episode. Both graphical and statistical measures will be used in the model performance evaluation. Graphical methods will include spatial distribution maps, scatter plots and time-series comparing model predictions to observations at regular TCEQ and EPA monitoring stations. To compare results from different drought parameterizations, regional absolute and relative difference plots of isoprene, ozone and isoprene oxidation products will be generated. Statistical methods will include computation of metrics of bias and error between predictions and observations for ozone and precursors using the guidance of U.S. EPA (2007). Statistical measures are shown in Table 2:

Table 2: Definition of Model Performance Statistical Measures

Statistical Measures	Definition
Mean bias	$\mathrm{MB} = \frac{1}{N}\sum_{i=1}^{N}(C_{m,i} - C_{o,i})$
Gross error	$\mathrm{GE} = \frac{1}{N}\sum_{i=1}^{N}\lvert C_{m,i} - C_{o,i}\rvert$
Root mean square error	$\mathrm{RMSE} = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(C_{m,i} - C_{o,i})^2}$
Normalized mean bias	$\mathrm{NMB} = \frac{\sum_{i=1}^{N} C_{m,i} - C_{o,i}}{\sum_{i=1}^{N} C_{o,i}}$
Normalized mean error	$\mathrm{NME} = \frac{\sum_{i=1}^{N}\left\lvert C_{m,i} - C_{o,i}\right\rvert}{\sum_{i=1}^{N} C_{o,i}}$
Mean normalized bias	$\mathrm{MNB} = \frac{1}{N}\sum_{i=1}^{N}\frac{C_{m,i} - C_{o,i}}{C_{o,i}}$
Normalized gross error	$\mathrm{NGE} = \frac{1}{N}\sum_{i=1}^{N}\frac{\left\lvert C_{m,i} - C_{o,i}\right\rvert}{C_{o,i}}$
Mean fractional bias	$\mathrm{MFB} = \frac{2}{N}\sum_{i=1}^{N}\frac{C_{m,i} - C_{o,i}}{C_{m,i} + C_{o,i}}$
Mean fractional error	$\mathrm{MFE} = \frac{2}{N}\sum_{i=1}^{N}\frac{\lvert C_{m,i} - C_{o,i}\rvert}{C_{m,i} + C_{o,i}}$
Accuracy of paired peak	$\mathrm{APP} = \frac{C_{p,opeak} - C_{o,opeak}}{C_{o,opeak}}$
Accuracy of unpaired peak	$\mathrm{AUP} = \frac{C_{p,ppeak} - C_{o,opeak}}{C_{o,opeak}}$

Note: C_m is the model-predicted concentration i, C_o is the observed i, and N equals the number of prediction-observation pairs drawn from all monitoring stations. The subscripts ppeak and opeak are the hours when predicted and observed peak concentrations occur.

5. Data Analysis, Interpretation, and Management

5.1 Data Reporting

The project team will issue monthly reports to the assigned AQRP project manager and a draft and fully revised final report at the end of the project. The reports will summarize steps that have been taken for quality assurance project data and results.

5.2 Audit of Data Quality

The 10% data quality audit requirement for data used in each task will be satisfied by:

Task 1: WRF model input data and configurations will be inspected first by Ph.D. student Peng Wang and second by Dr. Qi Ying. All WRF model results will be inspected first by Peng Wang and second by Dr. Qi Ying. Dr. John Nielsen-Gammon will independently check at least 10% of the model outputs.

Task 2: Measured isoprene flux and other associated data will be examined by first by Dr. Monica Madronich, and second by Dr. Gunnar Schade. Dr. Qi Ying will inspect at least 10% of the measured data independently.

Task 3: All meteorology and soil data needed to evaluate the drought parameterization will be inspected by Dr. Monica Madronich, and second by Dr. Gunnar Schade. Dr. Qi Ying will inspect at least 10% of the input data independently. The satellite PAR data will first be inspected by Dr. Gao and second by Dr. Ying.

Task 4: MEGAN model configuration and input data will be first inspected by Ph.D. student Peng Wang and second by Dr. Qi Ying. MEGAN generated emission fields will also be inspected by Ph.D. student Peng Wang and second by Dr. Qi Ying. At least 10% of the output fields will be independently checked by Dr. Gunnar Schade. LAI and PAR data needed for the MEGAN modeling will be inspected first by Dr. Huilin Gao and second by Dr. Ying. An independent check of 10% of the input LAI and PAR will be done by Dr. Gunnar Schade.

Task 5: Input data files needed to generate the anthropogenic emission files for modeling periods in 2007 and 2011 will be checked by Ph.D. student Peng Wang and second by Dr. Qi Ying. Generated anthropogenic emission files will be inspected by Ph.D. student Peng Wang and second by Dr. Qi Ying. Biogenic emission inputs are checked in Task 4 and meteorology inputs are checked in Task 1. Dr. Gunnar Schade will participate in the QA process of the CMAQ output data.

Data audit results will be documented in the draft and final report.

5.3 Data Summary for Reporting

Task 1: WRF Model results will be summarized and presented graphically, as time series and regional scalar and vector plots. Model performance statistics will be presented in a tabular form.

Task 2: Measured flux data, and other met and soil moisture data will be summarized in tabular form.

Task 3: Evaluation of different parameterizations will be presented graphically. The performance of each parameterization will be summarized in tabular forms. Regional plots will be used to summarize the satellite PAR and LAI data.

Task 4: Isoprene emissions generated using different soil moisture parameterization, and their absolute and relative differences will be presented graphically. Total emissions of different BVOCs will be summarized in tabular forms.

Task 5: To compare results from different drought parameterizations , regional absolute and relative difference plots of isoprene and ozone and isoprene oxidation products (methacrolein (MACR) and methyl vinyl ketone (MVL)) will be generated. Model results will be compared with observations graphically on time series and regional plots. Scatter plots may also be used. The normalized gross error parameter provides an overall assessment of model performance and can be interpreted as precision, and the normalized bias parameter measures a model's ability to reproduce observed spatial and temporal patterns and can be interpreted as accuracy. Therefore, modeled concentrations of isoprene, ozone and isoprene oxidation products will also be compared with observations using statistical measures recommend by the U.S. EPA (U.S. EPA, 2007), namely the unpaired predicted-to-observed peak ozone ratio (AUP), the normalized gross error (NGE), and the mean normalized bias (MNB). The U.S. EPA criteria (U.S. EPA, 2007) require an accuracy of unpaired peak ozone ratio (AUP) of $<\pm 20\%$, a mean normalized bias (MNB) of $\pm 15\%$ and a normalized gross error (NGE) of $< 35\%$ above a threshold ozone value of 60 ppb, and the AUP, MNB and NGE are defined in Table X.

QA Findings including any errors or incorrect descriptions will be corrected and reported in the final report.

5.4 Data Storage

Data generated for this project, including model inputs and final model outputs, will be securely archived during the project and transferred to the AQRP following the completion of the project. All data obtained for this project will be stored in electronic format. If data are provided on paper, the paper documents will be scanned to electronic PDF files for storage. Further details on storing data for WRF, MEGAN and CMAQ modeling are provided below. Details for flux data taken in Task 2 will be discussed in Part II of the QAPP document.

All input emissions inventories for air quality calculations and input data for biogenic emissions modeling and meteorological predictions will be stored on redundant arrays of inexpensive disks (RAIDs) to guard against hardware failure. Likewise, all WRF, MEGAN and CMAQ model output that is generated during the current project will be stored on RAIDs. Each input our output file will be assigned a unique name describing the type of file, the version, and the simulation date. A master description of all the data formats used for air quality, biogenic emissions and meteorology input and output files in the current project will be created at TAMU. Emissions inputs for air quality modeling will be created in Sparse Matrix Operator Kernel Emissions (SMOKE) formats and processed to CMAQ Input/Output Applications Programming Interface (IOAPI) format. All data format descriptions will be made available along with the data itself. A summary description of each file will be published on a password-protected website maintained by Dr. Qi Ying. Data files will be made available for download after the final year of the project. The download website will continue to be maintained after that time if it is under active use, or the files will be archived at TAMU and available by request to the project PI after that time. Data will be made available via network transfer, DVDs, or external hard drives (all media supplied by the requesting party).

6. Reporting

6.1 Deliverables

Monthly progress reports; draft and final project report. Other electronic data for WRF, MEGAN and CMAQ modeling, including all input and output files. Detailed deliverables and their due dates are listed below:

1. Executive summary. Due date: May 30, 2014.

2. Quarterly Reports. Quarterly Reports will provide a summary of the project for each reporting period. Due dates are listed in Table 3:

Table 3: Due dates for Quarterly Reports

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

3. Technical Reports. Technical Reports will be submitted monthly to the Project Manager and TCEQ Liaison as a Word document. Due dates are listed in Table 4:

Table 4: Due dates for technical reports

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

4. 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 are listed in Table 5.

Table 5: Due dates for financial status reports

Report	Period Covered	Due Date
FSR #1	Project Start – July 31, 2014	Friday, August 15, 2014
FSR #2	August 1 - 31, 2014	Monday, September 15, 2014
FSR #3	September 1 - 30, 2014	Wednesday, October 15, 2014
FSR #4	October 1 - 31, 2014	Monday, November 17, 2014
FSR #5	November 1 - 30 2014	Monday, December 15, 2014

FSR #6	December 1 - 31, 2014	Thursday, January 15, 2015
FSR #7	January 1 - 31, 2015	Monday, February 16, 2015
FSR #8	February 1 - 28, 2015	Monday, March 16, 2015
FSR #9	March 1 - 31, 2015	Wednesday, April 15, 2015
FSR #10	April 1 - 28, 2015	Friday, May 15, 2015
FSR #11	May 1 - 31, 2015	Monday, June 15, 2015
FSR #12	June 1 - 30, 2015	Wednesday, July 15, 2015
FSR #13	Final FSR	Wednesday, August 15, 2015

5. 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: Monday, May 18, 2015

6. 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.

7. 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.

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

6.2 Expected Final Products

An approvable final report for this project will be prepared and submitted by the end of this project. Multiple conference papers and/or peer-reviewed journal papers (e.g., papers in journal Atmospheric Environment) on isoprene emission characterization and WRF/CMAQ modeling of isoprene under drought and wet conditions are expected to be produced after completion of this project. Data acquired from field experiment will be included in monthly technical report and final report (see Part II of the AQRP for details). Modeling datasets to be submitted for archive include the following items:

1. All WRF modeling files, including raw input data to generate initial and boundary conditions, land use/land cover data, and WRF output files.
2. All MEGAN modeling files, including MODIS LAI datasets, satellite PAR, processed meteorological fields, PFT fields, emission factor fields, and MEAGN intermediate and final output files.
3. All CMAQ modeling files, including initial and boundary conditions for nested domains, photolysis rates, emissions, raw CMAQ output files, processed time series at monitors and corresponding observations.

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Quality Assurance Project Plan: Part II

Project 14-030

Improving Modeled Biogenic Isoprene Emissions under Drought Conditions and Evaluating Their Impact on Ozone Formation

Principal Investigator:

Dr. Qi Ying, Texas A&M University

Co-Principal Investigators:

Dr. Gunnar W. Schade, Texas A&M University

Dr. John Nielsen-Gammon, Texas A&M University

Dr. Huilin Gao, Texas A&M University

Summary of Project

QAPP Category Number: III

Type of Project: Measurement

QAPP Requirements: This QAPP requires descriptions of project description and objectives; organization and responsibilities; scientific approach; sampling procedures; measurement procedures; quality metrics; data analysis, interpretation, and management; reporting; and references.

QA Requirements:

Audits of Data Quality: 10% Required;

Report of QA Findings: Required in final report

Revision 1: June 11, 2014

DISTRIBUTION LIST

Elena McDonald-Buller, Project Manager, Texas Air Quality Research Program

Cyril Durrenberger, Quality Assurance Project Plan Officer, Texas Air Quality Research Program

Maria Stanzione, Program Manager, Texas Air Quality Research Program

Mark Estes, Project Liaison, Texas Commission on Environmental Quality

To be announced, Quality Assurance Project Plan Officer, Texas Commission on Environmental Quality

Contents

1. Project Description and Objectives

Biogenic volatile organic compounds (BVOCs) - mostly emissions of isoprene from deciduous tree species - contribute significantly to ozone production in Texas [1], particularly in the Houston area. Several ground based [2-6] and airborne measurements [5, 6] have been carried out in central and east Texas, which showed that isoprene abundances in the boundary layer are consistent with biogenic emissions models within a factor of two. Land use data bases used in this modeling contain dominantly isoprene-emitting oak, particularly post oak (*Q. stellata*)[7]. Oaks are a common part of the Texas landscape such as in the ecoregions of *Pineywoods*, *Post Oak Savannah*, *Blackland Prairie*, and the *Edwards Plateau*. It is notable that higher emitter densities were not always correlated to higher ambient isoprene abundances [5, 6], and it remains yet unknown whether these discrepancies occurred dominantly as a result of errors in emissions, or errors in transport and chemistry modeling [6]. The extreme Texas drought of 2011 brought very high ozone abundances in east Texas and since BVOCs are a dominant contributor to hydroxyl radical reactivity fueling ozone production, the BVOC, and particularly isoprene, emissions inventory for Texas is a crucial input parameter for ozone forecasting and modeling.

While boundary layer mixing ratios of biogenic VOC appear to be consistent with modeled emissions within the errors of modeled and measured data (factor 2) [6], it is unknown whether that supports current emission rate and chemical transport modeling or is caused by cancelling errors in these models. Direct isoprene flux measurements over an urban area in Houston [8] showed that surface area coverage of trees (biomass) and accurate local versus regional isoprene emitter information is critical in a heterogeneous landscape to validate isoprene emission modeling. Particularly during hot summer days when isoprene emissions and subsequent ozone production rates are expected to be high, emissions modeling needs to be reliable for accurate air quality assessments. In addition, the 2011 Texas drought demonstrated that reduced isoprene emissions from mature, field-grown trees can be triggered by low soil moisture levels (Barta, Gramann, White, and Schade, *AGU Fall Meeting 2011*, B54A-07) as drought progresses. However, the drought effect on isoprene emissions is not well studied, particularly in isoprene emitting oak species [9-15] growing in Texas. Individual studies suggest that aside from emissions reductions lagging photosynthesis reductions, the regular, strong temperature response of isoprene emissions may be altered under drought stress and emissions can be affected after drought relief (rewatering).

Hence, our objectives are to investigate the effects of drought stress on photosynthesis and isoprene emissions of typical Texas oak species. We will be using both field measurements on mature trees and greenhouse measurements on seedlings exposed to controlled drought conditions. Data will be used to forward a new drought parameterization for isoprene emissions that can be incorporated into the current emissions modeling framework used in Texas.

2. Organization and Responsibilities

Overall project organization and responsibilities are documented in the Part I of the QAPP. Dr. Qi Ying (PI) will oversee the progress of the entire project.

2.1. Organization and Responsibilities

Project Managers: Dr. Qi Ying, Associate professor (TAMU PI)

Dr. Gunnar W. Schade, Associate Professor (TAMU Co-PI)

Dr. Huilin Gao, Assistant Professor (TAMU Co-PI)

Dr. John Nielsen-Gammon, Professor (TAMU Co-PI)

Laboratory Manager: Dr. Monica Madronich, Postdoctoral Research Associate

Field team leader: Dr. Gunnar W. Schade, Associate Professor (TAMU Co-PI)

QA officer: TBD (TCEQ)

Data reviewers: Dr. Qi Ying, Associate professor (TAMU PI)

Dr. Gunnar W. Schade, Associate Professor (TAMU Co-PI)

The following are key personnel of this project (Task 2):

Dr. Gunnar W. Schade
Atmospheric Sciences
Texas A&M University
1104 Eller O&M Building
College Station, TX 77843-3150
ph.: (979) 845 0633
e-mail: gws@geos.tamu.edu
Fax: (979) 862-4466

Dr. Qi Ying
Civil & Environmental Engineering
Texas A&M University
College Station, TX 77845
ph.: (979) 845 9709
e-mail: qying@civil.tamu.edu
Fax: (979)

Dr. Monica Madronich

Atmospheric Sciences

Texas A&M University

1104A Eller O&M Building

College Station, TX 77843-3150

e-mail: monica.madronich@gmail.com

Fax: (979) 862-4466

The project is going to be directed and coordinated by Drs. Ying and Schade.

2.2. Project Schedule and Milestones

Table 1 Detailed Timetable for Task 2 (shading represents spin-up and -down times (line pattern), or presence and intensity of activity (light and dark grey color))

task / month	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun
Measurements		█	█	█	█	█							
phase I	▨												
phase II		█	█										
phase III			▨	█	█	▨							
data analysis		▨	▒	▒	▒	▒	▒	▒	▒				
Reporting	▒	▒	▒	▒	▒	▒	▒	▒	█	█	█	█	█

The following individual achievements (tasks list) are suggested as milestones, as tasks to be achieved in this order and within the time frame given to assure that the objectives of this project can be addressed.

a) June 2014
    a. assess seedling mortality rates
    b. maintain water status of all living seedlings
    c. begin leaf-level physiology and isoprene emission baseline measurements
    d. send out purchase orders for consumables
    e. execute 1st field trip to Freeman ranch for *Q. fusiformis* measurements, and two regular field trips
b) July 2014
    a. commence baseline measurements (phase II)
    b. maintain water status of all seedlings
    c. set up data logger for greenhouse gas environmental monitoring and soil moisture monitoring
    d. execute two regular field trips
c) August/September 2014
    a. evaluate baseline measurements
    b. select and mark trees for intermediate and drought treatments
    c. begin treatment schedule
    d. execute 2nd field trip to Freeman ranch for *Q. fusiformis* measurements, and two regular field trips
    e. suggest preliminary drought response parameterization based on field data in Sep. 2014
d) October/November/December 2014
    a. compare baseline to treatment measurements
    b. analyze observed drought responses of seedlings and field-grown mature trees
    c. execute two regular field trips in October
    d. submit data files to UT
e) spring 2015
    a. analyze drought response relationships; compare isoprene field data to seedling data
    b. provide (final) drought response parameterization
    c. submit data files to UT
    d. submit final report to UT

3. Scientific Approach

This project collects new data on isoprene emissions in Texas with a specific focus on the effects of drought on these emissions, and compares the results to published data in the scientific literature, as well as to model outputs based on that literature. Data quality objectives focus on measured isoprene fluxes, which are determined by a flow-through chamber approach.

3.1 Experimental Design

Concentrations of isoprene will be measured with an established analytical technique listed in Table 2 below. Measurement accuracy is most relevant. It is commonly dominated by the accuracy of the provided standard gas, the error made during its dilution into the matrix for calibration, and the precision of the measurement technique. Our quality objectives for these parameters are listed in Table 2.

Plants selected for this study include field-grown, mature trees and seedlings grown in a greenhouse. The former are selected based on availability at established field sites, which include local microclimate monitoring using a weather station (http://atmo.tamu.edu/oaktreeproject/). The latter were selected based on previous field measurement results and approximately 100 individuals were potted in spring 2014 for growth and use in this project.

3.2 Field measurement procedures

Field measurements are designed to obtain real-world, in-situ observations of photosynthesis and isoprene emissions under natural conditions. The trees' growth environment is monitored at a nearby weather station (Onset HOBO U30 with "smart sensors"), which records pressure, air temperature and relative humidity, wind speed and direction, rainfall and "leaf" wetness, volumetric soil moisture at 10 cm depth, photosynthetically active radiation (PAR), and ambient carbon dioxide (Vaisala GMP343 probe) and ozone (2BTEch model 202) mixing ratios. The stations record values every 10 s and store as 1-min averages. They are downloaded regularly (approx. biweekly), at which time the carbon dioxide probe is calibrated and the ozone instrument zeroed. Data is backed up to a portable hard disk upon return to the laboratory.

Both the field and greenhouse measurements consist of in-situ leaf-level measurements of plant physiological parameters (leaf temperature, CO_2 (assimilation, P_n) and H_2O (transpiration) exchange rates, stomatal conductance (g_s), and leaf internal $[CO_2]$ (C_i), and simultaneously emitted isoprene. The instrument employed is a 2010 model CIRAS 2 leaf photosynthesis analyzer with a 2.5 cm^2 leaf area cuvette attachment, appropriate for the investigated species, with temperature control from 10 °C below or above ambient, and light-level control from zero to above 2000 PAR (http://www.ppsystems.com/ciras2_portable_photosynthesis_system.htm). The system uses a pair of non-dispersive infrared (NDIR) analyzers to measure CO_2 and H_2O mixing ratios. The analyzers are regularly zeroed and balanced against each other for quality control. An instrument overhaul and a calibration check are budgeted.

The field data acquisition protocol is as follows:

1. turn on and equilibrate analyzer in the field (typically 20 min warm-up);
    1.1 obtain neutral "no-leaf" reading (zero fluxes) for quality control
    1.2 select CO_2 set-point (leaf exposure mixing ratio) to be 400 ppm; select temperature to be 30 °C and light level 1000 PAR units ("standard conditions")
    1.3. begin data recording
2. insert leaf in cuvette and wait for CO_2 set-point to be reached (5 min)
3. wait for leaf to equilibrate to cuvette conditions (3-10 min)
4. manually record equilibrium readings and sample volatiles (3 min)
5. confirm leaf equilibrium after sampling (1 min) for quality control
6. zero and balance the 2-channel NDIR analyzer regularly as required during field data acquisition (approximately hourly)
7. repeat 2.-5. for the next leaf

All measurements are taken from attached, intact leaves on the sun-exposed side of the tree that can either be reached from the ground or via a ladder. Sampling commences when targeted leaves have experienced full sun conditions for at least an hour prior to any measurements. Thus, field work does not usually begin before 10:00 h local standard time (LST) and typically ends before 18:00 h LST. After each measurement, the leaf is excised from the twig for subsequent laboratory based dry leaf mass measurements, which relate area-based to biomass based emissions (section B2.3).

All analyzer data are stored as ascii files on the analyzer's hard disk. Typical data density is 6 measurements per minute. Upon return to the laboratory data is downloaded and backed up onto a PC and a portable hard disk backup device before further processing.

3.3 Greenhouse measurement procedures

All greenhouse-grown seedling leaf measurements follow the same protocol as the field-based, mature tree measurements with the exception of leaf removal. After a leaf measurement, the seedling leaf will not be abscised so as to be available for another, future measurement. Instead, a protocol will be kept of

- pot number, seedling species and number of leaves per seedling
- leaf position (node) and size

until close to the end of the growing season. After the designated last measurement on a leaf, the leaf will be abscised and returned to the laboratory for dry weight determination.

Unlike the field-grown trees, seedlings growing in the greenhouse all experience the same physical environment (light, temperature, humidity). The control variable in the greenhouse is soil moisture as the driving force of drought stress (see workplan). Thus, our experimental design is a 1-factor approach, in which everything else but soil moisture is "held constant" at greenhouse environmental conditions

The greenhouse physical growth environment will be monitored using a Campbell Scientific Inc. data logger. Temperature and relative humidity will be monitored at two heights inside the greenhouse and one outside location for reference. Light (PAR) will be monitored close to the "canopy". Soil moisture will be monitored in 12 pots, four pots per treatment. For quality control, all soil moisture sensors (Decagon model EC5) will be compared in a single, wide diameter pot filled with the same soil mixture before deployment into the seedling pots. In addition, the four pots per treatment will be changed once to twice during the experiment to avoid continuous effects on seedlings, if any.

Greenhouse environment data will be downloaded once a week and processed to assure that watering schedules achieve the desired soil moisture levels per treatment, with corrective action being taken if pots fall outside a 10% relative variability margin.

Table 2: Data Quality Objectives (1 ppb = 10^{-9} mol mol^{-1})

Parameter	Sensitivity	Precision	Accuracy	comment
CO_2 / H_2O	0.1 ppm / 0.01 ppth	<0.5%	±2%	
isoprene	0.01 ppb (0.5 L sample)	<5%	< ±10%	or better
leaf mass	0.1 µg	<1 µg	±1 µg	or better
mass flow		±2%	±5%	factory calibrated
VOC standard	NA	±2%	±5%	or better

3. Sampling procedures

Gas sampling is carried out directly and indirectly. Photosynthesis parameters are measured directly through online NDIR analyzers. BVOCs are measured indirectly via solid adsorption and subsequent thermal desorption gas chromatography flame ionization detection (TD-GC-FID).

3.1 Photosynthesis analyzer gas sampling

The CIRAS 2 instrument aspirates ambient air through an inlet filter, which is then routed through user accessible and maintained absorption cartridges for CO_2 (Ascarite II) and water vapor (silca gel) in the back of the instrument. Under measurement conditions, all CO_2 and a selected amount of water vapor is scrubbed from the air stream before routing to the leaf cuvette. CO_2 from a commercial pressure cartridge ("soda chargers") is used to supply external CO_2 to achieve the desired set-point mixing ratio the leaf is exposed to. Instrument internal valve switching is used to determine NDIR analyzer zero and to balance the measurement and reference channels. Instrument span is stable over long time periods but can be checked by replacing aspirated ambient air with a span gas while using empty absorption cartridges.

The instrument flow through the leaf cuvette is settable and usually maintained at 350 mL min^{-1}. The internal flow towards the NDIR analyzers is 100 mL min^{-1} and not user changeable. Thus, an excess flow through the leaf cuvette of 250 mL min^{-1} is present during regular leaf physiology measurements.

3.2 BVOC sampling

BVOCs are sampled via adsorption onto standard prefilled ¼" OD, 0.15" ID, 3.5" long glass cartridges designed for use with thermal desorption instruments. We use both commercially obtained (Perkin-Elmer) and "homemade" glass cartridges. Either are filled with a combination of activated carbon adsorbents held in place by a glass wool plug. We use a packing of 125 mg Carbopack B and 55 mg Carbopack X of 60/80 mesh size (Supelco, Bellefonte, PA), separated by a glass fiber disk. For this project, we will produce an additional 24 cartridges filled with ~200 mg Tenax TA (Supelco, Bellefonte, PA) each as an alternative trapping material, which will be tested in the laboratory.

To sample BVOCs emitted from a leaf in the cuvette onto the adsorbent cartridges, the cuvette outflow was modified to allow parallel photosynthesis and emission sampling. The outflow line was substituted by a ¼" OD Teflon Y-tube in our system. One branch allowed air to be drawn by the system's internal pump at its rate of 100 mL min^{-1} for CO_2/H_2O gas exchange measurement, while the second branch was connected to an external sampling system. A 2-port Teflon, switch-activated solenoid valve (Biochem Fluidics, Boonton, NJ) opens the flow of air from the cuvette to the trap at the beginning of sampling. An external pump operated by the same switch aspirates 200 mL min^{-1} as controlled by a precision mass flow controller (GFC-17, Aalborg, Orangeburg, NY) over the cartridge for a user-selected time period. We typically collect a 0.5 L air sample (Table 2), i.e. operate the bypass for 2.5 minutes. During this time, the excess cuvette flow drops to 50 ml min^{-1}, but leaf physiology is monitored at the same time to account for possible deviations as a result of this reduced excess cuvette flow.

Two kinds of blanks are regularly sampled for quality control: Empty cuvette blanks at experimental conditions (no leaf in cuvette) and cartridge blanks are regularly taken to correct for variations in background BVOC concentrations, and possible adsorption of ambient air onto sampling cartridges during handling and transportation, respectively. Between samplings the cuvette is typically flushed with air for approximately 3 minutes to remove any residual VOCs. Empty cuvette blanks are sampled in the exact same manner as regular leaf emission samples, while cartridge blanks are only exposed to ambient air in the same fashion regular samples are during handling.

All sample tubes are capped with standard Teflon caps equipped with o-rings (Perkin Elmer, Buckinghamshire, UK). The tubes are kept in glass containers whose lids are lined with Teflon caps to minimize volatile adsorption. Filled and fresh adsorption tubes are stored in separate glass containers, transported to and from the field on cold packs inside an insulated box (cooler) to minimize sample desorption and diffusion. All cartridges are desorbed and their contents analyzed within 72 hours of collection. All cartridges are additionally "cleaned" (desorbed without preconcentration and measurement) the night prior to next day's usage using a cleaning method programmed into the ATD400 automatic desorber (section C1.1). Cartridge cleanliness is assessed via the cartridge blanks each measurement day.

The analytical system currently has available 48 adsorption cartridges filled with the Carbopack B/Carbotrap X mixture. An additional 24 cartridges filled with Tenax TA will become available and are designated specifically for this project. Both cartridge types will be tested for diffusive losses in the laboratory using two types of Teflon caps. All cartridges will carry assigned, numbered caps, such as to be able to pinpoint a cartridge that fails quality assurance procedures. No other cartridge identification is in place.

3.3 Leaf sampling

After a leaf measurement in the field, or after a final leaf measurement in the greenhouse in fall of 2014, leaves are detached and transported back to the laboratory inside a sealed container with the petioles immersed in water. In the laboratory, 2.85 cm^2 leaf disks are punched from the fresh tissue and dried for 24 h at 85ºC in a drying oven. Dry disks are weighed afterwards on a microgram precision balance inside a humidity controlled enclosure, and leaf specific mass in g DW cm^{-2} is calculated.

3.4 Sample custody

All samples will be in our direct custody between acquisition and processing. No gas sample cartridges will be shipped or transported by any other means than inside their designated glass storage containers. Samples are identified by their numbered caps, with cap number, sampling time and person taking and handling the sample identified via field notebook entries.

4. Measurement procedures

The project's central measurement technique is the determination of isoprene flux, F_{isop}, per leaf area using the difference in isoprene mixing ratio between reference air (C_{in}) and air exiting the leaf cuvette (C_{out}) (typically $C_{out} >> C_{in}$):

$$F_{isop} = V/\rho \times (C_{in} - C_{out})_{\mathrm{isop}} \qquad [\mathrm{g/s}] \qquad (1)$$

V is the cuvette air flow-through rate, ρ is air density. While the CIRAS 2 calculates the water and carbon fluxes internally, we use the instrument's recorded flow rate, in conjunction the measured mixing ratio difference between an empty cuvette measurement and a leaf measurement to calculate isoprene fluxes. Raw fluxes are then referenced to either leaf area, i.e. F_{isop}/2.5 cm^2 [$\mu\mathrm{g\ m}^{-2}\ \mathrm{h}^{-1}$], or specific leaf mass, i.e. F_{isop}/SLM [$\mu\mathrm{g\ gdw\ h}^{-1}$].

4.1 Isoprene mixing ratio determination

For both the field measurements and greenhouse measurements, BVOCs will be sampled using adsorption cartridges (section B2.2). Upon cartridge return to the laboratory, we employ a thermal desorption (TD) gas chromatography (GC) flame ionization detection (FID) technique. The TD instrument used is a Perkin-Elmer ATD400 thermal desorber; the GC-FID instrument is an HP5890 series II with electronic pressure control (EPC) board.

The system is operated with hydrogen as carrier and FID fuel gas, coming from a Matheson TriGas Chrysalis II model 250 HPNM hydrogen generator. The hydrogen is of 99.9999% purity and flowing through an additional indicating moisture trap for quality control. Pressure-controlled carrier gas flow is routed through the GC's injector toward the ATD400.

ATD400

The ATD400 is an automated adsorption cartridge processing unit providing for

- sample tube leak testing,
- sample tube purge,
- sample tube desorption at preset interval length and desorption temperature,
- sample preconcentration and focusing, and
- sample injection.

Operating similar to an autosampler, its mechanics driven by compressed air, the ATD400 first selects a cartridge from its carousel, takes its caps off and brings it into the flow path. It then pressurizes the tube for leak testing, evaluated via a timed pressure drop as evaluated by an internal pressure sensor. If found non-leaking, the tube is first purged with carrier gas to remove air, particularly oxygen, then thermally desorbed (primary desorption) by clamping an oven of ¾ of the tube's length sideways onto the cartridge.

After the preset desorption and preconcentration period, the oven is removed, the tube cooled, recapped, and placed back onto the carousel until the next cartridge is selected for analysis. The preconcentration and focusing trap is a narrow bore inert glass tube filled with a small Carbotrap X plug. It is cooled during the focusing step and rapidly heated after cartridge desorption to desorb all analytes (secondary desorption and injection) in a narrow band into the carrier gas stream. The desorbed sample is transferred via a heated capillary to the head of the chromatographic column and the ATD400 starts each chromatographic run automatically with secondary desorption. All transfer lines inside the ATD400 are made of glass-lined, inert SS tubing, and inert gas paths are routed using a central Valco valve, whose rotor was replaced in 2010.

The current, pre-evaluated settings are as follows:

- primary desorption temperature and time: 220 °C for 10 minutes
- transfer rate: 30-50 mL per minute
- preconcentration trap temperature: -5 °C
- secondary desorption temperature and time: 220 °C for 2 minutes
- turnaround time between cartridges: 45 minutes

The ATD400 is programmed via its own access panel, independent of the GC software. For quality control, it stores several "methods" and reports deviations from the programmed protocol during and after a series of cartridges is completed.

In addition to the analysis method used to process "loaded" cartridges, we use a "cleaning method" to desorb all cartridges intended for use the following day during the night prior. Cleaning settings are similar to regular desorption setting instead for the fact that a cartridge's volatiles content is discarded instead of analyzed, and turn-around time per cartridge is thus reduced to approximately 10 minutes.

GC-FID system

We operate a HP5890 series II GC with Chemstation software. Volatiles are separated on a 60-m × 0.25 mm MXT-624 Siltek® -treated stainless steel column (Restek Corporation, Bellefonte, PA) using a temperature program geared towards isoprene analysis. The oven/column temperature is initially held at 35°C for 4 min, than increased to 150°C at a rate of 10 °C min^{-1}. Then, temperature is increased to 220°C at 20°C min^{-1} heating rate and held for 11 min. The carrier gas (H_2) flow rate is set to approximately 2 mL min^{-1} at 40 °C and controlled for constant flow. The FID is operated at 250 °C with a typical 10:1 ratio of zero air and hydrogen using nitrogen as make-up gas. Zero air is produced by a zero air generator in the laboratory (AADCO, FL, model 737, fed by house compressed air).

The Chemstation software controls the GC temperatures and carrier gas flow rates, and records the FID signal. We program a set of cartridge measurements as a sequence using the same analysis method. Each cartridge in the sequence is uniquely identified by its cap number and the sample date in form of the file name as YYMMDD##. In addition, the sequence identifier includes leaf temperature, leaf external CO_2 mixing ratio, sample size, and sample location/site.

The system is calibrated using a single ppm-level isoprene-containing calibration gas. The calibration gas is diluted into zero air at ratios between 1:100 to 1:5000 using two precision flow controllers, one 0-10 mL min^{-1} for the calibration gas, and one 0-5000 mL min^{-1} for zero air. A calibration curve (spanning low ppb to low hundreds of ppb) is generated on a regular basis (3-pt for each measurement day, 6-8 pt every two months) using the same cartridges used for field sampling. For each calibration sample, part of the zero air diluent flow is routed through a wash bottle filled with high purity water from an ion-exchange system to create different humidity levels in order to simulate field sample conditions.

Instrument precision is based on repeatability of calibration samples at different mixing ratios. Sensitivity and linearity is based on FID response as evaluated from peak areas determined by the Chemstation software and calculated mixing ratios using calibration gas dilution ratios.

During each sampling day, a series of 3-4 calibration sample cartridges is produced in the morning, and these cartridges are transported, handled, and processed in the same manner as all other cartridges. Thus, field measurement precision is determined for each measurement day by the precision of the ad-hoc calibration curve obtained the day’s calibration samples.

5. Quality Metrics

Quality control (QC) and assurance (QA) is achieved through a series of samples and measures implemented during and after sampling and processing of samples.

5.1. Quality Control

QC measures include

i. regular zeroing and balancing of the NDIR analyzers as part of the CIRAS 2 system
ii. sample cartridge tracking for leakage and calibration gas repeatability
iii. “empty cuvette” blank sample collection for reference isoprene mixing ratio and cuvette system contamination tracking
iv. blank cartridge samples (unloaded) for diffusive contamination tracking (e.g. leaks)
v. duplicate sample taking to track leaf emission repeatability
vi. calibration sample acquisition and handling alongside regular sample taking
vii. detailed notebook entries on field activities accompanied by occasional photographs

Measure i is performed approximately hourly during instrument use at either field site or in the greenhouse. Measure ii is performed as a spot check by rotating different, random cartridges to act as daily calibration samples instead of selected cartridges. Measure iii includes 3-6 samples taken from an empty, balanced cuvette throughout a measurement day. Measure iv includes an additional 2-4 cartridges per measurement day exposed to ambient air or laboratory air for an appropriate amount of time reflecting regular sample handling. Measure v includes replicate samples taken immediately after a regular sample without changing any leaf conditions, and will be carried out once to twice per measurement day. Measure vi assures comparability from one sample day to another, including at least two, normally three to six calibration samples processed per measurement day. The associated calibration curves alongside the more detailed curves containing more concentration levels reveal the mixing ratios at which breakthrough becomes relevant (above approximately 150 ppb for the current cartridge filling, a mixing ratio not generally observed in any field sample; breakthrough will be assessed separately for the Tenax filling). Finally, measure vii assures the identification of deviations from the norm, and the proper association of results with the respective leaves and field conditions.

In addition, we will perform a renewed sample storage test to determine sample integrity over 72 hours at different temperatures as follows:

1. Two sets of calibration gas mixing ratios will be created at typical humidity levels, one high, one low ppb-level isoprene, both 0.5 L volume samples
2. A set of three cartridges each will be processed immediately after sampling
3. Another set of three cartridges each will be processed after 24, 48, and 72 hours following sampling
4. One set of (12+12) cartridges will be kept inside their glass storage container in a refrigerator at 4 °C, resembling field storage, one set inside another glass storage container at room temperature, resembling laboratory carousel storage time before processing

Our past storage test has shown that diffusive sample loss from the Carbopack/Carbotrap mix cartridges using the standard Teflon caps was less than 5% for all calibration gas compounds, including isoprene, after 72 hours.

Unless a day's of acquired samples are not processed due to analytical system failure, typical sample cartridge amounts of less than 40 guarantee that there are no samples stored more than 48 hours before being processed by the ATD-GC-FID system.

5.2. Quality Assurance

Quality assurance measures for the CIRAS 2 data include

i. spot checking of data integrity (e.g. noise specifications/behavior), and data consistency (e.g. between field notes and data records)

ii. removal of outliers during averaging/processing
iii. monthly span checks of the NDIR analyzers

Measure i will occur frequently during data processing when newly acquired data are processed for incorporation into a spreadsheet. Measure ii will occur at the same time when records are averaged to reflect leaf physiology during the isoprene sampling period. Measure iii is designed to make sure the instrument does not show a significant drift over longer time periods.

Quality assurance measures for the cartridge sampling and isoprene measurements include

i. successful demonstration of (i) a lack of sample loss during typical storage times; and (ii) a lack of breakthrough at a challenge mixing ratio of 100 ppb for the new Tenax cartridges
ii. checking of cartridge blanks for lack of unidentified VOC occurrences and lack of significance of known interferences, such as blank peaks
iii. subtracting empty cuvette blanks from leaf emission samples using an average of the nearest samples in time
iv. comparing measurement day calibration samples from one day to the next to ensure FID stability, and spot check individual cartridge integrity
v. comparing measurement day calibration samples to the extended calibration curve

Measure i will be established during the first month of the project. Measure ii to v are ongoing QA measures during data processing and analysis.

The calibration curve will be used to re-establish the current measurement accuracy and precision (cf. also Table 2) as determined from the regression curve and mixing ratio repeatability at typical mixing ratios of 10-100 ppb obtained from the field measurements. A new, NIST traceable isoprene containing calibration gas to be obtained for this project will be compared to the existing calibration gas via their calibration curves, and the new standard's accuracy as stated by the manufacturer will be used to determine the accuracy of the analytical system and, accordingly, of a single TD-GC-FID measurement.

6. Data analysis, interpretation, and management

6.1. Reporting requirements

The Schade group will report summary data monthly to TCEQ in form of Excel spreadsheets containing averaged leaf physiology data and associated isoprene emissions. Leaf Physiology data will be averaged over 1 minute prior to isoprene sampling. This period is the period during which the leaf attained equilibrium gas exchange inside the leaf cuvette and may vary from 1-5 minutes based on operator choice during field or greenhouse sampling. Only the last minute average prior to isoprene sampling will be reported for consistency. Data will include

- leaf external (C_r) and internal (C_i) CO_2 concentrations
- stomatal conductance (g_s) and net assimilation rate (P_n)
- chamber flow rate in mL min^{-1}
- isoprene peak areas from the Chemstation software
- isoprene mixing ratio of the leaf sample
- isoprene mixing ratio of the reference sample (empty cuvette)
- isoprene flux in $\mu mol\ cm^{-2}\ s^{-1}$ (and $\mu g\ gdw^{-1}\ h^{-1}$ for leaves from field measurements)
- leaf specific area, SLA, in $cm^2\ g^{-1}$ (if available from excised leaves from field measurements)
- the calibration curve for the measurement day

Further data analyses will be reported to the sponsor as they become available, such as temperature response curves, standard emission variability, and, at a later stage, soil moisture responses.

6.2. Validation and Audits of Data Quality

Data is assembled by the undergraduate student and postdoctoral research associate (PRA). The PRA and Co-PI will regularly spot check calculations made in the spreadsheet data files. Data will be backed up and cross-checked between the PRA and Co-PI and against the field and greenhouse notebooks before monthly submission to the sponsor. A minimum of 10% of the data will be audited. The results of the audits of data quality will be included in the final report.

6.3. Data Analysis

All leaf level standard emissions data will be compared to the measured soil moisture data. Temperature response curves will be modeled using the standard Guenther algorithm with additional consideration of recent temperature development in the field or greenhouse. Standard emissions and curves will be compared among leaves to determine variability (reported as one standard deviation), and within a day to determine potential diurnal development.

Soil moisture responses will be analyzed using the measured volumetric soil moisture and calculated Water-filled Pore Space (WFPS). Since the expected response is a drop in isoprene emission rates but may vary between species, between individuals, and between field-grown mature, and greenhouse grown trees, no single response function is expected to model observed responses. We will explore both linear and non-linear response functions, as well as potential thresholds.

6.4. Data storage and management

Data storage requirements do not exceed more than a few Gigabytes for the whole project. Data will be stored on onsite hard-disks in the Co-PI's laboratory and offices. The primary storage location will be the PRA's computer. Backups will be kept on a portable hard-disk intended for backups and on another computer used by the undergraduate student for data entry and manipulation.

Data backups will be performed on a weekly to monthly basis. Raw data are transferred immediately after a measurement day, and backed up to two different locations the next day. Chemstation raw data are backed up to a secondary hard drive weekly, and to another location by the end of the month. Processed data are backed up when ready for submission to the sponsor. Field and greenhouse notebooks are backed up via digitization. Original and digital copies of all notebooks will be stored in different locations during and after the project and will be kept for a decade after.

All personal computers run in the PI's research group are operated with daily updated Windows and Antivirus (AVG) software, and are biweekly to monthly scanned for malware and other threats. Access to all digital data is restricted by strong PC access passwords.

All acquired data is ultimately archived on DVDs. Raw data processing is achieved on personal computers of the Co-PI, postdoc, and undergraduate student. Freely available *R* software (http://www.r-project.org) is used to analyze and explore some of the processed data via writing out ascii files from the Excel spreadsheets. All processed data will also ultimately be archived on DVDs.

7. Reporting

The project's timeline and tasks are listed in section 2 of the Workplan. Progress reports will be sent to the UT project manager and TCEQ liaison once a month and through a final report as described in the sub-award contract. The monthly reports will contain the above (section E1) described data deliverables and a narrative describing project progress towards the objectives. The monthly progress report will be jointly drafted by the PRA and Co-PI, but its contents is solely the responsibility of the Co-PI.

The expected final product of this project is a suggested new drought parameterization for isoprene emissions that can incorporated into current isoprene emission modeling efforts, such as MEGAN. The project's final report will contain said suggested parameterization and the resulting evaluation of its implementation effects on ambient air quality as compared to no drought parameterization and the current, "simple" parameterization.

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