AQRP Monthly Technical Report

PROJECT TITLE	Improving Modeled Biogenic Isoprene Emissions under Drought Conditions and Evaluating Their Impact on Ozone Formation	**PROJECT #**	14-030
PROJECT PARTICIPANTS	Qi Ying, Gunnar W. Schade, John Nielsen-Gammon, Huilin Gao	**DATE SUBMITTED**	3/9/2015
REPORTING PERIOD	**From:** February 1, 2015 **To:** February 28, 2015	**REPORT #**	8

A Financial Status Report (FSR) and Invoice will be submitted separately from each of the Project Participants reflecting charges for this Reporting Period. I understand that the FSR and Invoice are due to the AQRP by the 15th of the month following the reporting period shown above.

Detailed Accomplishments by Task

Task 1: Meteorology simulation with WRF. Completed.

Task 2: Perform field and laboratory measurements on common Texas tree species

<u>Note</u>: Due to an additional project start delay from June to July and the unanticipated need to move all our seedlings to a different greenhouse in July, all monthly milestones described in the QAPP had to be moved by one month ahead

The spring 2015 milestones were addressed as follows:

a. analyze drought response relationships: could not be addressed yet since measurements so far have been unsuccessful (see previous monthly reports).
   compare isoprene field data to seedling data: post oak (*Quercus stellata*) basal (30 °C, 1000 µmol m^{-2}, s^{-1}) isoprene emissions measured on leaves on south facing branches of mature trees in the field are typically between 60 and 90 µg gdw^{-1} h^{-1} (basal emission rate listed by Geron et al., 2001, is 73 µg gdw^{-1} h^{-1}) equivalent to 25-47 nmol m^{-2} s^{-1} for typical specific leaf weights of 90-110 g m^{-2}. Potted post oak seedlings typically emitted 20-30 nmol m^{-2} s^{-1}, slightly less than field grown trees, but comparable. The respective numbers for field water oak (*Quercus stellata*) were similar (25-35 nmol m^{-2} s^{-1}; data from 2011, 2013 field seasons, similar to literature value of 81 µg gdw^{-1} h^{-1}) and also replicated in the potted seedlings in 2014 (20-30 nmol m^{-2} s^{-1}) but with significantly higher variability
b. provide final drought response parameterization: could not be addressed yet due to inconclusive data collected on seedlings last summer/fall
c. submit data files to UT: new data format was submitted for approval with last monthly report

Following up on last months report, we tested "isoprene" contamination on our adsorbent cartridges through distributing capped cartridges throughout laboratory for different lengths of time in an attempt to represent "open storage", such as when cartridges are being processed on the ATD400 caroussel. Cartridges ("passive samples") were placed in three locations in the laboratory during 3 days (1, back of the lab; 2, next to the GC; 3, next to chamber with isoprene emitting plant). Samples were also acquired "actively" with the pump at the same 3 locations (typical 500 mL sample). In addition, cartridges cleaned prior to analysis were also processed ("cleaned samples"). The results are depicted in Figures 1 through 4:

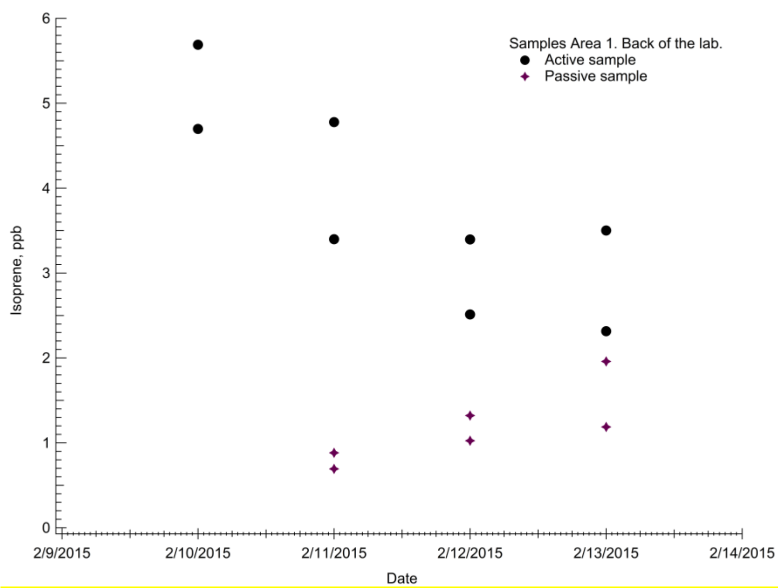

Figure 1: Isoprene equivalent abundance of the chromatographic peak eluting at the isoprene retention time for samples acquired in the back of the laboratory.

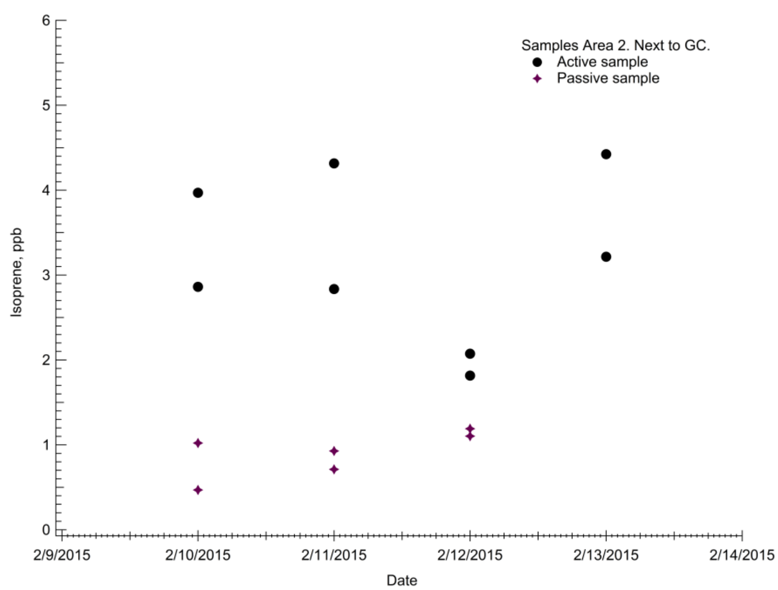

Figure 2: Same as Fig. 1 but for location next to the GC.

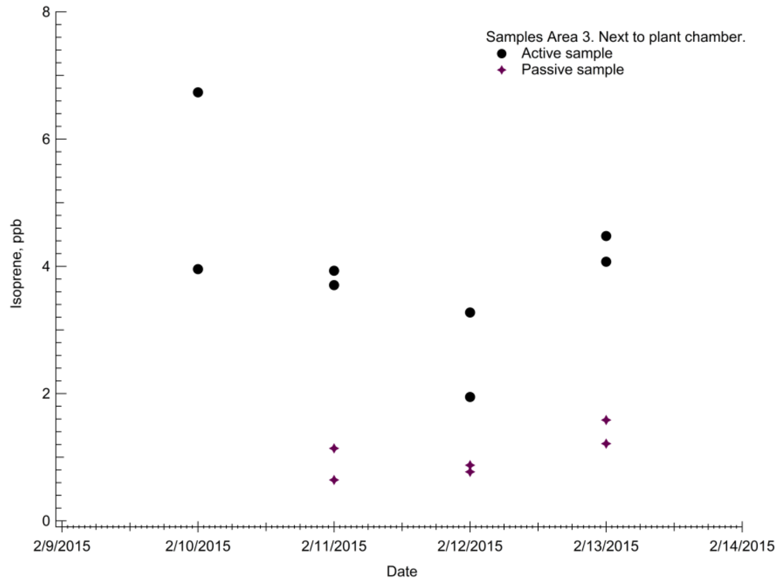

Figure 3: Same as Fig. 1 but for the laboratory location next to the plant chamber

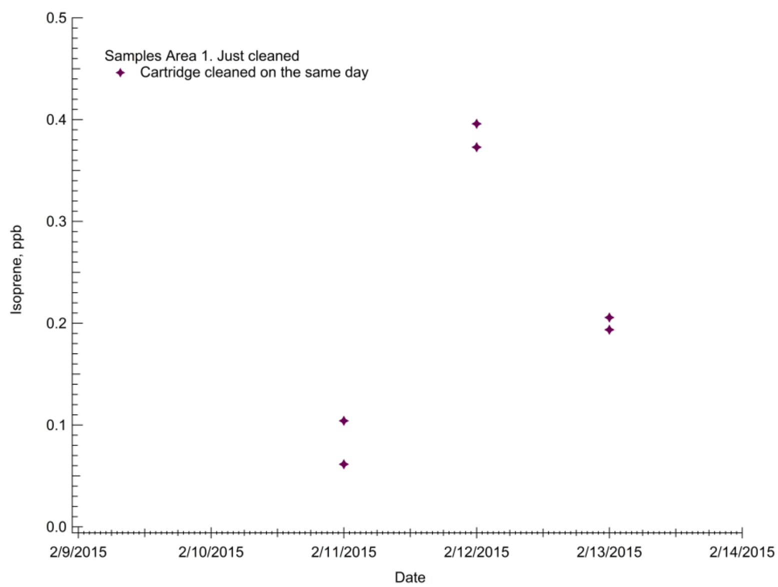

Figure 4: “Isoprene” peak abundance in just cleaned cartridge samples.

The results suggest that our laboratory contains 2-6 ppb of isoprene, likely due to the plant chamber and human respiration in the building. While cleaned cartridges contain less than 0.5 ppb isoprene equivalent when analyzed, on the order of 1 ppb may diffuse into the cartridges while they are processed in the laboratory 24-48 hours after sampling. Since typical isoprene amounts on samples taken from isoprene emitting leaves exceed 20 ppb, by subtracting the “empty cuvette” sample or blank amounts from the leaf-based samples, we avoid an up to 5% possible bias in our measurements.

Task 3: Evaluate drought parameterization for isoprene emissions – Not started yet. Waiting data from Task 2; and potentially a new parameterization scheme from Alex Guenther.

Task 4: Perform regional BVOC modeling using MEGAN – Completed. Both base case and the drought parametrization case have been completed for all three domains.

Task 5: Perform regional air quality simulations

A number of sensitivity runs were conducted to investigate the ozone over-prediction problems in summer. (1) We looked at the effect of boundary conditions of ozone on predicted ozone concentrations. The follow figures shows observed (red dot), predicted base case (black line) and predicted zero O3 boundary condition (in the 36 km domain) case (green line) at Sabine Pass (382050101) and at Waco (483901037) and at the FAA site at Dallas (484392003). Ozone concentrations at the Sabine Pass and Waco during mid-July are low, at 20 ppb for Sabine Pass and < 40 ppm for Waco. Base case predictions are much higher than observations. Using zero boundary condition leads to better predictions but does not completed solve the over-predictions seen on high ozone days, and leads to under-predictions on some days.

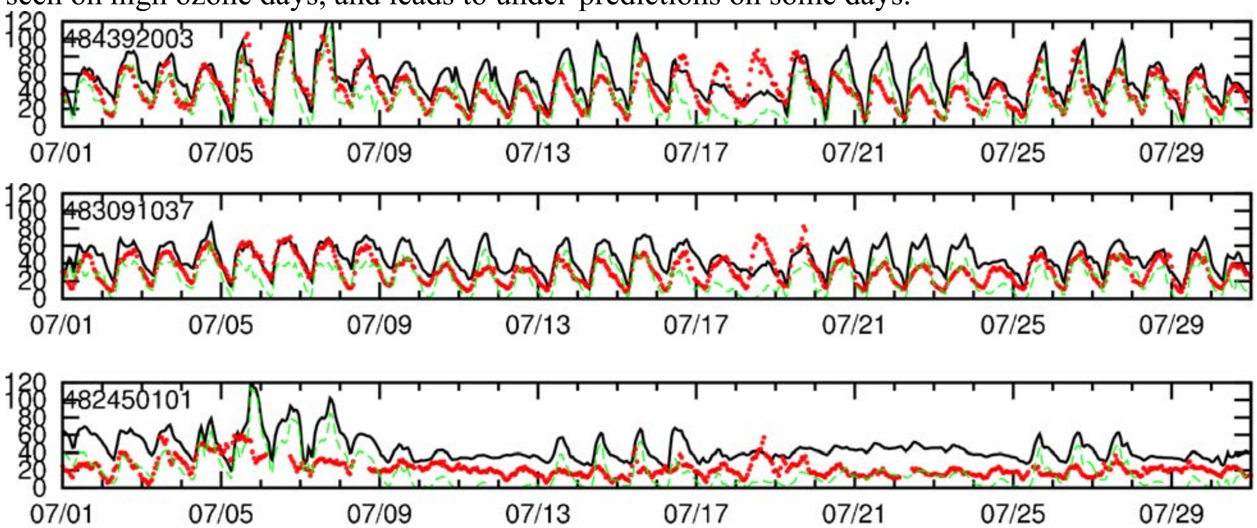

Figure 5: Predicted and observed ozone concentrations at three TCEQ sites. Unit is ppb. Observations are red dots; base case predictions are in black lines and sensitivity predictions are in green lines.

(2) We looked at the sensitivity of reducing isoprene emissions on predicted ozone concentrations. Two sets of runs were conducted, by reducing the isoprene uniformly across the domain by 50% and 90%. However, we failed to notice any significant changes in predicted ozone concentrations, and ozone is still significantly over-predicted, especially at urban sites, as shown in the following example for Port Arthur (482450011) and Houston Westhollow site in Houston (482010066) for 90% ozone reduction.

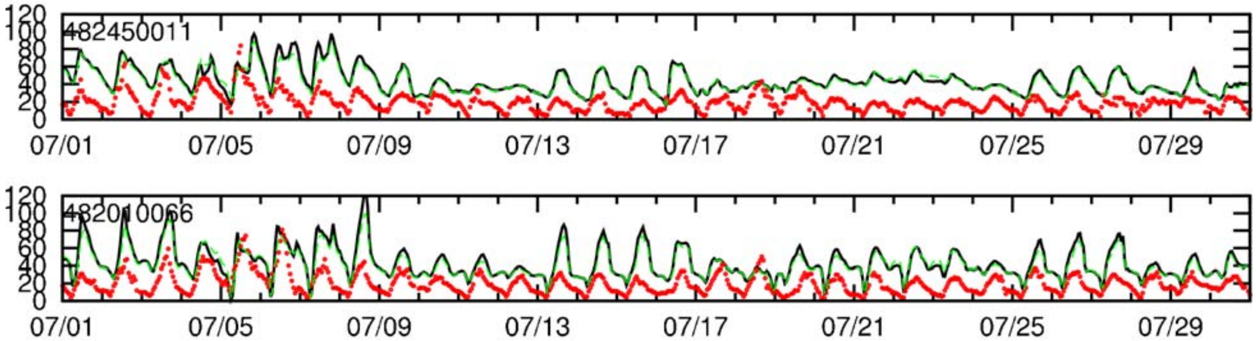

Figure 6: Predicted and observed ozone concentrations at two TCEQ urban sites. Unit is ppb. Observations are red dots; base case predictions are in black lines and sensitivity predictions are in green lines.

We then examined the time series and temperature and wind speed at the TCEQ stations. On a few days, temperature was significantly over-predicted and wind speed was over-predicted at the two stations, but it is unclear if this is the cause of the over-predictions.

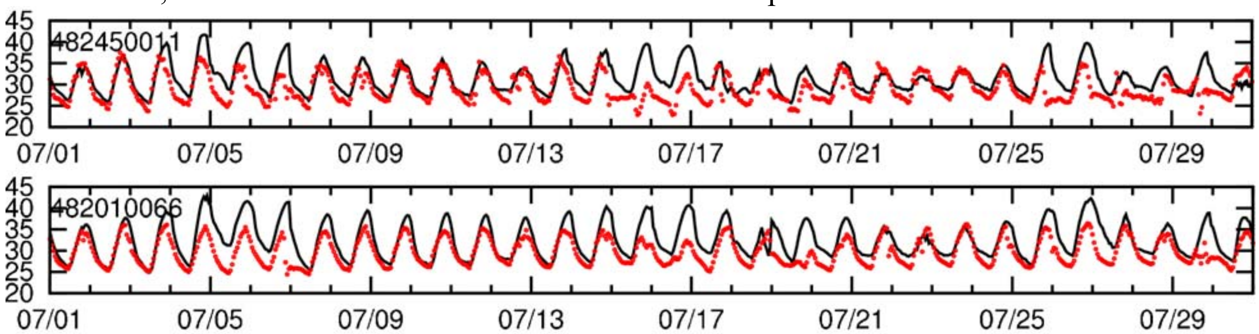

Figure 7: Predicted and observed temperature in July at two urban stations.

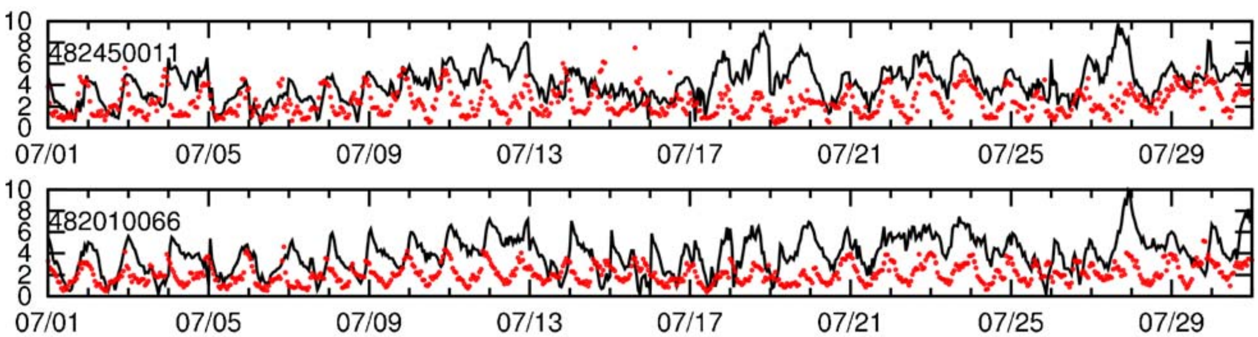

Figure 8: Predicted and observed wind speed in July at two urban stations.

(3) We also investigated the effect of PBL height on ozone predictions. Noticing that PBL height along the coast on some days are as predicted to be as low as 25 m, a sensitivity run was conducted by setting the minimum PBL to 200 m. However, no obvious change was observed.

(4) We examined predicted and observed NOx concentrations. NOx seems to be well predicted by ozone severely over predicted. For example, the following shows a comparison and ozone and NOx predictions at Texas Ave. in Houston:

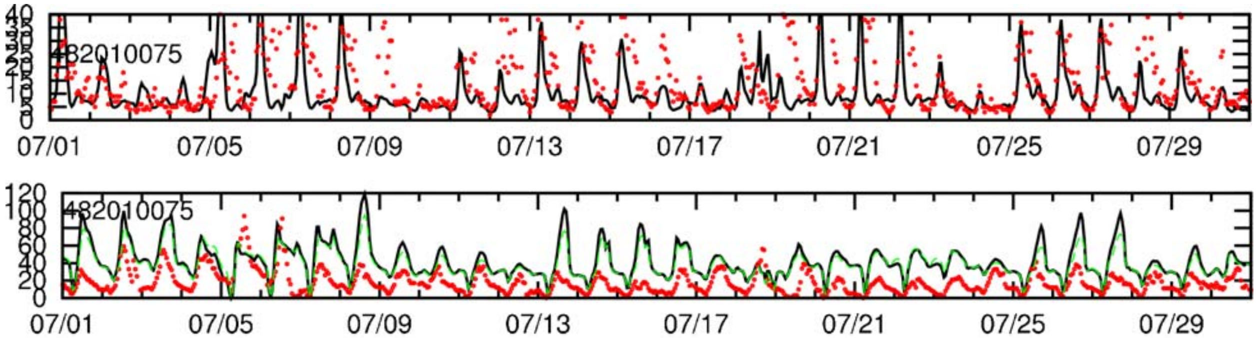

Figure 9: Predicted and observed NOx (top panel) and O_3 (bottom panel) in July at the Texas Ave. station in Houston.

Preliminary Analysis

Task 2: Figures 1-4 show very small, but significant amounts of background on our cartridges that can increase during "storage" (here: processing of cartridges in the laboratory). We account for that possible contamination by correcting measured fluxes with "empty cuvette" samples that have undergone the same processing, and via checking against blank samples for any additional contamination.

Task 5: Figure 5 suggests that lower background ozone concentrations might be needed to explain the lower observed concentrations at many of the sites during this episode. Isoprene over-prediction seems to have little correlation with ozone over-predictions, as shown in Figure 6. Biases in wind speed and temperature (Figures 7 and 8) could not explain the large over predictions of isoprene although over-prediction of temperature might have contributed to over-predictions on some days. Figure 9 shows that NOx is generally well predicted. Over-predictions of ozone are more severe on days when NOx concentrations are high, although the model seems to be able to capture the increase of NOx concentrations.

Data Collected

1. 3rd set of cartridge tests: Cartridge isoprene contents as a function of time for fixed isoprene mixing ratio collected, and for blanks

Identify Problems or Issues Encountered and Proposed Solutions or Adjustments

Ozone and isoprene over-predictions needs to be further studied. However, the two issues are not related. Isoprene over-prediction is more likely with MEGAN. (1) We plan to use the most recent BEIS vegetation distribution data and basal isoprene emission rates to generate the gridded emission factor field (EF), and use that as a MEGAN input instead of the default MEGAN file. (2) For ozone over-prediction, it seems that the over-prediction is a vertical mixing issue. Currently in CMAQ, adjustment of vertical turbulent diffusion coefficient (Kzz) occurs below 500 m: the Kzz values are set to 0.01 for rural areas and 1.0 for urban areas and linearly interpolated based on urban fraction. This might be inappropriate, especially on days with low PBL. We plan to test alternative vertical diffusion coefficient adjust schemes.

Goals and Anticipated Issues for the Succeeding Reporting Period

Goals

Task 2: 1) derive a better estimate of total, or a depth profile of soil moisture data during the 2011 field season in order to better relate isoprene emissions to soil moisture; 2) continue caretaking of the greenhouse-based seedlings, monitoring potential new growth as ambient insolation increases; monitor newly acquired and potted post oak and other seedling for growth. Routine sampling may begin as early as March 2015 since new leaves have been coming out on several of the greenhouse seedlings.

Task 5: 1) perform additional isoprene observation vs. prediction analyses for daily isoprene at PAMS sites to check the extent of the isoprene over-prediction problem; 2) generate biogenic emissions using the most recent BEIS 3.6 vegetation distribution and emission factor data (still use the MEGAN framework), and compare predicted isoprene emission rates with MEGAN predictions; 3) perform additional sensitivity runs to fix ozone over-prediction problem; 4) start base case simulation for 2007.

Detailed Analysis of the Progress of the Task Order to Date

Task 1: Completed.

Task 2: Major delay on task 2 due to inconclusive data last summer/fall. Will commence new measurements this spring, awaiting leaf-out and maturation.

Task 3: Waiting for new isoprene measurements and potentially new parametrization scheme from Alex Guenther.

Task 4: Completed.

Task 5: Isoprene over-predictions and ozone model performance problems in summer time need to be resolved.

Submitted to AQRP by: Qi Ying

Principal Investigator: Qi Ying