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**	1/13/2015
REPORTING PERIOD	**From:** December 1, 2014 **To:** December 31, 2014	**REPORT #**	6

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 in November 2014.

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 December milestones were addressed as follows:

a. Compare baseline to treatment measurements: After the gradual shutdown of isoprene emissions in senescing leaves in November, no further greenhouse measurements were conducted. Greenhouse seedlings were monitored for pests and watered when necessary. Note that temperatures in the greenhouse are still heat-supplemented, Figure 1.
b. Analyze observed drought responses of seedlings and field-grown mature trees: No additional analyses on greenhouse seedling data have been carried out since the last monthly report. However, we have carried out the first required cartridge testing, both for the Tenax® and the activated carbon adsorbent cartridges. A test was performed to determine the possible loss of (isoprene) sample when cartridges are stored. The length of this test was 4 days, while typical storage time in any of our experiments does not exceed 48 hours. Two different types of adsorbents were tested: Tenax, and the combination we use in our NSF project: $^{2}/_{3}$ Carbopack B, $^{1}/_{3}$ Carbotrap X. The first day 16 cartridges were filled (8 cartridges each adsorbent). During the next four consecutive days 2 cartridges each from storage were analyzed in the GC together with another 2 cartridges (from each adsorbent) that were filled up on the same day of the analysis. A total of 10 cartridges were analyzed every day, 4 cartridges from storage, 4 cartridges taken the same day, and 2 blanks. The time series tests are shown in Figures 2 and 3 for the two adsorbents, respectively. Similar to the first set of tests, in which isoprene emissions from individual leaves were collected back-to-back onto the two different cartridge types, no significant difference at the 95%-level was found between them.

Further, shown in Figure 4 is an experiment we carried out in our laboratory whole plant chamber and included in a combination analysis addressing isoprene emissions and drought presented by Monica Madronich at the AGU Fall Meeting in December (Poster A33H-3290: Effects of Drought Stress and Ozone Exposure on Isoprene Emissions from Oak Seedlings in Texas). It shows plant physiological parameters and isoprene emissions from a 3-yr old white oak tree seedling, from which we withheld water from the end of October for approximately two weeks. During this early experiment, only two daytime isoprene sampling times were maintained, but it serves as an example of the type of response we expect to observe from the seedlings.

c. **submit data files to UT: we need approval of the data format submitted with the previous monthly report before submitting more results to the sponsor.**

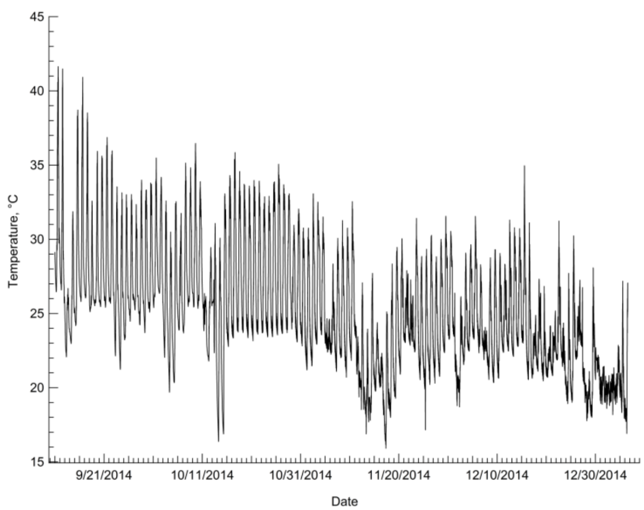


Figure 1: Greenhouse (air) temperatures mid-September through early January.

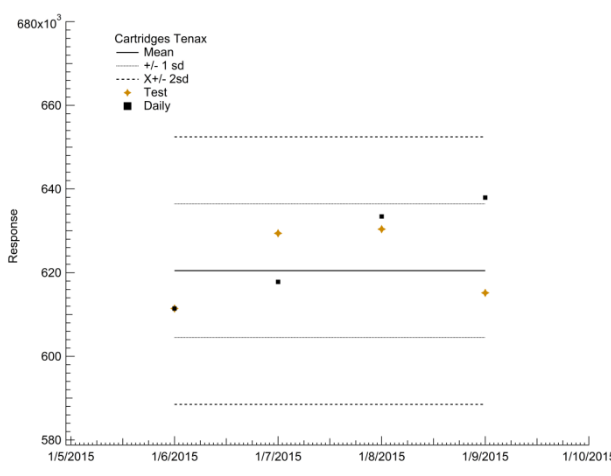


Figure 2: FID area response development for the isoprene peak from stored vs. freshly loaded cartridges using an isoprene mixing ratio of approximately 25 ppb, similar to what is typically found in cartridges taken from enclosed seedling leaves in the greenhouse.

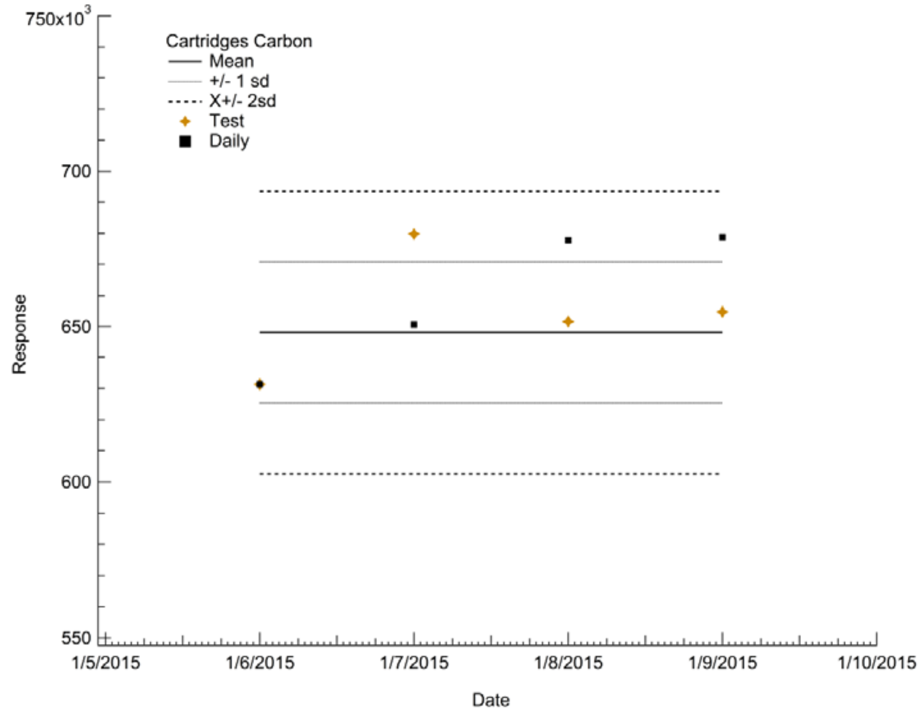


Figure 3: Same as Figure 2 but for the Carbopack/Carbotrap combination adsorbent cartridge.

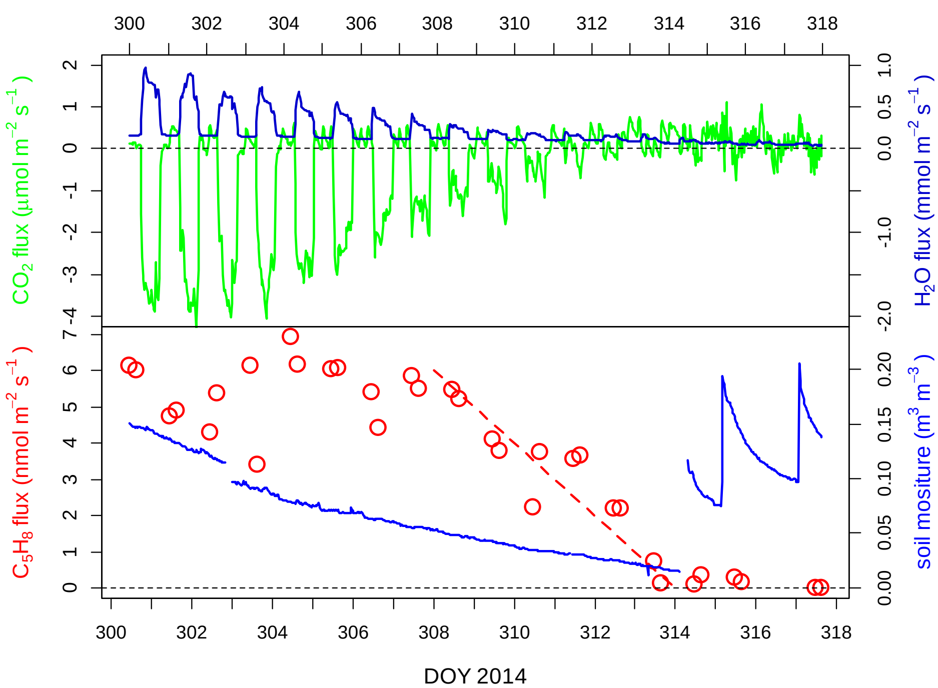


Figure 4: Physiological data (CO_2 and H_2O leaf-based fluxes) photosynthesis and isoprene emission rates from four water oak seedlings investigated, two each per treatment group. Error-bars show variability (standard error, se).

Task 3: Evaluate drought parameterization for isoprene emissions – waiting for alternative parameterization from Alex Guenther.

Task 4: Perform regional BVOC modeling using MEGAN

MEGAN emissions for base case (emissions without considering soil moisture effect on isoprene emissions) and case 1 (default MEGAN drought parameterization) have been generated for both 2007 and 2011. We are waiting for an alternative parameterization(s) from Alex Guenther. MEGAN processing is relatively fast and could be completed within a week for each set of new parametrizations.

Task 5: Perform regional air quality simulations

1. Emission processing for NEI 2011

Several errors in NEI emission processing were identified in the past month. Most of the errors were caused by using wrong input files for different source sectors, especially the on-road mobile sources (see discussion below), and missing source sectors such as peaking units for electrical power generation. These errors were fixed and we feel the current emission files are ready for production CMAQ modeling. A summary of the emission processing for NEI 2011 was given below.

The following NEI 2011 source sectors, as shown in Table 1, were processed using SMOKE v3.5.1. Details of the NEI 2011 as used in the EPA's 2011v6 platform can be found in ftp://ftp.epa.gov/EmisInventory/2011v6/v1platform/README_2011v6_package.txt. A short summary regarding point and on-road mobile source sectors is included in the following. In NEI 2011, emissions from electrical generating units (EGUs) are divided into three sectors: *ptegu*, *ptegu_pk* and *ptnonipm*. In older NEIs, the *ptegu* sector was called "*ptipm*" or "Integrated Planning Model". This sector incorporates Continuous Emissions Monitoring (CEM) hourly emissions for a majority of sources. The *ptegu_pk* sector includes units that only operate during times of peak demand, rather than for most or all of the year, as defined by EPA's Clean Air Markets Division (CAMD). Peaking units are kept in a separate sector by the EPA for the purposes of source apportionment in future modeling applications. This sector incorporates CEM hourly emissions for all sources. The *ptnonipm* sector includes emissions from all other industrial point sources.

On-road mobile emissions were processed using SMOKE-MOVES. The SMOKE-MOVES emission processing was done for three different types of emissions: (1) On-network emissions (*RatePerDistance*, or RPD); (2) Off-network emissions, fuel vapor venting (*RatePerProfile*, or RPP); and (3) Off-network emissions, non-venting (*RatePerVehicle*, or RPV). The RPD and RPV sectors were further divided into refueling and non-refueling subsectors. Different spatial allocation surrogates were used to improve spatial distribution of mobile source emission. For example, locations of gas stations along with population density data were used to allocate RPD and RPV refueling emissions. In order to match the SMOKE-MOVES annual emission totals with those provided by Texas and California, on-road mobile emissions from the two states were split into a separate sector. A control factor file was used to nudges the emissions so that the annual totals post-SMOKE-MOVES equal those provided by the states, at the county/SCC3 level in California, and at the county/SCC7 level in Texas. This method uses overall emissions totals provided by the state agencies, combined with SMOKE-MOVES temporal allocation. Speciation of the VOCs was done for the CB05 photochemical mechanism.

Table 1. Source sectors processed using SMOKE 3.5.1 for CMAQ modeling

Source sectors	**Type**	**Notes**
afdust	nonpoint	Area fugitive dust
ag	nonpoint	Agriculture ammonia sector
c1c2rail	nonroad	Class 1/Class 2 commercial marine vessels and locomotives
c3marine	nonroad	treated as point sources; Class 3 commercial marine vessels
nonpoint	nonpoint	Other non-point sources
nonroad	nonroad	Non-road mobile equipment sources
np_oilgas	nonpoint	Oil and gas extraction-related emissions
othar	nonpoint/nonroad	Area and nonroad mobile sources from Canada and Mexico
othon	onroad	Onroad mobile sources from Canada and Mexico
othpt	point	Offshore Class 3 CMV; drilling platforms; Canada and Mexico point sources
ptegu	point	Electrical generating unit; non-peaking units
ptegu_pk	point	Electrical generating unit; peaking units
ptfire	point	Wildfire and prescribed burning
ptnonipm	point	Other industrial point sources
pt_oilgas	point	Oil and gas extraction-related emissions
rateperdistance_catx	onroad, RPD	California and Texas on-road emissions[1]; on-network emissions[2]
rateperdistance_noRFL	onroad, RPD	On-road emissions for other states; on-network emissions
rateperdistance_Rfonly	onroad, RPD	Refuling emissions[3]; all states; on-network emissions
rateperprofile_catx	onroad, RPP	California and Texas on-road emissions; off-network emissions, fuel vapor venting
rateperprofile	onroad, RPP	On-road emissions for other states; off-network emissions, fuel vapor venting
ratepervehicle_catx	onroad, RPV	California and Texas on-road emissions; off-network emissions, non-venting
ratepervehicle_noRFL	onroad, RPV	On-road emissions for other states; off-network emissions, non-venting
ratepervehicle_RFLonly	onroad, RPV	On-road emissions for other states; off-network emissions, non-venting; refuel only
rwc	nonpoint	Residential wood combustion

[1] Total of the California and Texas emissions were adjusted to match the States' reported totals.
[2] On-network emissions include running emissions from rural and urban roads.
[3] Off-network emissions include start, evaporative and extended idle emissions.

The run scripts provided with the 2011v6 platform were modified so that emissions from all three CMAQ modeling domains can be generated. For the 4-km domain, spatial allocation surrogates for the United States were provided by the US EPA. However, spatial allocation surrogates for Mexico is not available but the 4-km domain does contain a small fraction of Mexico in the lower left corner. The Spatial Allocator program developed by the US EPA was used to re-grid the 12-km resolution emissions (othar and othon, see Table 1) into 4-km resolution emissions. As an example, Figure 5 shows daily emissions of NO and isoprene in the 36-km, 12-km and 4 km domains.

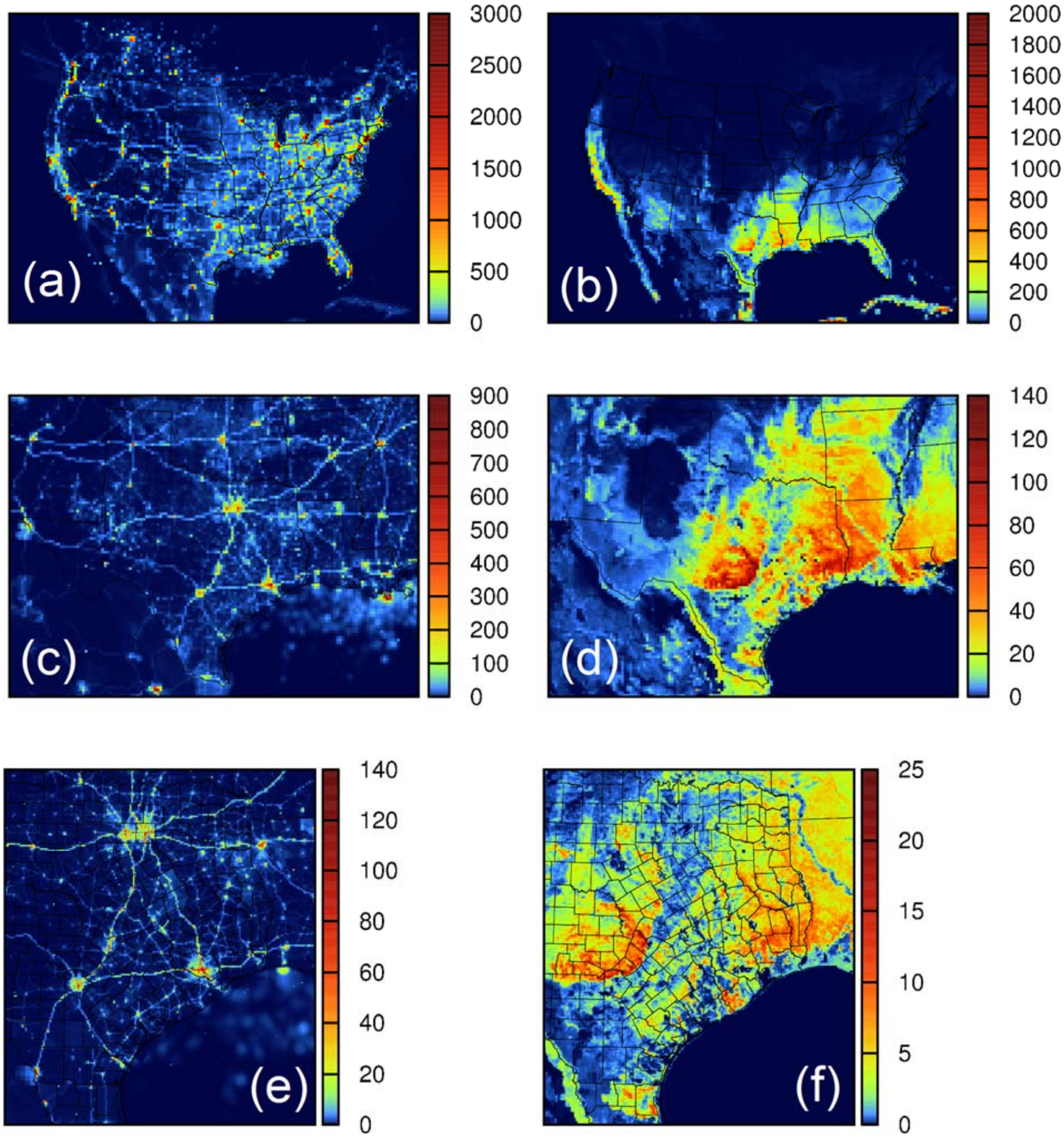


Figure 5. Daily surface level emissions of NO (a,c,e) and isoprene (b,d,f) for the 36-km (a,b) , 12-km (c,d) and 4-km (e,f) domains. Units are kmol/day per grid cell.

2. Preliminary CMAQ modeling

CMAQv5.0.1 was used for a preliminary modeling study with the 2011 emissions. The CMAQ model configuration was listed in Table 2.

Table 2. Configuration of CMAQ

Options	**Value**	**Notes**
Mechanism	cb05tucl	CB05 mechanism, including updates in toluene chemistry, homogeneous hydrolysis rate constants for N_2O_5, and chlorine chemistry.
Aerosol	AERO6	Version 6 of the aerosol mechanism - treatment of trace metals; aging of primary organics
Solver	EBI	
Plume rise	Inline	7 point source sectors
Dry deposition	Inline	
Photolysis	Inline	
Vertical diffusion	ACM2	
Lighting NOx	Not included	
Surface HONO	Enabled	
Biogenic emission	Pre-calculated MEGAN	

Timing test: A one-month preliminary CMAQ run for the 36-km resolution domain was completed (however, with incorrect emissions) on our small Linux cluster. On average, it takes about 55 minutes to complete one day simulation with 16 CPUs. Thus, it will take approximately 8 days for one year simulation (214 days from April 1 to October 31). For two years with at least three sets of emissions - this will take 8*2*3=48 days. This is not fast enough, as the 12-km and 4-km simulations will be considerably slower, due to finer grid size and larger domain size (4-km domain). We will move our production CMAQ simulation to the EOS/Ada clusters on TAMU. These large will allow multiple jobs to be conducted simultaneously, thus greatly reduce the computation time. An updated estimation of computation time will be available once we perform a test run on the EOS/Ada clusters.

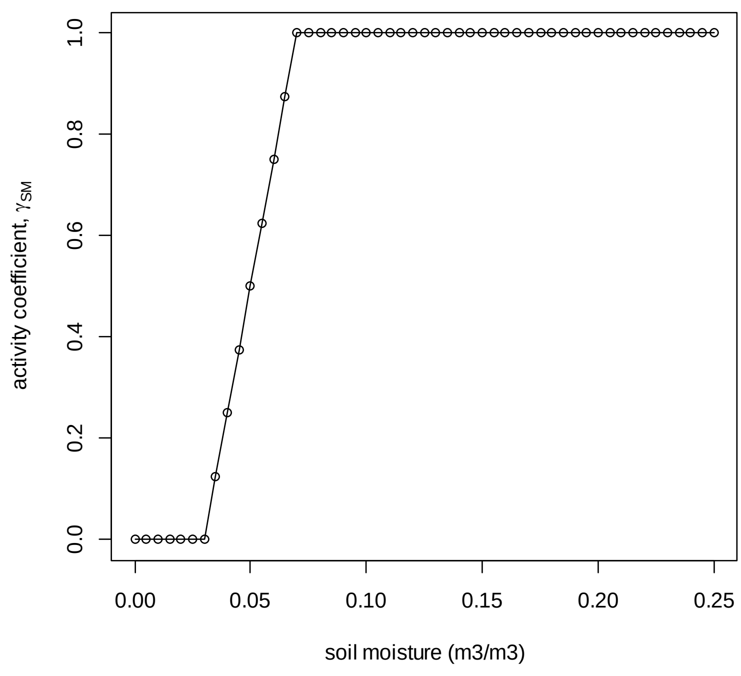
Preliminary Analysis

Task 2: Figures 2 and 3 show that no losses of isoprene are observed from the cartridges. All changes were within 5% of the initial mixing ratio with a non-significant increase of isoprene on the Tenax® cartridges. Since cartridges were stored the same way as field site or greenhouse acquired samples, i.e. on cold packs in a portable cooler, the only reason isoprene might increase on a cartridge is diffusion of isoprene or an underlying co-eluent onto the cartridge from laboratory air. We intend to take a series of lab air samples in January to evaluate that possibility.

Data shown in Figure 4 strongly suggests that the current (MEGAN) drought parameterization (Guenther el al., *Geosci. Model Dev.*, 5, 1471–1492, 2012) is reasonable:

$\gamma_{SM,isoprene} = 1$ for $\theta > \theta_1$
$\gamma_{SM,isoprene} = (\theta - \theta_w) / \Delta\theta_1$ for $\theta_w < \theta < \theta_1$, $\theta_1 = \Delta\theta_1 + \theta_w$
$\gamma_{SM,isoprene} = 0$ for $\theta < \theta_w$

in which θ is volumetric soil moisture, θ_w is soil moisture at the wilting point, and $\Delta\theta_1$ is an empirical soil moisture amount of 4% ($\Delta\theta_1$=0.04). According to this scheme, no isoprene is emitted after soil moisture drops below the wilting point. The function (θ_w=3%) looks like this:



Note that the drop is linear, which is seemingly matching the drop between doy 308 and doy 314 in Figure 4 (red dashed line), although a more curved function is possible, and may be evaluated when a higher data density is obtained. However, (i) the associated range of $\Delta\theta_1$ was smaller in our case (approx. 0.02 m^3/m^3), presuming the measured soil moisture was representative, which we cannot determine at this point due to the lack of a soil-specific sensor calibration to the organic-rich potting soil the seedling was in; and (ii) the wilting point, likely reached at doy 313 or 314, did not completely eliminate isoprene emissions. The latter was possibly due to non-uniform wilting of the various leaves on the plant. All leaves senesced during re-watering after doy 314, so we cannot conclude with high certainty that the drop in isoprene emission was solely due to the drought or also affected by senescence.

Data Collected

2nd set of cartridge tests: Cartridge isoprene contents as a function of time for fixed isoprene mixing ratio collected

Identify Problems or Issues Encountered and Proposed Solutions or Adjustments

Cluster disk failure due to power outage. We experienced an unexpected power outage in December 20, 2014, which leads to failure of 6 hard drives in the data storage system in our small research cluster. Luckily, these hard drives belong to several different RAID5 disk arrays and eventually all data were recovered. However, this caused the cluster to go offline for almost ten days. To reduce the possibility of data loss, we have since purchased several uninterruptable power supplies (UPSs) so that the cluster will gracefully powered itself off during a power outage. Additional daily incremental and weekly full backups for all source codes are implemented with copies stored on different machines to ensure data safety. Additionally, we will purchase additional storage to backup all data in the next couple of weeks.

Goals and Anticipated Issues for the Succeeding Reporting Period

Goals

Task 2: 1) Execute a 3rd set of cartridge tests in January; 2) continue to analyze chamber data as a supplement to the greenhouse measurements; 3) continue caretaking of the greenhouse-based seedlings, monitoring potential new growth as ambient insolation increases

Task 5: Finish 2007 NEI processing and perform QA/QC for the emissions. Complete simulations for 2011(base case and case 1).

Detailed Analysis of the Progress of the Task Order to Date

Task 1: Completed.

Task 2: Due to the delayed start of the project and ongoing issues, we are one to two months behind schedule (see proposed solution above and in last two reports).

Task 3: Waiting for a new drought parameterization but this would not slow down the progress of the project.

Task 4: Completed.

Task 5: On schedule.

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