AQRP Project 18-005

Next steps for improving Texas biogenic VOC and NO emission estimates

Final Report

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EXECUTIVE SUMMARY

Emissions of biogenic volatile organic compounds (BVOCs) from terrestrial ecosystems drive atmospheric distributions of ozone, particles and other constituents relevant for air quality. BVOC emissions are highly variable and can vary more than an order of magnitude over spatial scales of meters to kilometers and time scales of minutes to years. Estimating these emissions is challenging and yet accurate quantification and simulation of the magnitude and variation of these fluxes is a necessary step towards developing strategies for mitigating air pollution. Although there have been significant advancements in the procedures used to simulate biogenic emissions, the remaining uncertainties have limited predictability of Texas air quality simulations. This includes significant gaps in our understanding of biogenic emissions and their implementation in numerical models including isoprene, monoterpene and sesquiterpene emission factors and soil nitric oxide (NO) emissions.

The goal of Texas Air Quality Research Program (AQRP) Project 18-005 was to improve numerical model predictions of regional ozone and aerosol distributions in Texas by reducing uncertainties associated with quantitative estimates of biogenic volatile organic compound (BVOC) and soil NO emissions from Texas and the surrounding region. We aimed to improve the capability of the Model of Emissions of Gases and Aerosols from Nature (MEGAN) framework to estimate emissions of these compounds. This was accomplished by measuring isoprene, monoterpene and sesquiterpene emission factors of dominant urban and native Texas tree and crop species and integrate these results, and those from other studies, into an updated model, MEGAN version 3.1.

Our specific objectives included:

1. Conduct measurements of isoprene, monoterpene and sesquiterpene emission factors of important eastern Texas tree and crop species and investigate the variability within and among species and vegetation types.

2. Update the MEGAN model by incorporating an improved soil NO emission approach and integrating the emission factor data from objective 1 into the MEGAN emission factor processor.

3. Investigate the sensitivity of updated biogenic emissions estimated for Texas and surrounding regions.

All three objectives were accomplished as summarized by the following:

BVOC emission measurements

Terpenoid emission factors of dominant Texas species, including urban and native trees and agricultural crops, were successfully measured using three enclosure approaches. Each

approach is optimal for a specific subtask. One approach focused on rapid isoprene measurements to generate a large isoprene database for known isoprene-emitting trees, a second approach targeted speciated (88 compounds) terpenoid emissions of dominant Texas trees, and the final approach was used to investigate a broader range of BVOC from plant species (Texas crops) that were expected to have low terpenoid emissions. MEGAN model simulations show that the investigated plant species dominate the total BVOC emission from Eastern Texas.

About two-thirds of all trees emit isoprene at leaf-level rates less than ~ 0.1 nmol m^{-2} s^{-1} while the rest emit isoprene at rates that are several orders of magnitude higher. The Biogenic Emission Inventory System version 3 (BEIS3) model assigns a single leaf-level canopy-average emission factor equivalent to ~24 nmol m^{-2} s^{-1} to all isoprene-emitting trees in Texas. The leaf-level canopy-average isoprene emission factors measured for this study ranged from 27 to 43 nmol m^{-2} s^{-1} for 6 Texas isoprene emitting tree species. A large (37 to 54%) within-species emission factor variability was observed. This variability was reduced after accounting for the contribution of differences in the light environment. This was accomplished by applying an equation that accounts for variations in canopy leaf area index (LAI) depth. Isoprene emission factors for the same species differed by a factor of two for two different locations which may be due to environmental conditions or genetic differences. Measurements from a range of locations may be needed to accurately assign species-specific isoprene emission factors.

Speciated terpenoid emissions of 20 dominant Texas tree species were investigated using a glass enclosure with analysis by Thermal Desorption Gas Chromatography with Time-of-Flight Mass Spectrometer and Flame Ionization Detector (TD-GC-TOFMS/FID). These trees are associated with over half of the total terpenoid emissions in Eastern Texas. Eighty-eight different terpenoid compounds were detected including monoterpenes, aromatic monoterpenes, oxygenated monoterpenes, sesquiterpenes, a homoterpene and a diterpene. The observations were used to estimate emission factors for the nine MEGAN3.1 terpenoid emission categories. This includes the major contributors to total terpenoid emissions (e.g., pinenes) as well as minor compounds that have not typically been reported by previous BVOC emission studies. These minor compounds are individually small quantities but together make a significant contribution to the total terpenoid emission of some tree species. Of the 20 tree species, only sweetgum, loblolly pine and a few oaks had previously been investigated with high quality (j=4) emission measurements. Five species had no reported measurements and six species had reported measurements for isoprene but no other BVOC. Several of the investigated trees were found to be relatively low emitters (crepe myrtle, camphor, Chinese tallow tree) while others (Post oak, Southern live oak, Pecan, cedar elm and baldcypress) had monoterpene and/or sesquiterpene emission rates that are more than a factor of 8 higher than BEIS.

Low isoprene and monoterpene emission rates were observed for all 8 dominant Texas crop species investigated using the glass enclosure and Proton Transfer Reaction Time-of-Flight Mass spectrometer (PTRTOFMS) approach but observed sesquiterpene emissions were on a similar level as some tree species. Significant emissions of other biogenic VOC were observed including

acetaldehyde, acetone, acetic acid, and DMS. Methanol dominated emissions of all crops except for Bermuda grass and peanuts. Barley, Bermuda grass and wheat had the highest total emissions of BVOC other than methanol.

MEGAN3.1 model

The MEGAN model pre-processor and emission calculator codes were improved by updating the soil NO emissions code to the state-of-the-art approach developed by Hudman at al. (2012) and Rasool et al. (2016). The Emission Factor Processor code was modified to improve the approach used to assign default values. The input files were also updated to improve the default values and to incorporate the results of this study. The resulting codes are referred to as MEGAN3.1. Each version of each input file is assigned a unique name to ensure version control.

MEGAN3.1 Sensitivity and Assessment

Soil NO and BVOC emissions simulated using the SMOKE-BEIS, MEGAN2.1, MEGAN3 and MEGAN3.1 approaches were compared for a summer 2013 scenario across the TCEQ 12 and 36 km domains. MEGAN3.1 NO emission estimates tend to be a factor of 2 higher than BEIS and MEGAN3 and a factor of 2 lower than MEGAN2.1 although this varies by region in agreement with the results of Hudman et al. (2012). All four models have some similar features including high emissions in the Central US and some areas of California, and low emissions in the Rocky Mountain states.

In general, MEGAN3.1 estimated lower isoprene emissions and higher terpene emissions than MEGAN3. The lower MEGAN3.1 values are primarily due to an improved assignment of non-emitters. A lack of observations in the MEGAN3.0 database resulted in non-emitters, such as maple trees, being assigned a moderate (average of all trees) isoprene emission factor due to no data being available. MEGAN3.1 domain total isoprene emissions were about 10% lower than BEIS for the contiguous U.S. and the 12 km domain. In Texas, MEGAN3.1 isoprene was slightly lower than MEGAN3 and much lower than MEGAN2.1 or BEIS.

MEGAN3.1 total monoterpene emissions were about 36% higher than MEGAN3 for the contiguous U.S. and the 12 km domain primarily due to the addition and revision of emission factors input to the MEGAN EFP emissions database. In Texas, the MEGAN3.1 monoterpene emissions were higher than MEGAN3 and lower than MEGAN2.1 and BEIS. All four models predict relatively high monoterpene emissions in the southeastern US and Eastern Texas. MEGAN3.1 monoterpene emissions are higher than MEGAN3 and lower than BEIS throughout this region.

The MEGAN3.1 average leaf-level isoprene emission factor for 13 intensive aircraft flux measurement sites, 11.7 nmol m^{-2} s^{-1}, is within 5% of the aircraft-based isoprene emission factor while the MEGAN3.0 isoprene emission factor is about 20% higher than the aircraft

value. The MEGAN3.1 values are more highly correlated with the aircraft measurements than are the MEGAN3 values with r^2 values of 0.65 and 0.01 respectively. The results are similar for mixed forest sites but the MEGAN3.1 isoprene estimates for pine forests are 40% higher than aircraft-based flux measurements and values for oak forests are 25% lower. MEGAN3.1 tends to agree with the aircraft measurements at moderate isoprene levels (mixed forests), underpredict at high isoprene (oak forests) and overpredict for low isoprene landscapes (pine forests). These differences could be due to the different composition of isoprene emitting species in these forests or could be due to other factors such as differences in whether the isoprene emitters tend to be in the understory, where there is little light to drive isoprene emission as tends to occur in pine forests, or in the overstory, which tends to be the case for oak forests. As discussed in section 2.2.1, there may also be location driven differences associated with climate, stress, genetic populations, or other factors.

The MEGAN3.1 average leaf-level monoterpene emission factor for the 13 intensive aircraft sampling sites, 0.75 nmol m^{-2} s^{-1}, is a factor of 2.2 higher than the aircraft based monoterpene emission factor. Pine forests are a factor of 2.8 higher while oak forests are 45% higher. The MEGAN3.0 monoterpene emission factor is only 16% higher than the aircraft based emission factor. This is not surprising since the MEGAN3.0 emission factors are to a large degree based on these same aircraft measurements, due to the lack of high quality monoterpene emission factor data. The MEGAN3.1 values have a much larger variability than the MEGAN3 values due to the integration of the emission factors from this study into the MEGAN emission factor processor database. The MEGAN3.1 monoterpene emission factors tend to agree with the aircraft measurements at low monoterpene emission factors but overpredict for higher monoterpene emissions such as from pine forests. This could be due to uncertainties in the leaf enclosure measurements but it should also be recognized that the aircraft monoterpene flux measurements are near the detection limit of that system and are relatively more uncertain than the isoprene flux measurements.

Below, we list the conclusions of Project 18-005 and recommendations for further work.

Conclusions

- Multi-modal enclosure (isoprene-only, speciated terpenoids, comprehensive BVOC) measurement approach can effectively maximize regional characterization of a broad range of vegetation and chemical species.
- Species-average isoprene emission factors for Texas isoprene-emitting species (various oaks and sweetgum) varied from 27 to 43 nmol m^{-2} s^{-1} including 4 tree species (Post oak, Shumard oak, Swamp Chestnut oak, and Sweetgum) emitting ~30 nmol m^{-2} s^{-1} and 2 species (Southern live oak and Water oak) emitting ~40 nmol m^{-2} s^{-1}. Emission factor variability was reduced after accounting for light environment using a canopy LAI depth parameter.
- Very low emission rates of isoprene and monoterpenes were observed for Texas crop species in contrast to some literature reports. Significant crop emissions of sesquiterpenes,

acetaldehyde, acetone, acetic acid, and DMS were observed and methanol dominated all crop emissions except for Bermuda grass and peanuts. Barley, Bermuda grass and wheat had the highest BVOC emissions other than methanol.

- Eight-eight terpenoid compounds were emitted from 20 Texas trees. These compounds are mostly monoterpenes and sesquiterpenes but include some aromatic monoterpenes, oxygenated monoterpenes and sesquiterpenes, a homoterpene and a diteprene.
- The dominant Texas monoterpene is a-pinene and dominant Texas sesquiterpenes include b-caryophyllene, a-humulene and d-cadinene.
- Three urban Texas trees (crepe myrtle, camphor, and Chinese tallow tree) that are not included in the BEIS model were found to be very low emitters of terpenoid compounds.
- Total monoterpene emission factors for trees ranged from 2 to 6730 pmol m^{-2} s^{-1} and total sesquiterpene emission factors ranged from 0.2 to to 557 pmol m^{-2} s^{-1} with high and low emitters observed for both conifer and broadleaf tree species. Compared to BEIS, the measured values ranged from 90 times lower to 44 times higher.
- Five Texas tree species (post oak, southern live oak, pecan, cedar elm and baldcypress) had monoterpene and/or sesquiterpene emission factors that were a factor of 8 or more higher than the values used in BEIS.
- Relatively low monoterpene emission factors were observed for some common eastern Texas and southeastern US trees (loblolly pine and sweetgum) resulting in overall lower monoterpene emissions for MEGAN3.1 compared to BEIS for the TCEQ 12 km domain. The enclosure based emission factors may be biased by stress and may not be representative of regional emission behaviour.
- MEGAN3.1 has lower isoprene and higher monoterpene and NO emissions than MEGAN3 emissions. Compared to BEIS, MEGAN3 isoprene and monoterpene emissions are lower and NO emissions higher.
- The MEGAN3.1 isoprene emission factors are in good agreement with aircraft flux measurements. MEGAN3.1 monoterpene emission factors are a factor of two higher than aircraft based emission factors but agree within the large uncertainties of the aircraft flux measurements.

Recommendations for Future Work

- **ISOPRENE VARIABILITY:** Examine the location-dependent variability of isoprene emission factors and other leaf traits of a widespread isoprene emitting species (e.g., post oak, southern live oak, sweetgum) to characterize driving variables and establish the number of sites required to quantify representative isoprene emission factors.
- **CANOPY ENVIRONMENT:** Evaluate BEIS, MEGAN2, MEGAN3 and other canopy environment model simulations with light and temperature measurements throughout a range of tree canopies, especially in open and heterogeneous canopies.
- **CANOPY LOSS:** Conduct field measurements to develop and test a detailed 1D model of canopy and surface layer BVOC oxidation and deposition to improve biogenic emission

model evaluations by accurately relating emissions to concentrations and to provide the basis for representing these processes in 3D chemistry and transport models.

- **SHRUBLANDS:** Improve MEGAN3.1 desert, grass and shrubland landcover, especially shrub species composition and cover, and emissions data for west Texas and western US.
- **URBAN:** Improve MEGAN3.1 urban landcover, especially tree species composition and cover, and emission factors to reduce uncertainties that are otherwise expected to be much higher than in rural areas.
- **PREPROCESSOR:** Improve tools for pre-processing meteorological data for input to CAMx (i.e., WRFCAMx) to also provide input data for MEGAN3.1 in the required format.
- **TERPENOIDS AND STRESS:** Investigate terpenoid responses to drought, heat and other stress with field enclosure and ambient measurements to evaluate MEGAN3.1 estimates of stress induced emissions and reduce uncertainty in terpenoid emission factor estimates.
- **CONSTRAINING TERPENES:** Develop and apply an optimal (for cost, time, accuracy) approach for characterizing regional monoterpene and other terpenoid emission factors using a combination of enclosure and ambient terpenoid measurements.
- **MEGAN3.1:** MEGAN3.1 should be used for estimating emissions of NO, isoprene, monoterpene, sesquiterpenes and other biogenic emissions in Texas while continuing to improve MEGAN inputs, especially landcover and emissions data.

1.0 INTRODUCTION

This document provides the final report for the Texas Air Quality Research Program (AQRP) Project 18-005, "Next steps for improving Texas biogenic VOC and NO emission estimates". The project Co-Principal Investigators (Co-PIs) are Dr. Alex Guenther (UC Irvine) and Dr. Greg Yarwood (Ramboll Environ). The AQRP project manager is Dr. Elena McDonald-Buller at the University of Texas, Austin. The project liaison for the Texas Commission on Environmental Quality (TCEQ) is Mr. Doug Boyer.

The overall goal of Project 18-005 was to improve numerical model predictions of regional ozone and aerosol distributions in Texas by reducing uncertainties associated with quantitative estimates of biogenic volatile organic compound (BVOC) and nitric oxide (NO) emissions from Texas and the surrounding region. The overall benefit of this project is more comprehensive biogenic emission estimates for the Texas air quality simulations that are critical for scientific understanding and the development of regulatory control strategies that will enhance efforts to improve and maintain clean air.

1.1 Background

Emissions of reactive gases from the earth's surface drives the production of ozone and aerosol and other atmospheric constituents relevant for regional air quality. Emissions of some compounds, including BVOCs and NO, are highly variable and can vary more than an order of magnitude over spatial scales of a few kilometers and time scales of less than a day. This makes estimation of these emissions especially challenging and yet accurate quantification and simulation of these fluxes is a necessary step towards developing air pollution control strategies and for attributing observed atmospheric composition changes to their causes. Models assume that emission rates are the product of an emission factor (EF) and an emission activity factor, similar to the approach used for most anthropogenic emission estimates. While research activities tend to focus on emission activity factors, it is clear that uncertainties in EF make an important contribution and may even dominate the total uncertainty in BVOC emission rate estimates (Arneth et al. 2011, Guenther 2013). Although there have been significant advancements in the procedures used to simulate BVOC emissions, recent efforts have focused on emission activity processes and there have been few measurements of BVOC emission factors even though this remains a major outstanding contribution to the overall uncertainty. One of the difficulties in assigning emission factors is the large variability in reported rates which indicates that there are unaccounted processes driving this variability.

Soil microbes are thought to contribute about 15% of global NO emissions and 40 to 80% of total NO emissions in some agricultural regions with high fertilizer application rates (Hudman et al. 2012). BEIS3.6 and MEGAN3.0 use the approach of Yienger and Levy (1995) to estimate biogenic soil NO emissions, which captures some major features of soil NO emissions including biome specific emission factors and the major meteorological drivers of precipitation and temperature. Hudman et al. updated these procedures and integrated them on-line within the GEOS-Chem model and used satellite observations to show that the approach could reproduce the observed interannual variability (Hudman et al. 2012). Rasool et al. 2016 integrated the

Hudman et al. model into a special version of the CMAQ model and improved the driving variables. In both cases, the soil NO emission model has been coupled within a CTM. There remains an unmet need for using this improved approach to estimate soil NO emissions for off line simulations using air quality models such as CAMx (Ramboll 2018) or CMAQ model versions without the in-line update by Hudman et al.

1.2 Overview of Approach

The project aimed to reduce biogenic VOC and NO emission uncertainties to improve the ability of biogenic emission estimation tools to better predict emissions for air quality simulations. This was accomplished by field measurements and model development.

Our specific objectives included:

- Conduct field measurements of isoprene, monoterpene and sesquiterpene emission factors of important eastern Texas plant species and investigate the variability within and among species and vegetation types.
- Update the MEGAN3 model by incorporating an improved soil NO emission approach and integrating the emission factor data from objective 1 into the MEGAN emission factor processor.
- Update the MEGAN3 Emission factor processor including emission factors for regions outside of Texas and for compounds other than isoprene
- Prepare recommendation on isoprene emission factors including the scientific basis for choosing these factors.
- Investigate sensitivity of updated biogenic emissions estimated for Texas and surrounding regions.

1.3 Overview of Report

In Section 2, we describe measurements of biogenic terpenoid emissions. In Section 3, we report on our efforts to update the MEGAN3 model with improved soil NO emission calculations and improved BVOC emission factors for Texas and the surrounding region. Section 4 describes a sensitivity analysis of Texas biogenic emissions. In Section 5, we present conclusions and recommendations for future work. Finally, Section 6 contains results of the data quality audits.

2.0 TASK 1: MEASURE TEXAS BVOC EMISSION FACTORS AND THEIR VARIABILITY

2.1 BVOC Measurement Approaches

BVOC emission factor measurements characterizing dominant Texas tree species were made on mature field grown trees around Houston and Austin Texas during June 2019. Houston area tree species were identified by staff arborists on the U. Houston and Rice campuses. The three tree species studied near Austin were identified with a field guide with high confidence as there were only one or two species within each of those genera at these sites. Emission factors for dominant Texas crops were measured on mature plants grown in a UCI plant growth chamber during May to June 2019.

Three approaches were used to quantify BVOC emissions from important Texas plant species: 1) LICOR gas exchange system with Gas Chromatography with Quadrupole Mass Spectrometer (GCQMS) analysis in the field, 2) glass cuvette enclosure field system with laboratory GCTOFMS analysis, and 3) glass cuvette enclosure system with direct laboratory analysis by PTRTOFMS. These approaches are complementary and are suitable for investigating three major categories of Texas plants: 1) Isoprene-emitting trees, 2) other trees, and 3) crops. Isoprene emissions from isoprene-emitting trees were examined using the LICOR-GCQMS system which enabled measurements of a large number of trees and leaves under representative field conditions. Comprehensive speciated terpenoids from representative leaves of all trees were measured using the Glass-GCTOFMS system. Comprehensive BVOC emissions from crops were measured using the glass-PTRTOFMS system to assess total terpenoids (which were very low) and target BVOC other than terpenoids. Table 2-1 shows the number of trees and leaves investigated and the number of samples collected with each system for the 30 dominant Texas plant species investigated.

Table 2-1. Summary of all BVOC emission factor measurements.

Species (common name)	# of Plants	# of leaves	# of PTR MS	# of GCT	# of GCQ	ALL
Arachis hypogaea (Peanut)	3	8	8	4	0	12
Carya illinoinensis (Pecan)	1	3	0	6	0	6
Celtis occidentalis (Hackberry)	2	6	0	6	0	12
Cinnamomum camphora (Camphor)	1	3	0	6	0	6
Cynodon dactylon (Bermuda grass)	3	6	6	0	0	6
Glycine max (Soybeans)	3	7	7	0	0	7
Gossypium hirsutum (Cotton)	3	6	6	0	0	6
Hordeum vulgare (Barley)	3	6	6	0	0	6
Juniperus ashei (Ashe juniper)	2	8	0	16	0	16
Juniperus virginiana (redcedar)	1	3	0	6	0	6
Lagerstroemia indica (Crepe myrtle)	1	3	0	6	0	6
Liquidambar styraciflua (sweetgum)	3	11	0	6	22	28
Magnolia grandiflora (Magnolia)	1	3	0	6	0	6
Medicago sativa (Alfalfa)	3	8	8	0	0	8

Pinus echinata (Shortleaf pine)	1	2	0	4	0	4
Pinus palustris (Longleaf pine)	1	2	0	4	0	4
Pinus taeda (Loblolly pine)	2	7	0	14	0	14
Prosopis glandulosa (Honey mesquite)	2	8	0	16	0	16
Quercus fusiformis (Plateau live oak)	2	8	0	16	0	16
Quercus michauxii (Chestnut Swamp oak)	1	10	0	0	20	20
Quercus nigra (Water oak)	9	50	0	12	96	108
Quercus phellos (Willow Oak)	2	7	0	14	0	14
Quercus shumardii (Shumard oak)	2	8	0	13	59	72
Quercus stellate (Post oak)	4	25	0	13	59	72
Quercus virginiana (Southern Live Oak)	18	94	0	12	186	298
Taxodium distichum (Baldcypress)	1	3	0	12	0	12
Triadica sebifera (Chinese Tallow)	1	3	0	12	0	12
Triticum aestivum (Wheat)	3	6	6	0	0	6
Ulmus crassifolia (Cedar elm)	2	8	0	16	0	16
Zea mays (Corn)	3	6	6	0	0	6

The number (#) of plants and leaves measured and number of samples taken with each instrument are shown. Instruments include PTRTOFMS (PTR), GC-TOFMS/FID (GCT), GC-QMS (GCQ) and the total (ALL).

2.1.1 Isoprene emission, leaf traits and light environment measurements

Leaf environment and traits, including isoprene emission rate, specific leaf mass, leaf thickness, photosynthetic efficiency, photosynthesis and transpiration rates, etc., were measured on multiple leaves of six major isoprene-emitting Texas tree species including 1) an evergreen oak Quercus (Q.) virginiana (southern live oak), 2) four deciduous oaks including Q. michauxii (swamp chestnut oak), Q. stellata (post oak), Q. nigra (water oak), and Q. shumadii (Shumard oak) and 3) Liquidambar styraciflua (sweetgum). All species are found in landscapes near Houston, and were sampled on the U. Houston and Rice campuses. Quality Assurance and Quality Control (QA/QC) procedures were based on previous studies (Geron et al. 2016) and included 1) blanks measured from empty cuvette prior to emission measurements, 2) measurements made at both ambient and "standardized" light and temperature conditions, 3) mass spectrometer analysis for positive identification of isoprene, 4) replicate measurements, and 5) in-situ calibration after every fifth measurement using a standard cylinder referenced to a certified standard. Two environmental controlled LICOR6400 leaf enclosure systems were used as shown in Figure 2-1. These systems enable leaf-level measurements in a highly controllable temperature and light environment. For this study, emission factor measurements were made on leaves exposed to a temperature of 30^{o}C and photosynthetic photon flux density of 1000 μmol m^{-2} s^{-1} representing standard conditions for emission factors.

Along with photosynthesis and transpiration, the growth light environment of individual leaves was characterized using a fish-eye lens and digital image numerical analysis to quantify the daily total photon flux based on the approach of Niinemets et al. 2010. Additional leaf traits were measured using a handheld MultispeQ fluorometer/spectrometer to quantify parameters including photosynthetic efficiency, linear electron transfer, non-photochemical quenching and

leaf slope and aspect. The chlorophyll fluorescence measurement is an indicator of stress on a plant's photosynthetic apparatus. Figure 2-1 illustrates a typical deployment of the two LICOR systems on an oak tree at the Rice campus. Mature leaves were sampled over a range of light environments including relatively high light environments at the top of a tree and the southern edge of open canopies to the shaded portion of the lower canopy with a relatively low daily light level. Most sampled leaves were growing at a height of 2 to 3 meters but some leaves were sampled using a bucket lift, shown in Figure 2-2, to access mature leaves at the canopy top.

Figure 2-1. Ladder platform deployment of LICOR 6400 systems for isoprene measurements on an oak tree on the Rice University campus.

Figure 2-2. Bucket lift deployment of LICOR 6400 systems for isoprene measurements at the top of an oak tree on the Rice University campus.

The results of the measurements acquired with the approach described in this section are presented and discussed in section 2.2.1.

2.1.2 Speciated Terpenoid measurements using GCTOFMS/FID

Comprehensive terpenoid measurements were made on 20 Texas tree species including 4 of the isoprene-emitting tree species described in section 2.1.1 and 16 additional dominant Texas trees including 2 isoprene emitters (Quercus fusiformis known as Plateau live oak and Quercus phellos known as willow oak), 5 of the most common urban species in Houston (Triadica sebifera known as Chinese Tallow tree, Magnolia grandiflora known as Magnolia, Lagerstroemia indica known as crepe myrtle, Celtis occidentalis known as hackberry, and Cinnamomum camphora known as Camphor) and 9 native species (Pinus taeda known as loblolly pine, P. echinata known as shortleaf pine, P. palustris known as longleaf pine, Prosopis glandulosa known as honey mesquite, Juniperus ashei known as Ashe juniper, Juniperus virginiana known as eastern redcedar, Ulmus crassifolia known as cedar elm, Carya illinoinensis known as Pecan, and Taxodium distichum known as baldcypress). Most of these species are common in the region near Houston and were sampled on the U. Houston and Rice campuses. The three exceptions include Q. fusiformis (plateau live oak), J. ashei (ash juniper) and Prosopis glandulosa (mesquite) which are common on the Edwards Plateau and were sampled at the Wild Basin Wilderness preserve and Emma Long Metropolitan park near Austin Texas. QA/QC

procedures were based on previous studies (Geron et al. 2016) and included 1) blanks measured from empty cuvette prior to emission measurements, 2) measurements made on sun leaves, 3) mass spectrometer analysis for positive identification of isoprene, 4) replicate measurements, and 5) twice daily calibration using a certified standard. The two glass cuvette systems used for these measurements are shown in Figures 2-3 and 2-4. These light and temperature controlled systems measured emissions at controlled temperature and light conditions. For this study, leaves were typically exposed to 30^{o}C and 1000 micromol/m2/s photosynthetic photon flux density to establish speciated terpenoid emission factors at standard conditions. In some cases, especially while deployed at the Austin field sites, the ambient temperatures were so high that the system could only cool the enclosure down to around 31 or 32^{o}C and a temperature response algorithm was used to establish the emission at standard conditions.

In addition to measuring BVOC fluxes, photosynthesis and transpiration rates of each leaf were measured to quantify the physiological status of the leaf. Figures 2-3 and 2-4 illustrate a typical deployment of the glass cuvette systems on a mesquite tree near Austin TX. Mature sun leaves were sampled by accessing the edge of an open canopy at a height of 2 to 3 meters. The samples were collected on solid absorbent (Tenax and Carbograph 5TD) tubes that were sealed and shipped to the Guenther laboratory at UC Irvine for immediate analysis by Gas Chromatography with Time-Of-Flight Mass Spectrometry and Flame Ionization Detector (GC-

TOFMS/FID). This analytical system is capable of detecting over 100 individual terpenoid compounds.

Figure 2-3. Comprehensive terpenoid EF measurement systems enclosing 2 sets of leaves on a mesquite tree near Austin TX.

Figure 2-4. Comprehensive terpenoid EF measurement system control, power and CO2/H2O sensor.

The results of the measurements acquired with the approach described in this section are presented and discussed in section 2.2.2.

2.1.3 Comprehensive VOC screening using PTRTOFMS

Eight dominant Texas crops (Peanut, Bermuda grass, Soybeans, Cotton, Barley, Alfalfa, Wheat and Corn) were grown in a UCI growth chamber and screened for total BVOC including methanol, acetaldehyde, acetic acid, acetone, dimethyl sulfide (DMS), sum of methacrolein and methyl vinyl ketone, isoprene, benzene, toluene, total monoterpenes, and total sesquiterpenes. A Selected Reagent Ion Time-of-Flight Mass Spectrometer (Ionicon PTR-TOFMS 1000 Ultra) with an ion funnel was used to quantify emissions at high frequency (1 sample per second) allowing a large number of replicate measurements. The ion funnel focuses the ions into the transfer lens system to greatly improve ion transmission, leading to a lower detection limit of ~5 ppt (Ionicon, Innsbruck, Austria). The SRI-TOFMS instrument was operated in the standard H3O+ mode but the instrument's SRI NO+ ionization and fast GC capability, along with speciated terpenoid measurements using the system described in section 2.1.2, will be used in future efforts to confirm these compounds and identify additional individual compounds.

Figure 2-5. Comprehensive VOC screening using PTRTOFMS.

The results of the measurements acquired with the approach described in this section are presented and discussed in section 2.2.3.

2.2 BVOC measurement results

2.2.1 Isoprene emission, leaf traits and light environment measurements

The isoprene emission factor measurement approach described in section 2.1.1 provided emission factor estimates along with ancillary observations of plant traits and light environment (see Table 2-2). The average emission factor, measured at a temperature of 30°C and a Photosynthetic Photon Flux Density (PPFD) of 1000 μmol m^{-2} s^{-1}, of all leaves is 34.3 nmol m^{-2} s^{-1} which falls in the middle of the range of reported emission factors for Texas isoprene emitting trees (see Table 2-3). The observed average sun leaf emission factor for this study (Table 2-2) ranged from 28 nmol m^{-2} s^{-1} for Post oak (20% below the overall average) to 48 nmol m^{-2} s^{-1} for water oak (15% greater than the overall average). A large variability was observed with a range of a factor of 20 (4.6 to 102 nmol m^{-2} s^{-1}) and a standard deviation that is 46% of the mean value. The wide range of values published in the literature for each species (Table 2-3) may be

partially due to sampling bias and differences in measurement techniques but is likely also due to actual differences in emission factors for plants at different locations and experiencing different environmental conditions. The relatively lower quality measurements, classified as "j=0" data, in the MEGAN3 emissions database consistently have lower isoprene emission factors that are likely due to shading in the enclosures, plant stress and possibly sample degradation. However, there are large differences even for "j=4" higher quality measurements as shown in Table 2-3. Examples include the reported "j=4" isoprene emission factors for Turkey oak (24 to 79 nmol m^{-2} s^{-1}) and Black oak (33 to 72 nmol m^{-2} s^{-1}). These studies used the same or similar measurement approaches and so the results likely represent actual variability due to genetics and other factors. This indicates that emission factor measurements at multiple locations may be needed to characterize the regional average isoprene emission factor.

Table 2-2. Summary of measured isoprene emission factors (Isop., nmol m^{-2} s^{-1}) photosynthesis (Psyn, μmol m^{-2} s^{-1}) and stomatal conductance (Cond., mmol m^{-2} s^{-1}) rates, specific leaf area (SLA, cm^2 g^{-1}), relative chlorophyll (Chlor, %) and leaf thickness (μm).

Species	Location	position	Isop.	Psyn	Cond.	SLA	Chlor.	Thickness
Sweetgum	Rice	Sun	35.0	13.8	179	99	48	60
Sweetgum	Rice	Shade	10.7 (23.1)	4.28 (8.85)	45 (90)	183	48	50
Swamp oak	Rice	Sun	35.7	13.3	128	95		
Water oak	Rice	Sun	50.4	14.0	168	74	50	97
Water oak	Rice	Shade	9.9 (32.0)	4.64 (9.32)	41 (90)	138	49	70
Water oak	UH	Sun	37.9	15.0	200	84	42	110
Water oak	UH	Shade	12.1 (17.6)	4.95 (11.1)	46 (110)	113	47	65
Shum. oak	Rice	Sun	41.2	13.9	122	113	44	51
Shum. oak	Rice	Shade	8.2 (14.6)	3.1 (4.9)	23 (160)	195	47	88
Post oak	Rice	Sun	39.3	15.4	140	88		
Post oak	UH	Sun	20.9	12.8	161	83	49	93
Post oak	UH	Shade	8.1 (16.7)	6.0 (8.02)	195 (100)	105	54	57
S. Live Oak	Rice	Sun	41.1	16.5	167	64	58	107
S. Live Oak	Rice	Shade	13.5 (20.1)	4.18 (9.0)	37 (80)	94	56	99
S. Live Oak	UH	Sun	29.3	13.9	179	64	51	95
S. Live Oak	UH	Shade	8.1 (19.5)	4.02 (9.8)	54 (100)	84	46	113

Shade leaf isoprene, photosynthesis and stomatal conductance rates are shown for both measurements at ambient light and at PPFD=1000 (in parentheses).

It is well known that the light environment (daily total photons received) of the leaf can influence isoprene emission factors and is an important contributor to observed isoprene emission factor variability (Geron et al. 2001) but there has been little effort to quantify this (Niinemets et al. 2010). The observed average emission factor for all sun leaves (38.2 nmol m^{-2} s^{-1}) in this study is about a factor of 2 higher than the average for all shade leaves (19.2 nmol m^{-2} s^{-1}). The average photosynthesis rate of sun leaves, measured at a temperature of 30°C and PPFD of 1000 μmol m^{-2} s^{-1}, is about 65% higher than for shade leaves. Sun leaves also had higher (60%) stomatal conductance, lower (35%) specific leaf area and were 13% thicker. This demonstrates that the isoprene emission difference between sun and shade leaves is more pronounced than for other leaf traits.

BEIS3 assigns a single isoprene emission factor to all Texas isoprene emitting trees, a canopy average value of 24 nmol m^{-2} s^{-1}. MEGAN2.1 uses a canopy scale isoprene emission factor that cannot be directly compared with leaf scale emission factors but is roughly equivalent to ~34 nmol m^{-2} s^{-1} for sun leaves. The MEGAN2.1 EF is similar to the average sun leaf (11% lower) observed during this study while the BEIS3 value is similar (25% higher) to the average observed shade leaf value. The assignment of "sun" and "shade" designations to leaves during any field study is somewhat subjective with the leaf considered to be "shade" if it appears that other leaves would frequently block the sun and considered a "sun" leaf otherwise. For this study, we categorized leaves as sun or shade based on visual inspection and also quantified the light environment using measurements of leaf slope (with respect to horizontal), aspect and a fish-eye lens photograph of the canopy above the leaf. A canopy gap analysis program was used to quantify the canopy openness (27±9%, range: 7 to 48%), the daily photon flux (122±63 mol m^{-2} d^{-1}, range <10 to ~250), the fractions contributed by direct and diffuse light and a quantitative estimate of LAI depth which can be directly used in the MEGAN 3 model. This provided a continuous characterization of light environment, rather than the binary and relatively subjective categories of "sun" vs "shade" and enabled normalization of this influence with a standardization factor, LAI depth, to account for differences in light environment (see figure 2-6). LAI depth was used to account for emission variation due to differences in light environment by using the average LAI depth vs emission factor relationship, shown in Figure 2-6, to normalize the emission factors to a standard LAI depth of 1.5 m^2 m^{-2}. The isoprene emission factors normalized to a leaf temperature of 30°C, a photosynthetic photon flux density of 1000 μmol m^{-2} s^{-1} and an LAI depth of 1.5 m^2 m^{-2} (see Table 2-4), are ~30 nmol m^{-2} s^{-1} for four species (Post oak, Shumard oak, Swamp Chestnut oak and Sweetgum) and ~40 nmol m^{-2} s^{-1} for two other species (Southern live oak and Water oak). These values are well within the range of previously reported isoprene emission factors.

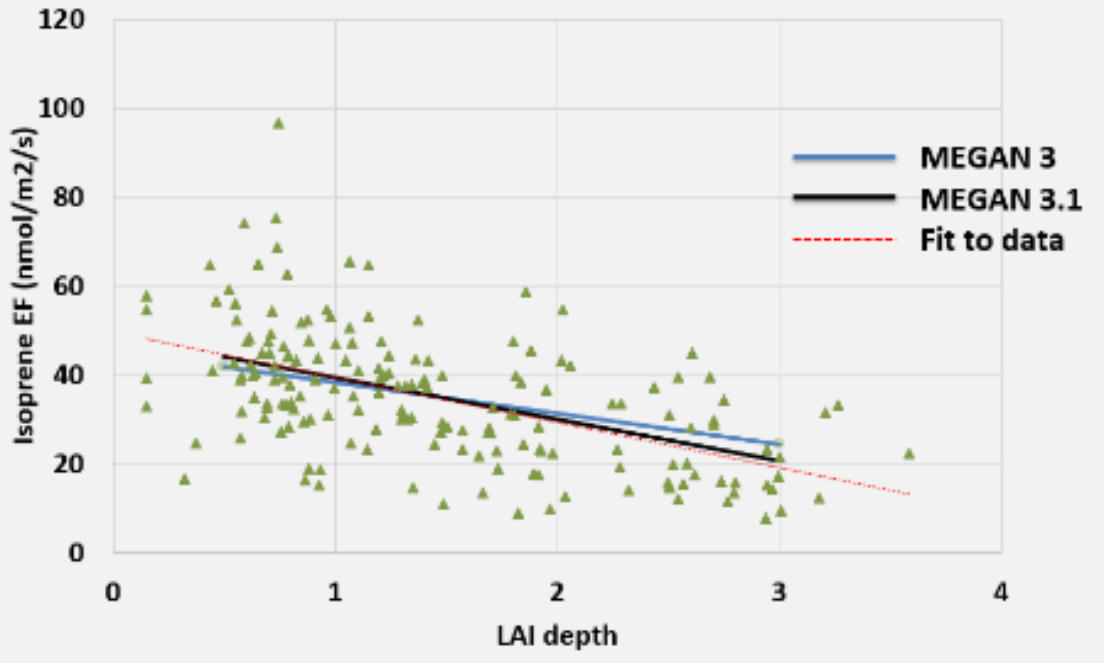

Figure 2-6. Observed relationship between isoprene emission factors and LAI depth for all leaves. Blue line is the relationship assumed in MEGAN3 (based on Niinemets et al. 2010), red line is the fit to these data, black line is the relationship assumed in MEGAN3.1.

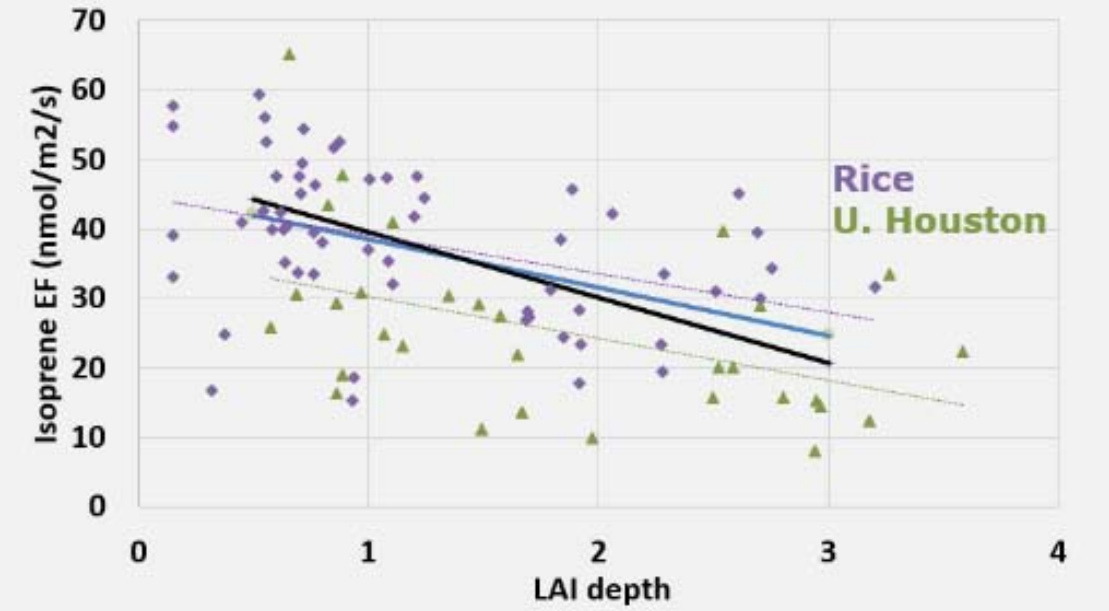

Figure 2-7. Same as in Figure 2-6 except that data is shown separately for Rice University campus (purple) and U. Houston campus (green).

Figure 2-7 shows that trees on the Rice University campus have higher isoprene emission rates than trees on the UH campus. Sun leaves at the Rice university campus were 88% higher for Post oak and ~ 35% higher for water oak and Southern live oak in comparison to sun leaves on the UH campus. There are at least four possible reasons for this difference: 1) LAI depth normalization does not sufficiently account for differences in light environment, 2) differences in the weather prior to the periods of measurements, 3) differences in chemical and physical climate or environmental stress at the two locations, and 4) genetic differences. Regarding the first possibility, our analysis of these data indicate that LAI depth does not fully represent light environment but actual light levels were not a better indicator of emission factors. More observations are needed to investigate this further. The second possibility is based on our knowledge that isoprene emission factors are higher during warm sunny periods than for cooler shadier periods (Guenther et al. 2012). While we considered this with the existing MEGAN light and temperature response functions, these algorithms may not be sufficiently accurate. The third possibility has been proposed by Lahr et al (2015) based on measurements of isoprene emission factors of post oak and sweetgum leaves at urban, suburban and rural sites near Houston. The mid-summer post oak isoprene emission factors at the suburban site (similar to Rice) were 38% higher than at the urban (similar to UH) site. However, they report that the sweetgum emissions were 43% lower at the urban site. Lahr et al. (2015) concluded that the difference in the isoprene emission factors at these sites was due to the location (urban, suburban, rural) but do not explain why post oak and sweetgum differ. The fourth possibility is based on Geron et al. (2001), Bäck et al. (2012) and other studies that have revealed large genetic variations in BVOC emission capacities within a species. The lineage of the trees on the two campuses is unknown but they likely represent different populations that could have different chemotypes within a species that differ in their isoprene emission capacity.

Table 2-3. Isoprene emission factors expressed per leaf area (nmol m^{-2} s^{-1}) and per leaf mass (μg g^{-1} h^{-1}) and specific leaf area (SLA, cm^2 g^{-1}). The type of measurement (E=enclosure, A=aircraft eddy covariance) and J value (0: low quality, 4: high quality) is indicated.

Species	Isoprene (area)	Isoprene (mass)	SLA	Type	J	Reference
BEIS3 (canopy average)	24	79	133			
MEGAN2.1 (Sun leaves)	34	84	90			
Liquidambar styraciflua (sweetgum)	4.7	11	96[a]	E	0	Helmig et al. 1999
	22	51	96[a]	E	0	Guenther 1996a
	34	80	96[a]	E	4	Guenther 1996a
	34	79	96[a]	E	4	Guenther 1996b
	37	77	87	E	4	Geron et al. 2001
	44			E	4	Lahr et al. 2015[b]
	25			E	4	Lahr et al. 2015[c]
	31			E	4	Lahr et al. 2015[d]
	40	97	98	E	4	Guenther 2019

	27			A	4	Yu et al. 2017
	35	84	99	E	4	This study[c]
Nyssa sylvatica		4.9			0	Helmig et al. 1999
(Blackgum)		15		E	4	Guenther 1996a
	30	87	119	E	4	Geron et al. 2001
	33			E	4	Guenther 2019
Quercus michauxii	36	100	113	E	4	This Study[c]
(Chestnut Swamp oak)						
Quercus alba	50	104	84	E	4	Geron et al. 2001
(White oak)	36			E	4	Geron et al. 2016
	31			E	4	Harley et al. 1997
	51			E	4	Harley et al. 1997
	33			E	4	Potosnak 1997
	39			E	4	Guenther 2019
Quercus rubra	30	76	101	E	4	Geron et al. 2001
(N. Red oak)	36			E	4	Geron et al. 2016
	50			E	4	Guenther 2019
Quercus nigra	46	92	81	E	4	Geron et al. 2001
(Water oak)	38	78	84	E	4	This Study[b]
	50	91	74	E	4	This Study[c]
Quercus phellos	48	105	88	E	4	Geron et al. 2001
(Willow Oak)						
Quercus shumardii	41	114	113	E	4	This Study[c]
(Shumard oak)						
Quercus stellata	39	77	80[a]	E	0	Helmig et al. 1999
(Post oak)	21	41	80[a]	E	0	Guenther 1996a
	43	84	80[a]	E	4	Guenther 1996a
	50	83	68	E	4	Geron et al. 2001
	36			E	4	Geron et al. 2016
	29			E	4	Lahr et al. 2015[b]
	40			E	4	Lahr et al. 2015[c]
	30			E	4	Lahr et al. 2015[d]
	39	84	88	E	4	This Study[c]
	21	42	83	E	4	This Study[b]
Quercus virginiana	40	52	54	E	4	Geron et al. 2001
(Southern Live Oak)	41	64	64	E	4	This Study[c]
	29	45	64	E	4	This Study[b]
Quercus (TX oaks)	39			A	4	Yu et al. 2017
Quercus falcata	13	29	88[a]	E	0	Helmig et al. 1999
(S. red oak)	57	127	88	E	4	Geron et al. 2001
Quercus coccinea	40	115	80	E	4	Harley et al. 1997
(Scarlet oak)						
Quercus laevis	16	35	87[a]	E	0	Guenther 1996a
(Turkey oak)	24	51	87[a]	E	4	Guenther 1996a

	79	171	87	E	4	Geron et al. 2001
Quercus prinus	23	50	89	E	4	Geron et al. 2001
(Chestnut oak)	50			E	4	Harley et al. 1997
Quercus velutina	72	178	103	E	4	Geron et al. 2001
(black oak)	33			E	4	Geron et al. 2016
	40			E	4	Harley et al. 1997
	33			E	4	Potosnak 1997

a: indicates literature value for SLA was used. b,c,d: indicates measurement location is urban (b), suburban (c), rural (d).

Table 2-4. Species-average isoprene emission factors (nmol m^{-2} s^{-1}) for canopy average, sun leaves, shade leaves, and leaves standardized to an LAI depth of 1.5.

Species	All	Sun	Shade	LAI = 1.5
Post Oak	24 ±13	28	17	27
Shumard Oak	27 ±15	39	15	28
Sweetgum	30 ±12	35	23	28
S. Live Oak	33 ±13	38	20	37
Swamp Ch. Oak	35 ±6	35	---	30
Water Oak	45 ±17	48	25	43

2.2.2 Speciated Terpenoid measurements using GCTOFMS/FID.

Speciated terpenoid emission factors for the 20 dominant Texas tree species listed in Table 2-5 were measured using the glass enclosure and GC-TOFMS/FID approach described in section 2.1.2. Leaves were measured at a temperature of ~30°C and a photosynthetic photon flux density (PPFD) of ~1000 μmol m^{-2} s^{-1} to establish emission factors at standard conditions. Eighty-eight terpenoid compounds were detected including 1 hemiterpene, 1 oxygenated hemiterpene, 2 hemiterpene oxidation products, 31 monoterpenes, 4 aromatic monoterpenes, 9 oxygenated monoterpenes, 32 sesquiterpenes, 6 oxygenated sesquiterpenes, 1 homoterpene, and 1 diterpene. On average, monoterpenes contributed 38% and sesquiterpenes 7% of the total non-isoprene total terpenoid emission for these tree species.

Monoterpene emissions were detected from all tree species (Table 2-5). The most common dominant monoterpene emitted was a-pinene, which was the major emission for about half of the tree species. Moderate to high total monoterpene emission rates with a high diversity (>5 monoterpenes) were observed for about half of the tree species. All three of the investigated species (crepe myrtle, Chinese Tallow, and Camphor) that are not included in the BEIS model had very low monoterpene emission rates (2 to 4 pmol m^{-2} s^{-1}). The monoterpene emission factors observed for three broadleaf species (Magnolia, mesquite, and post oak) are about a

factor of 2 higher than the BEIS values while four species (Pecan, southern live oak, baldcypress and cedar elm) are 8 to 44 times higher than the BEIS values. The post oak monoterpene emissions were dominated by the highly reactive monoterpene, beta-ocimene, which has been reported to be a stress-induced compound. Thus the observed high monoterpene emission may not be representative of all post oaks but may just indicate that these individuals were stressed. Two tree species (Loblolly pine and plateau live oak) had monoterpene emission factors that were a factor of 2 lower than the BEIS value and another two species (Longleaf pine and sweetgum) were 6 to 9 times lower (Table 2-5).

Half of the 20 tree species had total sesquiterpene emission factors exceeding 5 pmol m^{-2} s^{-1} (Table 2-5). The most common sesquiterpenes emitted were b-caryophyllene, a-humulene and d-cadinene which together were the major emission for about half of the tree species. The two juniper species (Ashe juniper and redcedar) had some of the lowest sesquiterpene emission rates. The highest sesquiterpene emissions (> 100 pmol m^{-2} s^{-1}) were observed for shortleaf pine, loblolly pine, baldcypress and post oak. These trees also tended to be the most diverse sesquiterpene emitters (>5 sesquiterpenes emitted). The observed sesquiterpene emissions for two species (Loblolly pine and southern live oak) were a factor of three higher than the BEIS values and another two species were 12 (Post oak) and 50 (Baldcypress) times higher. Five species (Ashe juniper, redcedar, plateau live oak, water oak, and cedar elm) had observed sesquiterpene emission factors that were 3 to 10 times lower than BEIS. The observed sesquiterpene emission factors for hackberry, sweetgum, magnolia and mesquite were 20 to 90 times lower than the BEIS values.

MEGAN3.1 assigns terpenoid compounds to nine of the twenty MEGAN emission classes. Oxidant reaction rates and aerosol yields of these terpenoids can vary by more than an order of magnitude demonstrating the need to categorize these compounds. The monoterpene emission factors for a- and b-pinenes (MEGAN emission class 3) and other highly reactive monoterpenes (MEGAN emission class 6) tended to dominate the observed total monoterpene emissions (see Table 2-6). The highly reactive sesquiterpene emissions (MEGAN class 9) were often a factor of 5 or more higher than the less reactive sesquiterpenes (MEGAN emission class 10). The emission factors for individual MEGAN emission classes (Table 2-6) ranged from less than 1 pmol m^{-2} s^{-1} to a maximum of 1800 nmol m^{-2} s^{-1} for pinene emissions from baldcypress. Total terpenoid emissions (excluding isoprene) ranged over a factor of 40 from ~0.06 nmol m^{-2} s^{-1} for Chinese tallow tree, hackberry and crepe myrtle to ~2 nmol m^{-2} s^{-1} for shortleaf pine and pecan. The highest total terpenoid (excluding isoprene) values are only ~6% of isoprene emission factors demonstrating how isoprene emitters can dominate regional total BVOC emissions even though they are a minority of trees. In addition to monoterpenes and sesquiterpenes, emissions of other terpenoids including aromatic monoterpenes (e.g. o-cymene, p-cymene, m-cymenene), oxygenated monoterpenes (e.g., alcohols, acetates, carbonyls), a homoterpene (dimethylnonatriene, DMNT), and a diterpene (Sandaracopimaradiene) were observed from some of these tree species but at relatively low rates.

Table 2-5. Observed total monoterpene (MT) and total sesquiterpene (SQT) leaf-level emission factors (pmol m^{-2} s^{-1}) and equivalent values for the BEIS model. "No Value" indicates that no value is included in BEIS.

Species	Observed MT	Observed SQT	BEIS MT	BEIS SQT
Pecan	1950	13	246	18
Hackberry	8.4	0.3	30	18
Camphor	3.4	1.1	No Value	No Value
Ashe juniper	211	2	122	15
Redcedar	118	5	122	15
Crepe myrtle	4.3	13	No Value	No Value
Sweetgum	75	1.1	460	28
Magnolia	1040	1	460	18
Shortleaf pine	1580	260	1430	34
Longleaf pine	162	54	1430	34
Loblolly pine	781	106	1430	34
Honey mesquite	39.5	0.2	15	18
Plateau live oak	12.8	6.5	31	18
Water oak	52.4	5	31	18
Willow oak	19.1	8.5	31	18
Post oak	69	214	31	18
South. live oak	281	54	31	18
Baldcypress	6730	557	282	11
Chinese tallow	2	0.6	No Value	No Value
Cedar elm	701	2.2	16	18

Table 2-6. Average emission factors (pmol m^{-2} s^{-1}) for MEGAN Emission Classes including MEC3 (pinenes), MEC4 (trienes), MEC 5 (other less reactive monoterpenes), MEC6 (other monoterpenes), MEC7 (aromatic C10), MEC8 (oxygenated monoterpenes), MEC9 (highly reactive sesquiterpenes), MEC10 (less reactive sesquiterpenes), and MEC17 (other stress compounds).

Species	MEC3	MEC4	MEC5	MEC6	MEC7	MEC8	MEC9	MEC10	MEC17
Ashe juniper	19	2	23	57	53	57	1	1	8
Baldcypress	1780	607	1585	1477	1251	34	549	8	85
Camphor	0	0	0.4	0	3	0	1	0.1	4
Cedar elm	510	20	29	115	27	0.3	2	0.2	14
Chinese Tallow	0.2	0.1	0.2	1	0.2	0.3	0.5	0.1	46
Crepe myrtle	2	0	0.2	0	2	0.1	12	1	50
Hackberry	4	0.1	0.3	1	3	0	0	0.3	42
Honey mesquite	4	0.1	0.4	6	25	4	0	0.2	32
Loblolly pine	575	7	31	136	31	0.5	89	17	0
Longleaf pine	39	18	16	61	26	2	48	6	167

Magnolia	322	30	117	425	132	15	1	0	0
Pecan	654	70	59	971	165	28	11	2	2
Plateau live oak	2	0.4	0.1	3	7	0.3	6	0.5	159
Post oak	2	32	1	15	17	2	188	26	287
Redcedar	5	6	0.5	78	26	2	4	1	96
Shortleaf pine	453	238	235	575	75	4	245	15	0
South. live oak	1	20	0.3	209	51	0.1	50	4	81
Sweetgum	22	1	1	25	25	1	1	0.1	330
Water oak	3	4	5	23	17	0.4	4	1	212
Willow oak	2	7	0.1	4	5	1	8	0.5	180

2.2.3 Comprehensive VOC screening using PTRTOFMS

BVOC emission factors of 8 dominant Texas crop species compiled in Table 2-7 were measured using the glass enclosure and PTRTOFMS approach described in section 2.1.3. Crop isoprene emission factors were less than 0.5% of the values determined for oaks and sweetgum (Table 2-2). This is in contrast to reports in the literature of moderate isoprene emission from some crops (e.g., Evans et al. 1982). Crop monoterpene emission factors were similar to those of the lowest emitting trees, e.g., Chinese tallow and camphor (Table 2-6). In contrast, crop sesquiterpene emissions were similar to those observed for many trees (Table 2-5). All 8 crops had significant emissions of other biogenic VOC compounds (Table 2-7). Methanol dominated all crop emissions except for Bermuda grass and peanuts. Some of the other dominant biogenic VOC emitted include acetaldehyde, acetone, acetic acid, and dimethyl sulfide (DMS). Barley, Bermuda grass and wheat had the highest total emissions of BVOC other than methanol.

Table 2-7. Observed isoprene, total monoterpenes (MT), total sesquiterpenes (SQT), acetaldehyde (Acetal.), acetone, acetic acid, dimethyl sulfide (DMS) and methanol emission factors (pmol m^{-2} s^{-1}) for eight Texas crops.

Species	Isoprene	MT	SQT	Acetal	Acetone	Acetic Acid	DMS	Methanol
Alfalfa	24	0	0	300	129	190	90	6650
Barley	122	19	411	698	311	568	80	4740
Bermuda grass	36	1	1170	238	108	589	42	0
Corn	10	9	67	14	48	17	55	5030
Cotton	0	0	0	0	0	155	83	18900
Peanut	43	5	0	204	95	251	161	0
Soybeans	12	102	0	63	80	28	105	3900
Wheat	17	53	718	125	42	80	0	4780

2.3 BVOC Measurement Deliverables

The BVOC emissions and ancillary measurements database described in this report are provided as a digital database.

3.0 TASK 2: MEGAN MODEL IMPROVEMENTS (MEGAN3.1)

3.1 Improved soil NO emission approach

An improved approach for estimating soil NO emissions, based on Hudman et al. (2012) and Rasool et al. (2016), was implemented in MEGAN3.1. Key improvements include 1) relating emissions to soil moisture, rather than precipitation, 2) decoupling water availability and temperature dependence and modifying the time scale, 3) improving gridded inventories for chemical fertilizers and manure, and 4) using MODIS-based growing season start and end dates for fertilizer application, and 5) including wet and dry nitrogen deposition, and 6) incorporating a representation of available N pool that includes natural, fertilizer and deposition sources. The resulting procedures were integrated into the GEOS-Chem model and evaluated using satellite observations to show that the approach could reproduce the observed interannual variability (Hudman et al. 2012).

The soil NO emission approach used in MEGAN3 and BEIS3.6 is based on Yienger and Levy (1995), a simple approach driven by landuse, temperature and precipitation that does not account for all of the observed variability. Soil moisture and landcover type, two of the key model inputs for estimating soil NO emissions using the Hudman et al. approach, were already available as inputs to MEGAN3 for estimating BVOC emissions. The daily fertilizer application rates, another required input, was implemented in MEGAN3.1 as a long-term average climatology. The climatological data can be replaced by year-specific fertilizer application data that users can calculate with the FEST-C modeling system (https://www.cmascenter.org/fest-c/) that uses the USDA EPIC model to simulate plant demand-driven fertilizer applications to commercial croplands throughout the contiguous US including Texas (Cooter et al. 2012).

Atmospheric nitrogen deposition inputs were implemented in MEGAN3.1 using a multi-year global climatology based on CESM CAM-Chem global nitrogen deposition estimates (Lamarque et al. 2012). As with fertilizer inputs, users can substitute the nitrogen deposition climatology data with specific model simulations or assimilated observations for a specific time period.

3.2 MEGAN Emission Factor Processor with new emissions data

The MEGAN3 framework includes an emission factor processor (EFP) that integrates plant species-specific emission factors and landcover data to generate landscape averaged emission factors. The EFP provides a transparent approach that enables users to determine the information that goes into the landscape average emission factor at any location in a model domain. The EF data generated by task 1 (see section 2) were compiled and integrated into the emissions comma separated values (CSV) input file for the EFP. The updated inputs were then used to estimate landscape average emission factor inputs for the MEGAN3.1 simulations described in section 4.

3.3 MEGAN3.1 Deliverables

The MEGAN3.1 emissions calculator and emission factor processor codes and associated input files and updated user guide were provided in a digital format and are also be available on the MEGAN Data Portal (bai.ess.uci.edu/ MEGAN).

4.0 TASK 3: MEGAN3.1 SENSITIVITY ANALYSIS OF TEXAS BIOGENIC EMISSIONS

4.1 MEGAN3.1 soil NO emissions

Soil NO emissions simulated using the SMOKE-BEIS, MEGAN2.1, MEGAN3 and MEGAN3.1 approaches were compared for the summer 2013 scenario for the TCEQ 12 and 36 km domains. MEGAN3.1 NO emission estimates tend to be a factor of 2 higher than BEIS and MEGAN3 and almost a factor of 5 higher than MEGAN2.1 (Figure 4-1) although this varies by region and, for example, MEGAN3.1 and BEIS are similar in Kentucky and Louisiana while MEGAN3.1 is a factor of 3 higher than BEIS in the central US states of Kansas and Nebraska (Figure 4-2). This is similar to the comparison reported by Hudman et al. (2012) for their new approach (the basis for MEGAN3.1) and the Yienger and Levy approach (the basis for MEGAN2.1, MEGAN3 and BEIS). All four models have some similar features including higher emissions in the Central US and California's Central Valley, and low emissions in the Rocky Mountain states (Figure 4-3). Also notable are the higher MEGAN3.1 emissions in northern and eastern Texas (Figure 4-5, 4-6).

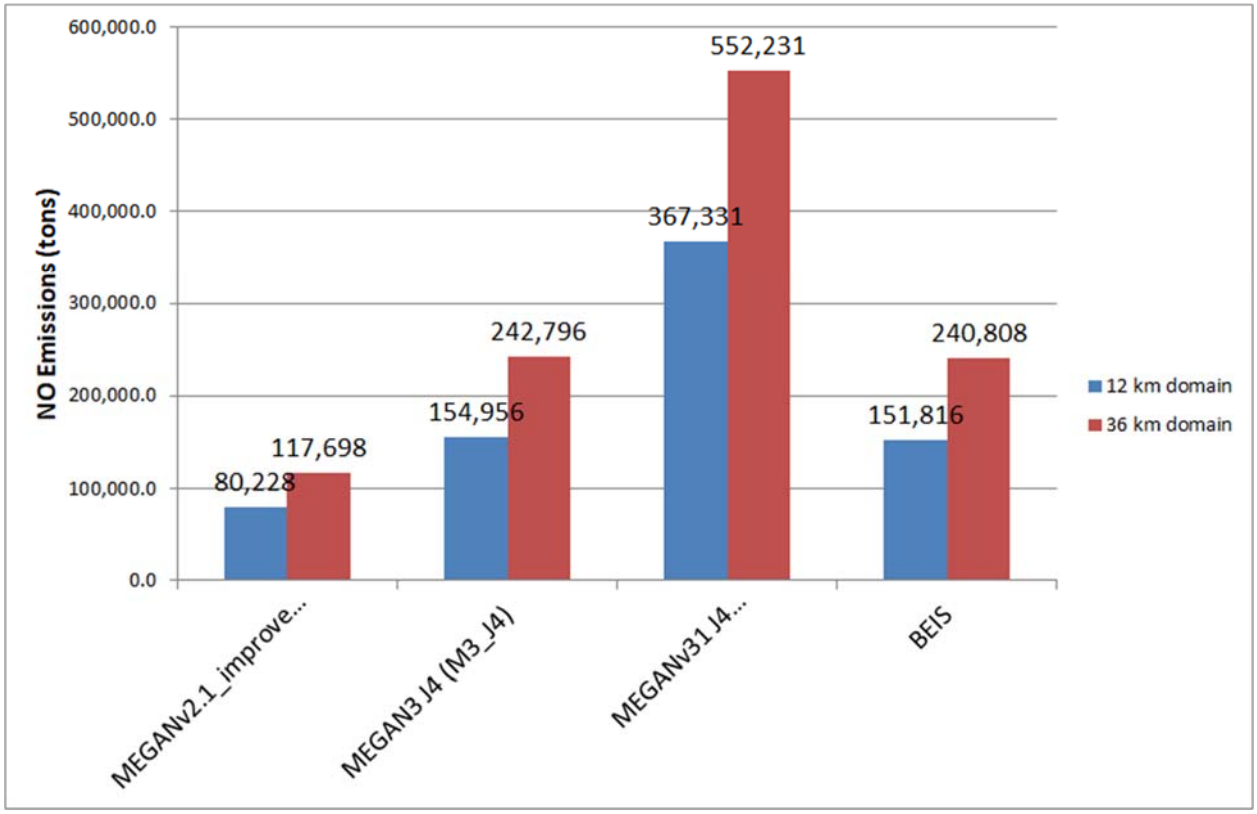

Figure 4-1. Total domain episode NO emissions (tons) for summer 2013 in the contiguous U.S. and the TCEQ 12 km domain estimated by MEGAN2.1, MEGAN3, MEGAN3.1 and BEIS models.

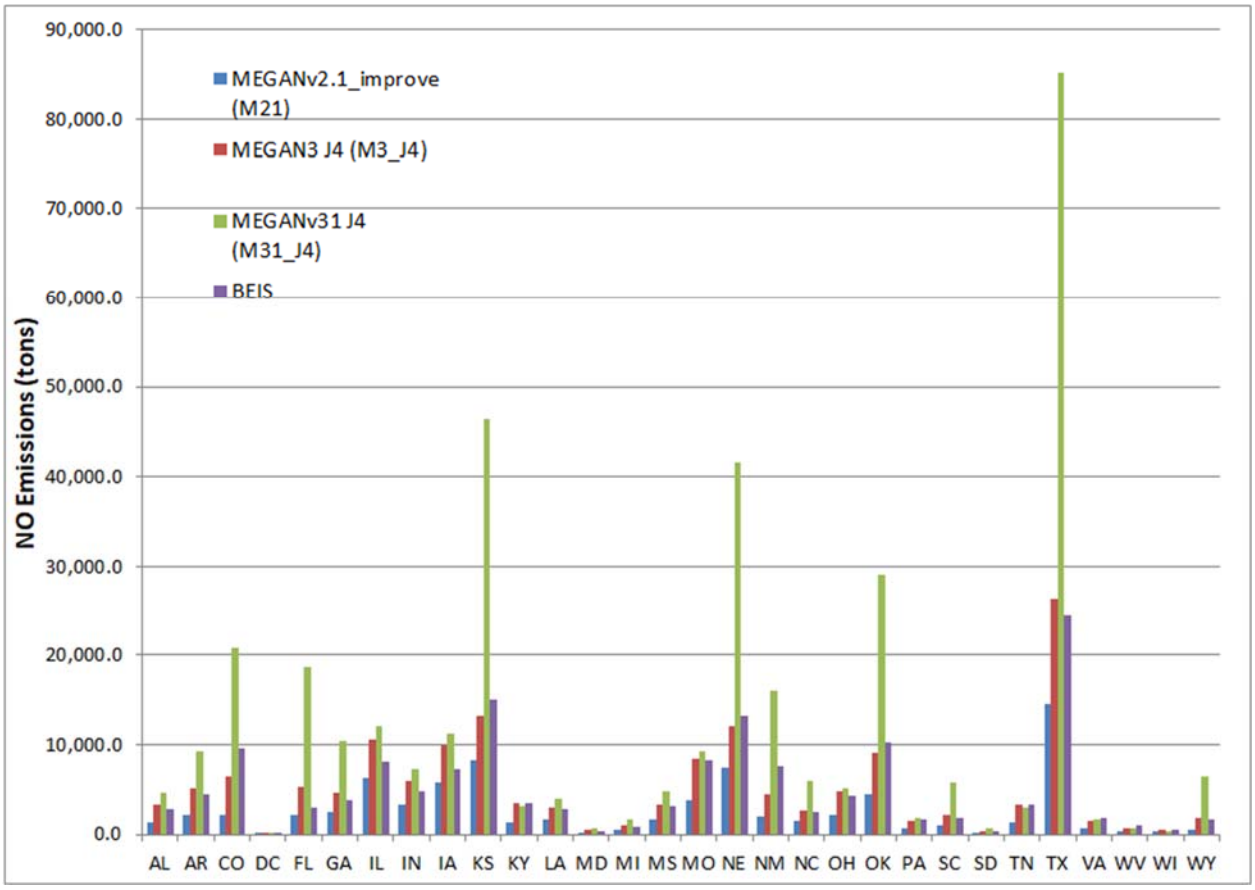

Figure 4-2. US State total NO emissions (tons) for summer 2013 in the TCEQ 12 km domain estimated by MEGAN2.1, MEGAN3, MEGAN3.1 and BEIS models.

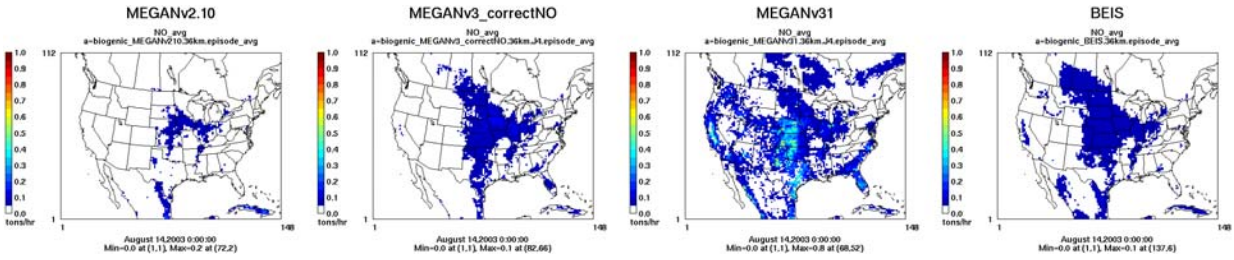

Figure 4-3. Episode average soil NO emissions (tons h^{-1}) simulated using SMOKE-BEIS, MEGAN2.1, MEGAN3 and MEGAN3.1 models for summer 2013 in the TCEQ 36 km domain.

A map showing difference in model estimates of soil nitrcic oxide emissions across the contiguous US

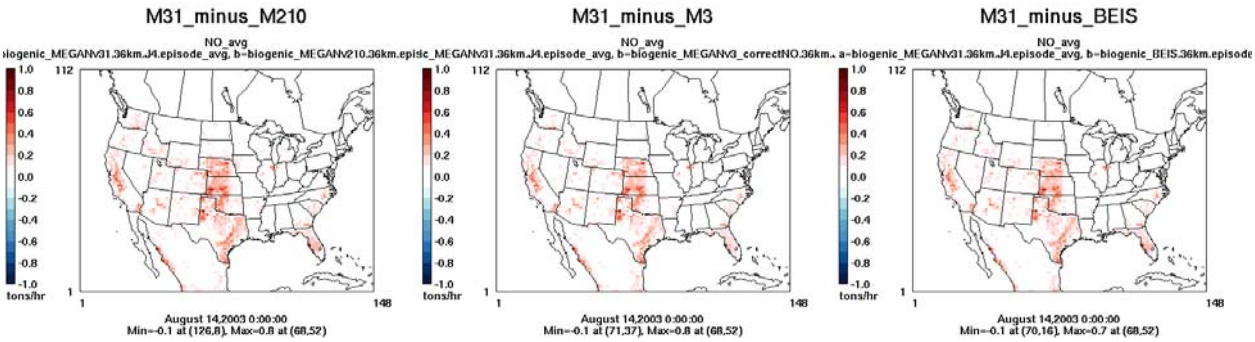

Figure 4-4. Difference (MEGAN3.1 minus other models) in soil NO emissions (tons h^{-1}) simulated, and shown in Figure 4-3, for summer 2013 in the TCEQ 36 km domain.

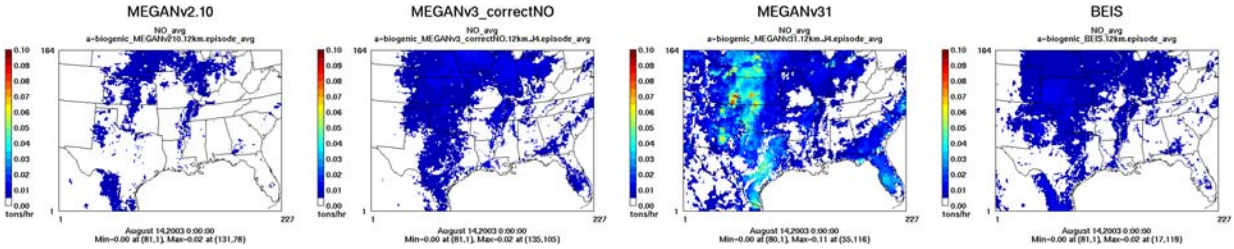

Figure 4-5. Episode average soil NO emissions (tons h^{-1}) simulated using SMOKE-BEIS, MEGAN2.1, MEGAN3 and MEGAN3.1 models for summer 2013 in the TCEQ 12 km domain.

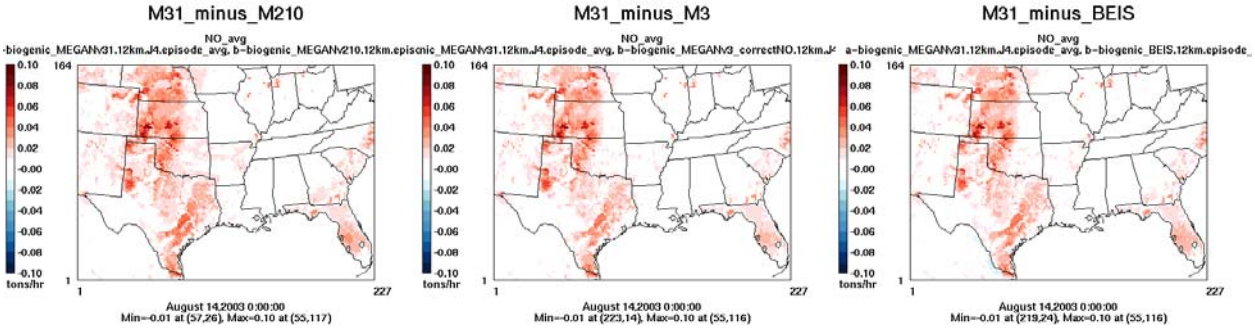

Figure 4-6. Difference (MEGAN3.1 minus other models) in soil NO emissions (tons h^{-1}) simulated, and shown in Figure 4-5, for summer 2013 in the TCEQ 12 km domain.

4.2 MEGAN3.1 BVOC emissions

BVOC emissions simulated using the SMOKE-BEIS, MEGAN2.1, MEGAN3 (with J=4) and MEGAN3.1 (with J=4) model approaches were compared for the summer 2013 scenario (June 1-July 15, 2013 period) for the TCEQ 12 and 36 km domains. In general, all four models have similar domain total isoprene emissions (Figure 4-7) although there are regional differences with MEGAN3.1 isoprene emission estimates lower than BEIS in shrublands and higher in southeastern US forests (Figure 4-10). MEGAN3.1 domain total isoprene emissions were about 10% lower than BEIS and 20% lower than MEGAN3 for the contiguous U.S. and the 12 km domain (Figure 4-7). In Texas, MEGAN3.1 isoprene was slightly lower than MEGAN3 but much lower than MEGAN2.1 or BEIS (Figure 4-8). All four models estimate higher isoprene emissions in the oak forest of the Ozarks and southeastern US (Figure 4-9, 4-11). MEGAN3.1 isoprene is higher than BEIS along the Texas-Louisana border and to the east but is lower in the rest of Texas (Figure 4-10, 4-12). MEGAN3.1 isoprene emissions are much lower than BEIS in central and west Texas and throughout the southwestern US. The development of the input data for MEGAN3.1 has focused on forested regions and additional efforts are needed to improve shrubland, grassland and cropland input data (both landcover and emissions) for the MEGAN emission factor processor. There are relatively few measurements in these landscapes making it difficult to assess which model has better performance.

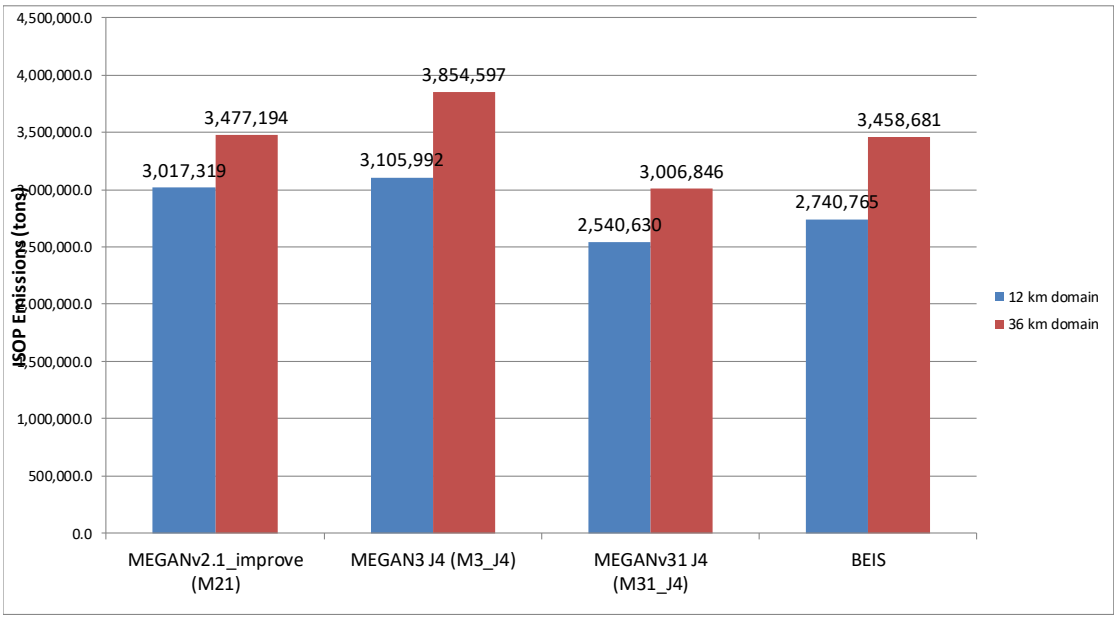

Figure 4-7. Total domain episode isoprene emissions (tons) for summer 2013 in the contiguous U.S. and TCEQ 12 km domain estimated by MEGAN2.1, MEGAN3, MEGAN3.1 and BEIS models.

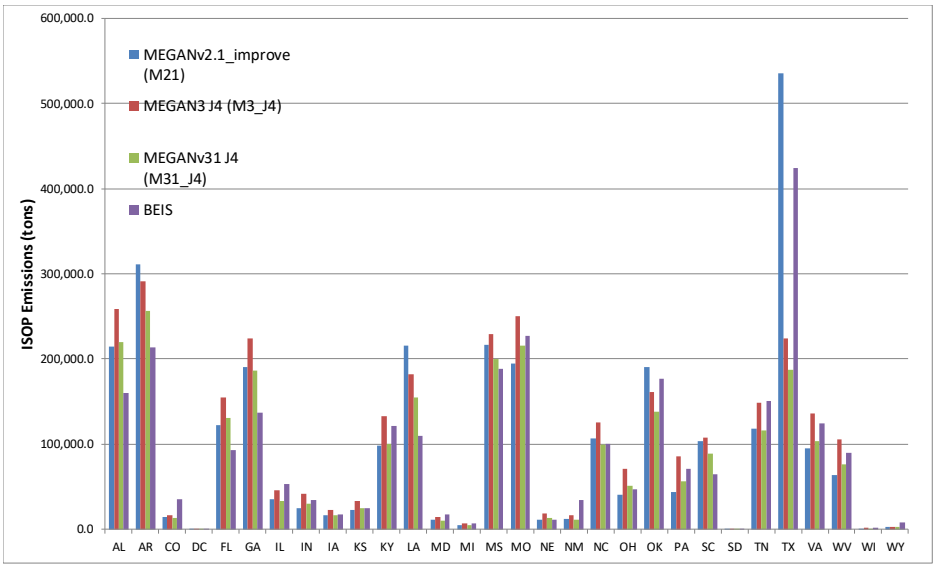

Figure 4-8. US State total isoprene emissions (tons) for summer 2013 in the TCEQ 12 km domain estimated by MEGAN2.1, MEGAN3, MEGAN3.1 and BEIS models.

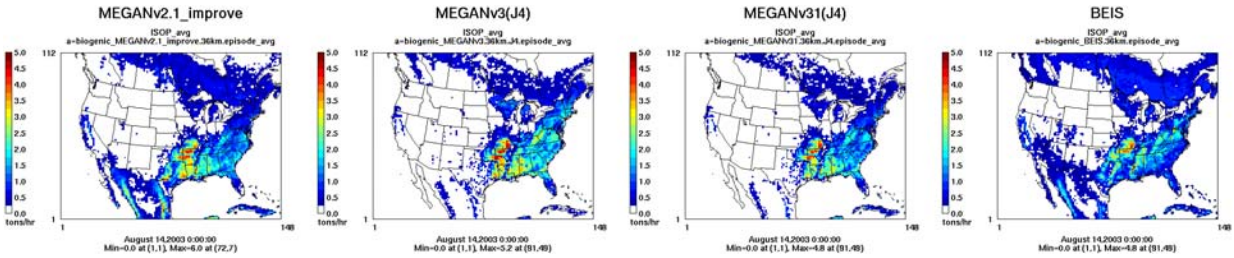

Figure 4-9. Episode average isoprene emissions (tons h^{-1}) simulated using SMOKE-BEIS, MEGAN2.1, MEGAN3 and MEGAN3.1 models for summer 2013 in the TCEQ 36 km domain.

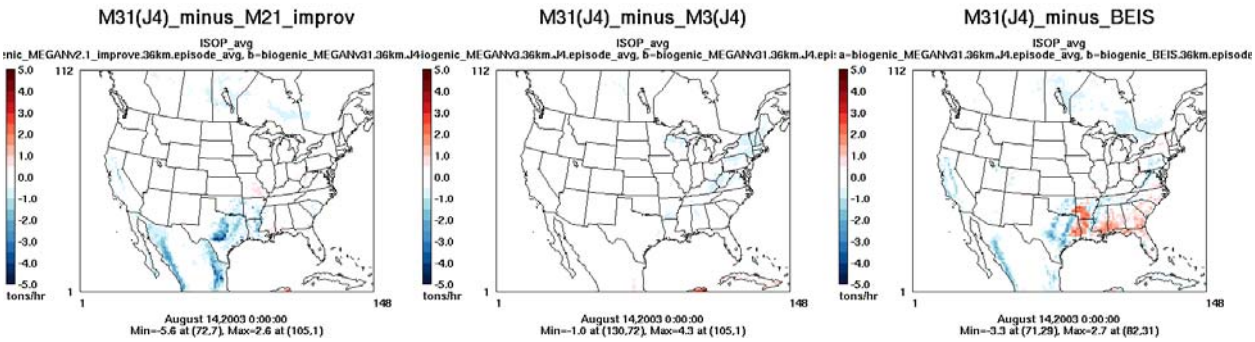

Figure 4-10. Difference (MEGAN3.1 minus other models) in isoprene emissions (tons h^{-1}) simulated, and shown in Figure 4-9, for summer 2013 in the TCEQ 36 km domain.

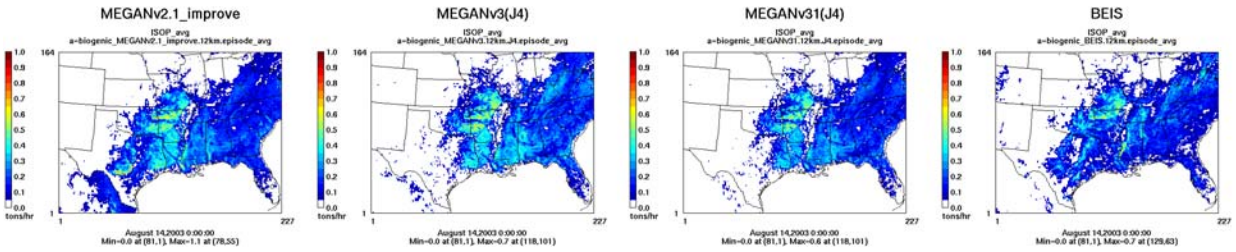

Figure 4-11. Episode average isoprene emissions (tons h^{-1}) simulated using SMOKE-BEIS, MEGAN2.1, MEGAN3.j=4 and MEGAN3.1.j=4 models for summer 2013 in the TCEQ 12 km domain.

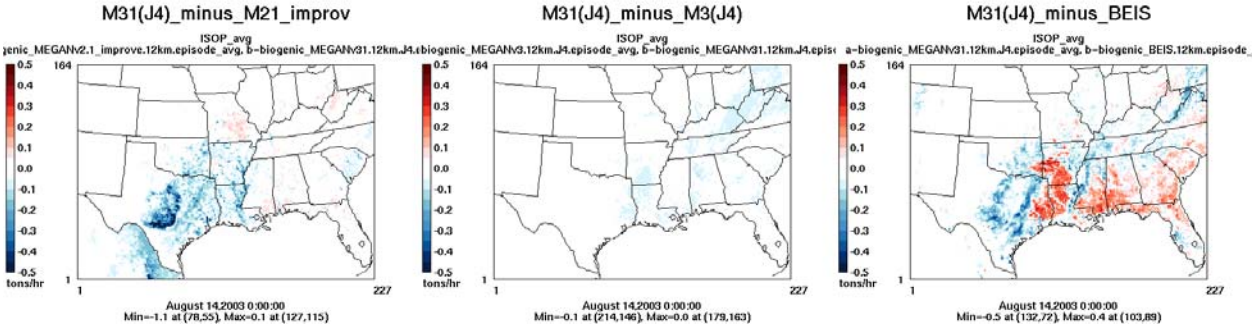

Figure 4-12. Difference (MEGAN3.1 minus other models) in isoprene emissions (tons h^{-1}) simulated, and shown in Figure 4-11, for summer 2013 in the TCEQ 12 km domain.

MEGAN3.1 total monoterpene emissions were a factor of 3 higher than MEGAN3 for the contiguous U.S. and the 12 km domain (Figure 4-13) primarily due to the addition of the emission factors measurements from this study (see Table 2-6) to the MEGAN EFP emissions database and because of an error identified in the MEGAN code. In Texas, MEGAN3.1 monoterpene emissions were higher than MEGAN3 and lower than MEGAN2.1 and BEIS (Figure 4-14). All four models predict higher monoterpene emissions in the southeastern US and eastern Texas (Figure 4-15, 4-17). MEGAN3.1 monoterpene emissions are higher than MEGAN3 and lower than BEIS throughout this region (Figure 4-16, 4-18). MEGAN3.1 terpene emissions are lower than BEIS in central and western Texas and throughout the southwestern US and the uncertainties are relatively high due to the lack of measurements. Improvements in the shrubland and grassland input data (landcover and emissions) are required for more reliable MEGAN3.1 (or BEIS) estimates in this region.

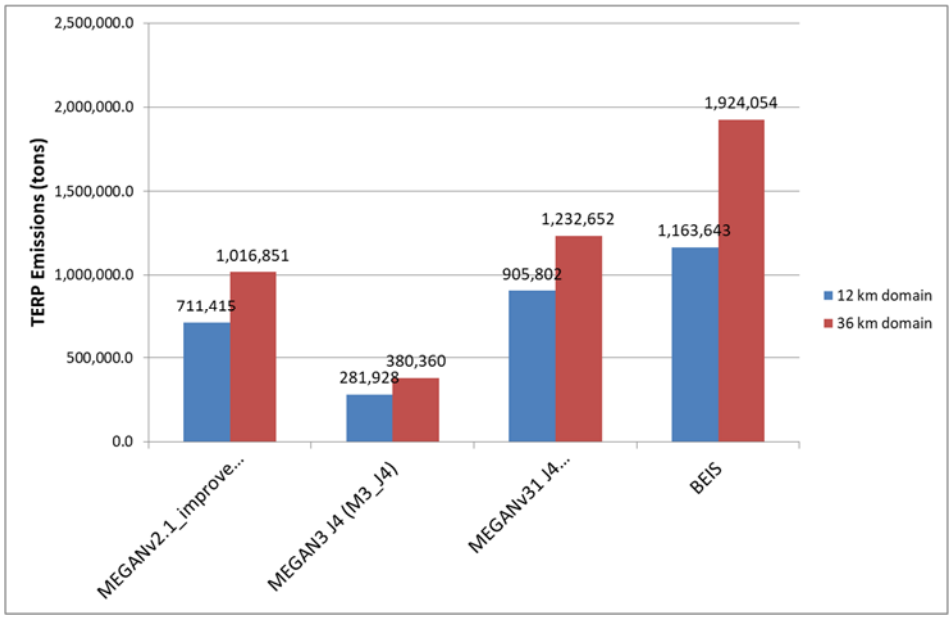

Figure 4-13. Total domain episode terpene emissions (tons) for summer 2013 in the contiguous U.S. and TCEQ 12 km domain estimated by MEGAN2.1, MEGAN3.j=4, MEGAN3.1.j=4 and BEIS models.

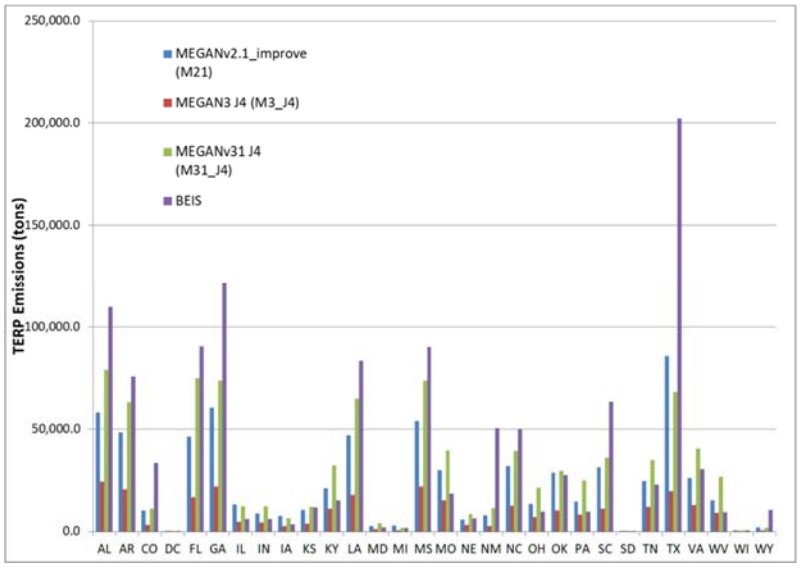

Figure 4-14. US State total terpene emissions (tons) for summer 2013 in the TCEQ 12 km domain estimated by MEGAN2.1, MEGAN3.j=4, MEGAN3.1.j=4 and BEIS models.

map of difference in model terpene emissoin estimates

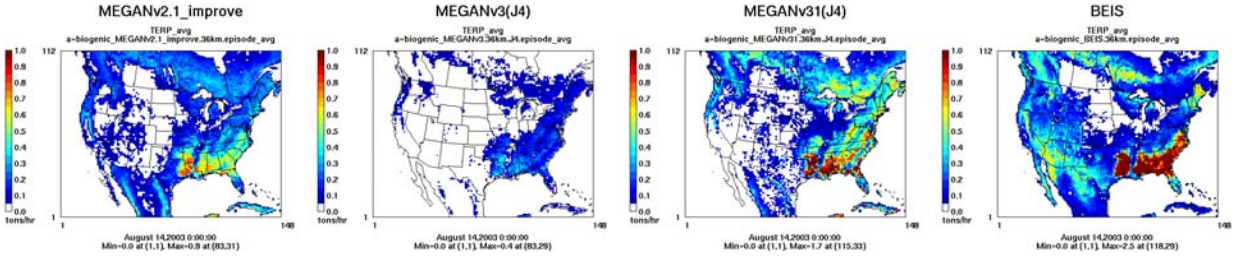

Figure 4-15. Episode average terpene emissions (tons h^{-1}) simulated using SMOKE-BEIS, MEGAN2.1, MEGAN3.j=4 and MEGAN3.1.j=4 models for summer 2013 in the TCEQ 36 km domain.

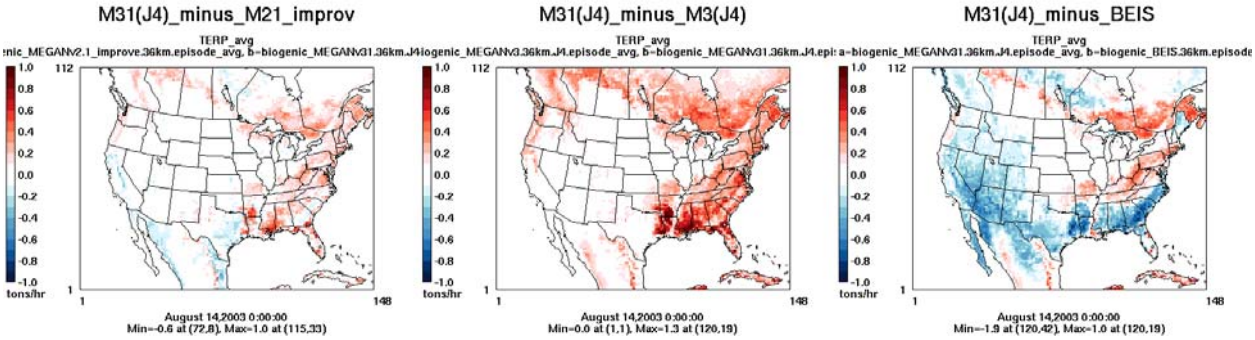

Figure 4-16. Difference (MEGAN3.1 minus other models) in terpene emissions (tons h^{-1}) simulated, and shown in Figure 4-15, for summer 2013 in the TCEQ 36 km domain.

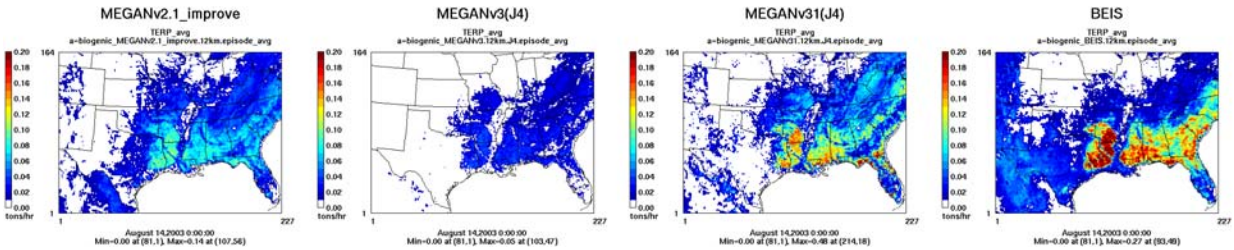

Figure 4-17. Episode average terpene emissions (tons h^{-1}) simulated using SMOKE-BEIS, MEGAN2.1, MEGAN3.j=4 and MEGAN3.1.j=4 models for summer 2013 in the TCEQ 12 km domain.

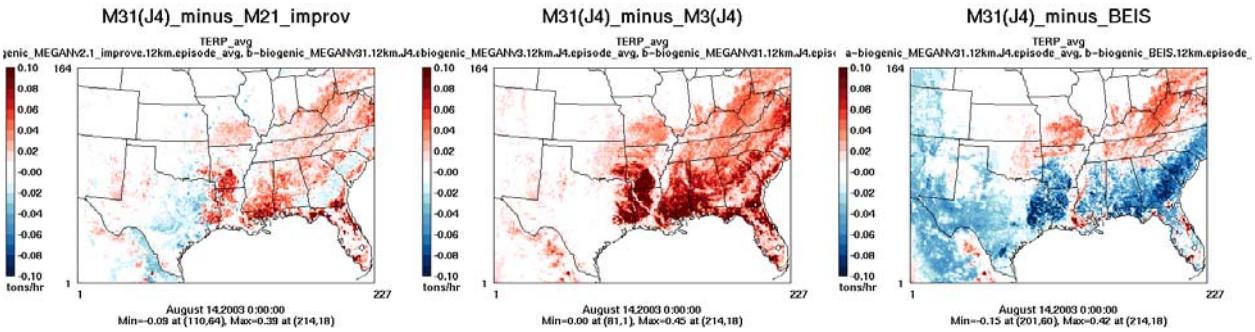

Figure 4-18. Difference (MEGAN3.1 minus other models) in terpene emissions (tons h^{-1}) simulated, and shown in Figure 4-17, for summer 2013 in the TCEQ 12 km domain.

Direct eddy covariance aircraft flux measurements, described in detail by Yu et al. (2017), were used to evaluate MEGAN3 (j=4) and MEGAN3.1 (j=4) emission factor estimates in the southeastern US. The aircraft data include intensive sampling results at 13 forested landscapes that are representative of the major landscape emissions types in eastern Texas and throughout the southeastern US. The NCAR C130 aircraft flew repeated racetrack patterns over each of the 13 forested landscapes and individual flux measurements (a total of ~1200 measurements with 29 to 239 measurements at each site) were averaged to characterize the representative isoprene and total monoterpene fluxes at each of the 13 forest sites. All 13 of the intensive sites fall within the TCEQ12 km domain (Figure 4-19) and include pine dominated forests (552 measurements), oak dominated forests (306 measurements) and mixed forests (464 measurements). Flights at multiple heights were used to extrapolate the measured flux down to the flux at the top of the canopy and account for flux divergence due to BVOC oxidation (Yu et al. 2017). Aircraft measurements of solar radiation and temperature were used to estimate light and temperature at the top of the canopy to drive the MEGAN3 canopy model and relate the observed emission to a leaf level emission factor at standard conditions. All of the intensive measurement sites were forested landscapes with a high vegetation cover (93 to 98%) dominated by trees (66 to 94%).

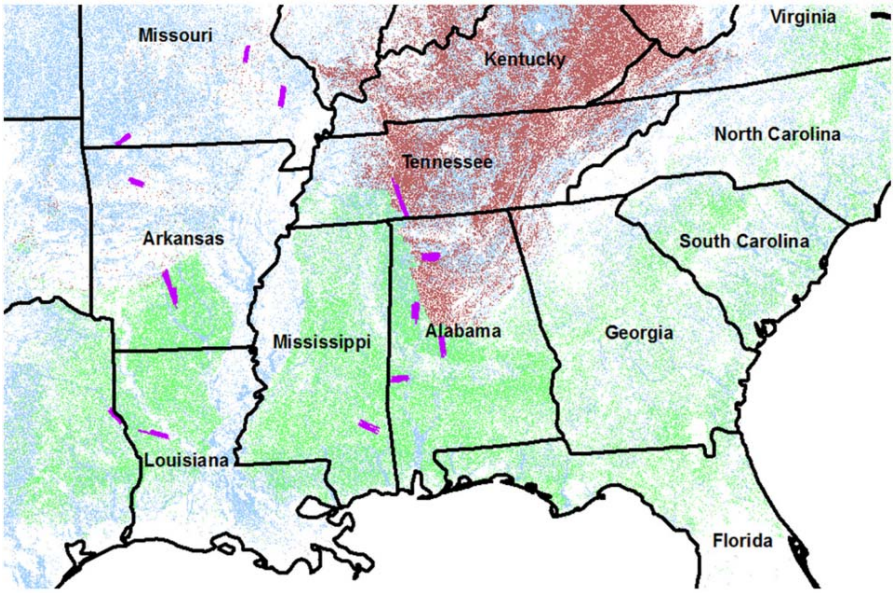

Figure 4-19. Location of aircraft eddy covariance flux intensive measurement sites (purple) and distribution of major forest types in Southeastern US including pine dominated forests (light green), oak dominated forests (brown), and mixed forests (blue).

The MEGAN3.1 (j=4) average leaf-level isoprene emission factor for the 13 intensive aircraft flux measurement sites, 11.7 nmol m^{-2} s^{-1}, is within 5% of the aircraft based isoprene emission factor while the MEGAN3.0 isoprene emission factor is about 20% higher than the aircraft based emission factor. Figure 4-20 shows that the MEGAN3.1 values are more highly correlated with the aircraft measurements than are the MEGAN3 values with r^2 values of 0.65 and 0.01 respectively. The results are similar for the average of the 4 mixed forest sites but the MEGAN3.1 estimates for pine forests are 40% higher than the aircraft values and the oak forests estimates are 25% lower. Figure 4-20 also shows that the MEGAN3.1 agrees with the aircraft measurements at moderate isoprene levels (mixed forests), underpredict at high isoprene (oak forests) and overpredict at low isoprene levels (pine forests). These differences could be due to uncertainties in emission factors of the various isoprene-emitting species in the different forests or could be due to other factors such as differences in whether the isoprene emitters tend to be in the understory where there is little light to drive isoprene emission, which tends to be the case for pine forests, or in the overstory, which tends to be the case for oak forests. As discussed in section 2.2.1, there may also be differences due to location associated with climate, stress, genetic population chemotypes, or other factors.

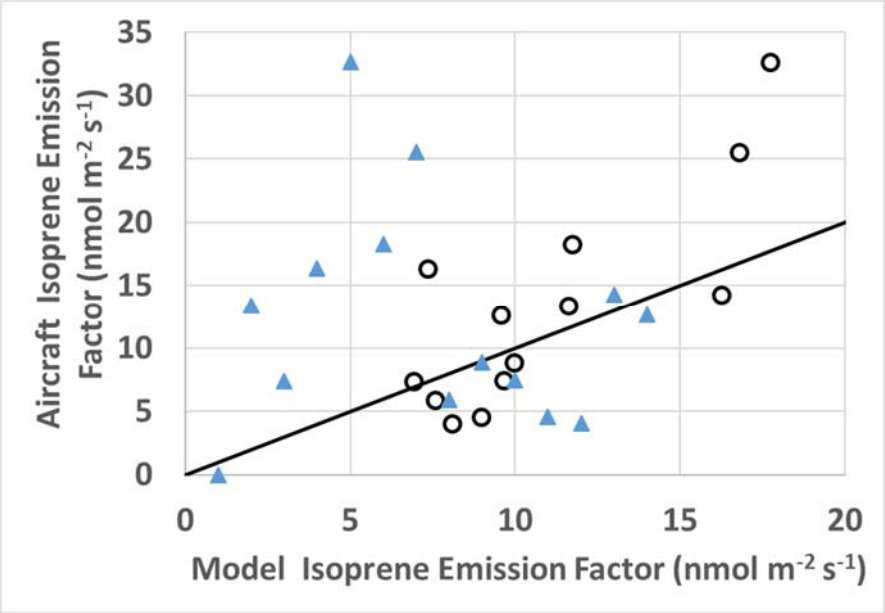

Figure 4-20. Scatterplot of isoprene emission factors based on aircraft observations and models including MEGAN3 (solid blue triangles) and MEGAN3.1 (open black circles) for 13 forests. Solid black line indicates 1:1 agreement.

The MEGAN3.1 (j=4) average leaf-level monoterpene emission factor for 9 intensive aircraft sampling sites, 0.75 nmol m^{-2} s^{-1}, is a factor of 2.2 higher than the aircraft based monoterpene emission factor. Aircraft monoterpene flux measurements were not available for the other four forest sites. MEGAN3.1 pine forest monoterpene fluxes are a factor of 2.8 higher while oak forests are 45% higher. The MEGAN3.0 monoterpene emission factors are only 16% higher than the aircraft based emission factors. This is because the MEGAN3.0 emission factors are partially based on the aircraft measurements, due to the lack of high quality monoterpene emission factor data. Figure 4-21 shows that the MEGAN3.1 monoterpene values have a higher variability than the MEGAN3 values. This is due to the integration of the emission factors from this study into the MEGAN emission factor processor database. Figure 4-21 also shows that the MEGAN3.1 monoterpene emission factors tend to agree with the aircraft measurements at low monoterpene emission factors but overpredict for higher monoterpene emissions such as from pine forests. This could be due to uncertainties in the leaf enclosure measurements but it should also be recognized that the aircraft monoterpene flux measurements are near the detection limit of that system and are relatively more uncertain than the isoprene flux measurements. The aircraft BVOC flux measurements account for chemical losses of BVOC during the transit from the canopy to the altitude of the aircraft measurement using the flux divergence measured between multiple heights. While this works well for compounds with a lifetime similar to isoprene, it does not account for losses of more reactive compounds which may even have substantial losses within the canopy.

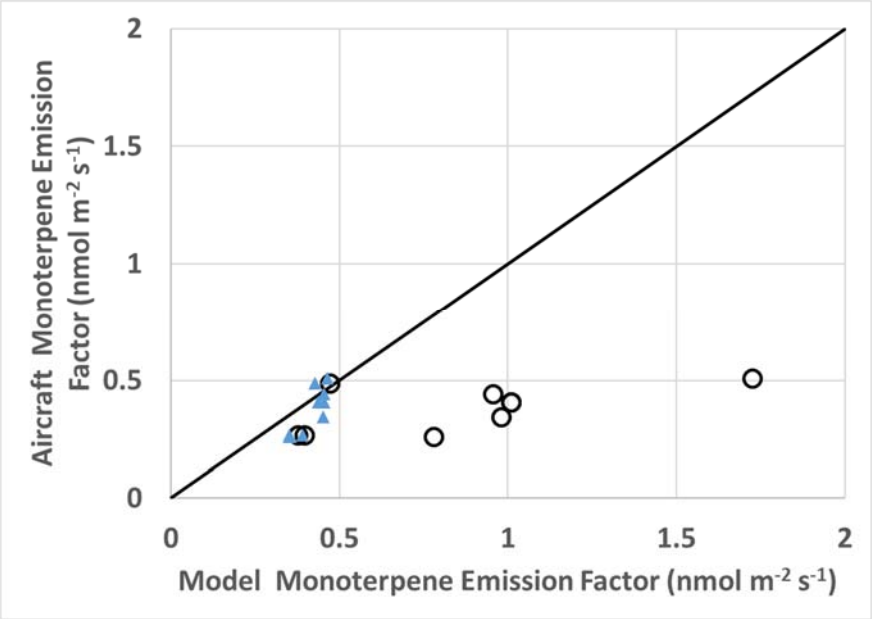

Figure 4-21. Scatterplot of monoterpene emission factors based on aircraft observations and models including MEGAN3 (solid blue triangles) and MEGAN3.1 (open black circles). Solid black line indicates 1:1 agreement.

4.3 MEGAN3 Deliverables

The MEGAN3.1 model output databases were compiled and delivered to the AQRP Project Manager at the conclusion of the project. This includes all MEGAN inputs and modeling files.

5.0 CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

Below, we provide a summary of findings of this study.

5.1 Summary of Findings

- Multi-modal enclosure (isoprene-only, speciated terpenoids, comprehensive BVOC) measurement approach can effectively maximize regional characterization of a broad range of vegetation and chemical species.
- Species-average isoprene emission factors for Texas isoprene-emitting species (various oaks and sweetgum) varied from 27 to 43 nmol m^{-2} s^{-1} including 4 tree species (Post oak, Shumard oak, Swamp Chestnut oak, and Sweetgum) emitting ~30 nmol m^{-2} s^{-1} and 2 species (Southern live oak and Water oak) emitting ~40 nmol m^{-2} s^{-1}. Emission factor variability was reduced after accounting for light environment using a canopy LAI depth parameter.
- Very low emission rates of isoprene and monoterpenes were observed for Texas crop species in contrast to some literature reports. Significant crop emissions of sesquiterpenes, acetaldehyde, acetone, acetic acid, and DMS were observed and methanol dominated all crop emissions except for Bermuda grass and peanuts. Barley, Bermuda grass and wheat had the highest BVOC emissions other than methanol.
- Eight-eight terpenoid compounds were emitted from 20 Texas trees. These compounds are mostly monoterpenes and sesquiterpenes but include some aromatic monoterpenes, oxygenated monoterpenes and sesquiterpenes, a homoterpene and a diteprene.
- The dominant Texas monoterpene is a-pinene and dominant Texas sesquiterpenes include b-caryophyllene, a-humulene and d-cadinene.
- Three urban Texas trees (crepe myrtle, camphor, and Chinese tallow tree) that are not included in the BEIS model were found to be very low emitters of terpenoid compounds.
- Total monoterpene emission factors for trees ranged from 2 to 6730 pmol m^{-2} s^{-1} and total sesquiterpene emission factors ranged from 0.2 to to 557 pmol m^{-2} s^{-1} with high and low emitters observed for both conifer and broadleaf tree species. Compared to BEIS, the measured values ranged from 90 times lower to 44 times higher.
- Five Texas tree species (post oak, southern live oak, pecan, cedar elm and baldcypress) had monoterpene and/or sesquiterpene emission factors that were a factor of 8 or more higher than the values used in BEIS.
- Relatively low monoterpene emission factors were observed for some common eastern Texas and southeastern US trees (loblolly pine and sweetgum) resulting in overall lower monoterpene emissions for MEGAN3.1 compared to BEIS for the TCEQ 12 km domain. The enclosure based emission factors may be biased by stress and may not be representative of regional emission behaviour.
- MEGAN3.1 has lower isoprene and higher monoterpene and NO emissions than MEGAN3 emissions. Compared to BEIS, MEGAN3 isoprene and monoterpene emissions are lower and NO emissions higher.

The MEGAN3.1 isoprene emission factors are in good agreement with aircraft flux measurements. MEGAN3.1 monoterpene emission factors are a factor of two higher than aircraft based emission factors but agree within the large uncertainties of the aircraft flux measurements.

5.2 Recommendations for Future Work

- **ISOPRENE VARIABILITY:** Examine the location-dependent variability of isoprene emission factors and other leaf traits of a widespread isoprene emitting species (e.g., post oak, southern live oak, sweetgum) to characterize driving variables and establish the number of sites required to quantify representative isoprene emission factors.
- **CANOPY ENVIRONMENT:** Evaluate BEIS, MEGAN2, MEGAN3 and other canopy environment model simulations with light and temperature measurements throughout a range of tree canopies, especially in open and heterogeneous canopies.
- **CANOPY LOSS:** Conduct field measurements to develop and test a detailed 1D model of canopy and surface layer BVOC oxidation and deposition to improve biogenic emission model evaluations by accurately relating emissions to concentrations and to provide the basis for representing these processes in 3D chemistry and transport models.
- **SHRUBLANDS:** Improve MEGAN3.1 desert, grass and shrubland landcover, especially shrub species composition and cover, and emissions data for west Texas and western US.
- **URBAN:** Improve MEGAN3.1 urban landcover, especially tree species composition and cover, and emission factors to reduce uncertainties that are otherwise expected to be much higher than in rural areas.
- **PREPROCESSOR:** Improve tools for pre-processing meteorological data for input to CAMx (i.e., WRFCAMx) to also provide input data for MEGAN3.1 in the required format.
- **TERPENOIDS AND STRESS:** Investigate terpenoid responses to drought, heat and other stress with field enclosure and ambient measurements to evaluate MEGAN3.1 estimates of stress induced emissions and reduce uncertainty in terpenoid emission factor estimates.
- **CONSTRAINING TERPENES:** Develop and apply an optimal (for cost, time, accuracy) approach for characterizing regional monoterpene and other terpenoid emission factors using a combination of enclosure and ambient terpenoid measurements.
- **MEGAN3.1:** MEGAN3.1 should be used for estimating emissions of NO, isoprene, monoterpene, sesquiterpenes and other biogenic emissions in Texas while continuing to improve MEGAN inputs, especially landcover and emissions data.

6.0 AUDITS OF DATA QUALITY

During this study, we performed Quality Assurance/Quality Control (QA/QC) procedures to ensure that all data and products generated are of known and acceptable quality. QA/QC procedures were performed in accordance with the Category III Quality Assurance Project Plan (QAPP) that was completed at the beginning of the study. In a Category III Project, data audits must be performed for at least 10% of the data sets and a report of QA findings must be given in the final report. A technical systems audit is not required. In this section, we report on the findings of our QA audits during this project.

6.1 BVOC emission and ancillary measurements

The UCI team reviewed more than 10% of the measurement data for quality assurance purposes before completing the analysis presented in Sections 4 and 5. Emission measurement data were evaluated against the quality metrics outlined in the QAPP for AQRP Project 18-005 and were found to be of acceptable quality.

Enclosure emission measurements are calculated by the following equation:

$$ER = Q\,[(C - C_b)/A]$$

where ER is the emission rate (nmol m^{-2} s^{-1}), C and C_b are the outlet and background mixing ratios respectively of the compound of interest (nmol mol^{-1}), Q is the flow rate of the air purging the enclosure (mol s^{-1}) and A is the area of leaf in the enclosure (m^{-2}). The background mixing ratio, C_b, accounts both for compounds that are able to pass though the VOC scrubber and any potential outgassing from contamination within the enclosure. For this study, C_b was consistently less than 6% of C for all compounds and contributed an uncertainty of <0.1 to 6% for various compounds. The enclosure flow rate (Q) was measured with a mass flow meter with a specified uncertainty of 5% that was checked using a Dry-Cal Definer volumetric flow meter (BIOS, Butler NJ) and corrected to standard conditions of temperature and pressure. Leaf Area, A, was determined with a digital photograph that was processed with a leaf area App. Tests with cut-outs of known area indicated that leaf area could be estimated within 7%. The dry mass of leaves was determined using a laboratory balance, verified using known weights, with a similar level of uncertainty. Multi-component commercial (Apel-Riemer) VOC standards were used to estimate response factors for the major BVOC for the two GC methods and PTR-MS. The responses were inter-compared with NIST certified alkane standards using a flame ionization detector, which has a consistent response for a wide range of hydrocarbons. This was used to estimate response factors for compounds that were not available in the commercial standards.

6.2 MEGAN Emissions Modeling Data

The MEGAN model was run by Ramboll using inputs developed by UCI. The Ramboll team member who performed the MEGAN modeling documented steps taken to obtain and process the MEGAN inputs, file paths to all inputs and outputs and provided a brief summary of the results. The documentation was used in the subsequent MEGAN modeling to ensure consistency in methods. Once the MEGAN modeling was completed, a Ramboll team member who had not performed the MEGAN modeling reviewed the modeling scripts for accuracy and then reviewed the model outputs. Model outputs for 10% of the episode days were reviewed using the PAVE visualization tool for completeness and compared with observations as well as the episode mean values reported in this document. All data for these days were examined for values that were outliers or otherwise unreasonable and none were found. A second Ramboll team member reviewed outputs for each day for the entire episode and found all values were reasonable. The MEGAN output data were determined to be correctly developed and complete and therefore suitable for the purposes of this study.

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