EXECUTIVE SUMMARY

The exchange of gases and aerosols between the Earth's surface and the atmosphere is an important factor in determining atmospheric composition and regional air quality. Accurate quantification of emission fluxes is a necessary step in developing air pollution control strategies. In some cases, emissions can be directly measured (e.g., point sources with continuous emission monitors) or can be estimated with reasonable confidence (e.g., point sources that have well-defined operating parameters). In contrast, large uncertainties are associated with area sources including emissions from vegetation, and in particular, emissions of biogenic volatile organic compounds (BVOCs). Vegetation is the largest source of VOC emissions to the global atmosphere. The oxidation of BVOCs in the atmosphere affects ozone, aerosol and acid deposition. Current BVOC emission estimates are based on measurements for individual plants that must be scaled up to represent landscapes and adjusted for environmental conditions. There is a critical need for independent BVOC emission inputs for air quality models.

Texas Air Quality Research Program (AQRP) Project 14-016 used aircraft observations from the 2013 Southeast Atmosphere Study (SAS) to assess and reduce uncertainties associated with a widely used BVOC emissions model, namely the Model of Emissions of Gases and Aerosol from Nature version (MEGAN; Guenther et al., 2012). The eddy covariance technique was used to directly quantify BVOC emission fluxes for all suitable aircraft observations from the SAS study.

The overall goal of this project is more accurate BVOC emission estimates that can be used in Texas air quality simulations that are critical for scientific understanding and the development of effective regulatory control strategies that will enhance efforts to improve and maintain clean air.

Estimation of Terpenoid Emissions Fluxes from Aircraft Data

Using a wavelet based approach, fluxes of isoprene and total monoterpenes were estimated using turbulence and proton transfer reaction-mass spectrometry (PTR-MS) measurements made onboard the C-130 aircraft during the 2013 SAS field campaign. Uncertainties associated with the estimated fluxes were also quantified. As expected, the highest isoprene fluxes were observed over broadleaf tree dominated woodland areas, while higher monoterpene fluxes were observed over areas such as longleaf pine woodland in Missouri and conifer and hardwood plantations in Louisiana, Texas, Arkansas and Alabama. The forests in these areas generally have higher fractions of high monoterpene emitting trees such as pines. Relatively low isoprene and monoterpene fluxes were observed over non-forested landscapes. These observations are consistent with a previous aircraft flux study in California (Karl et al., 2013; Misztal et al., 2014).

Subsampling was also performed for select C-130 flight legs to simulate the VOC sampling approach during SAS on the P-3 aircraft, which used a much longer sampling interval (15 seconds (s) versus 0.6 s on average for the C-130). The increased sampling interval in the P-3 data added significant uncertainty and error to calculated fluxes for sampling intervals greater

than a few seconds. Therefore, Fast Fourier Transform and wavelet based approaches were determined to be not suitable for analyzing VOC fluxes from the P-3 aircraft data in heterogeneous regions.

Instead, a mass balance approach was used to estimate isoprene emission fluxes from the NOAA P-3 and C-130 data. In a mass balance approach, it is assumed that the measured BVOC mixing ratio in the boundary layer reflects the equilibrium between emissions, chemical removal by hydroxyl (OH) radicals and entrainment out of the boundary layer (Warneke et al., 2010). The mass balance method requires specification of boundary layer height estimated from the aircraft data, k_{OH} is the rate coefficient for the BVOC+OH reaction, and [*OH*] is the concentration of OH radicals. The latter parameter was estimated using a parameterization from (Ehhalt and Rohrer, 2000) based on measured NO_2 mixing ratios, and j_{O1D} and j_{NO2} photolysis rates. The OH number density was measured onboard the C-130 during SAS and those data were used here to verify the validity of the OH estimate used for the mass balance approach. While there were significant differences between measured and calculated OH, the calculated OH, on average, agreed within 11% with the measurements.

The emission fluxes derived from the aircraft measurements using the mass balance approach were compared with emissions calculated using the BEIS and MEGAN models. For the purpose of these comparisons, the emissions were calculated along the flight tracks using the temperature and photoactive radiation (PAR) measured onboard the aircraft. The idea behind the approach is to use the aircraft data to constrain all the physical and chemical parameters that determine BVOC concentrations in addition to their emissions.

Isoprene emissions calculated from BEIS3.12, BEIS3.13, MEGAN2.0 and MEGAN 2.1 were compared to those calculated using the mass balance approach with measured isoprene mixing ratios from the following studies: Southeast Nexus (SENEX; the NOAA contribution to the Southeast Atmosphere Study [SAS] campaign), Nitrogen, Oxidants, Mercury and Aerosol Distributions, Sources and Sinks (NOMADSS), 2000 and 2006 Texas Air Quality Studies (TexAQS2000, TexAQS2006), International Consortium for Atmospheric Research on Transport and Transformation 2004 study (ICARTT2004) and the 1999 Southern Oxidant Study (SOS1999). The comparison showed that in general, MEGAN2.1 gives isoprene emissions that are higher than both BEIS3.12 and BEIS3.12 emissions and higher than fluxes inferred from NOMADSS aircraft measurements. The results from the C-130 (NOMADSS) and P-3 (SENEX) measurements during SAS compared very similarly with the emissions inventories. In general, MEGAN2.1 provides results that are higher than the emissions estimated from the measurements, whereas BEIS3.12 and BEIS3.13 estimates are lower. However, the uncertainties in the emissions estimated from the measurements are significant and do not allow a decision to be made as to which emissions model is more accurate. These conclusions are very similar to the observations made in previous NOAA work (Warneke et al., 2010)

Development of High Resolution Land Cover Data for MEGAN Modeling in Texas and the Southeastern US

Land cover characteristics including Leaf Area Index (LAI) and Plant Functional Type (PFT) are key driving variables for the estimation of biogenic VOC emissions by MEGAN and other biogenic emission models. Land cover and emission factor input data sets are considered the major uncertainties associated with BVOC emission estimates. We developed an updated LAI database for all of North America based on the 2013 MODIS (MOderate Resolution Imaging Spectroradiometer) satellite product (MCD15A2.005) and applied maximum green vegetation fraction from USGS (http://landcover.usgs.gov/green_veg.php), which is also based on MODIS remote sensing products. Spatial resolution of the LAIv data is approximately 900 meters. An updated 30-meter resolution PFT database (PFT16v2015) was developed for the continental US based on various ground survey, remote sensing and land surface model data products.

Emission Factor Database Development

The PFT16v2015 PFT database was developed for this project to provide the starting point for development of a high-resolution (30 m) emission factor (EF) database. An initial EF database, EFvE2015, was created using the same enclosure based emissions data used for the EF database, EFvE2011, described by Guenther et al. (2012) but with the new landcover data developed for this project and used for the new PFT database. The resulting EFvE2015 data were then compared with the EFvE2011 data. An additional database, EFvA2015, was created based on aircraft flux measurements and the new landcover and compared with the other EFs.

Compared with the EFvE2011 data, the EFvE2015 data predicts higher isoprene emission factors in some regions in the southeastern US, with the biggest differences in north Florida, central Texas, Oklahoma and Arkansas. Higher broadleaf deciduous tree coverages are also predicted for these areas in the PFT16v2015 database. On the other hand, lower broadleaf deciduous tree coverages were predicted by the PFT16v2015 database for southeast Missouri and northern Minnesota, which also has lower isoprene emission factors in the EFvE2015 database. The differences are mainly due to the incorporation of the LandFire existing vegetation type (EVT) data, which provides more spatial detail than the land cover dataset used to develop the EFvE2011 dataset.

Development of Airborne Emission Factors

Aircraft observations were used to evaluate and constrain MEGAN emission factors following the method of (Karl et al., 2013; Misztal et al., 2014) with some improvements and were used to develop the EFvA2015 emission factor database. The wavelet based approach provides isoprene and monoterpene flux data at high spatial resolution. However, the calculated fluxes are for the altitude at which the aircraft is flying and must be extrapolated to the surface level in order to be used to estimate EFs for biogenic VOCs. We applied a vertical flux divergence approach to perform this task. Surface fluxes of BVOCs were then calculated using a vertical flux divergence correction method (Misztal et al., 2014) that assumes a linear relationship between fluxes at different altitudes.

Converting the surface fluxes into EFs requires accurate estimates of meteorological conditions such as temperature, solar radiation and, to a lesser degree, other factors including soil

moisture, wind speed and humidity. The MEGAN model calculates BVOC emissions as the product of an EF and an emission activity factor (EAF) that accounts for the impact of driving variables including canopy environment. We calculated the EAF associated with each aircraft flux measurement and applied this factor to the extrapolated surface flux to obtain the emission factor for standard conditions.

EAFs were calculated using two different approaches. For one version, EAFs were calculated by executing a single point version of MEGANv2.1 for every flux measurement, using the LAIv and vegetation cover with meteorological fields extracted from the North American Land Data Assimilation System (NLDAS-2) forcing data and soil moisture data extracted from NLDAS-2 model data (VIC model). For the second version, EAFs were calculated using the regional MEGANv2.1 model with EFvE2011 emission factor database and meteorological driving variables derived from the Weather Research and Forecasting Model (WRF; Skamarock et al., 2008).

The correlation between EFvE2015 and airborne based EF suggest that the land cover data reasonably captures the variations of BVOC emissions among different EVTs. The correlations between airborne EF calculated using different approaches and the landcover based EFvE2015 data range from 0.32 to 0.73.

The airborne EFs calculated using WRF or using NLDAS meteorological data are considerably different. The WRF based EF values are consistently lower due to higher EAF values estimated by WRF. This is likely due to a high bias in solar radiation and temperature due to underestimates of aerosol and clouds. We have used the NLDAS data for our analysis because it includes assimilation of observed meteorology. However, the substantial differences (~37%) between the WRF and NLDAS results demonstrate the importance of having accurate meteorological observations to determine airborne EFs.

Development of MEGAN Biogenic Emission Inventories and Regional Photochemical Modeling

Using the landcover and emission factor databases described above, we prepared three sets of MEGAN v2.1 biogenic emissions for a June 1–July 15, 2013 modeling episode that encompassed the P-3 and C-130 SAS flights. The first inventory was a base-case biogenic emission inventory, which was developed using the MEGANv2.1 default landcover database, PFT16v2011, and default emission factors, EFv2011. This inventory is referred to as EFvE2011 below. Then, a second biogenic emission inventory (denoted by EFvE2015) was derived from updated inputs: the new high-resolution landcover database, PFT16v2015, and the EFvE2015 emission factor database described above. Finally, a third biogenic emission inventory was derived from the new high-resolution landcover database, PFT16v2015, and the EFvA2015 emission factor database; this inventory was used in a sensitivity test described below and is referred to as EFvA2015.

The three MEGAN emissions inventories were developed using temperatures and PAR from a WRF simulation of the June-July 2013 episode performed as part of this study. WRF was run with a new algorithm that accounts for the radiative effects of sub-grid scale cumulus clouds

(Alapaty et al., 2012; Herwehe et al., 2014) and has been shown to reduce surface downward shortwave radiation (DSW) and improve the simulation surface temperature and precipitation relative to the unmodified version of WRF.

Comparison of WRF modeled surface downward shortwave radiation (DSW) with visible satellite images for the C-130 flights and solar radiation measured at TCEQ monitoring sites indicated that, despite the additional cloud-radiation feedback, WRF underestimated the observed cloud field and overestimated DSW. Underestimating clouds and overestimating the available shortwave radiation very likely introduced a high bias in the MEGAN isoprene emissions through a high bias in PAR and affected the partitioning of surface heat and moisture fluxes.

The default (EFvE2011) and updated (EFvE2015) MEGAN biogenic emission inventories were compared against aircraft flux data and then evaluated using a photochemical grid model. The evaluation of the isoprene and monoterpene emissions against aircraft flux data showed that the MEGAN v2.1 isoprene emissions were consistently higher than the aircraft flux data calculated along the C-130 racetrack flight segments. This was true for both the default and updated MEGAN emission inventories. The default and updated MEGAN monoterpene emissions showed closer agreement with the airborne fluxes than the isoprene emissions, but the MEGAN monoterpene emissions were also generally higher than the airborne fluxes. The MEGAN monoterpene emissions had a spatial pattern similar to the airborne fluxes, with high emissions over the Texas-Louisiana border region, Mississippi and Alabama and lower emissions over southern Missouri and western Tennessee. The changes between default and updated inventories varied along the flight tracks, and it is difficult to assess which inventory showed better agreement with the airborne fluxes. The comparison between MEGAN emissions and the airborne fluxes is affected by the use of different meteorological data (WRF and NLDAS) in preparing the emissions flux estimates.

We performed regional photochemical modeling for June 1-July 15, 2013 time period of the C-130 and P-3 aircraft flights using both the default (EFvE2011) and updated (EFvE2015) MEGAN emission inventories. We evaluated modeled concentrations of terpenoid and other species against the aircraft measurements and compared modeled surface layer ozone to ground level ozone measured at rural sites. The Comprehensive Air Quality Model with Extensions (CAMx; Ramboll Environ, 2015) model has a high bias for surface ozone that is most pronounced at coastal sites during periods of onshore flow. This suggests that the model is affected by bias in the model boundary conditions for ozone and/or precursors.

Using both the default (EFvE2011) and updated (EFvE2015) MEGAN inventories, CAMx simulated spatial patterns of high and low isoprene that are similar to those of the aircraft observations. For example, both the modeled and the measured isoprene are relatively high in the region that includes northeast Texas, northwest Louisiana and southwestern Arkansas. Both observed and CAMx isoprene concentrations show hot spots in southeastern Missouri, central Alabama and central Georgia. Areas of low isoprene occur in the model and measurements in northern Indiana, northern Mississippi South Carolina, northeastern Kentucky and central

Texas. CAMx generally overestimates isoprene along the aircraft flight tracks with bias of 84% using the default EFvE2011 MEGAN emissions and 104% in the updated case with the EFvE2015 biogenic inventory.

Although the modeled high bias for isoprene relative to aircraft observations increased in the run using the updated EFvE2015 MEGAN emissions, the CAMx model's performance in simulating ground level ozone improved in the Houston area. The updated MEGAN inventory EFvE2015 has a significantly lower isoprene emissions factor and lower isoprene emissions in the Houston area, and this appears to reduce ground level ozone, bringing the model into closer agreement with observations. Kota et al. (2015) compared the gridded MEGAN isoprene emissions factor for the region north of Houston with isoprene emission factor estimates derived from a field study and found that the MEGAN emission factor was higher. Kota et al. determined that the overestimated isoprene emission factor caused a high bias in modeled isoprene concentrations in their Community Multiscale Air Quality (CMAQ) model simulation, but the isoprene overestimates did not significantly influence modeled ozone; this is in contrast to results of our CAMx simulations, in which changes in Houston area isoprene emissions strongly affected modeled ozone.

In the CAMx simulations, changes in surface ozone due to the change in the MEGAN emission inventory were relatively small outside of the Houston area and monitoring sites near the eastern border of Texas,

In the CAMx runs using default and updated EFvE2015 MEGAN emissions, modeled monoterpene concentrations were generally lower than the observed concentrations along the P-3 and C-130 flight tracks. Values of the coefficient of determination were lower for monoterpenes than for isoprene. In the run with updated EFvE2015 MEGAN emissions, the magnitude of the CAMx model's low bias for monoterpenes was reduced relative to the run with default emissions.

Four additional CAMx sensitivity tests were carried out.

1. We altered the CB6r2 chemical mechanism to increase the production of OH from the breakdown of isoprene following the mechanism of Peeters et al. (2013). The purpose of the test was to gauge the model's response to an isoprene mechanism that represents an upper limit on the production of OH from isoprene. Increasing OH production from isoprene reduces but does not eliminate the high bias in isoprene products.

2. Based on the high bias for isoprene noted in the CAMx run that used default MEGAN emissions, we reduced the MEGAN isoprene emissions by a factor of 2 for all grid cells and times and reran CAMx. For the P-3 data, the CAMx default run high bias for isoprene products (114%) changed to a low bias of -7% in the sensitivity test as a result of the lower isoprene emissions and atmospheric concentrations. For the C-130 data, the CAMx bias for isoprene products changed from 48% to -33%. The reduction in the

magnitude of bias for isoprene products in this sensitivity test suggests that the MEGAN isoprene emissions are overestimated in the default EFvE2011 case.

3. In June 2013, Nguyen et al. (2015) measured dry deposition velocities (V_d) for biogenic trace gases in an Alabama forest during the Southern Oxidant and Aerosol Study (SOAS). Comparison of CAMx V_d against the measurements showed Vd was underestimated in the model. We increased CAMx dry deposition of these species to improve agreement with the SOAS measurements. The effects of this test on modeled ozone and isoprene and monoterpenes species were small.

4. We ran CAMx with the EFvA2015 MEGAN emission inventory that used isoprene emission factors developed using SAS aircraft data. In the CAMx run with EFvA2015 MEGAN emissions, the high bias for isoprene decreased from 84%-113% in the default (EFvE2011) run and 104%-132% in the EFvE2015 sensitivity test to the range -5% to -16% in the CAMx EFvA2015 sensitivity test. The use of the EFvA2015 emission factors for isoprene in MEGAN improved the CAMx model's ability to reproduce the isoprene concentrations measured by the P-3 and C-130 aircraft. Although the high bias seen in the default EFvE2011 and EFvE2015 CAMx runs is reduced in the EFvA2015 sensitivity test, there was no improvement in correlation between observed and modeled values. R^2 values decreased slightly in the EFvA2015 sensitivity test relative to the CAMx runs using the default and EFvE2015 MEGAN emissions.

The best overall performance among all CAMx runs for a subset of species (isoprene, isoprene products, sum of monoterpenes, ozone, OH) occurred in the sensitivity test in which CAMx was run with the EFvA2015 MEGAN emissions that used emissions factors developed using the aircraft data. The CAMx bias for ozone was nearly unchanged across all CAMx runs. In the CAMx run with updated EFvE2015 MEGAN emissions, the CAMx bias for monoterpenes improved, but the overall bias for isoprene, isoprene products and OH increased. These results, taken together with the high bias in MEGAN isoprene emissions compared to the aircraft fluxes, suggest that MEGAN isoprene emissions are overestimated in both the default EFvE2011 and updated EFvE2015 inventories.

Conclusions

Below, we present conclusions drawn from the results of this study.

- Accurate meteorological input data, especially PAR and temperature, are critical for accurate BVOC emission calculations. Bias in weather model simulation of clouds and shortwave radiation introduces bias into the MEGAN emissions. Standard WRF simulations may result in considerable high bias in solar radiation and temperature due to model treatment of clouds. NLDAS appears to be better but also leads to overestimates. It should also be noted that bias in the PAR and temperature used to estimate emission factors from measured emissions will also introduce bias into the calculated emission factors. Data assimilation approaches (satellite and/or in-situ observations) are recommended for improving these inputs and they should be evaluated by comparison to observations.

- Landcover inputs (LAI and vegetation type) are also critical for BVOC emission modelling. LAI can vary considerably between years and we recommend using the provided 2013 LAI data for 2013 simulations and use the provided scripts and approach to calculate LAI for other years. We also recommend using the vegetation type distributions developed for this project.
- Emission factors are another key variable for BVOC emission modelling. We recommend using the new (aircraft based) isoprene emission factors (EFvA2015) developed for this project for BVOC emission modelling since both the eddy covariance and mixed layer approaches indicate this. However, more work still needs to be done to verify these emission factors and reconcile the substantial differences between leaf based, tower based, aircraft based and satellite based emission estimates. There is less evidence that the monoterpenes should be changed so we do not recommend changing the emission factors for monoterpenes from EFvE2015 to EFvA2015 at this time.

Recommendations

- We need to reconcile the substantial differences between leaf-scale, tower-scale and aircraft-scale emission estimates as well as comparisons to satellite based emission estimates.
- As is the case with most BVOC studies, we have focused on only a few compounds but there is evidence that other "unmeasured" compounds play an important role in atmospheric chemistry (e.g. Di Carlo et al., 2004; Goldstein and Galbally, 2007; Park et al., 2013; Jardine et al., 2015). New analytical techniques provide an opportunity for determining whether there are other important compounds and also for characterizing the contribution of these compounds (Pankow et al., 2012). New techniques include high sensitivity, high resolution, accurate mass, full scan mass spectrometry (time of flight and Orbitrap) and better approaches to minimize artifacts and losses (whole air sampling, removing oxidants with reactive alkenes).
- BVOC response to stress is recognized as potentially important but not well known component of BVOC emission models. These processes could lead to extreme (low or high) emission rates that could have an impact on air quality model results and should be quantified and evaluated.
- A good understanding of hydroxyl (OH) radical concentrations in forest environments is essential for modelling BVOC concentrations and for the interpretation of the measurements of BVOC fluxes. However, several detailed measurements have yielded significantly higher concentrations than can be explained using the known chemical reactions. Resolving this issue is important to advance the understanding of the effect of BVOC emissions on radical levels and ozone formation.
- Accurate meteorological data (PAR and temperature) is critical for accurate BVOC emission calculations. Bias in the WRF model's simulation of clouds and shortwave radiation introduces bias into the MEGAN emissions. The magnitude of this bias can be assessed by comparison of MEGAN emissions calculated along the aircraft flight track using

temperatures and PAR measured aboard the aircraft with MEGAN emissions calculated using WRF model temperatures and PAR. Improvements to the WRF model treatment of clouds and radiation that enable it to provide accurate inputs to MEGAN are needed for development of accurate BVOC emission inventories for photochemical modeling.

- Southern Oxidant and Aerosol Study (SOAS) dry deposition velocity measurements were very useful in constraining CAMx model dry deposition of oxygenated VOCs. Dry deposition measurements for other species/locations would be very helpful in improving models.
- The high resolution (1 m resolution) landcover data should be complemented with geolocated ground surveys of tree species composition and used to improve the MEGAN landcover in urban areas of Texas.