Determination of Biogenic Emissions from Aircraft Measurements During Four Campaigns and Comparison with Biogenic Emission Inventories

C. Warneke, S. McKeen, J.A. de Gouw, J. Brioude,
P. Goldan, W. Kuster, H. Stark, F. Fehsenfeld
NOAA Earth System Research Laboratory, 325 Broadway, Boulder, CO, 80305
carsten.warneke@noaa.gov

C. Wiedinmyer, A. Guenther
National Center for Atmospheric Research, Boulder, CO

L. Del Negro
Lake Forest College, Lake Forest, IL

ABSTRACT

During the NOAA SOS1999, TEXAQS2000, ICARTT2004 and TEXAQS2006 campaigns, airborne measurements of isoprene and monoterpenes were made in the eastern United States and in Texas, and the results are used to evaluate the biogenic emission inventories BEIS3.12, BEIS3.13, MEGAN and WM2001. Two methods are used for the evaluation. First, the emissions are directly estimated from the ambient isoprene and monoterpene measurements assuming a well-mixed boundary layer, and are compared with emissions estimated from the inventories extracted along the flight tracks. Second, BEIS3.12 is incorporated into the detailed transport model FLEXPART, which allows the isoprene and monoterpene mixing ratios to be calculated and compared to the measurements. The overall agreement for all inventories is within a factor of two and the two methods give consistent results. MEGAN is in most cases higher and BEIS3.12 and BEIS3.13 lower than the emissions determined from the measurements. Regions with clear discrepancies are identified. For example, an isoprene hotspot was expected from BEIS3 to the northwest of Houston, Texas, but was not observed in the measurements. Inter-annual differences in emissions were also observed: the isoprene emissions in Texas in 2006 were about a factor of two lower than in 2000.

INTRODUCTION

Because of the enormous impact of biogenic VOC emissions on the global and regional atmospheric chemistry that produces ozone and secondary organic aerosol [1, 2], biogenic VOCs are included in air quality forecast models, global chemistry and climate models and in regulatory regional models. The model input is usually in the form of off-line emission inventories. The most commonly used biogenic emissions inventory in North America is the EPA BEIS3 (Environmental Protection Agency Biogenic Emissions Inventory System 3) [http://www.epa.gov/asmdnerl/biogen.html], which includes isoprene, the monoterpenes and many other species. Another inventory, recently introduced by Guenther et al., is called MEGAN (Model of Emissions of Gases and Aerosols from Nature) [3], which is a detailed global inventory that includes over 100 species.

During the NOAA SOS1999, TEXAQS2000, ICARTT2004 and TEXAQS2006 campaigns, multiple flights on a large spatial scale were performed over forested areas in the eastern United States and in Texas. In this work we use the in-situ mixing ratio measurements of isoprene and monoterpenes from those field campaigns in an attempt to evaluate the available biogenic emission inventories EPA BEIS3.12, the latest version EPA BEIS3.13, MEGAN and an inventory developed by Wiedinmyer et al. for Texas only [4]. Two approaches are used for this evaluation. First, the emissions are estimated from the ambient measurements assuming a well-mixed boundary layer, and compared to the emissions from the inventories extracted along the flight tracks. Second, BEIS3.12 was incorporated into the Lagrangian transport model FLEXPART, and the calculated isoprene and monoterpene mixing ratios are compared to the aircraft measurements.

BODY

Measurement Campaigns and Instrumentation

The flight tracks of the NOAA WP-3 for SOS99, ICARTT2004 and TEXAQS2006 campaigns are shown in Figure 1A on top of the EPA BEIS3.13 summer isoprene base emissions map of the US. Base emissions are the isoprene emissions at standard conditions. Actual emissions deviate from the base emissions as a function of temperature and light. Flight tracks in the boundary layer are shown in black, the ones in the free troposphere in red. It can be seen that the area covered by the flight tracks includes a large part of the forested eastern half of the US including Texas, where large isoprene emissions are located. The flight tracks of the TEXAQS2000 study are shown in Figure 1B on top of the MEGAN isoprene base emission factors. In Figure 1C the BEIS3.13 summer monoterpene base emissions are shown.

During the ICARTT2004 and TEXAQS2006 campaigns, isoprene and monoterpene measurements were performed with the NOAA PTR-MS instrument (Proton-Transfer-Reaction Mass Spectrometer) on-board the NOAA WP-3 aircraft during multiple flights. During TEXAQS2000 isoprene was measured using the Innsbruck PTR-MS. A detailed description of the PTR-MS instrument and an inter-comparison with gas chromatography (GC) measurements from whole air samples (WAS) can be found elsewhere [5, 6]. During the flights isoprene and monoterpenes were measured for 1 second each every 17 seconds. During SOS99 isoprene was measured using an airborne gas chromatograph with a flame ionization detector (GC-FID). A 350 cm^3 STP sample was cryogenically acquired for 5 minutes every 15 minutes and analyzed in the remaining 10 minutes.

Isoprene Emissions Estimated with Emission Inventories

To calculate the actual isoprene emissions from BEIS3, the base emissions have to be multiplied with the temperature and light adjustment factors to account for environmental dependence of the isoprene emissions [7].

Equation (1) $$actual\,emission = base\,emission * c_t * c_l$$

where c_t is the temperature adjustment factor and c_l is light adjustment factor.
MEGAN is a biogenic emission inventory that was recently introduced by [3]. It is a global scale model with a base resolution of ~1 km^2 (30s latitude by 30s longitude) to enable both regional and global model simulations. Isoprene and other trace gases and aerosol emissions at every location are estimated by:

Equation (2) $$\text{Emission}=[\varepsilon][\gamma][\rho]$$

where ε is an emission factor for a compound at standard conditions (30^0 C and 1000 $\mu mol\ m^{-2}\ s^{-1}$ PAR), γ is an emissions activity factor that accounts for emission changes due to deviations from standard conditions and ρ is a factor that accounts for loss within the canopy.

For Texas only, a third isoprene emission inventory was used to compare with the measurement data. This inventory was developed by [4] and will be called WM2001 in the remainder of this manuscript. The light and temperature dependence for the WM2001 isoprene emission inventory are the same as in BEIS.

In this work, we extracted the base emissions and leaf-area index (LAI) along the flight tracks, and all other necessary parameters (shortwave radiation, zenith angle, ground temperature and pressure) were determined from the actual aircraft measurements. Figure 2 shows scatter plots of the isoprene base and actual emissions of BEIS3.13, MEGAN and WM2001 versus BEIS3.12, which shows MEGAN to yield the highest actual emissions, then BEIS3.12, then WM2001and the lowest BEIS 3.13.

Isoprene Emissions Estimated from the Aircraft Measurements

The isoprene emission flux along the flight tracks in the boundary layer can be modeled from the measured mixing ratio using a simple mixed boundary layer approach that takes the boundary layer height and the isoprene lifetime into account. The emissions can be estimated by:

Equation (3)

$$Emissions_{isoprene} - F_e = [isoprene] * BL_{height} * k_{OH} * [OH]$$

where [isoprene] is the measured concentration, BL_{height} the observed boundary layer height, k_{OH} the rate coefficients with OH, and [OH] the OH concentrations. F_e is the entrainment flux from the boundary layer into the free troposphere. The term k_{OH}*[OH] represents the inverse lifetime of isoprene due to reaction with OH (k_{OH} is 101×10^{-12} $cm^{-3}s^{-1}$ [8]). The entrainment flux from the boundary is estimated to be 30% from the emission flux.

The boundary layer height was determined for each profile flown by the WP-3 aircraft by looking at the isoprene, potential temperature and water vapor altitude profiles. A parameterization was used to estimate [OH] along the flight tracks [9], which makes use of photolysis frequency measurements of j_{O^1D} and j_{NO_2} as well as the measured NO_2 concentrations:

Equation (4)

$$[OH] = a(j_{O^1D})^{\alpha}(j_{NO_2})^{\beta}\frac{bNO_2+1}{cNO_2^{\,2}+dNO_2+1}$$

The parameters of [9] are α=0.83, β=0.19, a=4.1×10^9, b=140, c=0.41, and d=1.7, indicating a strong, slightly non-linear dependence of OH on j_{O^1D} and a small but highly non-linear contribution from j_{NO_2}. In Figure 3 the parameters needed for the calculation of the emissions from the measurements for the flight on September 16, 2006 in northeast Texas are shown. The observed isoprene mixing ratios color-coding the flight track in Figure 3A were high and highly variable. Figure 3B shows the boundary layer height, which was estimated to be 1.4 km for this flight, together with the OH concentration calculated according to Eq. (4) using the Ehhalt parameterization. Maximum OH values for this flight were around 10×10^6 molecules cm^{-3}. The emissions calculated from the mixing ratios are shown in Figure 3C as 1-second data and 5-minute averages together with the emissions calculated from BEIS3.12 and MEGAN. The overall uncertainty in estimating the emissions from the measurements is a factor of 2 (-50%, +100%). The uncertainties in the calculation of the emissions from the inventories are small in comparison. Therefore, the different emission estimates shown in Figure 3C for the September 16, 2006 flight in Texas agree within the estimated uncertainties on average.

Isoprene Mixing Ratios Estimated with FLEXPART Transport Model

The FLEXPART Lagrangian particle dispersion model [10] was used to simulate isoprene and monoterpene mixing ratios during ICARTT2004 and TEXAQS2006. FLEXPART used a temporal resolution of 3 h and 91 vertical levels and a horizontal resolution of 0.36^0 x 0.36^0. Isoprene emissions were taken from BEIS3.12 with a resolution of 0.3^0 x 0.3^0 for ICARTT2004 and 0.15^0 x 0.15^0 for TEXAQS2006. The temperature and light dependence of isoprene was calculated hourly for each isoprene emission grid with the EPA recommended canopy environment model by using the ECMWF 2 meter temperature and net solar radiation, interpolated linearly in space in time using the two nearest ECMWF fields. FLEXPART backward calculations were used to calculate the isoprene mixing ratio along flight tracks. The FLEXPART tracer that takes transport and emissions over the last hour into account was used to compare to the isoprene and monoterpene measurements.

Figure 4 illustrates the way FLEXPART is used to calculate the isoprene mixing ratio along the flight track. In Figure 4A the footprint calculated with FLEXPART for one point along the flight track during the September 16, 2006 flight is shown. The footprint gets folded in with the isoprene emissions at that location to calculate the mixing ratio. This is done for every second along the flight track. For isoprene we look only at transport times of one hour, which is only a very small region around the star that indicates the aircraft location. In Figure 4B the measured isoprene mixing ratio is shown together with the FLEXPART model results for this flight. The FLEXPART data shown here are the one-hour tracer. The observed isoprene mixing ratios were extremely variable during this flight and the model does not capture this small-scale variability, but the main features and the magnitude are described well. The overall uncertainty of this method is a factor of 2 (-50%, +100%) and therefore the model results shown in Figure 4B agree with the observations within the uncertainties.

Monoterpenes

Measurements of the sum of the monoterpenes are available for the ICARTT2004 and TEXAQS2006 campaigns. The emissions modeled from the observations are determined in the same way as described for isoprene earlier and are calculated as follows:

Equation (5) $$Emissions_{monoterpenes} - F_e = [monoterpenes] * BL_{height} * \left(k_{OH} * [OH] + k_{O_3} * [O_3]\right)$$

The emissions along the flight track from BEIS3.13 are calculated using aircraft data as described earlier and total monoterpenes were incorporated into FLEXPART using BEIS3.13 and mixing ratios were calculated along the fight tracks for emissions within the last hour of transport.

Quantitative Comparison

For each campaign we made scatter plots of the emissions of isoprene and the monoterpenes estimated from the measurements versus the emissions calculated from the different inventories. Furthermore the FLEXPART calculated mixing ratios were plotted versus the measured mixing ratios. The slopes and the correlation coefficients of all the linear fits are given in Table 1-3. The 5-minute averages were used and the linear fit was an orthogonal distance regression forced through zero.
The two different methods used to compare the isoprene measurements to the BEIS3.12 emissions database, the mixed boundary layer method (BEIS3.12 in Table 1) and the transport method (FLEXPART in Table 2), yield consistent results within about 30%. The slopes for the FLEXPART method is about 30% higher and the correlation coefficients for both methods are similar. This gives

good confidence in the validity of our approaches for this emissions inventory validation. A systematic difference of 30% is clearly within the uncertainties of both methods.

In an average sense, it can be concluded that BEIS3.12 estimates the magnitude of the isoprene emissions very well in Texas in 2006, overestimates in the northeast US in 2004 and underestimates in the southeast US in 1999 and in Texas in 2000. The correlation was the best for the comparison of SOS1999 data in the southeast US and the worst in Texas during TEXAQS2000. BEIS3.13 has for all three campaigns about 30% lower emissions than BEIS3.12, which yields under-predictions for all missions. The correlation between inventory and measurements is slightly improved compared to BEIS3.12.

As was seen earlier and also for the results in Table 1, MEGAN is almost a factor of two higher than BEIS3.12. For the southeast US and Texas in 2000 the agreement is very good to within 30%, whereas for the northeast US and Texas in 2006 MEGAN predicts higher emissions than modeled from the measurements. The correlation coefficients are about the same as for the comparison with BEIS3.12 ranging from R=0.59 to R=0.68.

The WM2001 inventory predicts emissions in Texas roughly in the same range as BEIS3.12 with a high correlation coefficient in 2006 and rather low in 2000.
For the monoterpenes (Table 3) the comparison with the two different methods is not as consistent as for isoprene, FLEXPART predicts a factor of two higher for TEXAQS2006 and within 20% for ICARTT2004, whereas for the mixed boundary layer method it is the other way round. This is likely caused by the larger errors involved with the monoterpenes analysis. Overall the comparison for ICARTT2004 and TEXAQS2006 is close to a factor of two, but the correlation coefficients for all comparisons are lower than for isoprene.

Regional and Inter-annual Differences

The data presented here are especially useful for looking at systematic regional differences because of the large number of flights and large area covered. The difference between FLEXPART using BEIS3.12 and the measurements during ICARTT2004 is used to color code the flight tracks plotted on the BEIS3.12 base emissions in Figure 5. Along the U.S.-Canadian border there is a large discontinuity in both the BEIS3.12 and BEIS3.13 base emissions, which is the result of different land-cover data used. This discontinuity at the border is not evident in the MEGAN inventory. Looking at the part of the flight track over Canada, it seems that FLEXPART using BEIS3.12 is higher lower than the mixing ratios from the measurements.

On average, in Texas the emissions estimated from the measurements are about a factor of two lower in 2006 compared to 2000 as can be seen in Table 1. The slopes of the 2006 comparisons are about a factor of two higher than the 2000 results indicating relatively lower emissions modeled from the observations at the same temperature and radiation in 2006 than in 2000.

CONCLUSIONS

Airborne isoprene and monoterpene measurements during four different field campaigns in the eastern US and in Texas were used to evaluate different available emission inventories (BEIS3.12, BEIS3.12, MEGAN and WM2001) using two different approaches. First, a mixed boundary layer method was used: the emissions are modeled from the ambient measurements using the isoprene and monoterpene lifetimes and the boundary layer height. The emission estimates from the measurements are compared to emissions calculated from the inventories, which are calculated using observations on the aircraft of all the necessary parameters, such as radiation and ground temperature. Second, a transport method was used: BEIS3.12 was incorporated into the detailed transport model FLEXPART and isoprene mixing ratios are calculated and compared to the measurements. Overall an agreement to better than a factor of two was found for all inventories and all campaigns and both methods yielded consistent results. Generally MEGAN is almost a factor of two higher than BEIS3.12, which is in turn about 30% higher than BEIS3.13. The emissions from MEGAN were somewhat higher than the emissions modeled from the isoprene measurements, whereas BEIS3.12 was somewhat lower.

Using this comparison, different areas were identified, where larger than expected differences were found. For BEIS3.12 and BEIS3.13 along the US Canada border and in Texas north of Houston discrepancies were discovered. In the same areas no differences were found with MEGAN, but for example MEGAN seem to over predict the emissions in northeast Texas in 2006.

Clear inter-annual differences in the emission strength between 2000 and 2006 were observed in Texas, which were likely caused by stronger influence of temperature and drought effects than the inventories can account for. MEGAN takes the previous 15-day temperature and radiation into account, which seems to improve the prediction of the inter-annual variation.

Within the uncertainties of the methods used here the most frequently used biogenic emissions inventories for the US generally agree with the observations for isoprene and the monoterpenes within a factor of 2. Discrepancies exist for certain areas and inter-annual changes need to be better accounted for. Since the biogenic VOCs have such large emissions more research needs to be done to improve the factor of two agreement.

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FIGURES

Figure 1. A: The flight tracks of the NOAA WP-3 aircraft during the NOAA TEXAQS2006, ICARTT2004 and SOS1999 campaigns (boundary layer in black and free troposphere in red) plotted on top of the EPA BEIS3.13 summer isoprene base emissions map of the United States. B: The MEGAN isoprene emission factor map with the TEXAQS2000 flight tracks. C: The BEIS3.13 monoterpene base emissions. The units of the emissions here and in the rest of the manuscript are (moles C km^{-2} h^{-1}) and the same color scale for the base emissions is used in all other Figures.

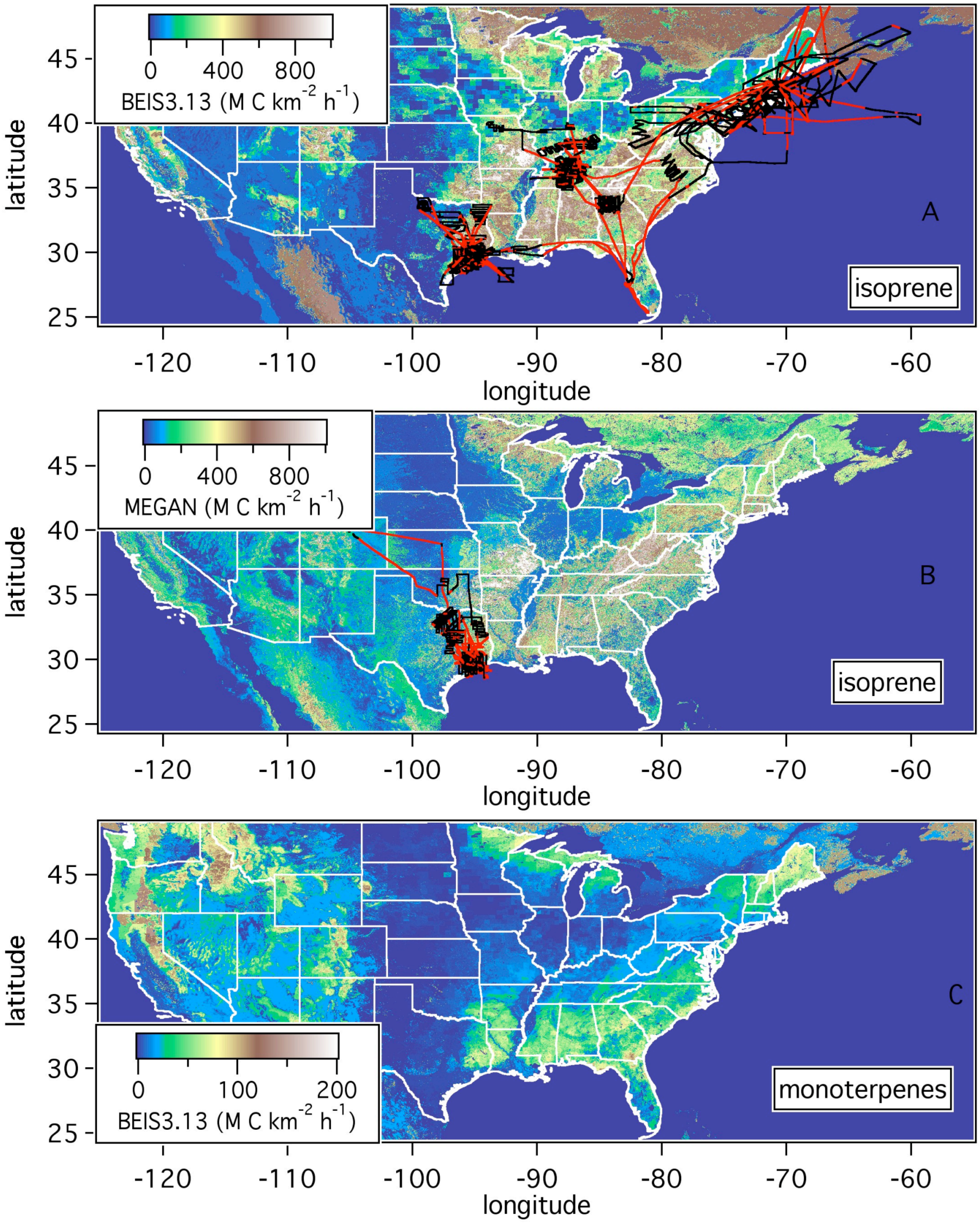


Figure 2. Scatter plots of the isoprene base and actual emissions of BEIS3.13, MEGAN and WM2001 versus BEIS3.12. The black dots are the 1-second data and the green circles are the 5-minute averages. The gray shaded areas indicate an agreement to within a factor of two and the solid red line is an orthogonal distance regression fit forced through zero.

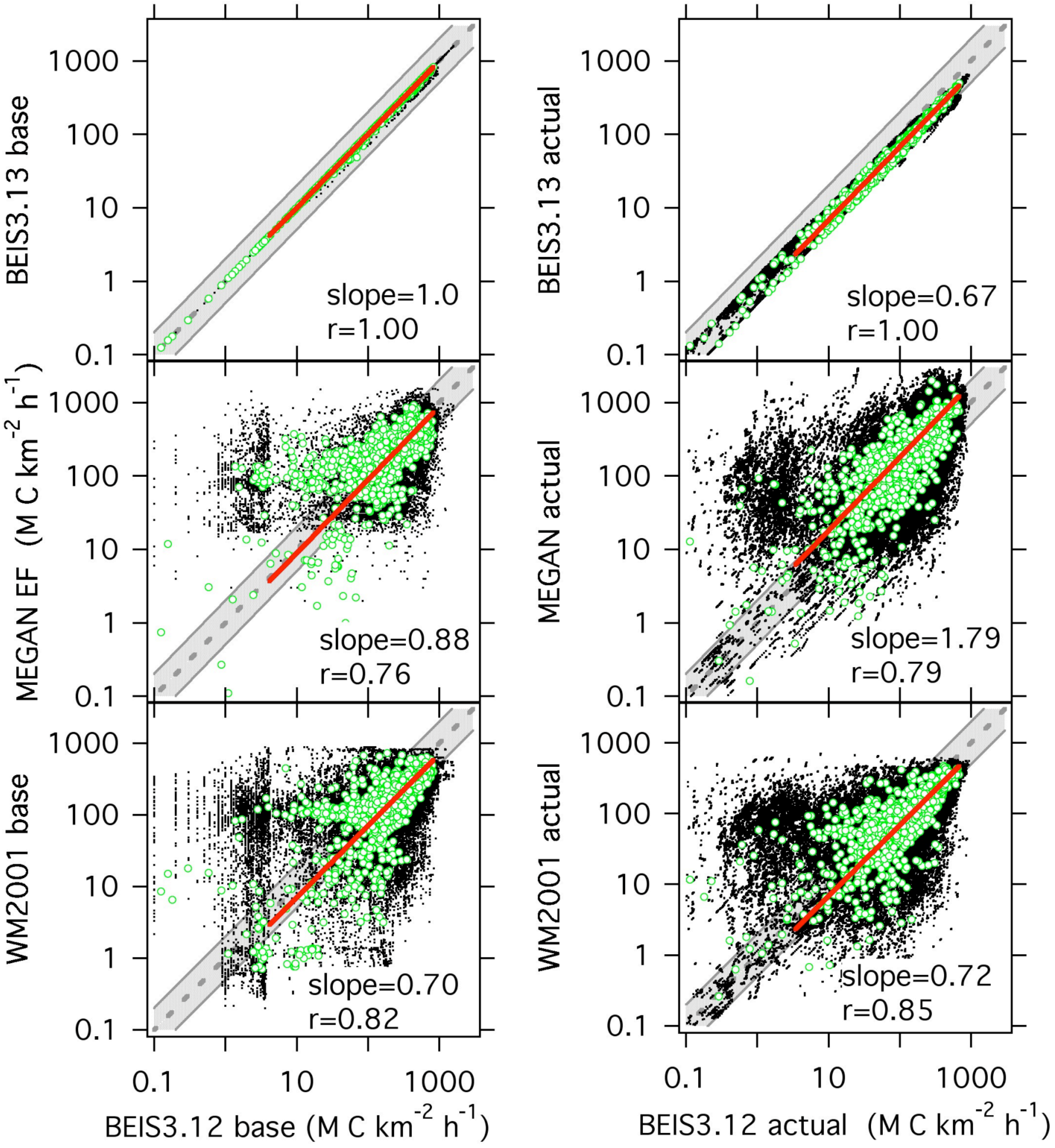
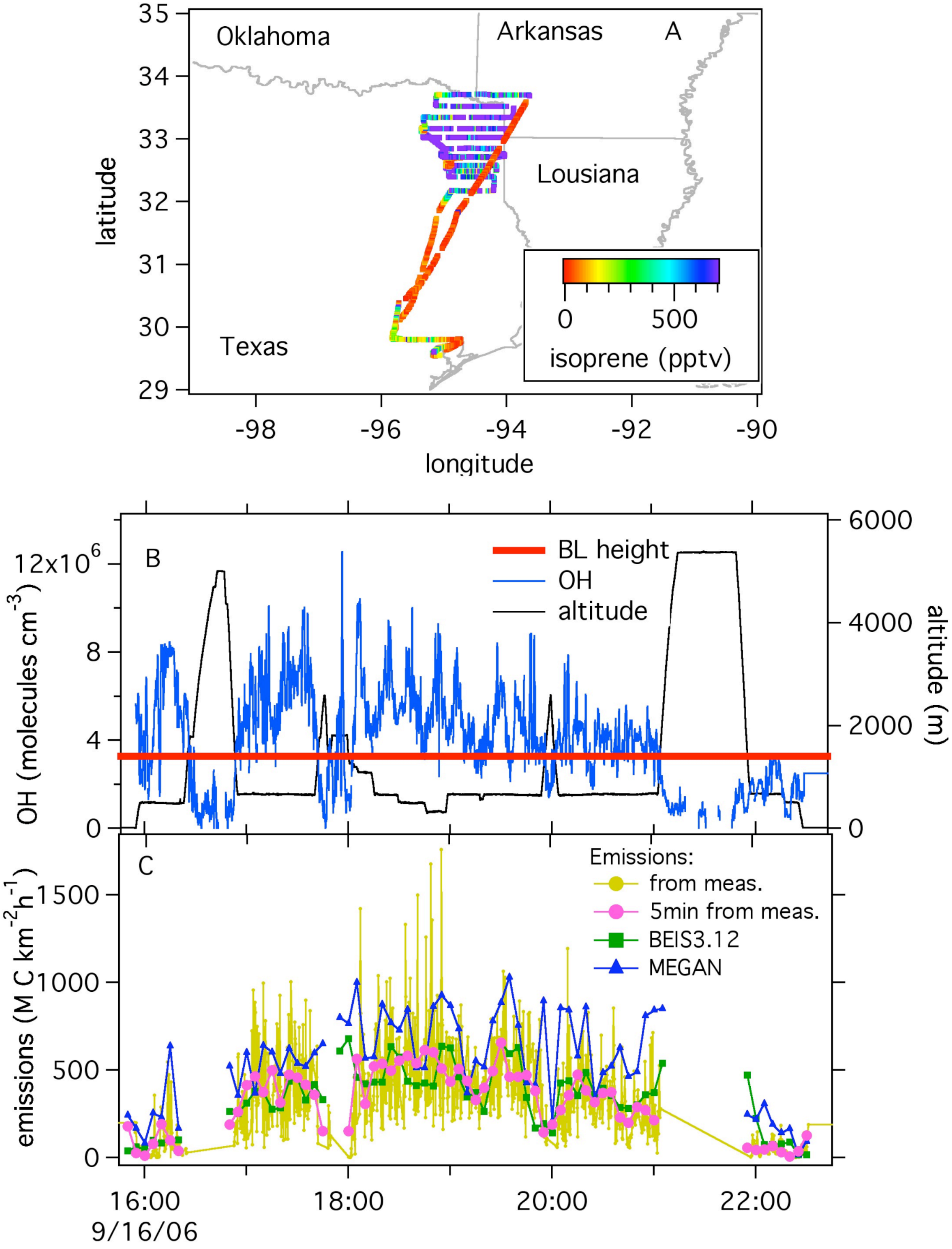


Figure 3. A: The flight track of the NOAA WP-3 from the TEXAQS2006 flight on Sep. 16, 2006 color coded with isoprene mixing ratios. B: The boundary layer height and the OH concentration used for modeling the emissions from the isoprene observations together with the aircraft altitude. C: The emissions modeled from the measurements and calculated from BEIS3.12 and MEGAN.



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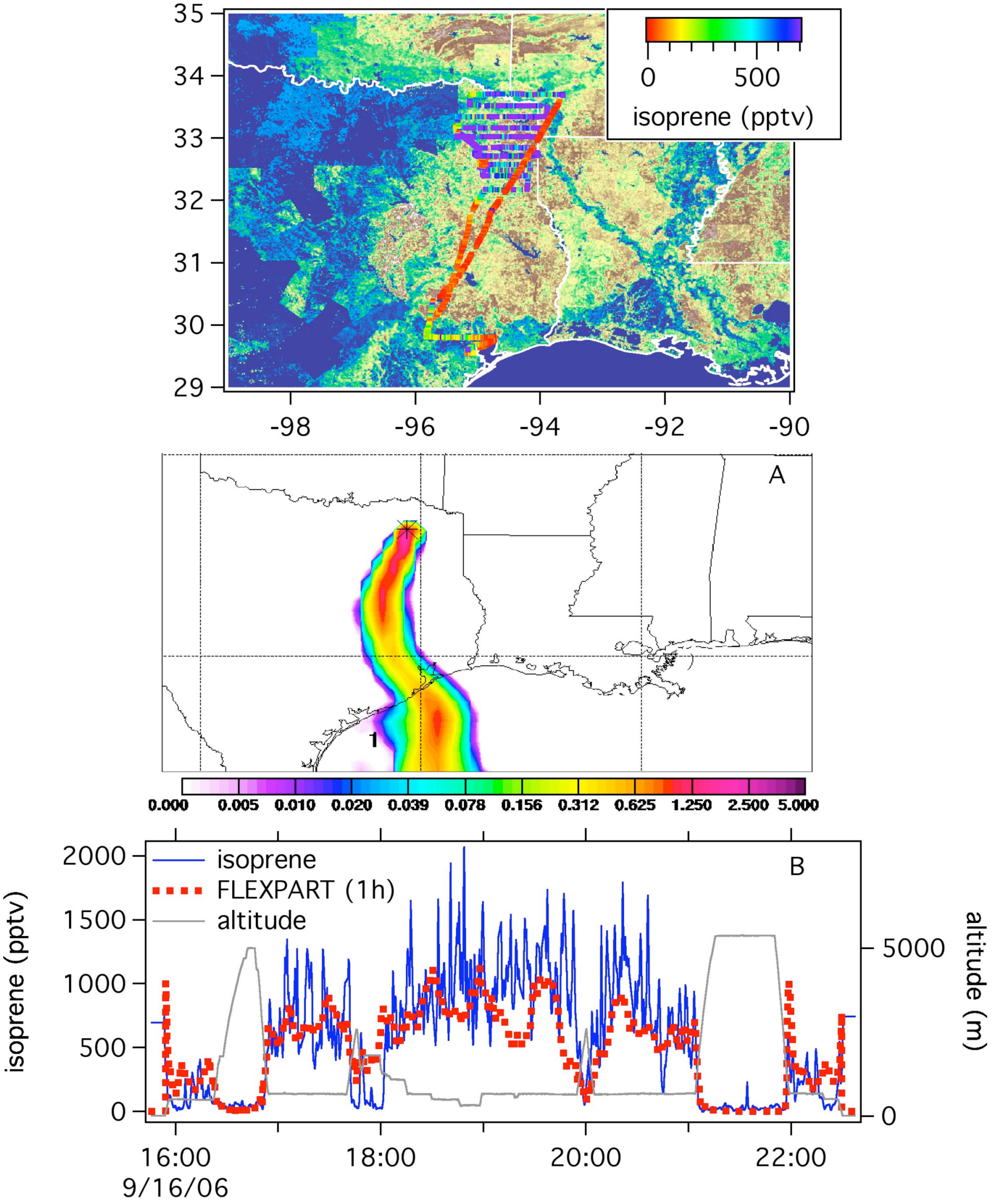
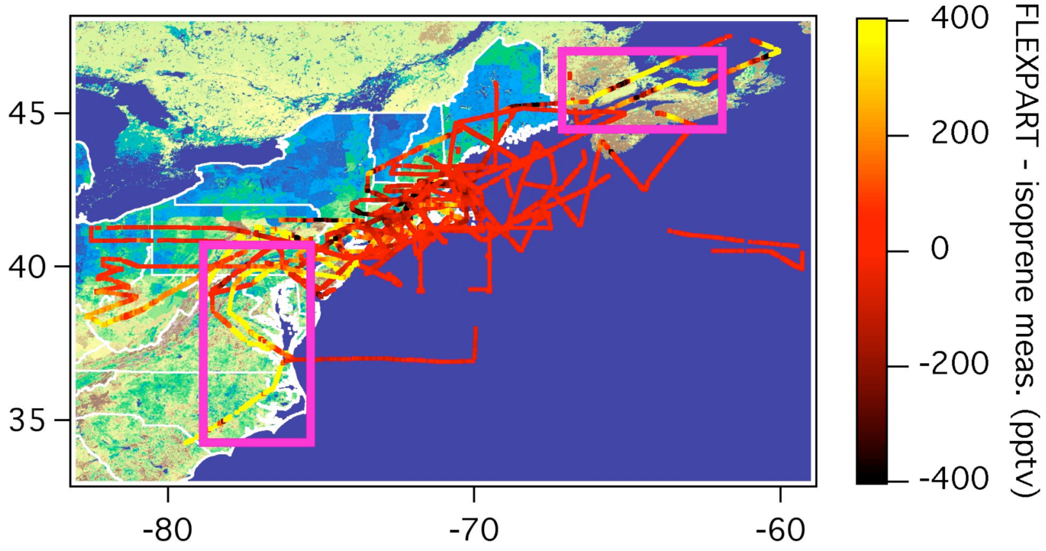


Figure 5. The flight tracks of the NOAA WP-3 during the ICARTT2004 campaign color coded with the difference of the isoprene from FLEXPART using BEIS3.12 with isoprene measurements on top of the BEIS3.12 base emissions. The pink squares indicate areas were significant differences were observed.



TABLES:

Table 1. The slope and the correlation coefficient R (in brackets) for linear fits of scatter plots for the isoprene emissions determined from the biogenic emission inventories versus the emissions modeled from the measurements using the mixed boundary layer method. The linear fit is an orthogonal distance regression forced through zero.

	BEIS3.12 Isoprene	BEIS3.13 Isoprene	MEGAN Isoprene	WM2001 Isoprene
SOS1999	0.61 (0.73)	0.43 (0.75)	1.09 (0.59)	N/A
TEXAQS2000	0.47 (0.62)	0.34 (0.64)	1.30 (0.68)	0.50 (0.52)
ICARTT2004	1.65 (0.66)	0.98 (0.67)	2.83 (0.68)	N/A
TEXAQS2006	0.98 (0.69)	0.60 (0.70)	1.81 (0.63)	0.68 (0.73)

Table 2. The slope and the correlation coefficient R (in brackets) for linear fits of scatter plots for the mixing ratios calculated with FLEXPART versus measured mixing ratios. The linear fit is an orthogonal distance regression forced through zero.

	FLEXPART Isoprene
SOS1999	N/A
TEXAQS2000	N/A
ICARTT2004	2.05 (0.61)
TEXAQS2006	1.30 (0.75)

Table 3. The slope and the correlation coefficient R (in brackets) for linear fits of scatter plots for the monoterpene emissions determined from the biogenic emission inventories versus the emissions modeled from the measurements using the mixed boundary layer method and scatter plots of the mixing ratios calculated with FLEXPART versus measured mixing ratios. The linear fit is an orthogonal distance regression forced through zero.

	BEIS3.13 Monoterpenes	FLEXPART Monoterpenes
SOS1999	N/A	N/A
TEXAQS2000	N/A	N/A
ICARTT2004	2.26 (0.53)	1.12 (0.55)
TEXAQS2006	1.22 (0.41)	1.96 (0.43)

KEYWORDS

Biogenic VOCs
Biogenic VOC emission inventory
MEGAN
BEIS
top-down evaluation