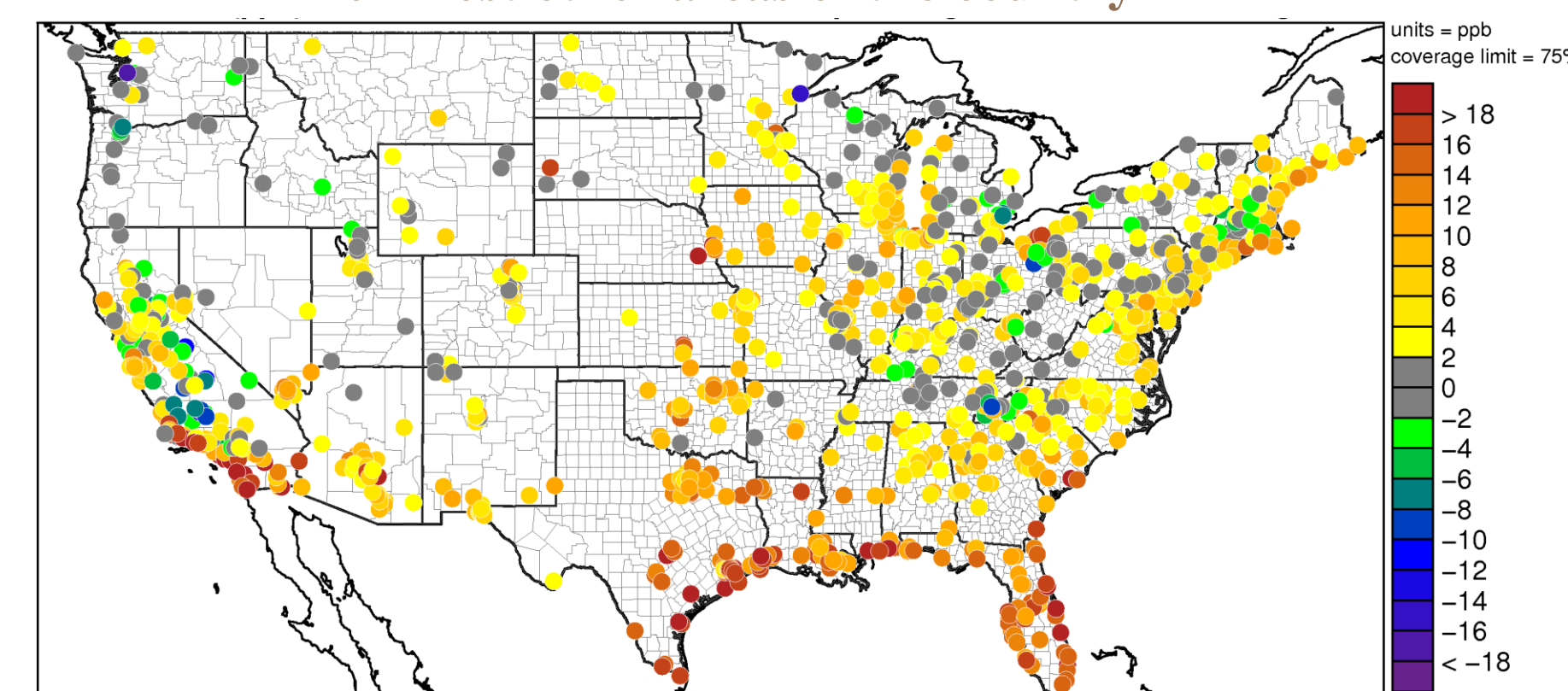


## Motivation

Past studies have documented the tendency for regional photochemical models to over-predict ozone (O<sub>3</sub>) concentrations along the Gulf of Mexico coast in the US (Yarwood et al., 2012; Environ, 2012; Simon et al., 2012; Smith et al., 2013). It has been suggested that this over-prediction is, at least in part, due to missing/under-estimated marine O<sub>3</sub> loss mechanisms in the model including: underestimate of O<sub>3</sub> deposition velocity over sea-water and O<sub>3</sub> destruction by halogen chemistry .

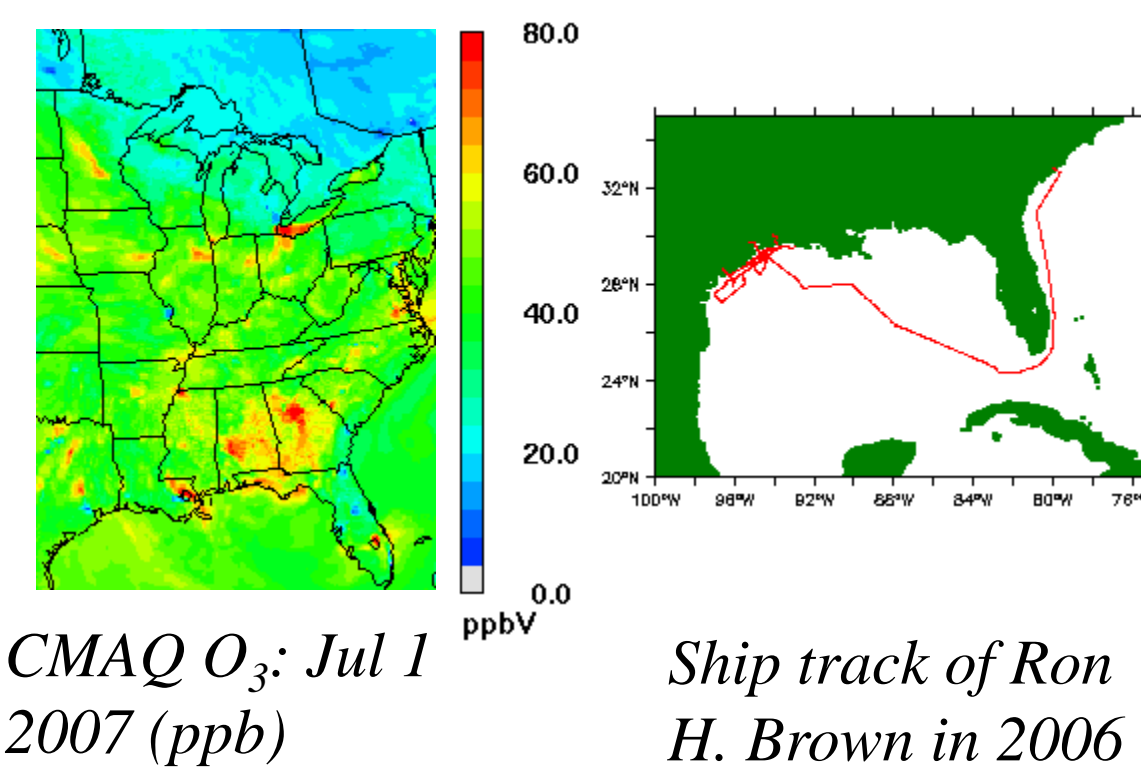
New analysis of a 2007 CMAQ model simulation support these conclusions

### 1. Ozone bias is larger along the Gulf of Mexico coast than for most other areas of the country



Mean Bias in MDA8 O<sub>3</sub> from 2007 CMAQv5.01 Simulation: Jun-Aug

### 2. Measurements of O<sub>3</sub> concentrations over the Gulf of Mexico are generally lower than modeled concentrations



- The Ron H. Brown was in the open gulf of Mexico for ~4 days during the 2006 TEXAQ5 II field study (Helmig et al., 2012)
- Measured O<sub>3</sub> ranged from 0-35 ppb
- Median O<sub>3</sub> was ~26 ppb
- Modeled O<sub>3</sub> over the Gulf of Mexico (2007) was generally closer to 40 ppb

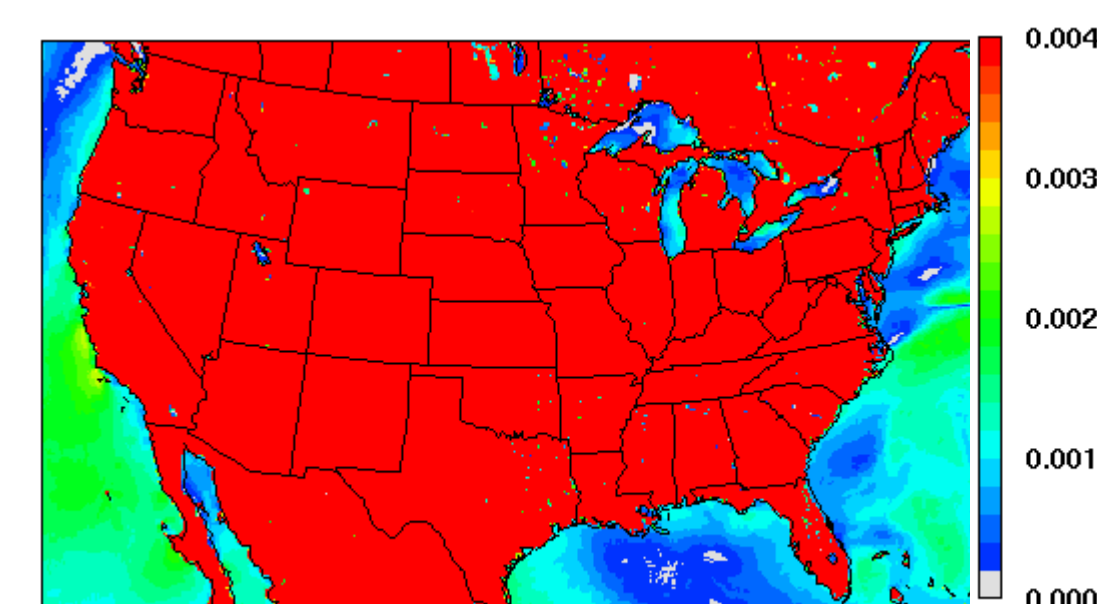
### 3. Measurements of O<sub>3</sub> deposition velocity over the Gulf of Mexico are about an order of magnitude larger than modeled deposition velocities

Table 3. Summary and Statistical Evaluation of Ozone Deposition Velocity Results, With Results for TexAQ5 Broken Up Into TexAQ5<sub>Land</sub> (Land- and Coast-Influenced Regions) and TexAQ5<sub>Sea</sub> (Open Ocean) and GOMECC Data Broken Up Into Subsets for the Gulf of Mexico (GOM) and North Atlantic Region (ATL) Measurements\*

	Mean	Median	250%	750%	No.	NF	T1 (h)	T2 (h)
TexAQ5 <sub>Land</sub>	0.22	0.056	0.024	0.19	6388	3059	1098	510
TexAQ5 <sub>Sea</sub>	0.55	0.27	0.122	0.547	3521	1106	587	194
TexAQ5 <sub>GOM</sub>	0.036	0.034	0.002	0.064	3067	1953	511	326
STRATUS	0.0090	0.0090	0.0041	0.037	1662	1336	277	223
GOMECC <sub>Land</sub>	0.019	0.018	-0.0063	0.045	3496	1784	580	297
GOMECC <sub>GOM</sub>	0.014	0.019	-0.014	0.041	1100	663	183	111
GOMECC <sub>ATL</sub>	0.022	0.018	-0.0061	0.044	2350	1121	397	187
GAZY	0.010	0.0090	-0.0075	0.024	4628	2745	771	458
AMMA	0.026	0.020	-0.0029	0.044	2568	1147	428	191

\*No is the total number of 10 min flux data points, and NF is the remaining number of data points after filtering (10 min averages). T1 is the total time of collected data; T2 is the total time of good data (left after filtering).

Table from Helmig et al. (2012)



CMAQ O<sub>3</sub> deposition velocity: Jul 1 2007 (cm/s)

## Marine O<sub>3</sub> Loss Sensitivity Analysis

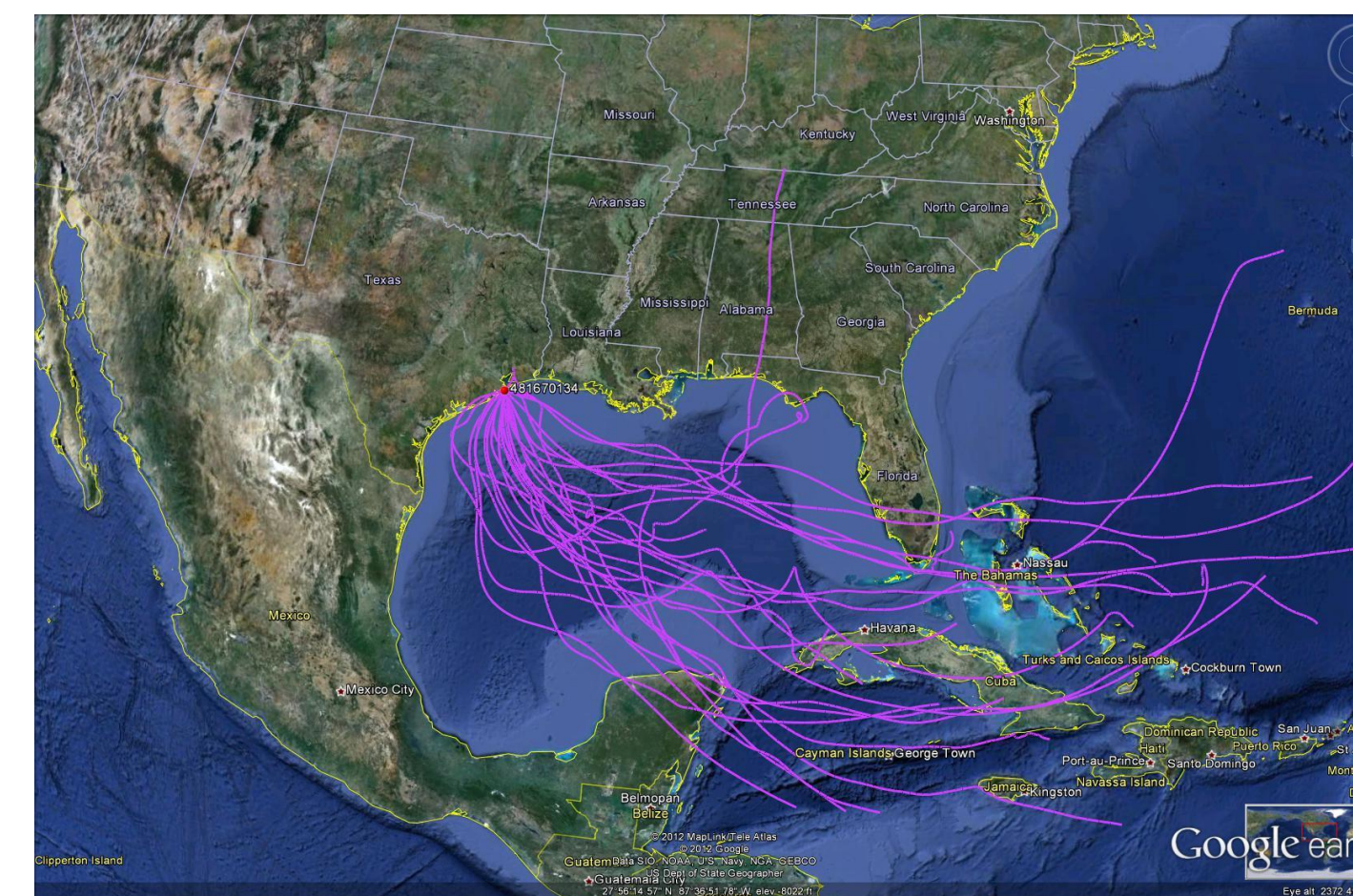
To investigate this phenomenon further, we performed a CMAQ sensitivity simulation with a first-order O<sub>3</sub> loss reaction over marine grid cells in the boundary layer

- July-Aug 2007
- CMAQv5.0.1, WRFv3.3
- O<sub>3</sub> loss rate = 2.0x10<sup>-6</sup> s<sup>-1</sup> (based on Read et al., 2008)
- O<sub>3</sub> deposition velocity over water set to 0.034 cm/sec based on Helmig et al. (2012)
- See Sarwar et al. (poster #11) for more sophisticated evaluation of marine O<sub>3</sub> chemistry

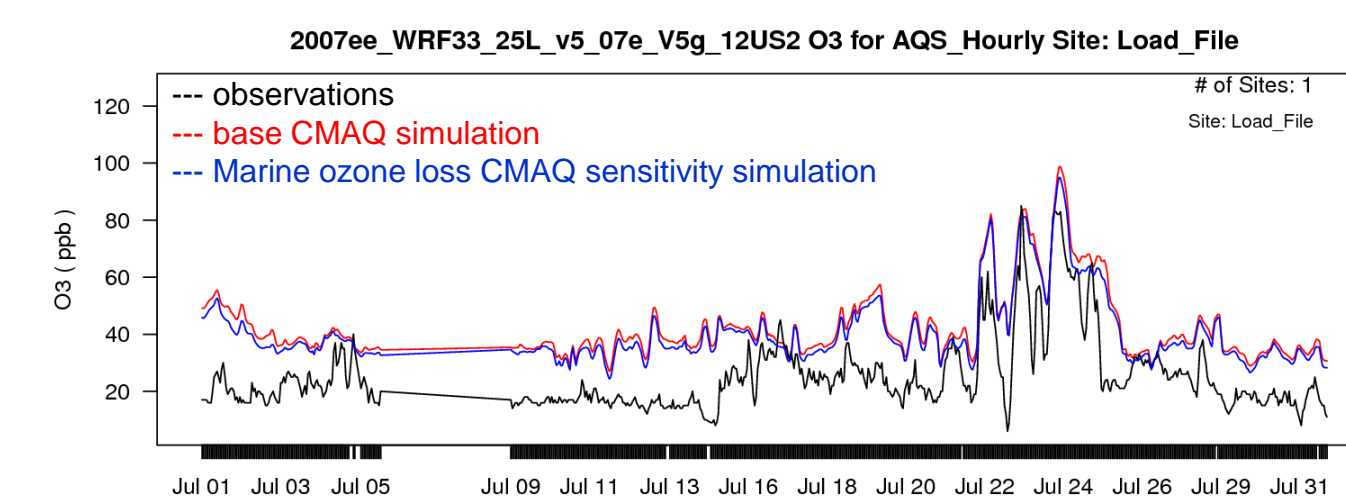
## Galveston, Texas Case Study

Galveston's location as a coastal site that can be influenced by marine as well as continental and urban air masses makes it an ideal case study for further investigating the causes of coastal O<sub>3</sub> over-predictions

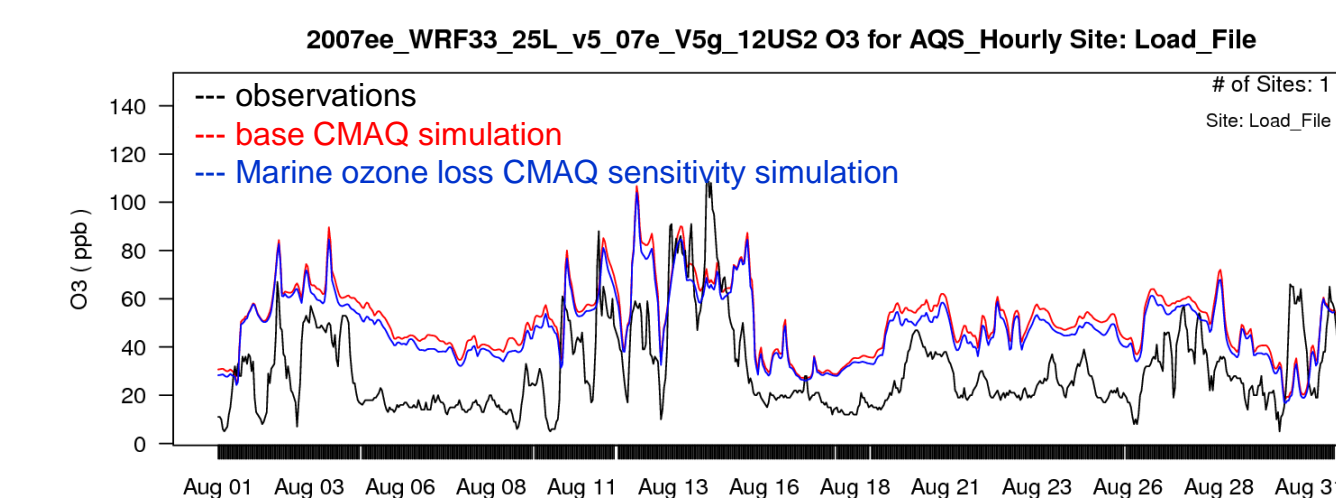
### 1. 120-hr back trajectories on days with the poorest model performance during the summer of 2007, suggest that O<sub>3</sub> over-prediction is associated with onshore flow from the Gulf of Mexico (similar to Smith et al., 2013)



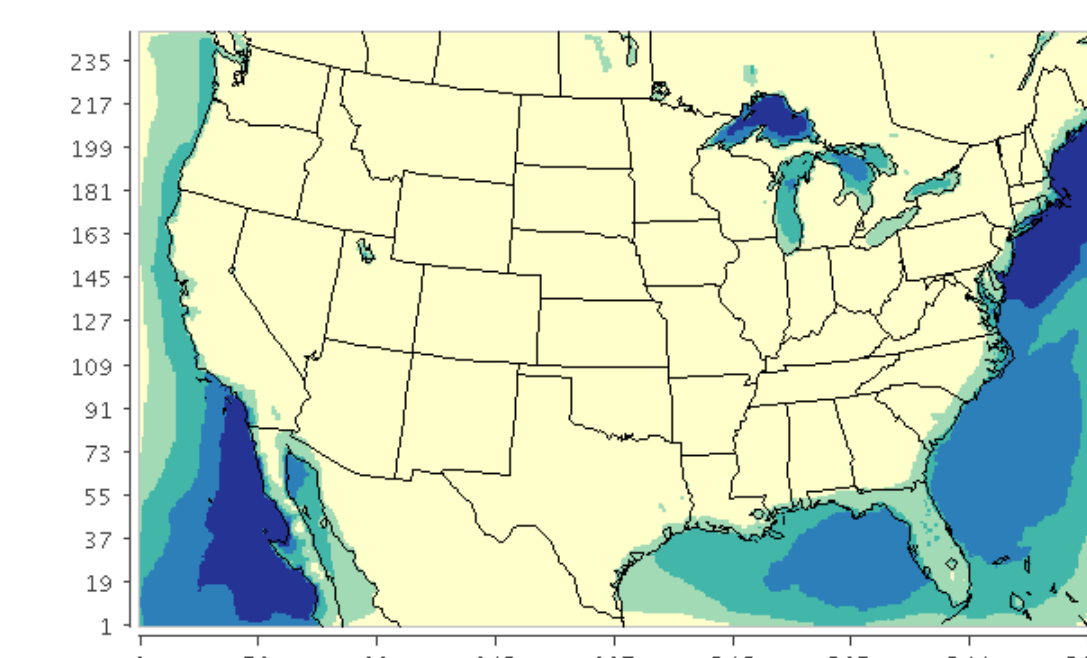
### 2. The largest model over-predictions occur on low O<sub>3</sub> days. Despite reducing O<sub>3</sub> concentrations over marine grid cells, the sensitivity simulation did little to improve this model over-prediction at the Galveston monitor



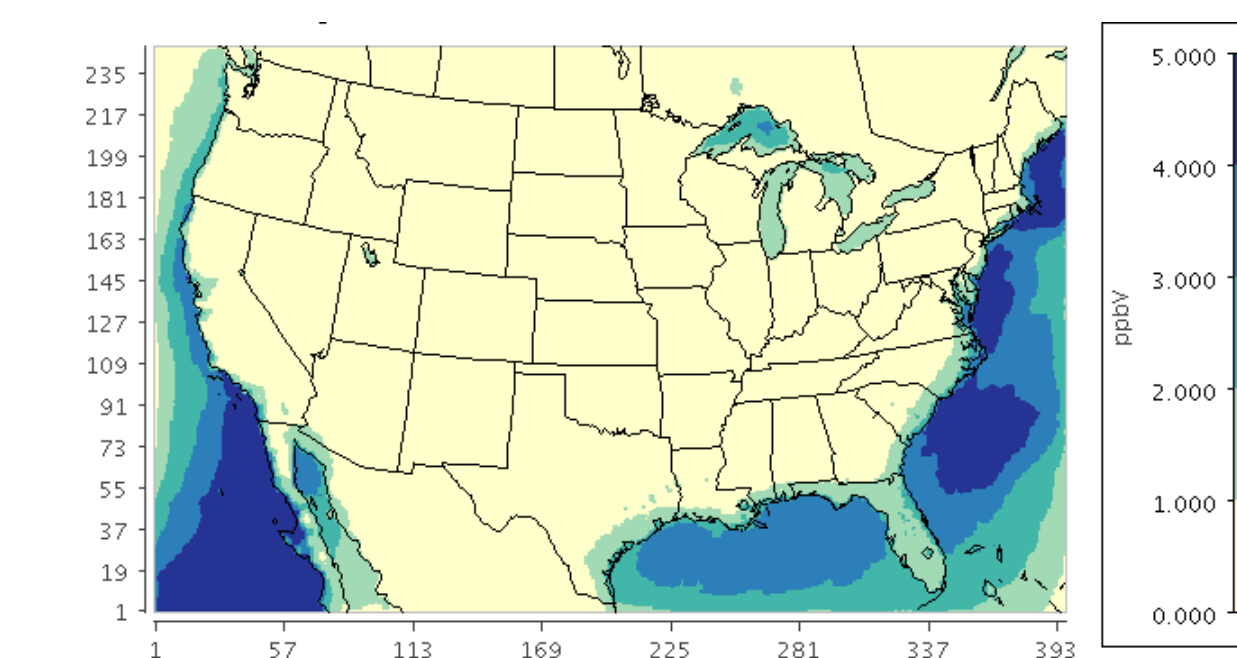
Hourly time series of observed and modeled O<sub>3</sub> in Galveston, TX: Jul 2007



Hourly time series of observed and modeled O<sub>3</sub> in Galveston, TX: Aug 2007

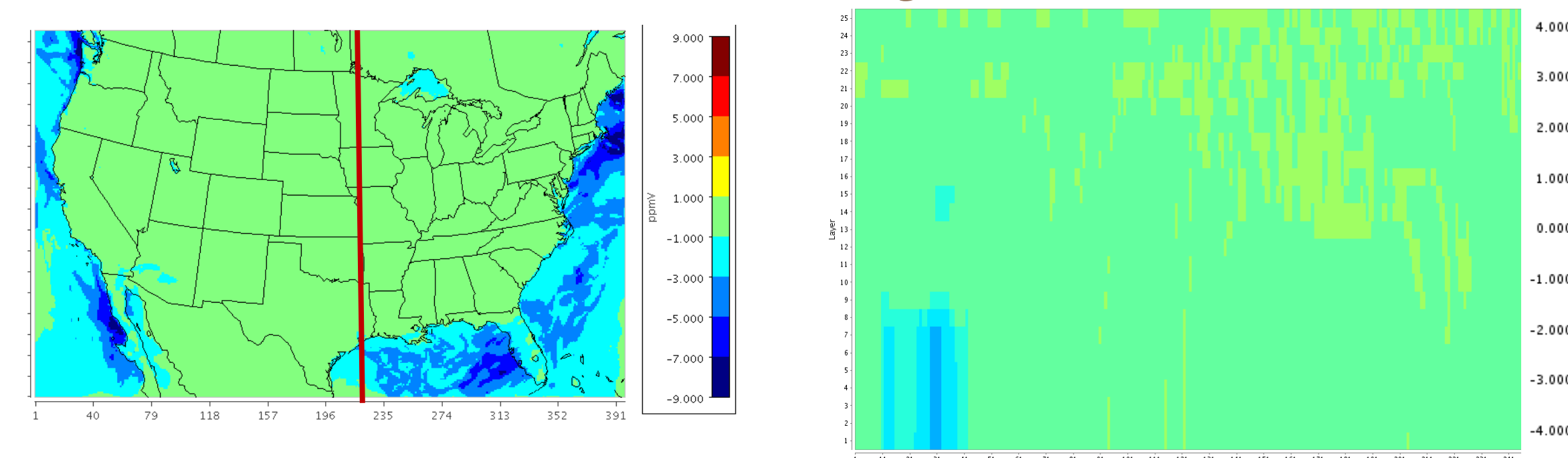


Mean decrease in hourly O<sub>3</sub> from the marine O<sub>3</sub> loss sensitivity simulation: Jul 2007



Mean decrease in hourly O<sub>3</sub> from the marine O<sub>3</sub> loss sensitivity simulation: Aug 2007

### 3. A vertical profile of the O<sub>3</sub> response to the modeling sensitivity simulation shows that O<sub>3</sub> reductions occur in the lowest 7-9 model layers (400-800 m) over marine grid cells



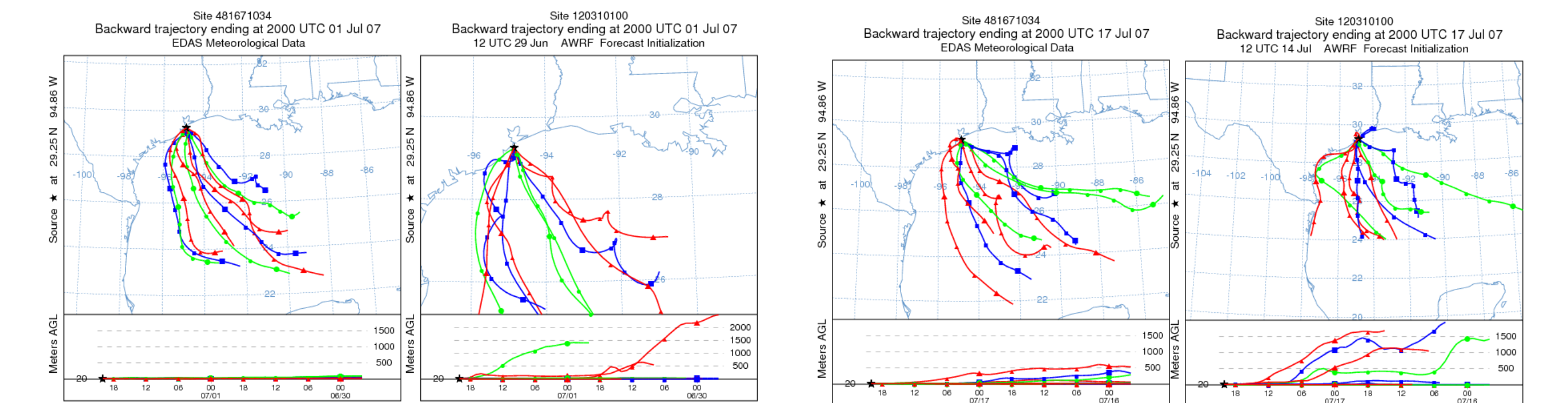
Decrease in O<sub>3</sub> from the marine O<sub>3</sub> loss sensitivity simulation: July 13, 2007 17:00 UTC in the first model layer (left) and for the vertical profile cross section for transect shown in red (right)

- Galveston observed Jul 13 MDA8: 16.5 ppb
- Galveston modeled Jul 13 MDA8: 38.9 ppb

## Comparison of WRF and EDAS Back Trajectories

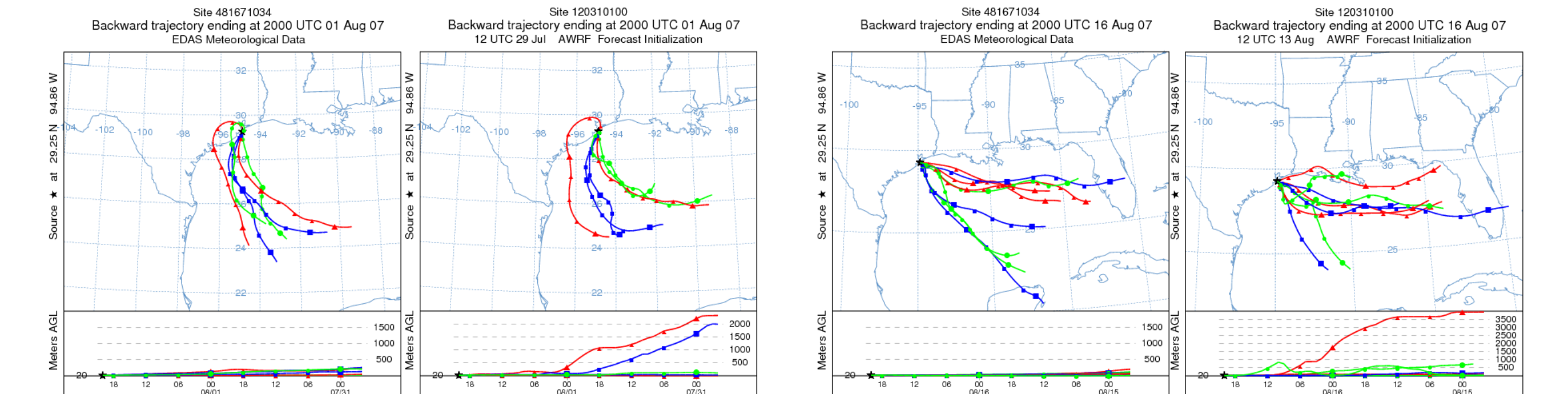
To further investigate why the marine O<sub>3</sub> sensitivity simulation did not substantially lower O<sub>3</sub> in Galveston on low O<sub>3</sub> days that were predominately marine influenced, we compare HYSPLIT back trajectories from the model simulation (WRF) versus those from the Eta Data Assimilation System (EDAS) during the summer of 2007.

- Back trajectories were evaluated for a starting location of Galveston, Texas at a height of 20m
- All back trajectories were run for 48 hours starting 2pm local time on all days for which MDA8 O<sub>3</sub> was less than 35 ppb
- HYSPLIT was run using the default model vertical velocities for both WRF and EDAS



Back trajectories from EDAS (left) and WRF (right) on July 1, 2, 3, 4, 10, 11, 12, 13, 14, 15

Back trajectories from EDAS (left) and WRF (right) on July 17, 18, 19, 20, 26, 27, 28, 29, 30, 31



Back trajectories from EDAS (left) and WRF (right) on August 1, 5, 6, 7, 8, 9

Back trajectories from EDAS (left) and WRF (right) on August 16, 17, 18, 21, 22, 23, 24, 25, 29

- These plots show that both EDAS and WRF consistently predict that air originates from marine locations on low ozone days. The horizontal back trajectories cover similar horizontal extents.
- These plots also show, that on some days, WRF vertical mixing is substantially greater than EDAS vertical mixing. WRF back trajectories often reach up to 1000-1500 m while EDAS back trajectories generally stay within 500 m of the surface
- This suggests that although the marine O<sub>3</sub> loss sensitivity depletes O<sub>3</sub> in the marine boundary layer, WRF may be drawing down higher O<sub>3</sub> air from aloft resulting in higher surface O<sub>3</sub> at coastal sites
- If this is the case, then coastal O<sub>3</sub> concentrations will not be substantially impacted on these days unless either 1) coastal WRF treatment is modified to reduce vertical mixing or 2) marine O<sub>3</sub> loss were to extend above the marine boundary layer
- This analysis is not conclusive but raises questions about the combined effect of processes included in the air quality model, the meteorological model and the boundary condition representations on coastal O<sub>3</sub> predictions

## References

Environ (2012) Final Report: Improving CAMx Performance in Simulating Ozone Transport from the Gulf of Mexico. Prepared for Texas Commission on Environmental Quality, Austin, TX, September 2012, project number 06264081, Work Order NO. 582-11-10365-FY12-05  
 Helmig et al. (2012) Atmosphere-ocean ozone fluxes during the TexAQ5 2006, STRATUS 2006, COMECC 2007, GasEX 2008, and AMMA 2008 cruises. Journal of Geophysical Research, vol 117, D04305.  
 Read, K.A., et al. (2008) Extensive halogen-mediated ozone destruction over the Atlantic Ocean. Nature, 453, 1232-1235.  
 Simon et al. (2011) Policy-driven EPA priorities for improvements to the CMAQ photochemical modeling system, CMAS conference, Chapel Hill, NC, October 2011  
 Smith et al., (2013) Characterization of Gulf of Mexico Background Ozone Concentrations, CMAS conference, Chapel Hill, NC, October 2013  
 Yarwood et al., (2012) Modeling ozone depletion in the marine boundary layer caused by natural iodine emissions, CMAS conference, Chapel Hill, NC, October 2012