Addressing model over-prediction of ozone influx from the Gulf of Mexico

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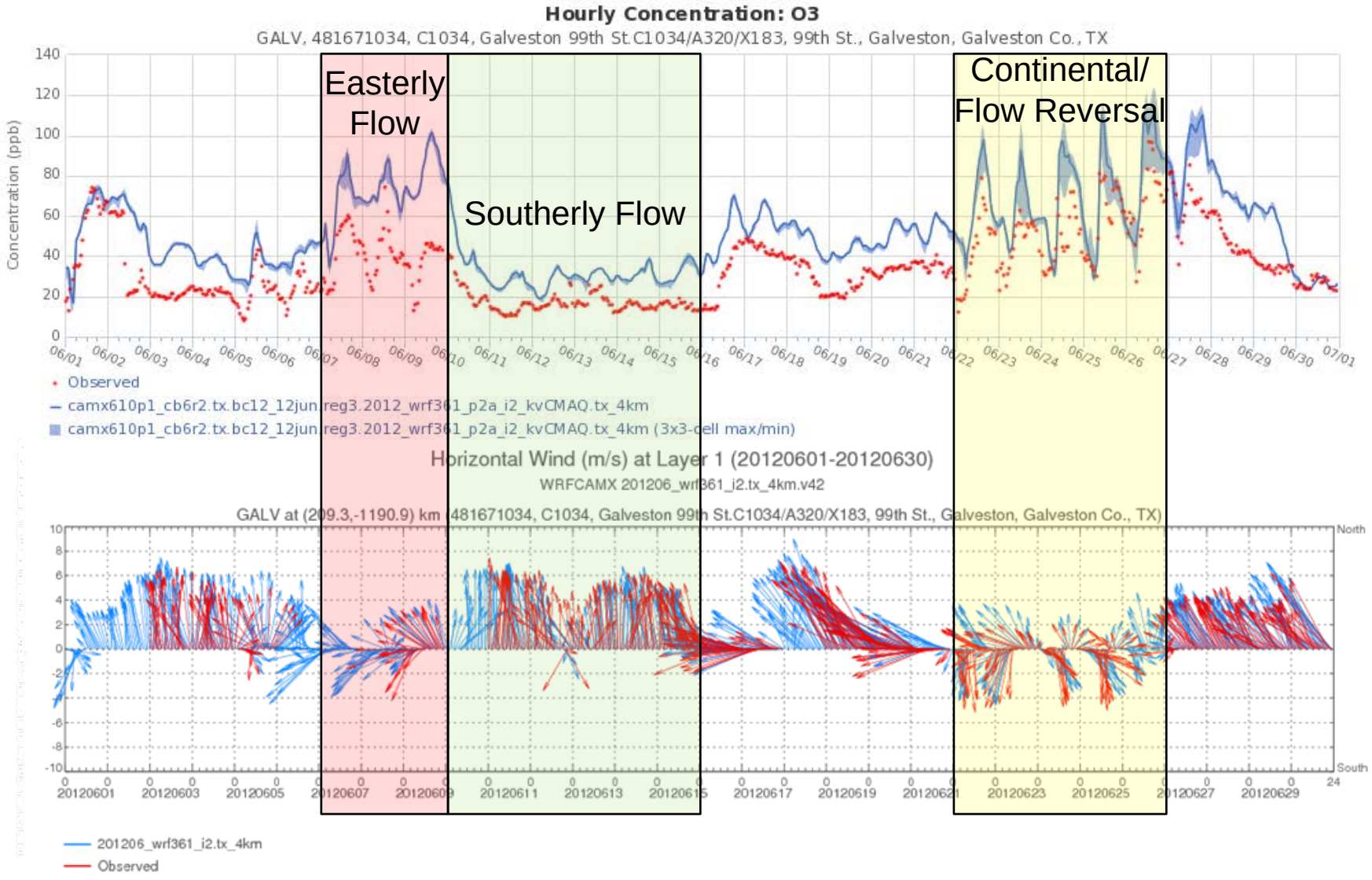
Introduction

- Regional photochemical models are known to over-predict ozone concentrations transported onshore from the Gulf of Mexico.
- Chlorine, iodine, and bromine along with numerous compounds containing them are known to participate in ozone formation and/or destruction.
- Halogen chemistry results in significant depletion of ozone in maritime environments.
- Global models also over-predict marine ozone concentrations, adding to bias through derived boundary conditions.

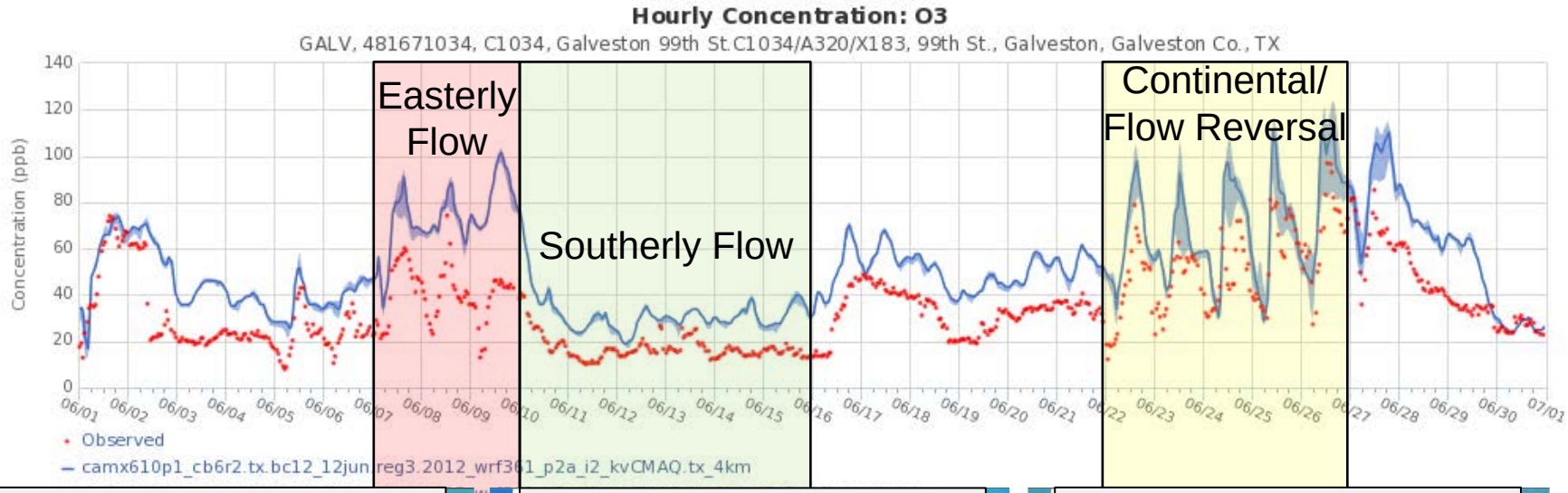
Three Meteorological Regimes

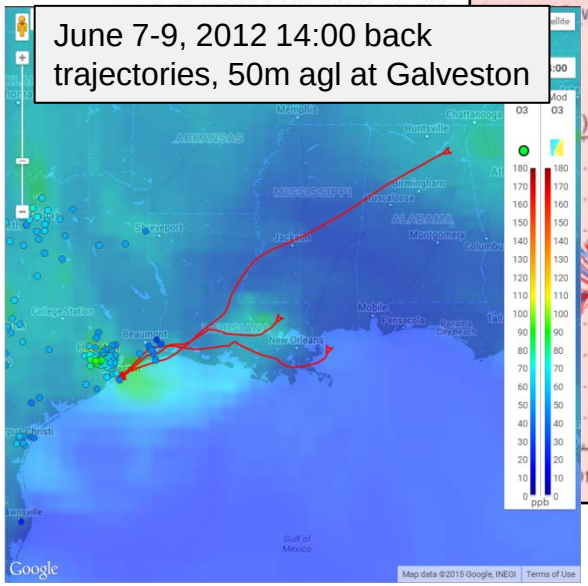
June 2012

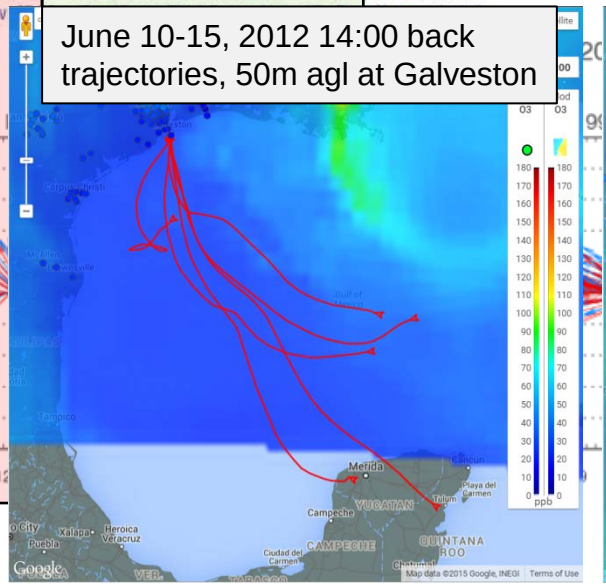


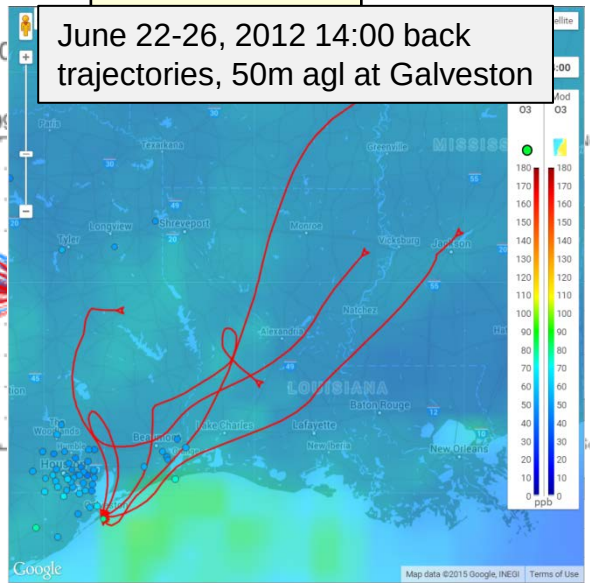
Three Meteorological Regimes

June 2012









Halogen Chemistry in CAMx

- Augmented version of CB6r2: CB6r2**h**
- Iodine, Bromine and Chlorine pathways
- Adds 88 reactions and 41 species to CB6r2 (in addition to current 216 reactions involving 75 species)
- CAMx run time with CB6r2h ~ 1.6X longer than CB6r2 (when aerosols are not explicitly modeled)

Ozone Destruction Pathways

Chlorine Cycles:

	ClO + HO_2 cycle	***ClO + ClO cycle***	***$ClNO_3$ + H_2O cycle***
	$Cl + O_3 \rightarrow ClO + O_2$	$(Cl + O_3 \rightarrow ClO + O_2) \times 2$	$Cl + O_3 \rightarrow ClO + O_2$
	$ClO + HO_2 \rightarrow HOCl + O_2$	$ClO + ClO \rightarrow Cl_2 + O_2$	$ClO + NO_2 \rightarrow ClNO_3$
	$HOCl + h\nu \rightarrow Cl + OH$	$Cl_2 \rightarrow 2\ Cl$	$ClNO_3 + H_2O$ –aer $\rightarrow HOCl + HNO_3$
			$HOCl + h\nu \rightarrow Cl + OH$
Net:	**$O_3 + HO_2 \rightarrow OH + 2\ O_2$**	**$2\ O_3 \rightarrow 3\ O_2$**	**$O_3 + NO_2 + H_2O \rightarrow O_2 + HNO_3 + OH$**

Bromine Cycles:

	BrO + HO_2 cycle	***$BrNO_3$ + H_2O cycle***	***HOBr + HBr cycle***
	$Br + O_3 \rightarrow BrO + O_2$	$Br + O_3 \rightarrow BrO + O_2$	$Br + O_3 \rightarrow BrO + O_2$
	$BrO + HO_2 \rightarrow HOBr + O_2$	$BrO + NO_2 \rightarrow BrNO_3$	$BrO + HO_2 \rightarrow HOBr + O_2$
	$HOBr + h\nu \rightarrow Br + OH$	$BrNO_3 + H_2O$ –aer $\rightarrow HOBr + HNO_3$	$Br + R\text{-}H \rightarrow HBr + R$
		$HOBr + h\nu \rightarrow Br + OH$	$HOBr + HBr$ –aer$\rightarrow Br_2 + H_2O$
			$Br_2 \rightarrow 2\ Br$
Net:	**$O_3 + HO_2 \rightarrow OH + 2\ O_2$**	**$O_3 + NO_2 + H_2O \rightarrow O_2 + HNO_3 + OH$**	**$O_3 + HO_2 + R\text{-}H \rightarrow 2\ O_2 + H_2O + R$**

Ozone Destruction Pathways (cont.)

Iodine Cycles:

	IO + HO2 cycle	***IO + IO cycle***	***IO + NO2 cycle***
	I + O3 → IO + O2	(I + O3 → IO + O2) x 2	I + O3 → IO + O2
	IO + HO2 → HOI + O2	IO + IO → I + OIO	IO + NO2 → IONO2
	HOI + hν → I + OH	OIO + hν → I + O2	IONO2 + hν → I + NO3
			NO3 + hν → NO + O2
			NO + O3→ NO2 + O2
Net:	**$O_3 + HO_2 \rightarrow OH + 2\ O_2$**	**$2\ O_3 \rightarrow 3\ O_2$**	**2 O3 → 3 O2**

These cycles are referred to as catalytic cycles because the halogen atoms are regenerated in the reactions and therefore one I, Cl, or Br atom can potentially destroy many O_3 molecules.

Halogen Emissions

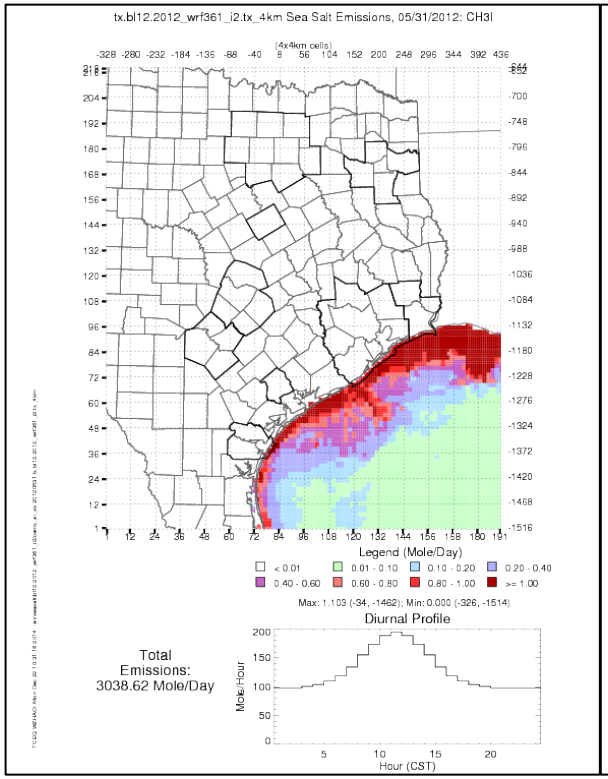
- Molecular iodine (I_2, CB6h species I2) emissions from seawater are assigned a constant flux of $4X10^8$ molecules $cm^{-2}sec^{-1}$.
- Chlorine and bromine-content of sea salt aerosols (SSCL and SSBR, respectively) are assumed to be produced by oceanic turbulence, bubble breaking, and viscous shear and are modeled using the CAMx sea-salt preprocessor.

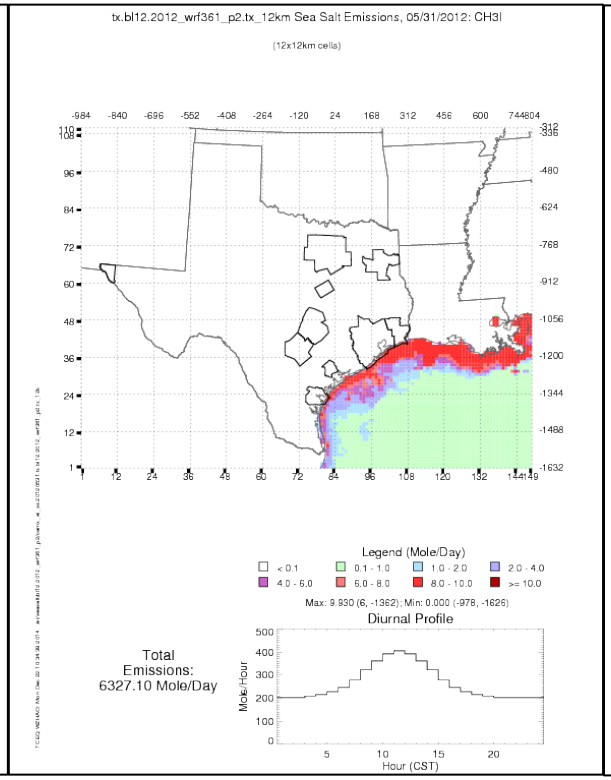
Halogen Emissions

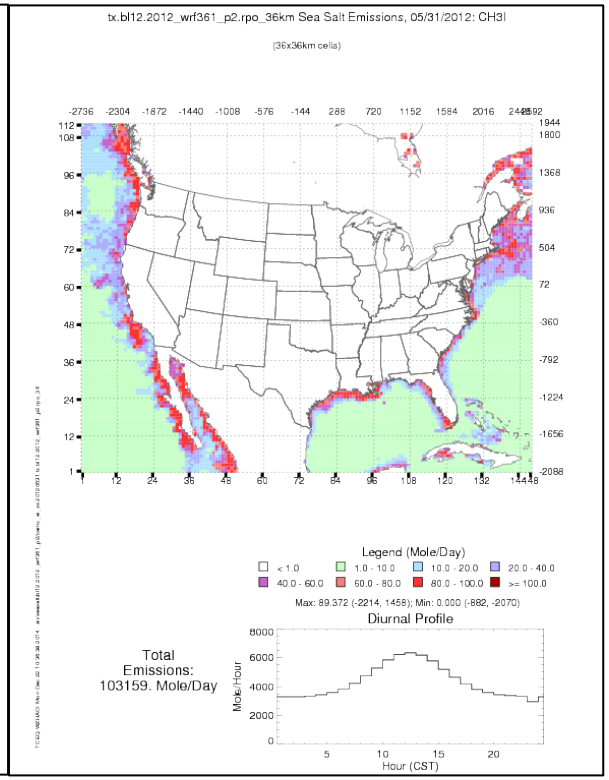
- Halomethanes are generated by organic sources and allocated spatially according to monthly average chlorophyll-a observations from the SeaWIFS satellite. These include:
  - Iodomethane (CH_3I, CH3I)
  - Diiodomethane (CH_2I_2, MI2)
  - Chloroiodomethane (CH_2ICl, MIC)
  - Bromoiodomethane (CH_2IBr, MIB)
  - Chlorobromomethane (CH_2BrCl, MBC)
  - Dibromomethane (CH_2Br_2, MB2)
  - Dichlorobromomethane ($CHBrCl_2$,MBC2)
  - Chlorodibromomethane ($CHBr_2Cl$, MB2C)
  - Bromoform ($CHBr_3$, MB3)

Halogen Compound Emissions:
iodomethane (CH_3I)

May 2012, Each Day

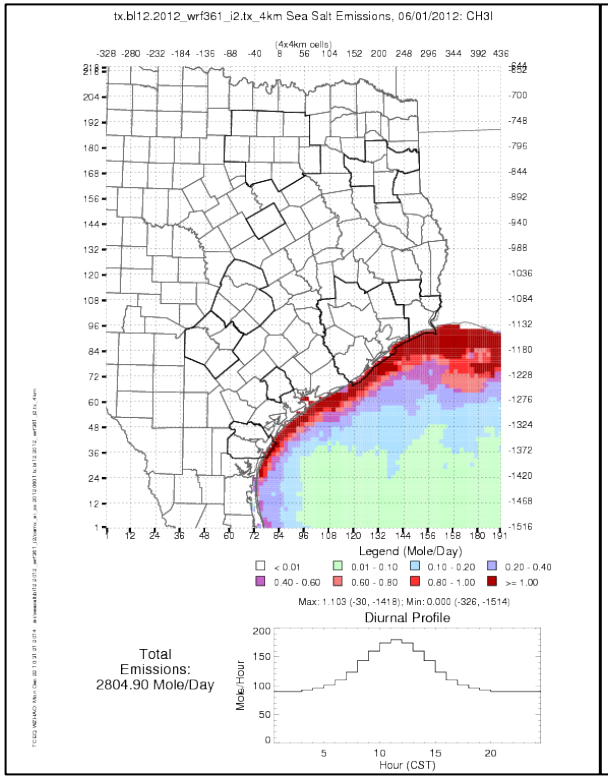


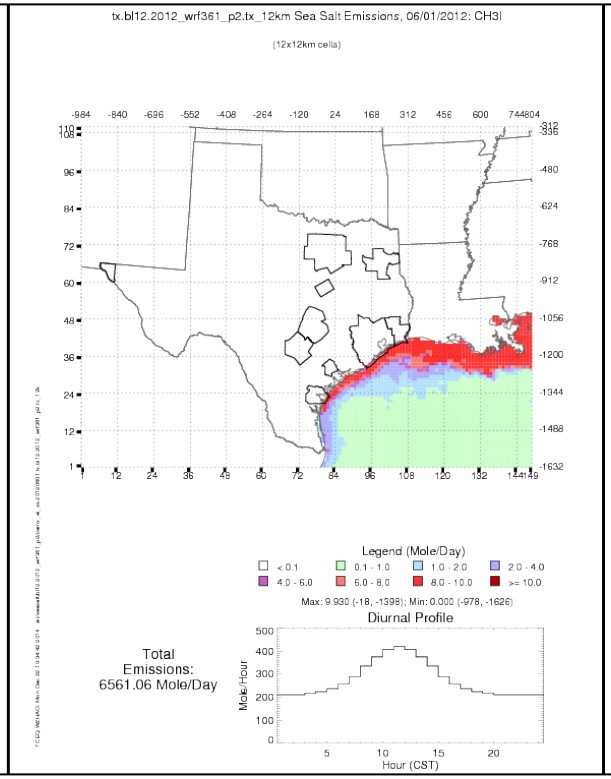


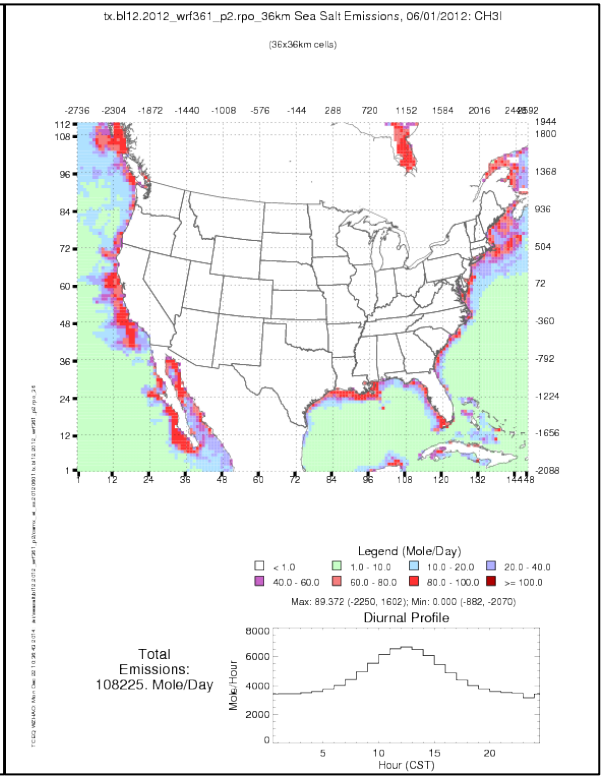


Halogen Compound Emissions:
iodomethane (CH_3I)

June 2012, Each Day

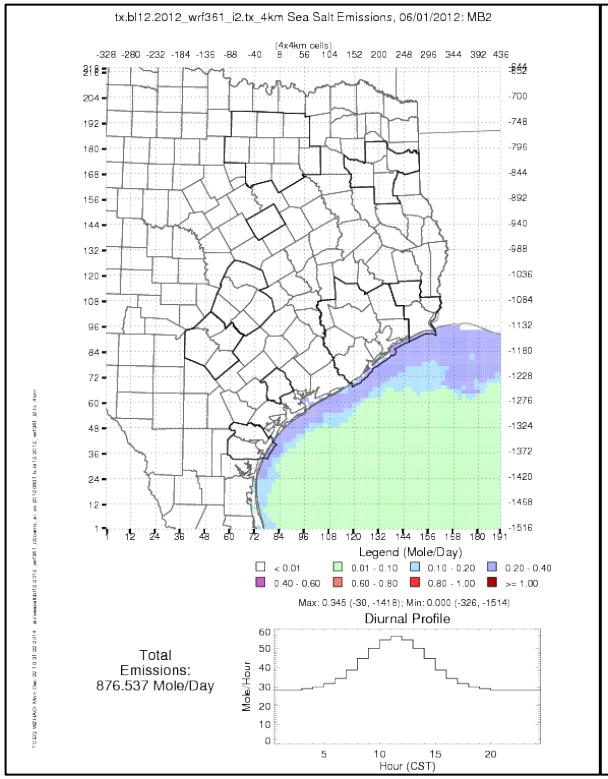


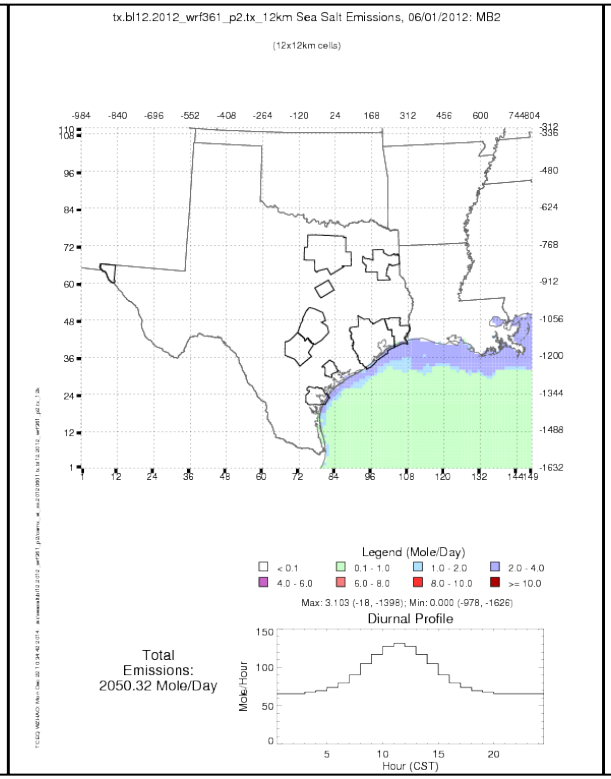


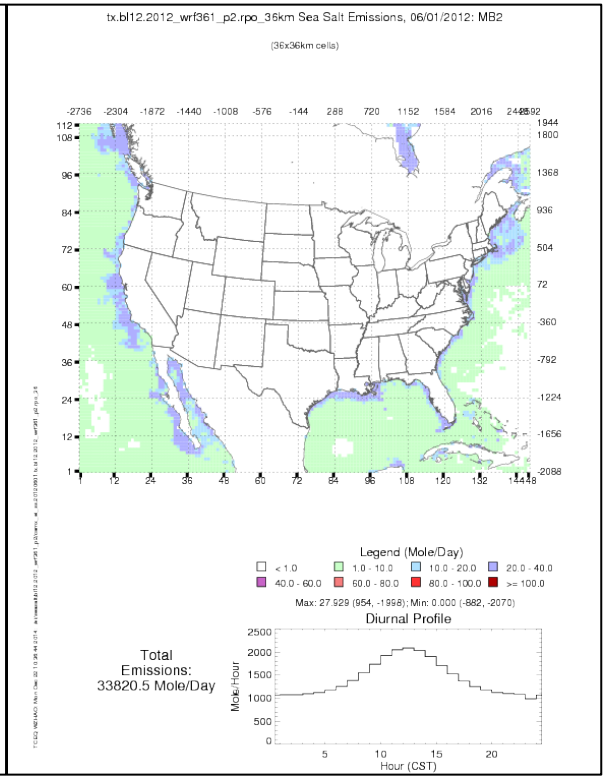


Halogen Compound Emissions:
dibromomethane (CH_2Br_2)

June 2012, Each Day

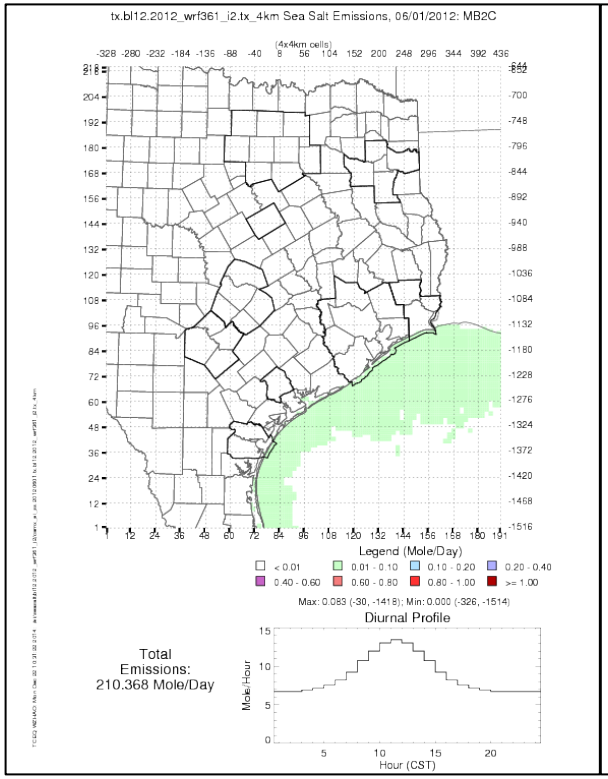


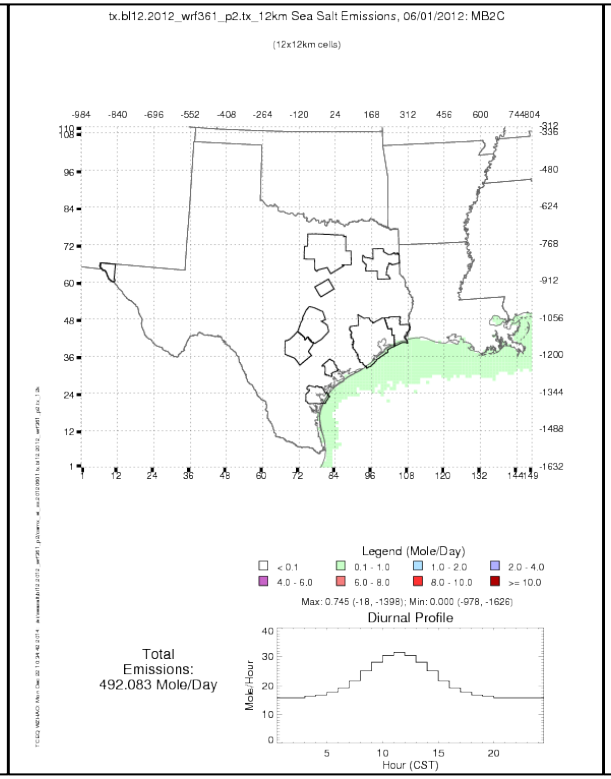


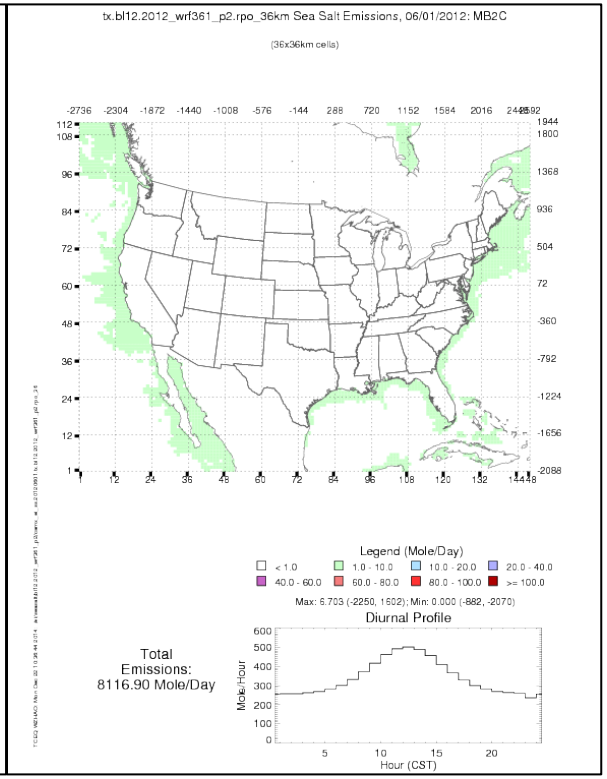


Halogen Compound Emissions:
chlorodibromomethane ($CHClBr_2$)

June 2012, Each Day

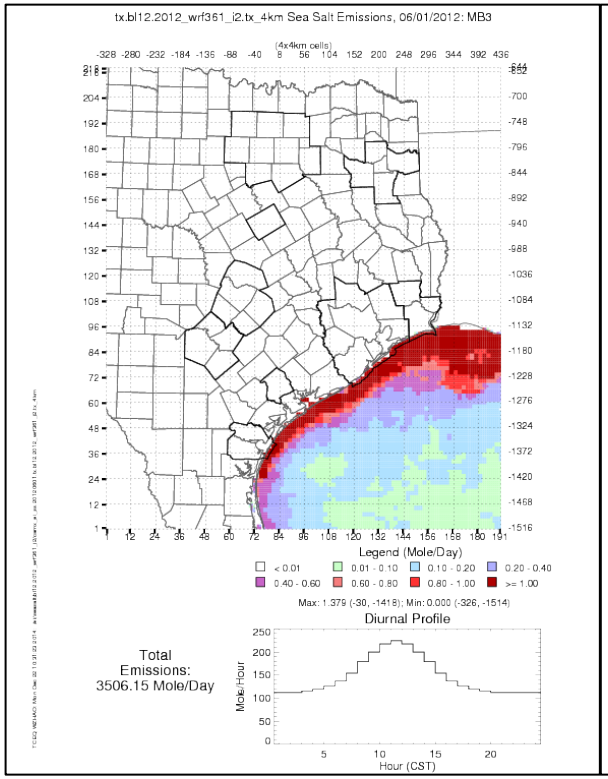


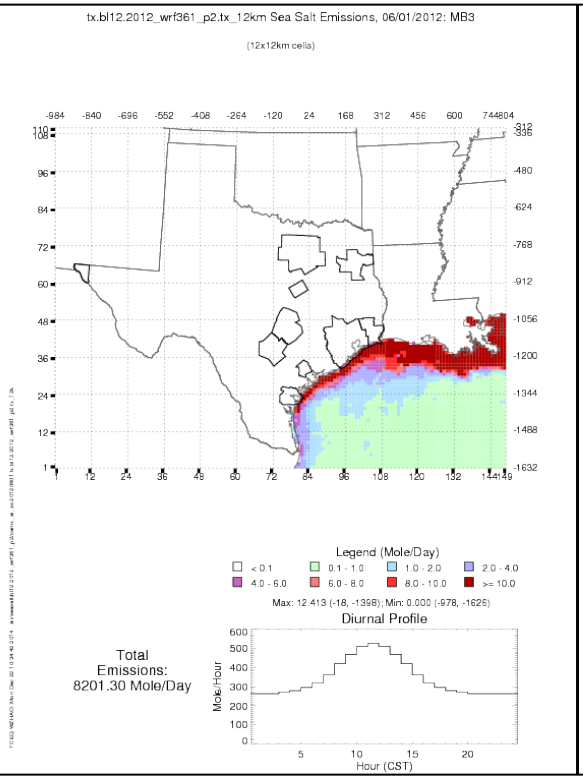


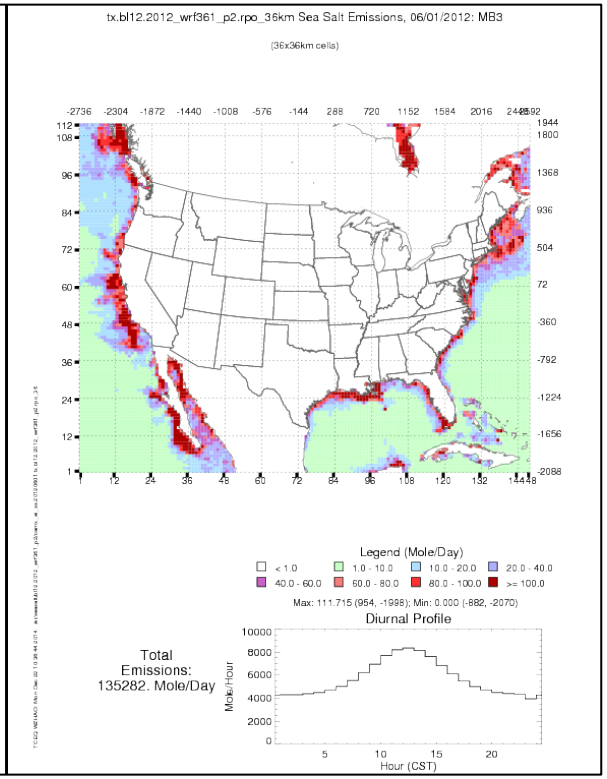


Halogen Compound Emissions:
bromoform ($CHBr_3$)

June 2012, Each Day

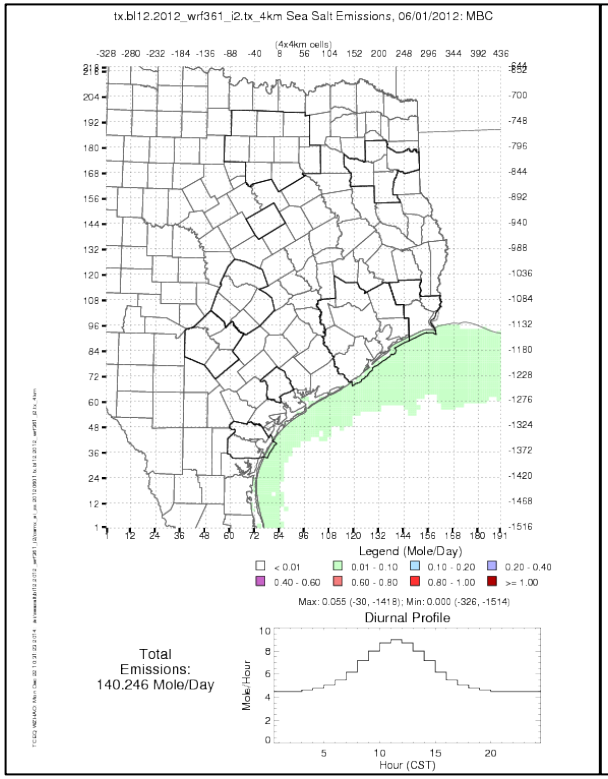


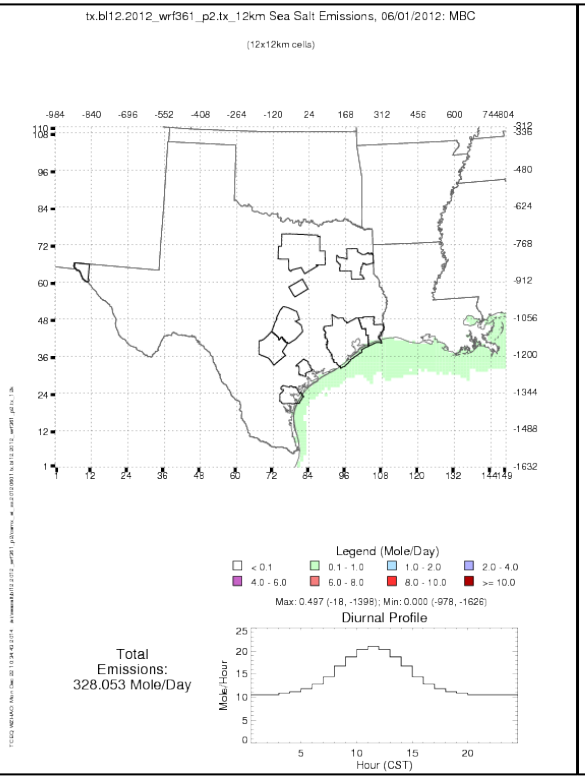


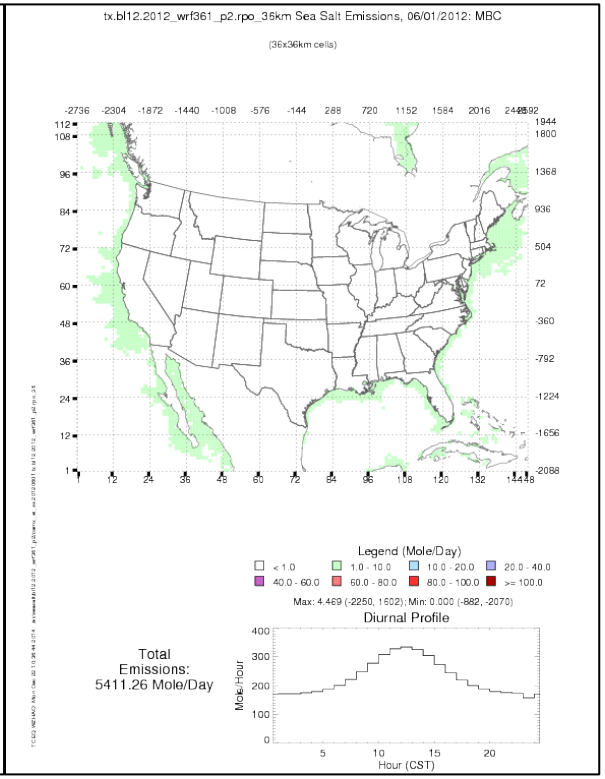


Halogen Compound Emissions:
chlorobromomethane (CH_2ClBr)

June 2012, Each Day

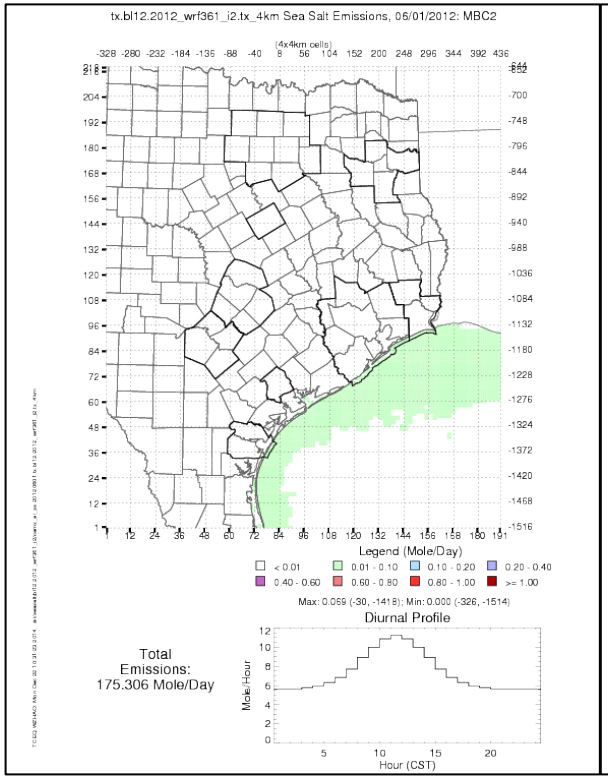


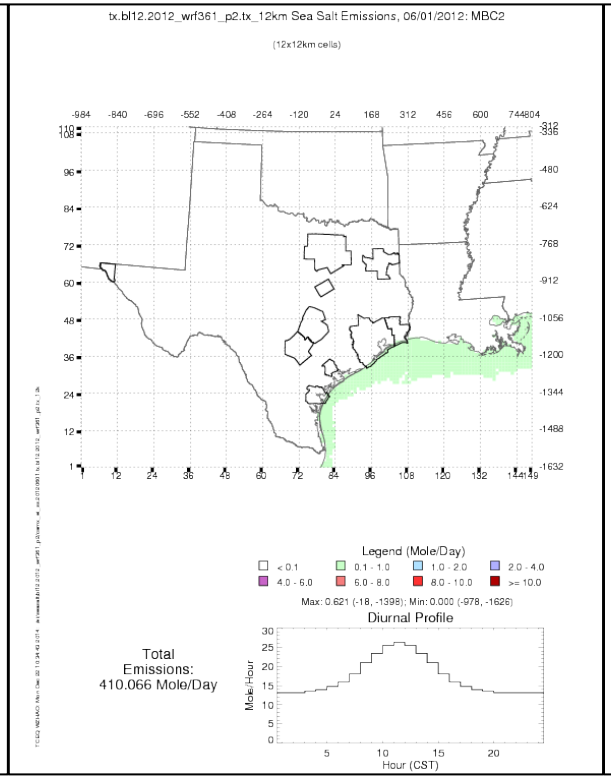


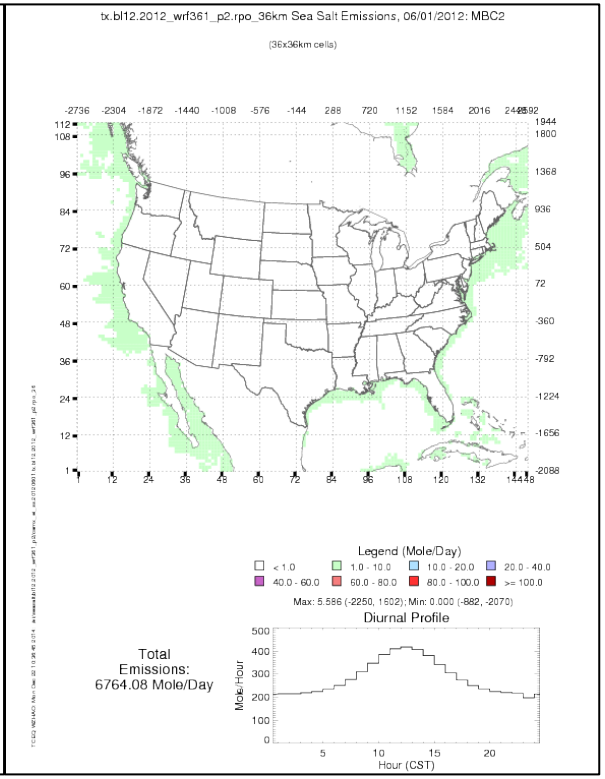


Halogen Compound Emissions:
dichlorobromomethane ($CHCl_2Br$)

June 2012, Each Day

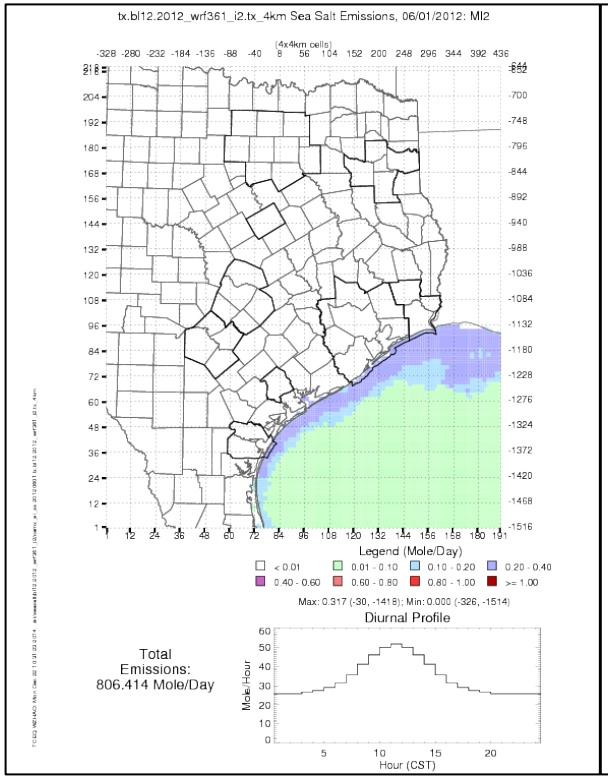


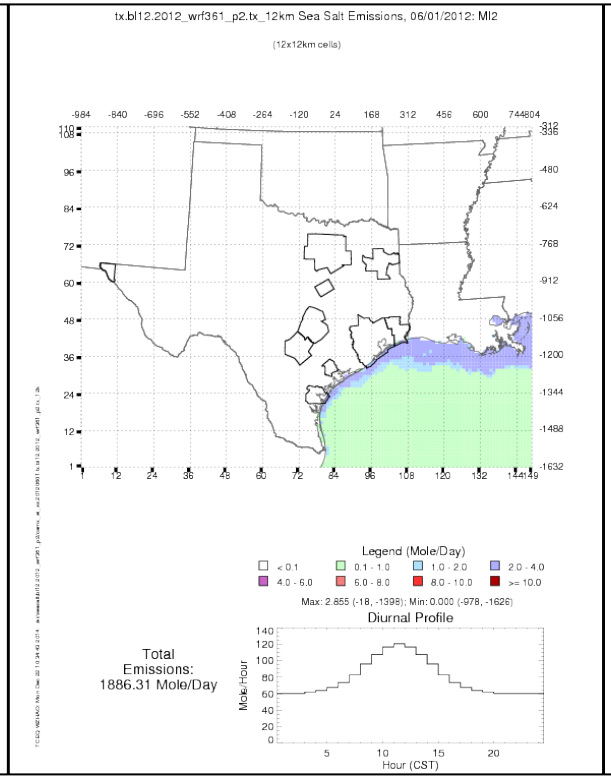


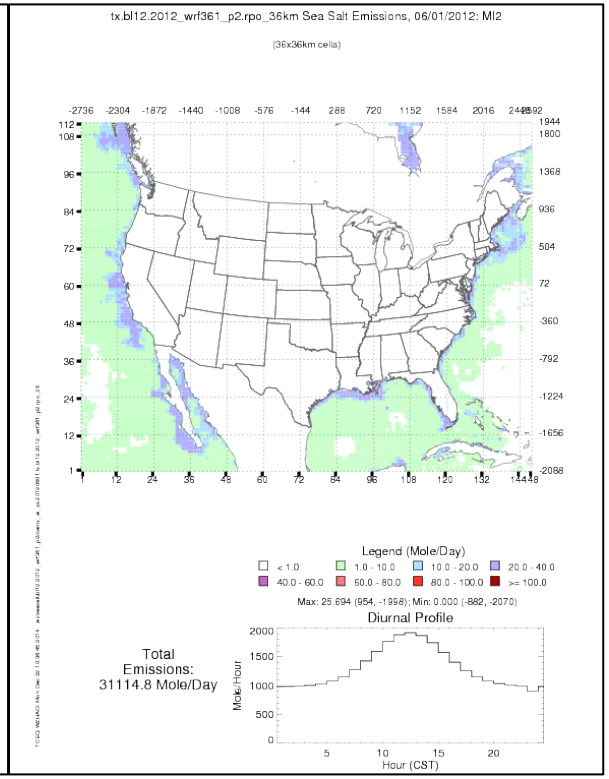


Halogen Compound Emissions:
diiodomethane (CH_2I_2)

June 2012, Each Day

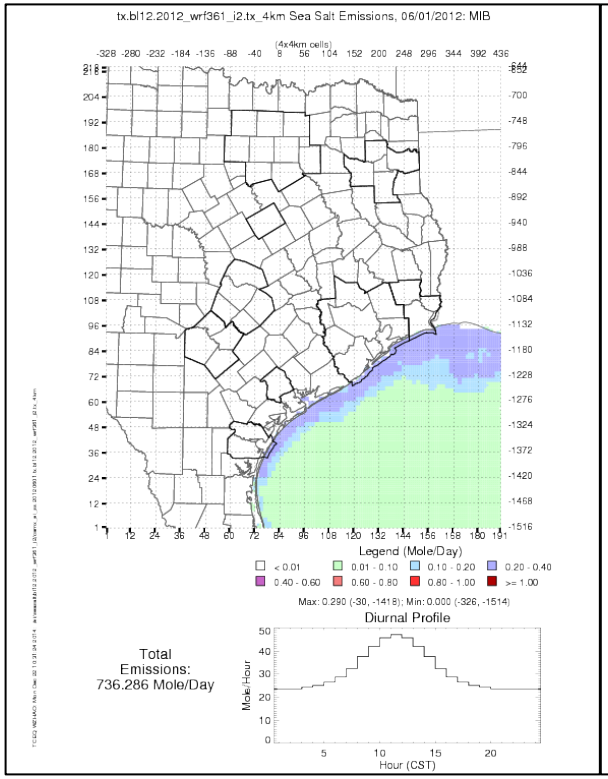


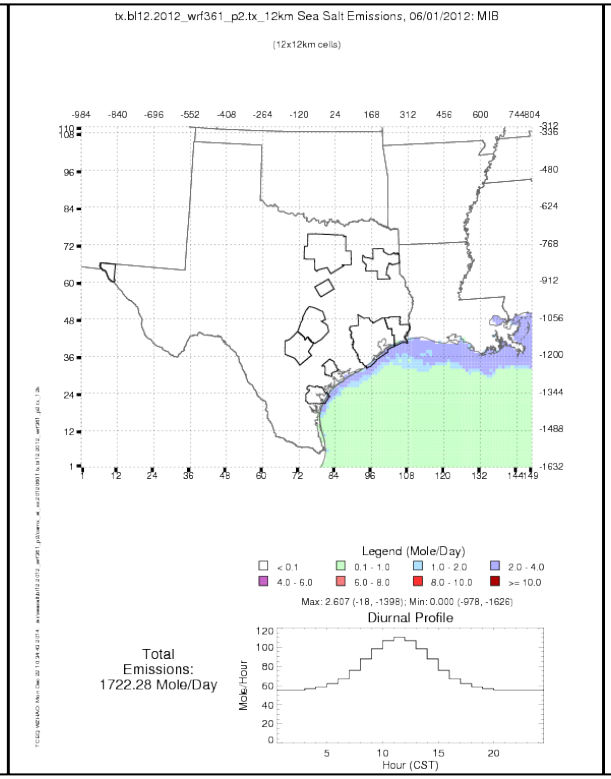


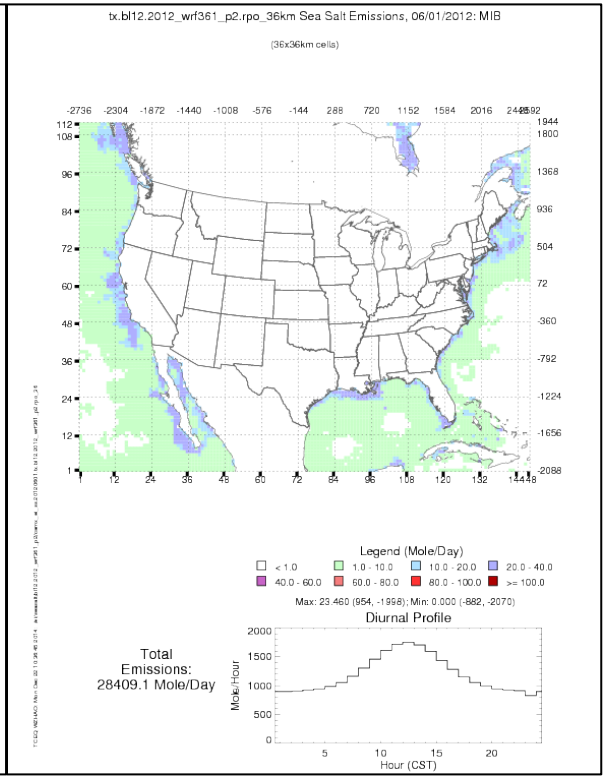


Halogen Compound Emissions:
bromoiodomethane (CH_2IBr)

June 2012, Each Day

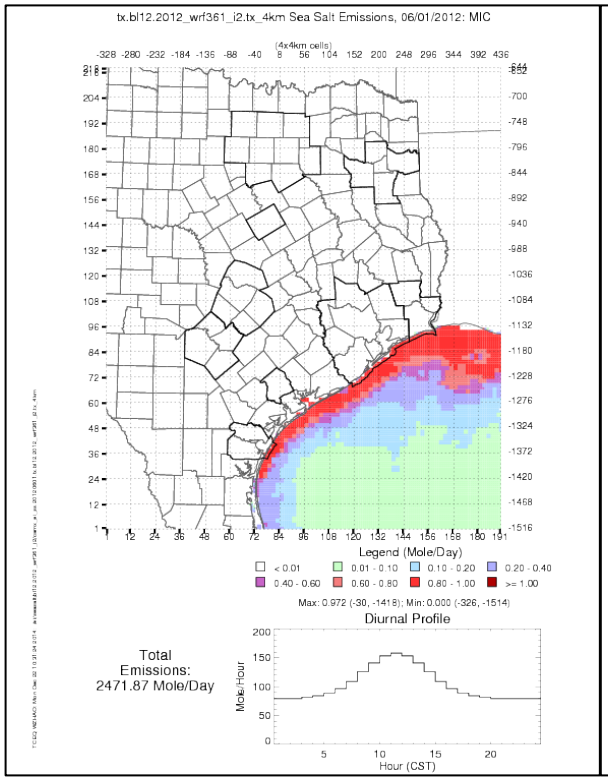


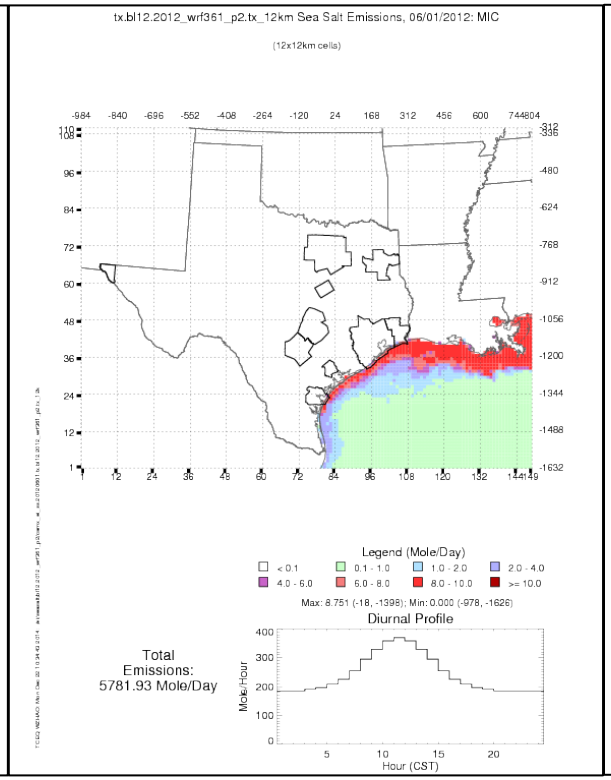


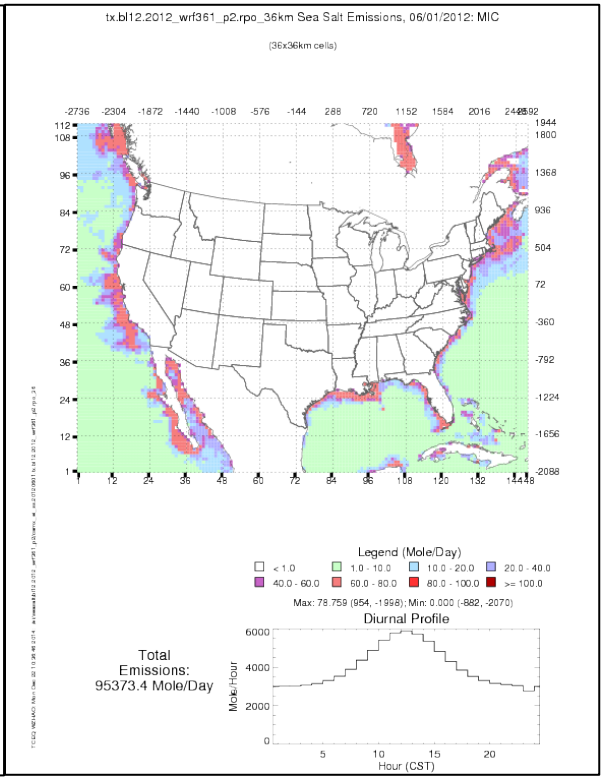


Halogen Compound Emissions:
chloroiodomethane (CH_2ClI)

June 2012, Each Day

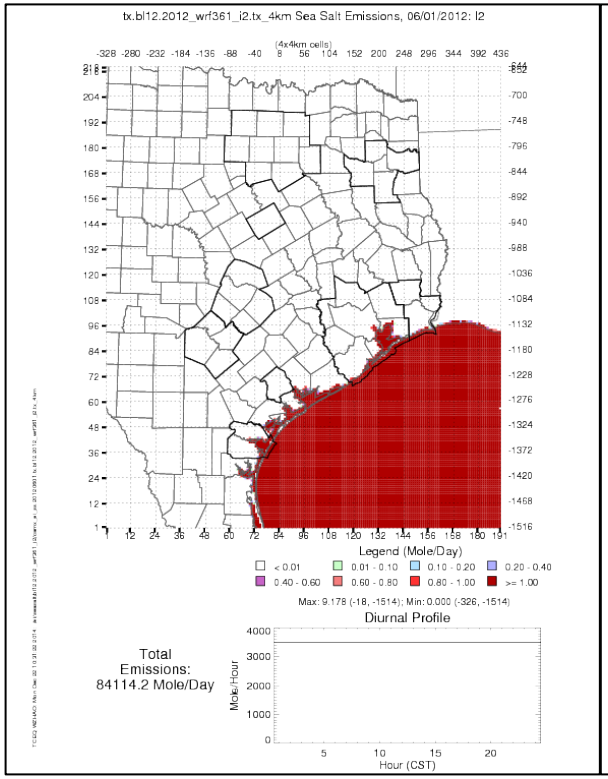


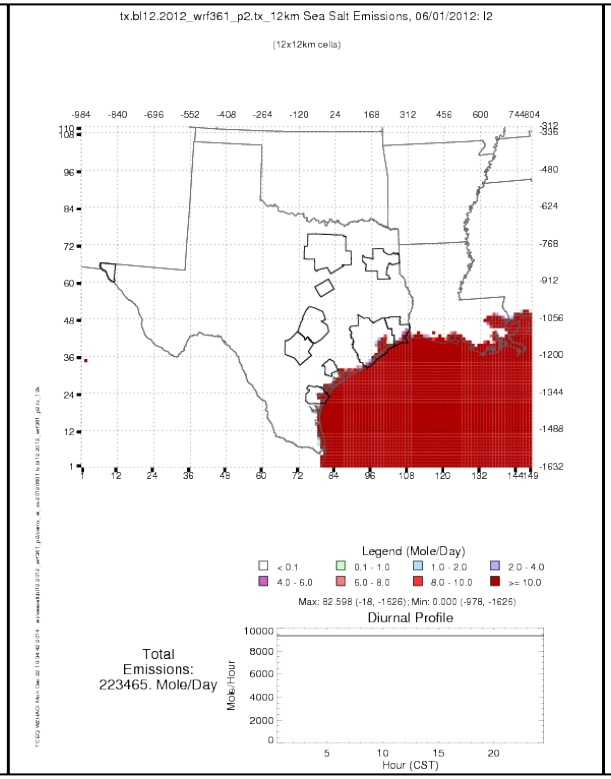


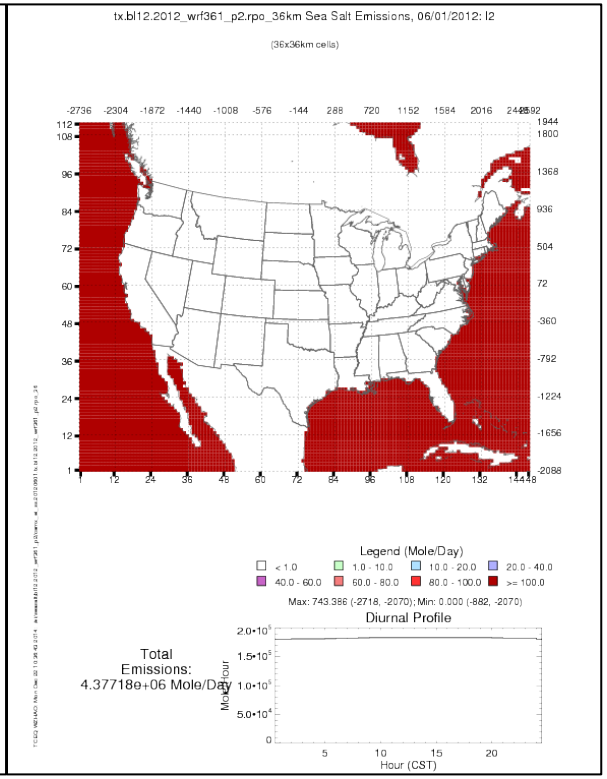


Halogen Compound Emissions:
Iodine (I_2)

Constant, Every Day

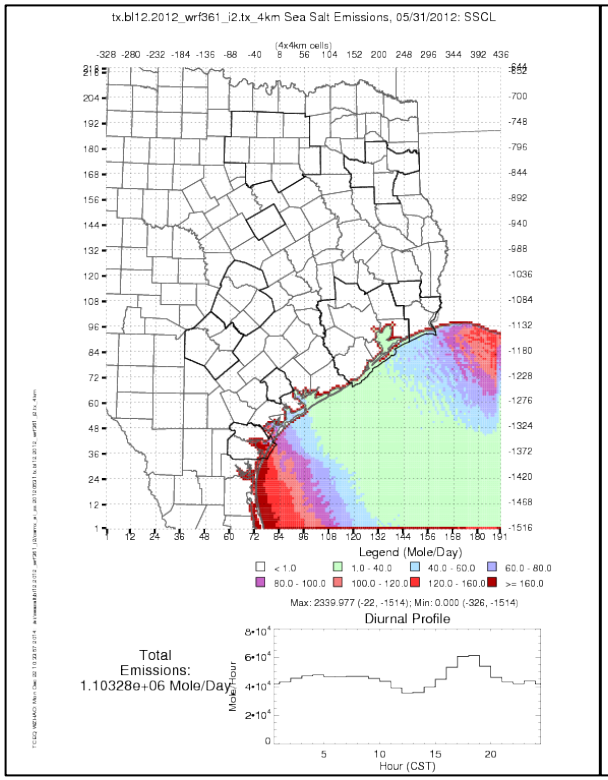


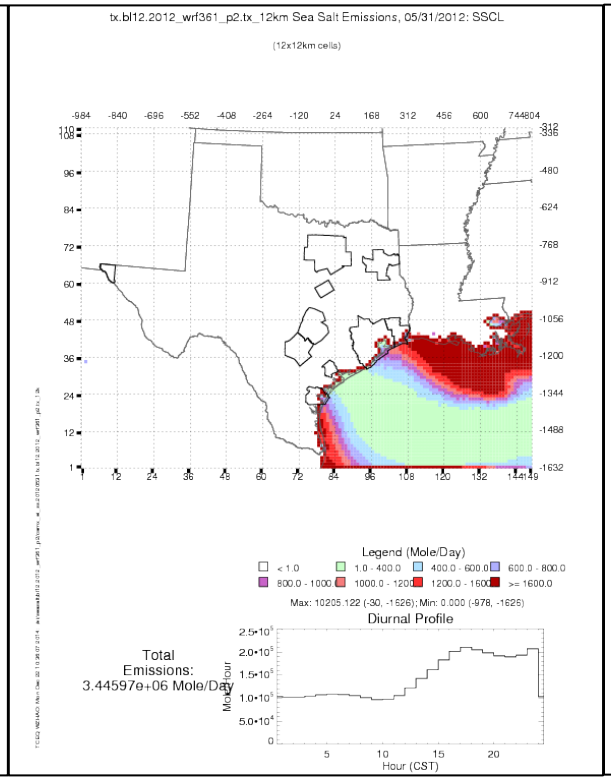


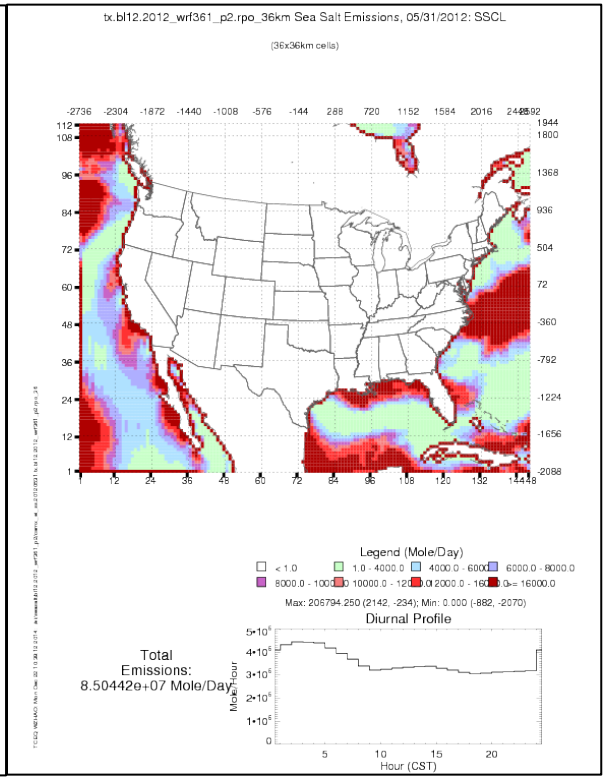


Halogen Compound Emissions:
Chloride from Sea Salt

May 31, 2012

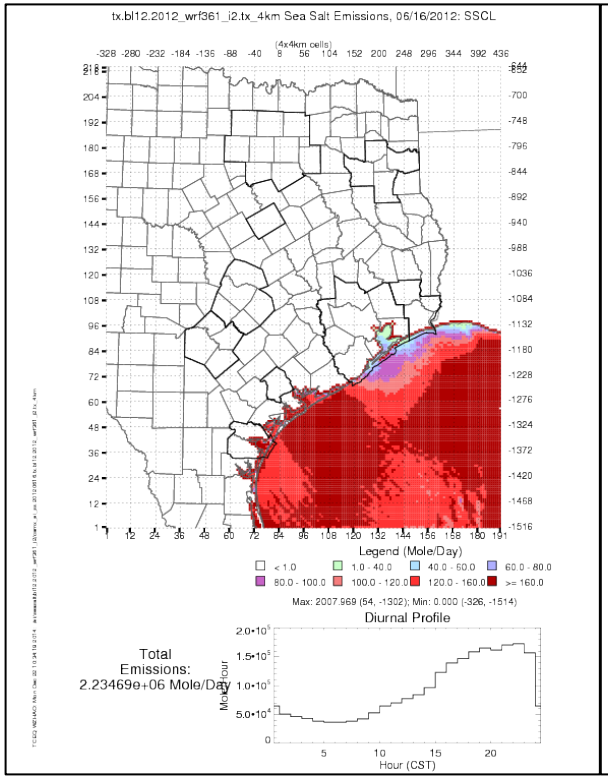


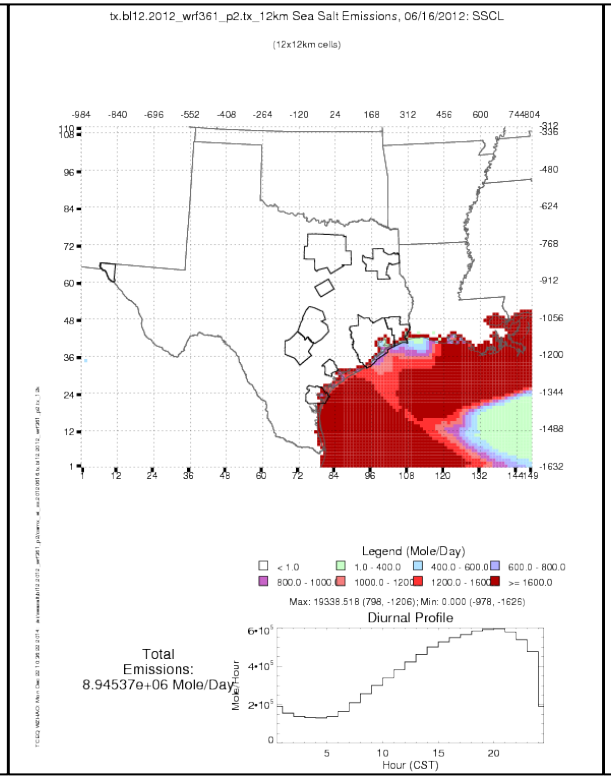


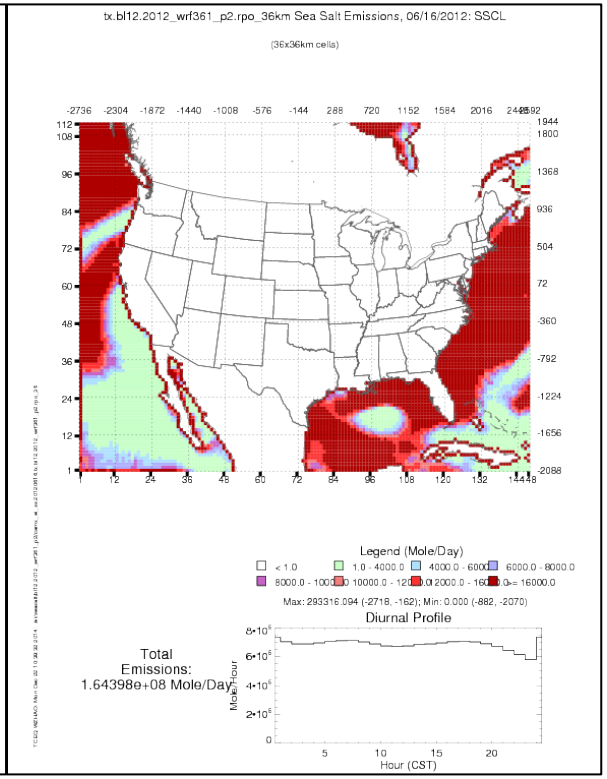


Halogen Compound Emissions:
Chloride from Sea Salt

June 16, 2012





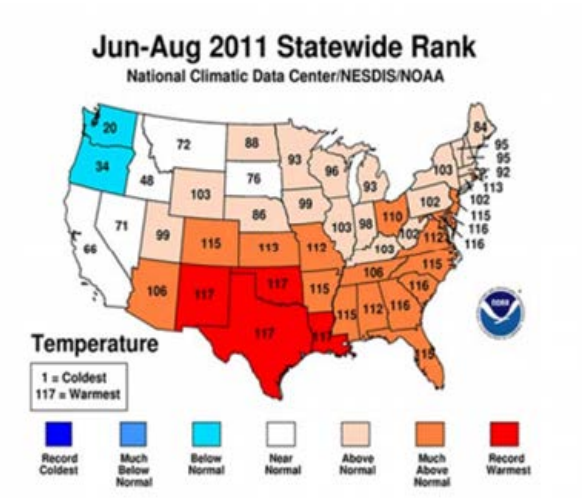


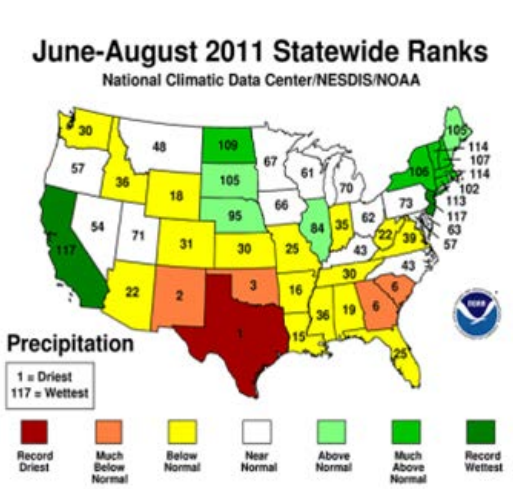
The TCEQ 2012 Modeling Platform

- Same Continental U.S. (CONUS) grid as EPA 2011 modeling platform, 36 km coarse grid
- 2012 ozone season (May through September)
- Nested 12-km South-Central US and 4-km East Texas grids
- Updated emissions
  - MEGAN 2.10 biogenics with high-resolution LULC data (Guenther 2008 30-second data)
  - Link-based on-road emissions in Houston and Dallas-Fort Worth areas
- CAMx with CB6 chemistry

The TCEQ 2012 Modeling Platform

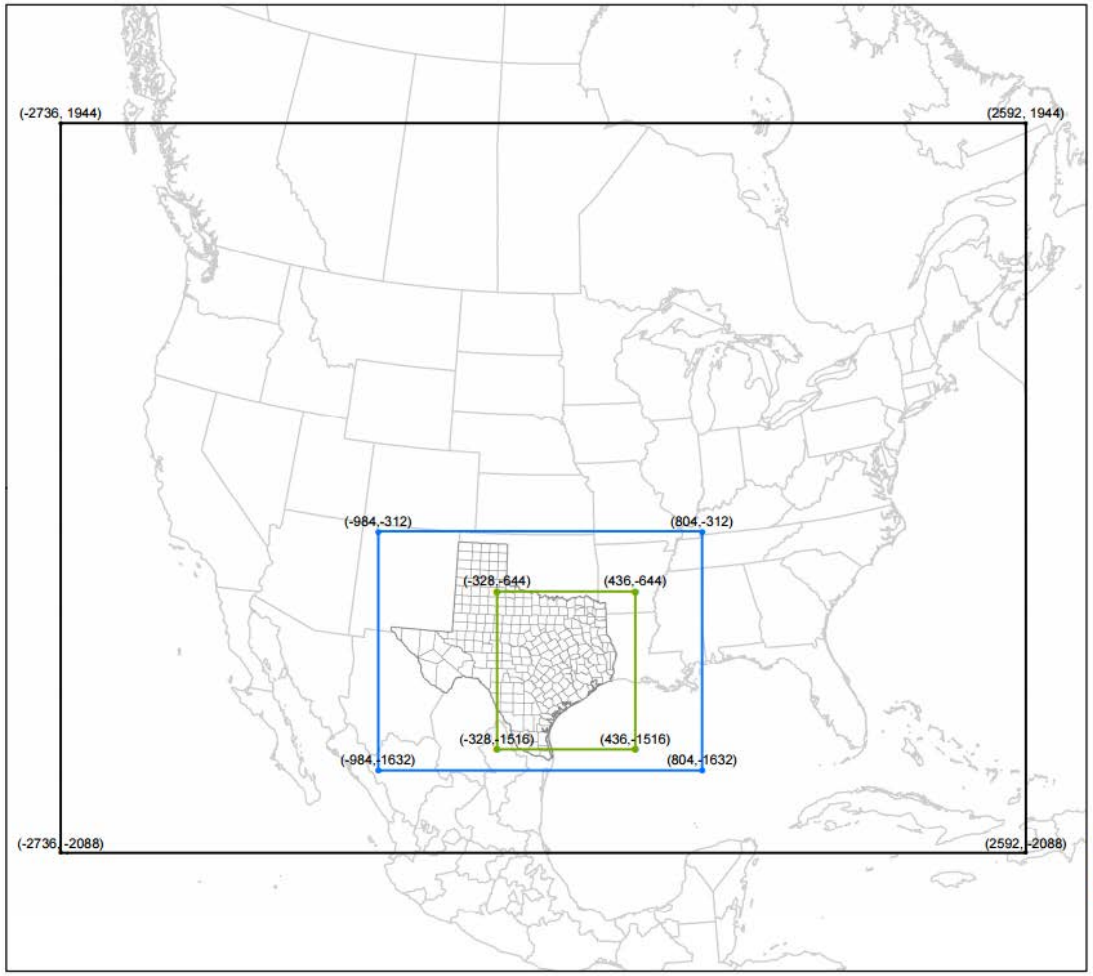
- GEOS-Chem V9-01-03 boundary conditions
- WRF 3.6.1
  - 38 vertical layers
  - Pleim-Xiu land-surface model
  - YSU PBL scheme
  - WRFCAMx w/ 100 m K_V patch
- Not based on Texas' hottest, driest year on record!

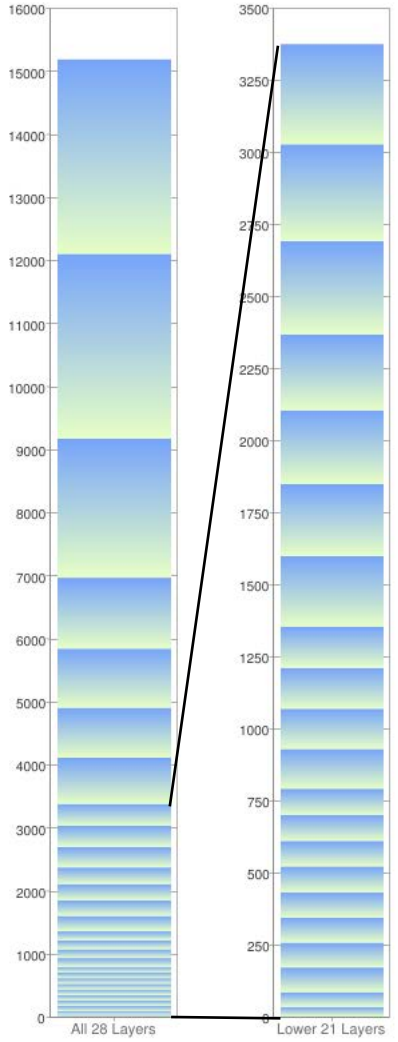




The TCEQ 2012 Modeling Platform

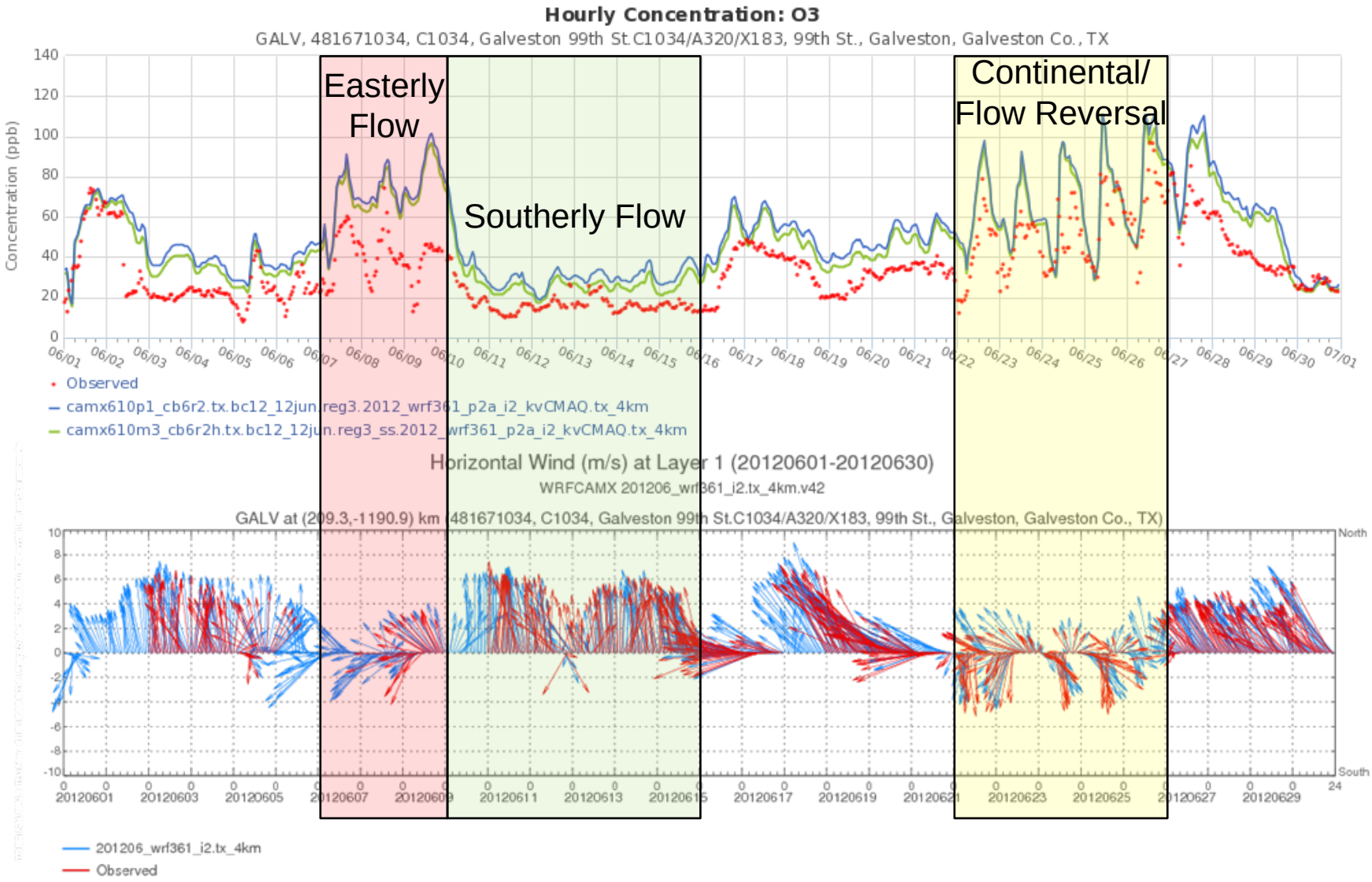
Texas Ozone Modeling Domains





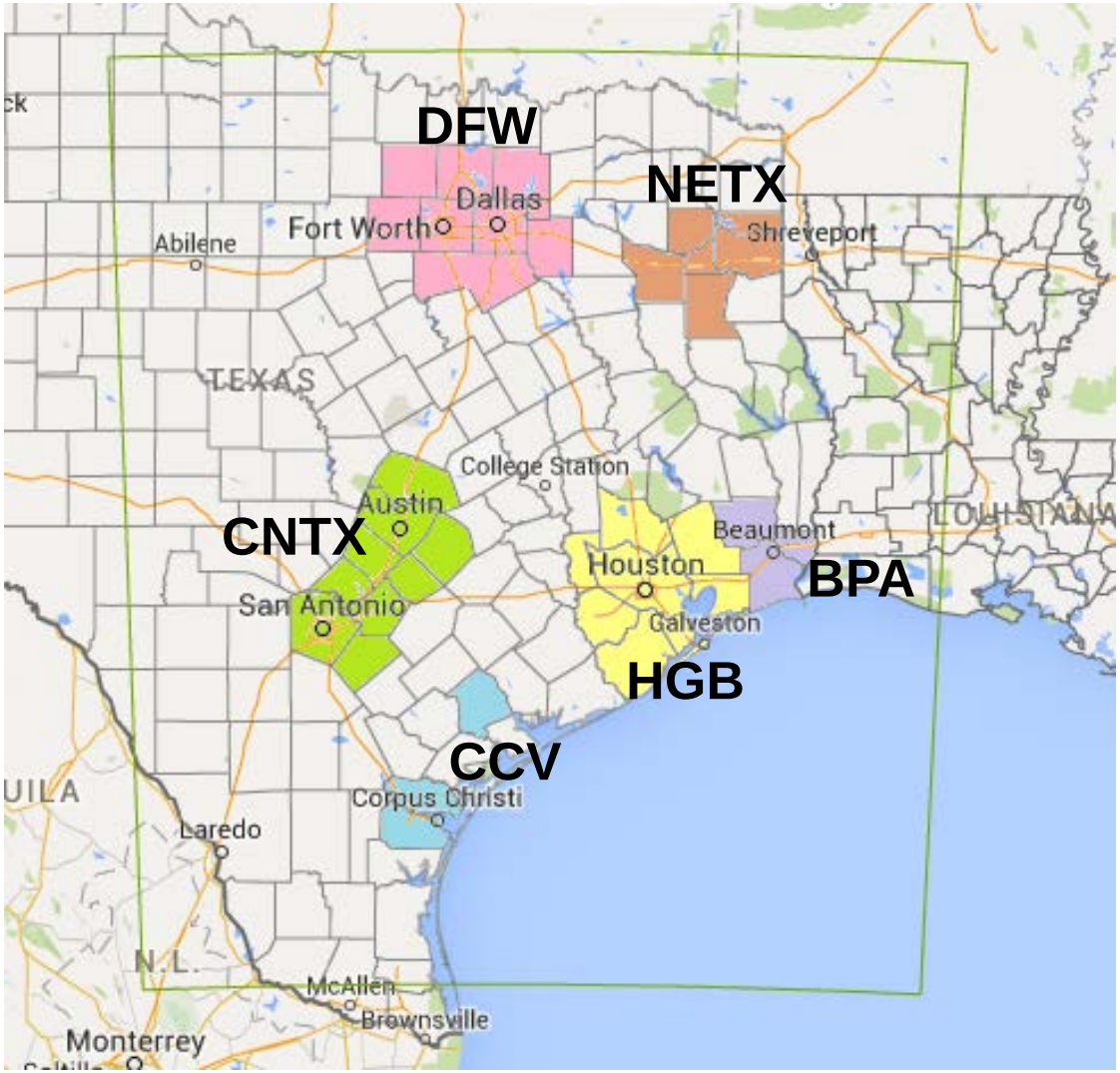
Model Performance Comparison

Galveston C1034



Model Performance Comparison

Eastern Texas (4 km grid)



Area	Number Monitors
Dallas-Fort Worth (DFW)	17
Houston-Galveston-Brazoria (HGB)	46
Beaumont-Port Arthur (BPA)	8
Northeast Texas (NETX)	3
Central Texas (CNTX)	17
Corpus Christi-Victoria (CCV)	10
Other areas	7
Eastern Texas Total (4 km grid)	109

Model Performance Comparison

Eastern Texas (4 km grid)

Maximum Daily 8-Hour (MDA8) Ozone Performance

All Model Observation Pairs

AREA	Bias (ppb)		RMSE (ppb)	
	CB6r2	CB6r2h	CB6r2	CB6r2h
Dallas-Fort Worth	7.90	6.35	10.42	9.08
Houston-Galveston-Brazoria	12.95	10.40	16.42	14.12
Beaumont-Port Arthur	13.78	11.10	16.11	13.71
Northeast Texas	9.99	8.39	12.62	11.17
Central Texas	8.37	6.40	10.80	9.23
Corpus Christi-Victoria	7.79	4.50	11.62	9.28
All Eastern Texas	10.50	8.21	13.84	11.85

Model Performance Comparison

Eastern Texas (4 km grid)

Maximum Daily 8-Hour Ozone Performance

Observed MDA8 O_3 ≥ 60 ppb

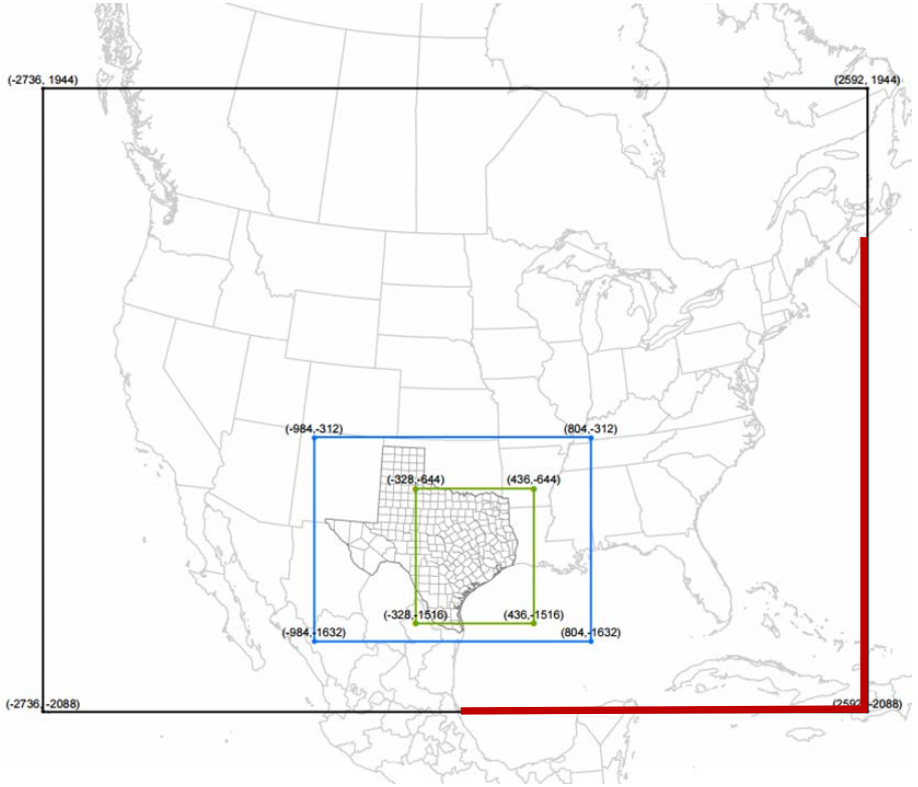
AREA	Bias (ppb)		RMSE (ppb)	
	CB6r2	CB6r2h	CB6r2	CB6r2h
Dallas-Fort Worth	3.85	2.86	7.90	7.30
Houston-Galveston-Brazoria	4.07	2.59	12.41	11.69
Beaumont-Port Arthur	5.44	3.89	10.84	9.89
Northeast Texas	4.96	4.02	8.83	8.32
Central Texas	1.31	0.19	5.73	5.44
Corpus Christi-Victoria	-4.63	-6.55	8.35	9.31
All Eastern Texas	3.13	1.85	9.97	9.42

Marine Boundary Conditions

- Boundary conditions for regional modeling applications are typically extracted from global models such as GEOS-Chem and MOZART.
- Comparison of marine boundary conditions with near-shore monitors indicates that they over-predict ozone over ocean waters.
- Halogen chemistry is being included in newer versions of the global models.

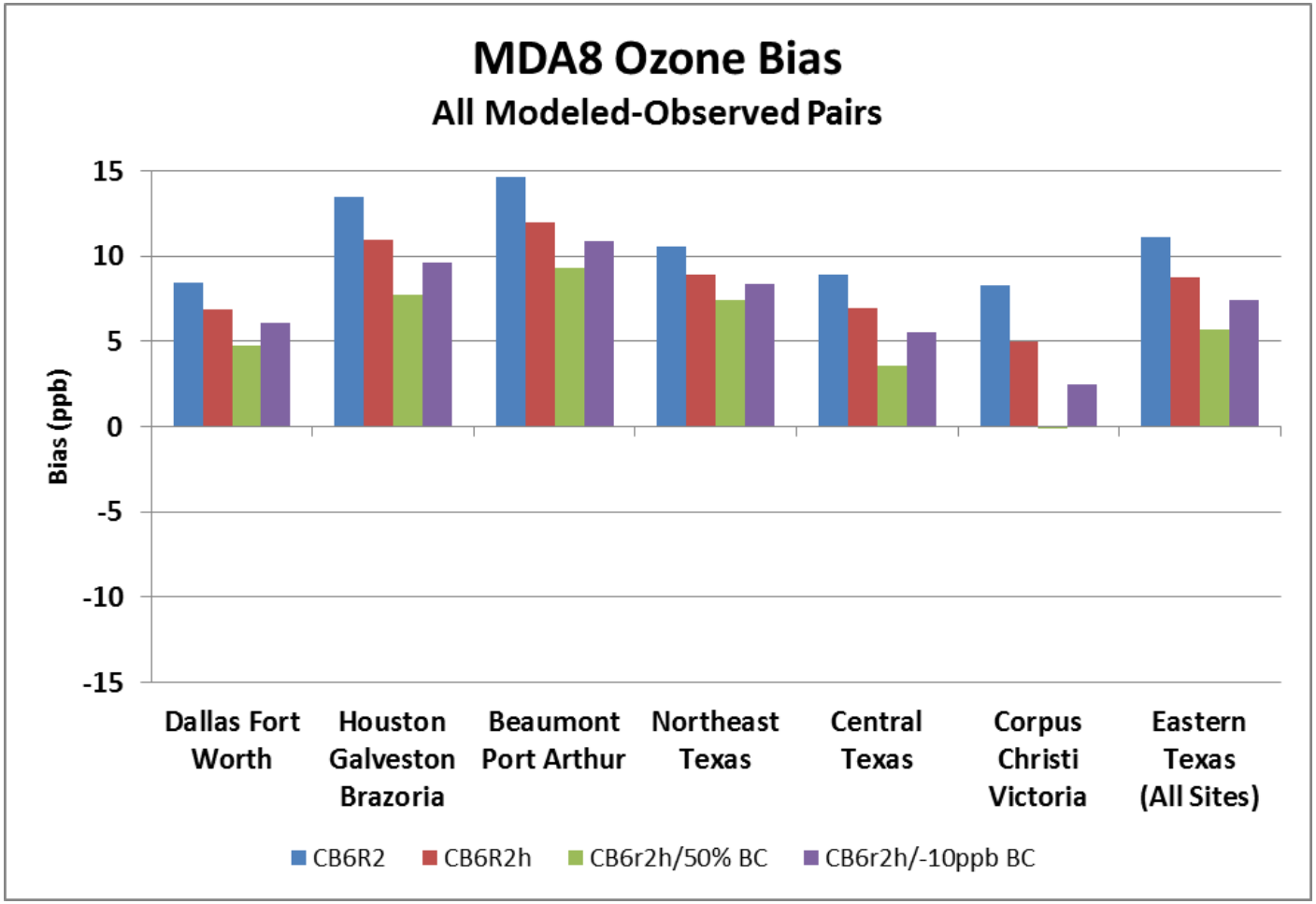
Boundary Conditions Sensitivities

- Two model runs to assess the sensitivity of MDA8 Ozone in eastern Texas to marine boundary conditions:
  - Marine boundary concentrations of all pollutants south and east of Texas reduced by 50%.
  - Marine boundary concentrations of ozone south and east of Texas reduced by 10 ppb.



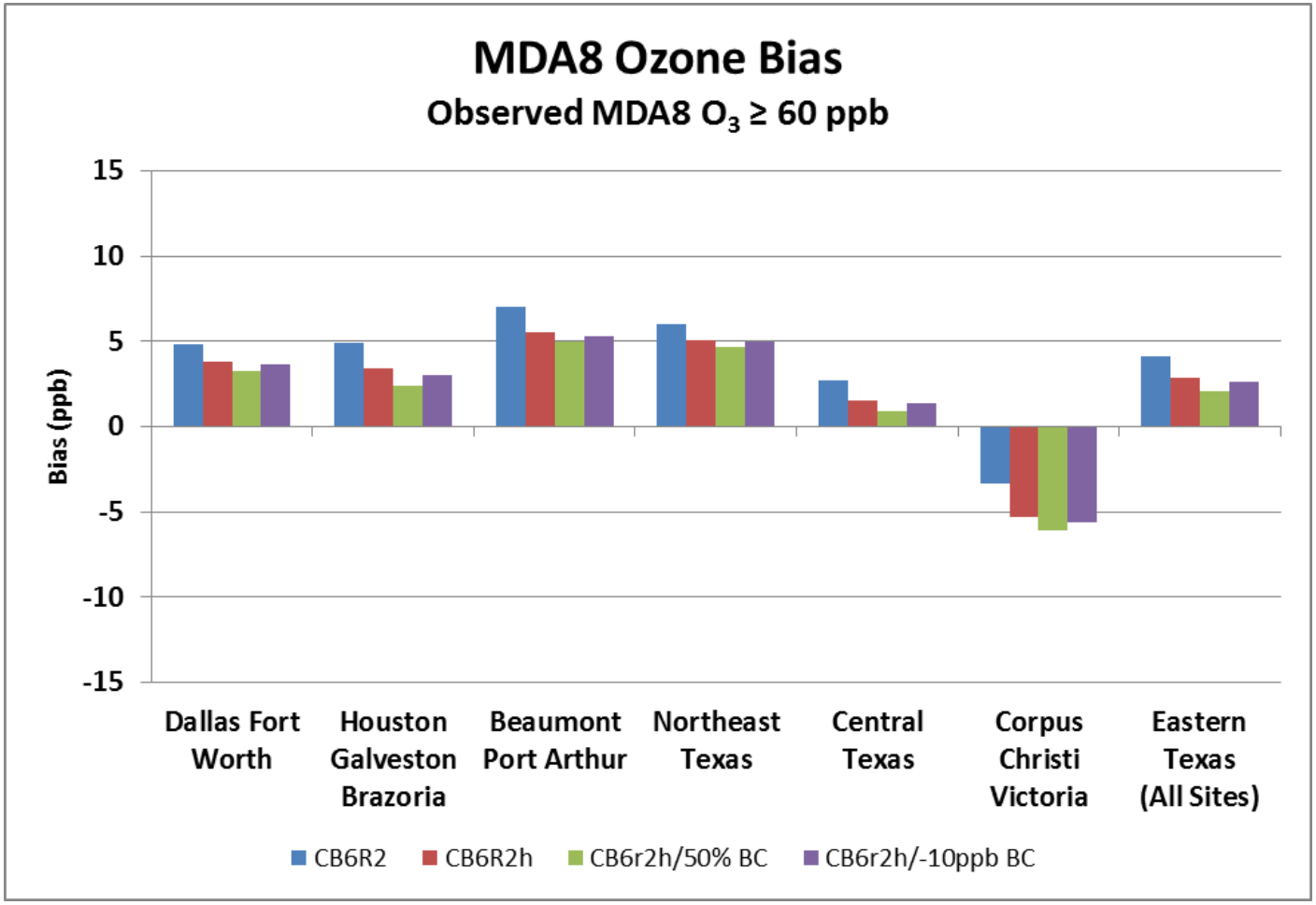
Model Performance Comparison

Eastern Texas (4 km grid)



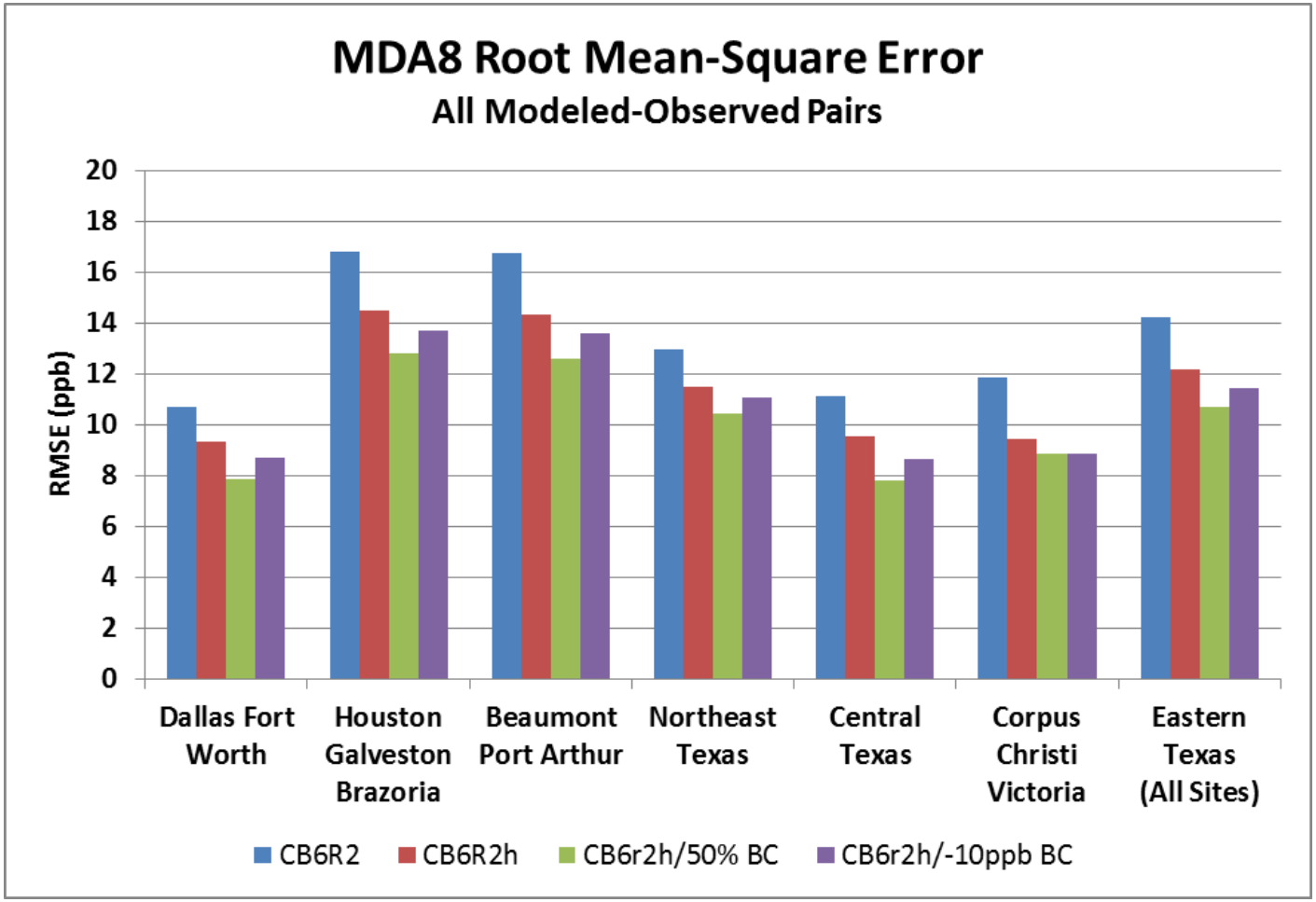
Model Performance Comparison

Eastern Texas (4 km grid)



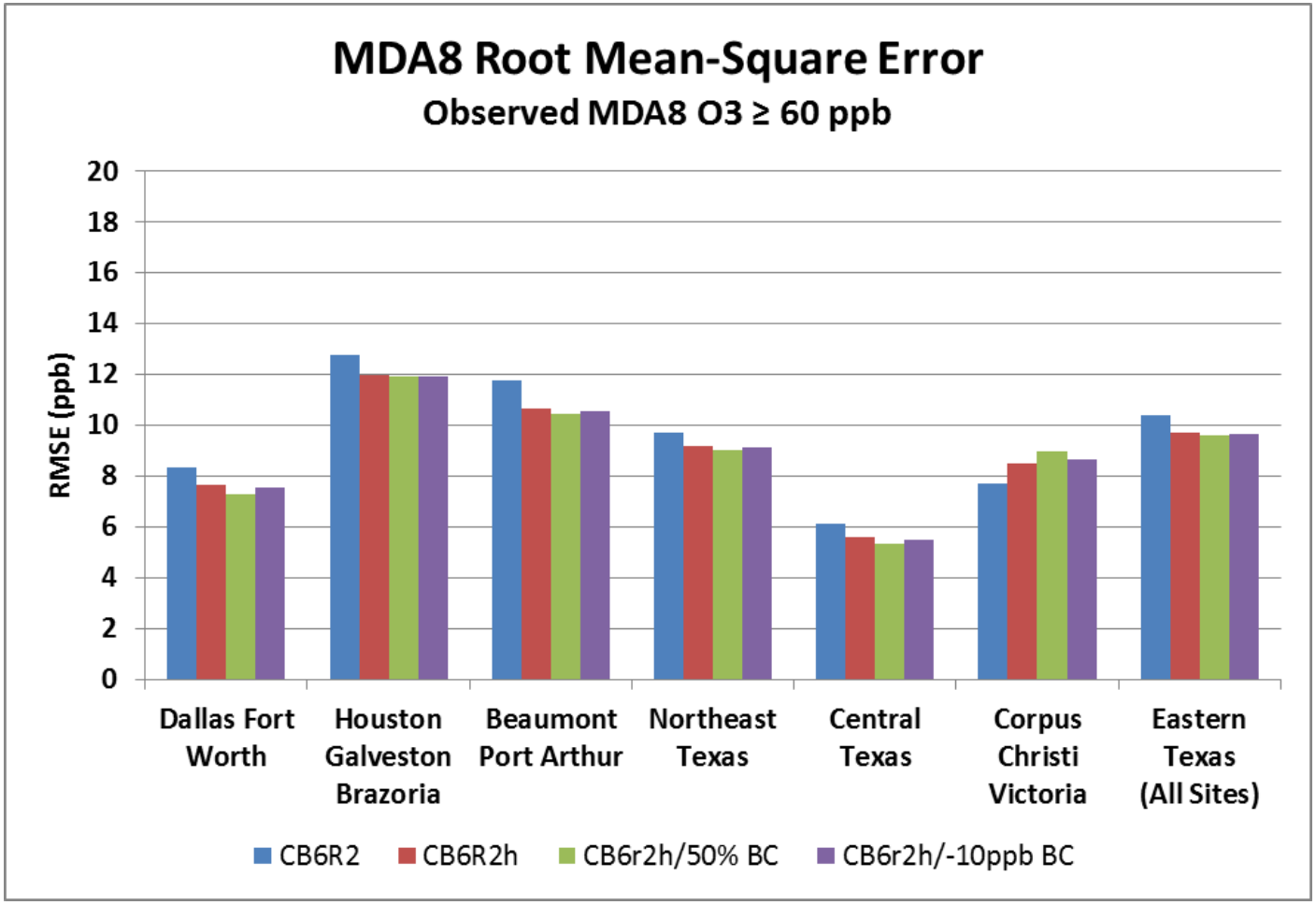
Model Performance Comparison

Eastern Texas (4 km grid)



Model Performance Comparison

Eastern Texas (4 km grid)



Conclusions

- Models over-predict ozone concentrations transported onshore from the Gulf of Mexico.
- Model performance can be significantly improved through use of halogen chemistry and through reduced marine boundary conditions.
- Smaller but still significant improvements are seen for MDA8 concentrations ≥ 60 ppb.
- Halogen chemistry increases CAMx execution time by about 60% when explicit aerosols are not being modeled.

Future Needs

- Faster halogen chemistry code to reduce long execution times
- Monitoring of halogen products at Galveston (summer, 2016)
- New boundary conditions from a global model with native halogen chemistry ("almost there" in GEOS-Chem)
- Investigation of iodine feedback loop – ozone deposition on ocean waters releases I_2, which in turn reacts with ozone

Resources

- The TCEQ 2012 modeling platform can be accessed at: https://www.tceq.texas.gov/airquality/airmod/data/tx2012 (currently June is online but other months should be available soon).

- Ozone background references:
  - Estes, M., D. Johnston, F. Mercado and Smith, J (2014) Regional background ozone in the eastern half of Texas, Presented at CMAS 2014 http://www.cmascenter.org/conference/2014/agenda.cfm
  - Smith, J., F. Mercado and M. Estes (2013). Characterization of Gulf of Mexico Background Ozone Concentrations, Presented at CMAS 2013 http://www.cmascenter.org/conference/2013/agenda.cfm

- Marine halogen chemistry references:
  - Yarwood, G., J. Jung, U. Nopmongcol and C. Emery (2012) Improving CAMx Performance in Simulating Ozone Transport from the Gulf of Mexico, Final Report for Work Order No. 582-11-10365-FY12-05
  - Yarwood, G., T. Sakulyanontvittaya, U. Nopmongcol and B. Koo (2015). Ozone Depletion by Bromine and Iodine over the Gulf of Mexico, Final Report for Work Order No. 582-11-10365-FY14-12 https://www.tceq.texas.gov/airquality/airmod/project/pj_report_pm.html

Resources

- Modeling references:
  - ENVIRON (2014) User's Guide to CAMx version 6.10, available at http://www.camx.com/
  - Yantosca, et al., 2014, GEOS–Chem v9–02 Online User's Guide, http://acmg.seas.harvard.edu/geos/doc/man/.

- Also see:
  - Monks, et al., 2015, Tropospheric ozone and its precursors from the urban to the global scale from air quality to short-lived climate forcer, Atmos. Chem. Phys., 15, 8889–8973, 2015