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Gulf of Mexico Ozone Deposition:
Air Quality Model Enhancements

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Background

Ozone deposition to the ocean surface is an important removal pathway (Galbally and Roy 1980; Gallagher et al. 2001), and since this can play a major role in the ozone budget in the marine boundary layer and influence onshore/inland distribution of ozone, it must be accounted for in regional air-quality models.

The chemical enhancement of the ozone deposition to the sea surface due to iodine-containing emissions and on the subsequent iodine chemistry responsible for the halogen activation and ozone loss must be assessed.

Present regulatory ozone modelling often does not account for the changes in the ozone deposition rates in the coastal waters and such omission can lead to the overestimation of the impact of offshore oil and gas operations when developing the state implementation plans for the new eight-hour ozone standard.

Purpose

1. Modify the CMAQ dry deposition module for ozone to seawater surfaces using the improved algorithm to estimate the surface resistance in the iodine reaction process, and to perform sensitivity test to calculate the change in the ozone deposition rates for the different meteorological condition and algae distributions.
2. Develop an iodine-extended atmospheric chemistry module in CMAQ, perform the model run based on new MMS 2000 Gulf of Mexico emission inventory incorporating the biogenic iodine emission from the algae density and distribution, and finally to quantify the ozone loss and budget in the Gulf of Mexico marine boundary layer.

Outline in This Presentation

1. Modification of Model-3/CMAQ dry deposition (M3DDEP) module for ozone deposition to sea water

2. Estimation of dissolved iodide concentration from the data set of chlorophyll from satellite

3. Simulations of CMAQ for three different modeling cases for one month.

4. Analyses of iodine effects on dry deposition velocities and fluxes for ozone

Modification of Ozone Deposition Modules in CMAQ

Water surface resistance (r_{gw}) of the Model-3/CMAQ dry deposition (M3DDEP). Module in MCIP (version 3.0)

$$r_{gw} = \frac{H}{\alpha^* \times 4.8 \times 10^4 \times u_*} = \frac{\text{non - dimensional Henry's law constant}}{\text{chemical enhancement factor} \times \text{transfer velocity}}$$

This formulation cannot account for ozone deposition taking place without wind, though substantial ozone deposition occurs by chemical reactions (mainly iodide reactions) at low wind speeds (Gabally and Roy 1980).

Modified model including both chemical and physical processes as parallel resistances for ozone deposition to sea water (Chang et al. 2004):

Wind-induced physical transport and chemical reaction (A) Wanninkhof 1992; Liss and Merlivat 1986; Slinn et al. 1978 and molecular ozone transfer process including chemical reactions (B) Garland et al. 1980.

$$A = \frac{H}{\alpha k_w}$$

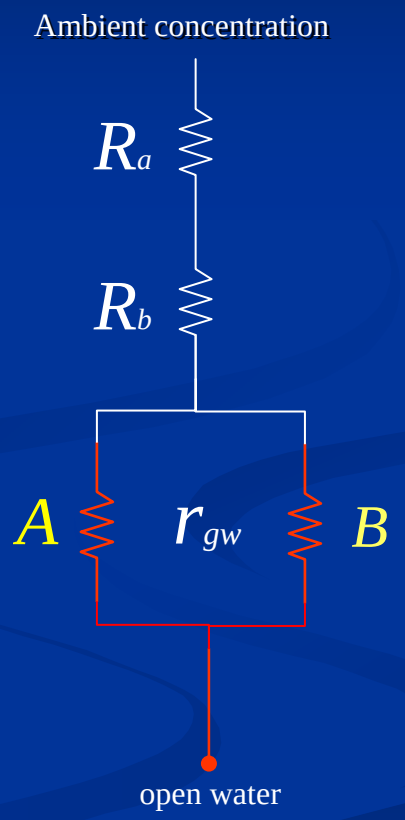
α : chemical enhancement factor

$$B = \frac{H}{\sqrt{\lambda D}}$$

λ (chemical loss rate) $= \sum_i k_i C_i$

k_i and C_i : kinetic rate constant of a species i

$$\frac{1}{r_{gw}} = \frac{1}{A} + \frac{1}{B}$$



$$V_d = (R_a + R_b + r_{gw})^{-1}$$

$$r_{gw} = \frac{H}{\alpha k_w + \sqrt{\lambda D}} = \frac{1}{p k_w + q} \qquad q = \frac{\sqrt{(\sum_i k_i C_i) \times D}}{H}$$

p Interactions between wind-induced turbulent transport and chemical enhancement: 1.75 m/s (Chang et al. 2004)

k_w Transfer velocity calculated by a relationship suggested by Wanninkhof (1992), wind dependent variable

q Deposition velocity due to only to molecular gas-transfer

C_i Concentration of species (iodide, DMS and alkenes) reacting with ozone:

[iodide] : 20 – 400 nM (Campos et al.. 1996 and 1999)

(the strongest candidate to enhance ozone deposition)

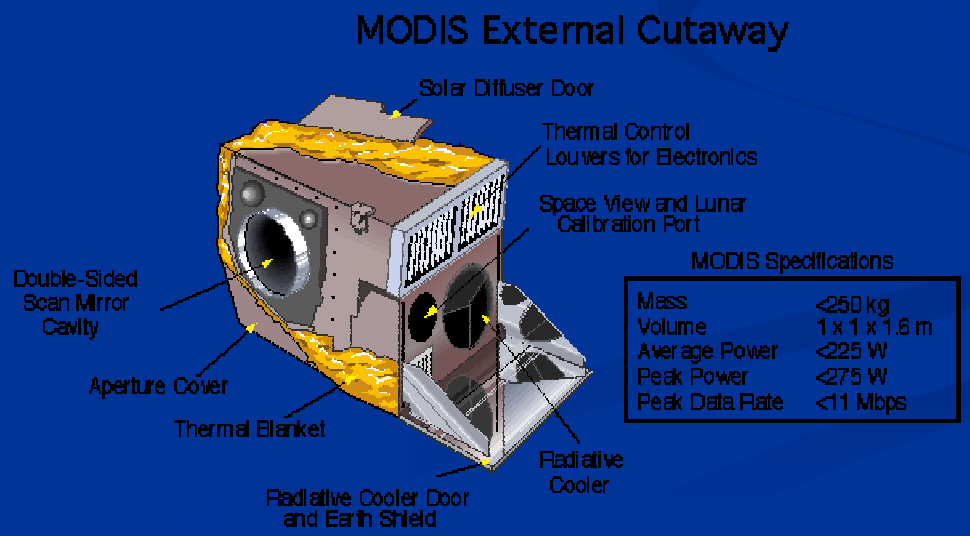
[DMS] : 0.04 – 316 nM (Kettle et al. 1999)

(potential candidate to elevate q when only at extremely high concentration)

Estimation of Iodide Concentrations from Satellite Data

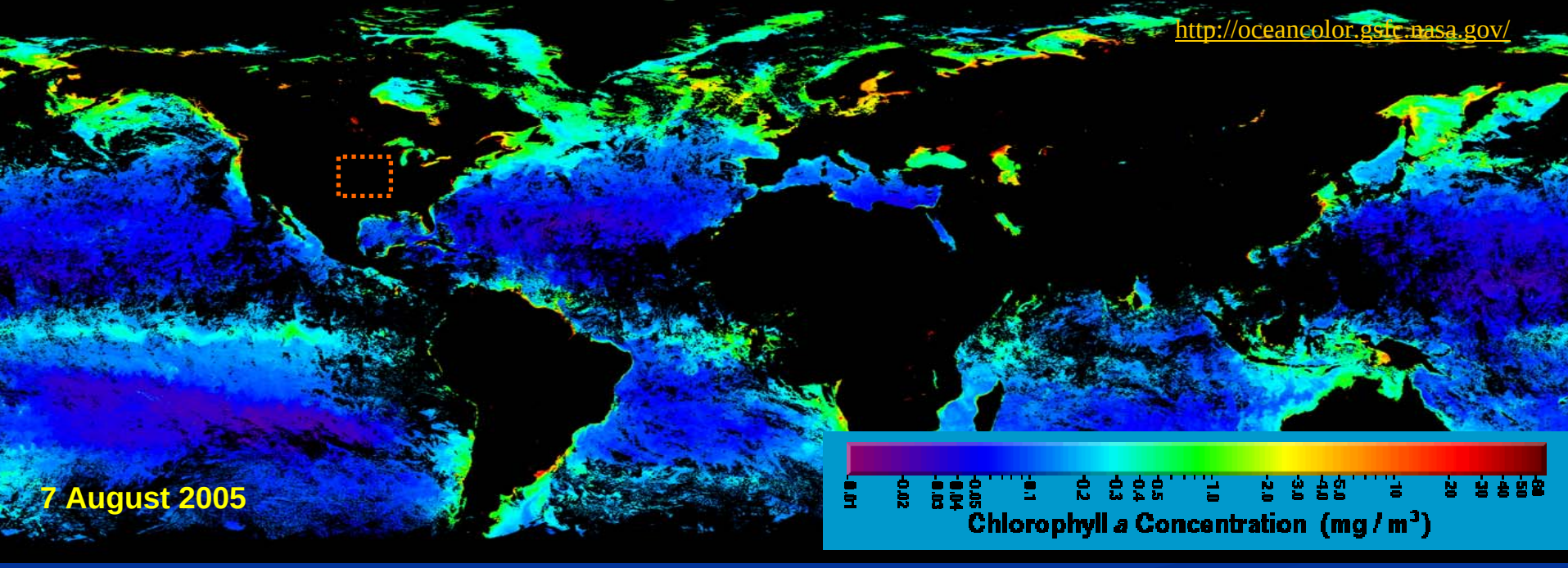
Indirect estimation of iodide concentration from satellite-derived estimates of near-surface chlorophyll concentrations

1. Ocean chlorophyll data from MODIS (Moderate Resolution Imaging Spectroradiometer) onboard AQUA satellite was scaled by a linear regression model based on:
   - Chlorophyll was highly correlated with iodide based on field measurements (Rebello et al. 1990)
   - Most of the iodide concentrations measured in the surface sea water was roughly in the range from 100 to 400 nM (Campos et al.. 1996; Wong and Zhang 1992).
2. Weekly gridded iodide concentration input data were generated from chlorophyll-iodide processor

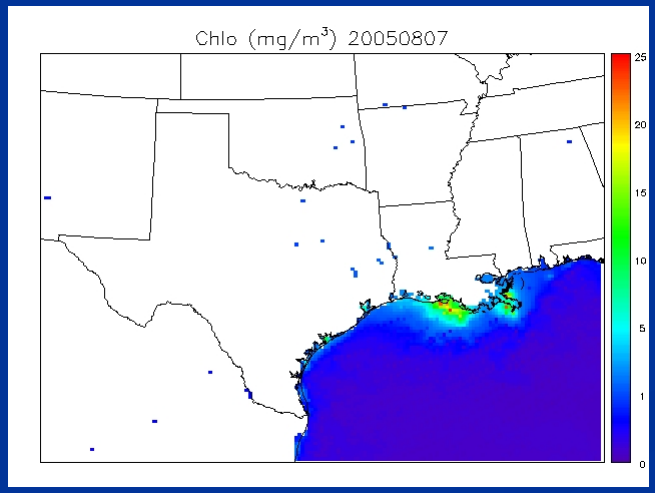


MODIS (Moderate Resolution Imaging Spectroradiometer) Onboard AQUA Satellite

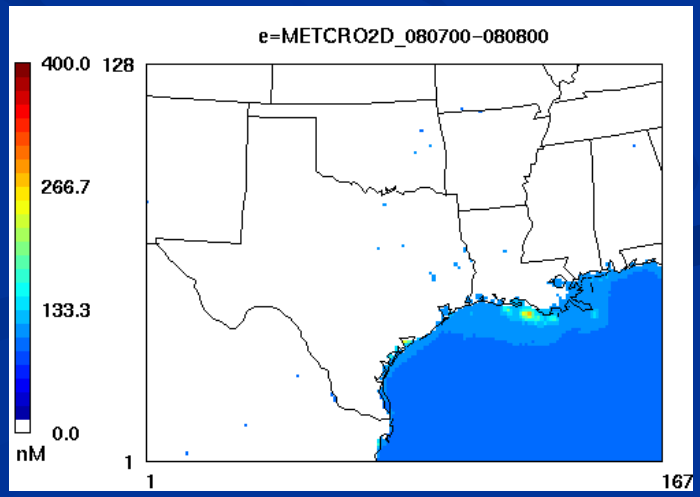
http://oceancolor.gsfc.nasa.gov/



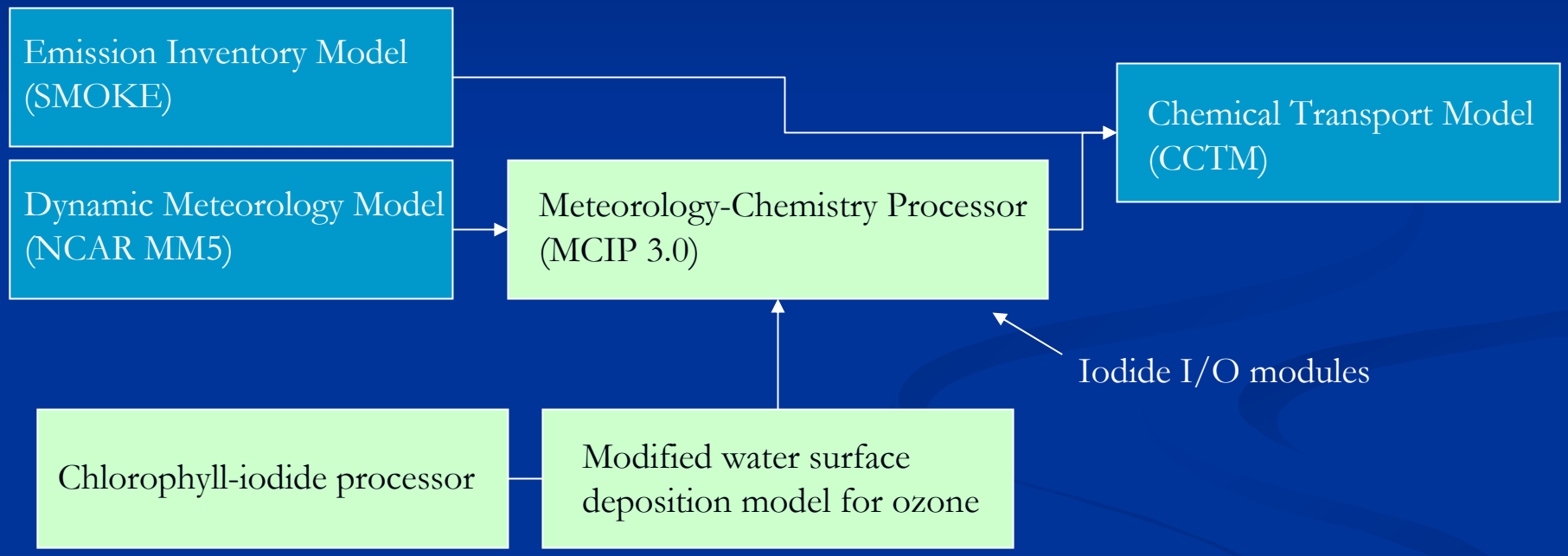
Gridded chlorophyll concentrations by interpolating weekly satellite observations spatially



Iodide concentrations generated from weekly gridded chlorophyll data (linear fit at present)

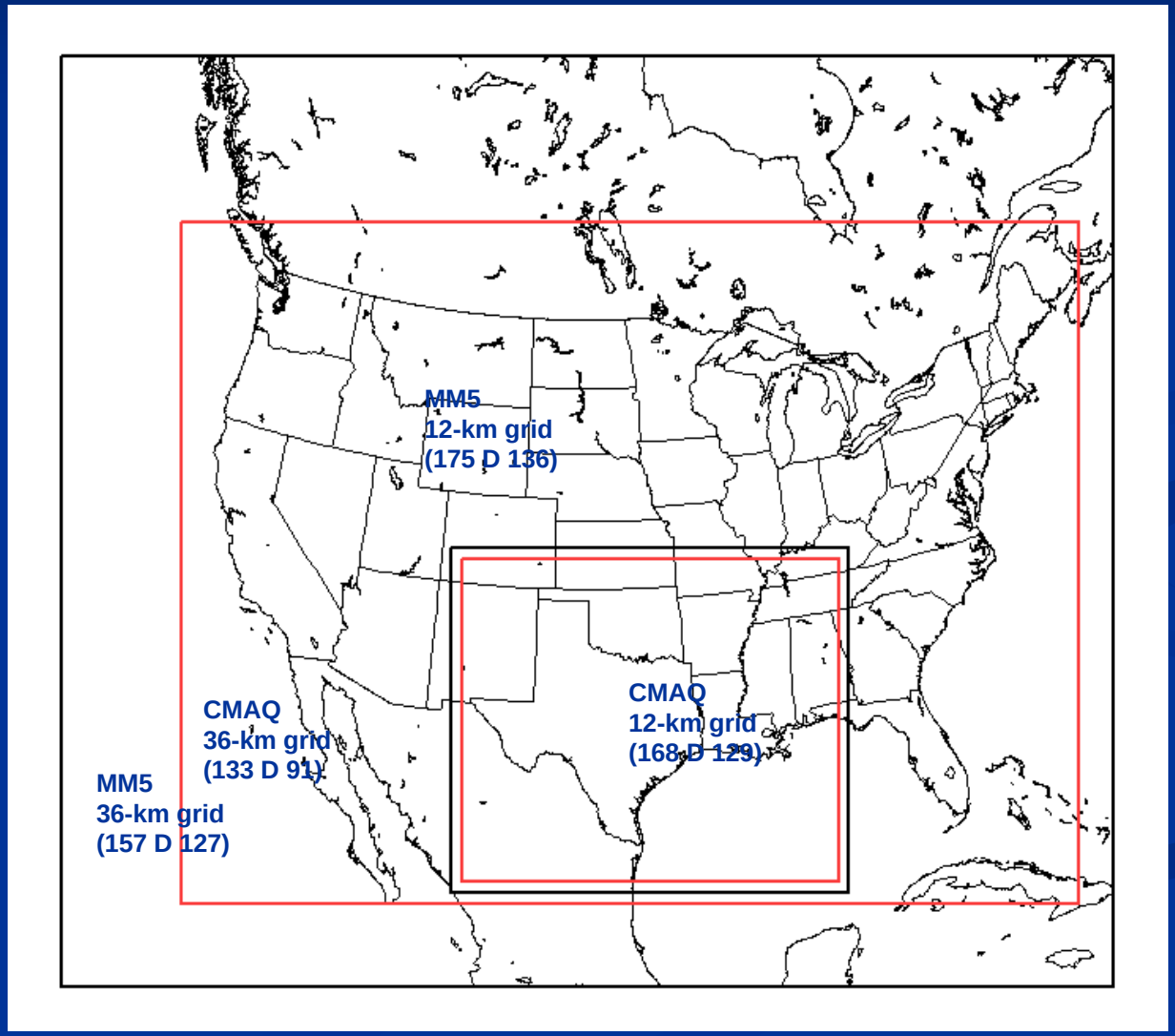


CMAQ Modeling Linked with Modified Ozone Dry Deposition Modules



Modeling Domain

Lambert 36 and 12-km grid nests used for MM5/CMAQ modeling
The 12-km grid covers Texas-Louisiana-Mississippi



MM5 Configuration

- Land use data: USGS (36, 12 km) and TFS-LULC 2000 (4 km)
- Initial/lateral boundary conditions: NCEP "ETA" model analysis fields
- 43 vertical full-sigma levels
- Nestdown process

Physics Options

Option	Scheme
Radiation	RRTM
Explicit moisture	Simple Ice (Dudhia)
Cumulus parameterization	Grell
PBL physics	MRF
Land surface physics	Noah Land-Surface Model

MCIP & CCTM Configuration

The MCIP options used in processing the MM5 out fields were:

- The "pass-through" option where PBL values as estimated by MM5 were used directly
- Radiation fields from MM5 files were used
- Original/modified Model-3/CMAQ dry deposition (M3DDEP) routine

The CMAQ chemical transport model (CCTM) ran with

- 23 vertical layers selected from 43 layers in MM5
- CB-IV gas-phase chemistry mechanism
- RADM-type aqueous chemistry and subgrid cloud processes
- Efficient Euler backward iterative (EBI) solver.
- Piecewise parabolic method (PPM).
- Eddy diffusivity theory
- Boundary conditions provided by a global 3D chemistry/transport model, GEOS-CHEM (resolution of 2° latitude by 2.5° longitude)

Modeling Results

Modeling period: August 2005

Month-long simulations with CMAQ for three different modeling cases:

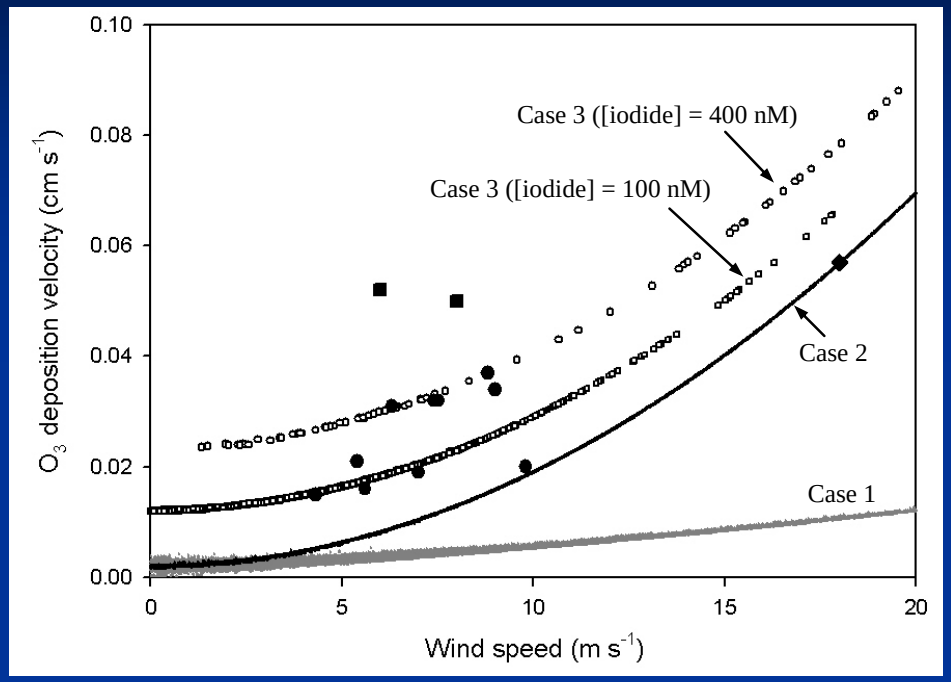
Case 1: Original M3DDEP in MCIP3.0

Case 2: Modified M3DDEP without iodide reaction

Case 3: Modified M3DDEP with iodide reaction

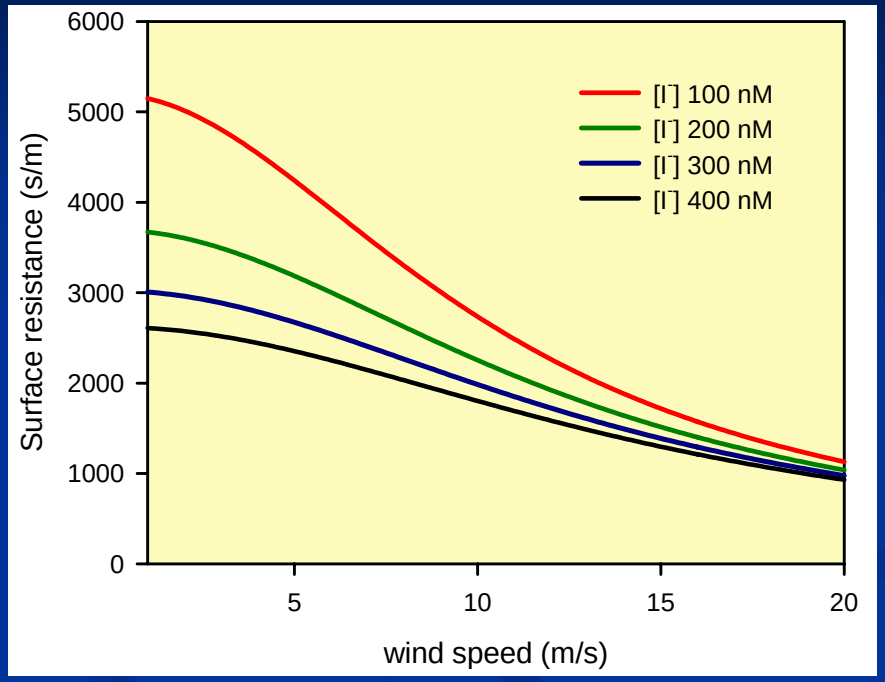
Evaluation

Dry deposition velocity for ozone



Dry deposition velocity for ozone as a function of wind speed. Two curves for Case 3 indicates deposition velocities corresponding to different iodide concentrations (100 and 400 nM) extracted from model results during August, 2005. The filled circles indicate observations of Kawa and Pearson (1989). Solid squares and a solid diamond indicate observations of Lenschow et al. (1982) over the Gulf of Mexico and the North Pacific, respectively

Surface resistance for ozone (Case 3)



Surface resistance for ozone as a function of wind speed. All curves are corresponding to different iodide concentrations (100, 200, 300 and 400 nM)

Monthly Averaged Dry Deposition Velocity

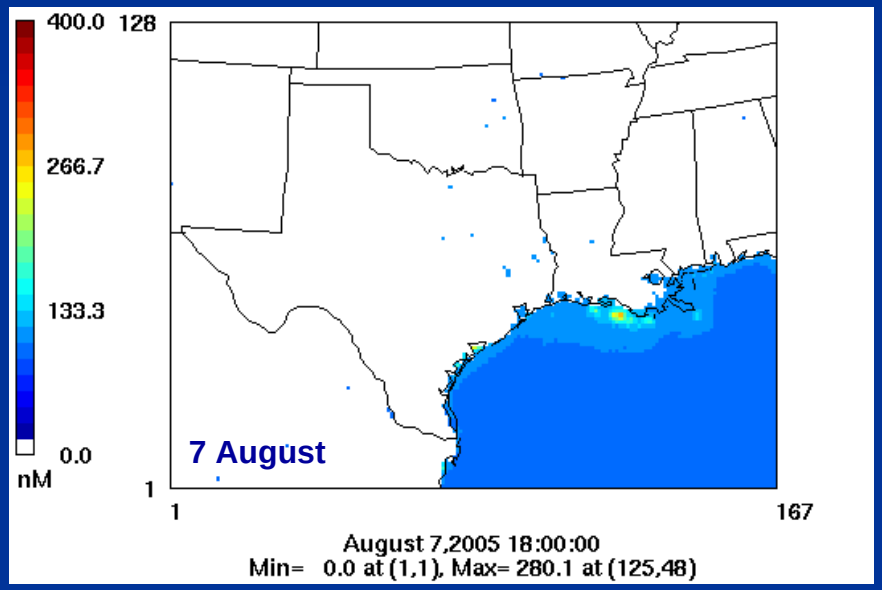
Case	Dry deposition velocity for ozone (cm/s)			10-m wind speed (m/s)
	Average ± S.D.	Max.	Min.	
1	0.0028 ± 0.0008	0.0059	0.0021	4.19 ± 1.85 Max. = 10.26 Min. = 2.26
2	0.0062 ± 0.0047	0.0244	0.0031	
3	0.0167 ± 0.0047	0.0349	0.0135	

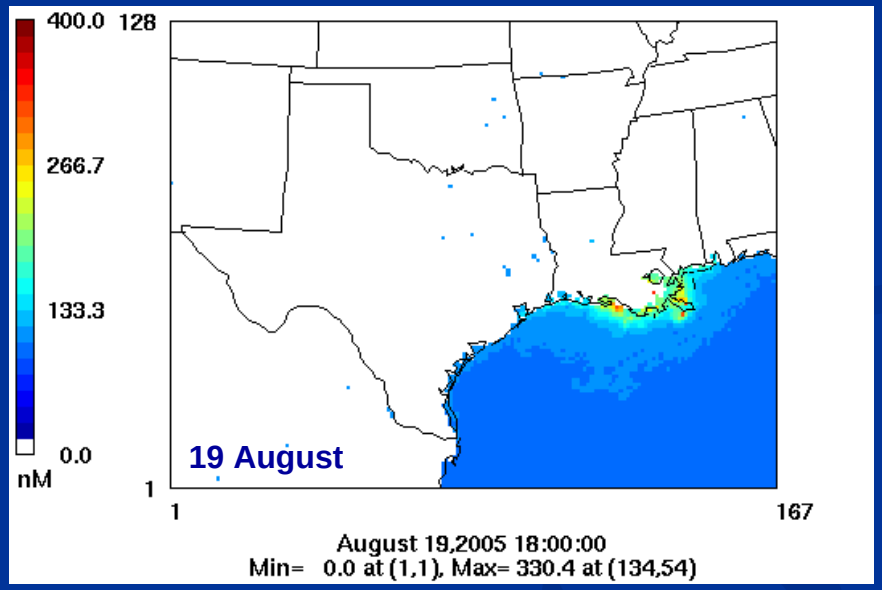
Surface dry deposition velocities for ozone and 10-m wind speed from the different modeling cases. The values were averaged for the entire sea area in a regional domain (12 km cell size) over a period of one month. Note that maximum and minimum values are those among daily averages.

Case Study (7th, 19th August)

To better understand the dependency of deposition velocity on wind speed, two days (7th and 19th August) with the lowest and highest average wind speeds during August (except hurricane period) were selected.

Distribution of iodide concentrations

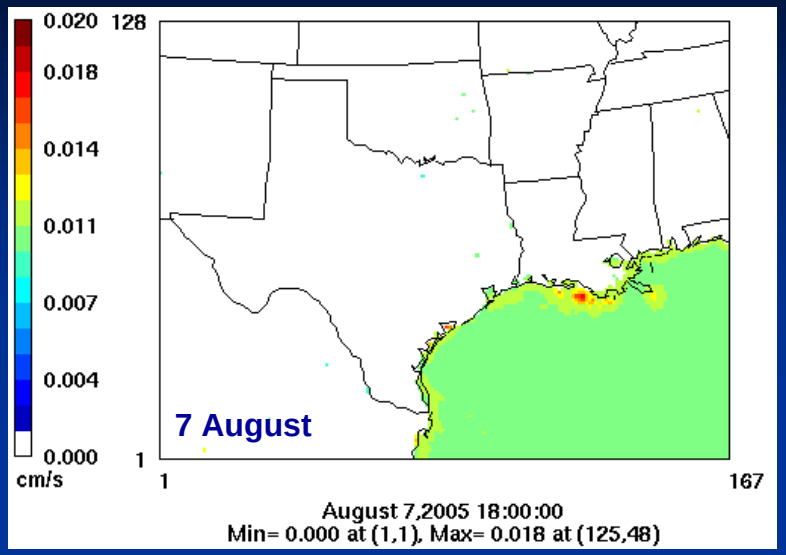


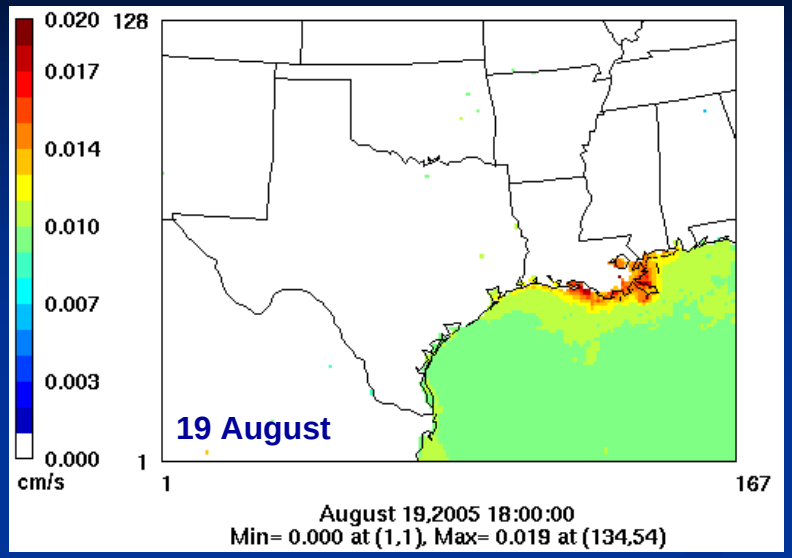


Iodide concentrations from satellite-derived estimates of near-surface chlorophyll concentrations for a 12-km regional domain at noon on 7 August (left) and 19 (right).

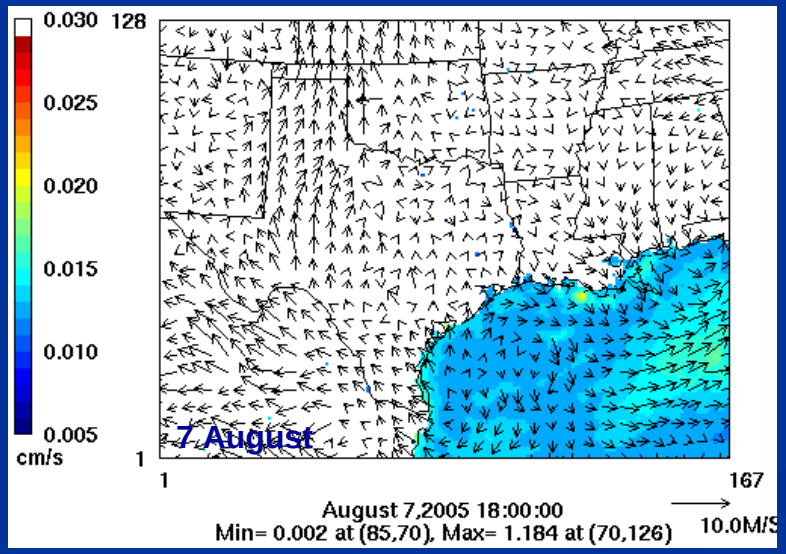
Dry Deposition Velocities for Case 2 and 3

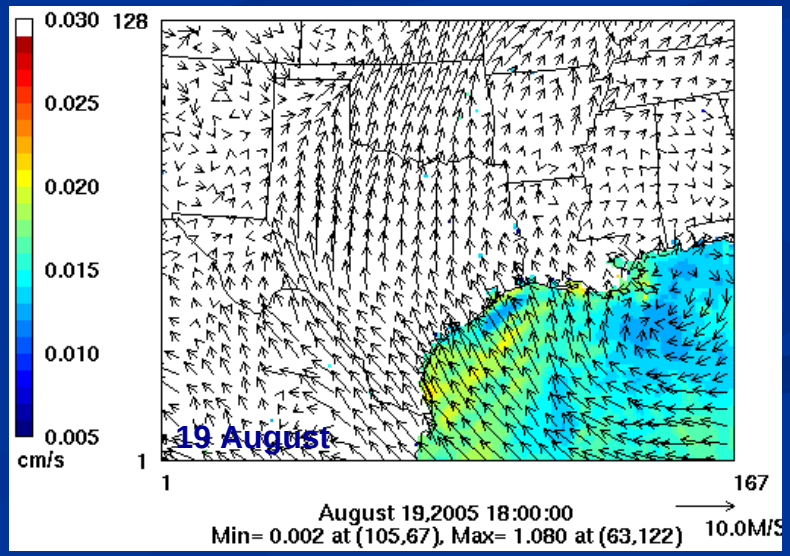
UTC time





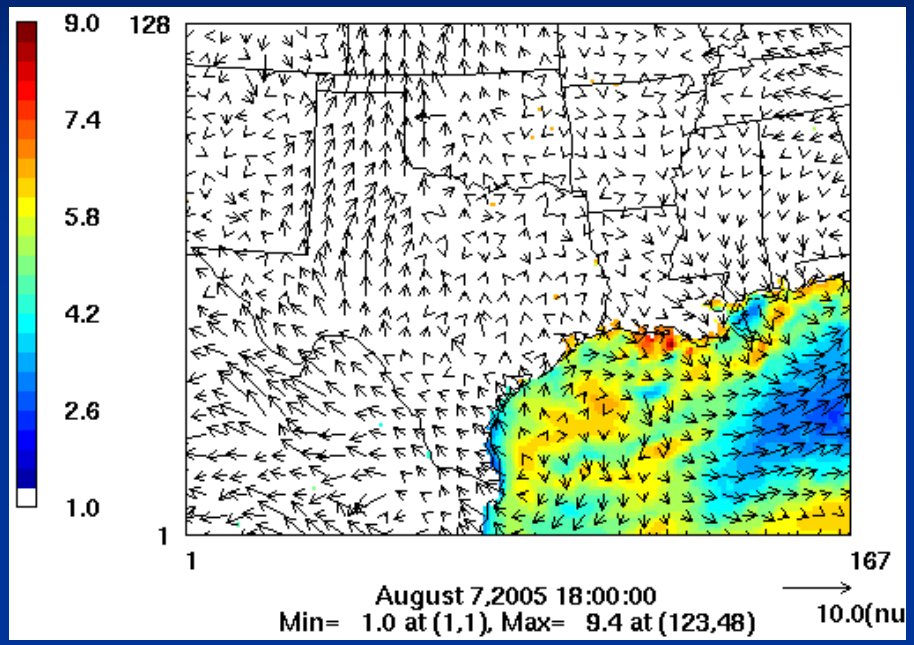
Differences in Dry Deposition Velocity (Case 3 Minus Case 2)



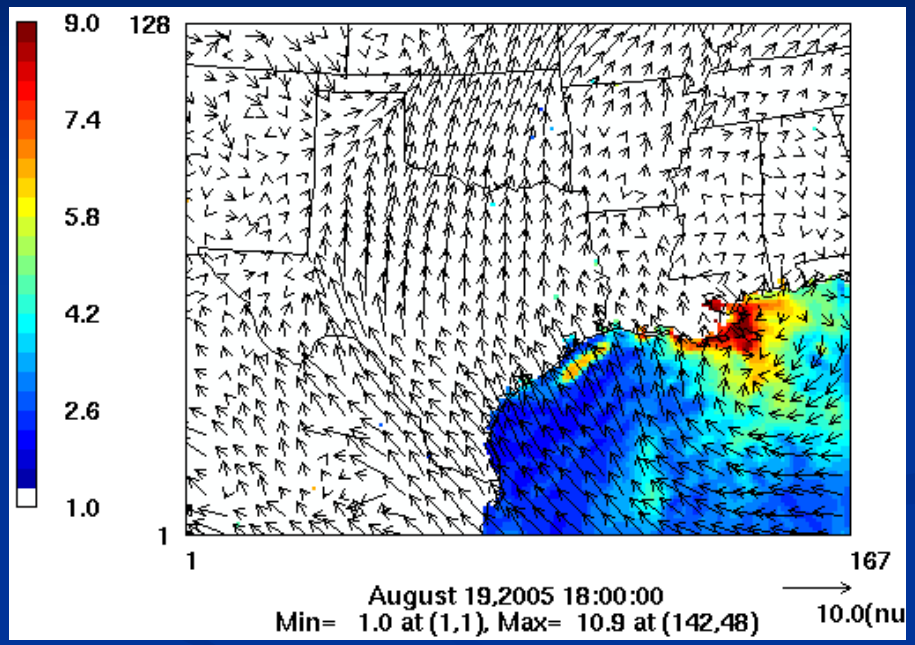


Ratio of Dry Deposition Velocities for Case 3 to Case 2

7 August



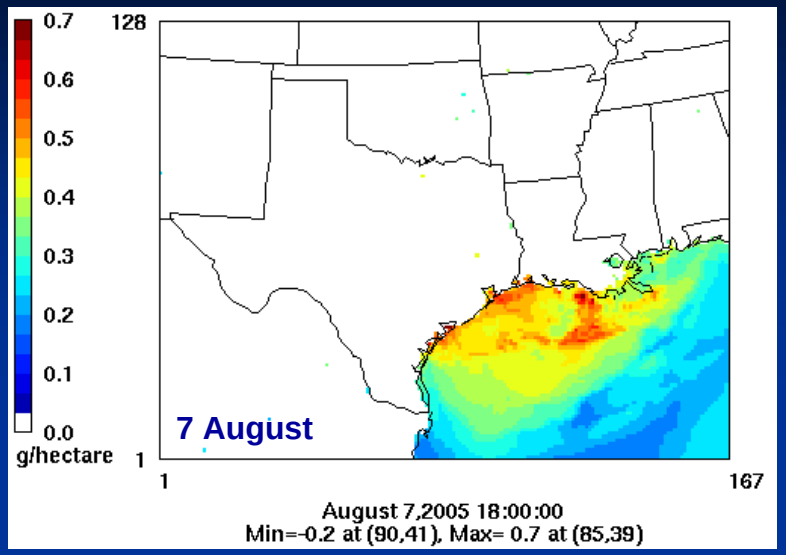
19 August

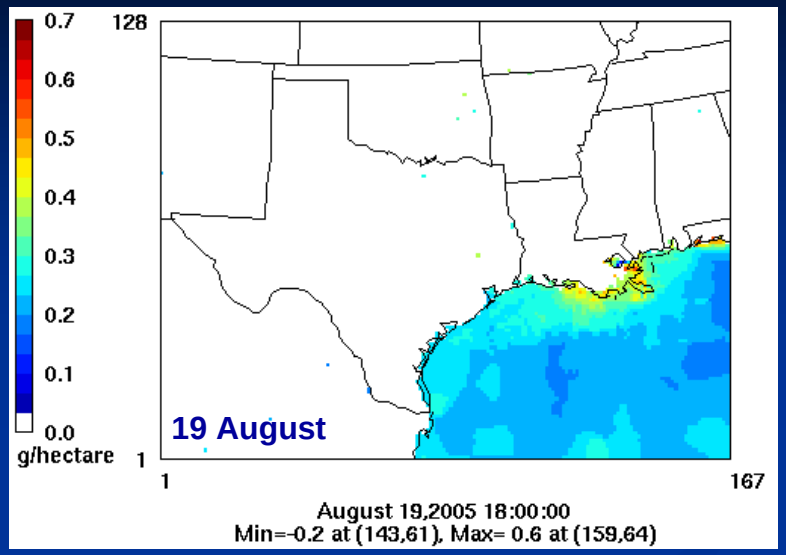


This indicates significant contribution of iodide reactions to the total deposition velocity at low wind speed.

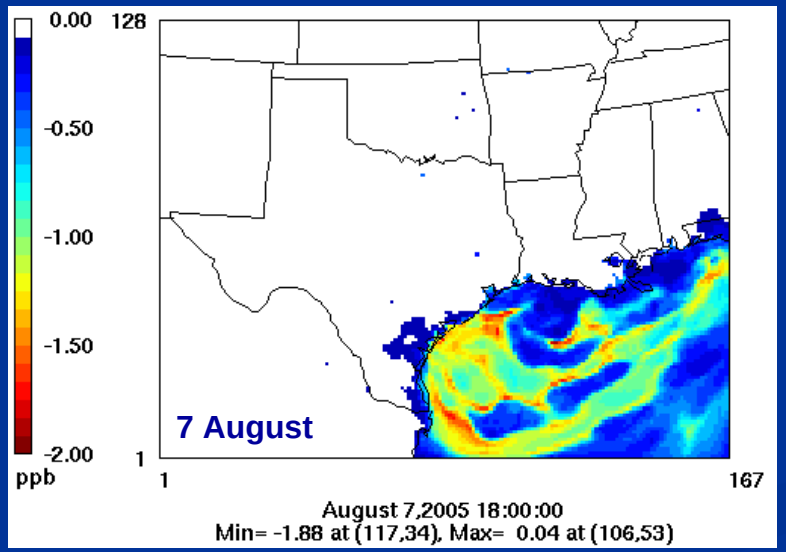
High ratio values represent impacts of differences in both the iodide concentration and wind speed.

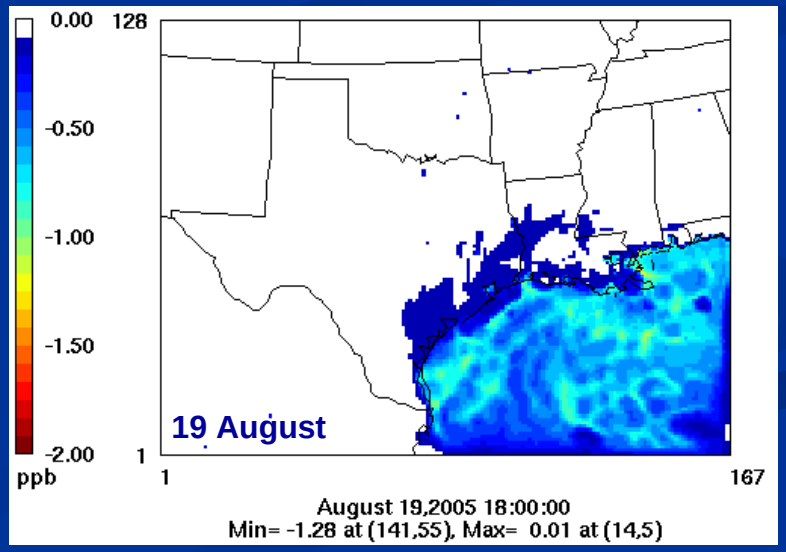
Differences in Surface Ozone Deposition (Case 3 Minus Case 2)



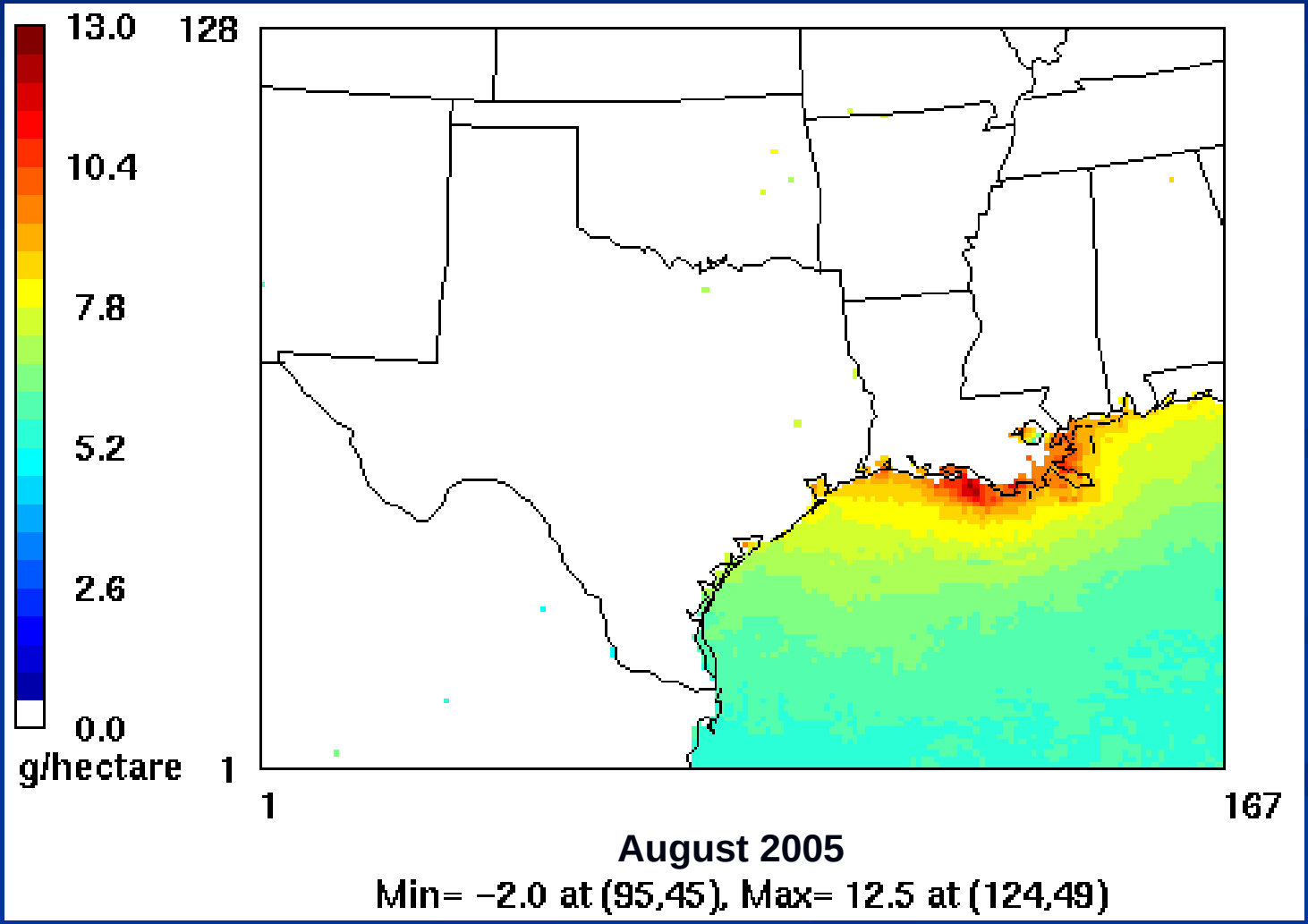


Differences in Surface Ozone Concentration (Case 3 Minus 2)





Differences (Case 3 Minus Case 2) in 24-Hour Cumulative Ozone Deposition Amount (Monthly Mean)



Summary & Future Plan

- Ozone dry deposition velocity can increase by about 63% due to iodide effect alone
- A large difference between deposition velocities for Case 2 and 3 were found along the cost due to iodide effects
- Iodide reactions clearly contributed to the total deposition velocity at low wind speed.
- Simulated ozone dry deposition amount between Case 2 and 3 showed that significant ozone loss can take place by iodide reaction

The additional analysis includes:

- Statistical analysis of modeling results
- Analyses of the effects on ambient ozone concentrations at the coastal area in different meteorological conditions
- Algorithm design for adding gas-phase iodine reaction process into the chemistry mechanism in CMAQ

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