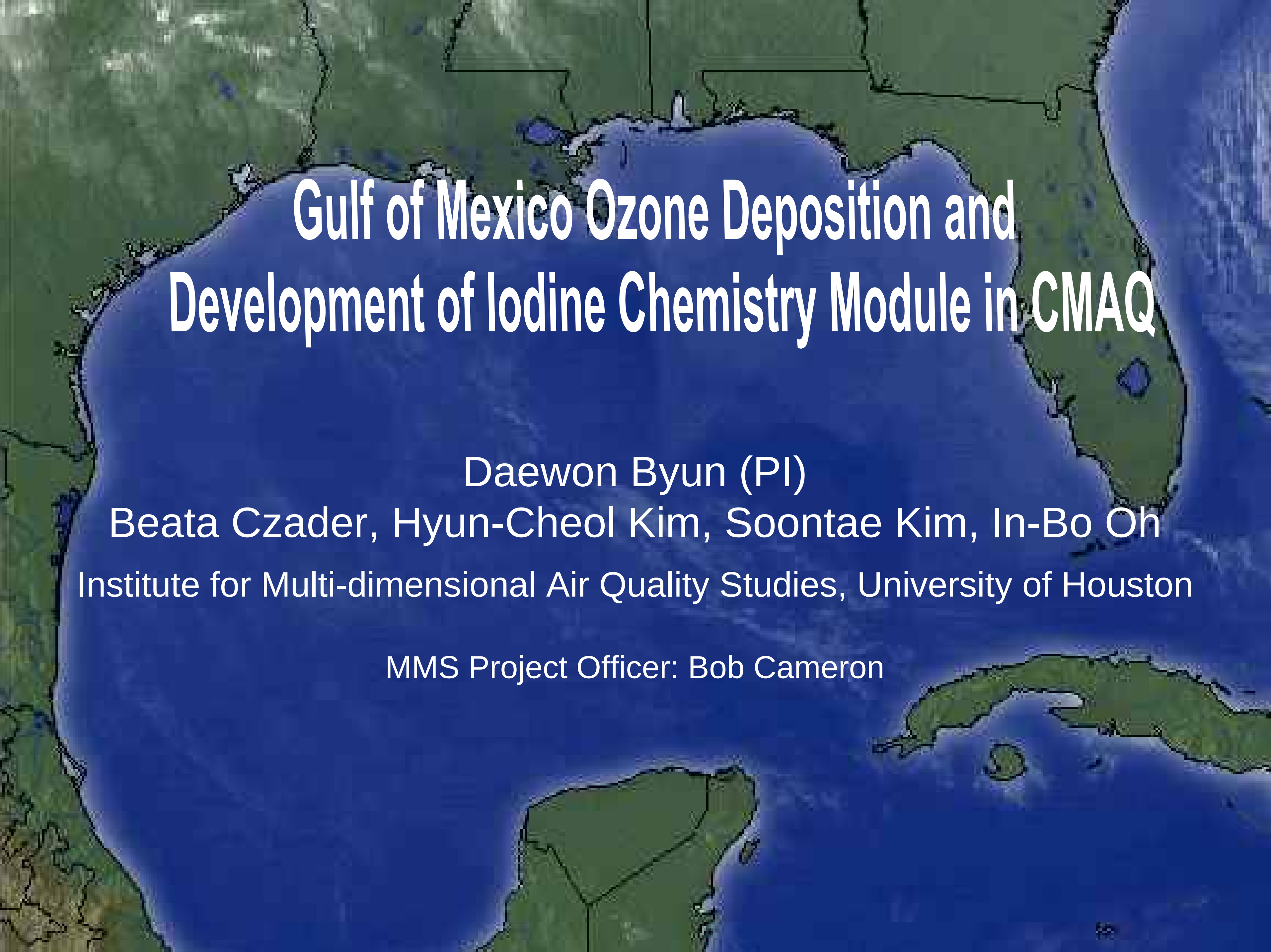

Gulf of Mexico Ozone Deposition and Development of Iodine Chemistry Module in CMAQ

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MMS Project Officer: Bob Cameron

Background (1)

- Iodine from the microalgae in the sea surface of coastal area can affect atmospheric chemistry through the titration reaction of ozone and iodine as well as photochemical reactions involving chlorine, iodine and other halogens from phytoplankton in the coastal waters.

- The former changes ozone deposition flux to the ocean surface (Galbally and Roy 1980; Gallagher et al. 2001) and this can play a major role in the ozone budget in the marine boundary layer and influence onshore/inland distribution of ozone.

Background (2)

- Iodine and other halogens also involve in homogeneous and heterogeneous reactions with anthropogenic and natural emissions that subsequently change concentrations of ozone and atmospheric particular matter.

- Present regulatory ozone modelling often fails to account for these effects 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 tests to calculate the change in the ozone deposition rates for the different meteorological condition and iodide distributions.

2. Develop 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 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. Analyses of iodine effects on dry deposition velocities, deposition amounts, and air concentrations 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 byitself 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 following 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)

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

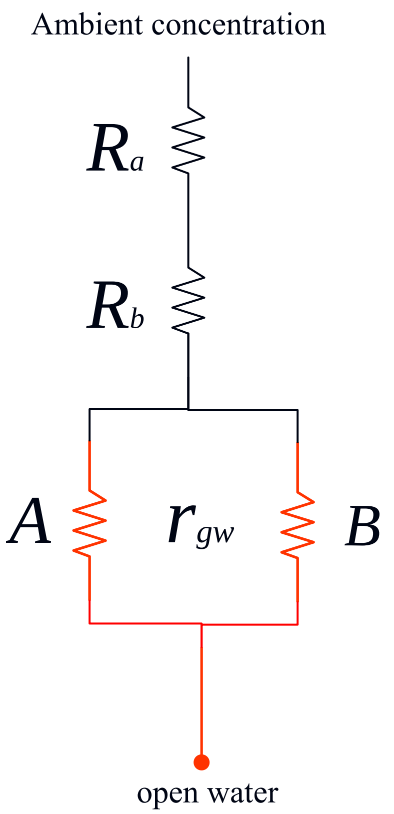
α : chemical enhancement factor

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

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:

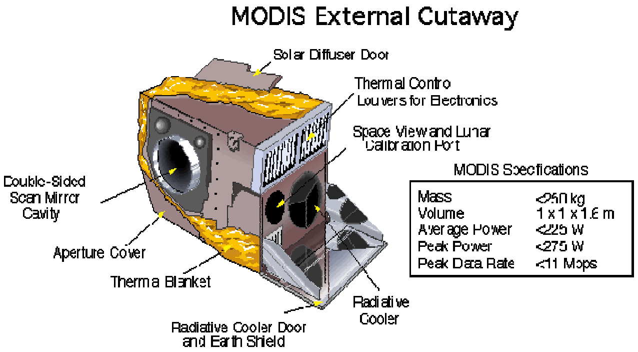
[iodide] : 20–400 nM (Campos et al. 1996 and 1999)
(the strongest candidate to enhance ozone deposition)
[DMS] : 0.04–316 nM (Kettle et al. 1999)
(potential candidate to elevate q when only at extremely high concentration)

Chlorophyll_a Concentration Measurements

- MODIS (Moderate Resolution Imaging Spectroradiometer) onboard AQUA satellite
- SeaWiFS (Sea-viewing Wide Field-of-view Sensor) onboard SeaStar
- The Coastal Zone Color Scanner (CZCS) on the NIMBUS-7

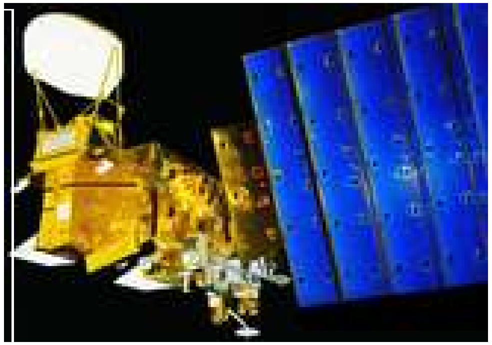
http://modis.gsfc.nasa.gov/

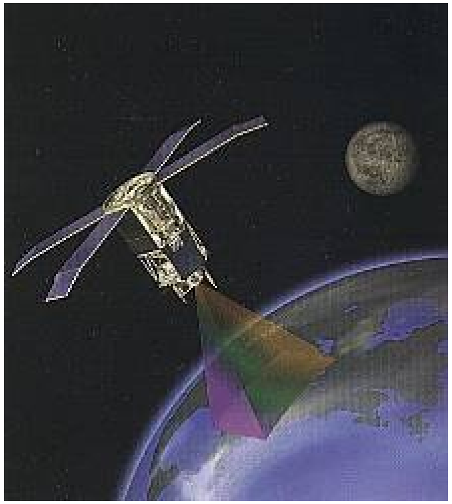
http://oceancolor.gsfc.nasa.gov/SeaWiFS/



MODIS Specifications

Mass	<250 kg
Volume	1 x 1 x 1.6 m
Average Power	<225 W
Peak Power	<275 W
Peak Data Rate	<11 Mbps

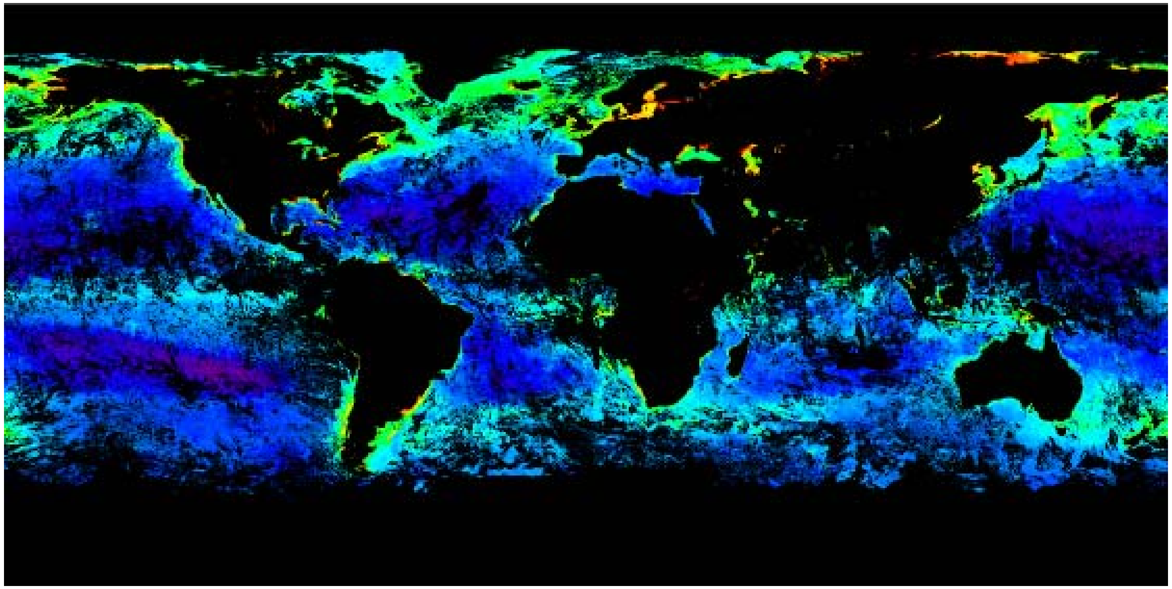




MODIS Chlorophyll_a Concentration

- MODIS (Moderate Resolution Imaging Spectroradiometer) onboard AQUA satellite

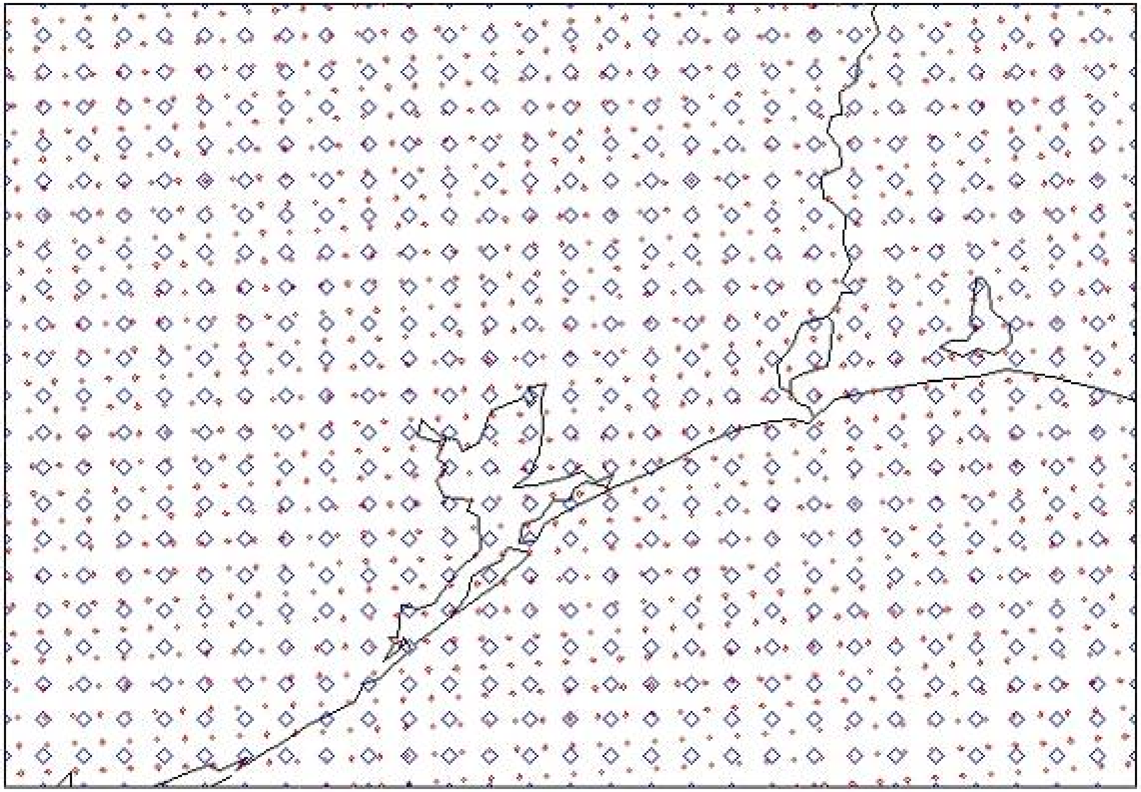
- 4, 9 km resolution
- daily, 3day, weekly(8day), and monthly data are available



9 km weekly

Grid Points

CMAQ grid points are based on LCC map projection, and MODIS CHLO data are based on LL



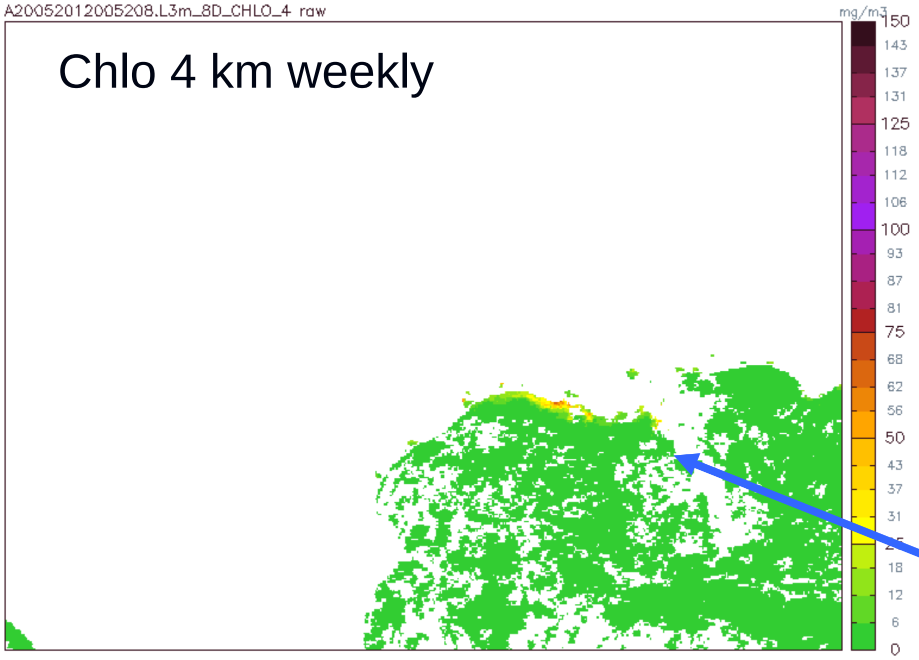
◊ CMAQ grid

● CHLO grid

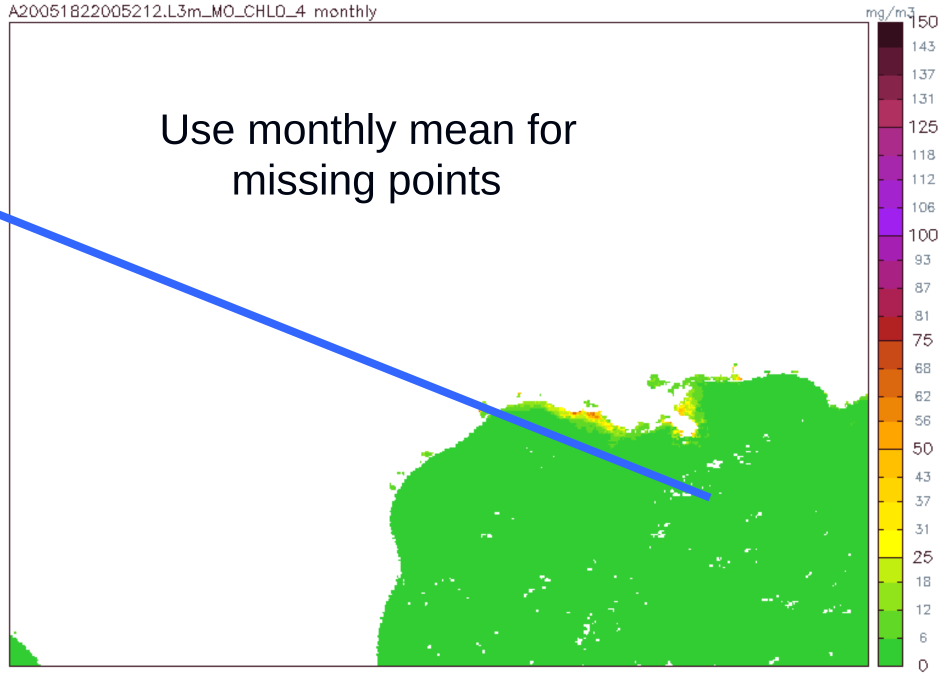
Regridding MODIS Chlorophyll_a

MODIS Chlo 4km weekly data was regridded into CMAQ 12 km grid

For missing points, monthly mean data was used

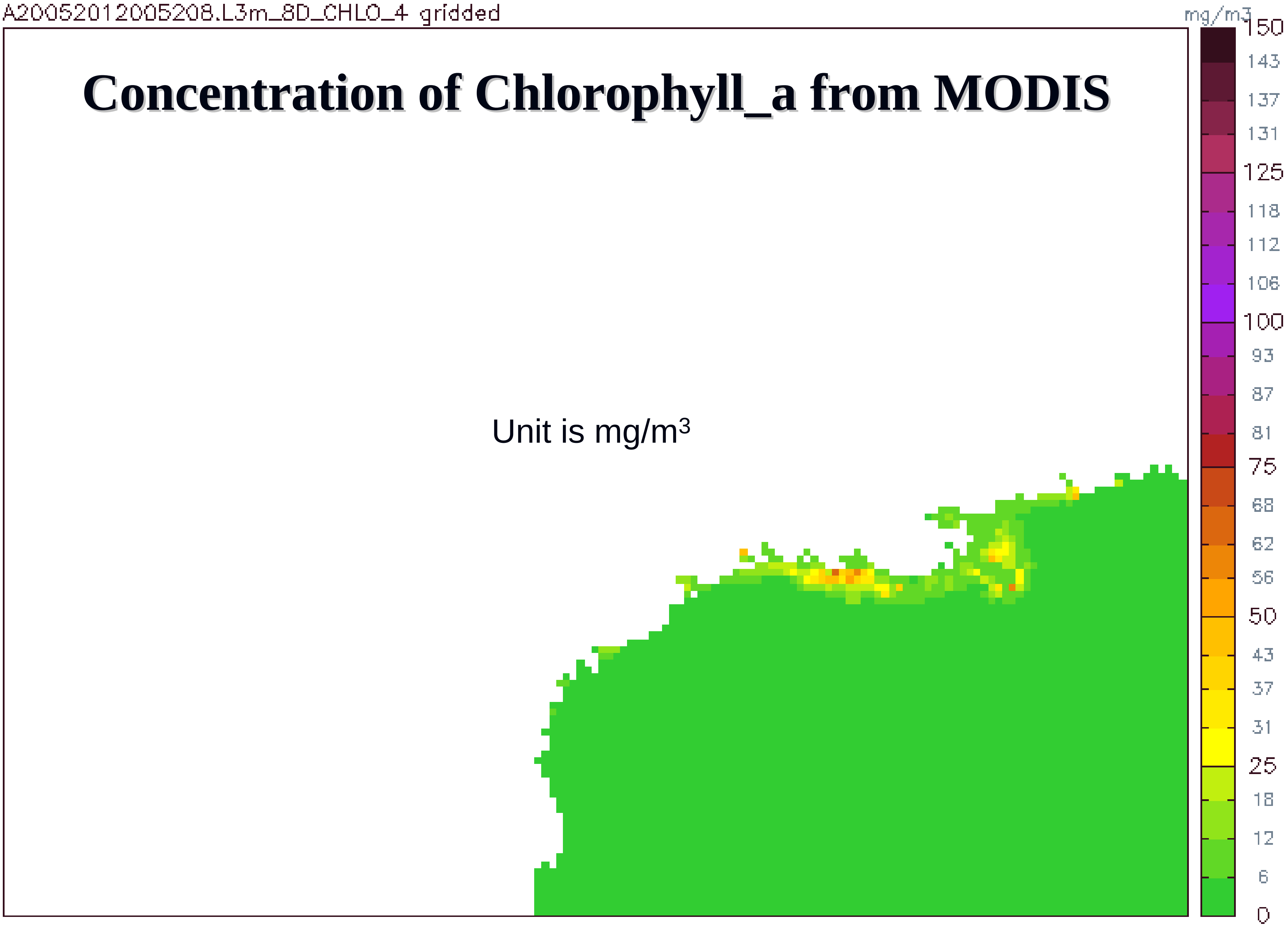


Chlo 4 km weekly



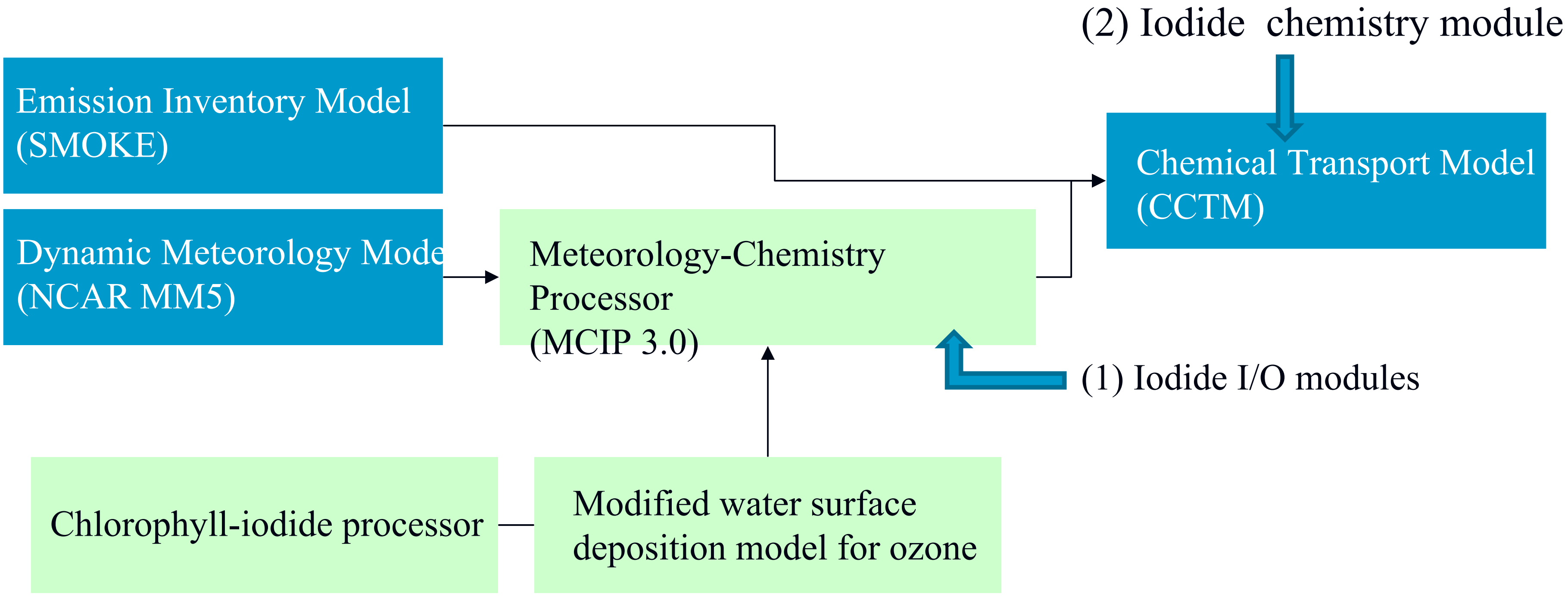
Use monthly mean for missing points

Concentration of Chlorophyll_a from MODIS



Unit is mg/m^3

CMAQ Modeling Linked with Modified Ozone Dry Deposition Modules



(2) Iodide chemistry module

Emission Inventory Model (SMOKE)

Dynamic Meteorology Mode (NCAR MM5)

Meteorology-Chemistry Processor (MCIP 3.0)

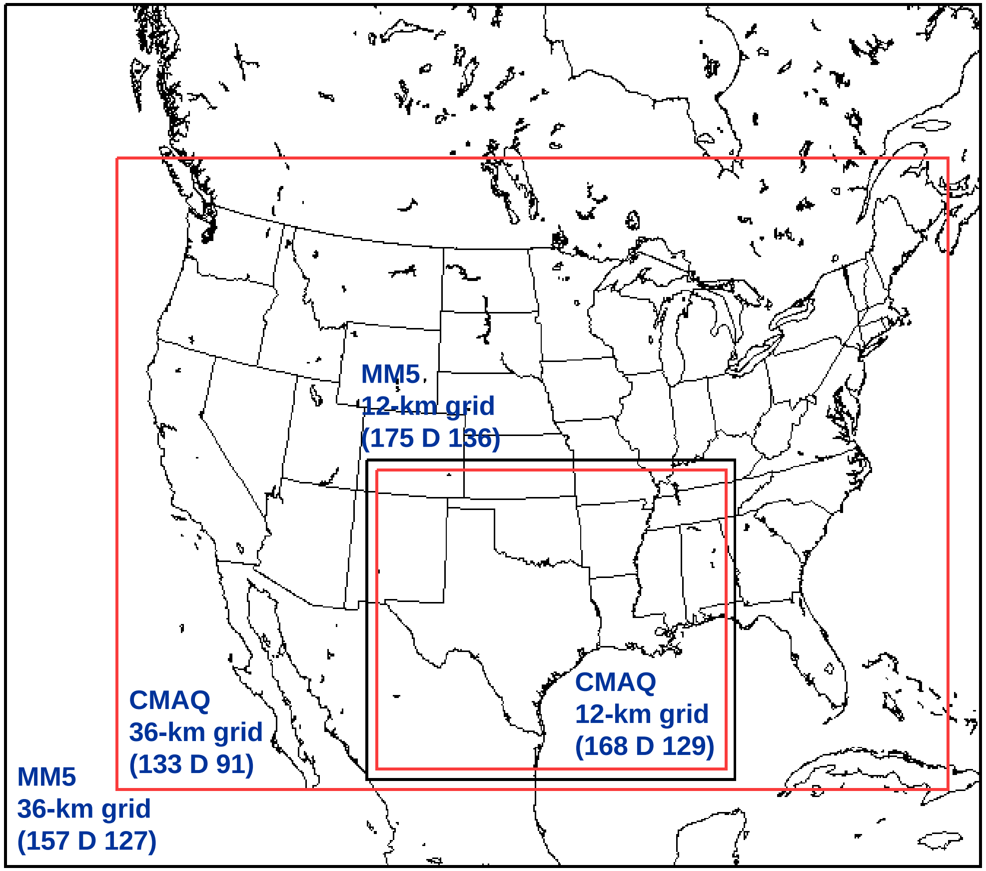
Chemical Transport Model (CCTM)

(1) Iodide I/O modules

Chlorophyll-iodide processor

Modified water surface deposition model for ozone

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

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:

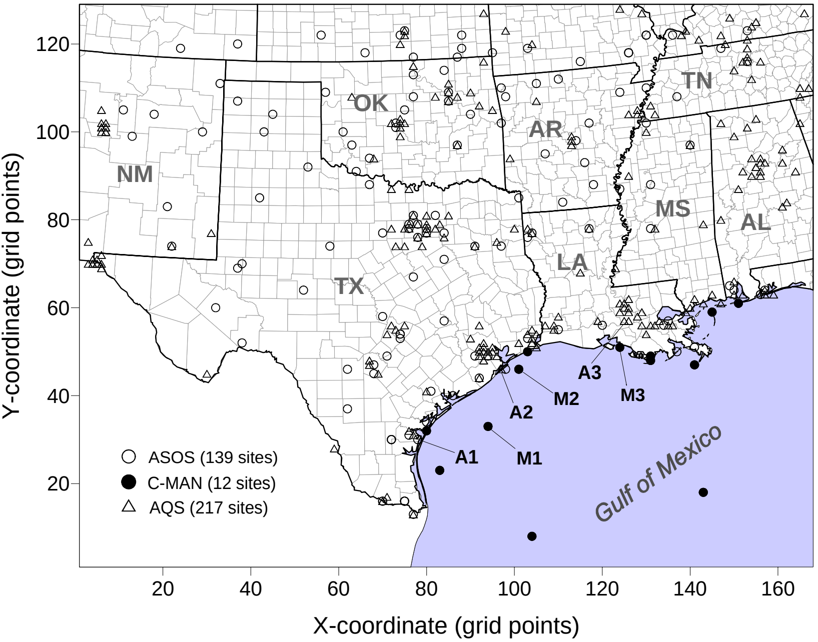
- The “pass-through” option where PBL values as estimated by MM5 were used directly
- Radiation fields from MM5 files were used
- Original/modified Model-3/CMAQ dry deposition (M3DDEP) routine

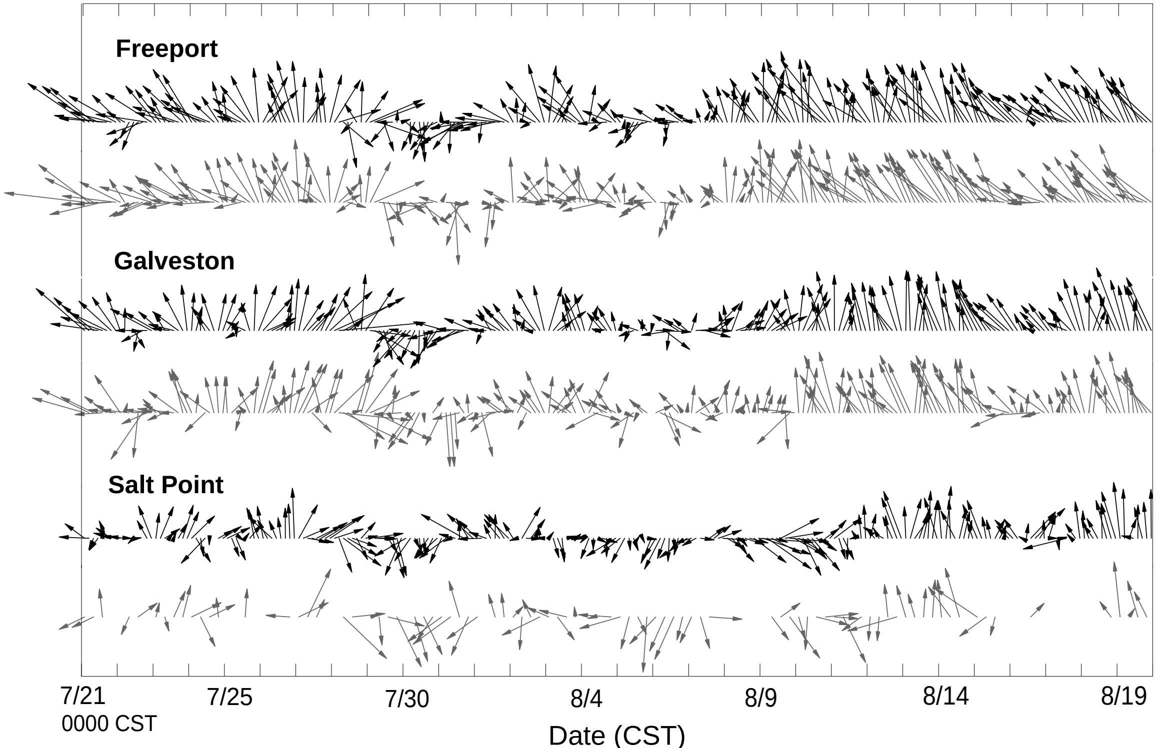
The CMAQ chemical transport model (CCTM) ran with

- 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)

Meteorological Simulations

21 July – 20 August 2005

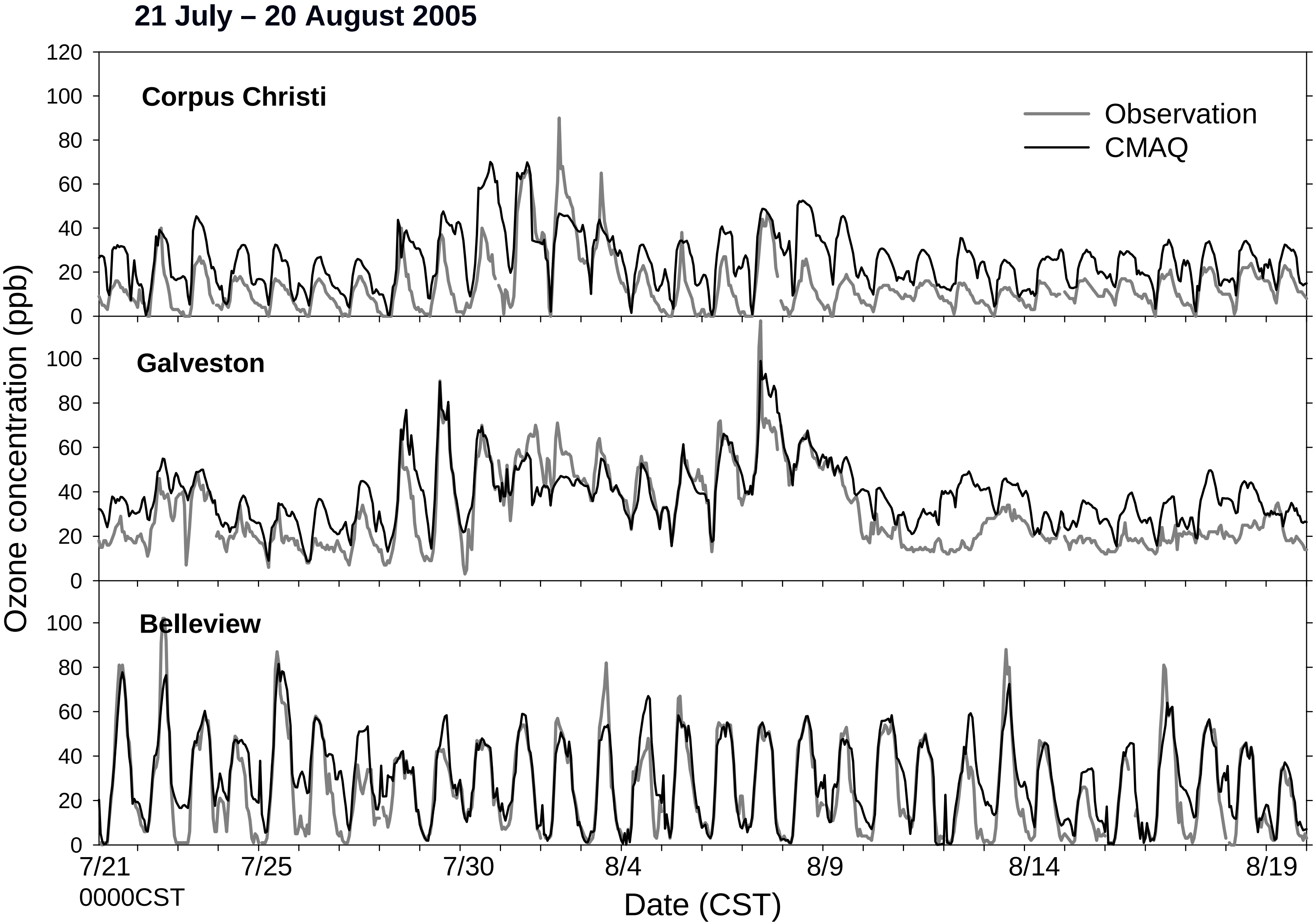




Simulated ⟶

Observed ⟶

Simulated Ozone Concentrations at Coastal Sites



One-month Average Dry Deposition Velocity

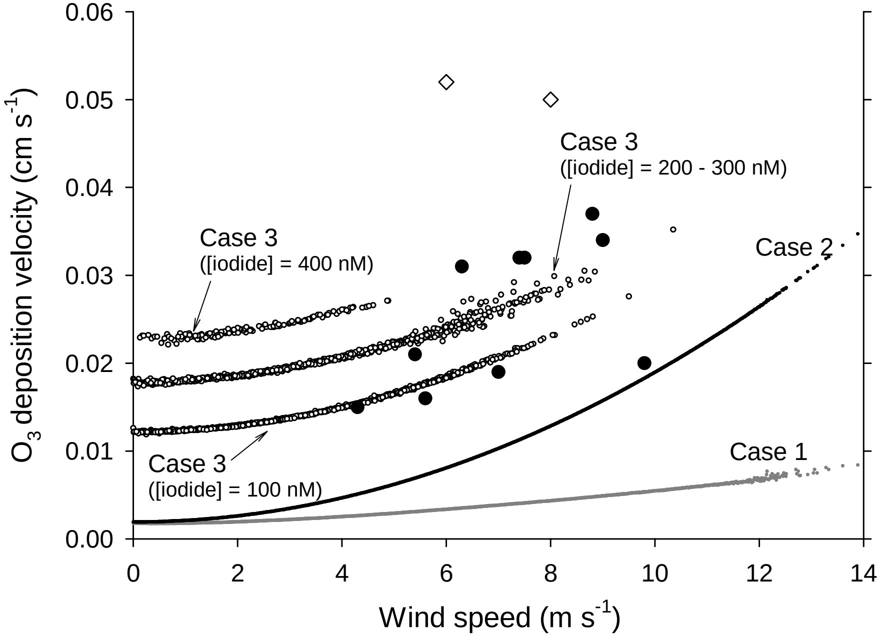
Case	Dry deposition velocity for ozone (cm/s)			10-m wind speed (m/s)
	Average ± S.D.	Max.	Min.	
1	0.0028 ± 0.0008	0.0059	0.0021	4.19 ± 1.85 Max. = 10.26 Min. = 2.26
2	0.0062 ± 0.0047	0.0244	0.0031	
3	0.0167 ± 0.0047	0.0349	0.0135	

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.

Simulated ozone dry deposition velocities can increase by about 63% due to iodide effect alone

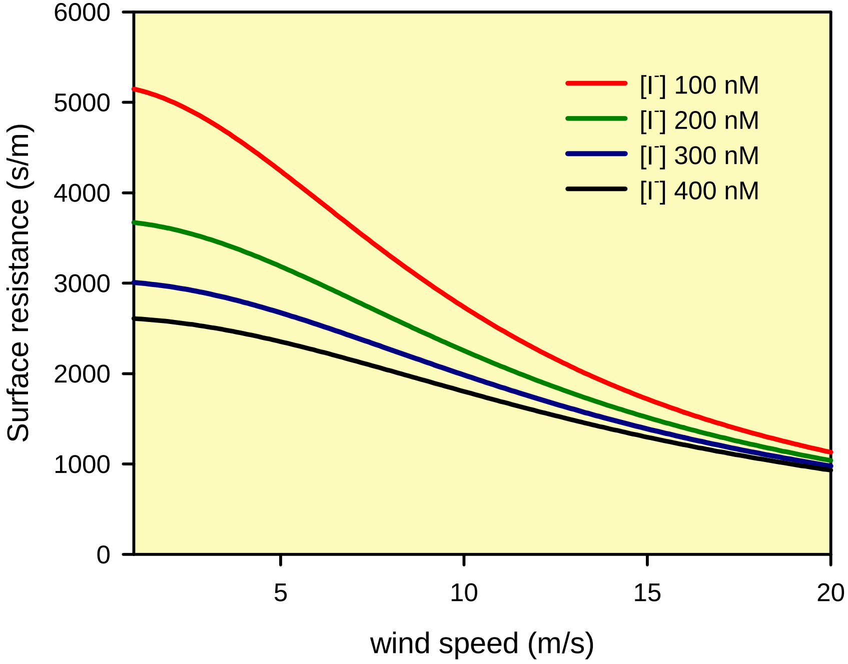
Evaluation

Dry deposition velocity for ozone

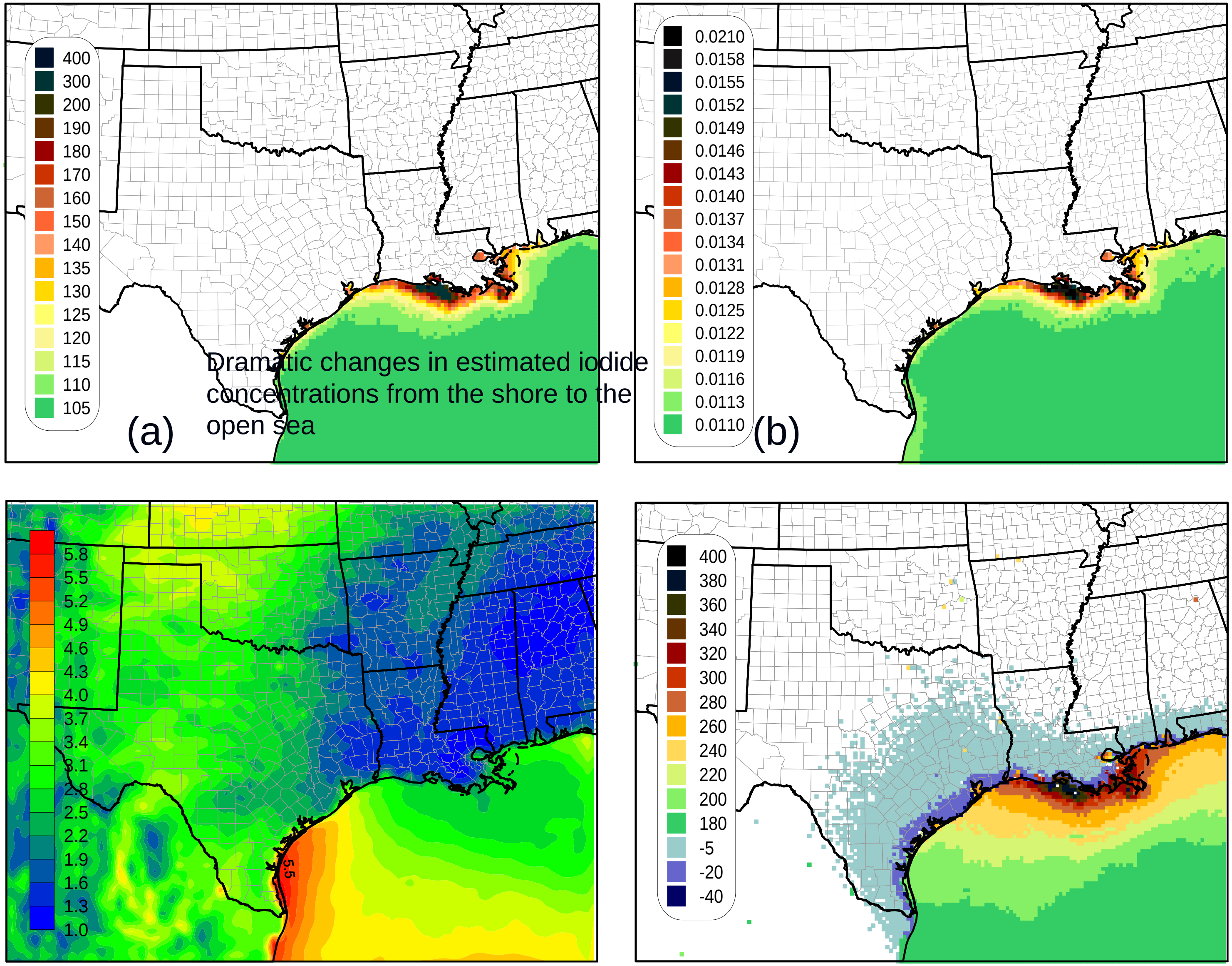


Dry deposition velocity for ozone as a function of wind speed. The individual curves are for different modules: M3DDEP (Case 1); modified M3DDEP without iodide reaction (Case 2); modified M3DDEP with iodide reaction (Case 3). Two curves for Case 3 indicates deposition velocities corresponding to different 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)

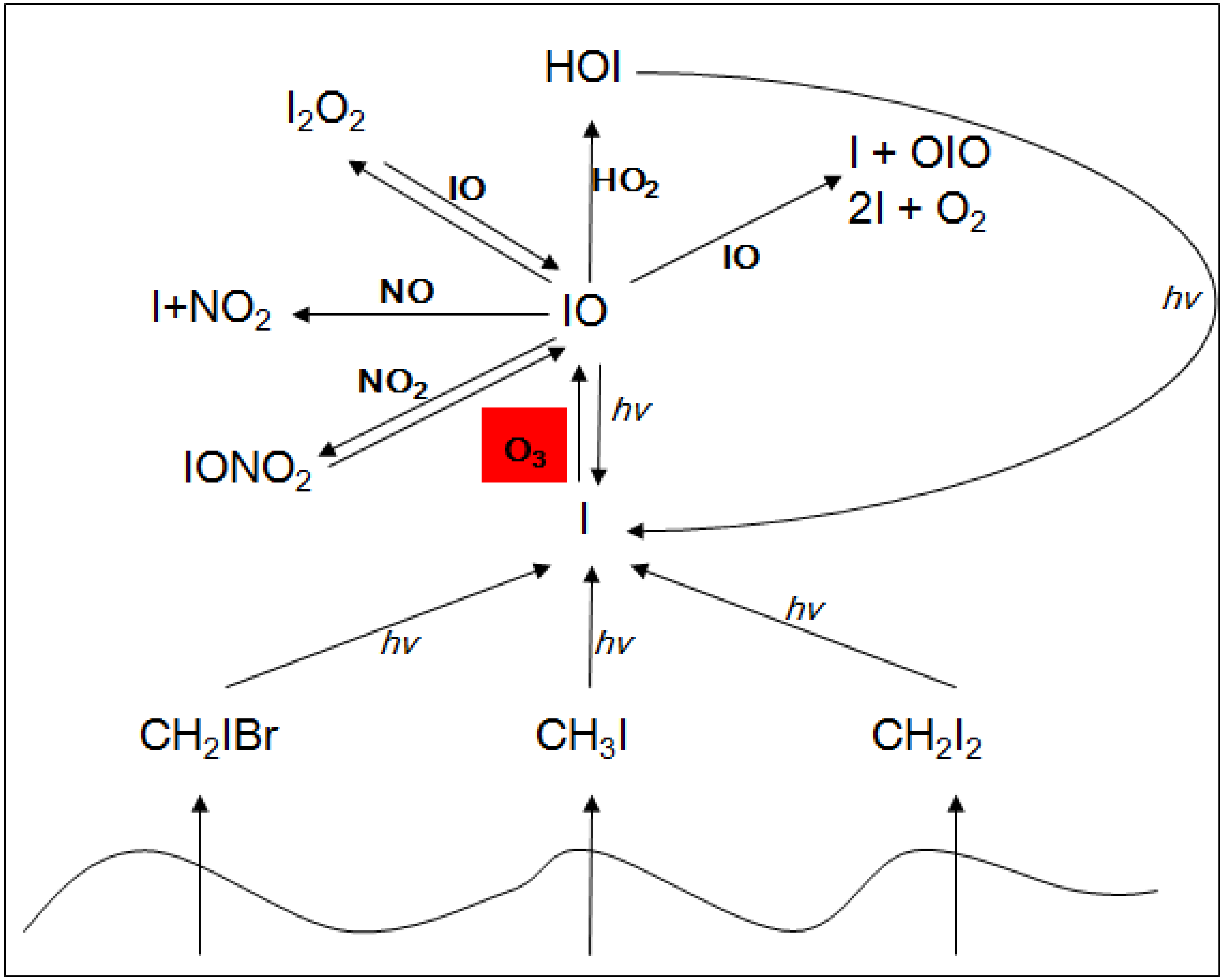


Dramatic changes in estimated iodide concentrations from the shore to the open sea

Large dry deposition velocity near the coast of New Orleans

(a) Estimated iodide concentrations (nanomole L^{-1}, nM) from satellite-derived estimates of near-surface chlorophyll concentrations for a 12-km regional domain, differences between Case 2 and 3 (Case 3 minus 2) in (b) ozone dry deposition velocities (cm s^{-1}), (c) 10-m wind speeds (m s^{-1}) and (d) differences in ozone deposition amounts accumulated over the one-month period (g hectare^{-1}). All values but the dry deposition amounts are averaged for each grid cell over the one-month period.

Gas Phase Iodine Chemistry in the Marine Boundary Layer



Chemical Mechanism Implemented in CMAQ

	Mechanism based on McFiggans et al., 2000 and Vogt et al. 1999.	Mechanism added into CMAQ CB4 reaction mechanism	Notes
(R1)	$I + O_3 \rightarrow IO + O_2$	$I + O_3 \rightarrow IO$	1
(R2)	$I + HO_2 \rightarrow HI + O_2$	$I + HO_2 \rightarrow HI$	1
(R3)	$I + NO_2 + M \rightarrow INO_2 + M$	$I + NO_2 + M \rightarrow INO_2$	1
(R4)	$IO + NO \rightarrow I + NO_2$	$IO + NO \rightarrow I + NO_2$	
(R5)	$IO + HO_2 \rightarrow HOI + O_2$	$IO + HO_2 \rightarrow HOI$	1
(R6)[a]	$IO + IO \rightarrow I_2O_2$	$IO + IO \rightarrow I_2O_2$	
(R7)[a]	$IO + IO \rightarrow 2I + O_2$	$IO + IO \rightarrow 2I$	1
(R8)	$IO + NO_2 + M \rightarrow IONO_2 + M$	$IO + NO_2 + M \rightarrow IONO_2$	
(R9)	$IONO_2 \rightarrow IO + NO_2$	$IONO_2 \rightarrow IO + NO_2$	
(R10)	$OH + HI \rightarrow I + H_2O$	$OH + HI \rightarrow I$	1
(R11)	$HOI + OH \rightarrow IO + H_2O$	X	2
(R12)	$ION_2 \rightarrow I + NO_2$	$ION_2 \rightarrow I + NO_2$	
(R13)	$I + NO_3 \rightarrow IO + NO_2$	$I + NO_3 \rightarrow IO + NO_2$	
(R14)	$CH_3I + hv \rightarrow CH_3 + I$	$CH_3I + hv \rightarrow I + XO2 + FORM + HO2$	3
(R15)	$CH_2I_2 + hv \rightarrow CH_2 + 2I$	$CH_2I_2 + hv \rightarrow 2I + 2HO2 + CO$	4
(R16)	$CH_2IBr + hv \rightarrow CH_2 + I + Br$	$CH_2IBr + hv \rightarrow I + Br + 2HO2 + CO$	4
(R17)	$IO + hv \rightarrow I + O$	$IO + hv \rightarrow I + O$	
(R18)	$HOI + hv \rightarrow I + OH$	$HOI + hv \rightarrow I + OH$	
(R19)	$INO_2 + hv \rightarrow 0.5\,(I + NO_2) + 0.5\,(IO + NO)$	$INO_2 + hv \rightarrow 0.5\,(I + NO_2) + 0.5\,(IO + NO)$	
(R20)	$IONO_2 + hv \rightarrow 0.5\,(IO + NO_2) + 0.5\,(I + NO_3)$	$IONO_2 + hv \rightarrow 0.5\,(IO + NO_2) + 0.5\,(I + NO_3)$	
(R21)	$HI + hv \rightarrow H + I$	$HI + hv \rightarrow HO2 + I$	5

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M$$

$$CH_3O_2 \begin{cases} + NO \rightarrow CH_3O + NO_2 \\ + NO_2 + M \leftrightarrows CH_3OONO_2 + M \\ + HO_2 \rightarrow CH_3OOH + O_2 \end{cases}$$

$$CH_3OOH + hv \rightarrow CH_3O + OH$$

$$CH_3OOH + OH \rightarrow CH_3O_2 + H_2O$$

$$CH_3O + O_2 \rightarrow HCHO + HO_2$$

→ based on Vogt et al. 1999

→ $H + O_2 \rightarrow HO_2$

Photolysis rates: CH3I, CH2I2, CH2IBr, IO, HOI, INO_2[a], BrONO2[b]

IUPAC values

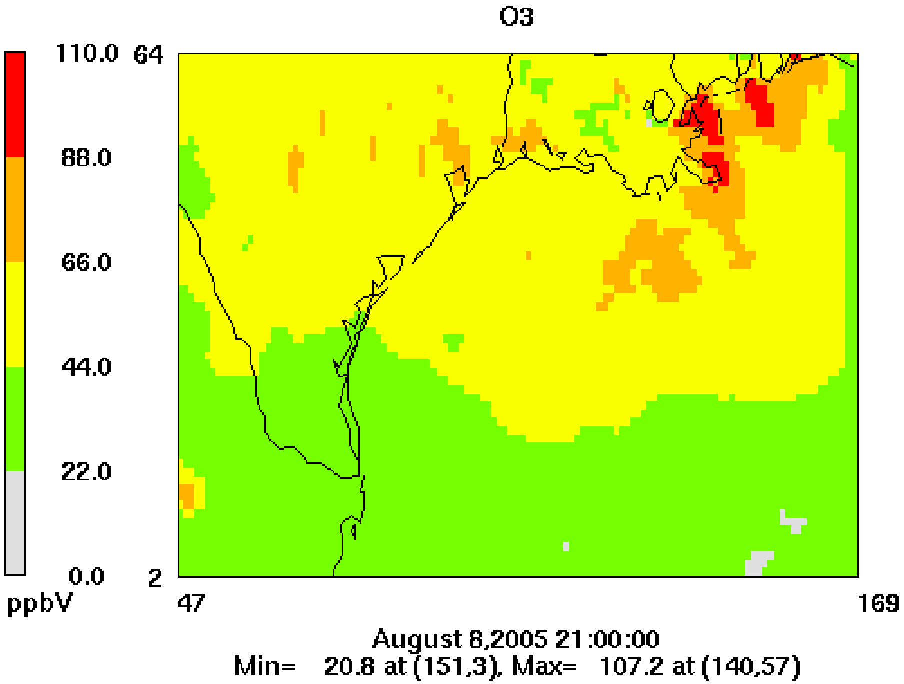
$BrNO_2$ Carter 2007

no data available $BrNO_2$

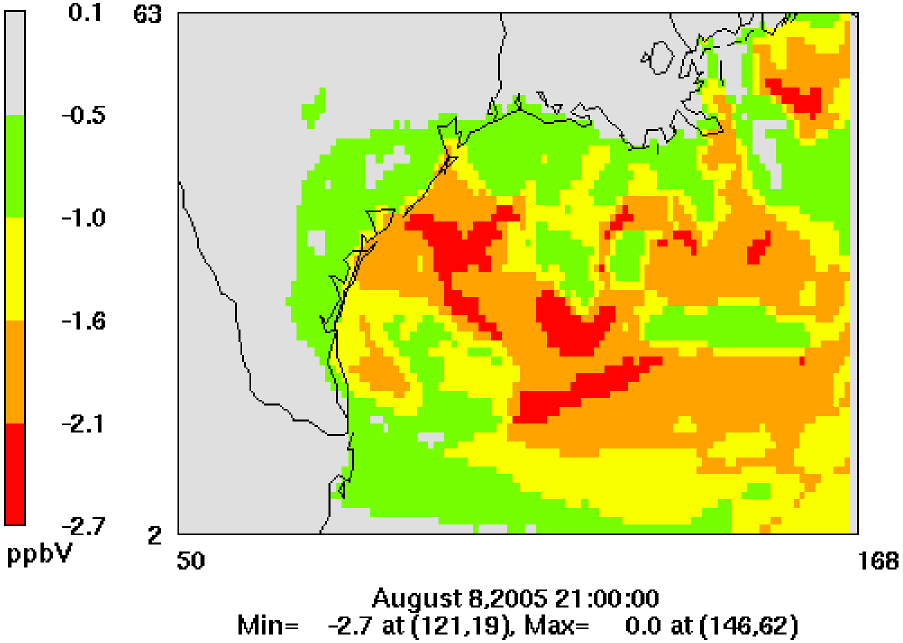
Modeling the Effects of Halocarbon Emissions on Ozone Concentration in the Gulf of Mexico

Phase 1

Emissions of CH_3I assumed to be **constant** at the rate of 1.395x10-7 moles/s (Carpenter 2003; Vogt et al. 1999) for CMAQ modeling



O3 (iodine) – O3 (base)



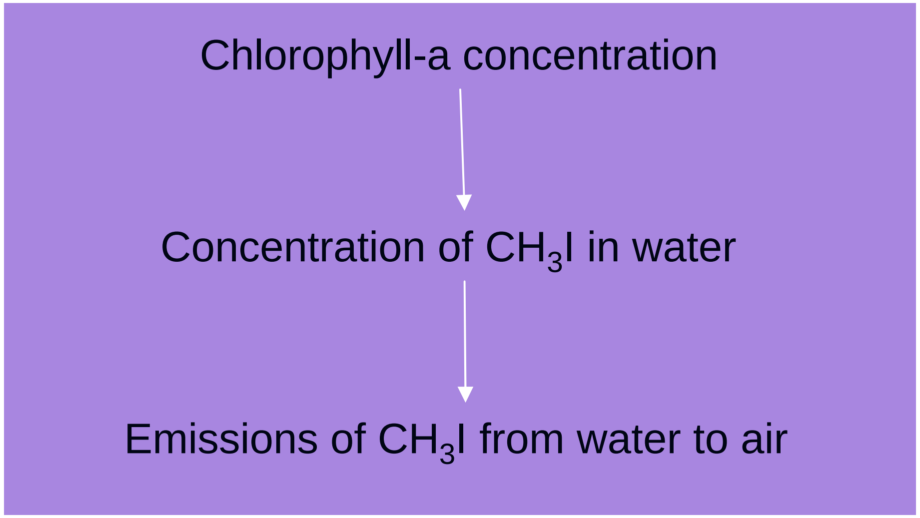
up to 5% ozone decrease in the Gulf of Mexico

CH_3I Emission Estimates

CH_3I emissions are **<u>not constant</u>**

Phase 2

CH_3I emissions can be estimated from the chlorophyll-a satellite data



Chlorophyll-a concentration

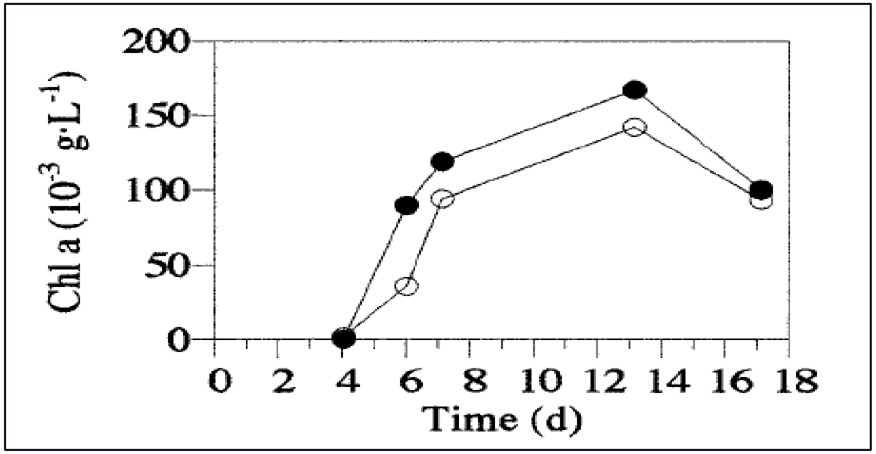
Concentration of CH_3I in water

Emissions of CH_3I from water to air

Methyl iodide (CH_3I) Concentration in Water Based on Chlorophyll-a Concentration

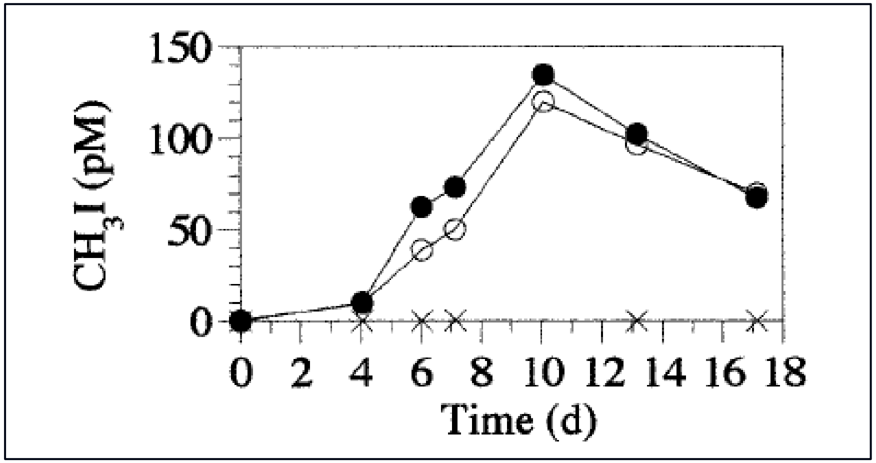
0.2 – 1.2 pmol CH_3I per µg Chlo-a per day

(Scarratt and Moore 1999)



2.8 – 8 pmol CH_3I per µg Chlo-a per day

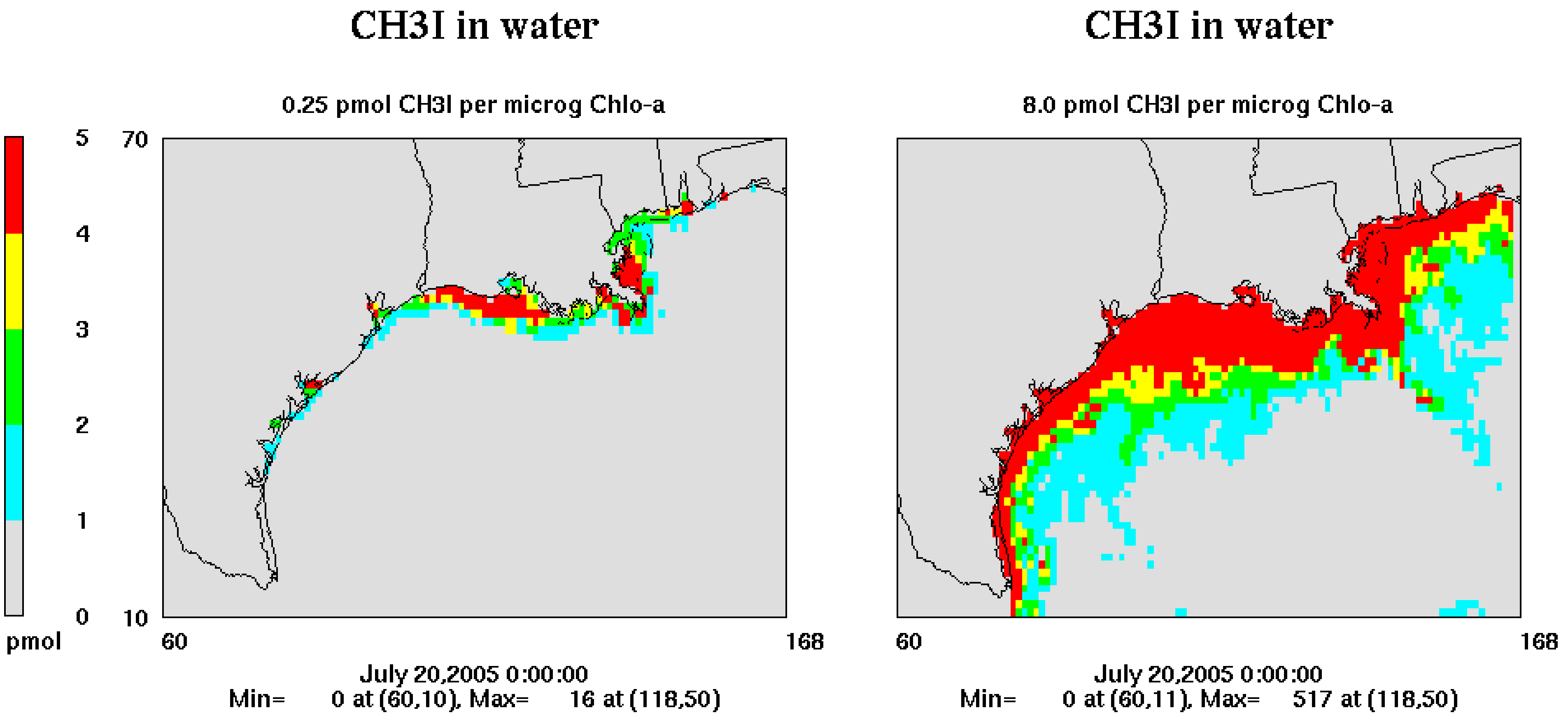
(Moore and Groszko 1999)



Methyl iodide (CH_3I) Concentration in Water Based on Chlorophyll-a Concentration

0.2 – 1.2 pmol CH_3I per µg Chlo-a per day (Scarratt and Moore 1999)

2.8 – 8 pmol CH_3I per µg Chlo-a per day (Moore and Groszko 1999)



1 – 7 pmol/L CH3I measured in NW Atlantic and Pacific (Moore and Groszko 1999)

The Ocean to Air Flux of Methyl Iodide (1)

Sea-air flux estimate (Liss and Slater 1974)

$$F = k\,(c_w - c_a/H)$$

the exchange constant

CH_3I concentration in the water and air

Henry's constant

We follow Moore and Groszko et al. (1999) simplified approach assuming that $c_w >> c_a$

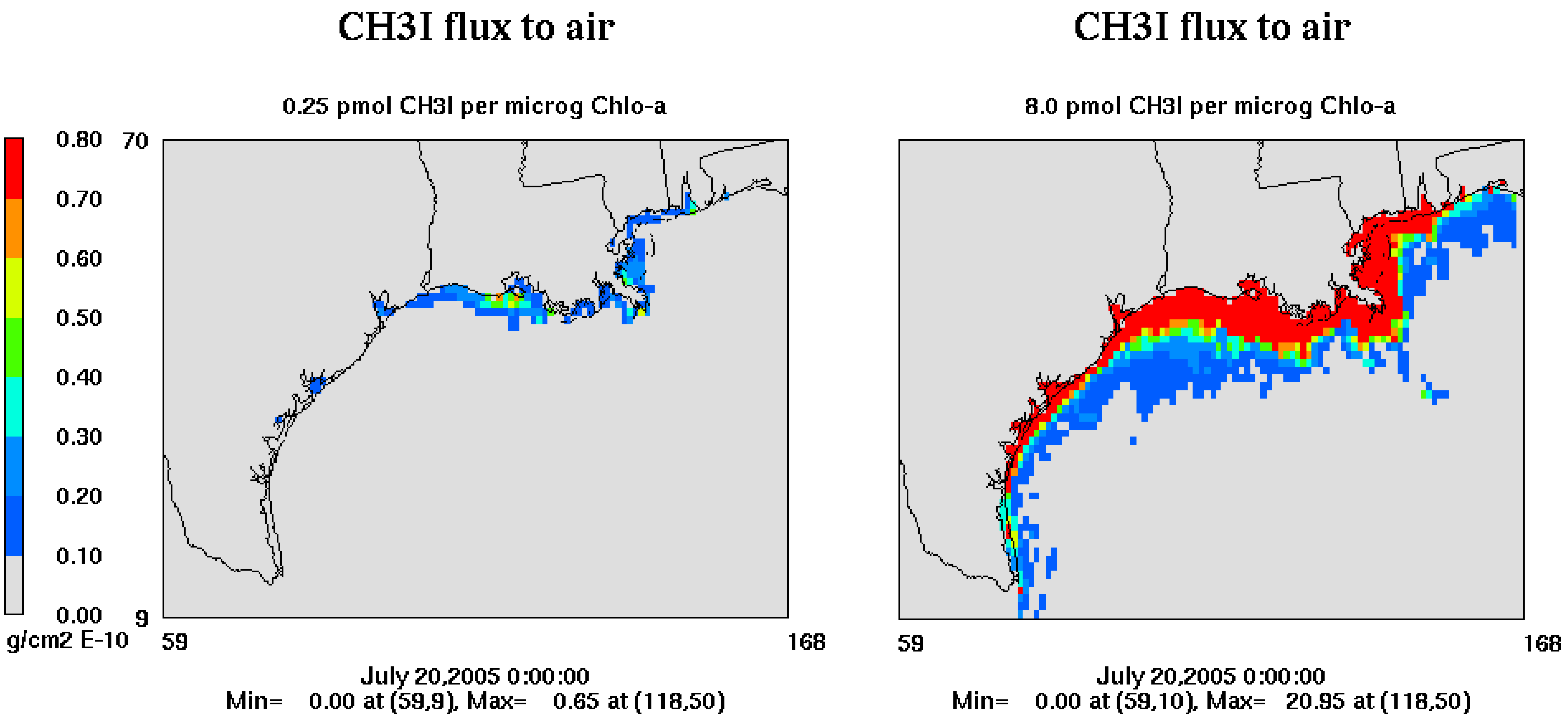
$$F = k \cdot c_w = 0.31 \cdot u^2 \cdot \left(\frac{S_c}{660}\right)^{-\frac{1}{2}} \cdot c_w$$

wind speed

Schmidt number

S_c not available for CH_3I, we use scaled S_c for CH_3Br following De Bruyn and Sattzman (1974)

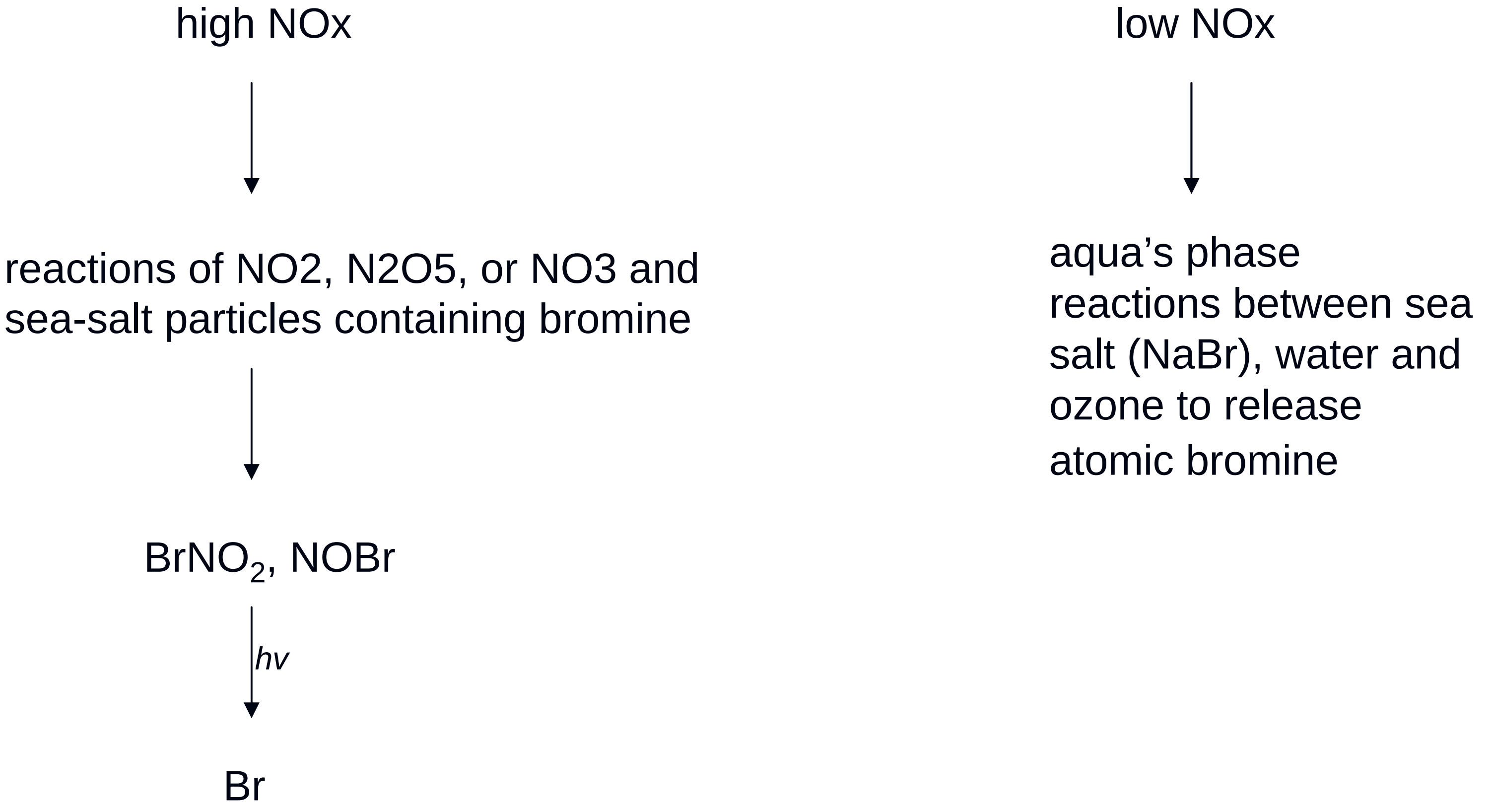
The Ocean to Air Flux of Methyl Iodide (2)



$9.2 \cdot 10^{-11}$ g/cm^2 in Southtern Pacific (Shon and Kim 2002)
$2.3 \cdot 10^{-10}$ g/cm^2 in Pacific (Moore and Groszko 1999)
$3.5 \cdot 10^{-10}$ g/cm^2 in Atlantic (Moore and Groszko 1999)

Ozone Decay Due to Heterogeneous Chemistry

Ozone reactions with reactive halogens in association with sea-salt aerosols may lead to ozone destruction in the marine boundary layer just after sunrise [Nagao et al. 1999]



high NOx

reactions of NO2, N2O5, or NO3 and sea-salt particles containing bromine

BrNO$_2$, NOBr

$h\nu$

Br

low NOx

aqua’s phase reactions between sea salt (NaBr), water and ozone to release atomic bromine

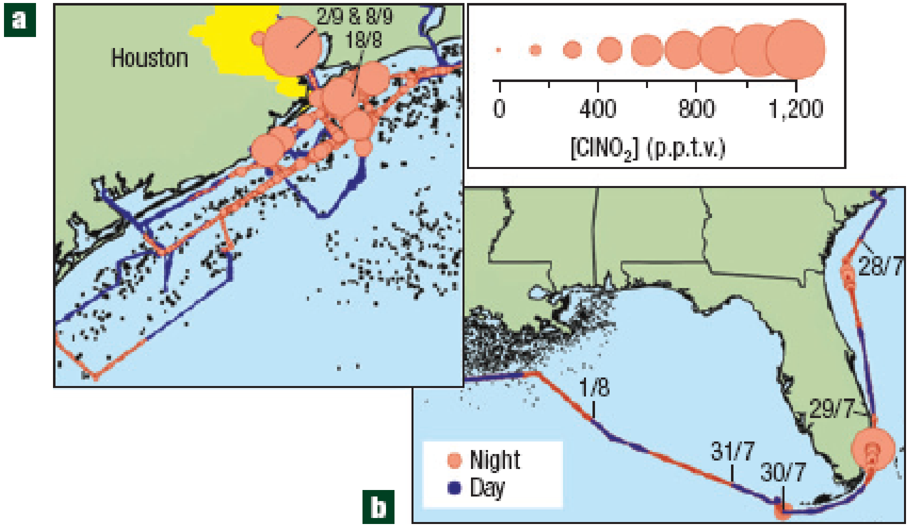
Importance of Nitryl Chloride $ClNO_2$ in the Polluted MBL

High levels of nitryl chloride in the polluted subtropical marine boundary layer,
Osthoff et al. Nature Geoscience, April 2008

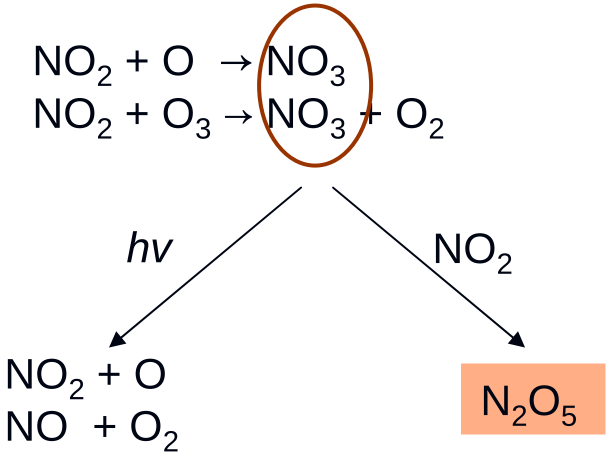
$$NaCl_{(s,aq)} + N_2O_5 \rightarrow ClNO_2 + NaNO_{3\,(s)}$$

$$\Big\downarrow hv$$

$$Cl + NO_2$$



- ☐ correlation of $ClNO_2$ concentrations to N_2O_5, which is a source of $ClNO_2$



$$NO_2 + O \rightarrow NO_3$$
$$NO_2 + O_3 \rightarrow NO_3 + O_2$$

hv

NO_2

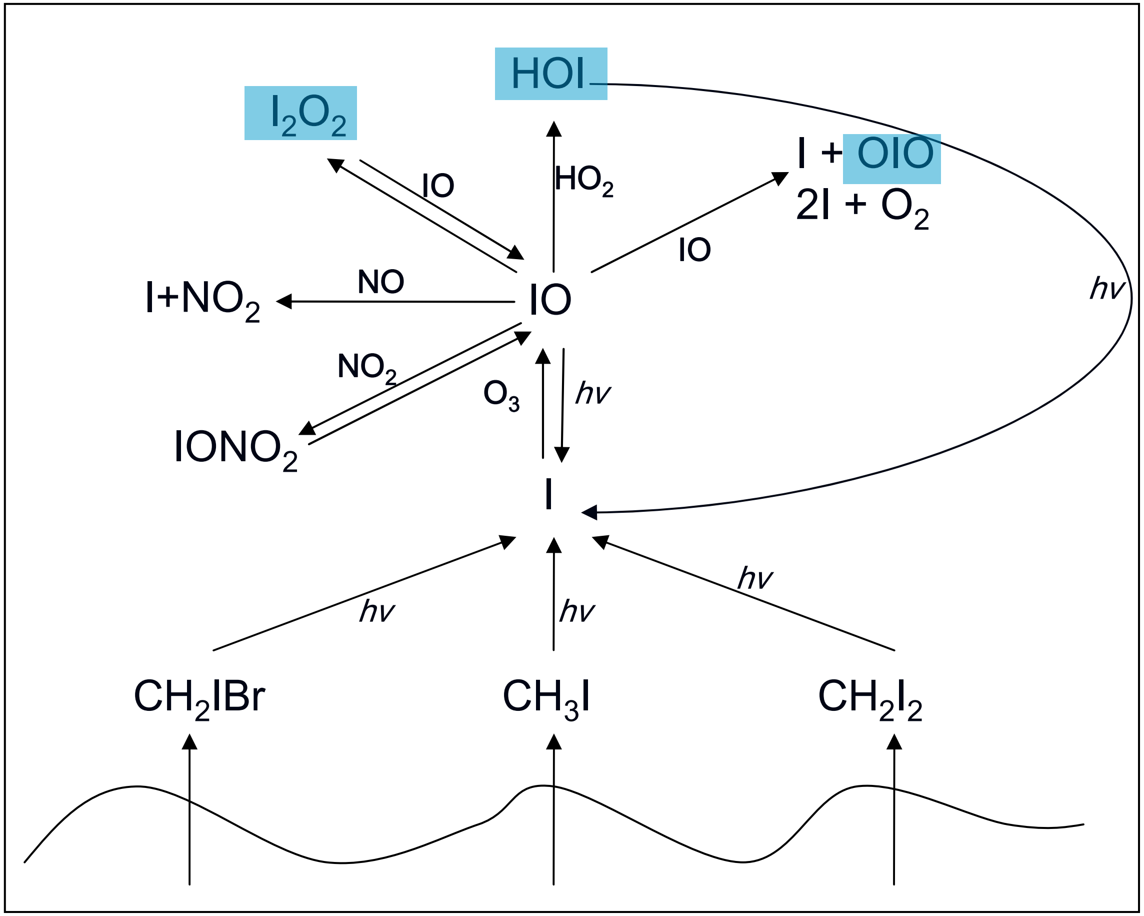
$$NO_2 + O$$
$$NO + O_2$$

N_2O_5

Particle Formation from Iodocarbons

The particles present in the marine boundary layer may act as cloud condensation nuclei (CCN) which are origins of marine clouds.

🟦 condensable iodine vapors (CIV)



- New particle formation through nucleation, condensation and coagulation;
- Condensation on existing thermodynamically stable cluster embryos, such as ammonium sulfate clusters

Project will not be continuing …

- PI now with NOAA Air Resources Lab
- To work on CMAQ/PM modeling issues continuously

References

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