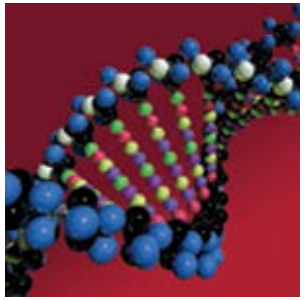
Modeling ozone depletion in the marine boundary layer caused by natural iodine emissions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Acknowledgment

Sponsored by the Texas Commission on Environmental Quality

Background

- Ozone modeling for Texas with CAMx using 2-way nested 36, 12, 4 km grids
  - Houston/Galveston/Brazoria
  - Dallas/Fort-Worth
  - Near-nonattainment areas
    - Austin
    - Beaumont/Port-Arthur
    - Corpus Christi
    - El Paso
    - Northeast Texas
    - San Antonio
    - Victoria
    - Waco
- Several areas of interest located on the Gulf Coast

CAMx ei_tx_4km Domain

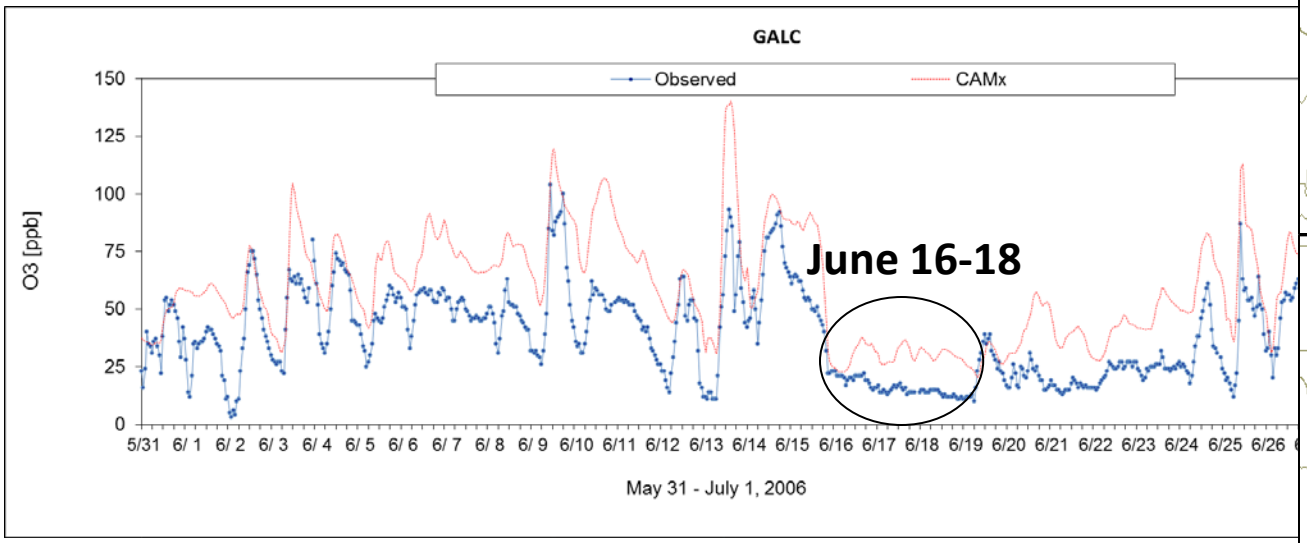
CAMx tx_12km Domain

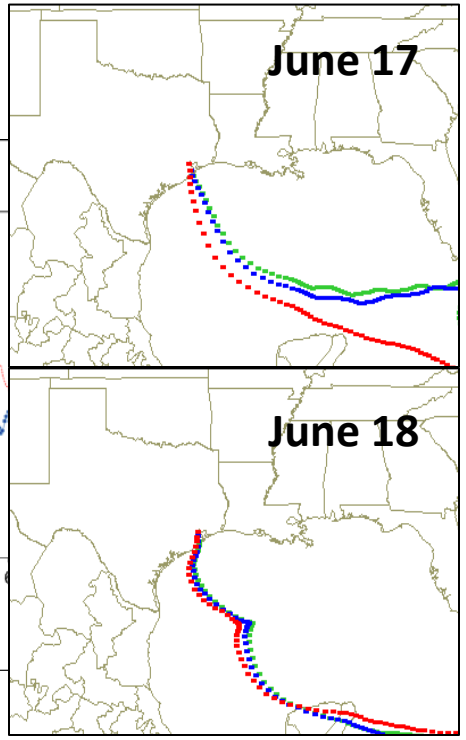
CAMx us_36km Domain

CAMx rpo_36km Domain

Background

Ozone at Galveston: June 2006

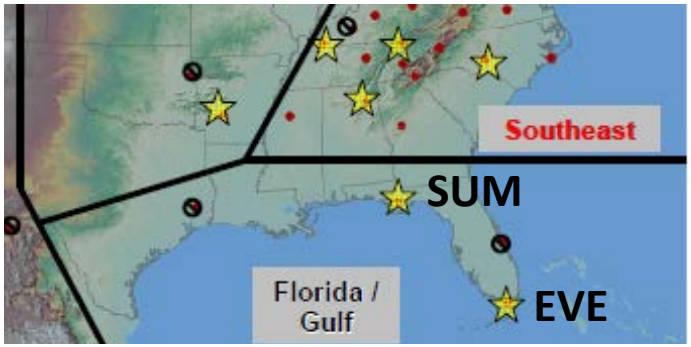


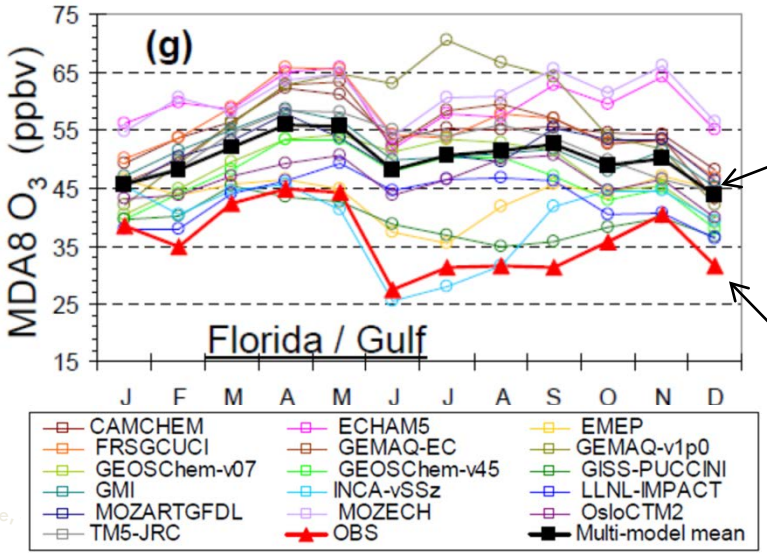


- Ozone over-predicted at monitors on the Gulf Coast
  - Example shows Galveston for June 2006
  - Observed ozone only15-20 ppb during persistent onshore flow
  - CAMx regional model biased high by 10-15 ppb
- Many global models biased high for Gulf Coast (next slide)

Ozone Bias in Global Models for the Gulf

- 20 global models compared in HTAP 2007 interim assessment
  - Task Force on Hemispheric Transport of Air Pollution
- Models compared to Sumatra and Everglades CASTNET monitors in Florida
  - Observed summer minimum in MDA8 O_3 (June-September)
  - Most models over predict, including GEOS-Chem and MOZART
  - Fiore et al (2008) and Reidmiller et al. (2009; www.atmos-chem-phys.net/9/5027/2009/)





Multi-Model Mean

Observed average of SUM and EVE

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Several Potential Causes Investigated

- Ozone deposition velocity too low over water
  - Improved CAMx using $V_d(O_3)$ measurements from TexAQS 2006
  - Tended to increase ozone
- CAMx ozone boundary condition (from GEOS-Chem) too high over the Gulf
  - Most global models are biased high over the Gulf
  - Potential explanations: coarse resolution (~200 km) and lacking iodine chemistry
- Iodine chemistry destroys ozone over the Gulf
  - Chemistry proposed in early 1990s and well documented
  - CAMx shows potential ozone reductions of ~5 ppb over Gulf
  - Bromine also destroys ozone and is synergistic with iodine

Ozone Depletion by Iodine

- I-atoms destroy ozone catalytically
  - Single I-atom can destroy hundreds of O_3 molecules
- Proposed by Chameides and Davis (1980)
  - Confirmed by field studies in Ireland, tropical Atlantic (Cape Verde Islands), Tasmania, etc.
  - Very active research field driven by interest in particle nucleation by iodine oxides (I_2O_4, I_2O_5, etc.)
- Why do iodine and chlorine behave differently?
  - Cl-atoms react with VOCs, I-atoms don't
  - I-atoms destroy O_3 unless stored in a temporary reservoir or converted to aerosol
  - Br-atoms more like I than Cl

Chemical Mechanisms

Cycle 1: IO + IO cycle

$$(I + O_3 \rightarrow IO + O_2) \times 2$$

$$IO + IO \rightarrow OIO + I$$

$$OIO + hv \rightarrow I + O_2$$

$$2O_3 \rightarrow 3O_2$$

Cycle 2: IO + HO_2 cycle

$$I + O_3 \rightarrow IO + O_2$$

$$IO + HO_2 \rightarrow HOI + O_2$$

$$HOI + h\nu \rightarrow I + OH$$

$$HO_2 + O_3 \rightarrow OH + 2O_2$$

Cycle 3: IO + NO_2 cycle

$$I + O_3 \rightarrow IO + O_2$$

$$IO + NO_2 \rightarrow IONO_2$$

$$IONO_2 + h\nu \rightarrow I + NO_3$$

$$NO_3 + h\nu \rightarrow NO + O_2$$

$$NO + O_3 \rightarrow NO_2 + O_2$$

$$2O_3 \rightarrow 3O_2$$

Reactive iodine species in a semi-polluted environment

Anoop S. Mahajan,[1] Hilke Oetjen,[1] Alfonso Saiz-Lopez,[2] James D. Lee,[3] Gordon B. McFiggans,[4] and John M. C. Plane[1]

GEOPHYSICAL RESEARCH LETTERS, VOL. 36, L16803, doi:10.1029/2009GL038018, 2009

- Cycle 2 favored at low NOx e.g. in un-polluted marine boundary layers
- Cycle 3 can operate at high NOx
- All cycles begin with I + O_3 => IO + O_2 and differ in how IO is converted back to I
- The sum of I + IO indicates potential for ozone destruction; I + IO observed at ppt concentrations during daylight

CAMx Iodine Mechanism

- Implemented for CB6
  - 33 reactions of 17 iodine-containing species
  - Easily implemented for other mechanisms

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Oceanic Emissions of I-atom Precursors

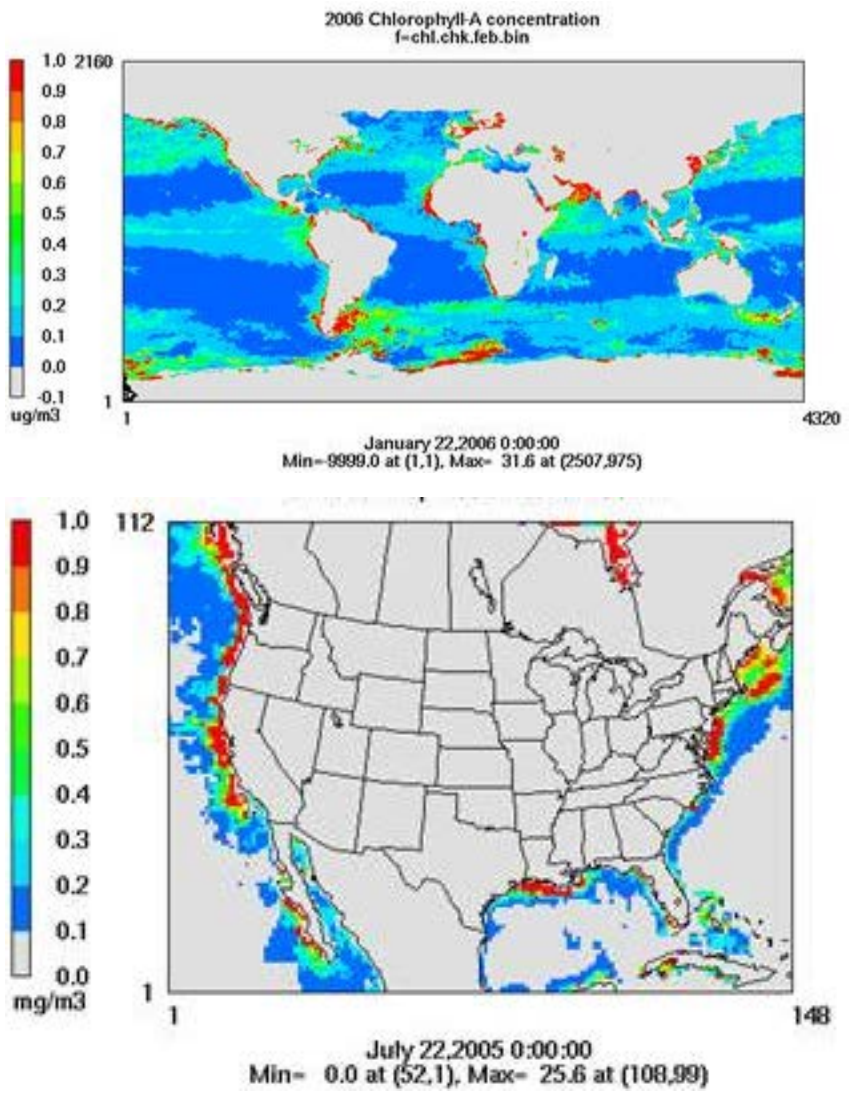
- Volatile organo-iodine compounds (VOIs)
  - CH_3I, CH_2I_2, CH_2ClI, CH_2BrI (halo-methanes)
  - Photolysis liberates I-atoms in days to minutes
  - Photobiological source of VOIs
    - Macroalgae (seaweed)
  - Photochemical source of VOIs
    - Sunlight and dissolved organic carbon (DOC)
- Molecular iodine (I_2)
  - Photolysis to I-atoms occurs in minutes
  - Reaction with NO_3 at night produces I-atom
  - Emissions may result from reactions of deposited O_3

Oceanic VOI Emissions for CAMx

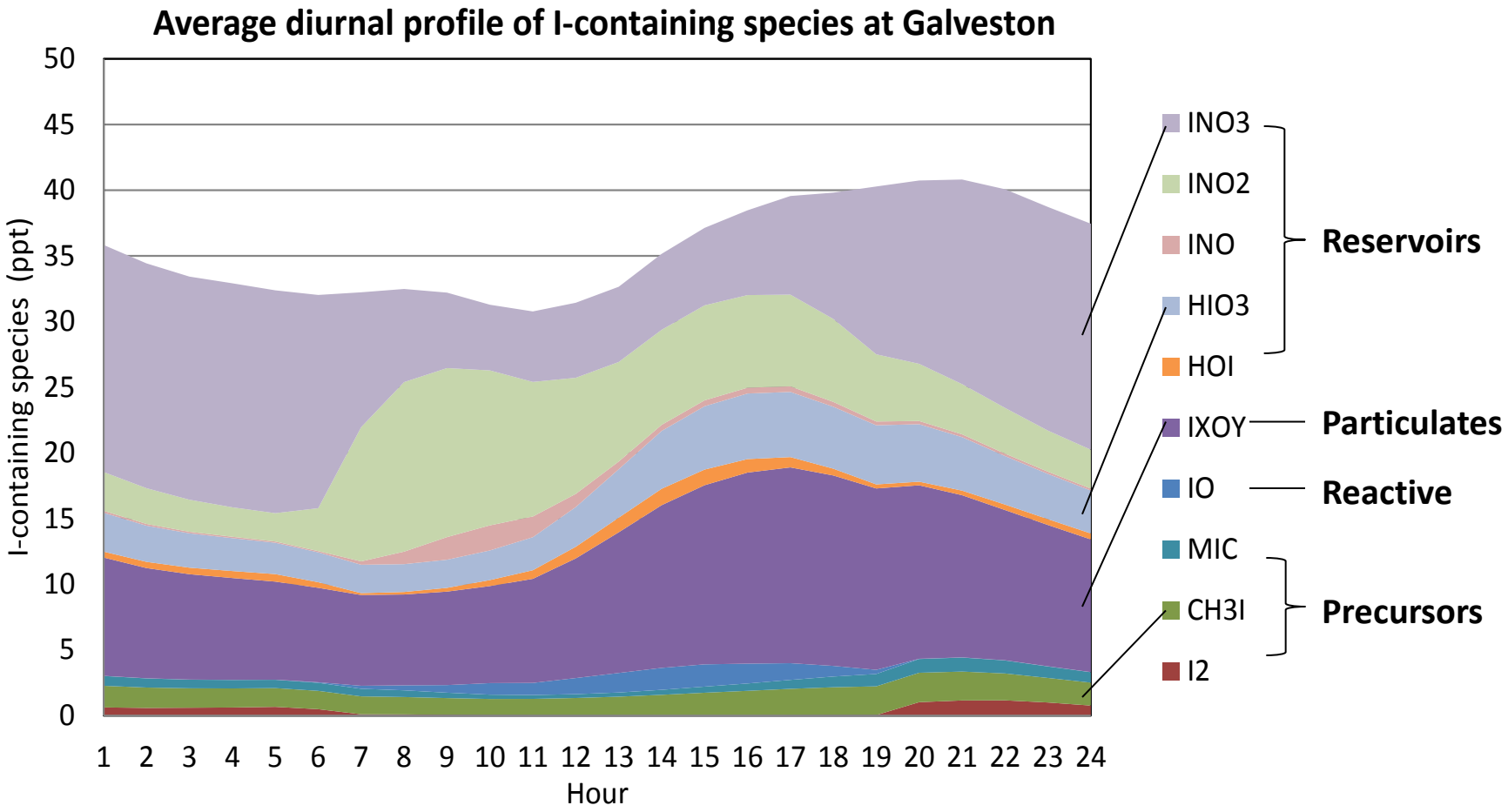
- Organic iodine emissions based on water content of chlorophyll-a
  - SeaWiFS satellite data provide global coverage, monthly averages
- Calibrated to global emission estimates

VOI Species	Emission (Gg/yr)
CH3I	213
CH2I2	234
CH2IBr	87
CH2I2	116

2006 Chlorophyll-a (ug/m^3) from SeaWiFS

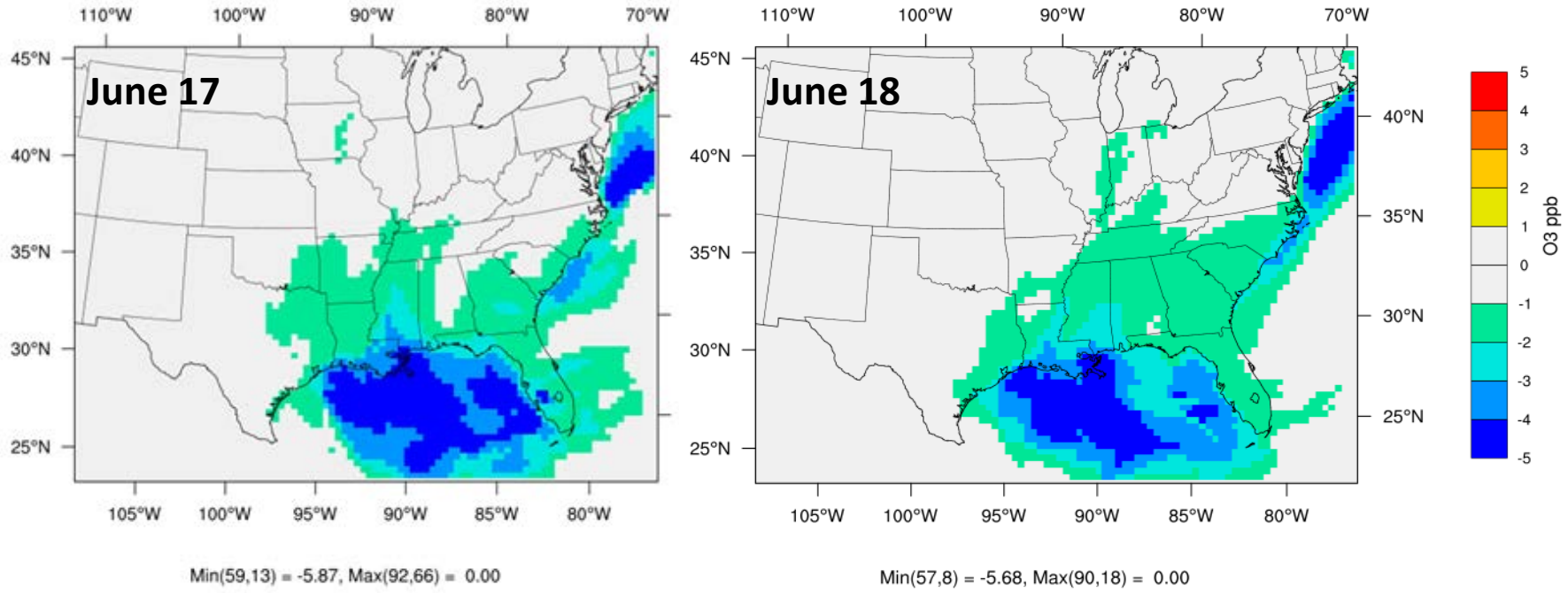


Iodine Speciation at Galveston, TX



Monthly average diurnal profile for species containing 1% or more of iodine

Ozone Depletion by Iodine Chemistry



- Change in MDA8 O_3 due to iodine emissions/reactions on days with persistent onshore flow
- ~5 ppb ozone reductions over wide areas of Gulf
- Reductions influence coastal monitors and cities

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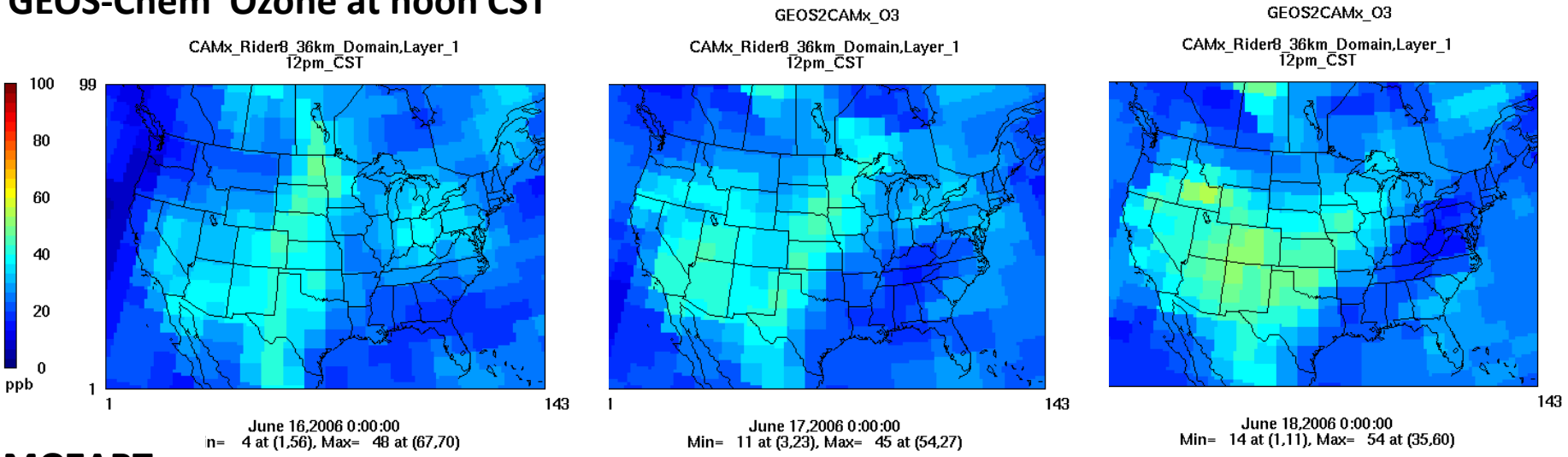
Iodine Chemistry Conclusions and Recommendation

- Iodine chemistry could cause up to ~5 ppb ozone depletion over the Gulf and at coastal monitors
  - Emissions are uncertain
  - Chemistry is uncertain, but constrained to match field studies
- Field studies find that Bromine and Iodine cause comparable ozone depletion, and acted synergistically
  - Also include bromine emissions/reactions
- Consider potential interaction between ozone deposition and I_2 emission from oceans
  - High ozone concentrations raise ozone deposition, raise I_2 emission, raise ozone destruction rate by iodine chemistry

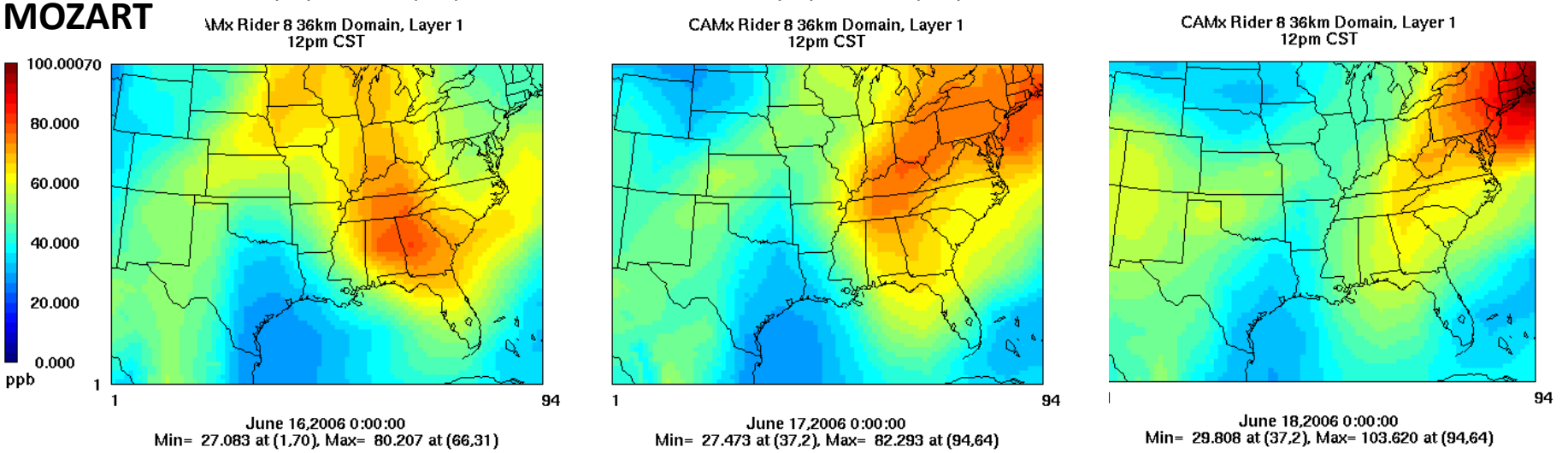
End

GEOS-Chem and MOZART: June 16-18, 2006

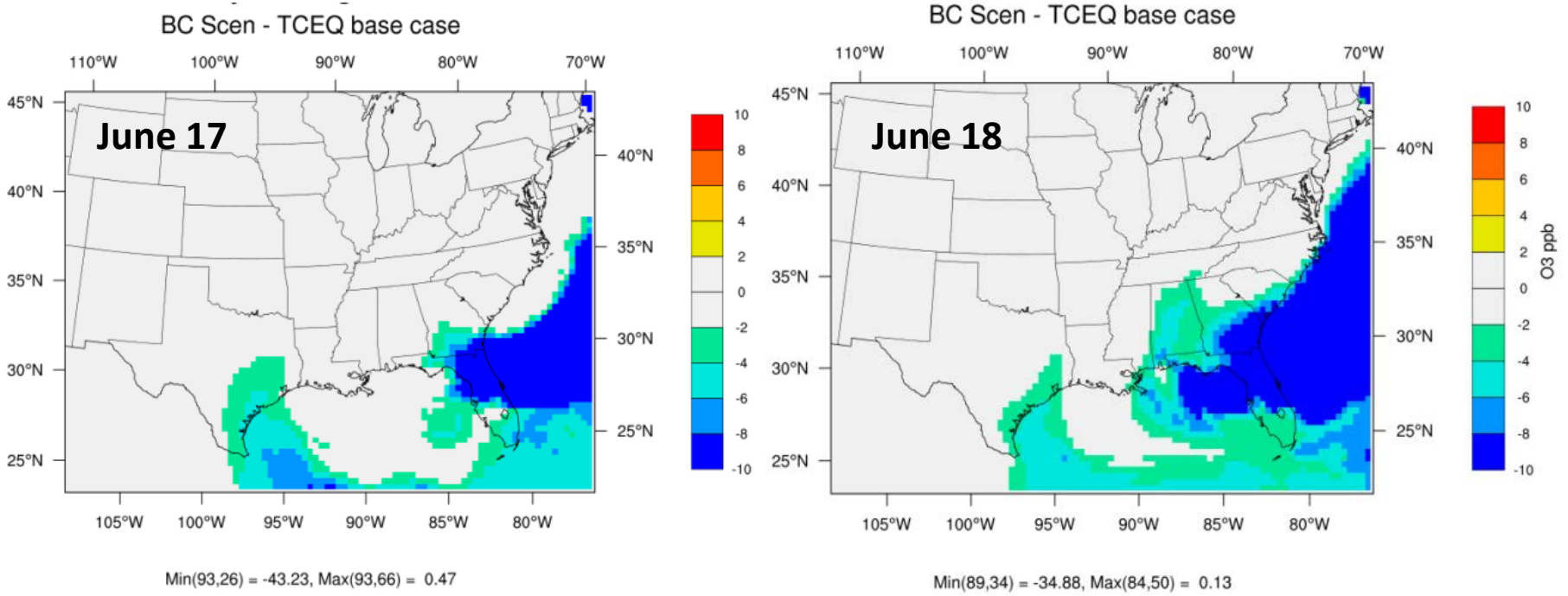
GEOS-Chem Ozone at noon CST



MOZART



Ozone Sensitivity to CAMx Boundary Conditions



Difference in MDA8 ozone on June 17 and 18, 2006 due to capping the Ozone BCs over the Gulf of Mexico and Atlantic Ocean to values from the tropical Atlantic