Modeling Hg(II) reduction through condensed phase photochemistry with dicarboxylic acids

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2011 CMAS Conference, October 25th
Chapel Hill, NC

Outline

- Overview of aqueous phase reduction and motivation
- Model simulations
  - Condensed phase reduction schemes
    - None, $HO_2^{\cdot}$, C2-C4 dicarboxylic acids (DCA)
  - July-August and January-February simulations
- Evaluation against MDN observations
  - Domain wide statistics
  - Regional differences
- Conclusions

Office of Research and Development
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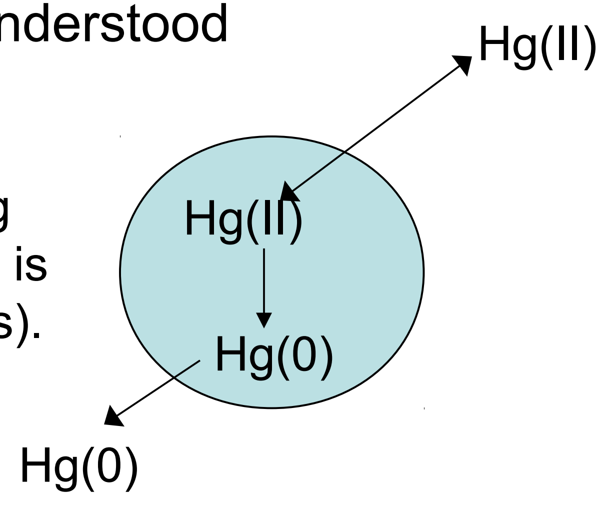
Atmospheric Hg

- Mercury deposition is the primary source of mercury contamination in ecosystems
  - Reactive gas phase mercury, Hg(II), deposits readily
  - Gaseous elemental mercury, Hg(0), not as apt to deposit through wet and dry pathways
  - Atmospheric Hg is primarily (~99%) present as Hg(0)
- In soils or the water column Hg can be transformed into organic Hg compounds
  - Potent neurotoxins
- Hg(II) is reduced in cloud droplet to form Hg(0)
  - Though mechanisms are not well-understood

Hg(II) is reduced to Hg0 during aqueous processing, but there is debate about the mechanism(s).



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Motivation

- Most atmospheric models parameterize condensed phase Hg(II) by $HO_2^{\cdot}$ or scaled to OH
  - Reduction by $HO_2^{\cdot}$ has been shown to be improbable under environmental conditions
  - Scaled rates do not represent real atmospheric chemical processes
- Recent laboratory experiments (Si and Ariya, 2008; Bartels-Rausch et al 2011) and observations (Wang and Hintelmann, 2009) indicate photoinduced reduction of Hg(II) by DCA
  - Second order photoreduction of Hg(II) observed with oxalic, malonic and succinic acids
- A reduction mechanism proposed by Si and Ariya, 2008 is investigated in a regional scale modeling study

Model Simulations

- Changes to aqueous phase Hg chemistry
  - CMAQ estimates cloud secondary organic aerosols (SOA)
    - Oxalic acid is the dominant product of glyoxal oxidation and dominates over other DCAs
  - Same model run but the cloud SOA (primarily oxalic acid) reduction pathway instead of $HO_2^{\cdot}$
- 2002 January-February and July-August model runs
  - No condensed phase, $HO_2^{\cdot}$ and DCA reduction mechanism cases simulated
  - Evaluated against mercury deposition network (MDN) wet deposition observations

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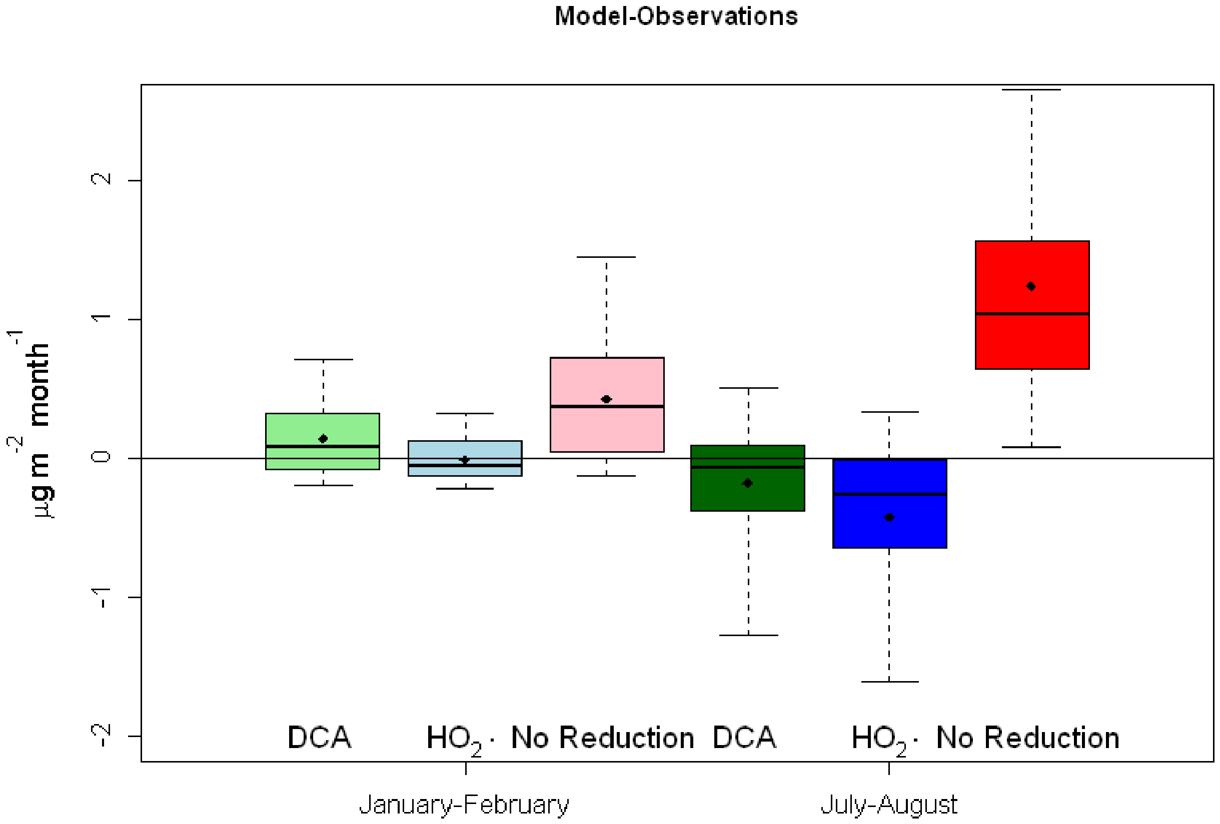
Domain Wide Evaluation

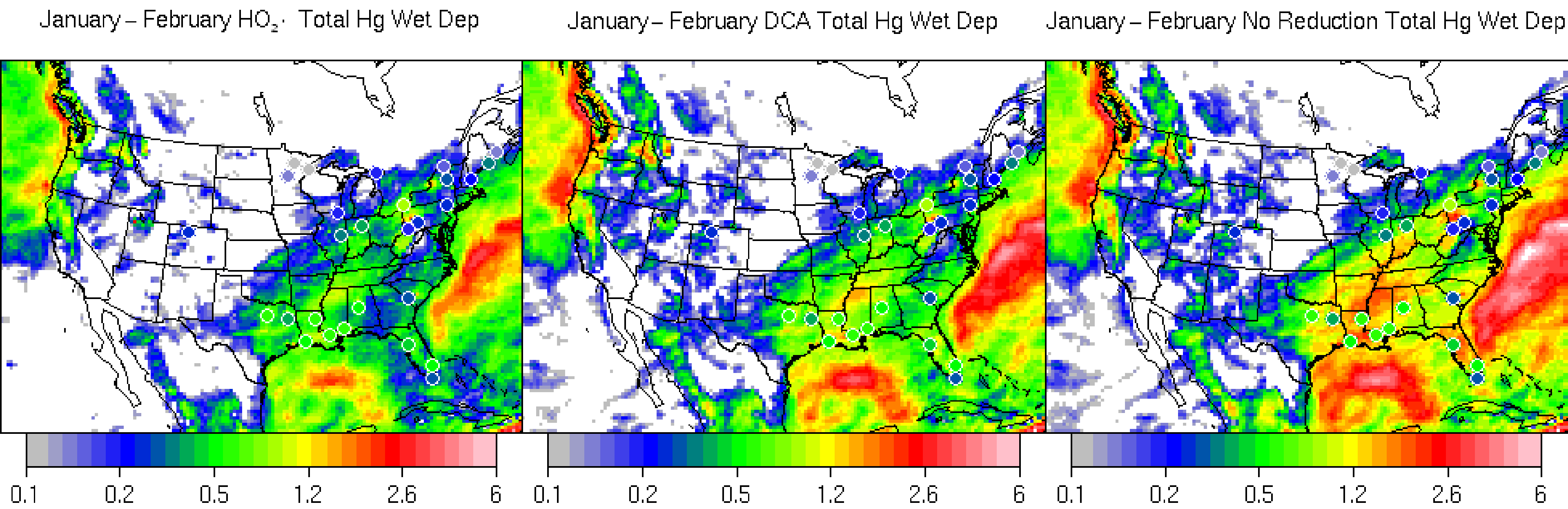


- Reduction scheme is necessary to capture observations
- DCA mechanism reduced bias and error in wet deposition estimates in July-August simulations
- DCA mechanism increased bias and error in wet deposition estimates in January-February simulations

Domain Wide Evaluation

		r	MB	ME	NMB	NME
MM5 Precip.	Jan. -Feb.	0.815	4.2 mm mon^{-1}	16.9 mm mon^{-1}	9.0%	37.5%
	Jul. -Aug.	0.729	33.7 mm mon^{-1}	59.3 mm mon^{-1}	74.4%	132.3%
No Reduction	Jan. -Feb.	0.726	0.423 μg m^{-2} mon^{-1}	0.471 μg m^{-2} mon^{-1}	111%	123%
	Jul. -Aug.	0.787	1.233 μg m^{-2} mon^{-1}	1.234 μg m^{-2} mon^{-1}	117%	117%
HO2 Reduction	Jan. -Feb.	0.718	-0.014 μg m^{-2} mon^{-1}	0.149 μg m^{-2} mon^{-1}	-4%	39%
	Jul. -Aug.	0.655	-0.428 μg m^{-2} mon^{-1}	0.508 μg m^{-2} mon^{-1}	-41%	48%
DCA Reduction	Jan. -Feb.	0.714	0.139 μg m^{-2} mon^{-1}	0.231 μg m^{-2} mon^{-1}	36%	60%
	Jul. -Aug.	0.738	-0.184 μg m^{-2} mon^{-1}	0.381 μg m^{-2} mon^{-1}	-17%	36%

Jan.-Feb. Hg Wet Deposition



- Less variability between model simulations than July-August simulations
- DCA over predicted wet deposition in Gulf States
- Jan.-Feb. wet deposition more sensitive to boundary condition Hg(II) concentrations

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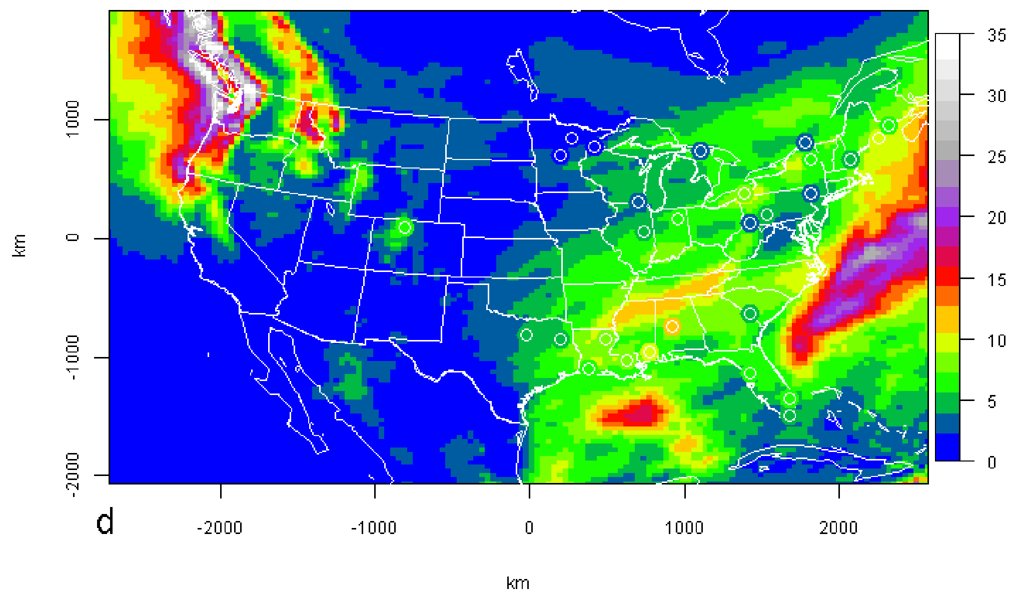
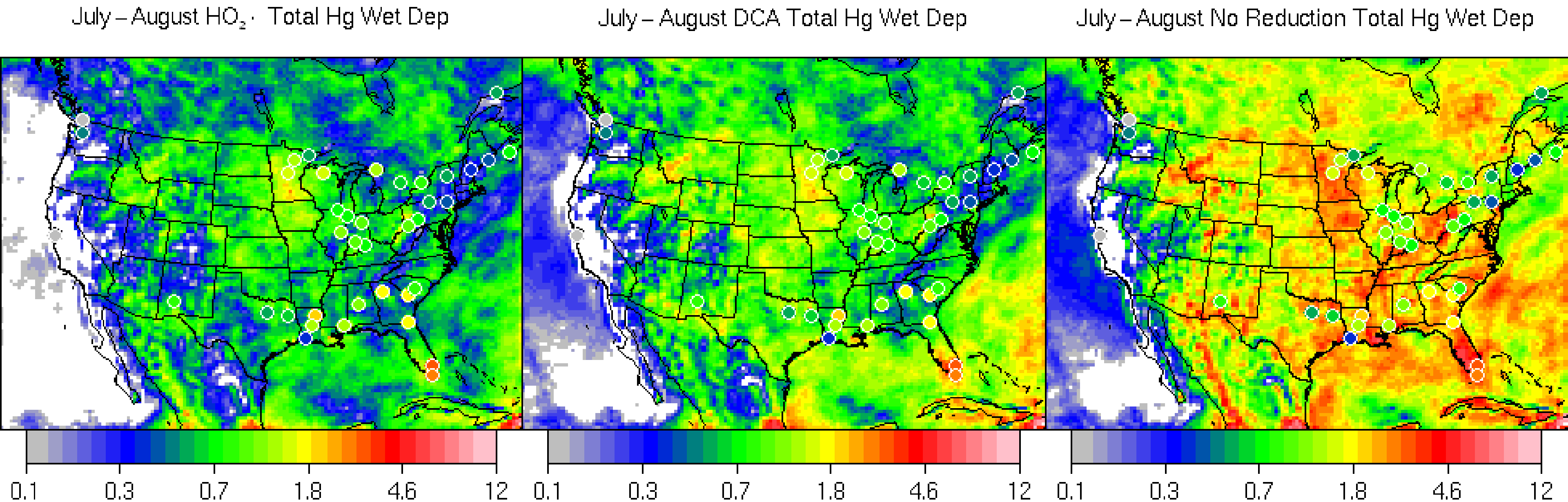
Jan.-Feb. Precipitation

January-February Precipitation cm



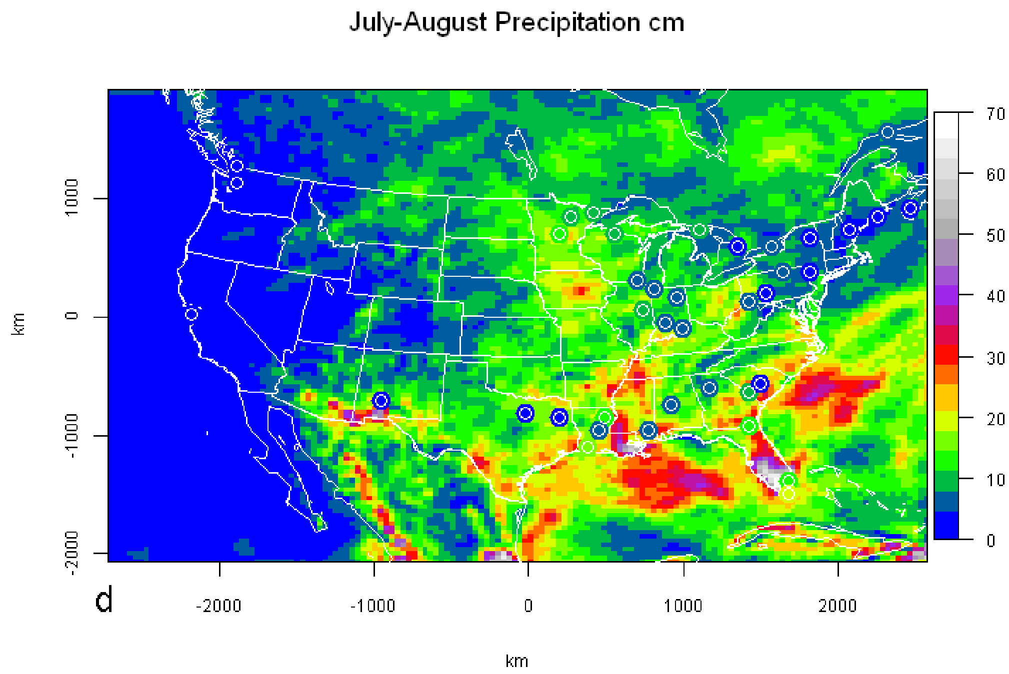
- Precipitation is over estimated in the North East

July-August Hg Wet Deposition



- DCA mechanism reduces under prediction in Southeast and Midwest
  - Increases wet deposition in the west and over the oceans where observations are sparse
- No reduction scheme over predicts wet deposition domain wide

July-August Precipitation



- Precipitation is over estimated in the south and around Indiana
- Bias in TX and IA correspond to model over estimates in the DCA and no reduction cases

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Conclusions

- Condensed phase reduction of Hg(II) by DCA has been parameterized in CMAQ
  - More probable than $HO_2^{\cdot}$ and more physically descriptive than scaled reduction mechanisms
- Improved July-August total Hg wet deposition performance when compared to MDN observations
  - When Hg total deposition peaks in most locations
- Some degredation in January and February wet deposition performance
  - Absolute increase in Jan. & Feb. bias is less than the improvements in July & Aug.
  - May be related to model boundary conditions
- Available in CMAQ 5.0 Multipollutant

Questions?