ATMOSPHERIC DEPOSITION OF NUTRIENTS AND CONTAMINANTS

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2008 Greater Everglades Ecosystem Restoration Conference, July 28 – August 1
Naples, FL

Objectives

- Provide an overview of the importance of atmospheric deposition as a contributing source or flux of three key contaminants to the Everglades –

  Mercury
  Sulfur
  Phosphorus

- Examine the implications of these fluxes and inherent uncertainties with respect to Everglades restoration

Forms of Atmospheric Deposition

- **Wet Deposition**
  - Scavenging of airborne particulates and gases by rainfall
- **Dry Deposition**
  - Gravitational settling of airborne particulates
  - Impaction of particles and gases to surfaces (*e.g.*, vegetative surfaces, aquatic surfaces)

Atmospheric Fluxes of Hg to a Forested Canopy

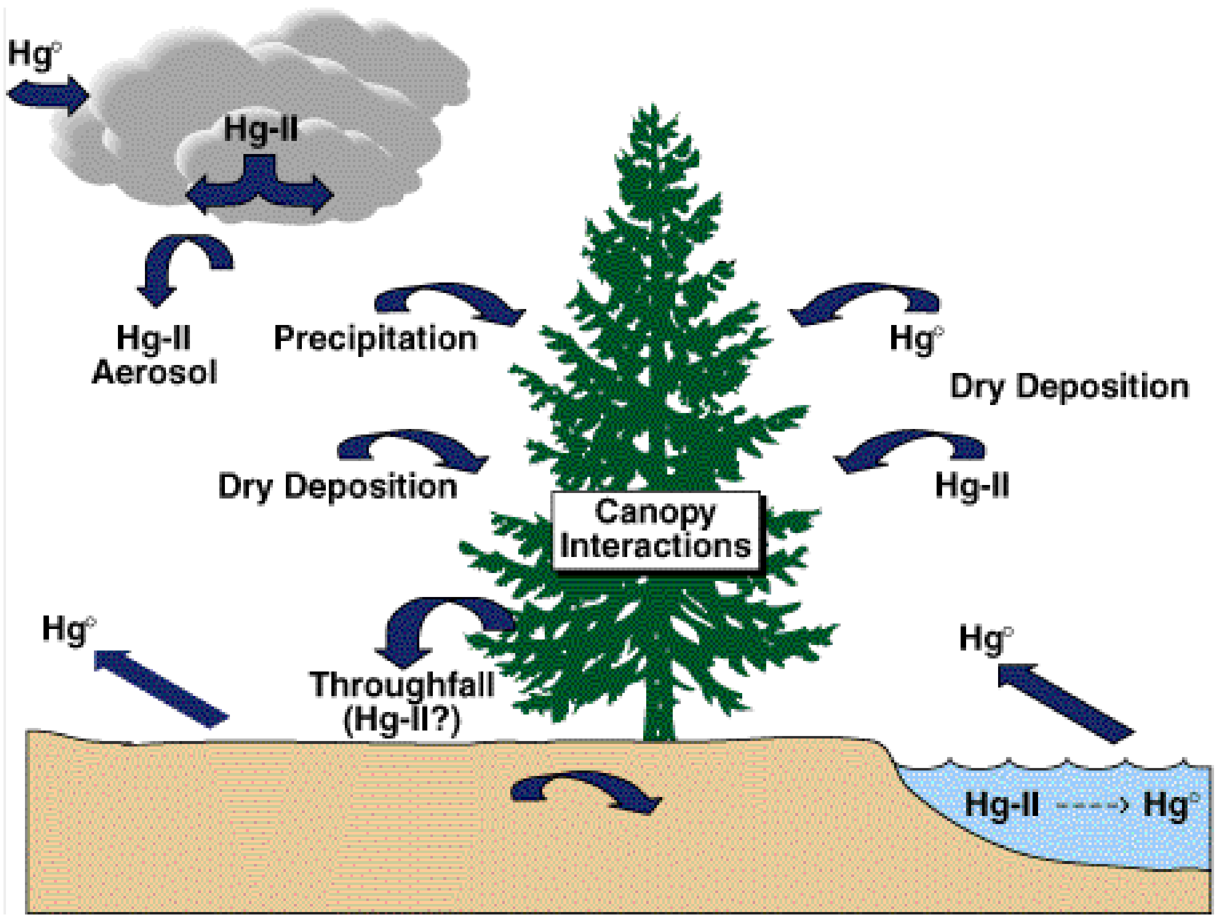


Figure from http://www.esd.ornl.gov/iab/iab4-17.htm

Wet Deposition Monitoring
NADP/MDN Site FL11, ENP Beard Research Center

http://nadp.sws.uiuc.edu/sites/siteinfo.asp?id=FL11&net=NTN

Dry Deposition Measurements

- Direct Methods
  - Surface analysis (*e.g.*, foliar extraction, throughfall and stemflow, surrogate surfaces, isotopic tracers, watershed mass balance)
  - Atmospheric flux methods (*e.g.*, eddy correlation and gradient method where ambient measurements are combined with micrometeorological measurements to determine flux)
- Indirect Methods
  - Concentration monitoring

    Based on: $F = V_{dep} \times C$
  - Inferential monitoring – involves additional measurements to refine estimate of V_{dep}

Summary of Major Studies of Contaminant Deposition in South Florida and the Everglades

Study	Wet	Bulk	Dry
	Mercury		
Guentzel *et al.* (2001)	Yes	Yes	$Hg_{particulate}$
Dvonch *et al.* (1999)	Yes		$Hg_{particulate}$
Marsik *et al.* (2007)			Surrogate water surface; inferential model coupled with Hg speciation
MDN (1996 – present)	Yes	No	No
Atkeson *et al.* (2003)	Modeled		Modeled

Summary of Major Studies of Contaminant Deposition in South Florida and the Everglades

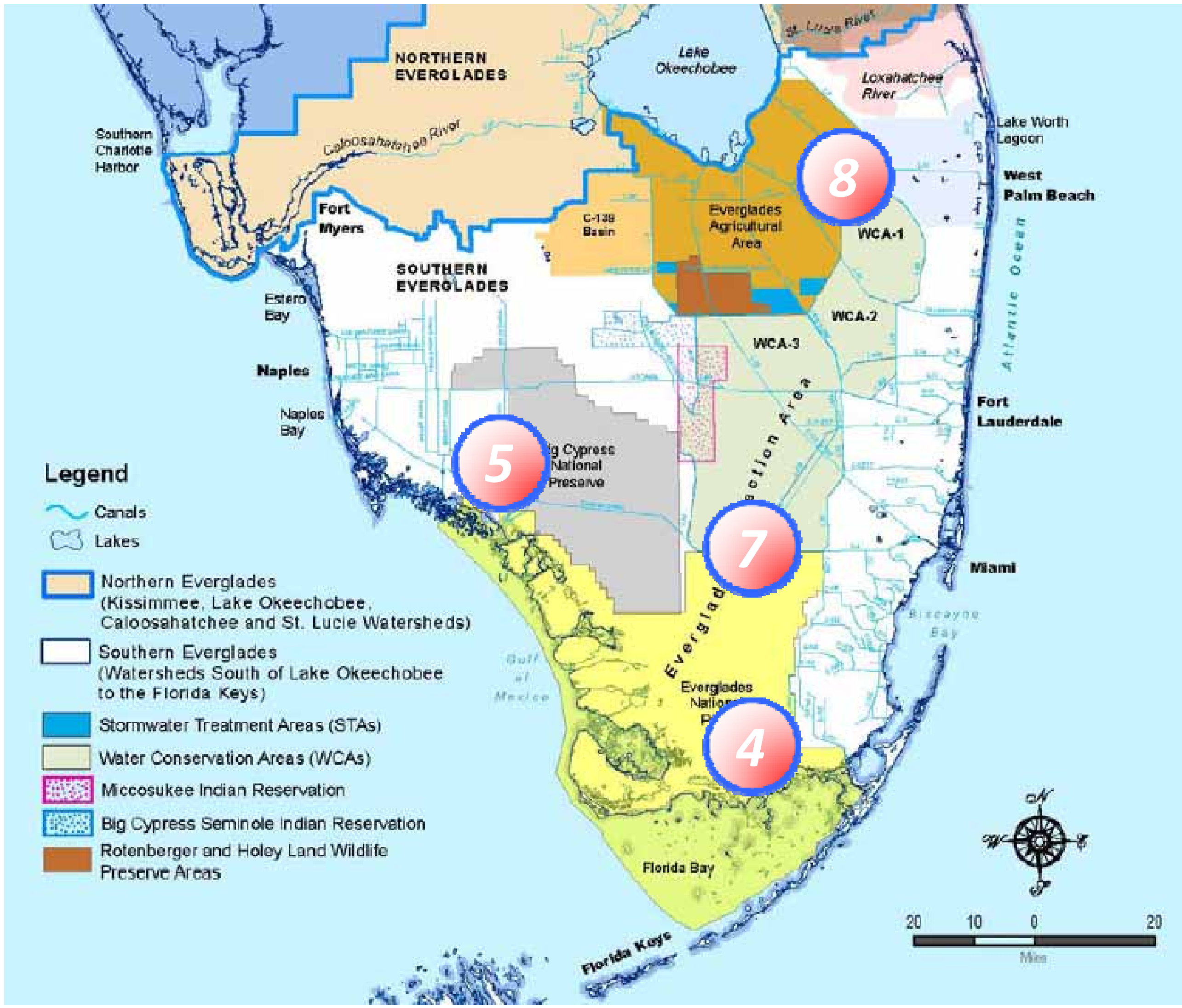
Study	Wet	Bulk	Dry
		Phosphorus	
Brezonik *et al.* (1983)	Yes	Yes	Yes
Pollman *et al.* (2002)	Yes	Yes	No
Ahn and James (1999, 2001)	Yes		Yes
		Sulfate	
NADP (1980 – present)	Yes	No	No
CASTNET (1998 – present)			Ambient air measurements of S species coupled with estimates of v_{dep} from meteorology

Wet and Dry Deposition of TN and TP at Four Sites in Florida. From Brezonik*et al.* (1983)

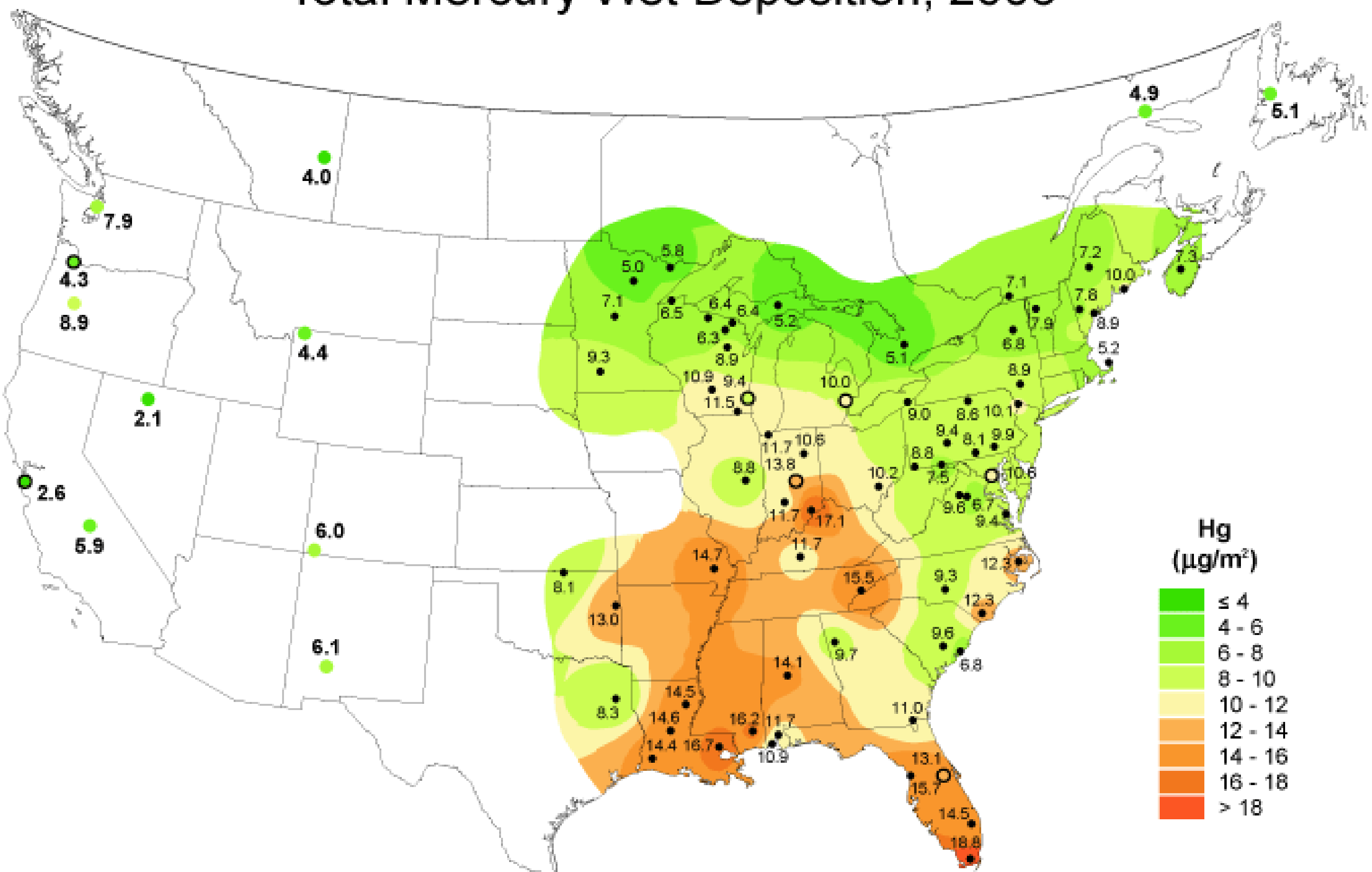
	TN g/m²-yr			TP mg/m²-yr		
Site	Wet	Dry	Total	Wet	Dry	Total
Gainesville	0.63	0.28	0.91	16	42	58
Cedar Key	0.52	0.25	0.77	6	18	24
Apopka	0.47	0.34	0.81	9	48	57
Belle Glade	0.64	0.49	1.13	12	84	96
Mean	0.57	0.34	0.91	11	48	59
% Wet			63			19

Wet Deposition of TP (µg/L) in the Everglades

Data from Pollman *et al.* (2002)

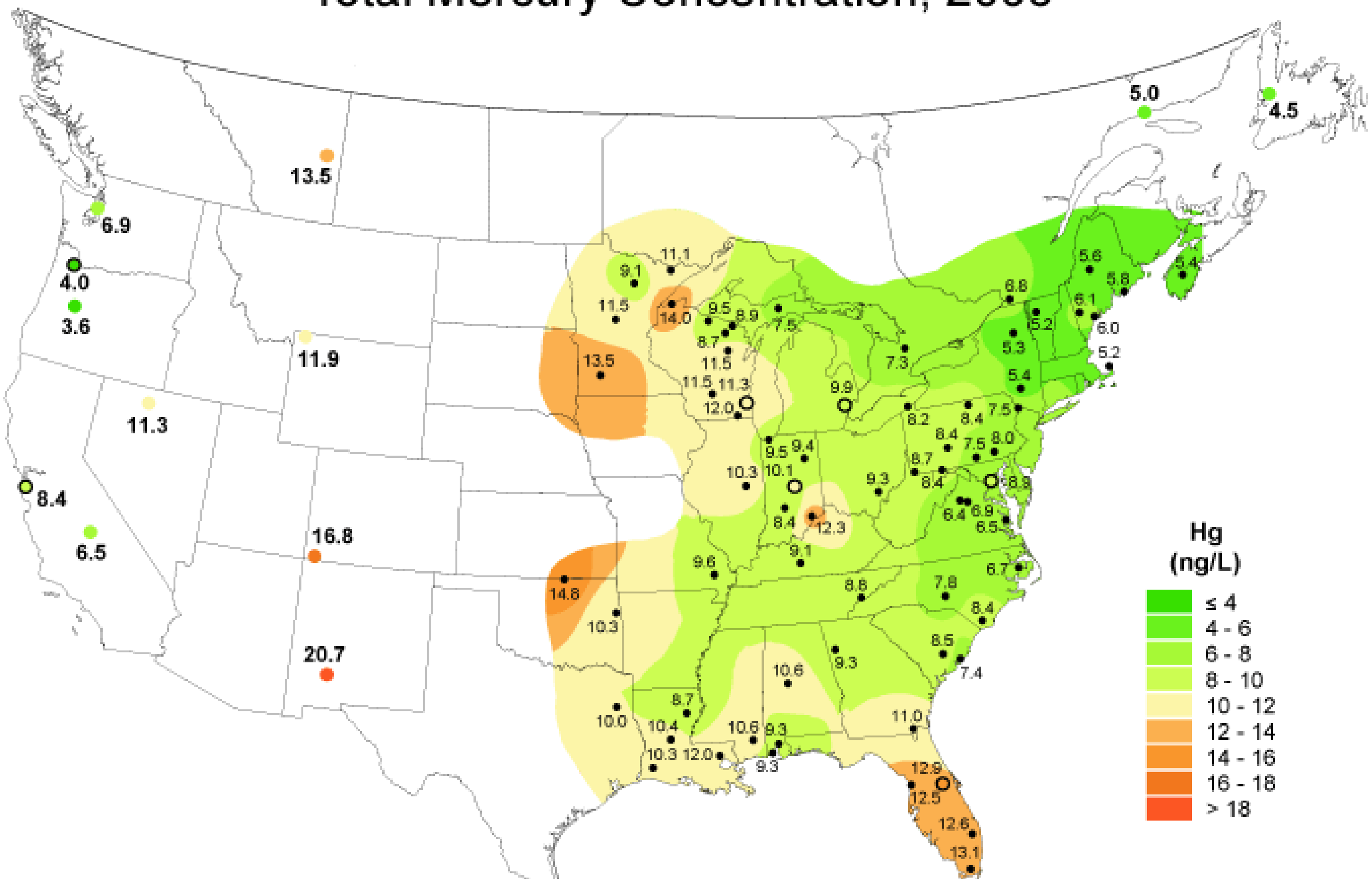


Total Mercury Wet Deposition, 2006



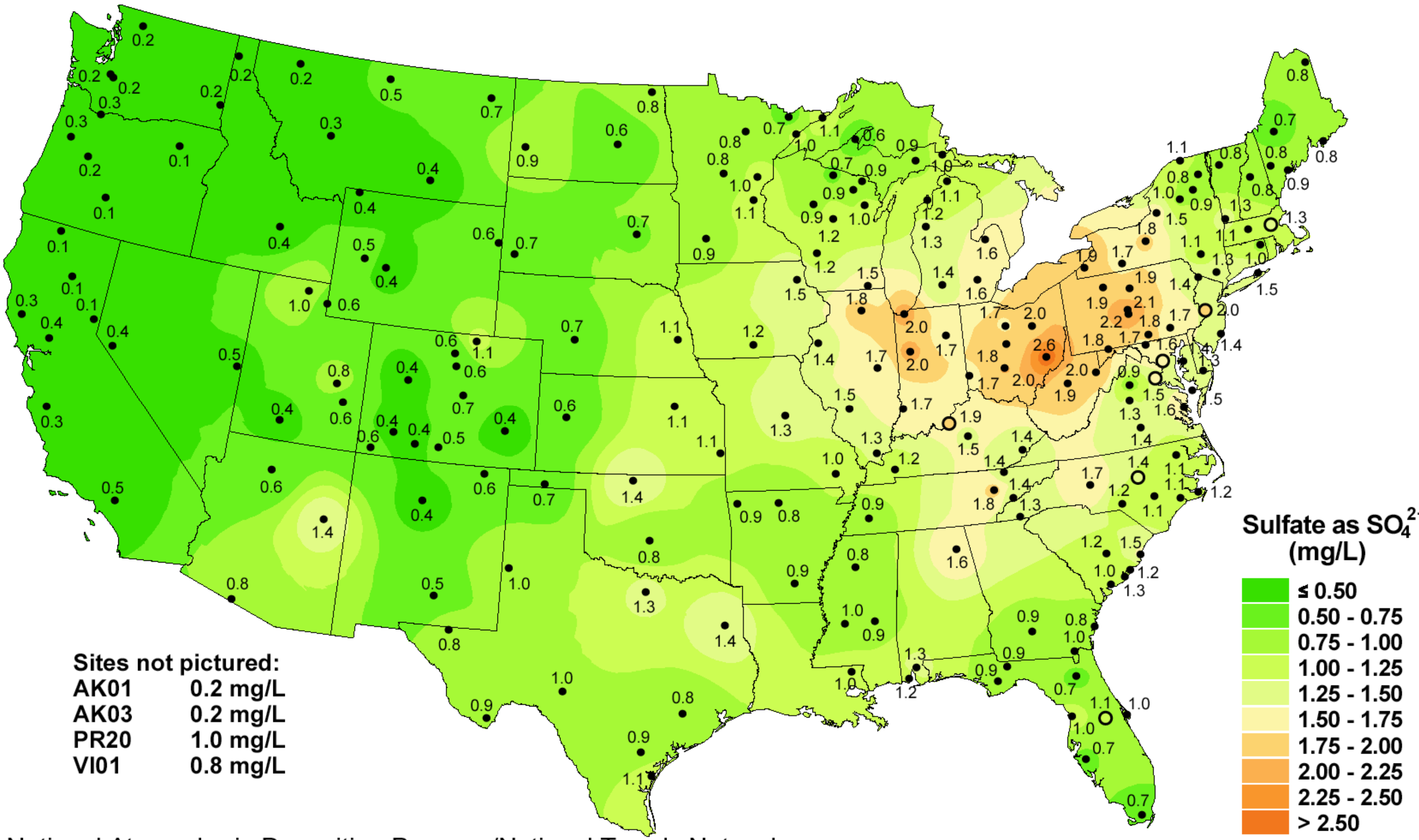
National Atmospheric Deposition Program/Mercury Deposition Network

Total Mercury Concentration, 2006



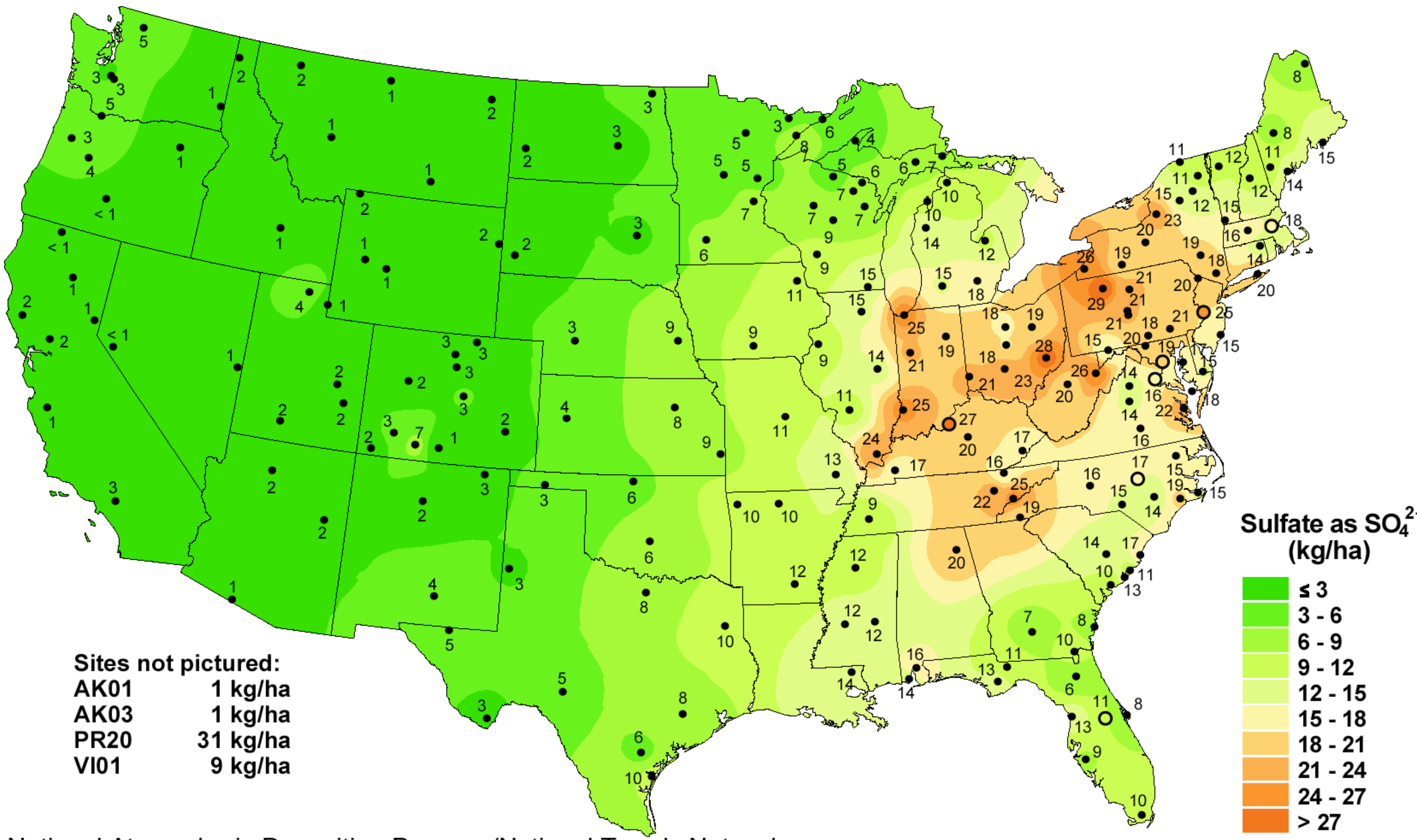
National Atmospheric Deposition Program/Mercury Deposition Network

Sulfate ion concentration, 2006



National Atmospheric Deposition Program/National Trends Network
http://nadp.sws.uiuc.edu

Sulfate ion wet deposition, 2006



National Atmospheric Deposition Program/National Trends Network
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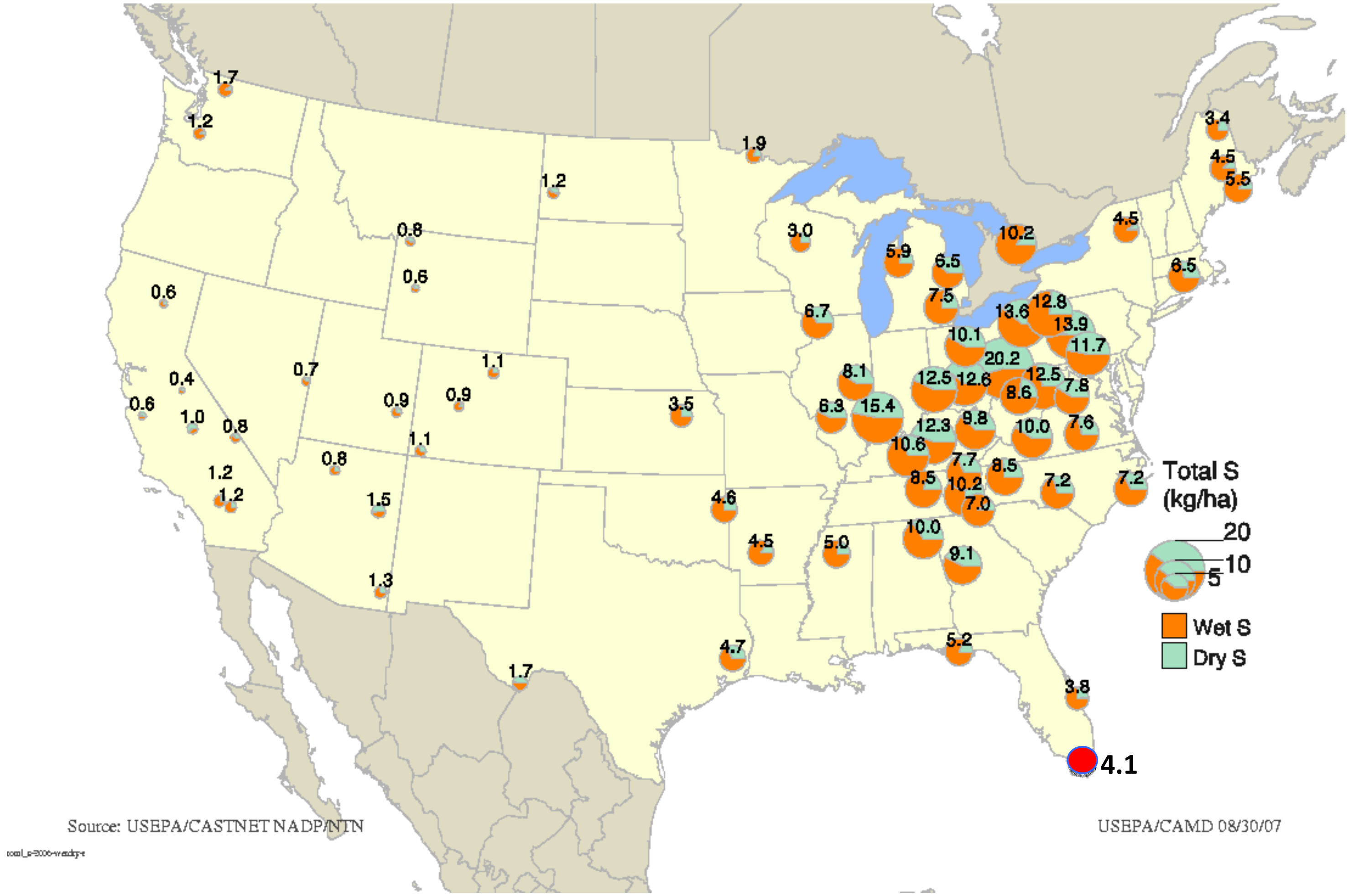
Total (Wet + Dry) S Deposition



http://www.epa.gov/castnet/maptotal.html

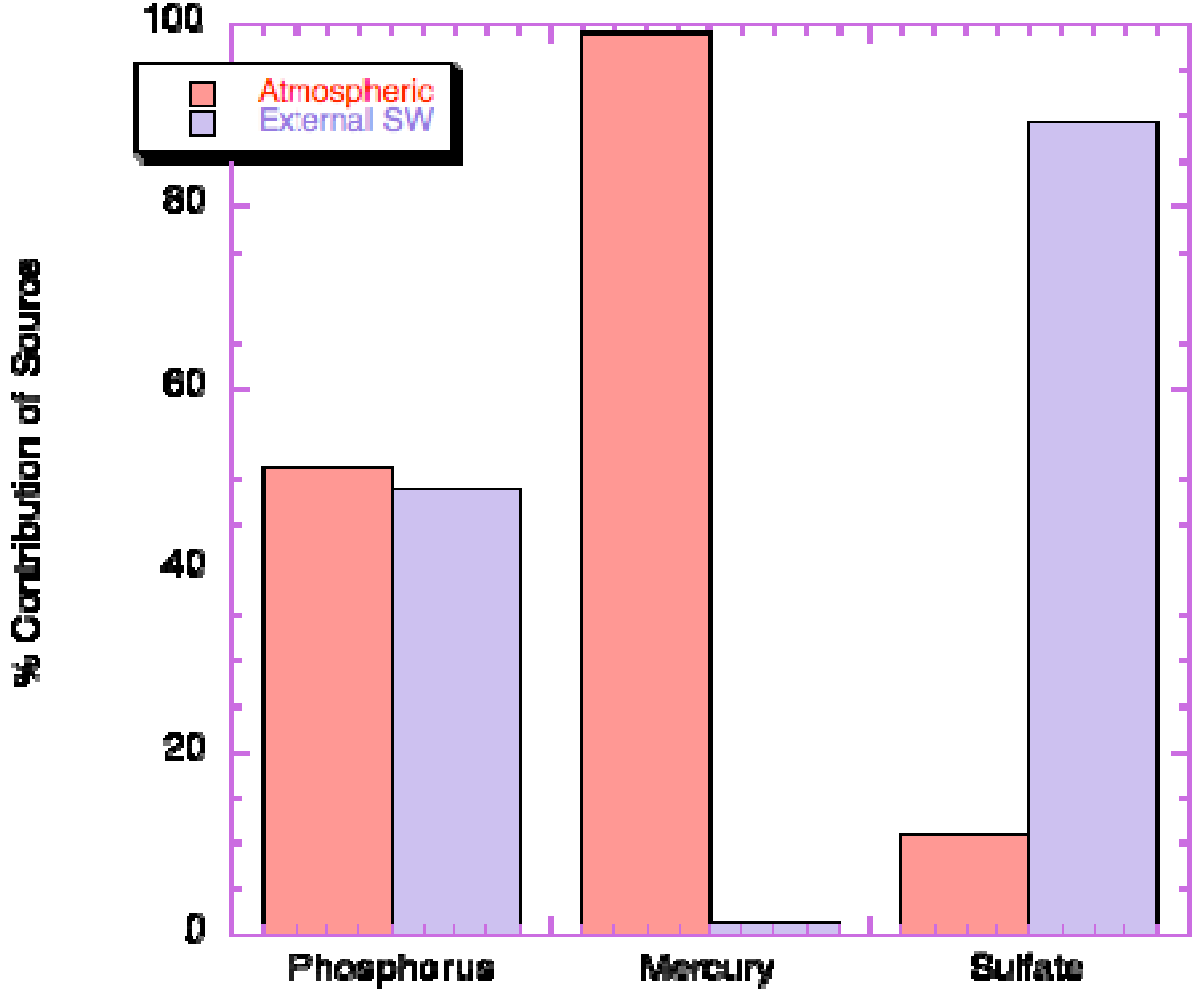
Are Atmospheric Fluxes of Hg, S, and P Important Sources to the Everglades?

Contaminant Loading Calculations to the Everglades Protection Area

- Flows for external surface water inflows from SFER 2007, WY2002-2006
- Data for discharge structures obtained from DBHYDRO for Hg_{total} and SO4.
- Fluxes calculated as:

- TP surface water inputs from SFER (2007).

Relative Contribution of External Surface Water Inputs and Atmospheric Deposition to Contaminant Loading to EPA



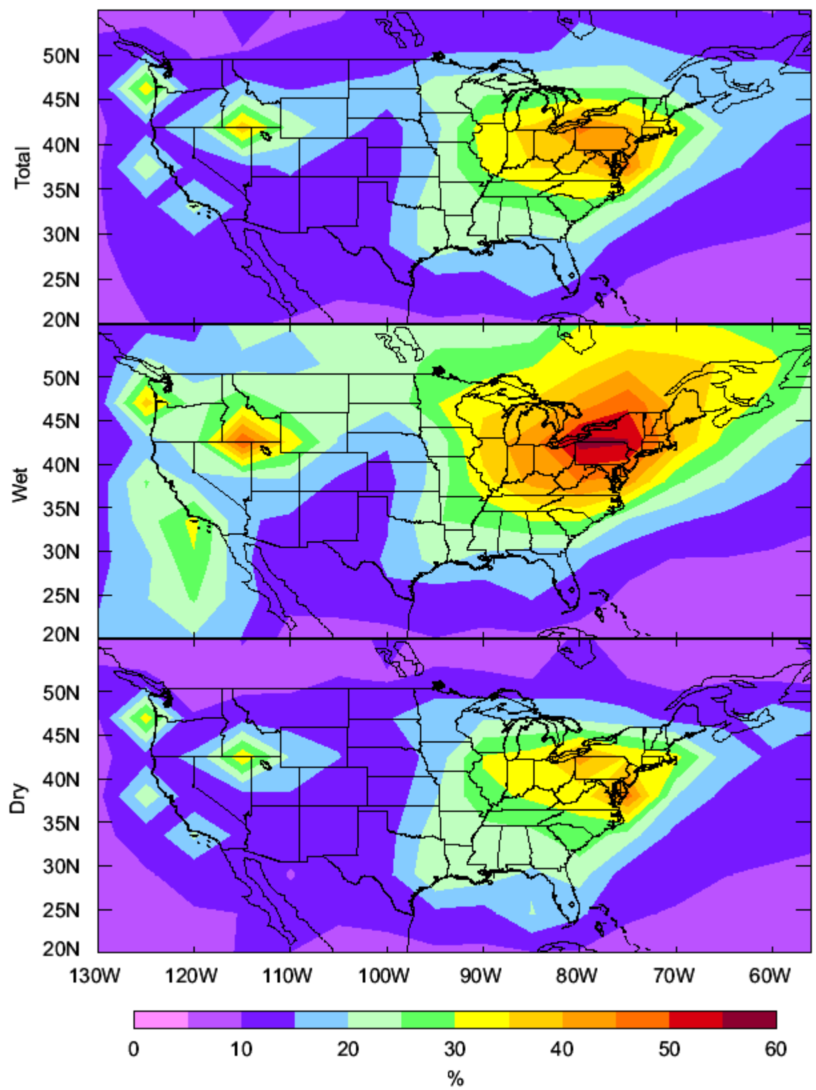
Assumes the following dry:wet deposition ratios:
TP = 1:1
Hg = 1:2
SO4 = 1:4.4

Sources of Hg Deposited in the Everglades

Study	Analysis	Contributions from North American sources	Local Contributions
Seigneur et al. (2003)	Global scale modeling (100 km x 100 km grid)	17%	
Carlton et al. (2004)	Global scale modeling (20 km x 20 km grid)	8%	
Selin and Jacob (2008)	Global scale modeling (4 x 5 grid)	15%	
Guentzel et al. (2003)	Ambient measurements + box model calculations		30 - 46% summertime wet deposition
Dvonch et al. (1999)	Multi-element tracer studies + stack gas measurements, 1995 – 1996.		71 – 73% along eastern border of Everglades
Pollman et al. (2007)	Analysis of coupled changes in emissions with measured changes in atmospheric flux		1991 – 51% 1995-96 – 21% 2000 – 9%

GEOS-Chem modeled contributions of North American Hg emission sources to wet and dry deposition of Hg.

From Selin and Jacobs, *Atmospheric Environ., 2008.*



1. Wet contributions between 10 and 15%.
2. Dry contributions between 15 and 20%.
3. Contribution to total deposition is ~ 15%.

1. Model resolution not sufficient to capture near field contributions
2. Emissions inventory for Florida sources (magnitude and speciation) likely not accurate

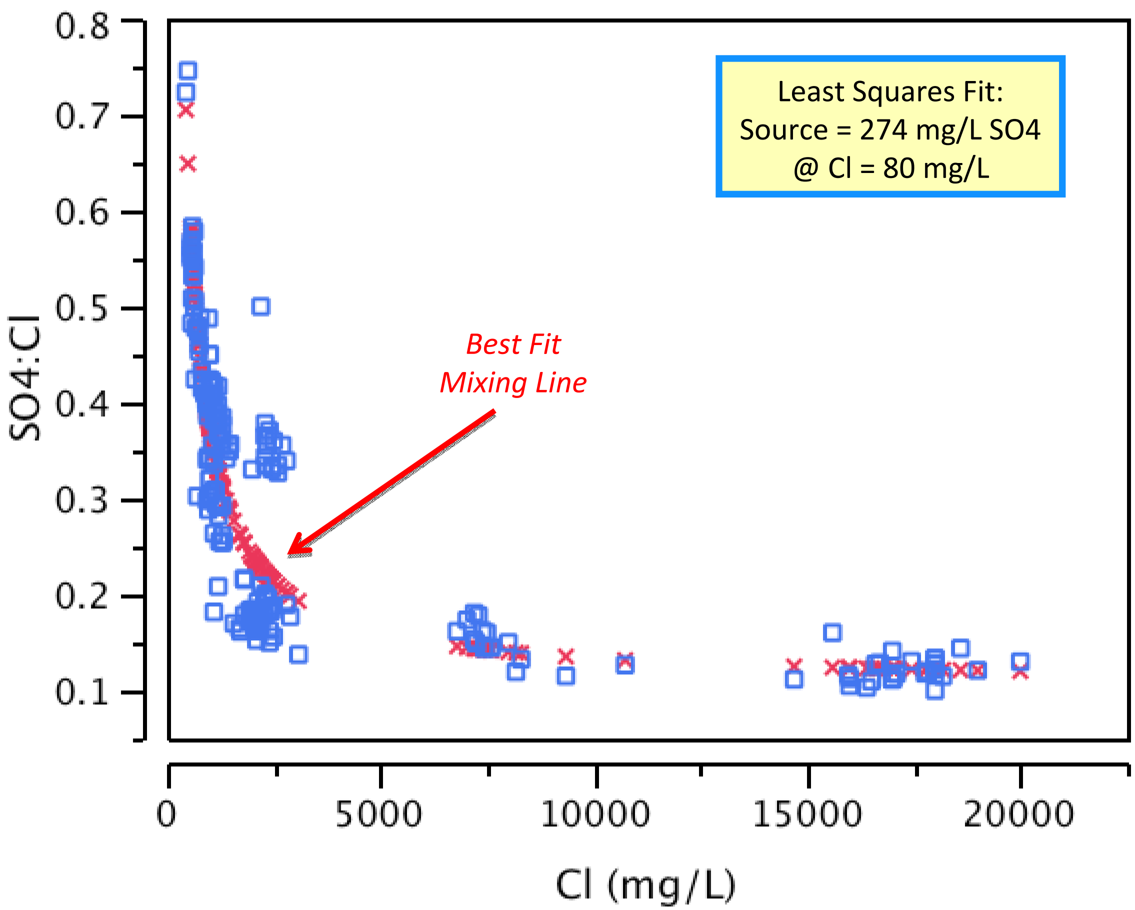
Sources of Sulfate Entering the Everglades

1. Atmospheric deposition directly to the Everglades Protection Area contributes only 11% of the total S load entering the system.

2. Does rainwater mixed with connate seawater discharging from the EAA constitute a significant source?

Plot SO_4:Cl *vs.* Cl in Deep Groundwater.

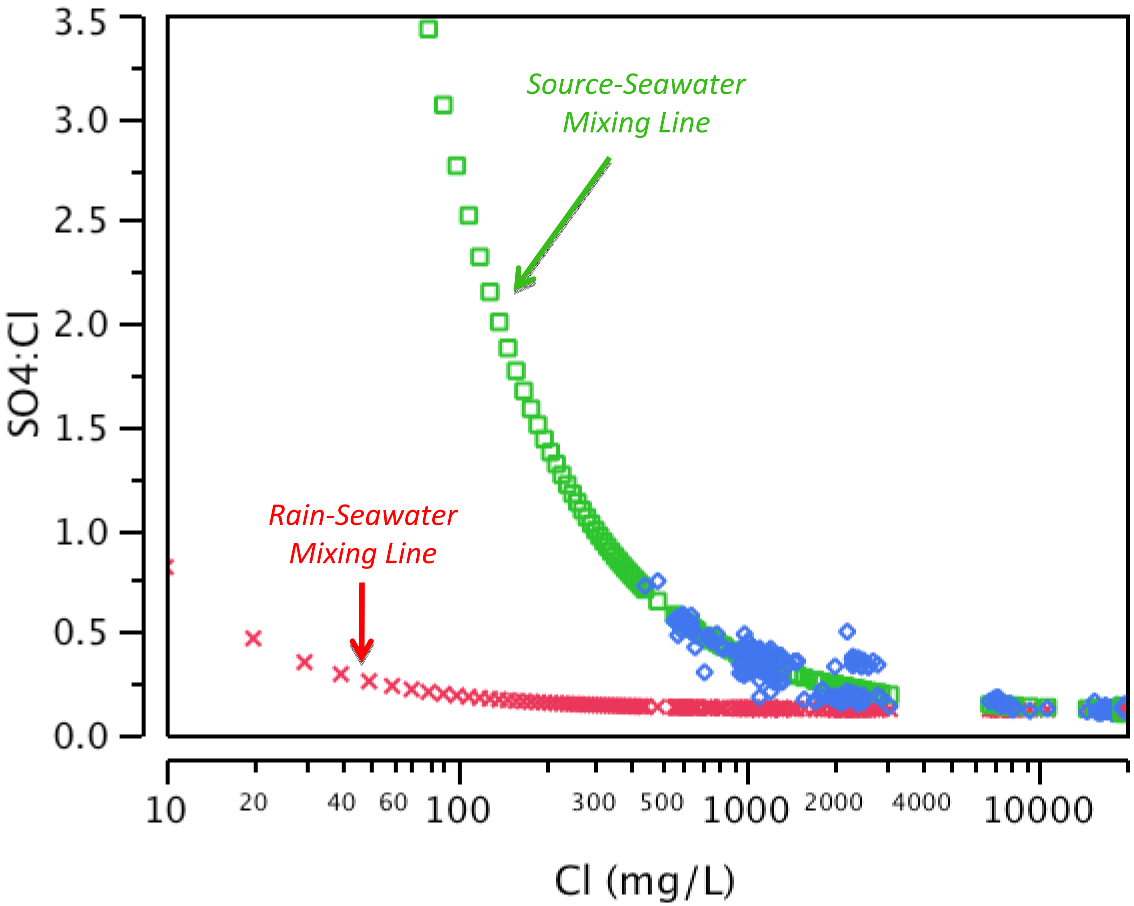
Data from DBHYDRO



Results indicate additional source water with high SO_4:Cl mixing with connate seawater

File: SFWMD Wells – Deep Subset

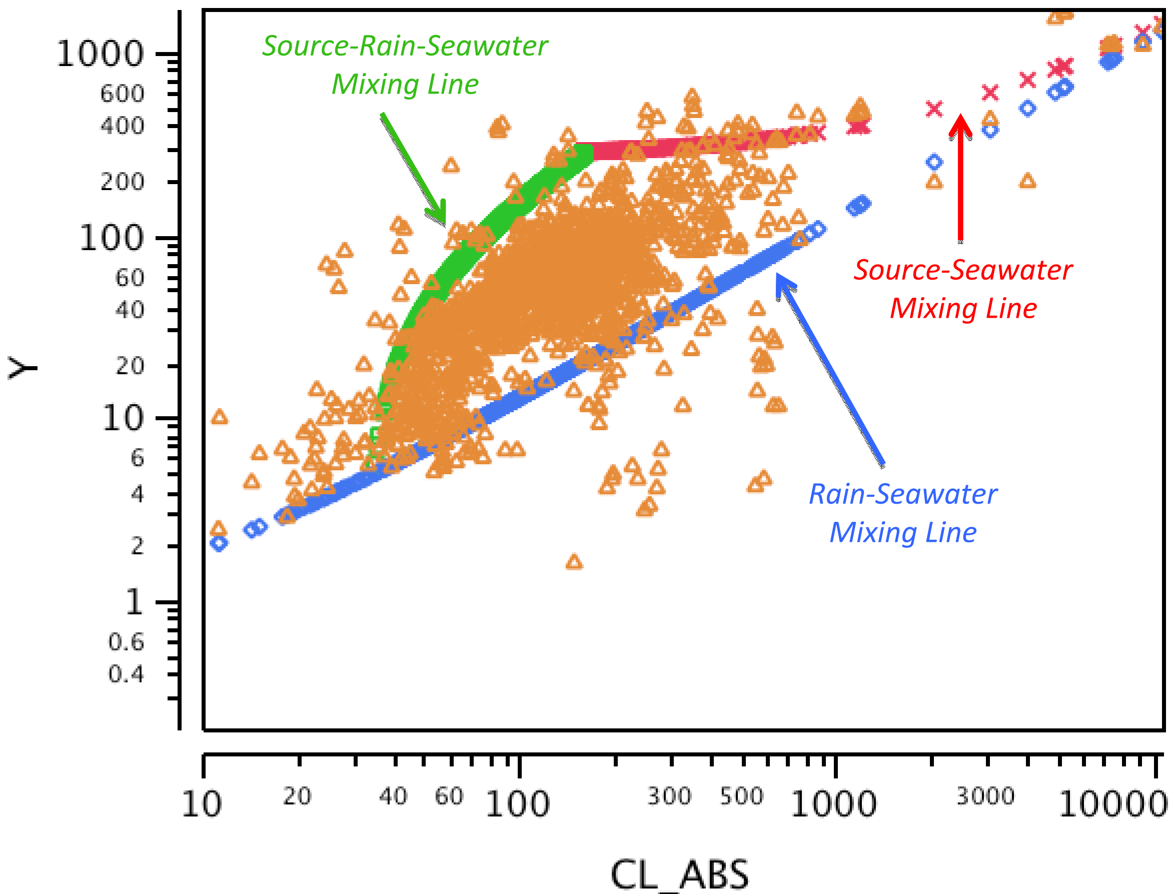
Plot of Unknown Source-Connate Seawater and Rainwater-Connate Seawater Mixing Lines



Results show that the unknown source of SO_4 clearly cannot be rainwater mixing with connate seawater.

File: SFWMD Wells – Deep Subset

SO_4 concentrations in EAA surface and groundwaters as a function of Cl.



1. Most waters sampled are enriched relative to rain-SW mixing line.
2. Sample SO_4 concentrations largely reflect dilution of source contributions by mixing with rainwater and/or connate seawater.

File: Na-Cl-SO4 No DL

Vertices at Cl = 35 and 160 mg/L

Is Dry Deposition of P Important to the Everglades?

- Total magnitude of dry deposited P is unknown, but could range from ½ to 10x of P wet deposited in the marsh.

- Much of the dry deposited P may be associated with very large particles (> 10 μM) that travel only short distances. Therefore much of the dry deposited P may constitute *net* deposition rather than a true external input.

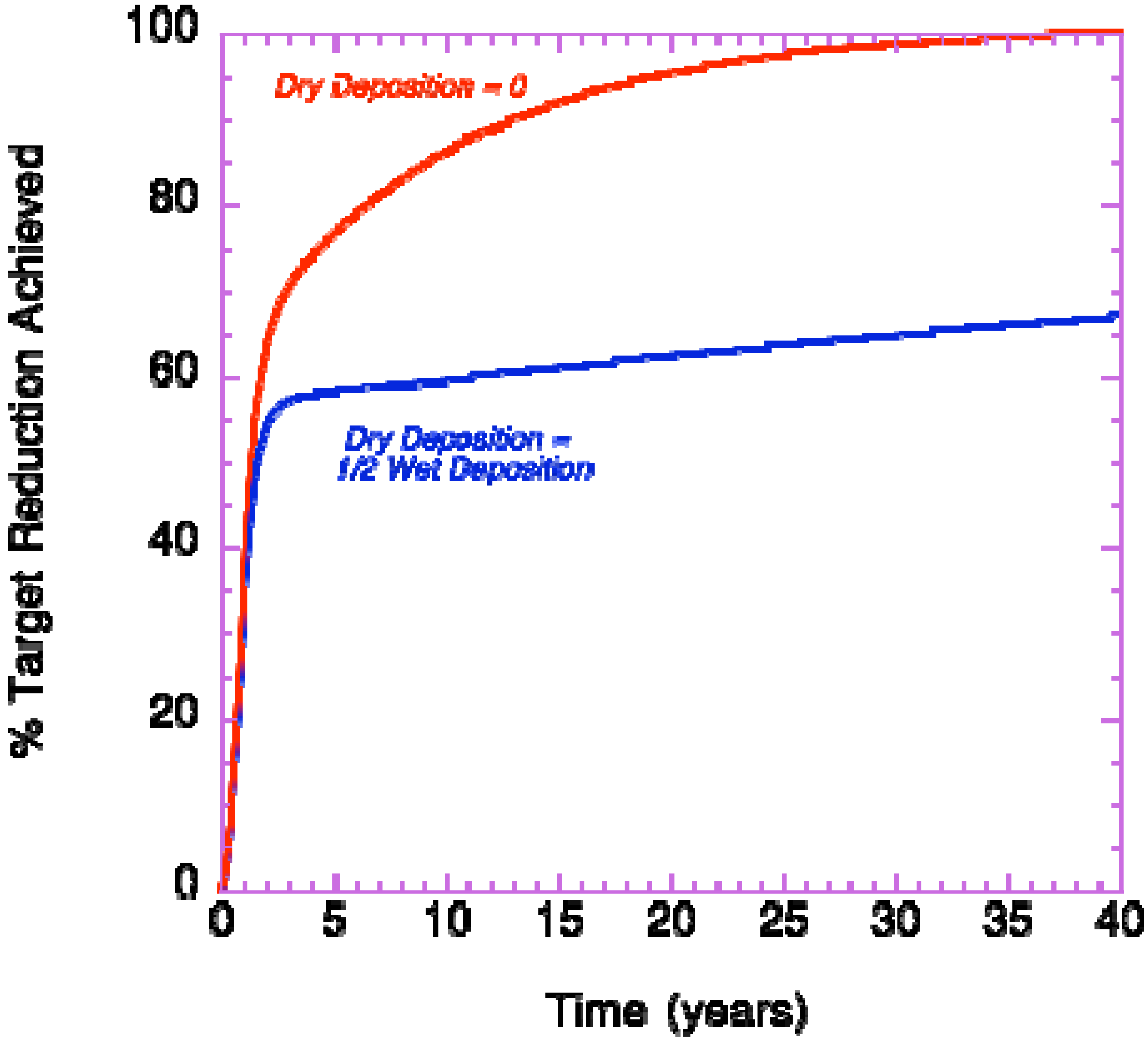
- Speciation of dry deposited P is critical with respect to having any real effect on P cycling in the water column and surficial sediments.

Is Dry Deposition of P Important to the Everglades?

- Depending on the magnitude of dry deposited reactive or labile P, failure to include this load will lead to improperly calibrated mass balance models.

- In addition, failure to account for this flux will lead to underestimates of both the rate and magnitude of recovery of the Everglades to reductions in P inputs from surface runoff.

Simulated Effect of Not Including Dry Deposition in Predicting Recovery of WCA-2A to 50% Reduction in Surface Inputs of P



Not including dry deposition in model results in:

1. ***Under-predicting*** the ***magnitude*** of recovery (in this case ~ 33% after 50 years);
2. ***Over-predicting*** the ***rate*** of recovery

Conclusions
Phosphorus

- Depending upon the magnitude of dry deposition, atmospheric deposition of P may equal or exceed external surface water inputs to the EPA.
- Reality is that very little is known about dry deposition of phosphorus. Bulk deposition measurements – which are unreliable for several reasons – are the only source of information specific to the Everglades.
- Source and nature of dry deposition is important. Is dry deposited P merely recycled P (in which case it does not contribute to the *net* load) or does it reflect a true external input?
- The magnitude of labile dry deposited P has important consequences for predicting the rate and magnitude of recovery of the Everglades to reductions in P loadings.
- Models that fail to account for this input very likely will predict more rapid rates and a greater of recovery than will occur given a specified reduction in surface water inputs of P to the Everglades.

Conclusions
Hg

- Nearly all of the Hg entering the Everglades is derived from atmospheric deposition.
- The extent to which these inputs can be controlled by reducing local emissions is both uncertain and controversial.
- The Statewide Florida Mercury TMDL should resolve this issue in part through implementation of an intensive "supersite" in Broward County to monitor mercury and trace element chemistry coupled with an improved emissions inventory and source receptor modeling.

Conclusions
SO4

- Most (89%) of the Hg entering the Everglades Protection Area is derived from surface water inputs.
- Mixing ratio analyses indicate that most of the sulfate leaving the EAA is enriched from an unspecified source.
- Restoration of the Everglades with respect to sulfur enrichment thus necessitates identifying the source (which is clearly neither connate seawater or rainwater) and eliminating or controlling it.