Atmospheric Mercury Measurements and Modeling at the Grand Bay NERR

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NOAA Air Resources Lab, Silver Spring, Maryland

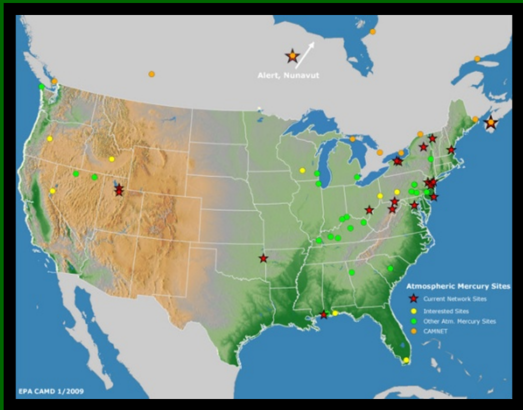
Gulf of Mexico Alliance Mercury Forum

May 10-12, 2010

Mote Marine Lab,

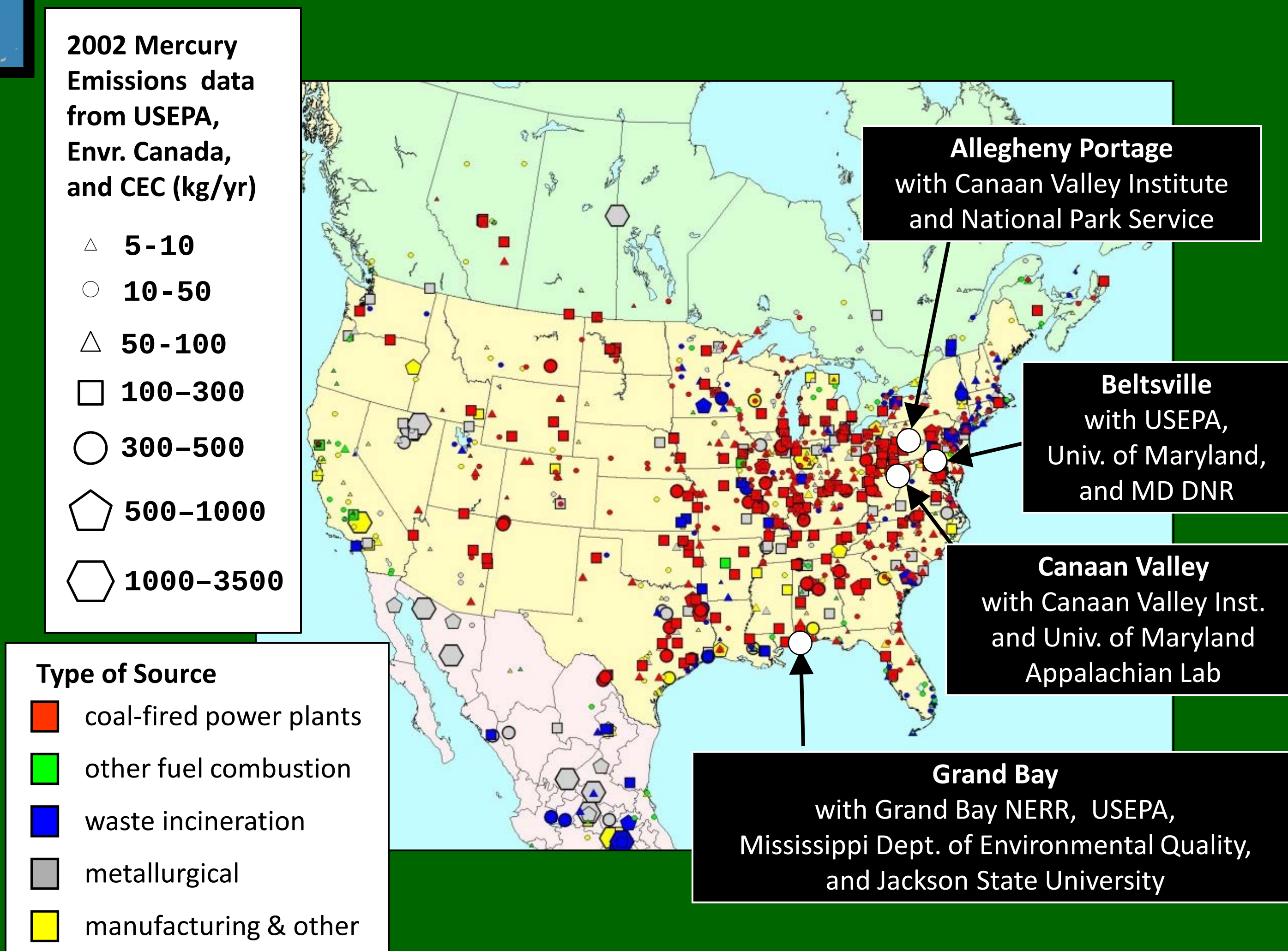
Sarasota, FL

http://www.arl.noaa.gov/mercury.php

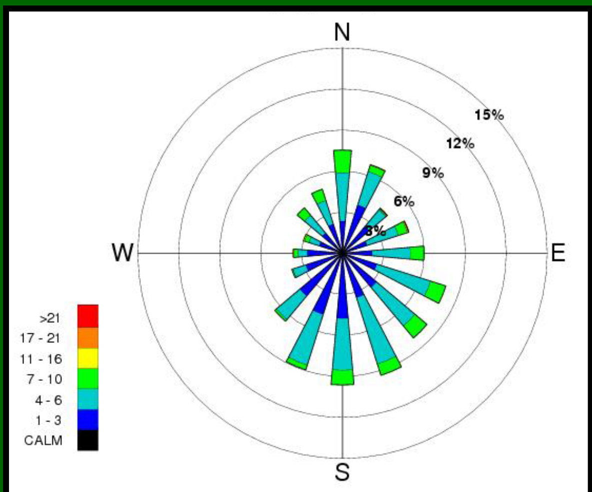


Four Collaborative Comprehensive Atmospheric Mercury Measurement Sites

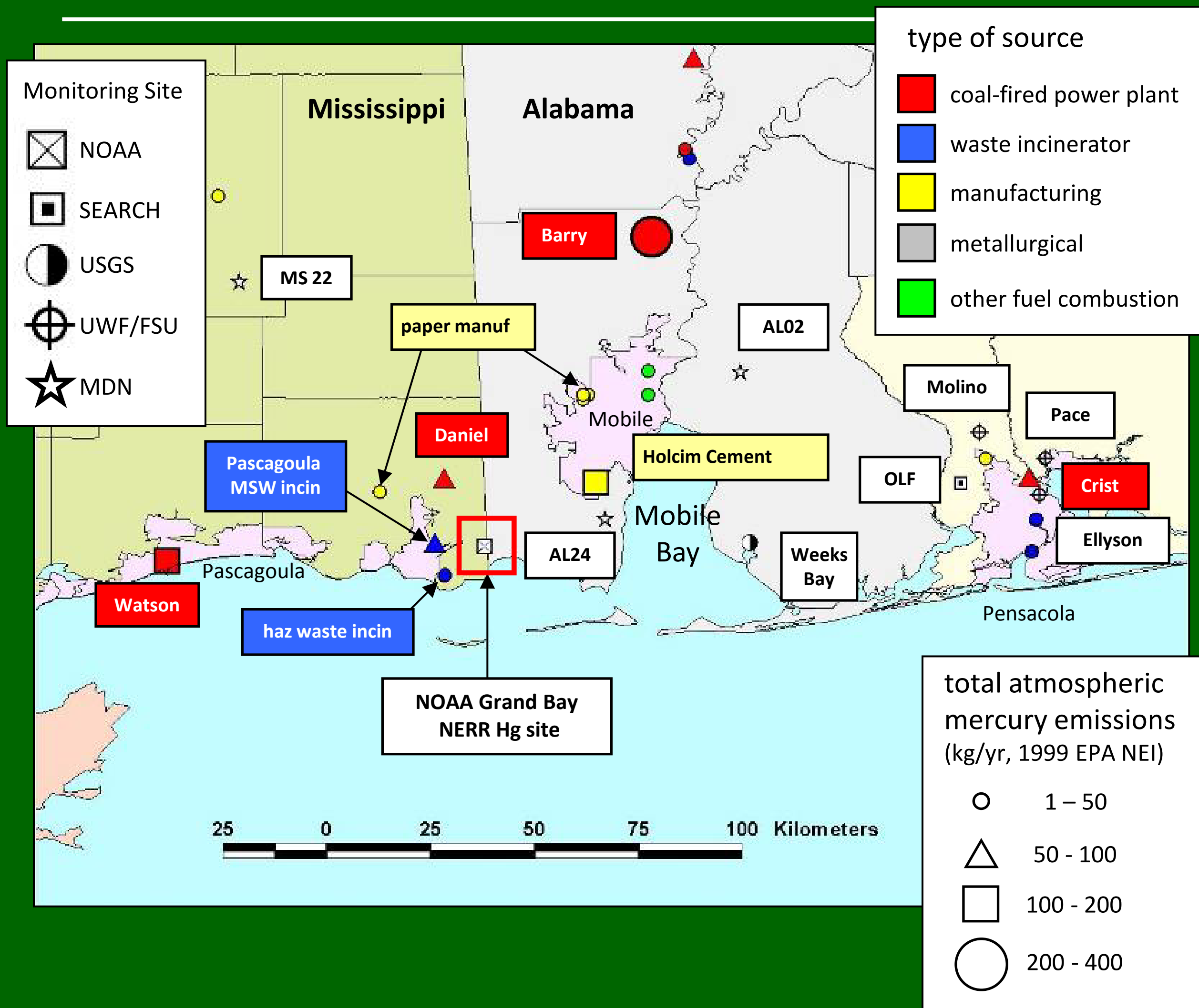
Part of AMNet, an emerging inter-agency speciated mercury ambient concentration measurement network



Grand Bay NERR site often sees Gulf of Mexico air masses, but is potentially influenced by several regional mercury emissions sources



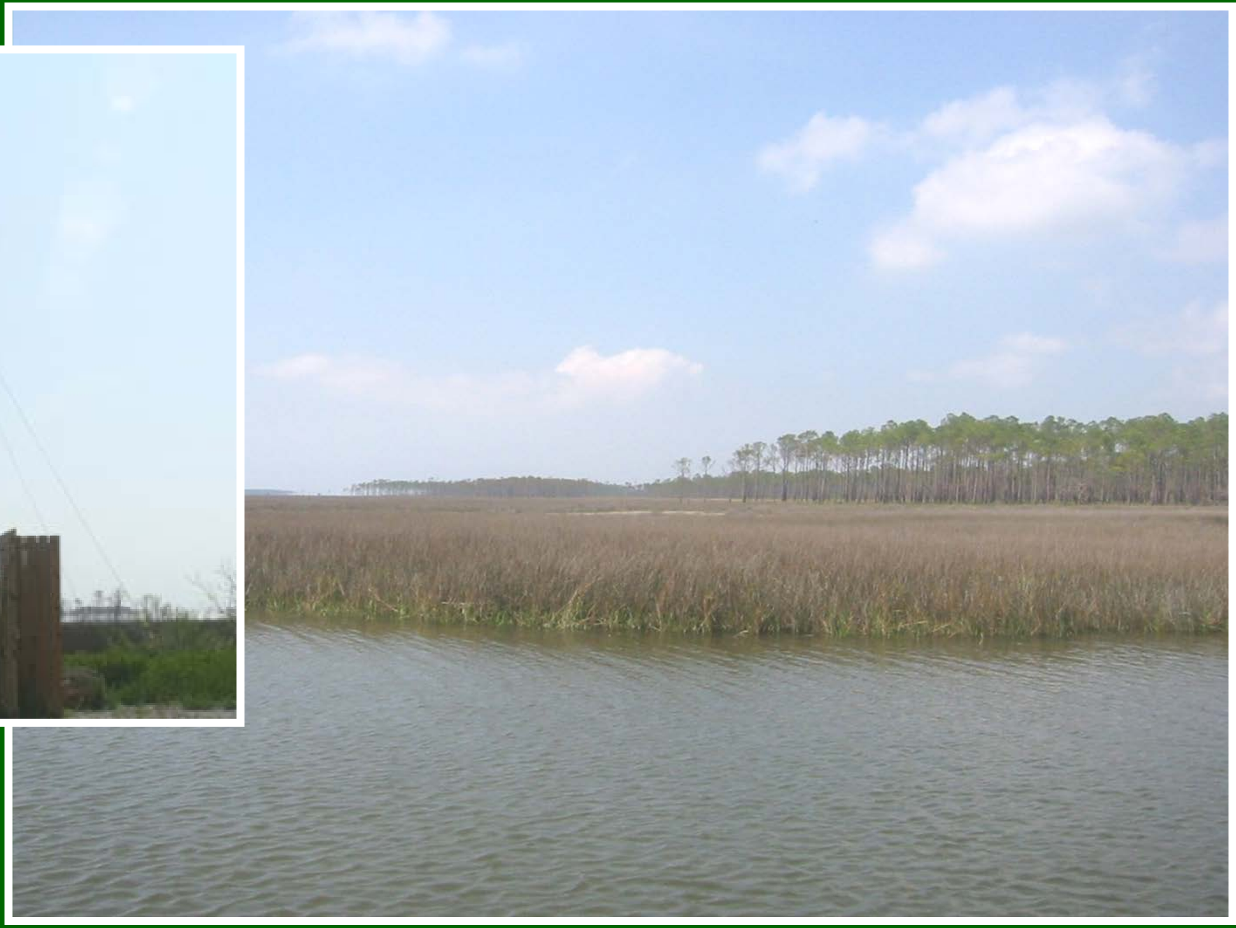
where the wind comes from that we see at Grand Bay



Atmospheric Mercury Monitoring Station at the Grand Bay NERR

mercury and trace gas monitoring tower (10 meters)

view from top of the tower



Some of the instrumentation inside the trailer at the Grand Bay NERR site

Measurements began in 2006 and the site has evolved over time

2005-2006: site selection

Sept 2006: Speciated Hg, SO_2, O_3, and CO measurements begin at "inland" site

2005 2006 2007 2008 2009 2010

Feb 2007: Meteorological measurements added

Oct 2007: Move to "coastal" site near Pavillion; 2nd Tekran speciated Hg measurement suite added

Jan 2008: NO/NO_y added

Aug 21 – Oct 5, 2008: site shut down due to threat of hurricanes

Jan 2010: Black Carbon added

2010: MS DEP adds comprehensive suite of wet deposition measurements with funding from USEPA

Summer 2010: Field Intensive (being planned)

Atmospheric mercury measurements are very challenging

"Hmmm... maybe better if the tower goes vertical?"

The people who are making the measurements

Jake Walker
Site Operator,
Grand Bay NERR

Winston Luke
Principal Investigator, NOAA
Air Resources Lab

Paul Kelley
Instrument engineer,
data acquisition and
management,
NOAA Air Resources Lab

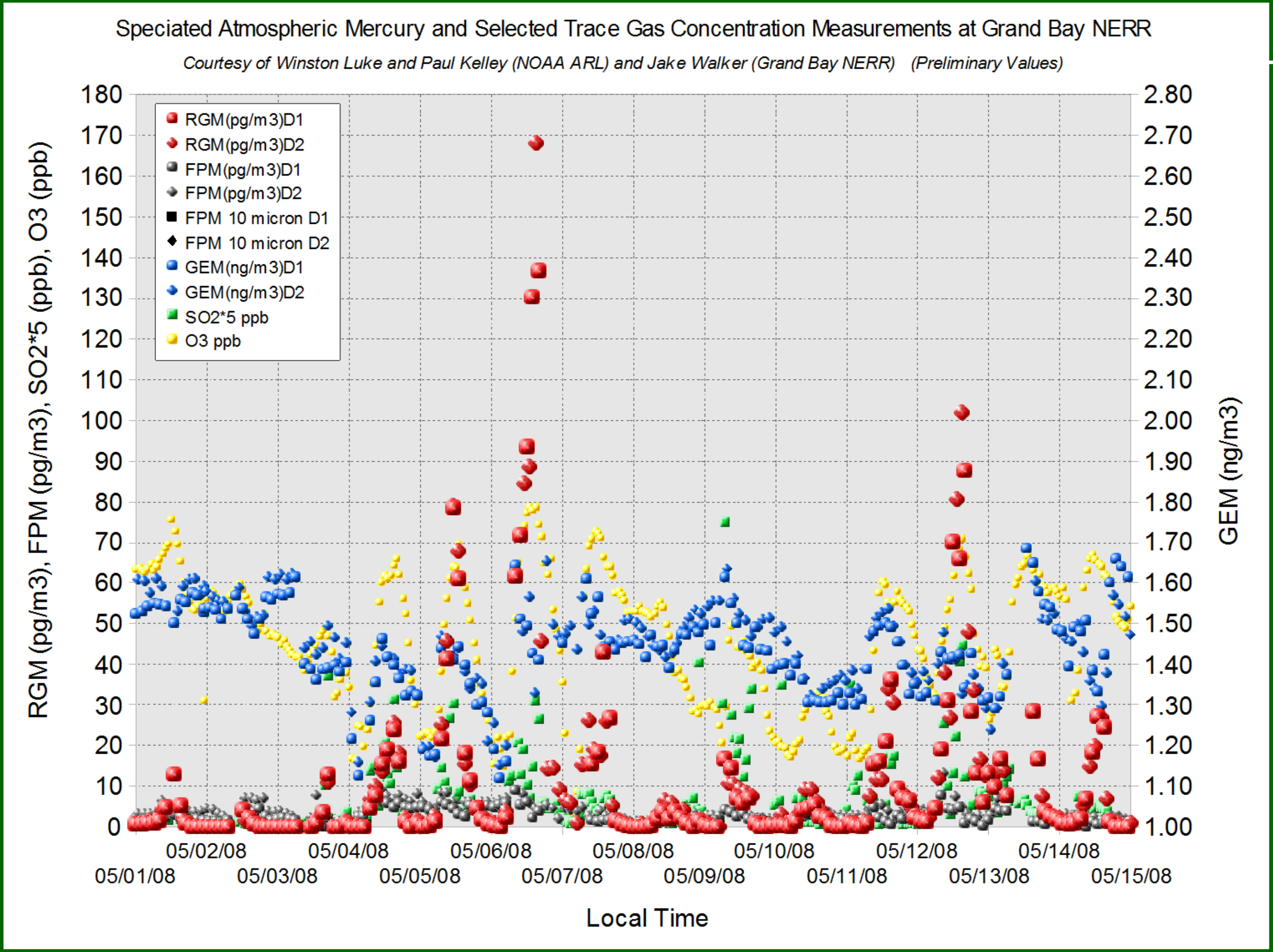
Current Atmospheric Measurements of Ambient Air Concentrations and Meteorological Data

Elemental mercury (two instruments)	"Speciated" Atmospheric Mercury Concentrations
Fine particulate mercury (two instruments)	
Reactive gaseous mercury (two instruments)	
Sulfur dioxide	Trace gases and other measurements to help understand and interpret mercury data
Ozone	
Carbon Monoxide	
Nitrogen Oxides (NO, NOy)	
Aerosol Black Carbon	
Wind speed, Wind Direction	Meteorological Data
Temperature, Relative Humidity	
Precipitation Amount	

Wet Deposition Measurements added in 2010 by the Mississippi Department of Environmental Protection (Henry Folmar, Becky Comyns, others), with funding from the USEPA

Precipitation	Continuous digital measurement of precipitation amount
Major Ions pH, SO_4^{-2}, NO_3^-, PO_4^{-3}, Cl^-, NH_4^+, Ca^{+2}, Mg^{+2}, K^+, Na^+	Weekly measurements of concentrations in precipitation (NADP-NTN)
Total Mercury	Weekly measurements of concentration in precipitation (NADP-MDN)
Methyl Mercury	Monthly measurements of concentration in precipitation (composite)
Selected Trace Metals As, Cd, Cr, Cu, Pb, Ni, Se, Zn	Weekly measurements of concentrations in precipitation (MDN Heavy Metal Protocol)

Example of Ambient Concentration Measurements at the Grand Bay site

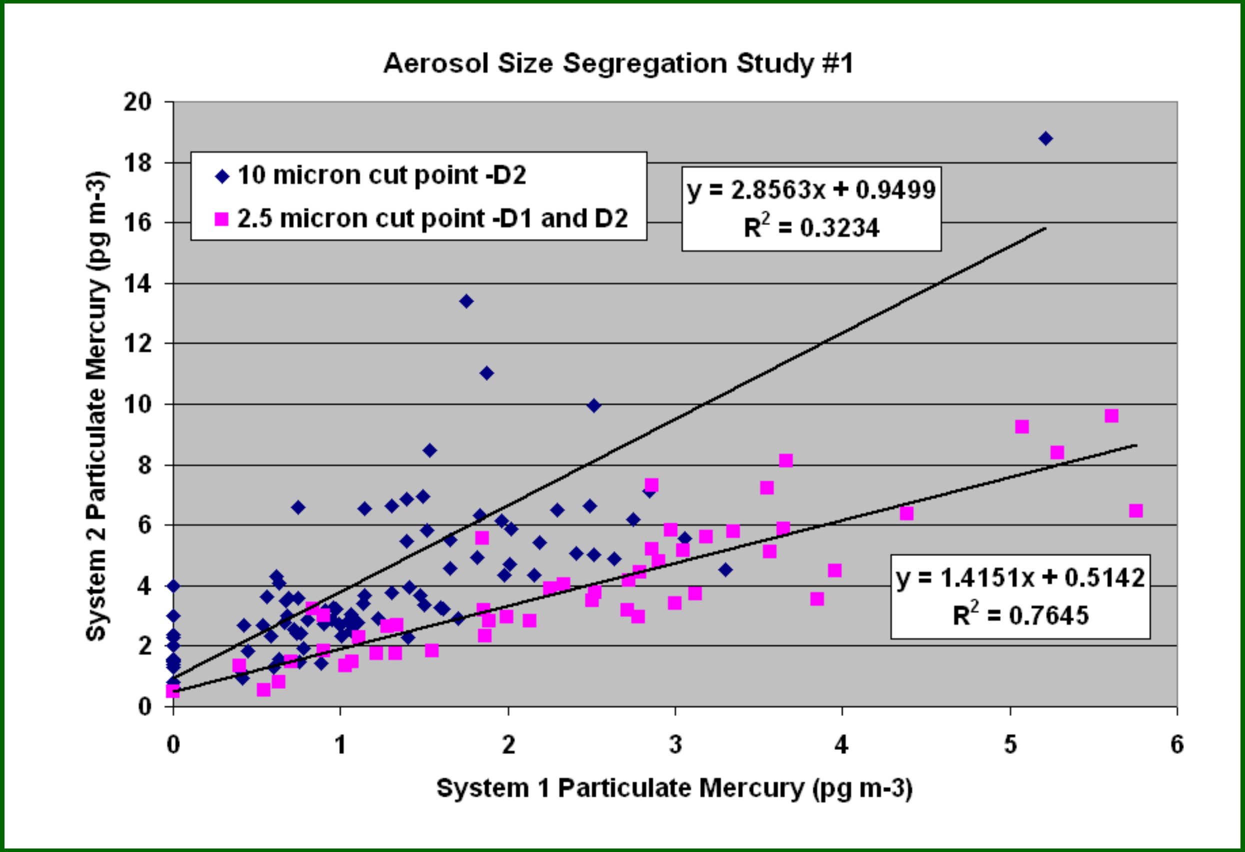


The two sets of speciated mercury measurements generally track each other well

Sometimes we see relatively pronounced peaks in one or more forms of mercury (in this example, RGM)

With two speciation units, can get continuous data and can also carry out methodological experiments

- **PINK data points:** two systems were configured identically, to allow only particles less than 2.5 microns to be analyzed
- **BLUE data points:** System 2 was altered to allow particles up to 10 microns to be analyzed
- Results suggest that there may be as much mercury in the coarse (sea salt) aerosol fraction as in the fine fraction.

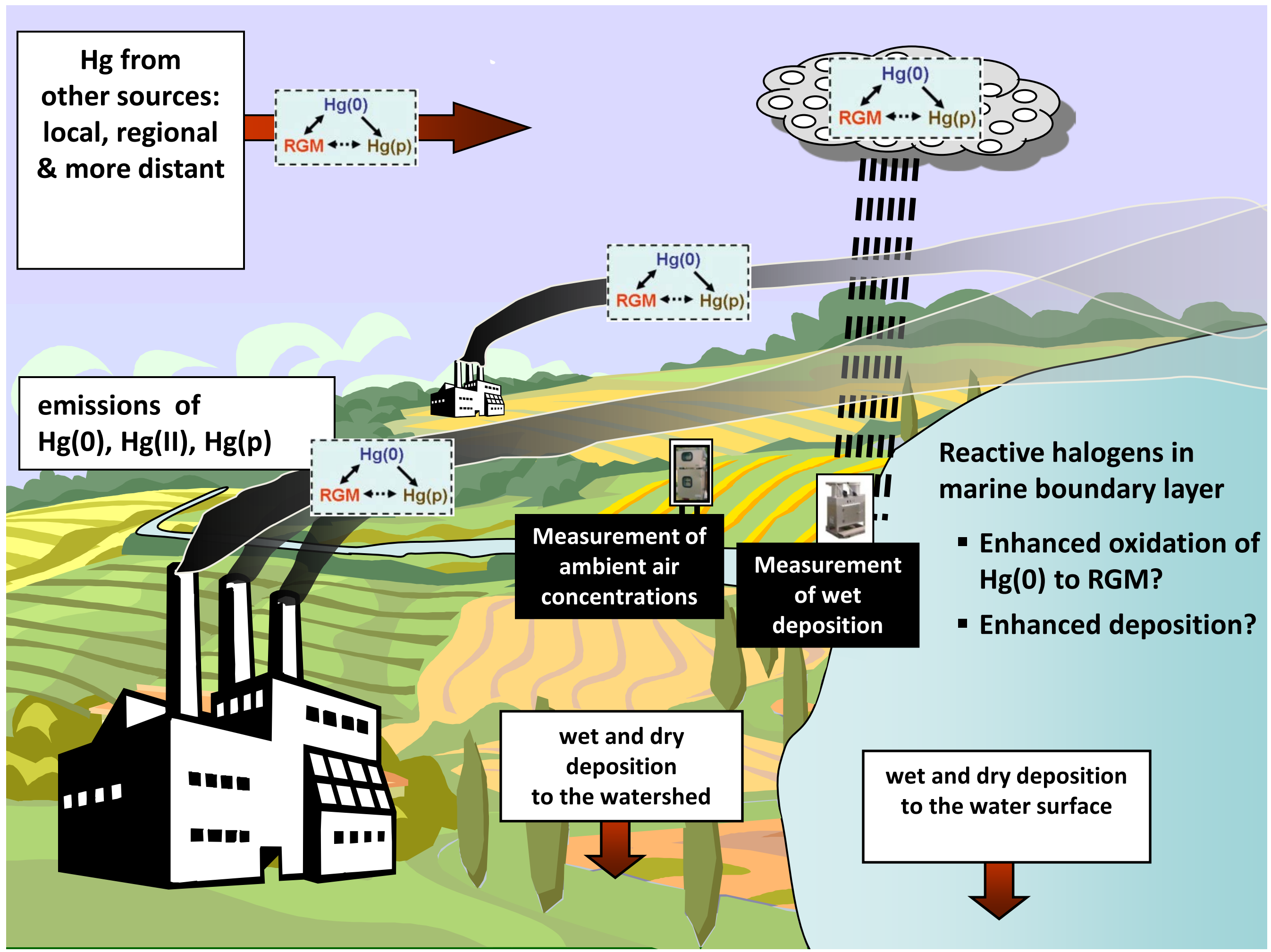


Grand Bay Field Intensive Scheduled for July-Aug 2010

Ground-Based Measurements	
(ongoing) mercury, trace gas, black carbon, met data	• Winston Luke and Paul Kelley (NOAA ARL), • Jake Walker (Grand Bay NERR)
(ongoing) wet deposition: major ions, mercury, methyl-Hg, trace metals Will try to switch to event-based during intensive	• Mississippi State Dept of Env Protection/EPA • Jake Walker (Grand Bay NERR)
ambient concentrations of BrO at the surface via Chemical Ionization Mass Spectrometry (and possibly other Br compounds, e.g., Br2, BrCl, and HOBr	• Greg Huey (Georgia Tech)
isotopic mercury analysis of event-based precipitation and aerosols	• Bill Landing, Flip Froelich (Florida State Univ)
trace metal analysis of size-segregated aerosol Spring 2010 and possibly during intensive	• Mark Engle (USGS)
Aircraft and Above Surface Measurements	
aircraft flights measuring concentrations of Hg^0 (Tekran), total and "speciated" RGM (coated/uncoated denuders), O_3, SO_2, and particle count	•Stephen Corda, John Muratore, & colleagues (Univ. of Tennessee Space Institute – UTSI) • Hynes and Swartzendruber (Univ of Miami) • Luke and Kelley (NOAA ARL)
vertical distribution of O_3 and met data above the site (ozonesondes)	• Luke and Kelley (NOAA ARL) • Jake Walker (Grand Bay NERR)

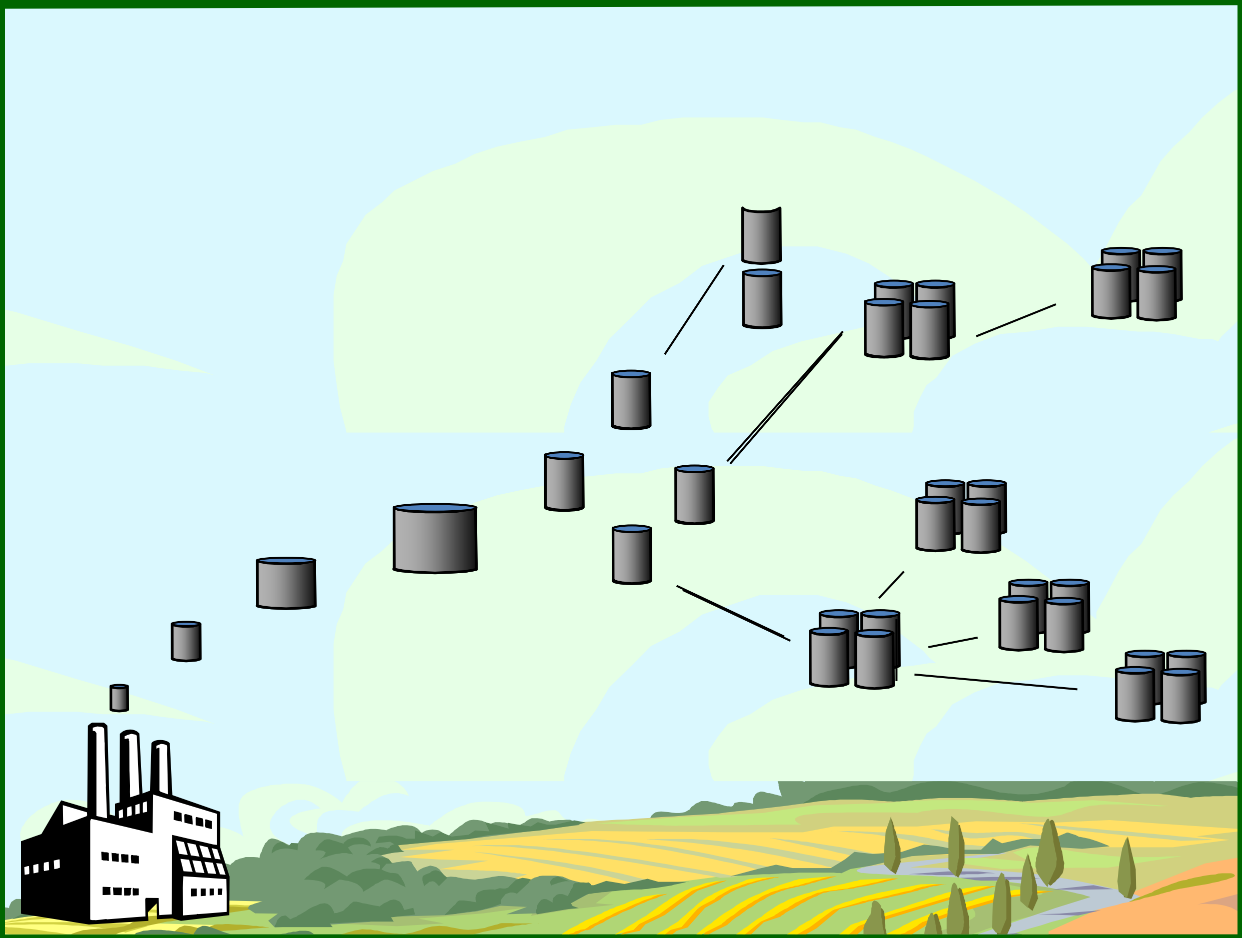
Atmospheric Fate and Transport: Measurements and Modeling

- ❑ Model evaluation?
- ❑ Source attribution for deposition?
- ❑ Want to provide deposition estimates to GOM ecosystem models



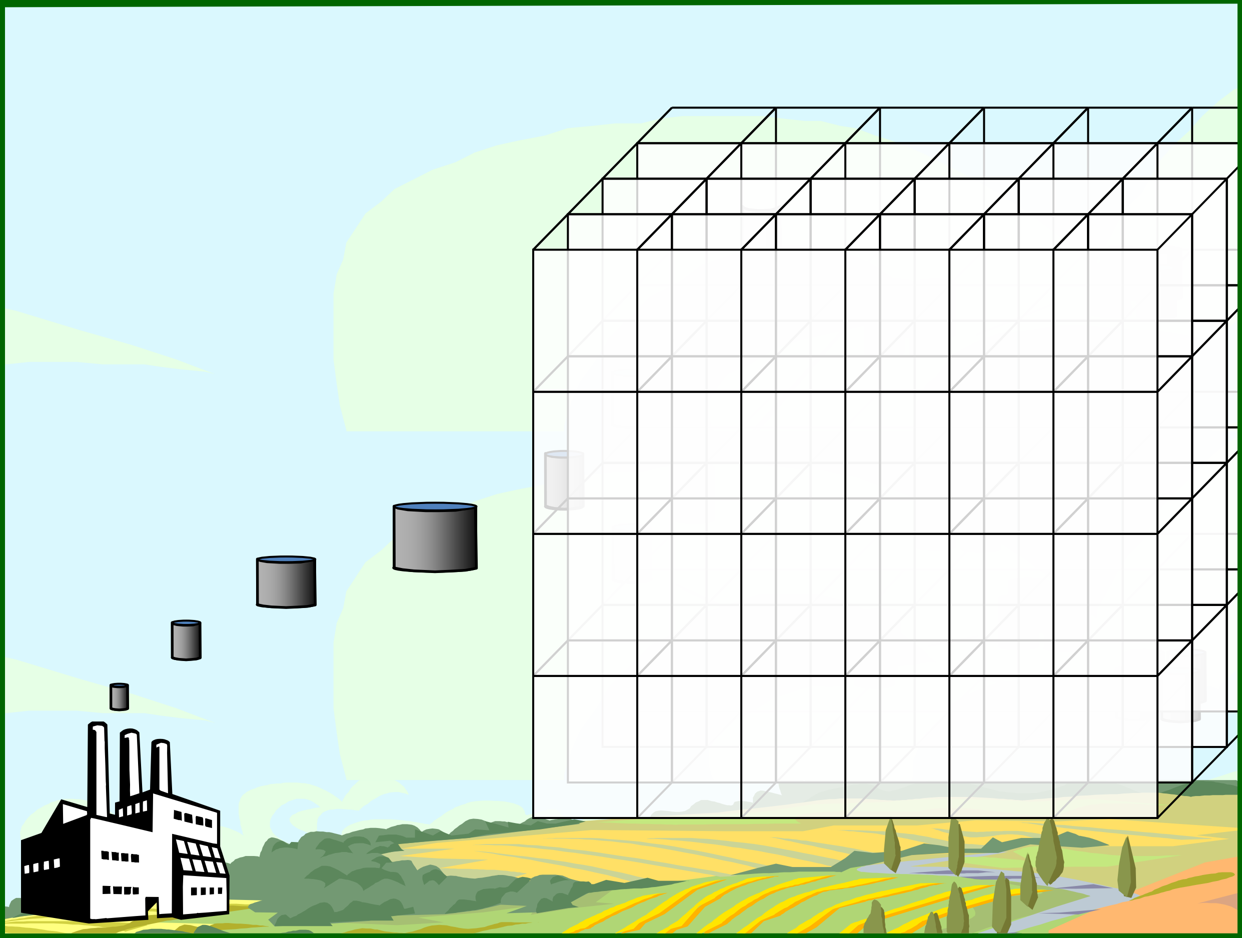
HYSPLIT-Hg -- a specially configured version of the HYSPLIT atmospheric fate and transport model

- Puffs or particles emitted from a source
- Chemistry, dispersion and deposition simulated
- Puffs grow and split
- Splitting can overwhelm computational resources



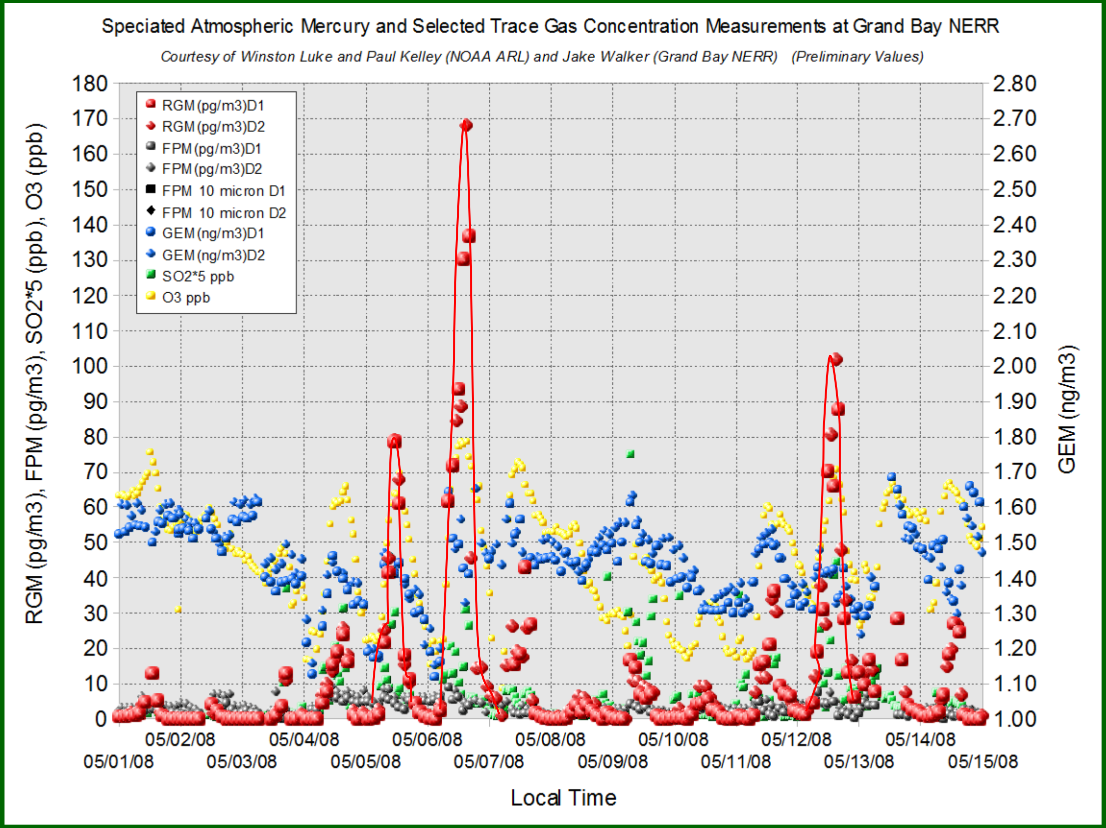
HYSPLIT-Hg now includes an integrated Eulerian grid

- In HYSPLIT (4.9), puffs are "transferred" to an Eulerian grid after a specified time (e.g., 96 hrs)
- the mercury in those puffs is simulated on that grid from then on…
- Combines plume simulation in short-range with Eulerian simulation for long-range transport



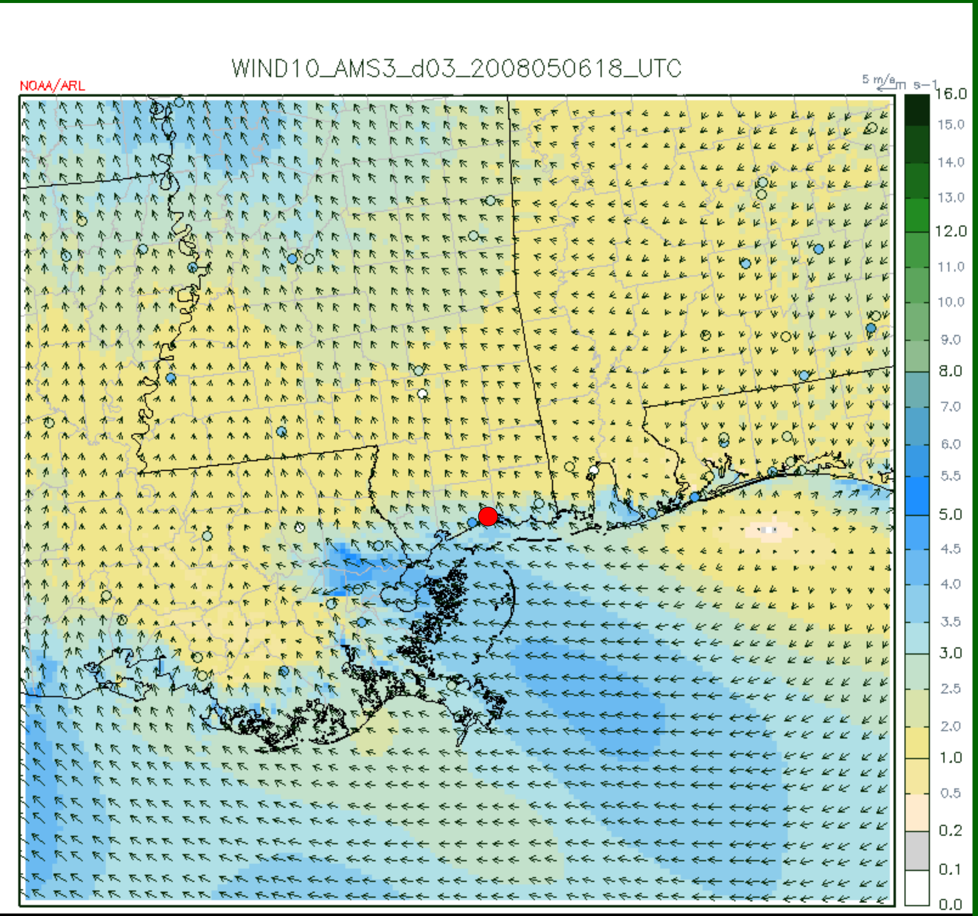
Initial Model Evaluation focusing on episodes

- Can the model reproduce episodes of high measured mercury concentrations?
- Can the model reproduce high mercury wet deposition episodes?



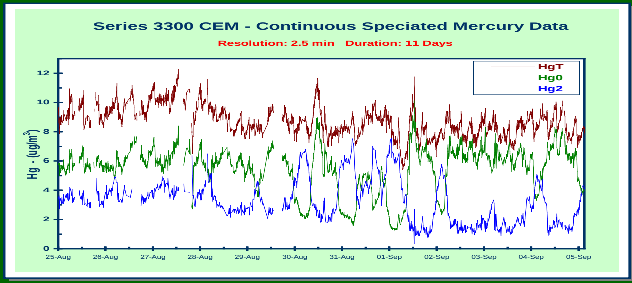
Meteorological data: a critical model input

- During model evaluation exercises, want to diagnose weaknesses in model physics and chemistry, without large influence of met data errors
- Would like to examine trade-off between high-resolution and coarser met data sets, which are more routinely available
- Dr. Venkata Dodla (JSU) and Dr. Fantine Ngan (NOAA ARL) are creating high resolution, ground-truthed met data sets for episodes in the region around the site (e.g., horizontal resolution of 4 km)



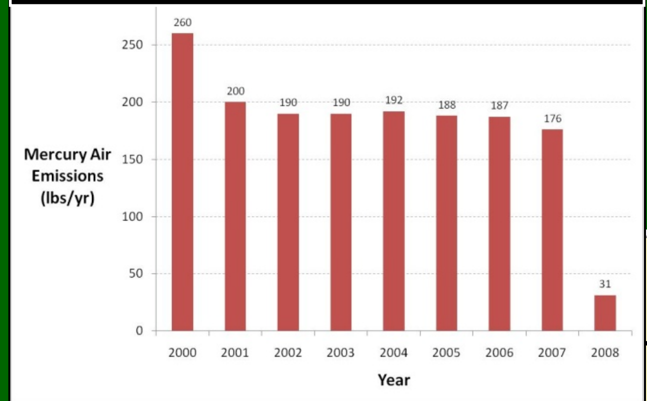
Wind speed (shaded) & wind vector (arrows) on 5/6/08, 18 UTC (approx time of episode peak)

Emissions data: a critical model input



- In model evaluation, want to diagnose weaknesses in model without large influence of emissions errors
- Need accurate, speciated emissions estimates for all sources impacting the site – *for the time period of the episode*
- Need accurate emissions data for any assessment
- We all need accurate emissions information.
- How can we share what we already have, and improve the information where needed?

Lowman reported dramatic drop in mercury emissions in 2008 TRI



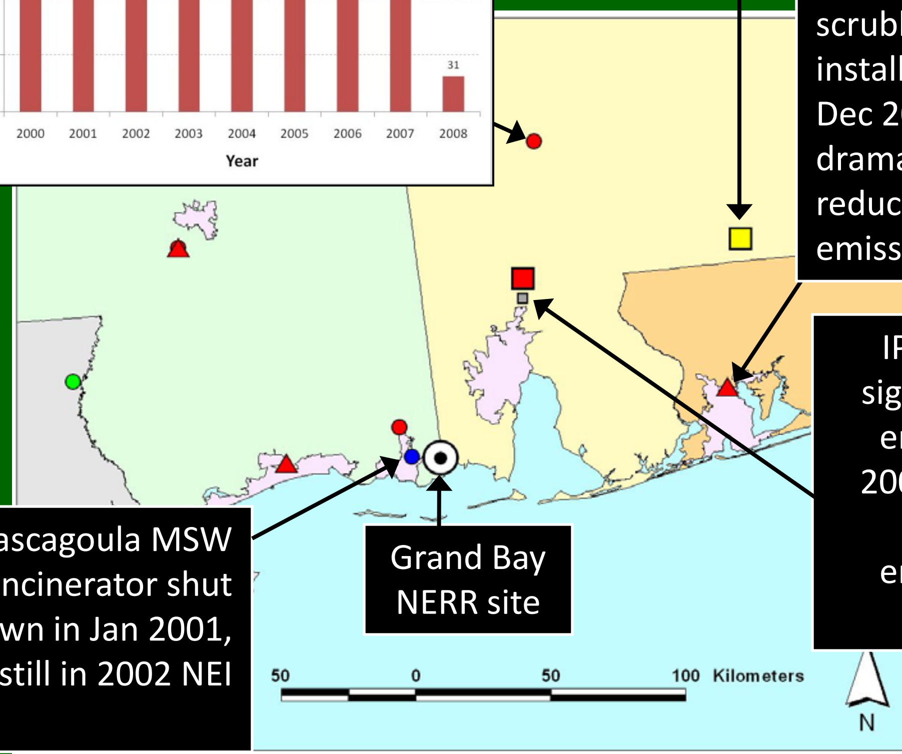
Brewton paper mill : Hg emissions in 2002 NEI , but do not appear in 2000-2008 TRI

CRIST: New scrubber installed Dec 2009 will dramatically reduce RGM emissions

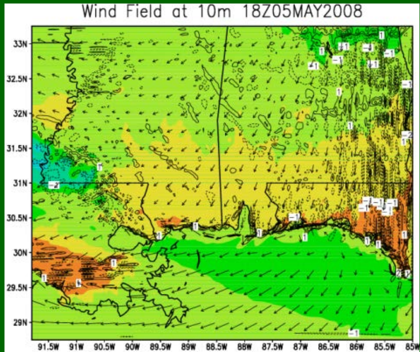
IPSCO Steel: significant Hg emissions in 2002 NEI, but negligible emissions in 2008 TRI

Pascagoula MSW Incinerator shut down in Jan 2001, but still in 2002 NEI

Grand Bay NERR site

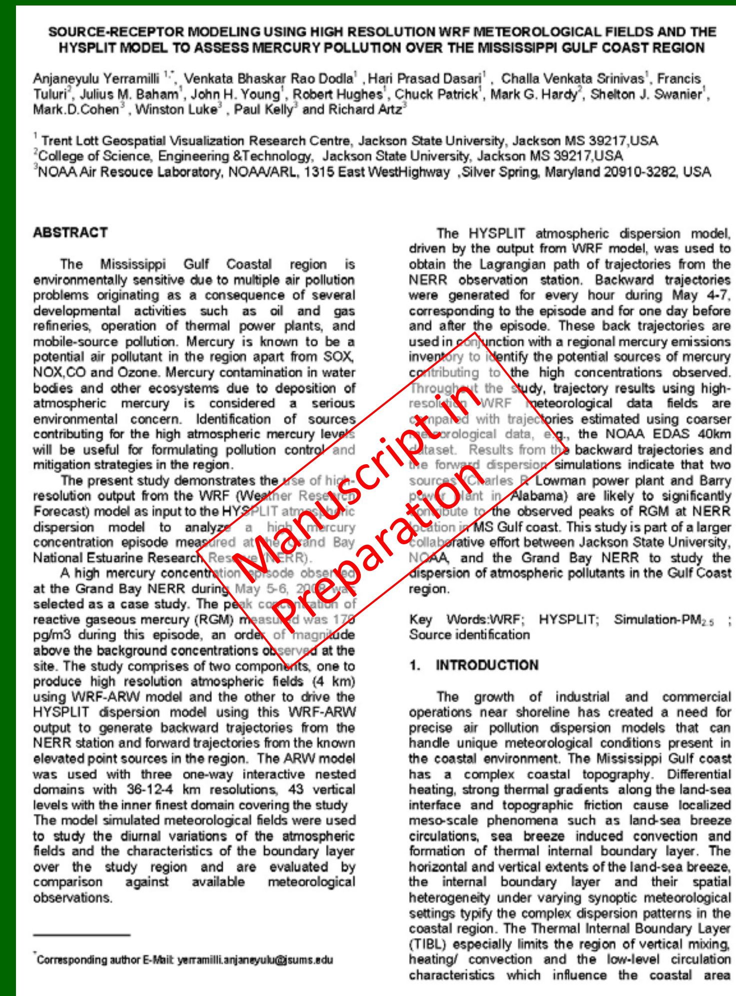


Large mercury emissions point sources from USEPA 2002 National Emissions Inventory (NEI)



Collaboration with Jackson State University on atmospheric mercury modeling in the region

- led by Shelton Swanier and Anjaneyulu Yerramilli, the director of the *Trent Lott Geospatial and Visualization Center*
- Manuscript in preparation analyzing the May 5-6 2008 high-RGM episode at the site.
- High-resolution met data (4 km) is being generated and utilized
- **ALSO:** JSU Professor *Jerzy Leszczynski* and colleagues are carrying out computational chemistry estimates of atmospherically relevant reactions of mercury



SOURCE-RECEPTOR MODELING USING HIGH RESOLUTION WRF METEOROLOGICAL FIELDS AND THE HYSPLIT MODEL TO ASSESS MERCURY POLLUTION OVER THE MISSISSIPPI GULF COAST REGION

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ABSTRACT

The Mississippi Gulf Coastal region is environmentally sensitive due to multiple air pollution problems originating as a consequence of several developmental activities such as oil and gas refineries, operation of thermal power plants, and mobile-source pollution. Mercury is known to be a potential air pollutant in the region apart from SOX, NOX,CO and Ozone. Mercury contamination in water bodies and other ecosystems due to deposition of atmospheric mercury is considered a serious environmental concern. Identification of sources contributing for the high atmospheric mercury levels will be useful for formulating pollution control and mitigation strategies in the region.

The present study demonstrates the use of high-resolution output from the WRF (Weather Research Forecast) model as input to the HYSPLIT atmospheric dispersion model to analyze a high mercury concentration episode measured at the Grand Bay National Estuarine Research Reserve (NERR).

A high mercury concentration episode observed at the Grand Bay NERR during May 5-6, 2008 was selected as a case study. The peak concentration of reactive gaseous mercury (RGM) measured was 170 pg/m3 during this episode, an order of magnitude above the background concentrations observed at the site. The study comprises of two components, one to produce high resolution atmospheric fields (4 km) using WRF-ARW model and the other to drive the HYSPLIT dispersion model using this WRF-ARW output to generate backward trajectories from the NERR station and forward trajectories from the known elevated point sources in the region. The ARW model was used with three one-way interactive nested domains with 36-12-4 km resolutions, 43 vertical levels with the inner finest domain covering the study The model simulated meteorological fields were used to study the diurnal variations of the atmospheric fields and the characteristics of the boundary layer over the study region and are evaluated by comparison against available meteorological observations.

The HYSPLIT atmospheric dispersion model, driven by the output from WRF model, was used to obtain the Lagrangian path of trajectories from the NERR observation station. Backward trajectories were generated for every hour during May 4-7, corresponding to the episode and for one day before and after the episode. These back trajectories are used in conjunction with a regional mercury emissions inventory to identify the potential sources of mercury contributing to the high concentrations observed. Throughout the study, trajectory results using high-resolution WRF meteorological data fields are compared with trajectories estimated using coarser meteorological data, e.g., the NOAA EDAS 40km dataset. Results from the backward trajectories and the forward dispersion simulations indicate that two sources (Charles R Lowman power plant and Barry power plant in Alabama) are likely to significantly contribute to the observed peaks of RGM at NERR location in MS Gulf coast. This study is part of a larger collaborative effort between Jackson State University, NOAA, and the Grand Bay NERR to study the dispersion of atmospheric pollutants in the Gulf Coast region.

Key Words:WRF; HYSPLIT; Simulation-$PM_{2.5}$; Source identification

1. INTRODUCTION

The growth of industrial and commercial operations near shoreline has created a need for precise air pollution dispersion models that can handle unique meteorological conditions present in the coastal environment. The Mississippi Gulf coast has a complex coastal topography. Differential heating, strong thermal gradients along the land-sea interface and topographic friction cause localized meso-scale phenomena such as land-sea breeze circulations, sea breeze induced convection and formation of thermal internal boundary layer. The horizontal and vertical extents of the land-sea breeze, the internal boundary layer and their spatial heterogeneity under varying synoptic meteorological settings typify the complex dispersion patterns in the coastal region. The Thermal Internal Boundary Layer (TIBL) especially limits the region of vertical mixing, heating/ convection and the low-level circulation characteristics which influence the coastal area

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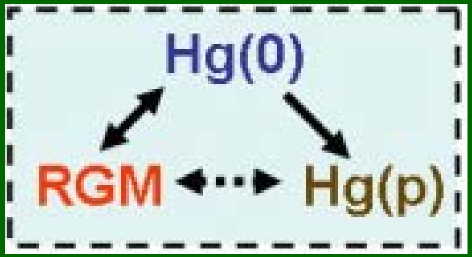


(Evolving) Atmospheric Chemical Reaction Scheme for Mercury

- Complete?
- Accurate?
- Concentrations of Reactants?
- What is RGM?

	Reaction	Rate	Units	Reference
	GAS PHASE REACTIONS			
?	$Hg^0 + O_3 \rightarrow Hg(p)$	3.0E-20	cm^3/molec-sec	Hall (1995)
	$Hg^0 + HCl \rightarrow HgCl_2$	1.0E-19	cm^3/molec-sec	Hall and Bloom (1993)
	$Hg^0 + H_2O_2 \rightarrow Hg(p)$	8.5E-19	cm^3/molec-sec	Tokos et al. (1998) (upper limit based on experiments)
	$Hg^0 + Cl_2 \rightarrow HgCl_2$	4.0E-18	cm^3/molec-sec	Calhoun and Prestbo (2001)
?	$Hg^0 + OH \rightarrow Hg(p)$	8.7E-14	cm^3/molec-sec	Sommar et al. (2001)
new	$Hg^0 + Br \rightarrow HgBr_2$			
	AQUEOUS PHASE REACTIONS			
	$Hg^0 + O_3 \rightarrow Hg^{+2}$	4.7E+7	$(\text{molar-sec})^{-1}$	Munthe (1992)
	$Hg^0 + OH \rightarrow Hg^{+2}$	2.0E+9	$(\text{molar-sec})^{-1}$	Lin and Pehkonen(1997)
	$HgSO_3 \rightarrow Hg^0$	$T^{*}e^{((31.971^{*}T)-12595.0)/T}$ sec^{-1} [T = temperature (K)]		Van Loon et al. (2002)
?	$Hg(II) + HO_2 \rightarrow Hg^0$	~ 0	$(\text{molar-sec})^{-1}$	Gardfeldt & Jonnson (2003)
	$Hg^0 + HOCl \rightarrow Hg^{+2}$	2.1E+6	$(\text{molar-sec})^{-1}$	Lin and Pehkonen(1998)
	$Hg^0 + OCl^{-1} \rightarrow Hg^{+2}$	2.0E+6	$(\text{molar-sec})^{-1}$	Lin and Pehkonen(1998)
	$Hg(II) \leftrightarrow Hg(II)_{(soot)}$	9.0E+2	liters/gram; t = 1/hour	eqlbrm: Seigneur et al. (1998) rate: Bullock & Brehme (2002).
	$Hg^{+2} + hv \rightarrow Hg^0$	6.0E-7	$(\text{sec})^{-1}$ (maximum)	Xiao et al. (1994); Bullock and Brehme (2002)

HYSPLIT Training

http://www.ertcorp.com/HYSPLIT

Acknowledgements

- **Jake Walker, Mark Woodrey, Glen Ruple (*Grand Bay National Estuarine Research Reserve*)**
- **Shelton Swanier, Jerzy Lesczcynski, Yerramilli Anjaneyulu, Venkatesh Dodla, Hari Dasari, & others *(Jackson State Univ.)***
- **Steve Brooks *(NOAA ATDD and Canann Valley Institute)***
- **Glenn Rolph, Barbara Stunder, Ariel Stein, Steve Fine (*NOAA Air Resources Laboratory*)**
- **David Schmeltz, Tim Sharac, Rick Haeuber, Sam Napolitano (*US EPA Clean Air Markets Division*)**
- **Gary Matlock, Russell Callender, Jawed Hameedi (*NOAA NOS Nat'l Centers for Coastal Ocean Science)***
- ***U.S. Fish and Wildlife Service -- Grand Bay National Wildlife Refuge***

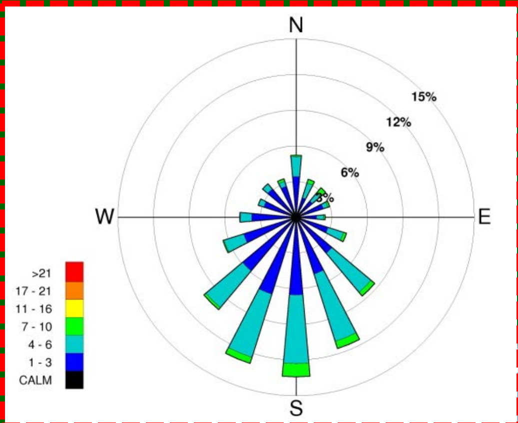
Summary of NOAA ARL Mercury Measurement Sites

● NOAA-led measurement
● Co-located measurement

Site	Collaborators / Co-locators	Ambient Air Measurements: Mercury Speciation	Ambient Air Measurements: SO_2	Ambient Air Measurements: O_3	Ambient Air Measurements: NO/NO_y	Ambient Air Measurements: CO	Ambient Air Measurements: Carbon black	Precipitation: Major Ions (NTN)	Precipitation: Mercury (MDN)	Precipitation: Trace Metals	Dry Deposition: Surrogate Surface	Dry Deposition: Throughfall	Other: Meteorology
Beltsville (MD)	▪ ***PI = Winston Luke (NOAA)*** ▪ EPA Clean Air Markets Division ▪ Univ of Maryland ▪ Maryland DNR ▪ MACTEC ▪ USGS	NOAA-led (2)	Co-located	Co-located	Co-located	Co-located		Co-located	Co-located			Co-located	Co-located
Grand Bay (MS)	▪ ***PI = Winston Luke (NOAA)*** ▪ Grand Bay NERR ▪ MS Dept Envr Quality ▪ U.S. EPA ▪ U.S. Fish & Wildlife Agency	NOAA-led (2)	NOAA-led	NOAA-led	NOAA-led	NOAA-led	NOAA-led	Co-located	Co-located	Co-located			NOAA-led
Canaan Valley (WV)	▪ **PI = Steve Brooks(CVI/NOAA** ▪ Canaan Valley Institute ▪ Univ Md Frostburg Appalachian Lab ▪ USGS	NOAA-led		NOAA-led				NOAA-led	NOAA-led		NOAA-led	Co-located	NOAA-led
Allegheny Portage (PA)	▪ ***PI = Steve Brooks (CVI/NOAA)*** ▪ Canaan Valley Institute ▪ Pennsylvania DEP ▪ National Park Service	NOAA-led						Co-located	Co-located				

Where in the world is Bill Landing?

We may be able to measure atmospheric impacts at the site from the BP / DEEPWATER HORIZON oil spill



Wind Rose estimated for the Grand Bay NERR site, for the months of May and June, from 2004-2009