

# **Atmospheric mercury measurements in the Gulf of Mexico and mid-Atlantic regions: Early results from an emerging monitoring network**

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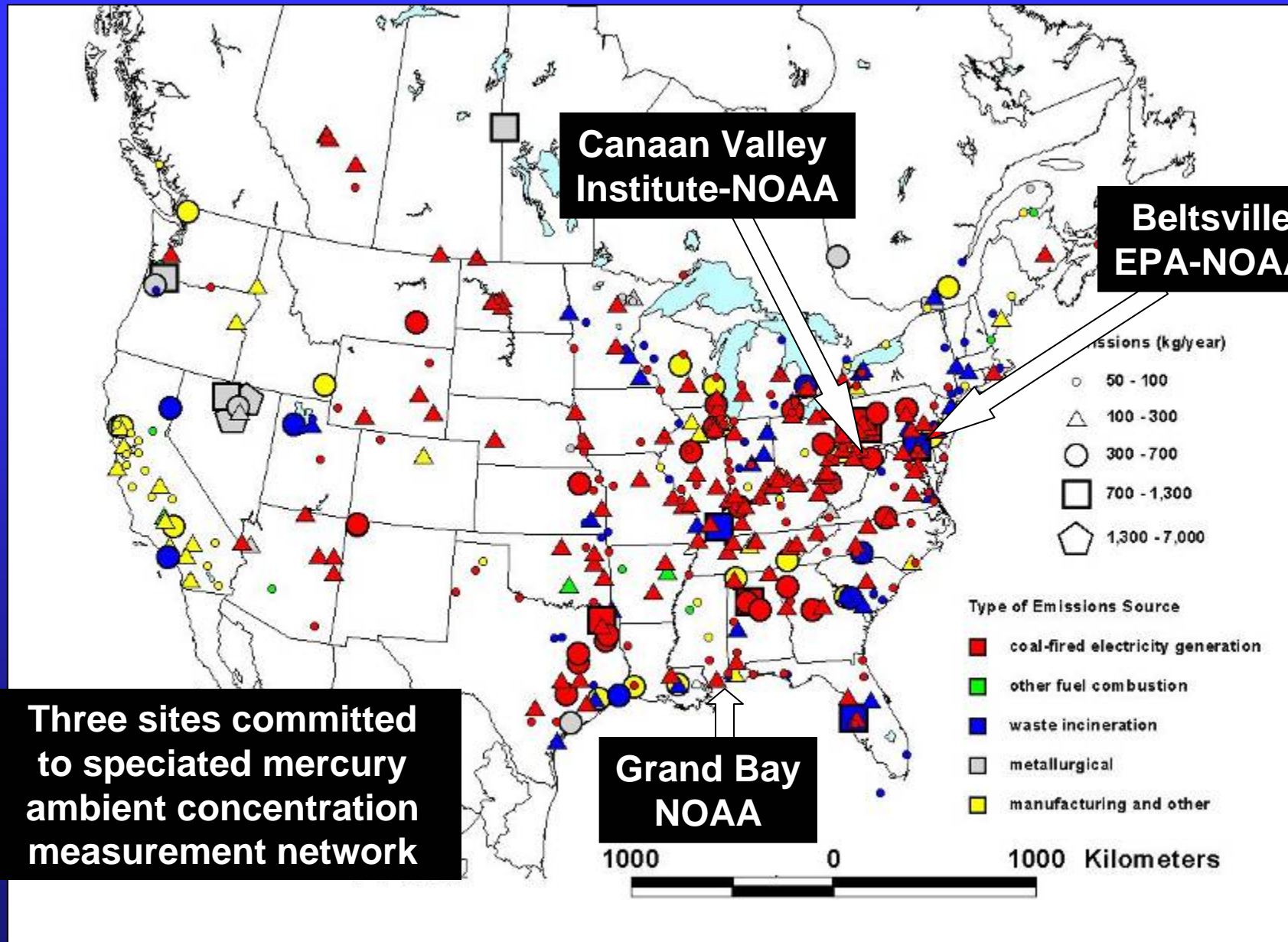
**NOAA/Air Resources Laboratory, Silver Spring, MD**

**Jake Walker**

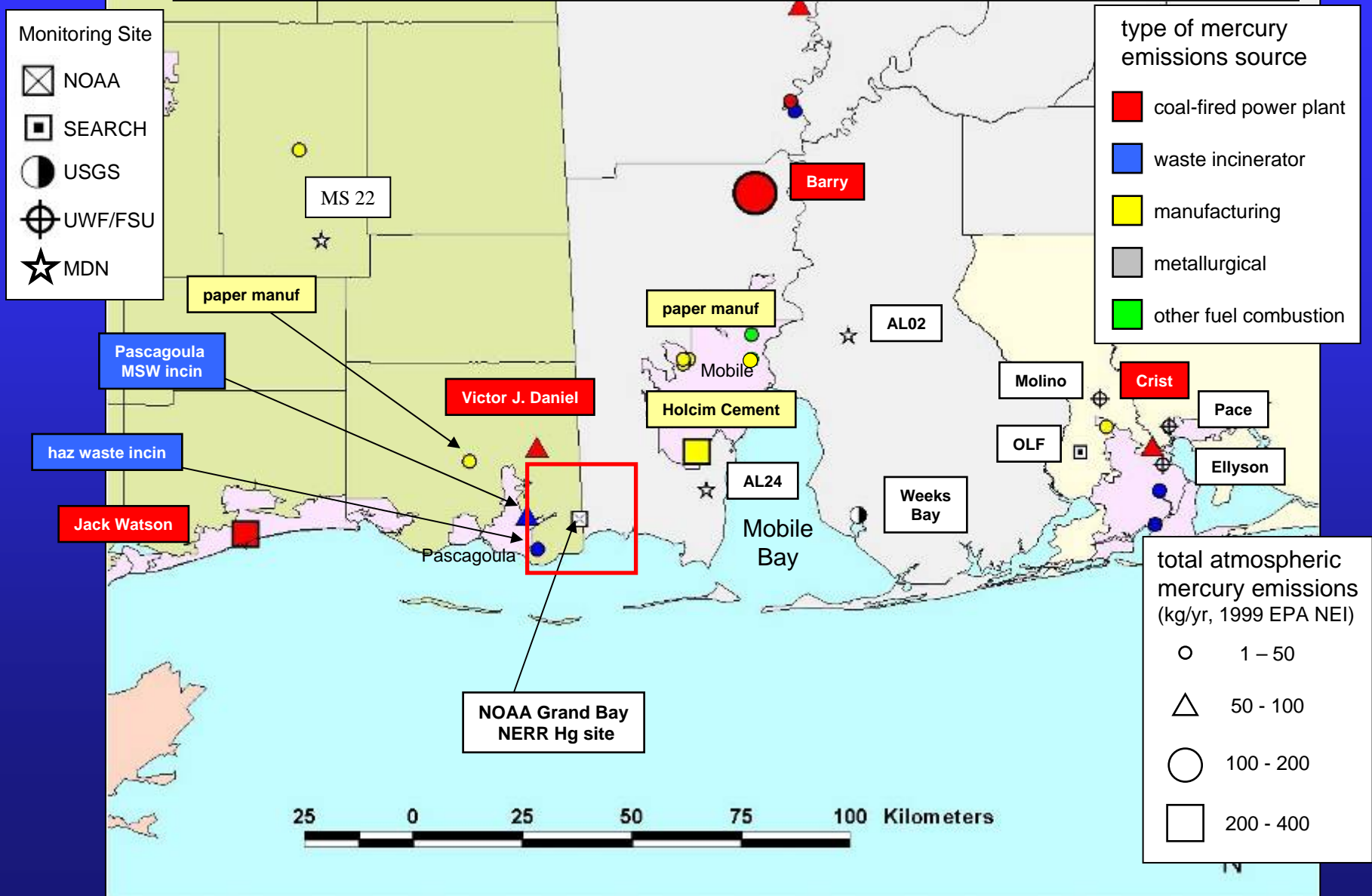
**Grand Bay National Estuarine Research Reserve, Moss Point, MS**

**Prepared for NADP 2007 Technical Committee Meeting  
Boulder, CO, Sept. 10-13, 2007**

# NOAA Mercury Sites



# Location of the NOAA Grand Bay NERR Atmospheric Mercury monitoring site, other atmospheric Hg monitoring sites, and major Hg point sources in the region (EPA 1999 NEI emissions inventory)

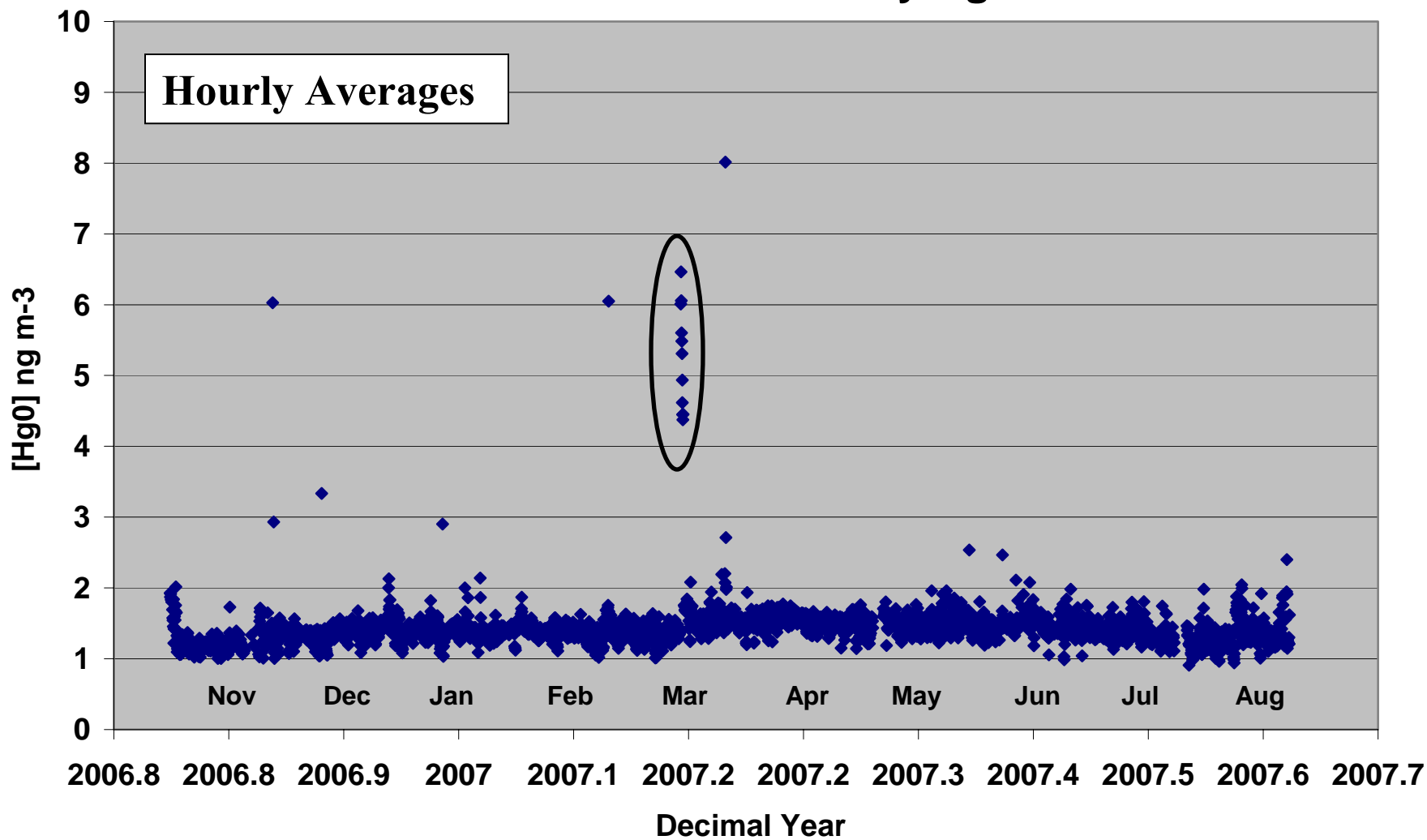


# Measurements at Grand Bay NERR, MS

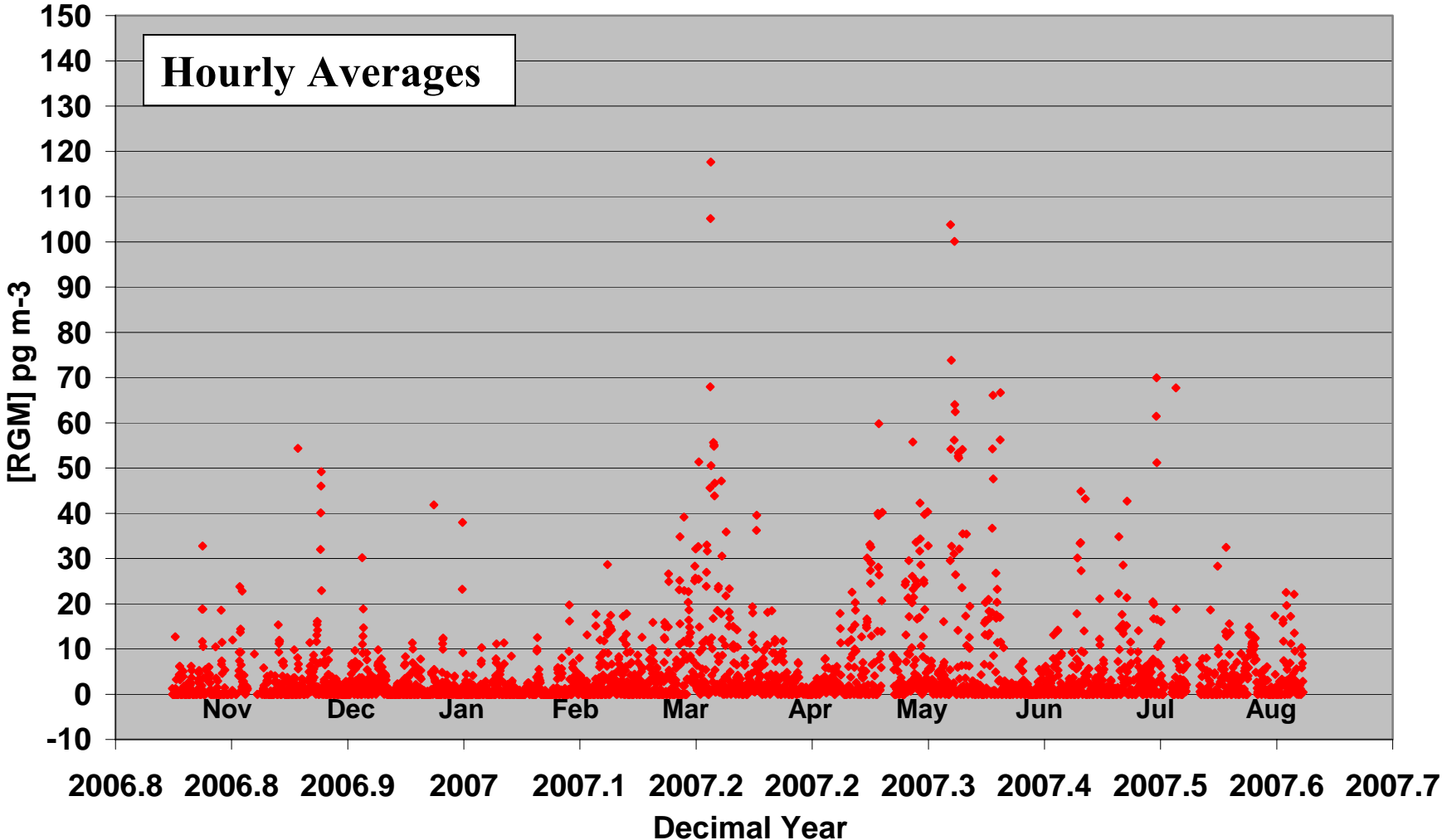


- Tekran speciation system ( $\text{Hg}^0$ , RGM,  $\text{Hg-p}$ ) installed Sept. 29, 2006
- Ancillary measurements ( $\text{CO}$ ,  $\text{O}_3$ ,  $\text{SO}_2$ ) added October 20, 2006
- Sampling Height 4 m
- Meteorological measurements (T, RH, WS, WD, Solar, Precip Rate/Amount) added March 1, 2007; nearby FWS station provided earlier measurements

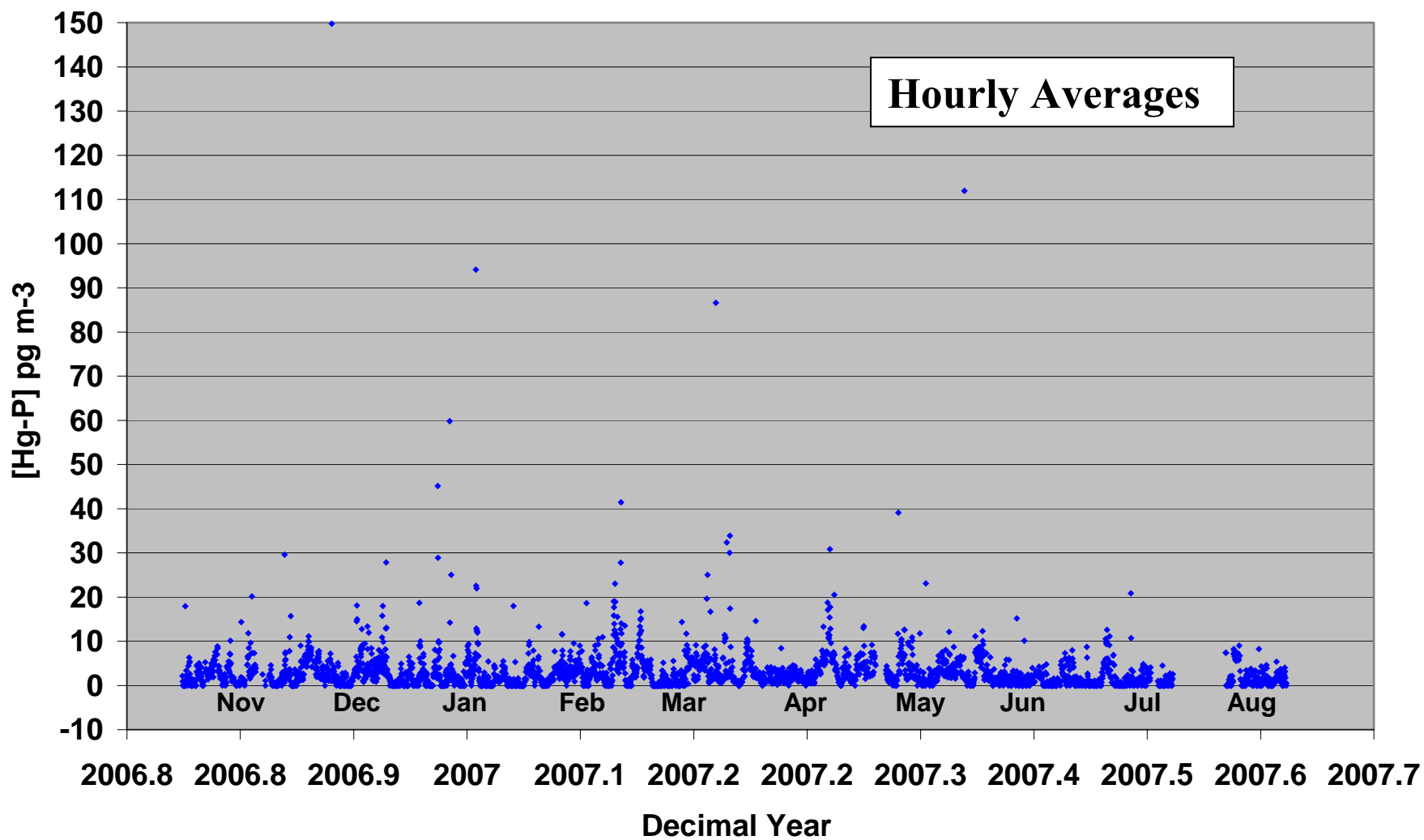
# Time Series Grand Bay Hg<sup>0</sup>



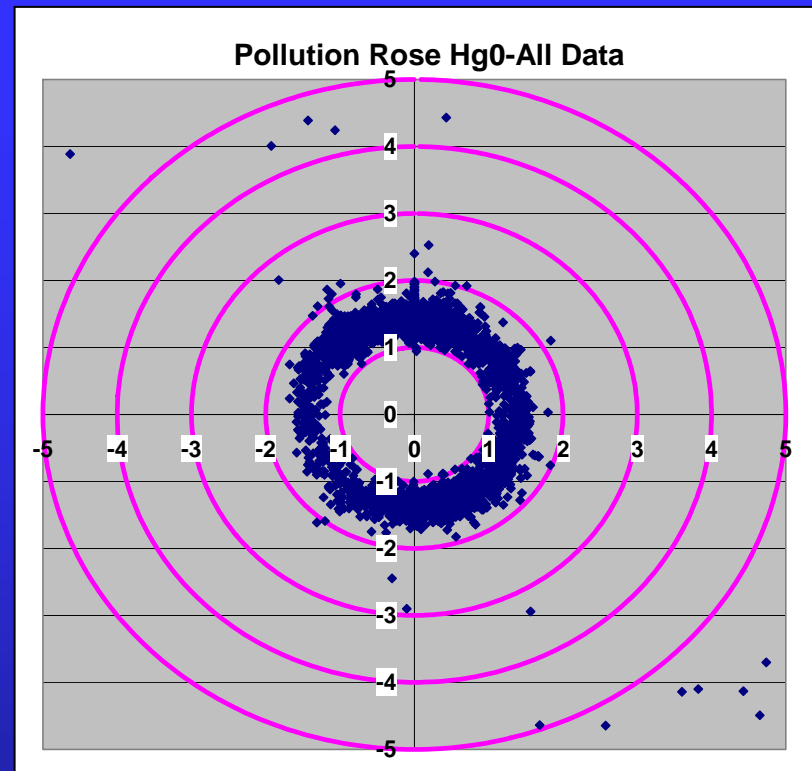
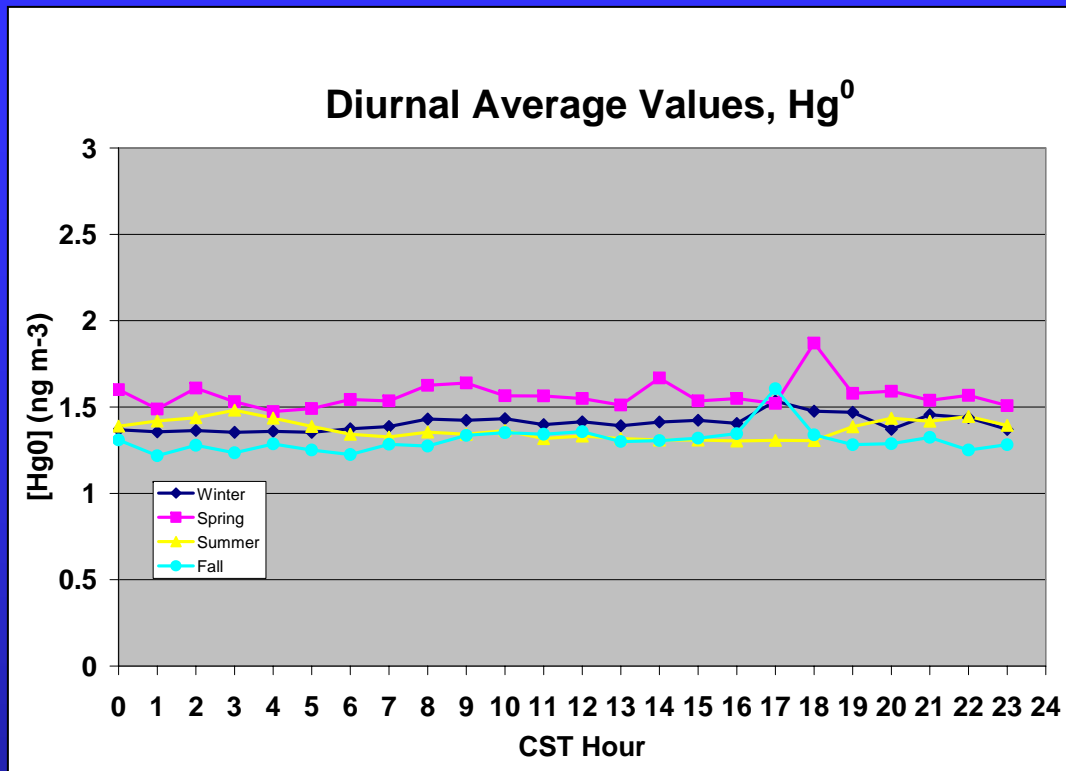
# Time Series Grand Bay RGM



# Time Series Grand Bay Hg-P



# Elemental Mercury ( $\text{Hg}^0$ )



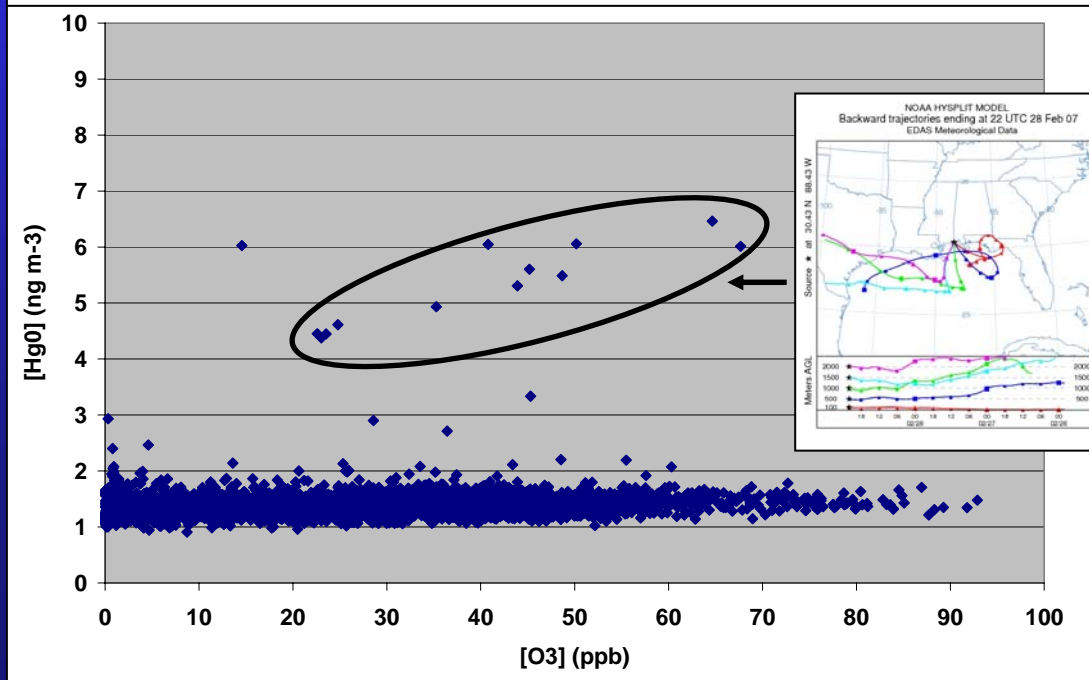
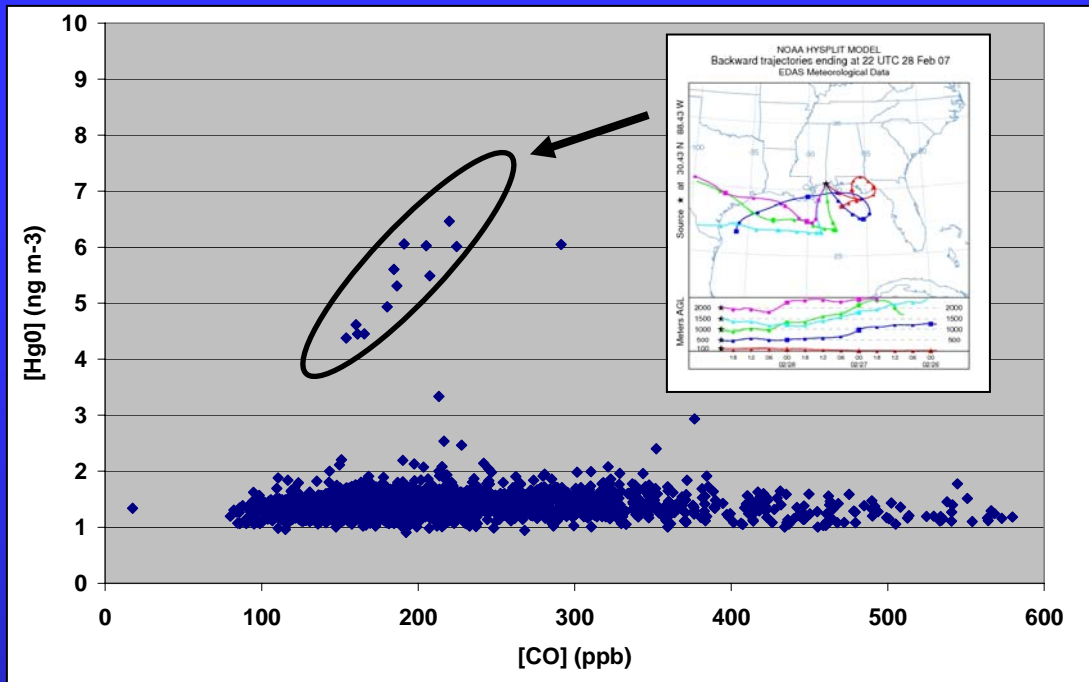
**As expected, with a few exceptions  $\text{Hg}^0$  concentrations show little or no diurnal variation or dependence on wind direction**



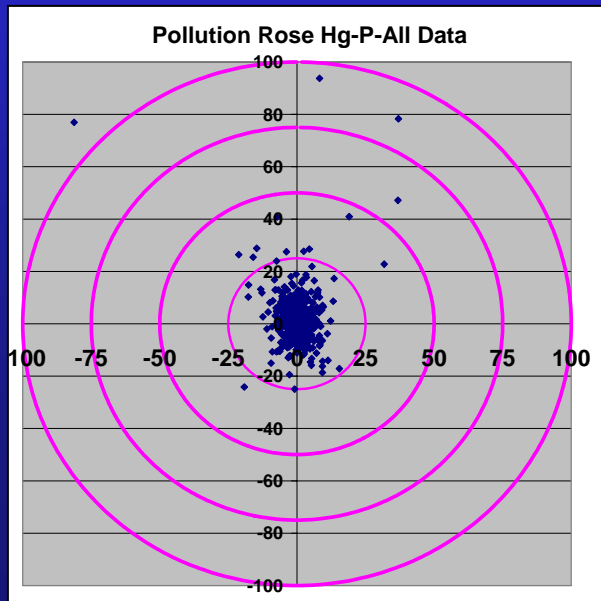
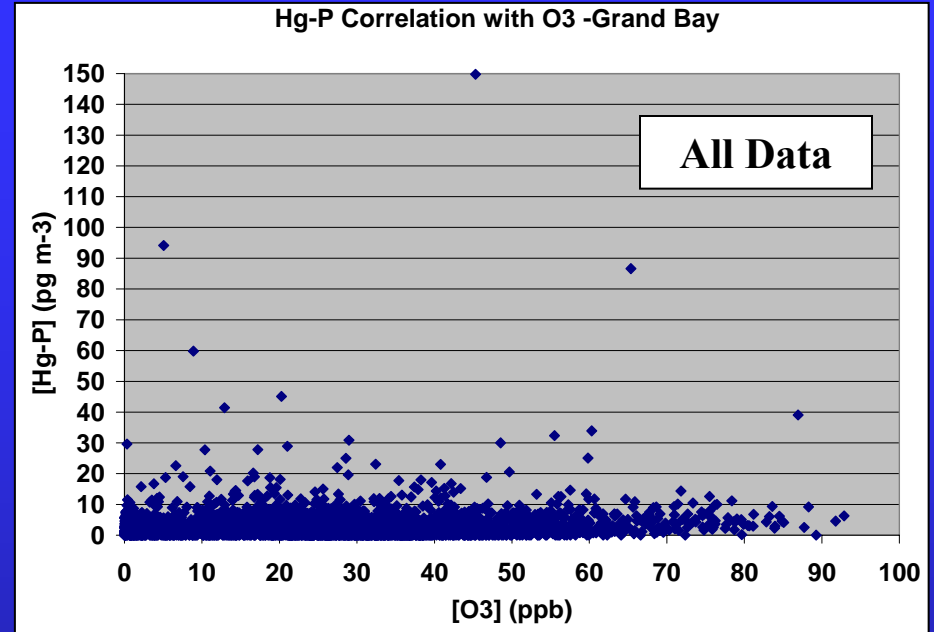
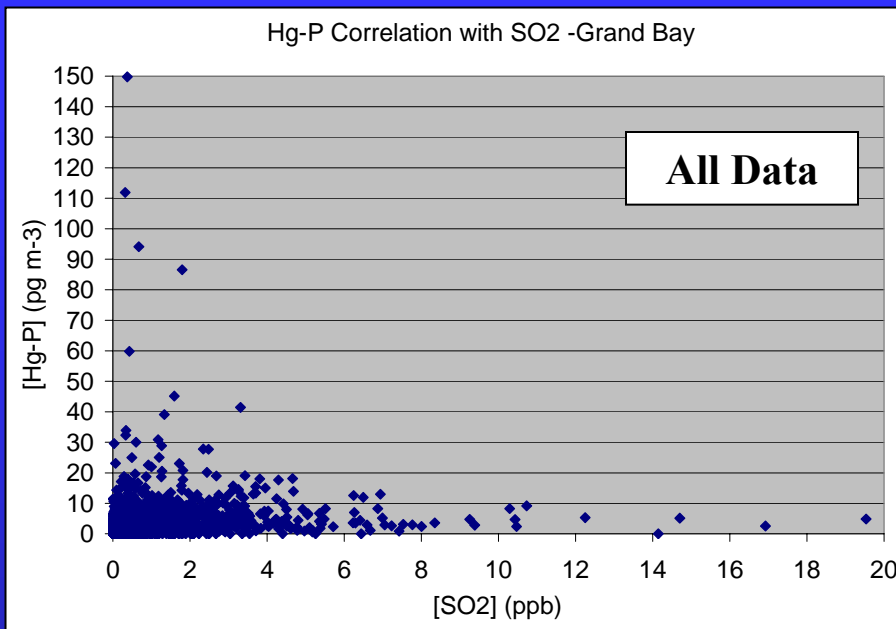
# Overnight Event Feb. 28-March 1

Strong correlation  
between  $\text{Hg}^0$  and  
 $\text{CO}$ ,  $\text{O}_3$ .

Suggests combustion  
(natural sources?)  
and transport from  
source regions to  
West. RGM, Hg-P  
ca  $20 \text{ pg m}^{-3}$   
during episode

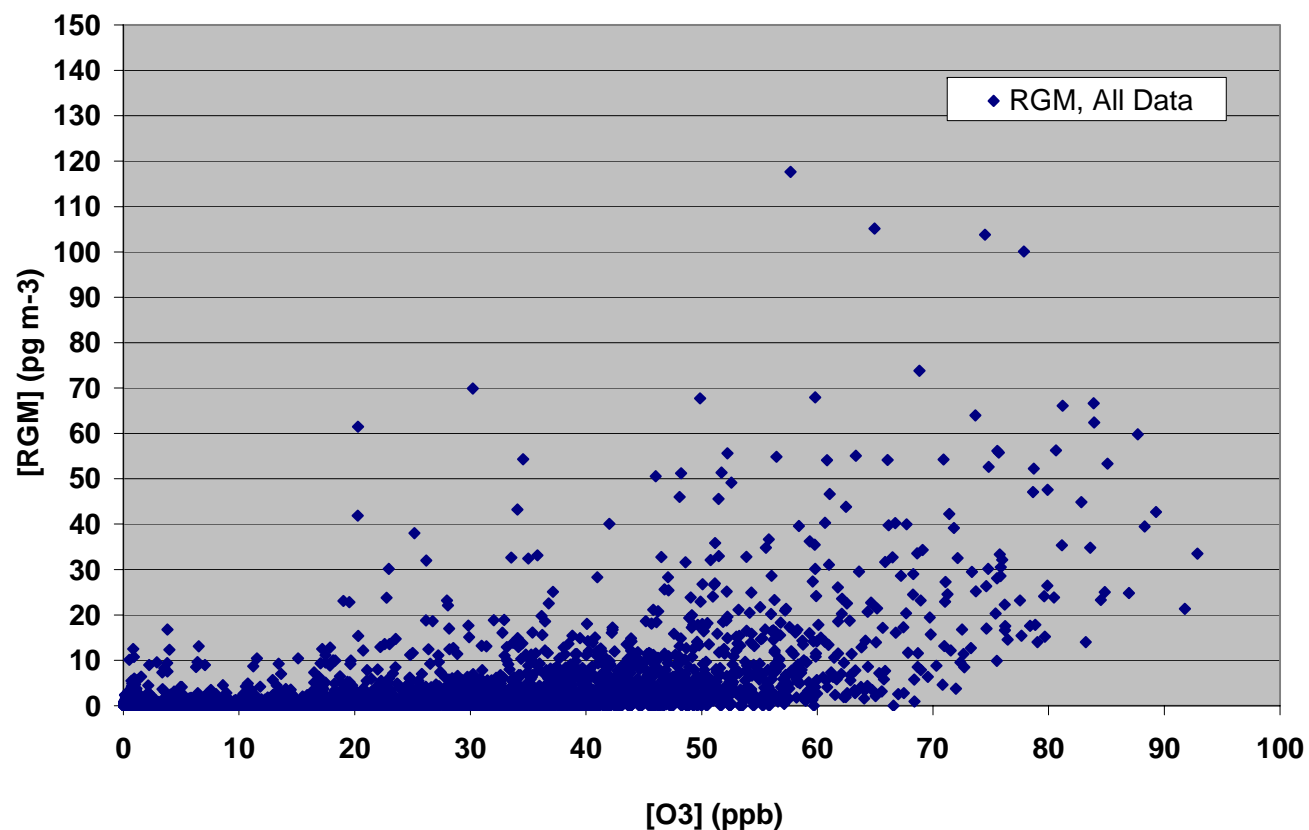


# Particulate Mercury (Hg-P)



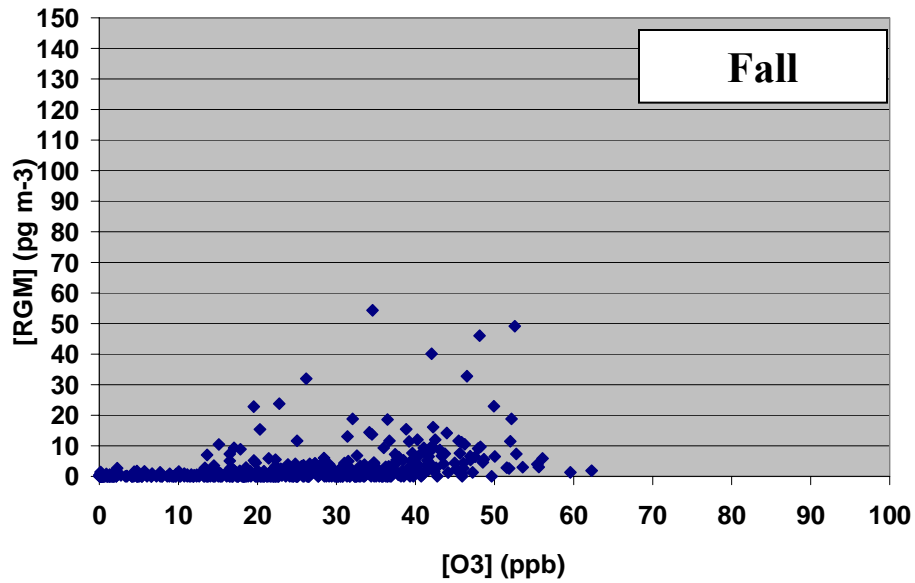
**With the exception of a few well-defined transport events, Hg-P displays no consistent relationship with WD, and exhibits little or no correlation with other trace species**

RGM Correlation with O<sub>3</sub> -Grand Bay

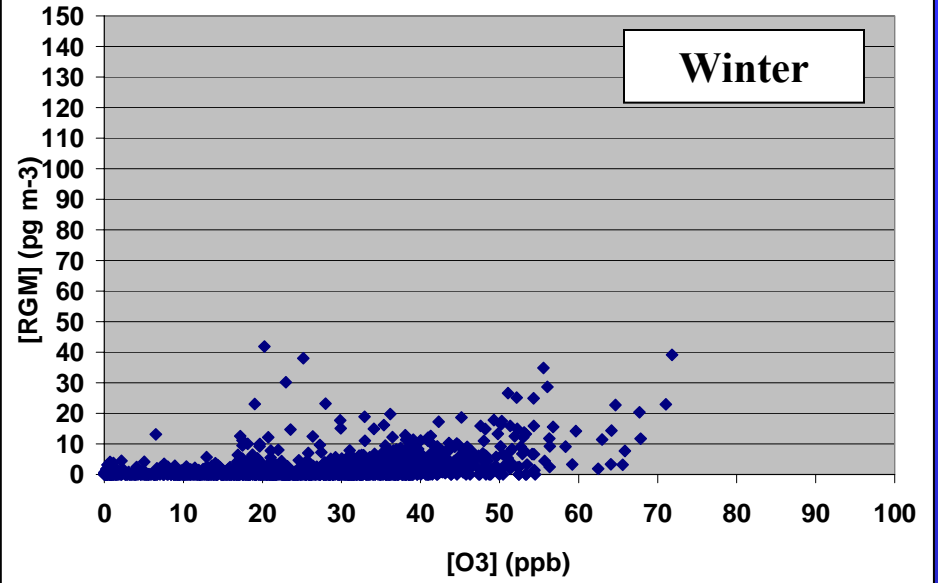


**Strongest correlations seen between RGM and O<sub>3</sub>, most of which is driven by seasonal dependence – RGM concentrations are highest, relationship with O<sub>3</sub> is strongest in Spring.**

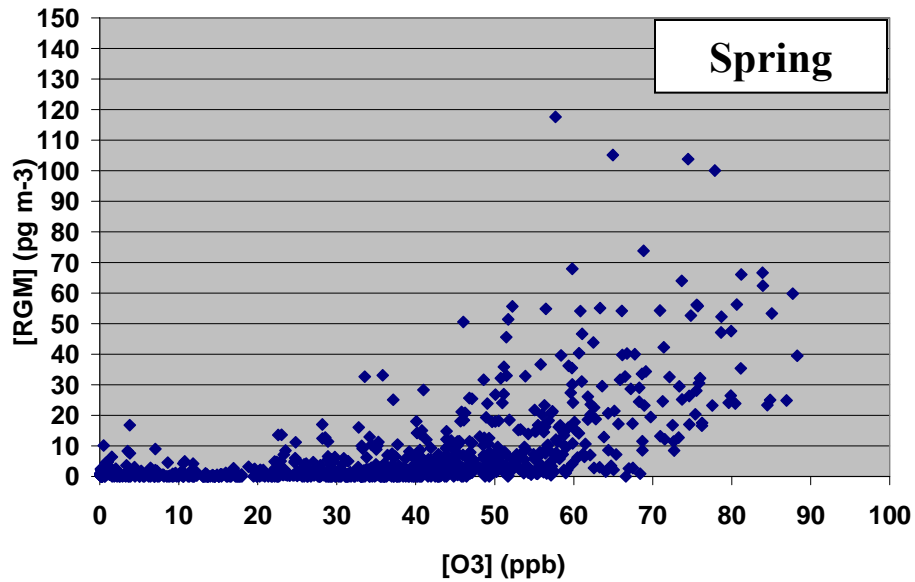
RGM Correlation with O3 -Fall



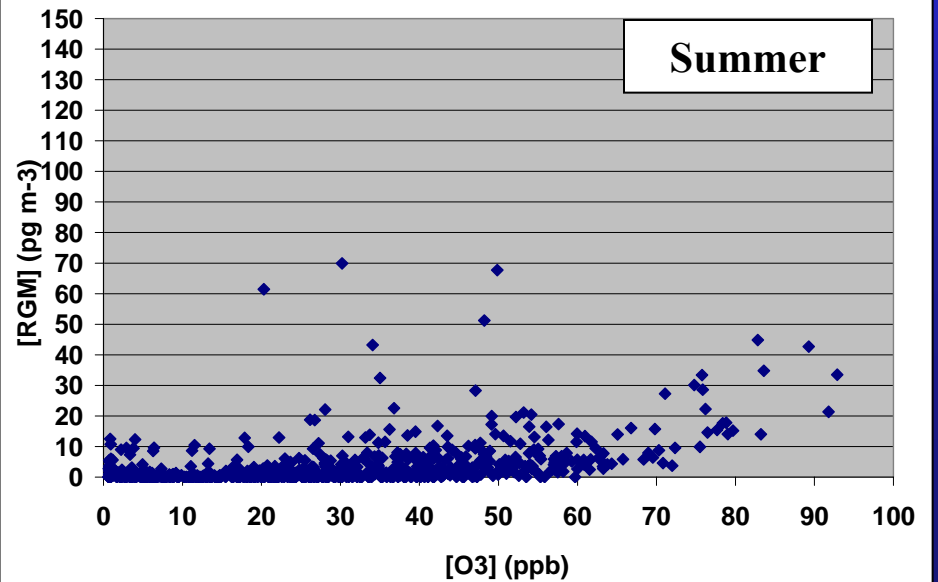
RGM Correlation with O3 -Winter

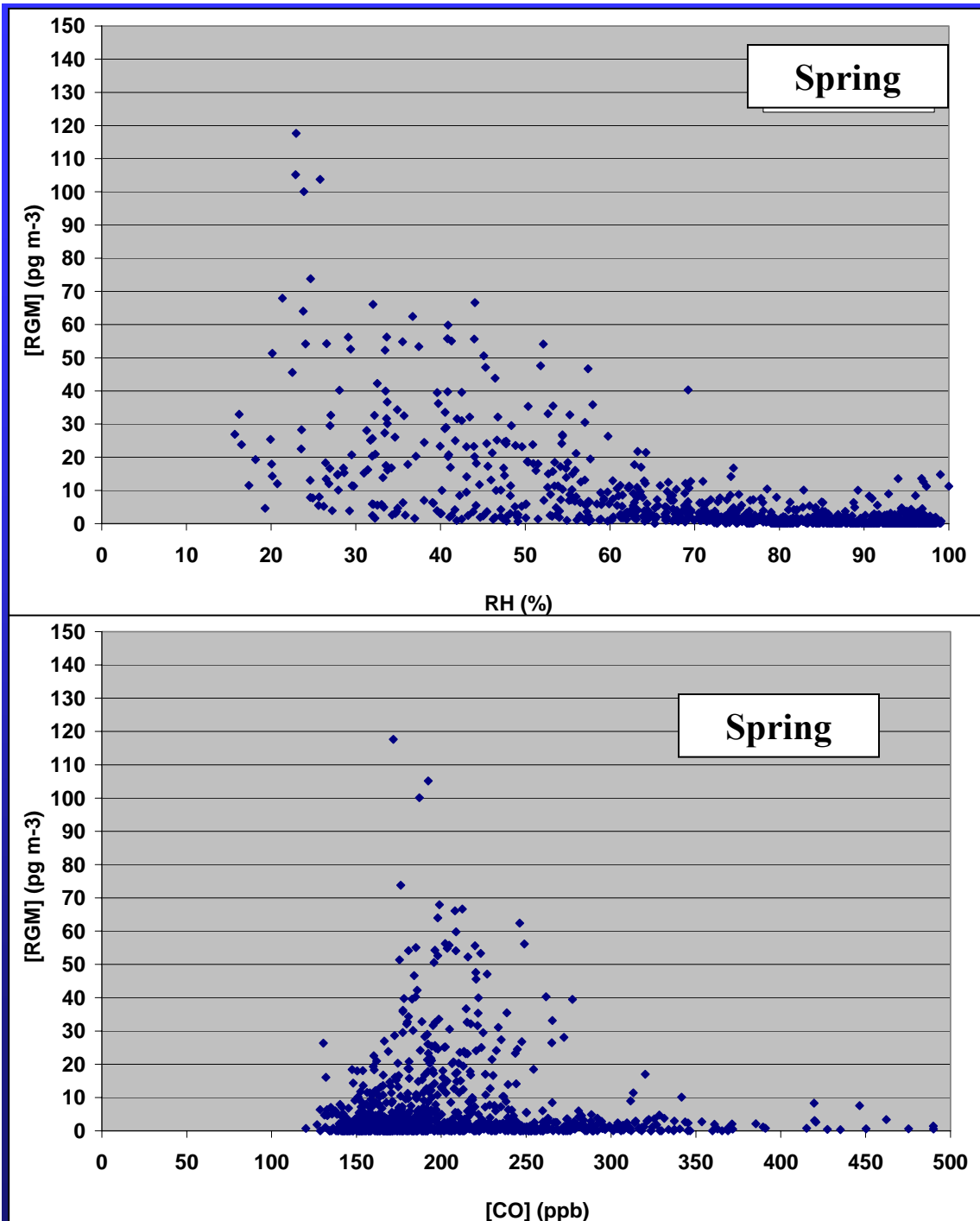


RGM Correlation with O3 -Spring



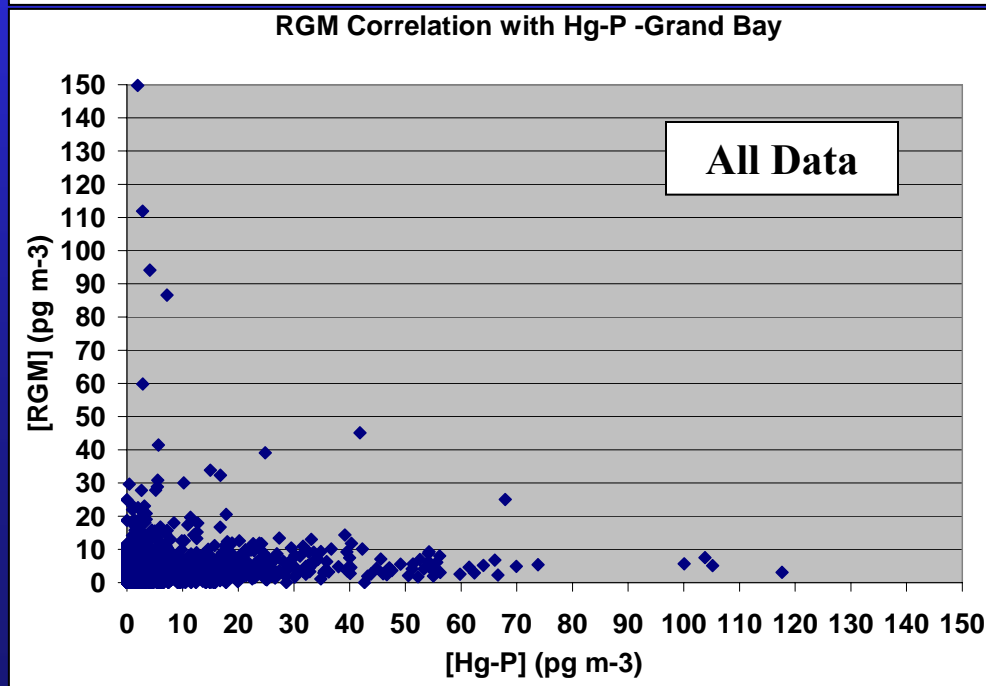
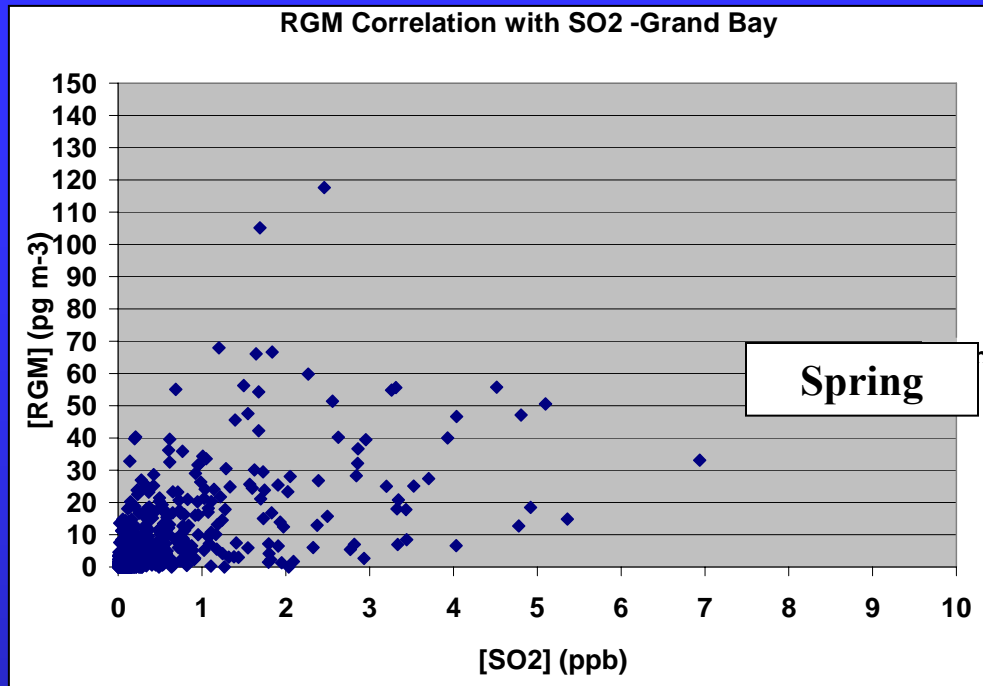
RGM Correlation with O3 -Summer





**Association of peak RGM with low RH and CO concentrations typical of continental influence suggests highest Spring peaks of RGM are seen in post-frontal activity, with transport from upwind continental sources to the North**

**RGM/RH relationship is tricky, as phase partitioning may also be at issue**



**Poor correlation with SO<sub>2</sub> suggests:**

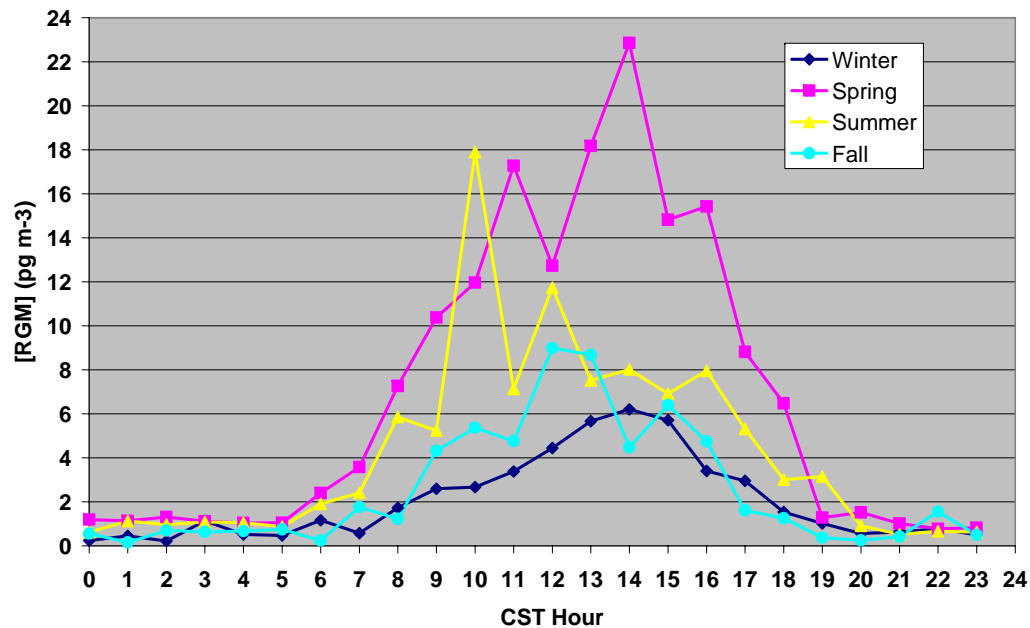
**A mix of primary sources with varying emission characteristics**

**A mix of primary and secondary sources of RGM**

**Different chemical processing and removal rates of SO<sub>2</sub> and RGM during transport**

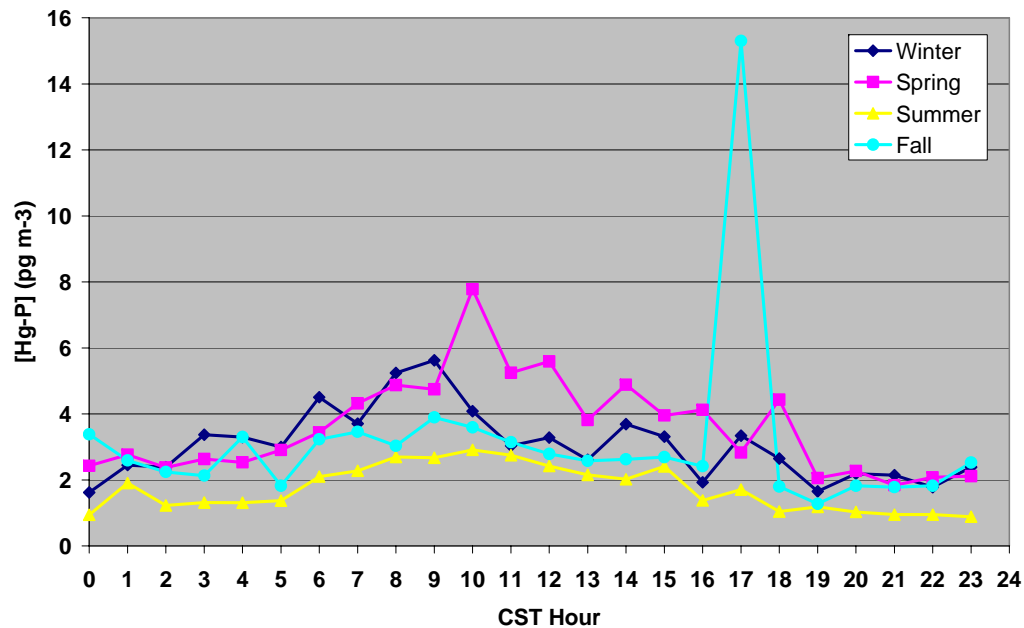
**Lack of correlation –RGM and Hg-P suggests different sources and/or removal rates of these species**

Diurnal Average Values, RGM

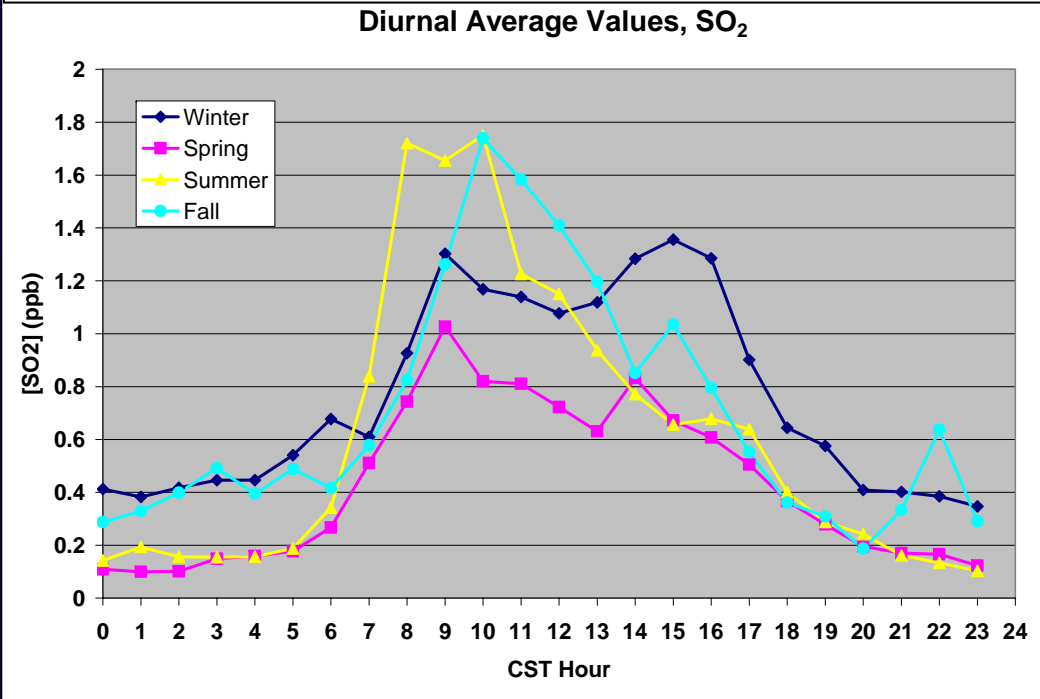
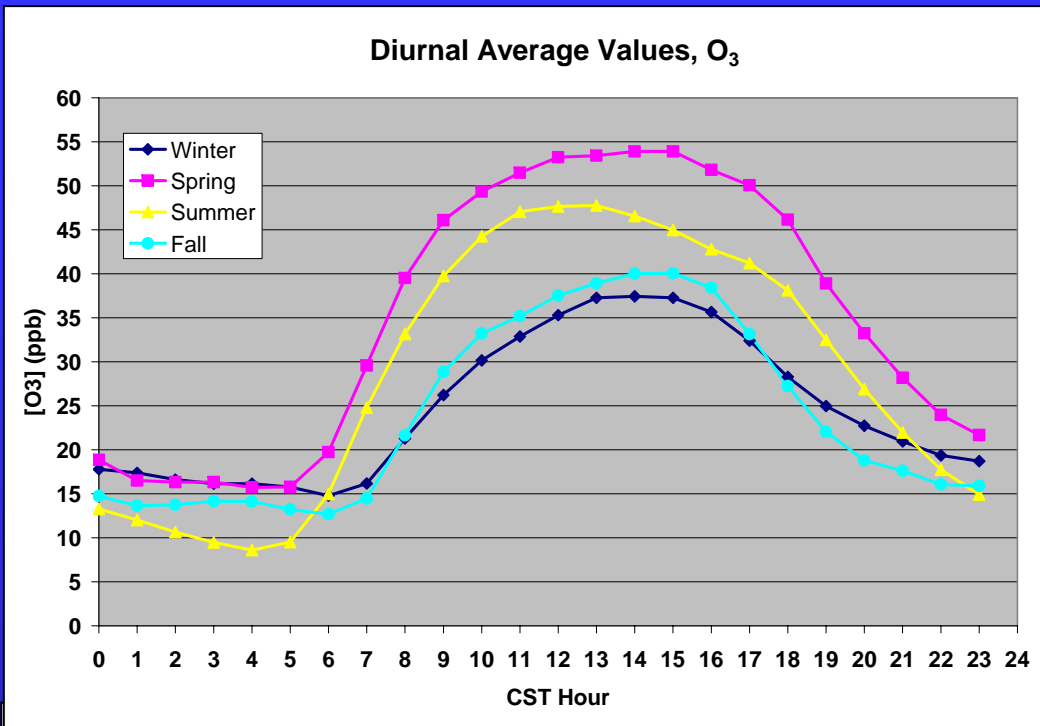


Significant diurnal patterns seen in both RGM and Hg-P, but amplitude of diurnal Hg-P profile is much smaller.

Diurnal Average Values, Hg-P



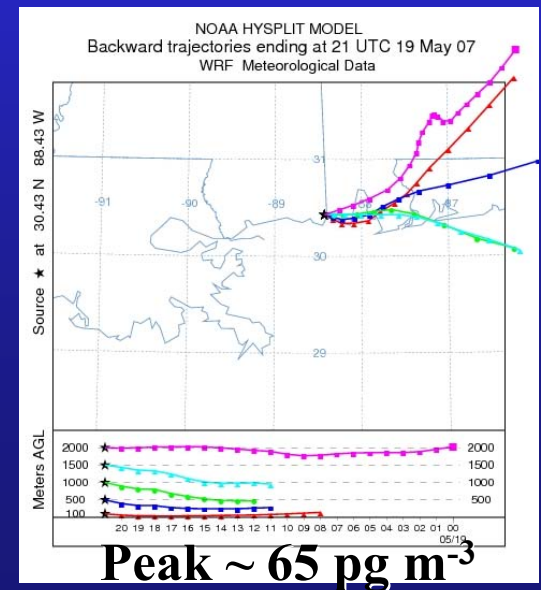
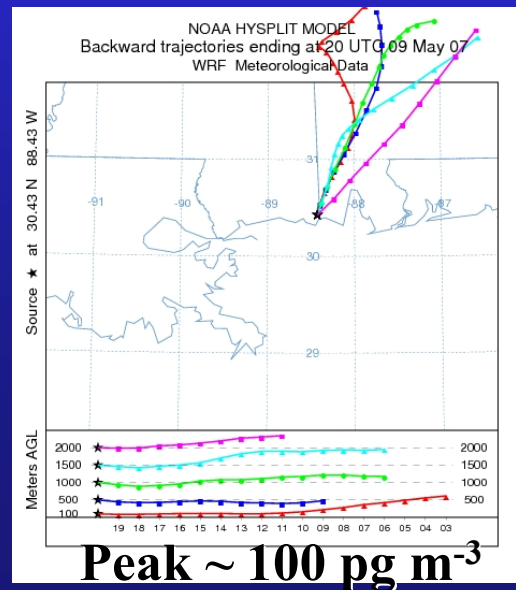
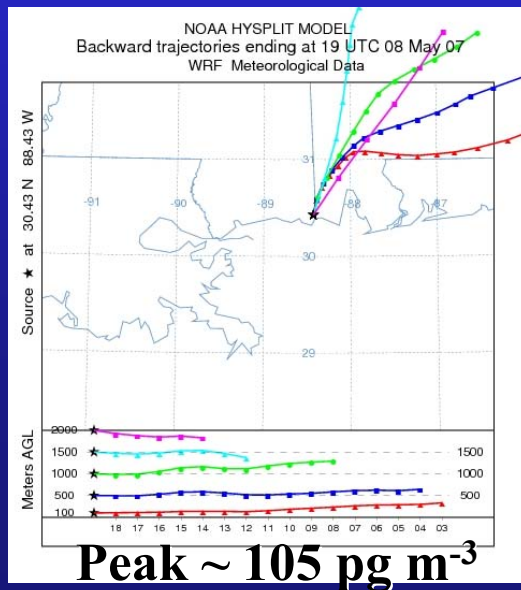
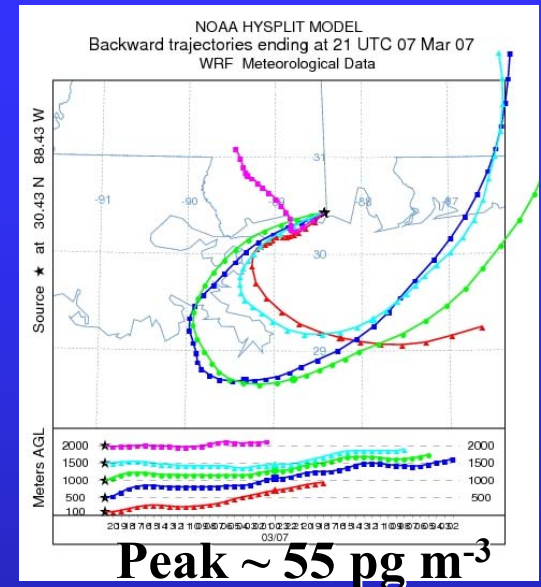
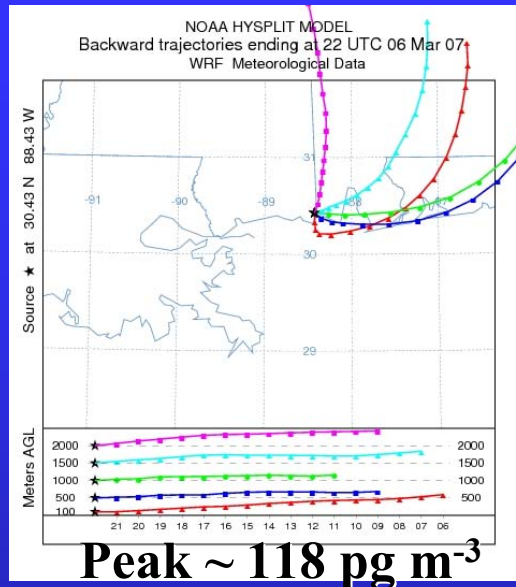
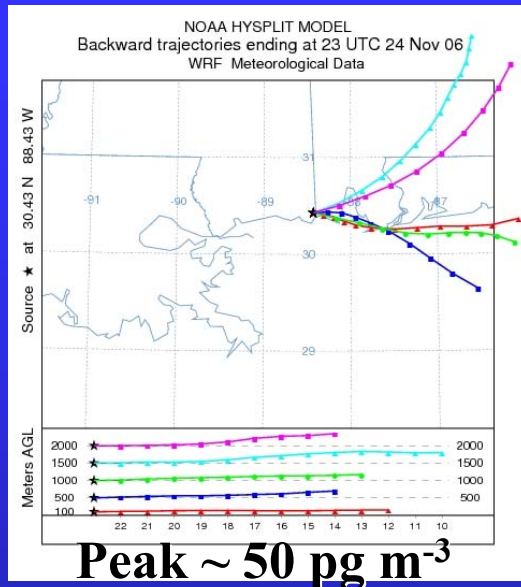
Highest RGM and Hg-P concentrations seen in Spring



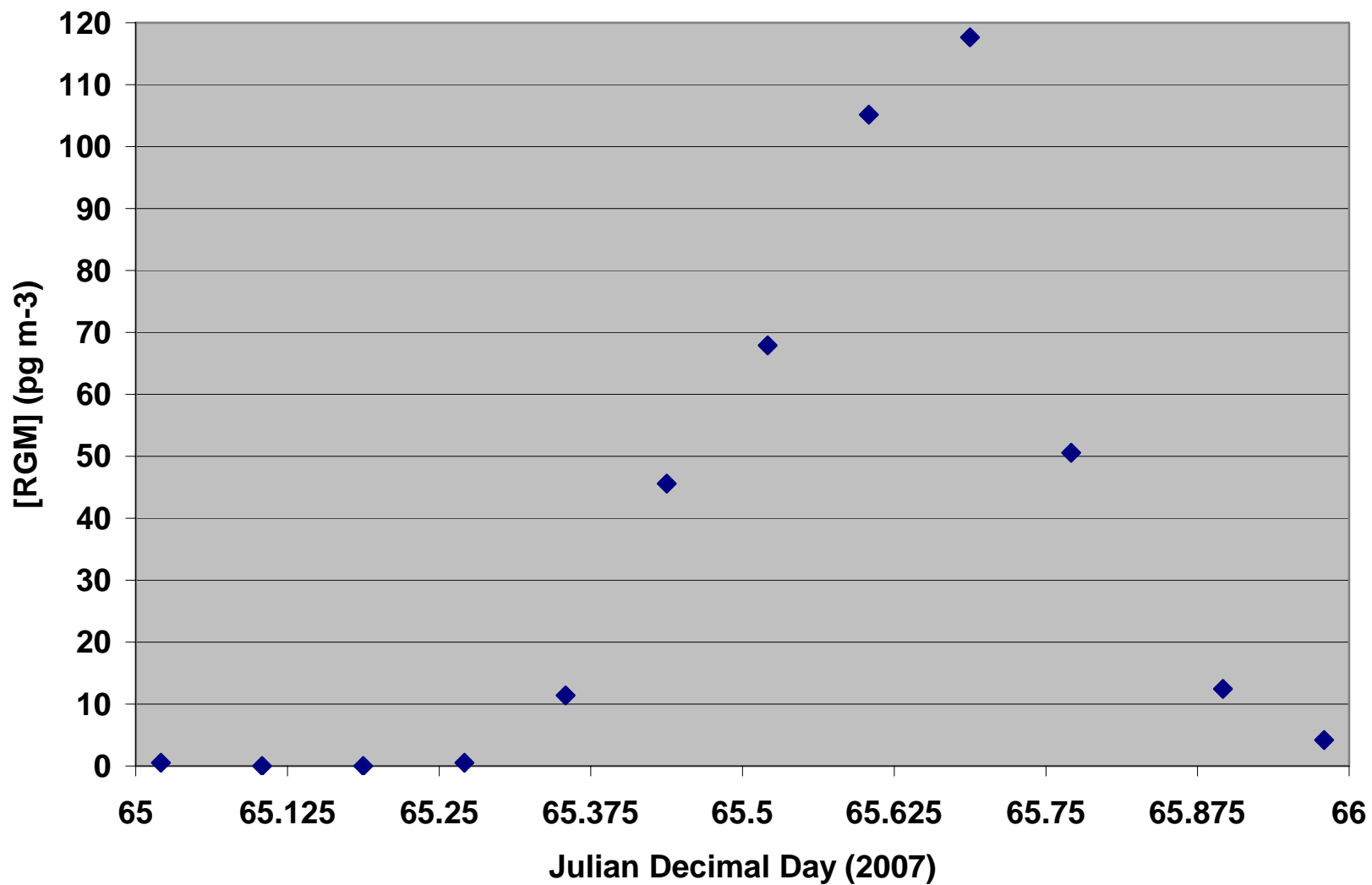
**Similarity to O<sub>3</sub> and SO<sub>2</sub> diurnal profiles confirms the importance of downward mixing in the development of the daytime boundary layer, but does not allow us to differentiate between primary and secondary sources of the mercury species.**



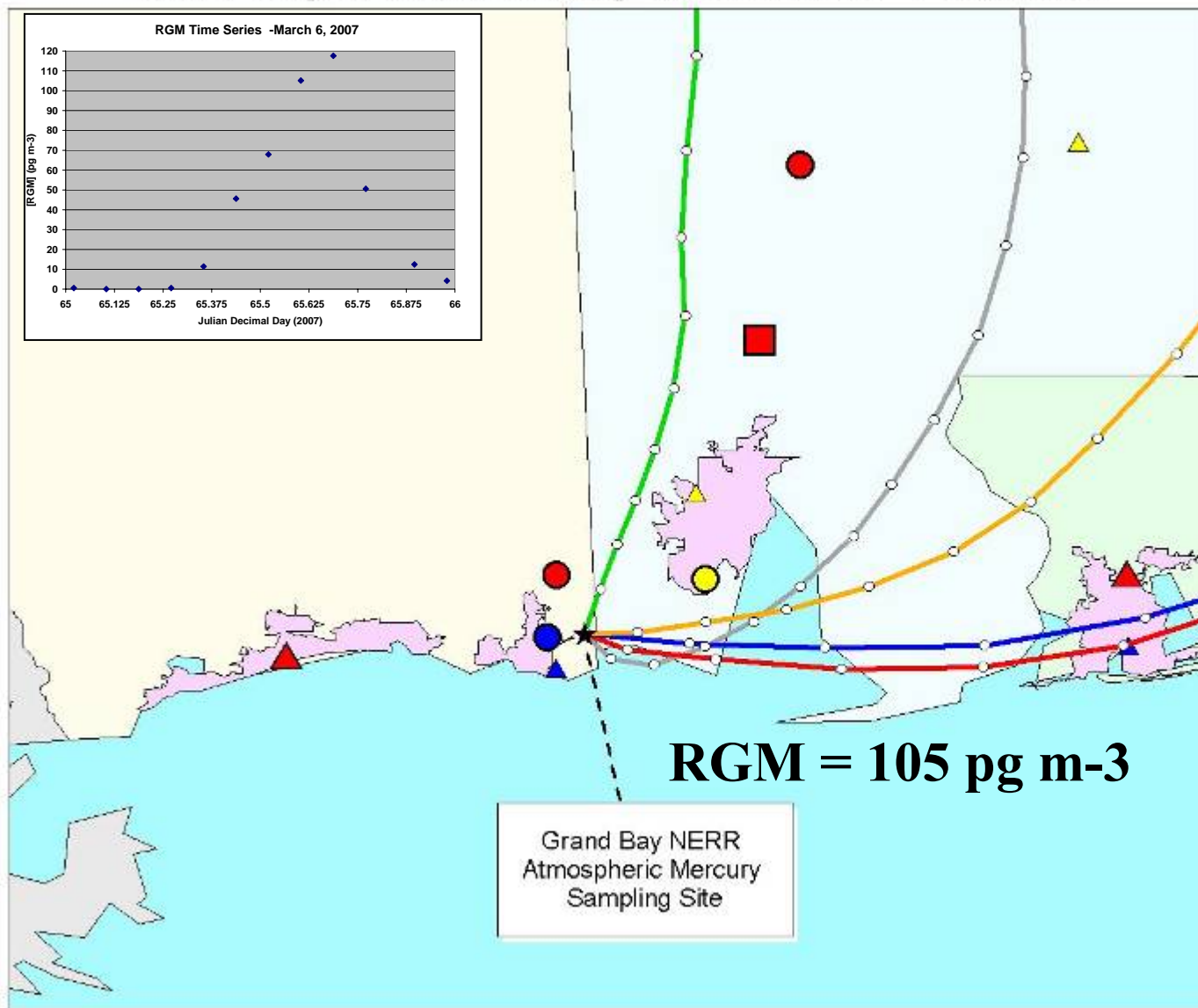
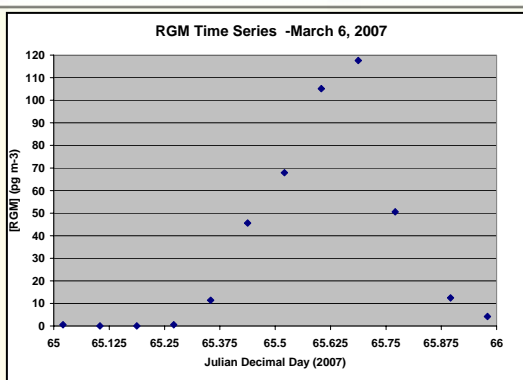
# Higher RGM Associated with N-E trajectories



### RGM Time Series -March 6, 2007



# Back Trajectories Arriving at 3/06/2007 14:00 CST



Large sources of 1999 RGM (Reactive Gaseous Mercury) emissions (kg/yr) based on USEPA data from 1999 Nat'l Emissions Inventory

Size and shape of symbol denotes amount of RGM emitted (kg/yr)

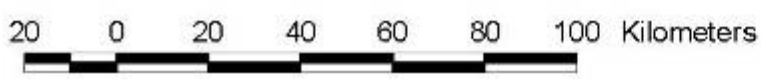
- △ 5 - 10
- 10 - 50
- △ 50 - 100
- 100 - 300

Color of symbol denotes type of mercury source

- coal-fired electricity generation
- other fuel combustion
- waste incineration
- metallurgical processes
- manufacturing/other

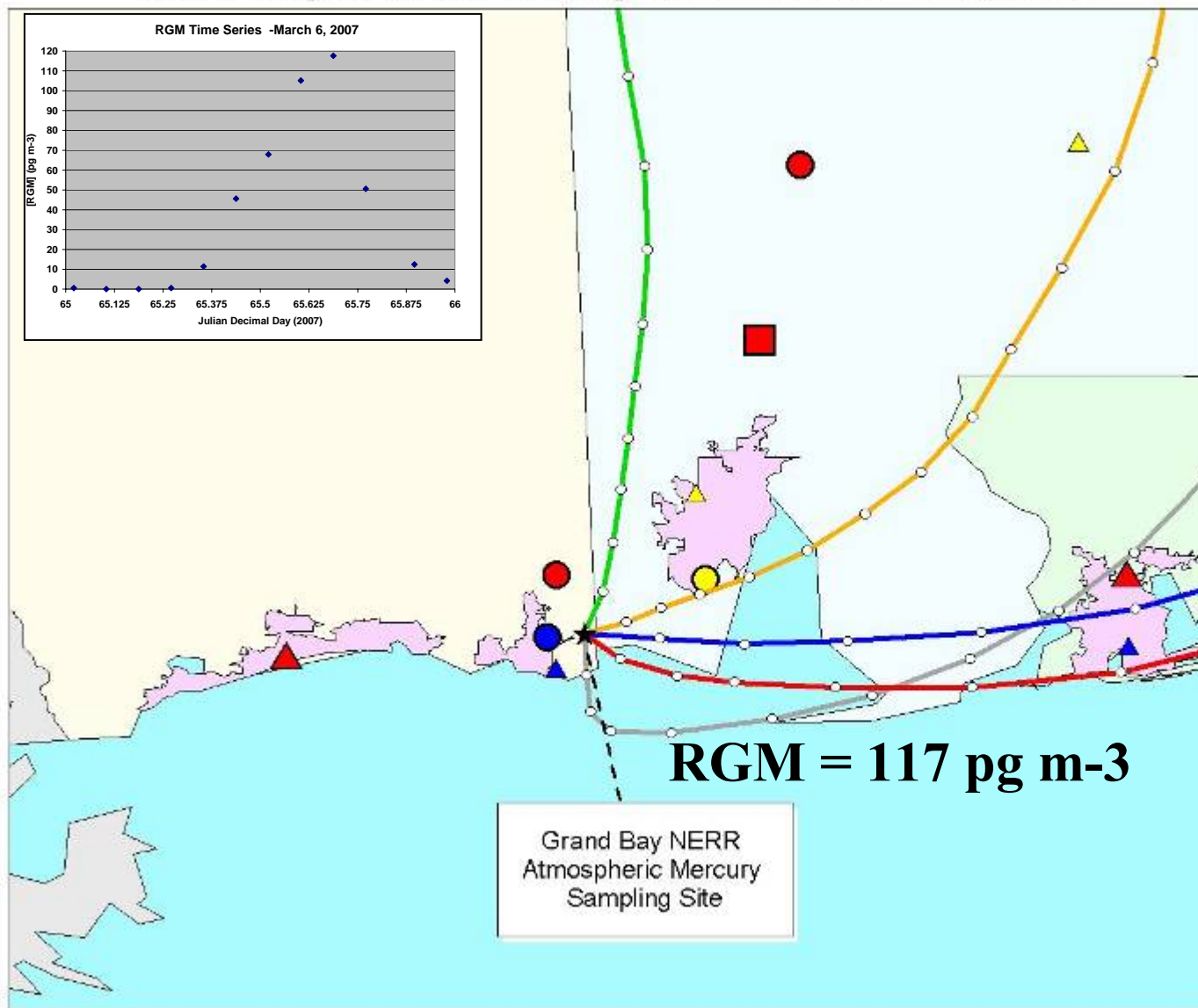
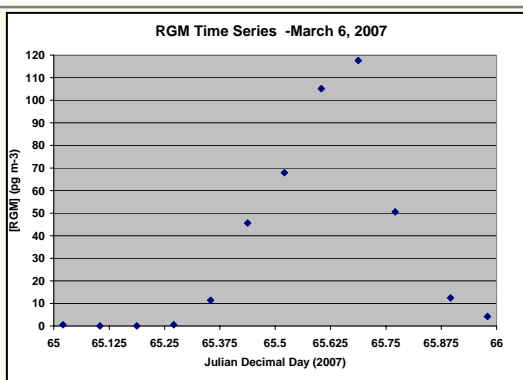
Back-trajectories starting at indicated height (m). Circles on trajectories mark the hourly position of the trajectory.

- ~ 100
- ~ 500
- ~ 1000
- ~ 1500
- ~ 2000



urbanized areas

# Back Trajectories Arriving at 3/06/2007 16:00 CST



Large sources of 1999 RGM (Reactive Gaseous Mercury) emissions (kg/yr) based on USEPA data from 1999 Nat'l Emissions Inventory

Size and shape of symbol denotes amount of RGM emitted (kg/yr)

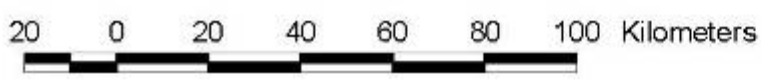
- △ 5 - 10
- 10 - 50
- △ 50 - 100
- 100 - 300

Color of symbol denotes type of mercury source

- coal-fired electricity generation
- other fuel combustion
- waste incineration
- metallurgical processes
- manufacturing/other

Back-trajectories starting at indicated height (m). Circles on trajectories mark the hourly position of the trajectory.

- ~ 100
- ~ 500
- ~ 1000
- ~ 1500
- ~ 2000

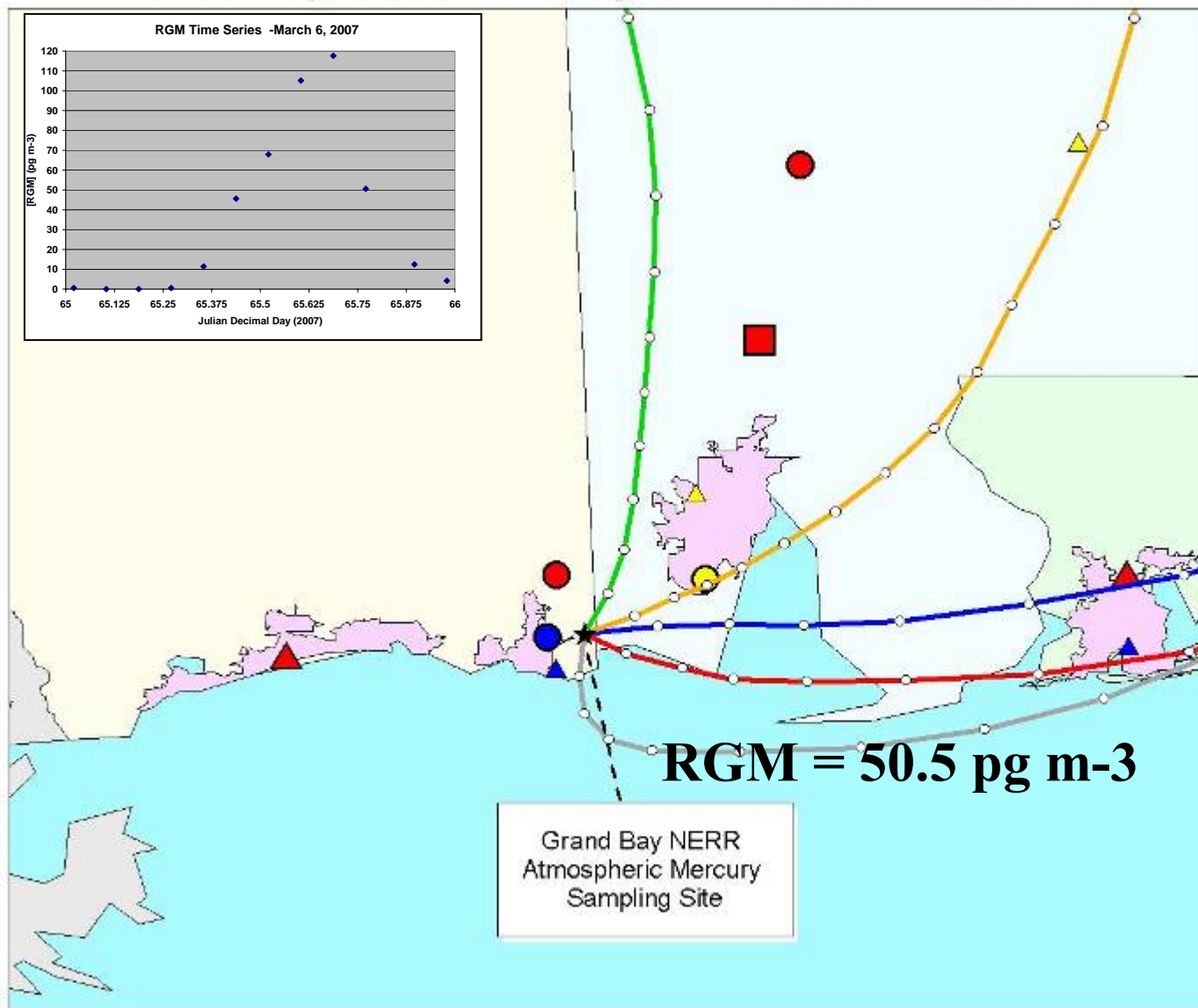
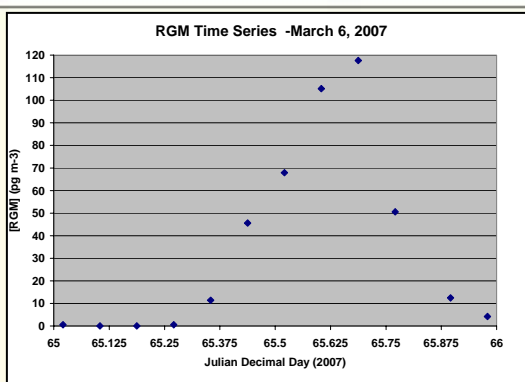


urbanized areas

Grand Bay NERR  
Atmospheric Mercury  
Sampling Site

**RGM = 117 pg m<sup>-3</sup>**

# Back Trajectories Arriving at 3/06/2007 17:00 CST



Large sources of 1999 RGM (Reactive Gaseous Mercury) emissions (kg/yr) based on USEPA data from 1999 Nat'l Emissions Inventory

Size and shape of symbol denotes amount of RGM emitted (kg/yr)

- △ 5 - 10
- 10 - 50
- △ 50 - 100
- 100 - 300

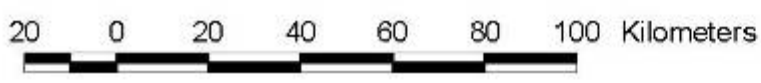
Color of symbol denotes type of mercury source

- coal-fired electricity generation
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- waste incineration
- metallurgical processes
- manufacturing/other

Back-trajectories starting at indicated height (m).

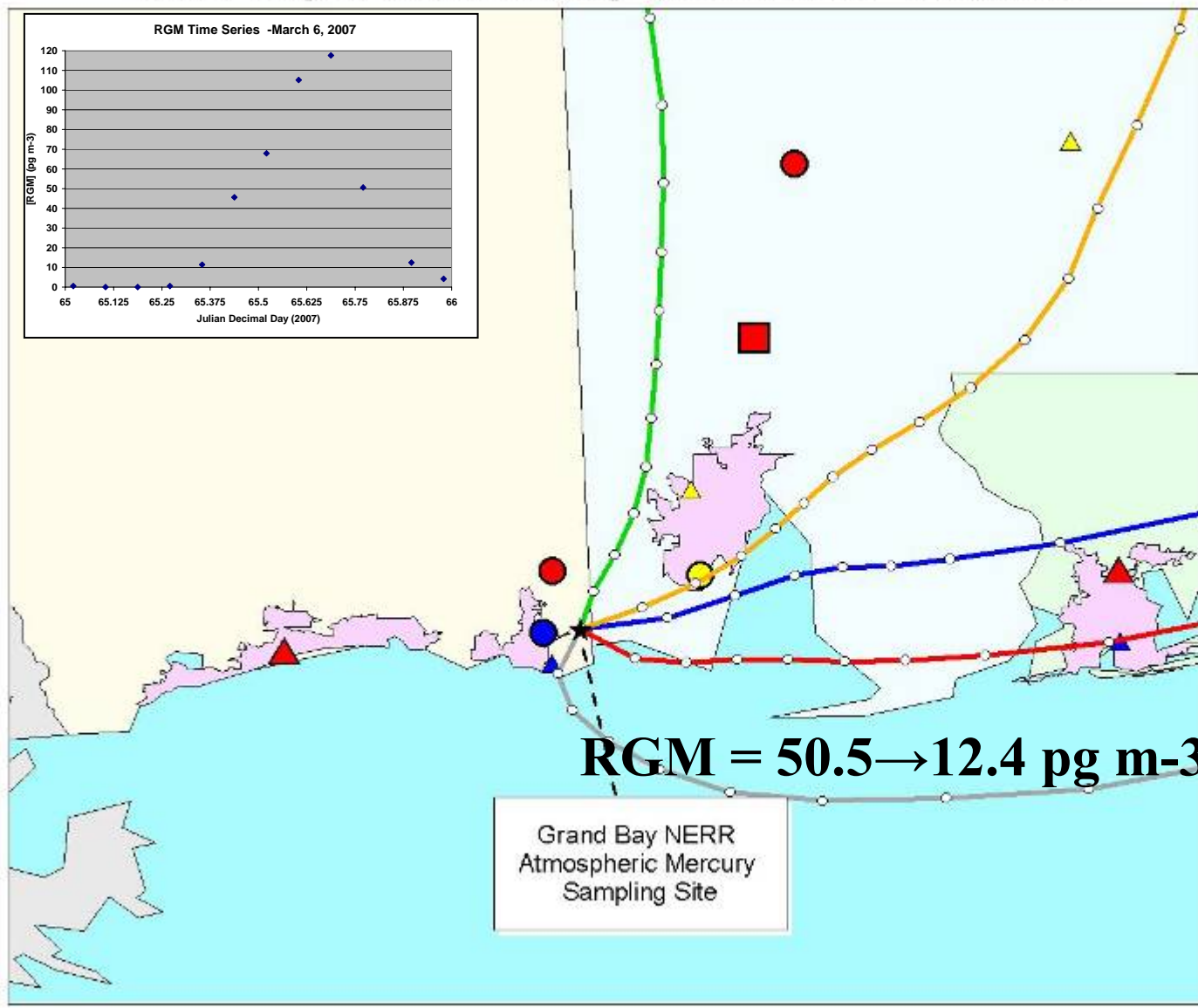
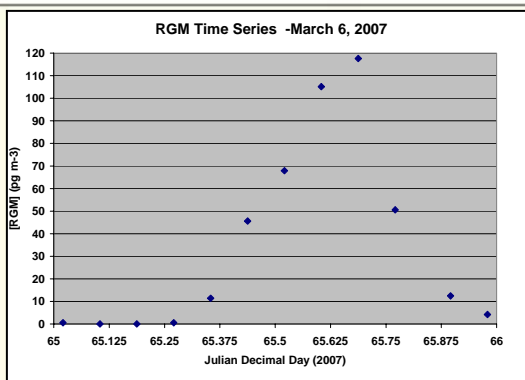
- ~ 100
- ~ 500
- ~ 1000
- ~ 1500
- ~ 2000

Circles on trajectories mark the hourly position of the trajectory.



urbanized areas

# Back Trajectories Arriving at 3/06/2007 19:00 CST



Large sources of 1999 RGM (Reactive Gaseous Mercury) emissions (kg/yr) based on USEPA data from 1999 Nat'l Emissions Inventory

Size and shape of symbol denotes amount of RGM emitted (kg/yr)

- △ 5 - 10
- 10 - 50
- △ 50 - 100
- 100 - 300

Color of symbol denotes type of mercury source

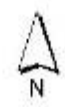
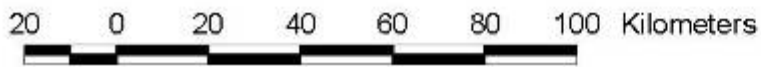
- coal-fired electricity generation
- other fuel combustion
- waste incineration
- metallurgical processes
- manufacturing/other

Back-trajectories starting at indicated height (m). Circles on trajectories mark the hourly position of the trajectory.

- ~ 100
- ~ 500
- ~ 1000
- ~ 1500
- ~ 2000

**RGM = 50.5 → 12.4 pg m<sup>-3</sup>**

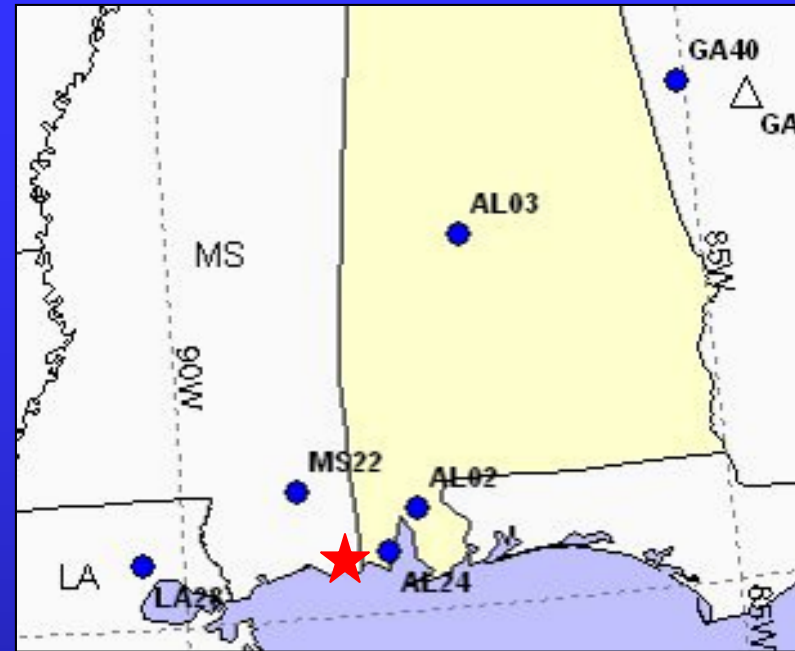
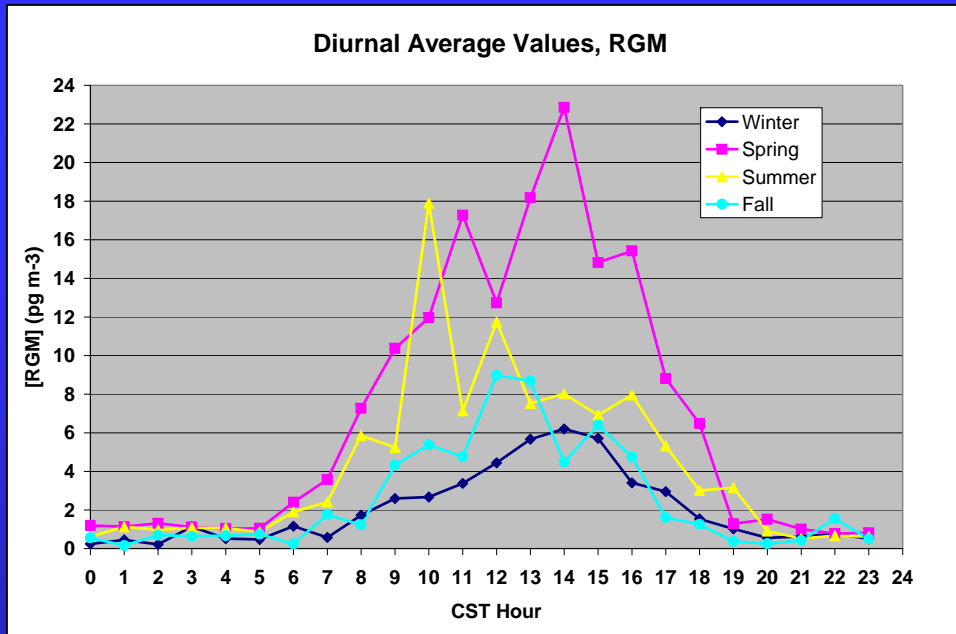
Grand Bay NERR Atmospheric Mercury Sampling Site



urbanized areas



# Deposition Estimates



**RGM + Hg-P Dry Deposition ( $\text{ng m}^{-2} \text{day}^{-1}$ );  
assumes  $V_d = 2.5 \text{ cm s}^{-1}$  and  $0.3 \text{ cm s}^{-1}$  mid day average**

	Fall	Winter	Spring	Summer
<b>Dry Dep, Grand Bay (2006-2007)</b>	5.4	4.3	14.2	8.6
<b>Wet Dep, AL24 (2005-2006)</b>	13.5	24.8	31.6	34.6
<b>Wet Dep, MS22 (2005-2006)</b>	11.9	28.2	28.5	65.3
<b>Wet Dep, AL02 (2005-2006)</b>	24.7	21.6	31.3	34.6



# Summary and Conclusions

- **Grand Bay NERR Site typically exhibits rural/remote characteristics with generally low concentrations of all species, but with occasional transport related episodes of higher concentrations.**
- **Elemental Hg shows little variation, little or no dependence on WD, and no discernible diurnal pattern, as expected.**
- **Hg-P behaves similarly, but with more transport related episodes and a modest diurnal profile.**
- **RGM exhibits a more pronounced diurnal profile. Both RGM and Hg-P profiles show increases in daytime, coincident with O<sub>3</sub> and SO<sub>2</sub> peaks, illustrating the importance of downward mixing of an aloft reservoir with the breakup of the nocturnal boundary layer. Photochemical (secondary) production may also be occurring.**

# Summary and Conclusions

- **RGM correlates most closely with O<sub>3</sub> in Springtime, and is associated with dryer air characteristic of continental emissions (CO ca 200 ppb).**
- **These results suggest RGM is transported from northerly continental sources following cold-frontal penetration in Spring. Reduced frequency of cold frontal passage at the site in Summer leads to lower RGM levels, more sporadic transport to the site from upwind sources.**
- **No evidence of strong, substantial RGM production or transport in marine (Gulf) air masses. Hg in coarse aerosols?**
- **Dry deposition estimates, when compared with nearby MDN deposition records, suggest wet deposition dominates the removal of reactive mercury species at the site, especially in Winter. If substantial Hg exists in the coarse aerosol fraction, the reported dry dep fluxes are under reported.**

# Recent Developments and Future Activities at Grand Bay NERR



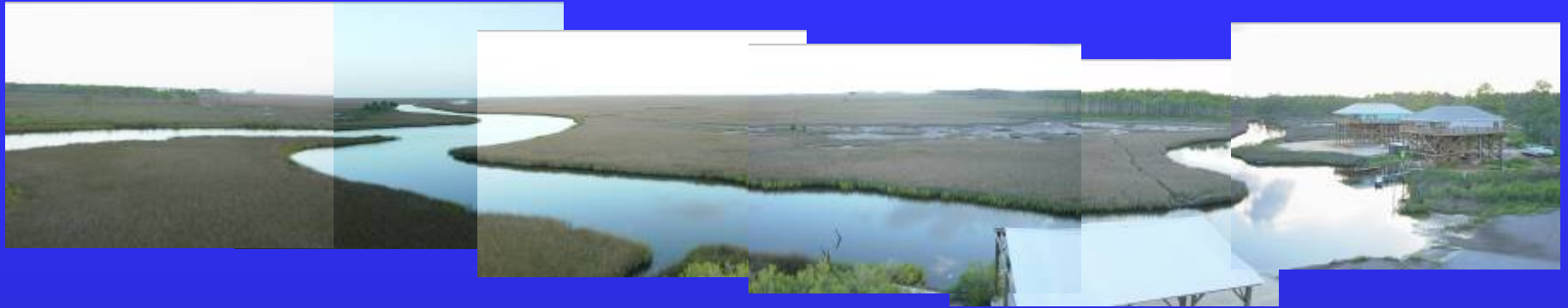
- Migration from old trailer and site to new trailer at permanent site (water's edge, 2 miles distant)
- Addition of 10m walk-up scaffold
- Addition of second Tekran System

Synchronous sampling –precision, QA/QC studies, investigation of Hg/aerosol size, etc.

Asynchronous sampling for true continuous measurements

- Addition of NO/NO<sub>y</sub> monitor

# Pictures of Permanent Monitoring Site



View from top of 10 m tower looking at the southerly (prevailing wind) sampling sector over the U.S. Fish and Wildlife Service Pavilion at Grand Bay NERR



# **Acknowledgments**

**We would like to thank Gary Matlock and Russell Callender of NOAA's National Centers for Coastal Ocean Science for their generous financial support, and to Durwin Carter (Manager, Grand Bay National Wildlife Refuge) and David Ruple (Manager, Grand Bay National Estuarine Research Reserve) for their ongoing support and assistance of this project.**