Atmospheric mercury measurements in the Gulf of Mexico ~~and mid-Atlantic~~ region~~s~~: Early results from an emerging monitoring network

Winston Luke, Mark Cohen, Paul Kelley, Steve Brooks

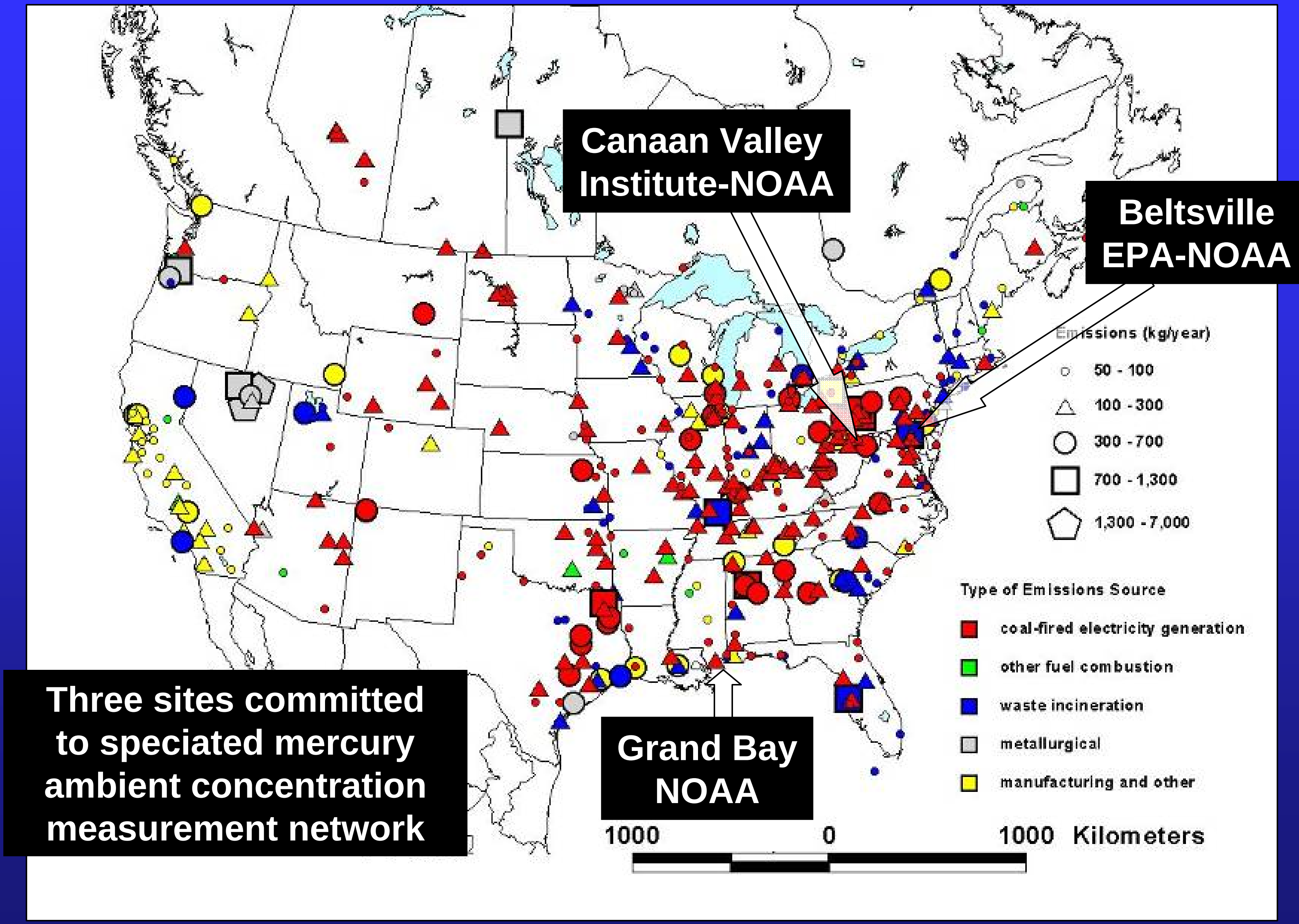
NOAA/Air Resources Laboratory, Silver Spring, MD

Jake Walker

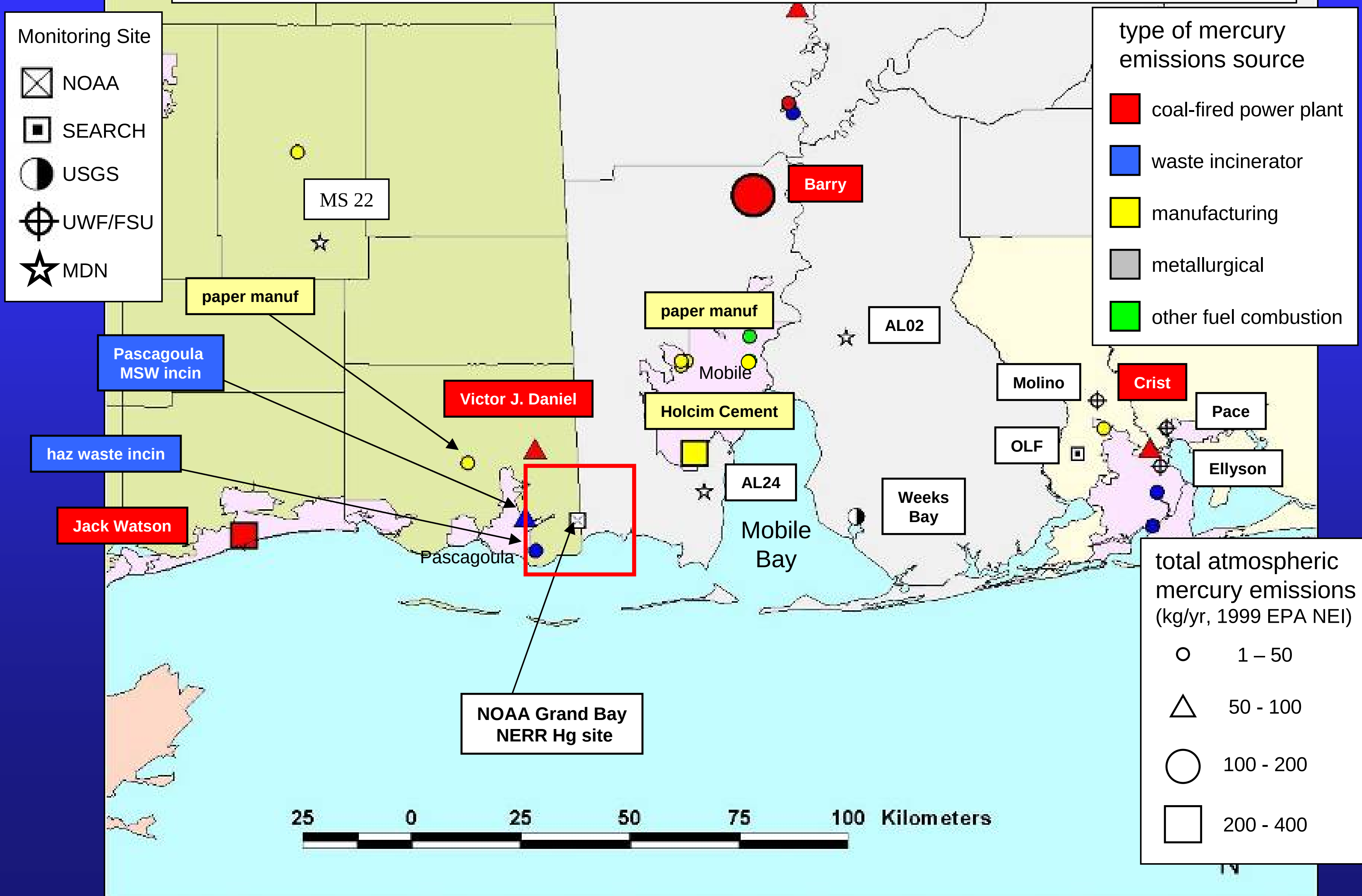
Grand Bay National Estuarine Research Reserve, Moss Point, MS

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

NOAA Mercury Sites

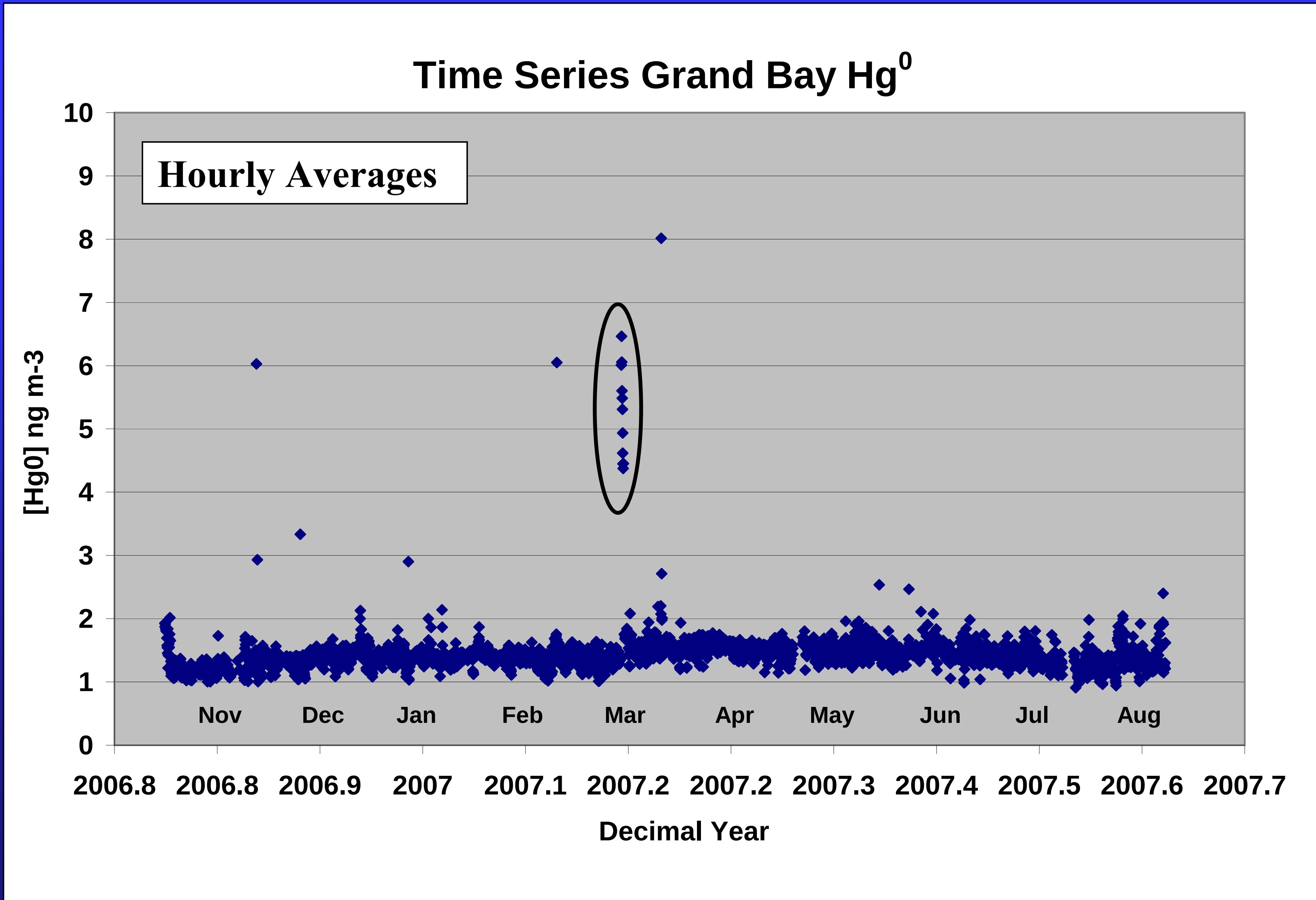


Location of the NOAA Grand Bay NERR Atmospheric Mercury monitoring site, other atmospheric Hg monitoring sites, and major Hg point sources in the region (EPA 1999 NEI emissions inventory)

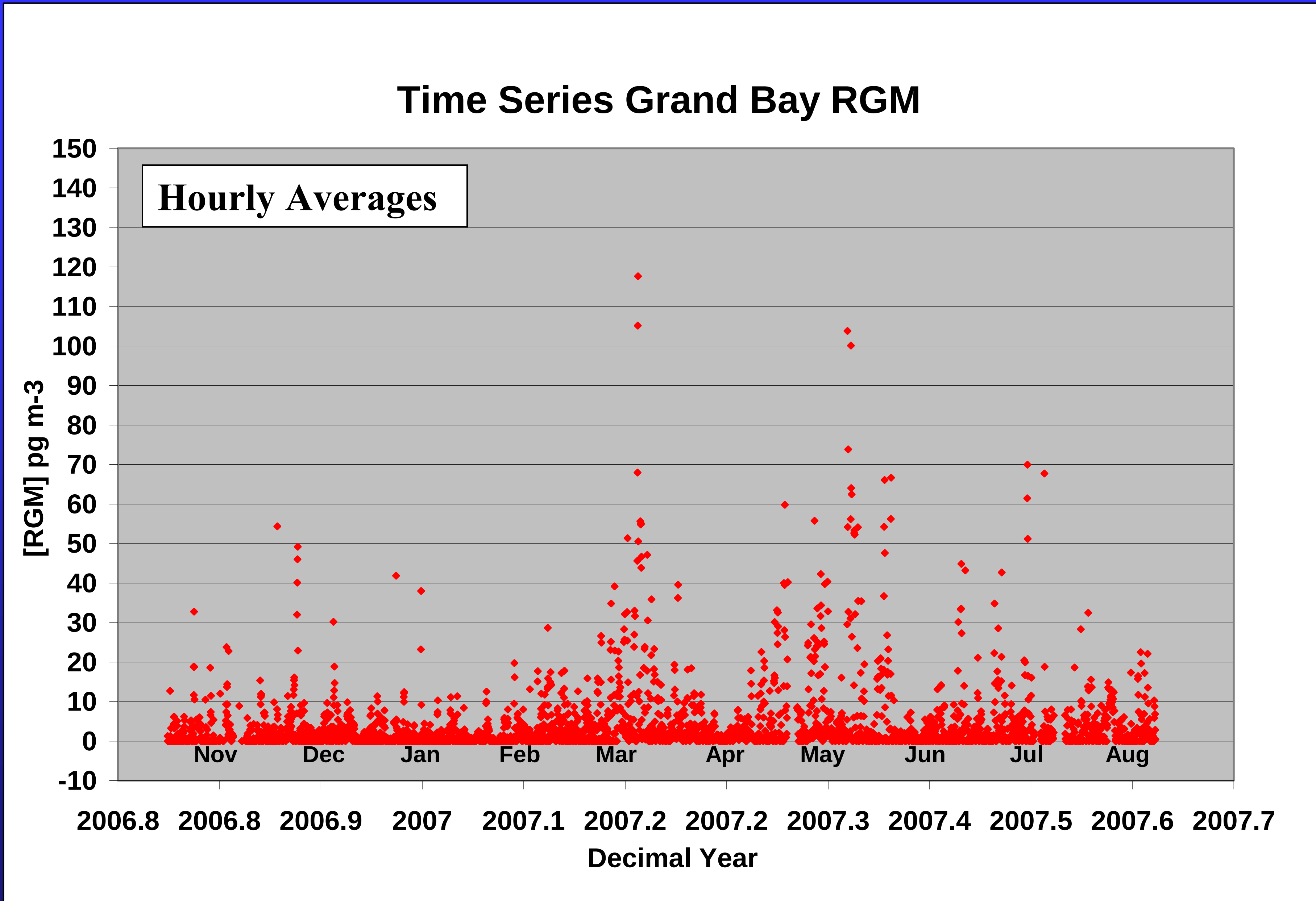


Measurements at Grand Bay NERR, MS

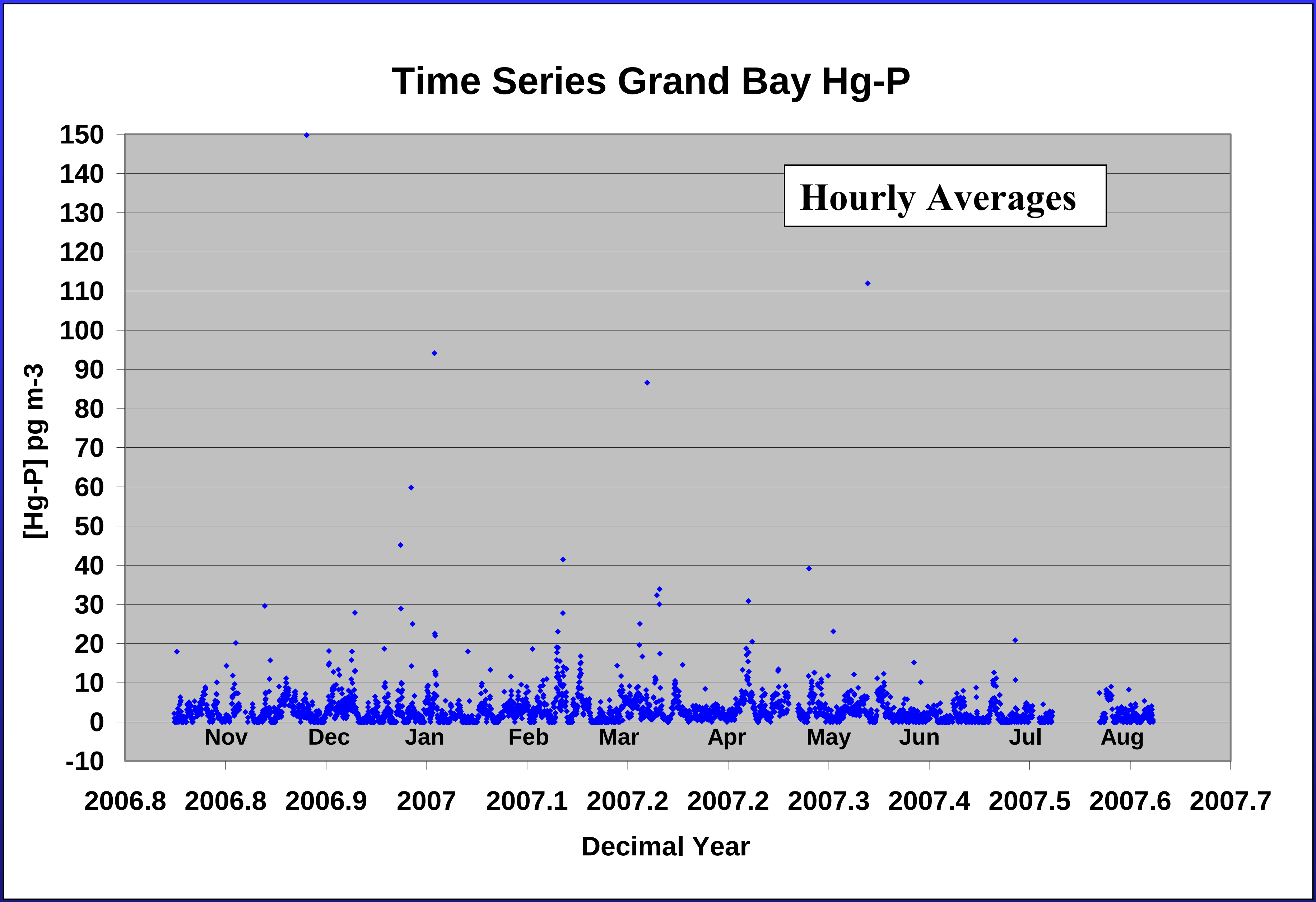
- **Tekran speciation system (Hg^0, RGM, Hg-p) installed Sept. 29, 2006**
- **Ancillary measurements (CO, O_3, SO_2) added October 20, 2006**
- **Sampling Height 4 m**
- **Meteorological measurements (T, RH, WS, WD, Solar, Precip Rate/Amount) added March 1, 2007; nearby FWS station provided earlier measurements**



Time Series Grand Bay Hg^0
Hourly Averages
[Hg0] ng m-3
10
9
8
7
6
5
4
3
2
1
0
Nov
Dec
Jan
Feb
Mar
Apr
May
Jun
Jul
Aug
2006.8
2006.8
2006.9
2007
2007.1
2007.2
2007.2
2007.3
2007.4
2007.5
2007.6
2007.7
Decimal Year

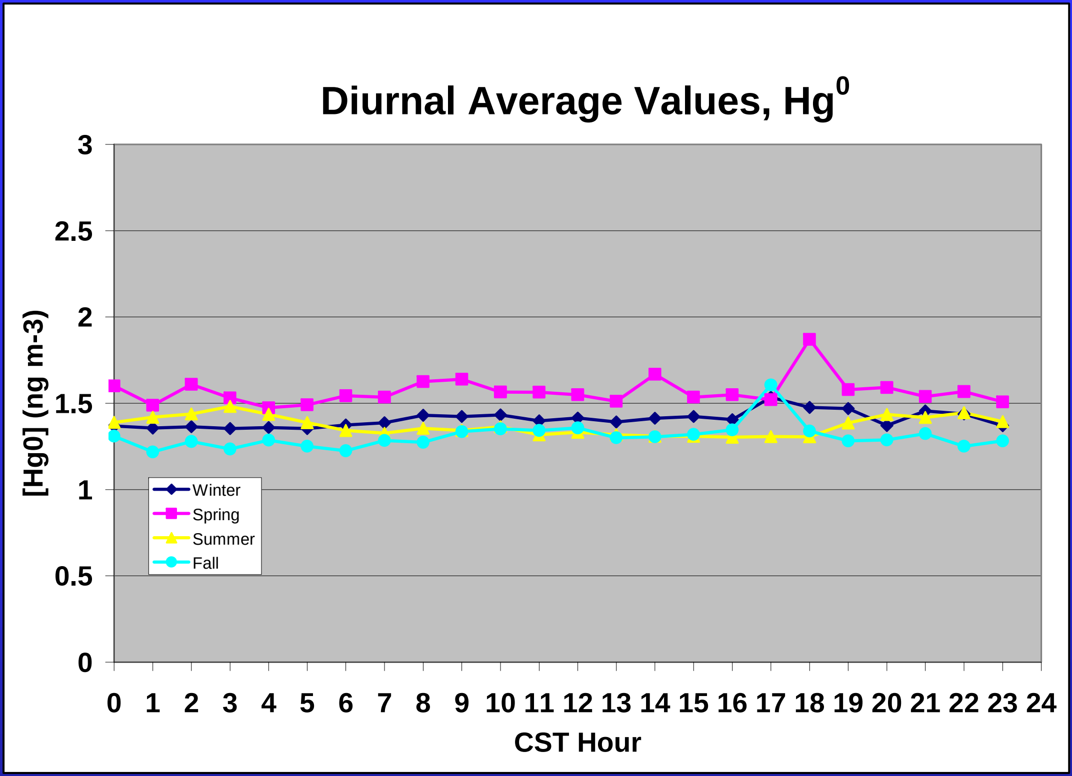


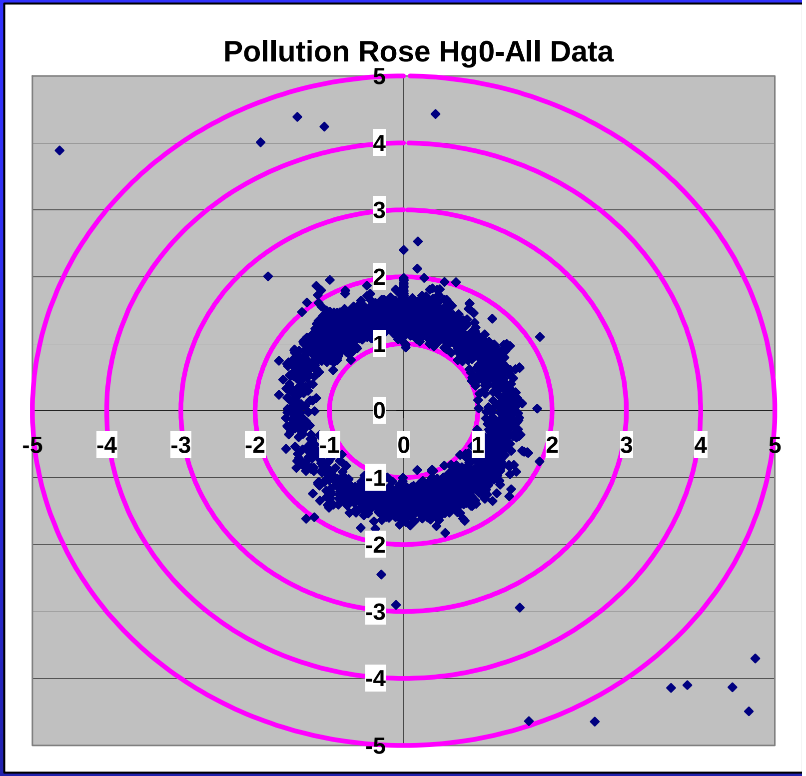
Time Series Grand Bay RGM
Hourly Averages
[RGM] pg m-3
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
Nov
Dec
Jan
Feb
Mar
Apr
May
Jun
Jul
Aug
2006.8
2006.8
2006.9
2007
2007.1
2007.2
2007.2
2007.3
2007.4
2007.5
2007.6
2007.7
Decimal Year



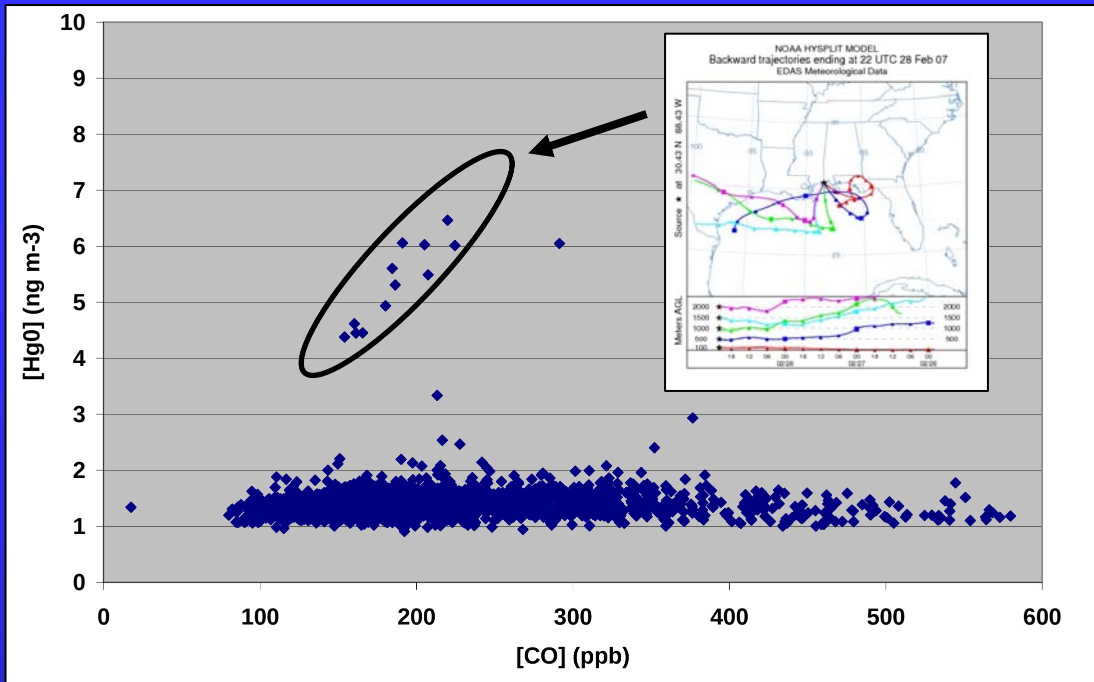
Time Series Grand Bay Hg-P
Hourly Averages
[Hg-P] pg m-3
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
Nov
Dec
Jan
Feb
Mar
Apr
May
Jun
Jul
Aug
2006.8
2006.8
2006.9
2007
2007.1
2007.2
2007.2
2007.3
2007.4
2007.5
2007.6
2007.7
Decimal Year

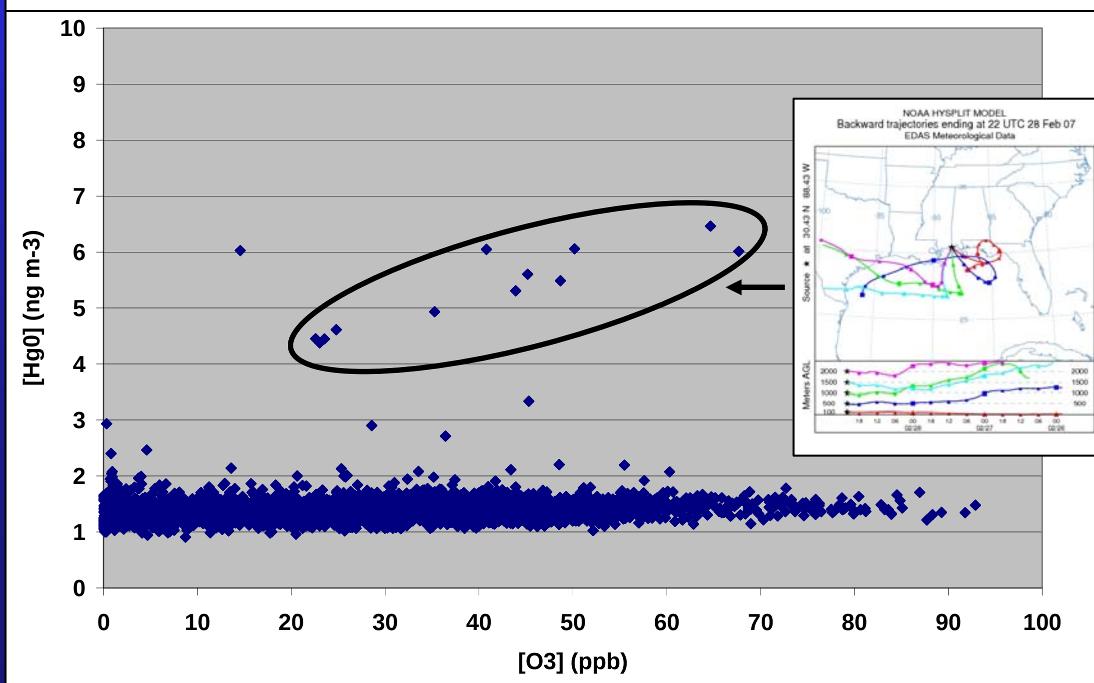
Elemental Mercury (Hg^0)





As expected, with a few exceptions Hg^0 concentrations show little or no diurnal variation or dependence on wind direction



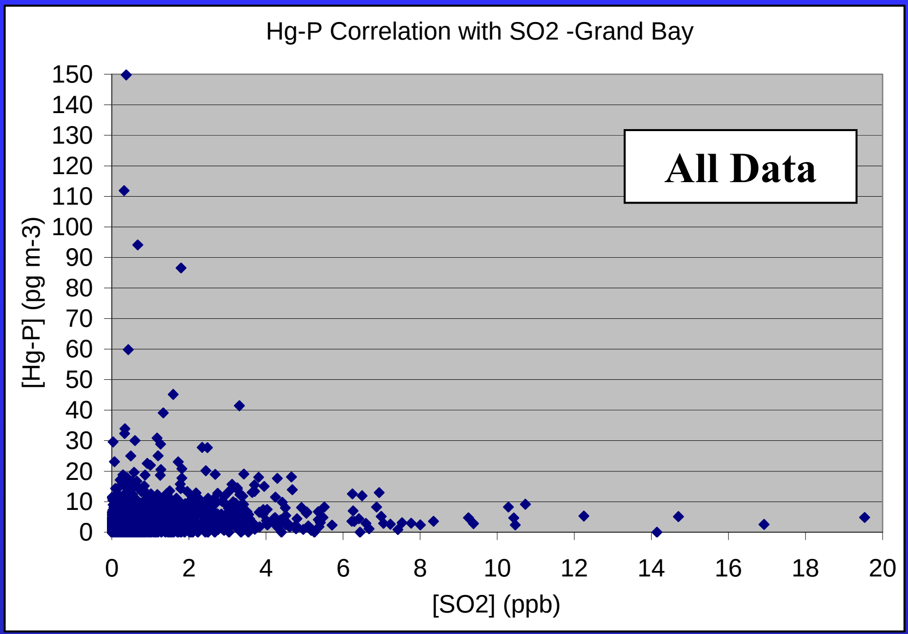


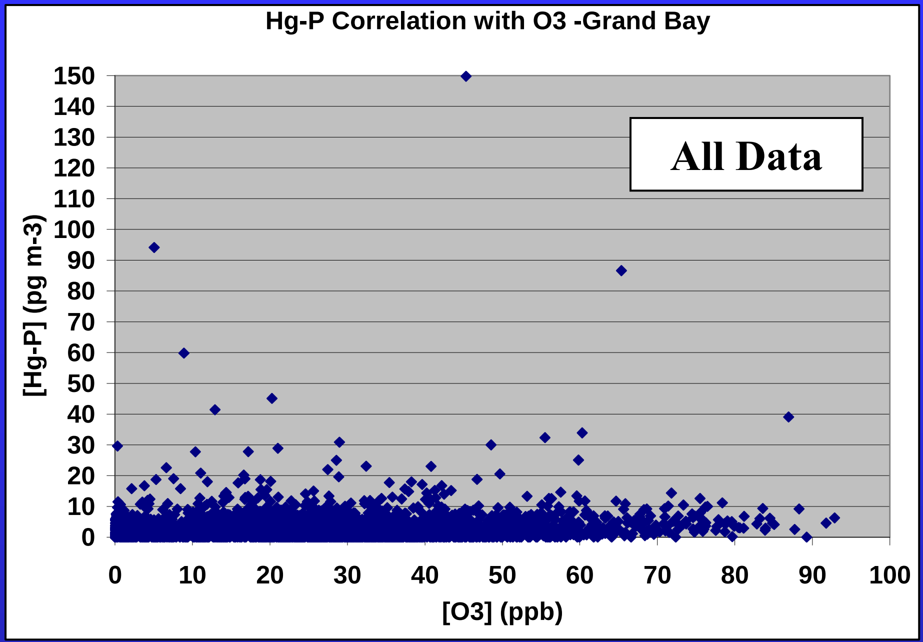
Overnight Event Feb. 28-March 1

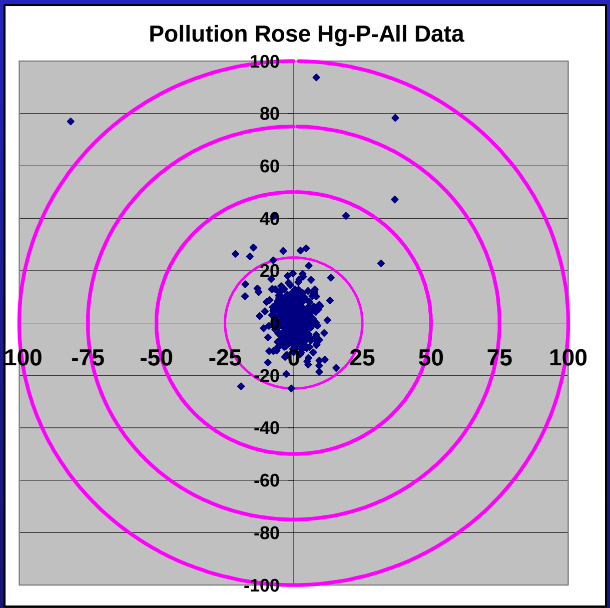
Strong correlation between Hg^0 and CO, O_3.

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

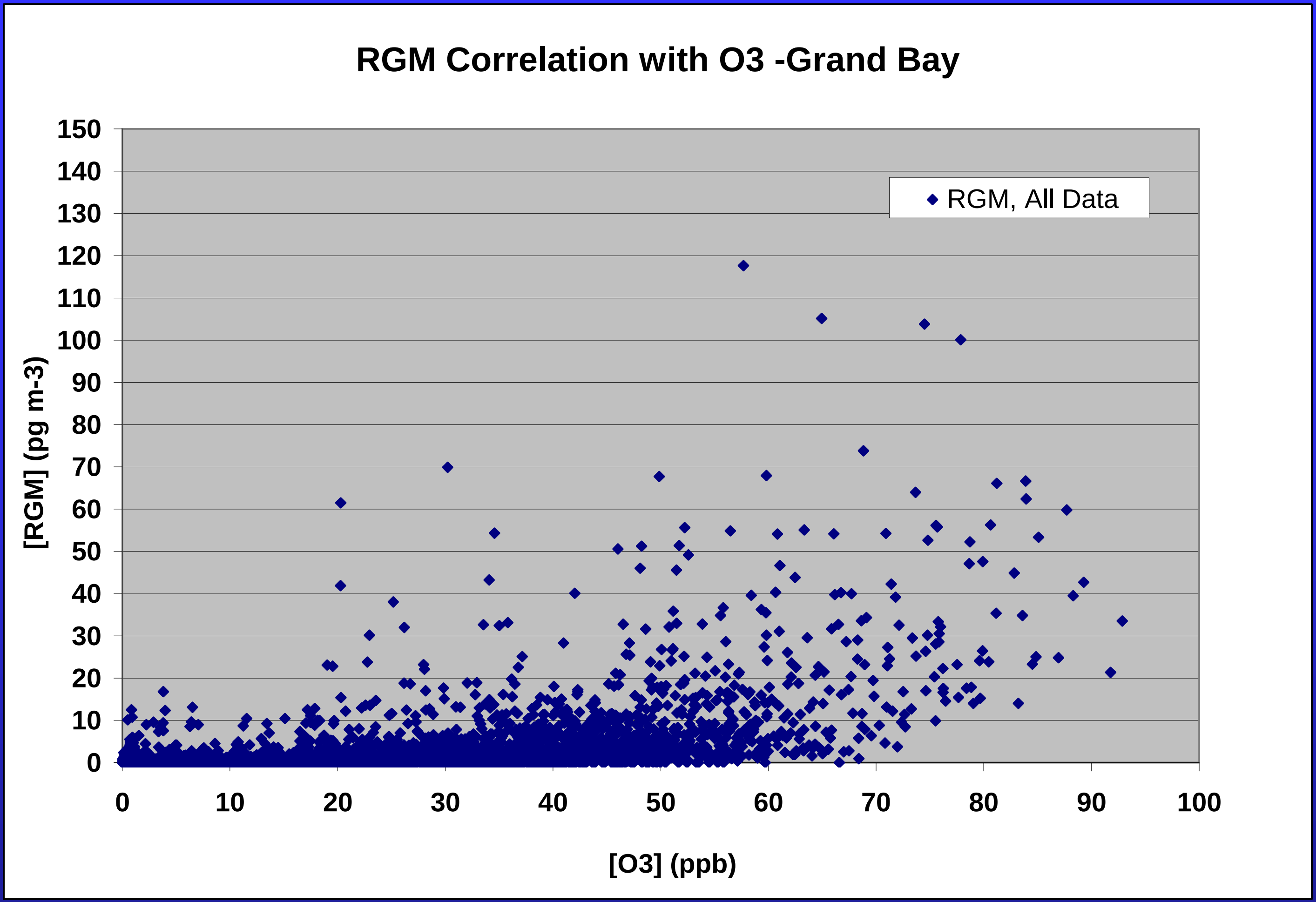
Particulate Mercury (Hg-P)



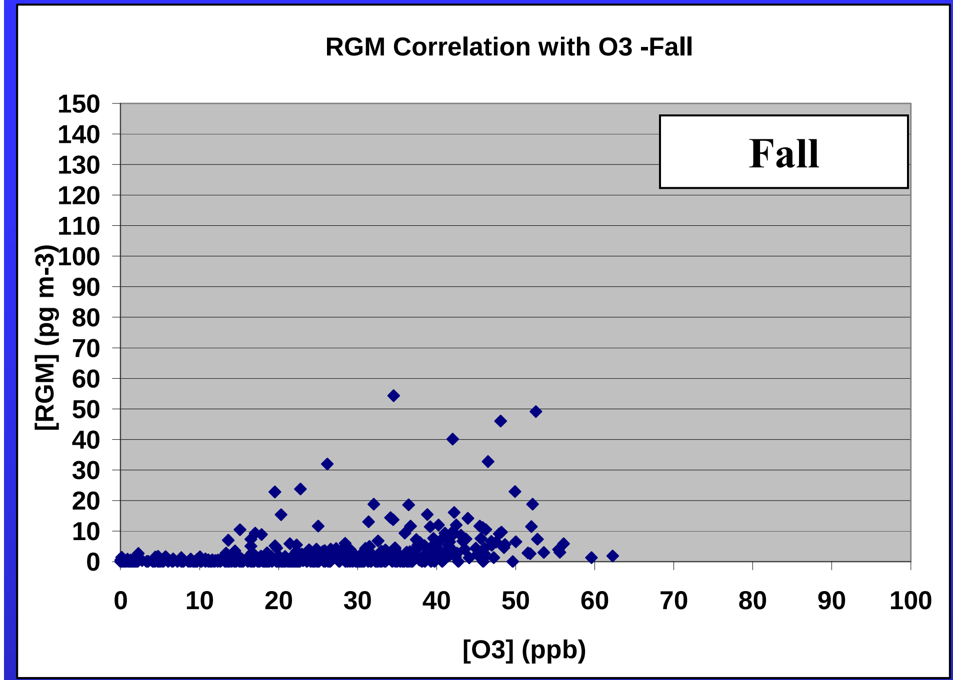




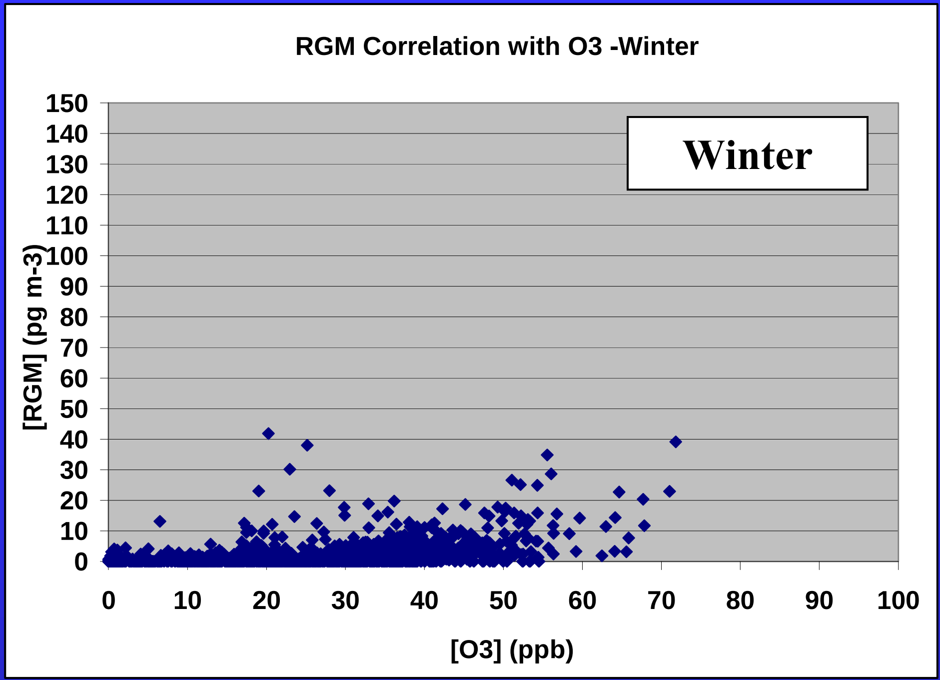
With the exception of a few well-defined transport events, Hg-P displays no consistent relationship with WD, and exhibits little or no correlation with other trace species



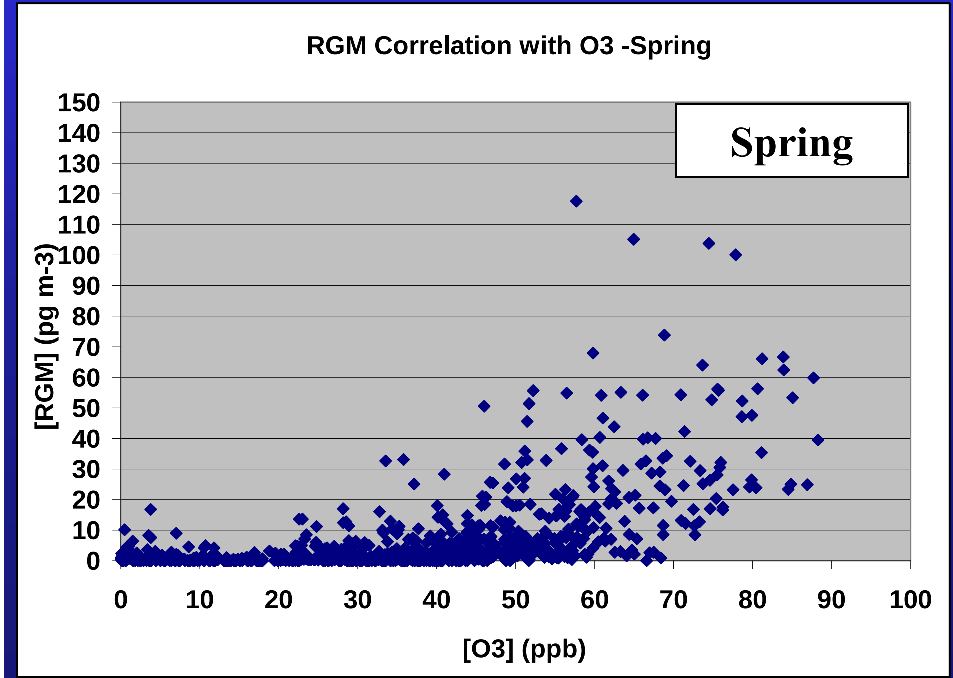
Strongest correlations seen between RGM and O_3, most of which is driven by seasonal dependence – RGM concentrations are highest, relationship with O_3 is strongest in Spring.



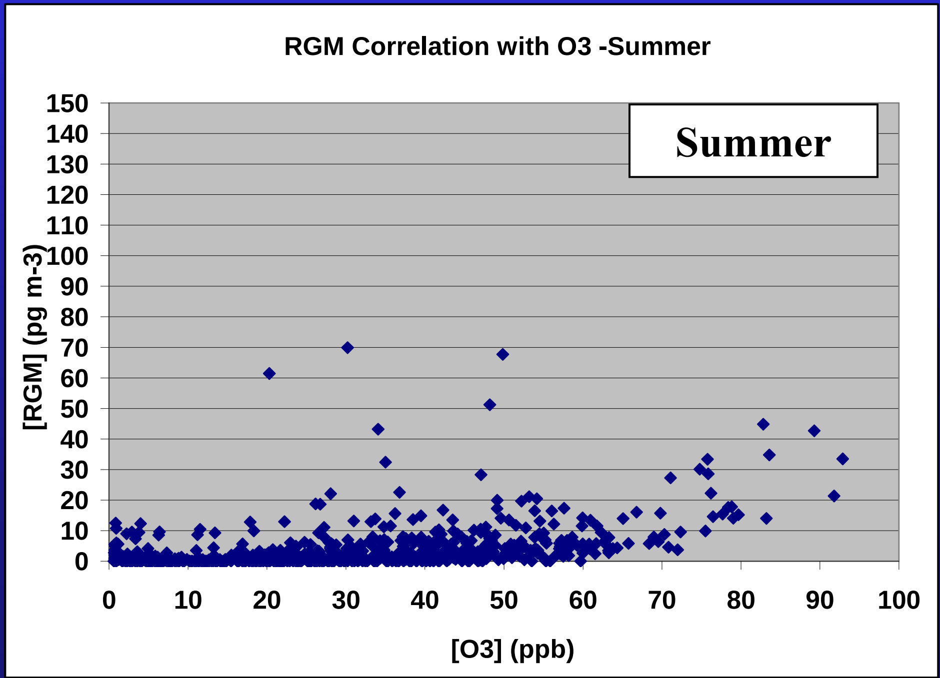
RGM Correlation with O3 -Fall
Fall
[RGM] (pg m-3)
[O3] (ppb)



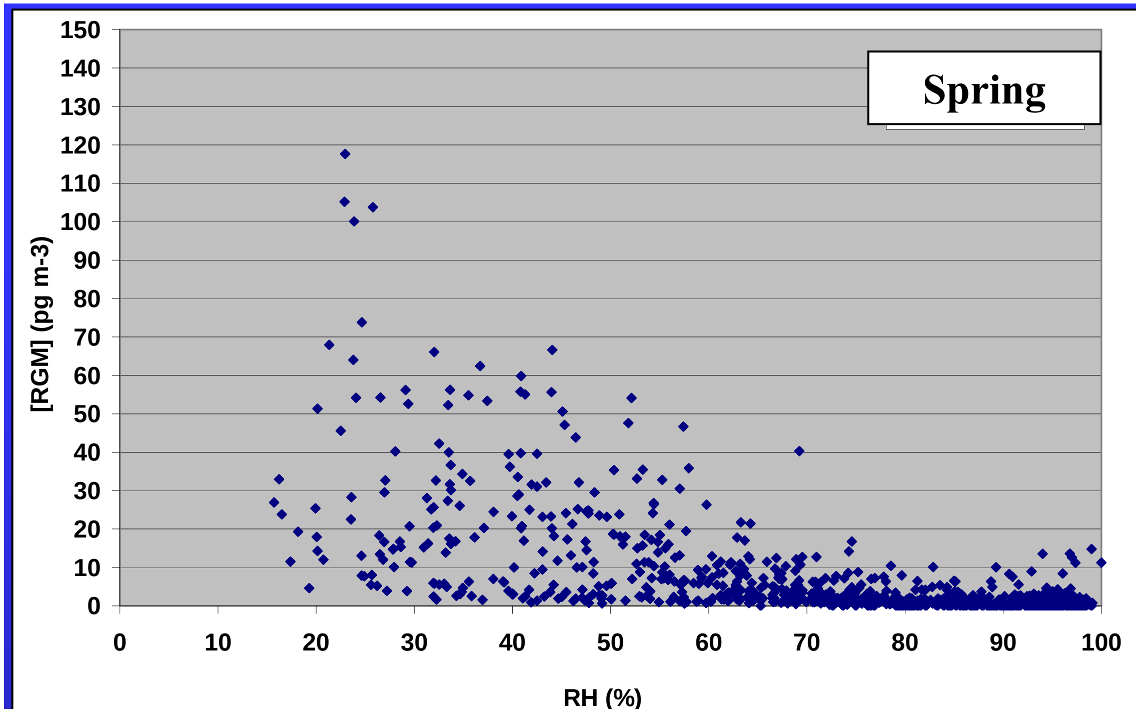
RGM Correlation with O3 -Winter
Winter
[RGM] (pg m-3)
[O3] (ppb)

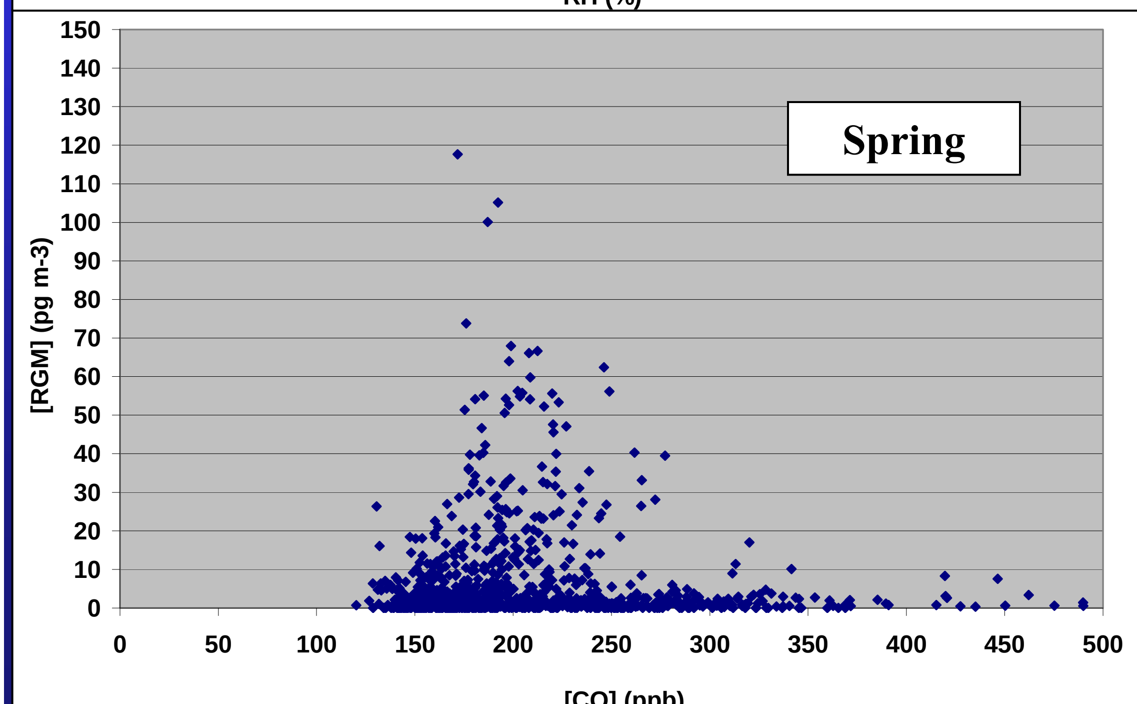


RGM Correlation with O3 -Spring
Spring
[RGM] (pg m-3)
[O3] (ppb)



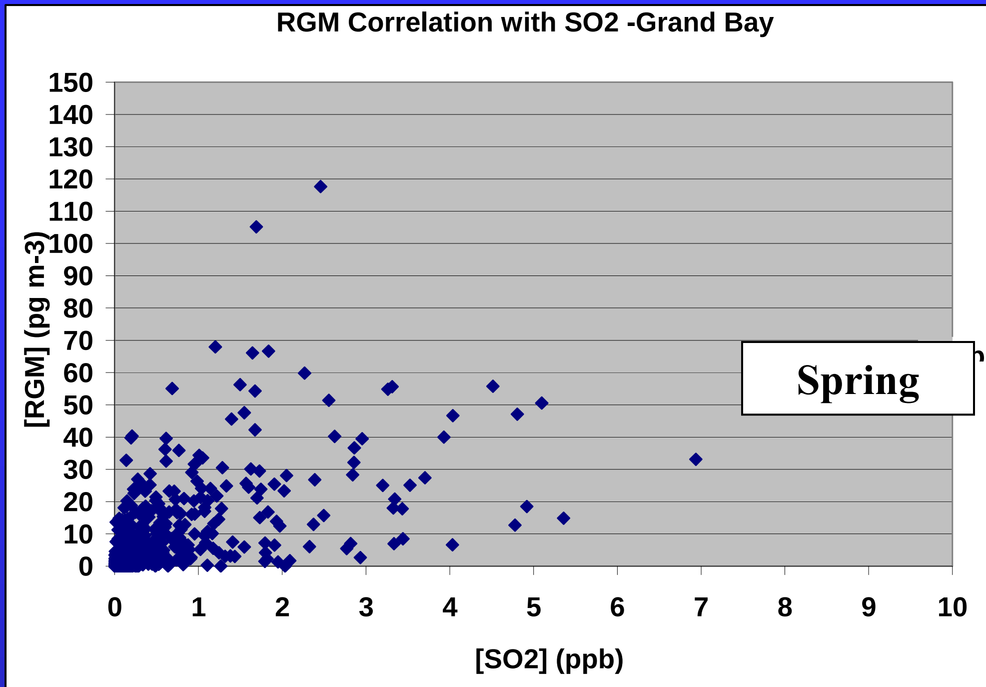
RGM Correlation with O3 -Summer
Summer
[RGM] (pg m-3)
[O3] (ppb)

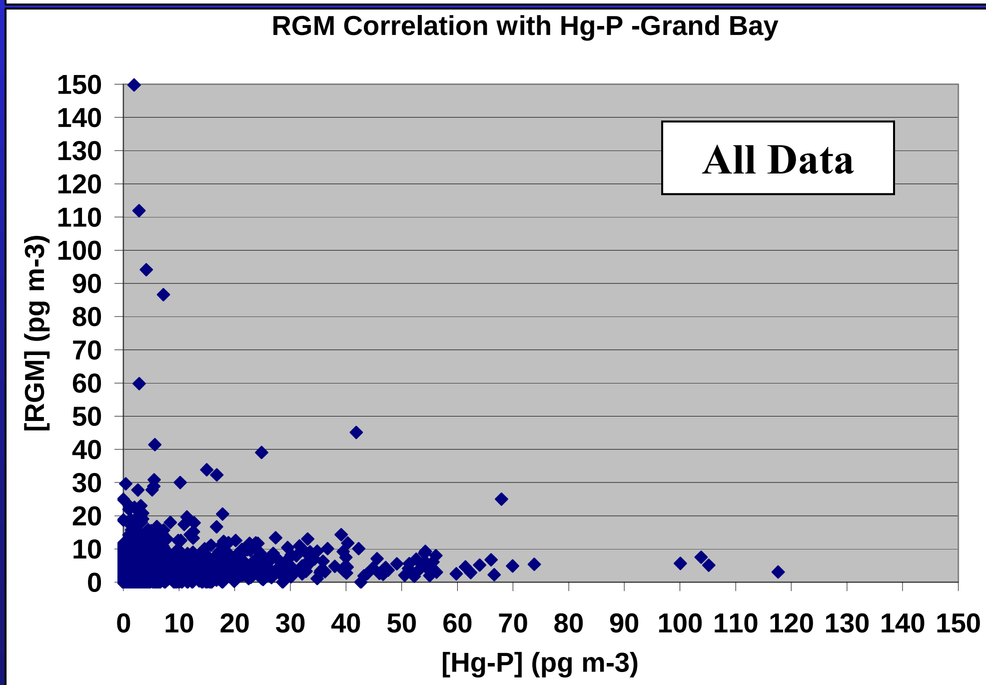




Association of peak RGM with low RH and CO concentrations typical of continental influence suggests highest Spring peaks of RGM are seen in post-frontal activity, with transport from upwind continental sources to the North

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





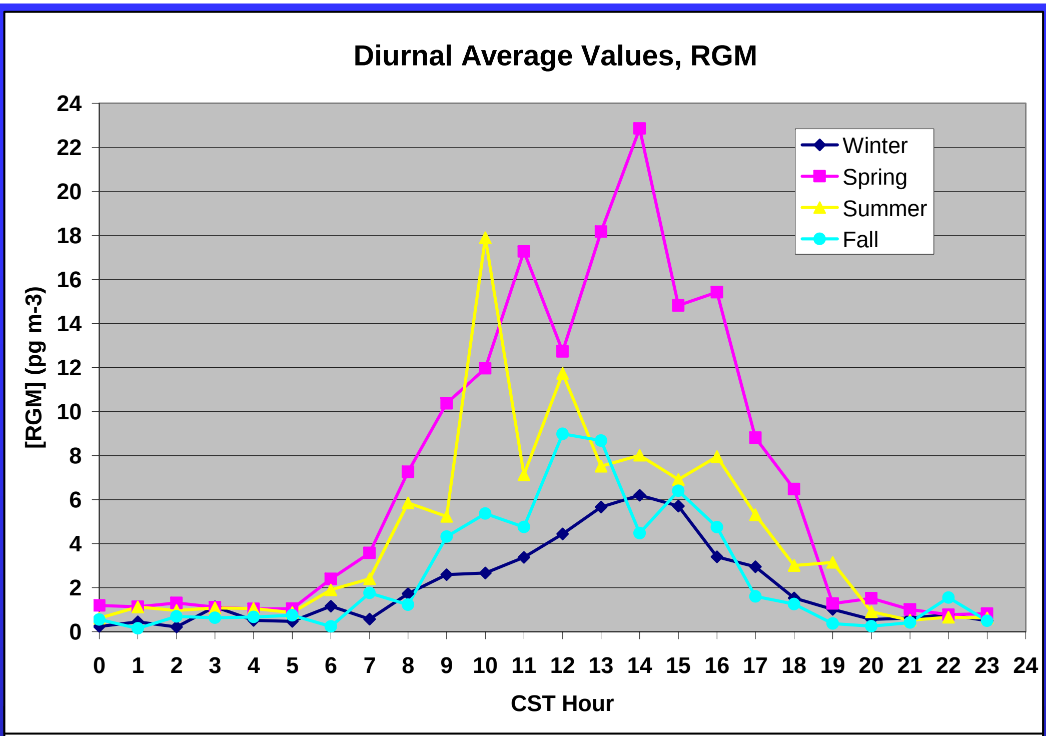
Poor correlation with SO_2 suggests:

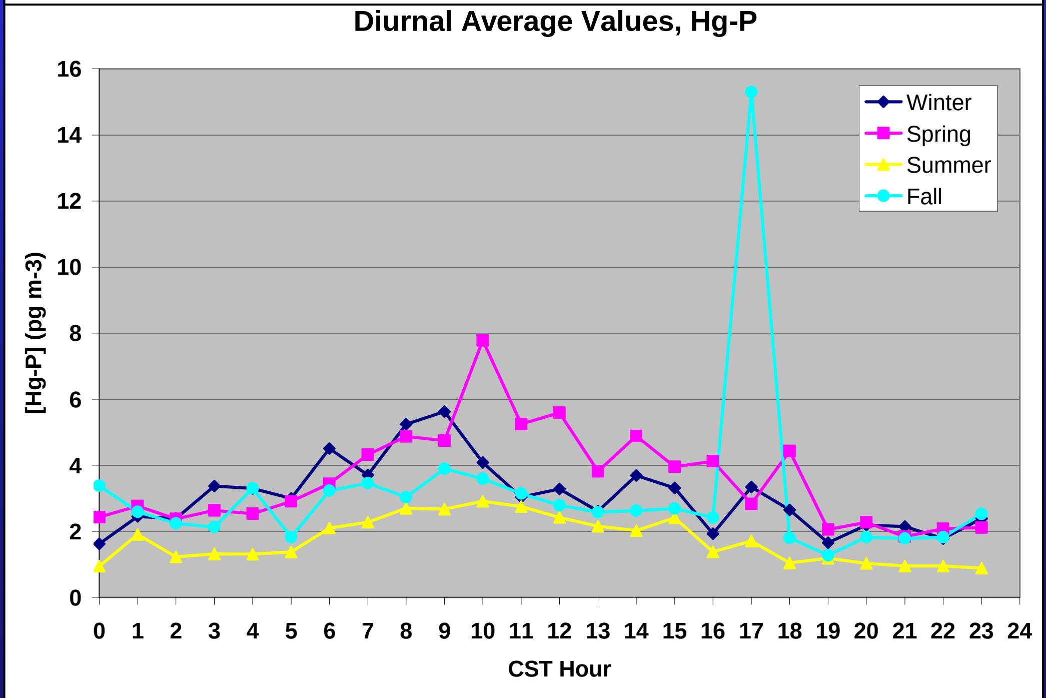
A mix of primary sources with varying emission characteristics

A mix of primary and secondary sources of RGM

Different chemical processing and removal rates of SO_2 and RGM during transport

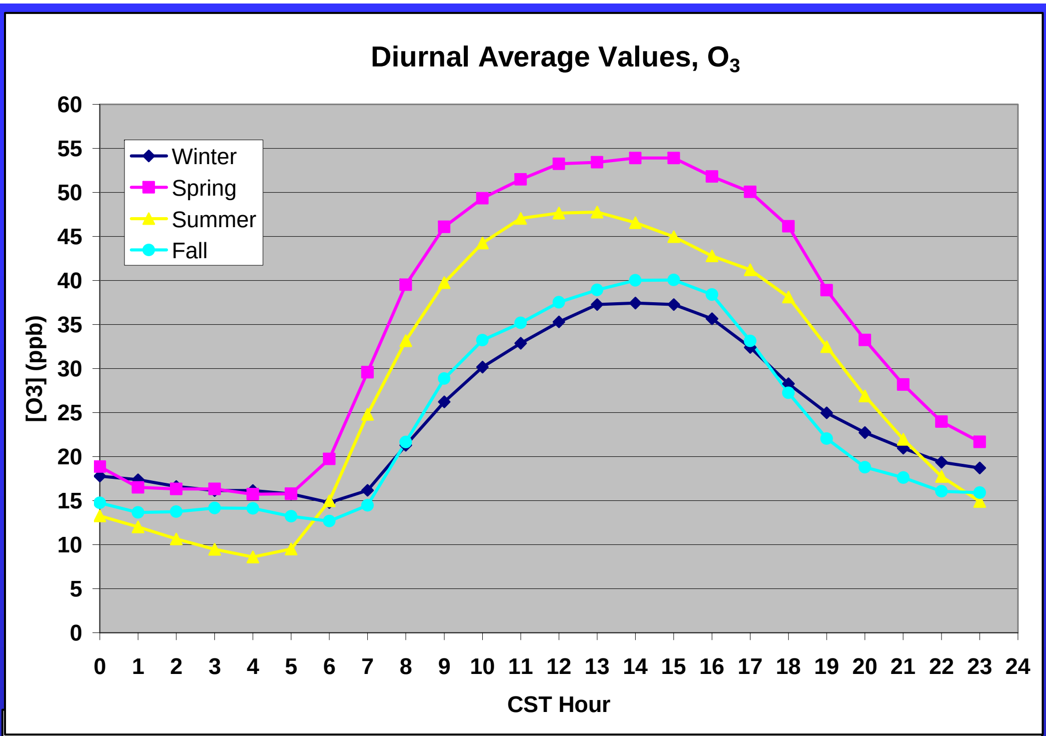
Lack of correlation –RGM and Hg-P suggests different sources and/or removal rates of these species

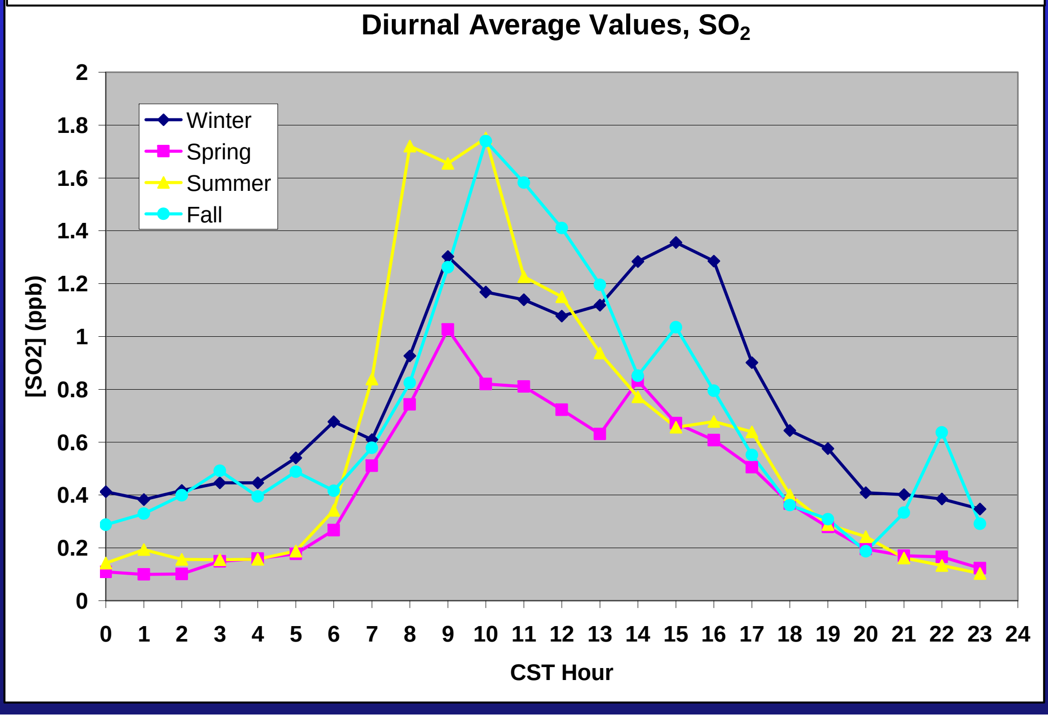




Significant diurnal patterns seen in both RGM and Hg-P, but amplitude of diurnal Hg-P profile is much smaller.

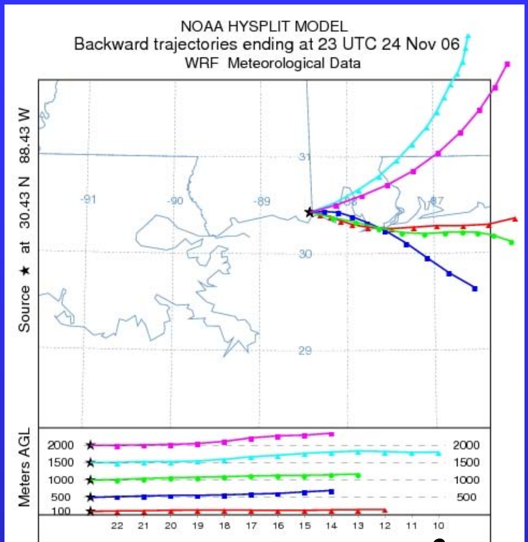
Highest RGM and Hg-P concentrations seen in Spring



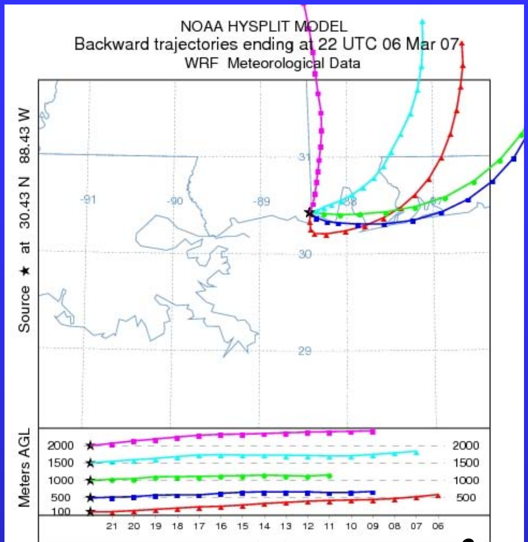


Similarity to O_3 and SO_2 diurnal profiles confirms the importance of downward mixing in the development of the daytime boundary layer, but does not allow us to differentiate between primary and secondary sources of the mercury species.

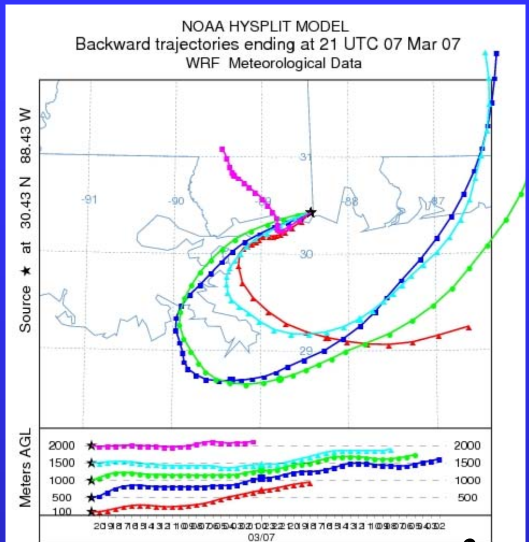
Higher RGM Associated with N-E trajectories



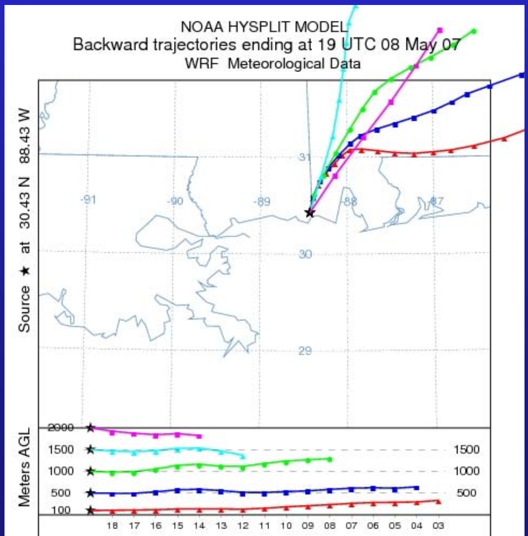
Peak ~ 50 pg m^{-3}



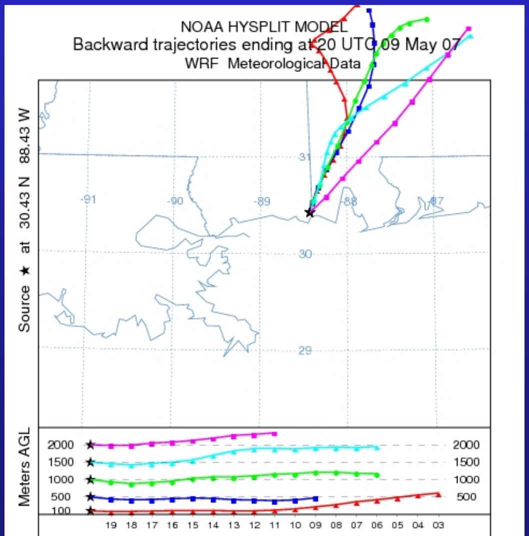
Peak ~ 118 pg m^{-3}



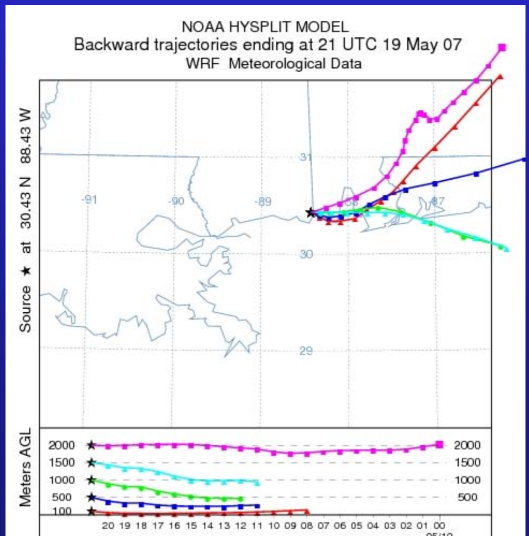
Peak ~ 55 pg m^{-3}



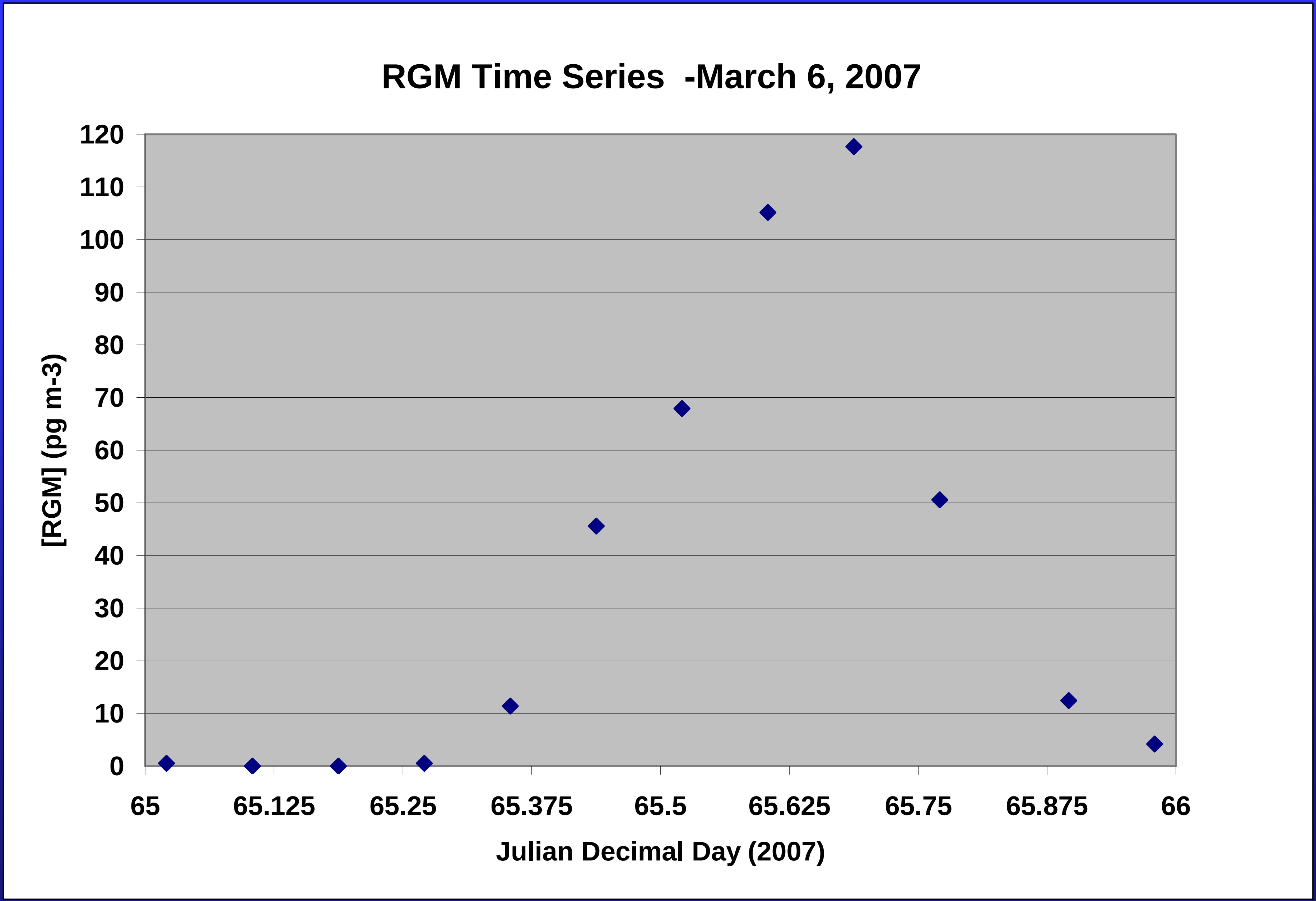
Peak ~ 105 pg m^{-3}



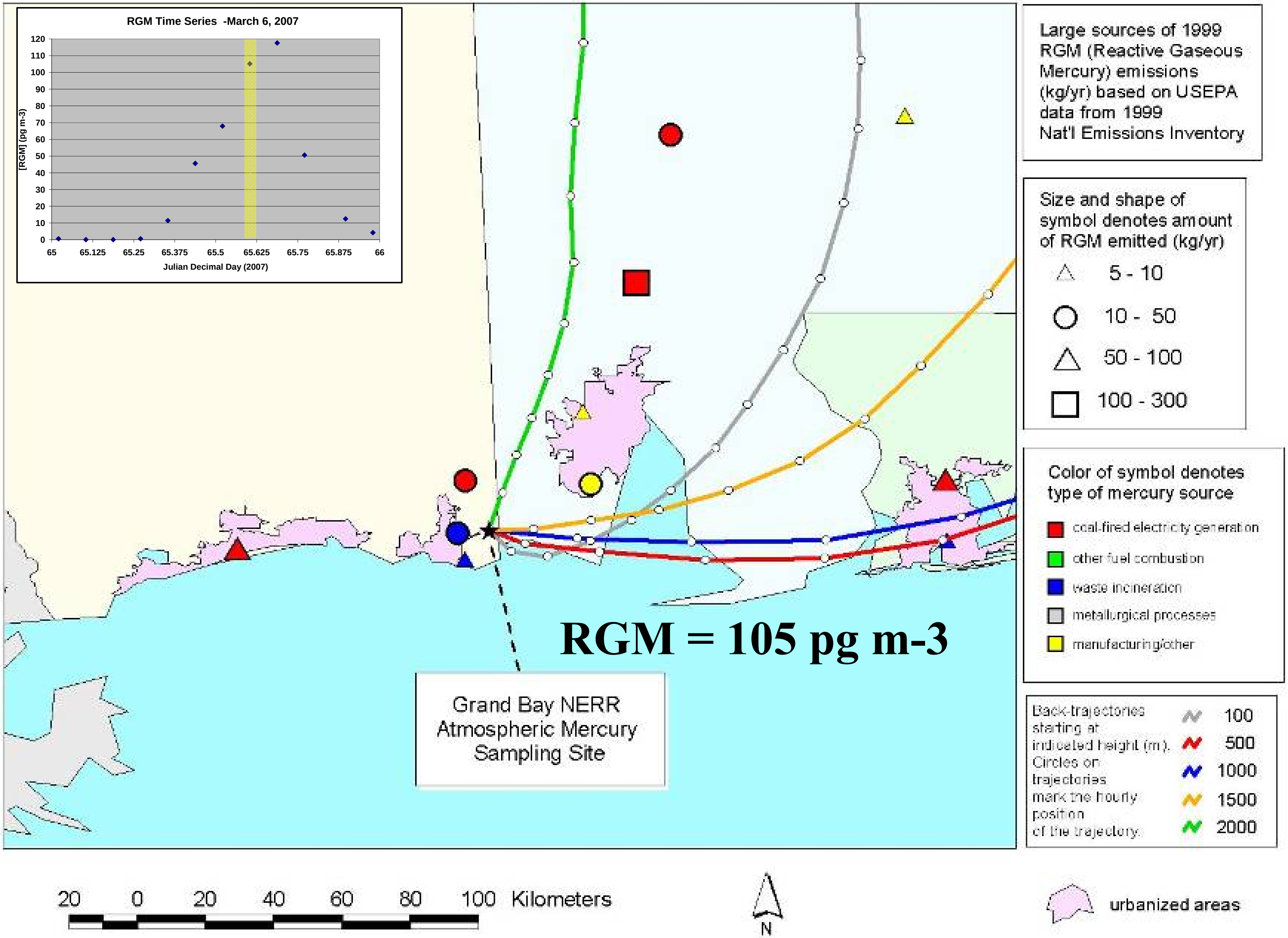
Peak ~ 100 pg m^{-3}



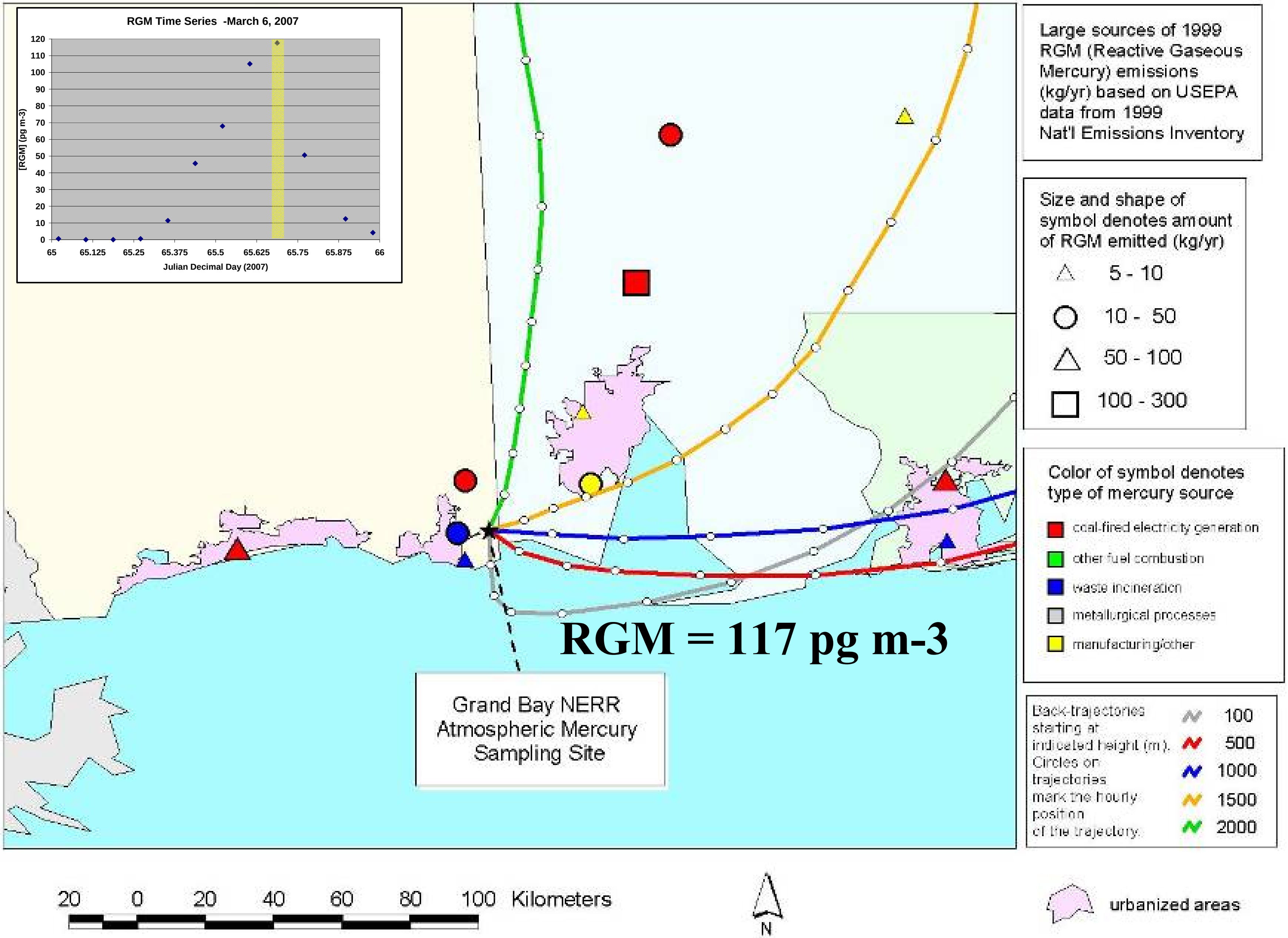
Peak ~ 65 pg m^{-3}


RGM Time Series -March 6, 2007
[RGM] (pg m-3)
120
110
100
90
80
70
60
50
40
30
20
10
0
65
65.125
65.25
65.375
65.5
65.625
65.75
65.875
66
Julian Decimal Day (2007)

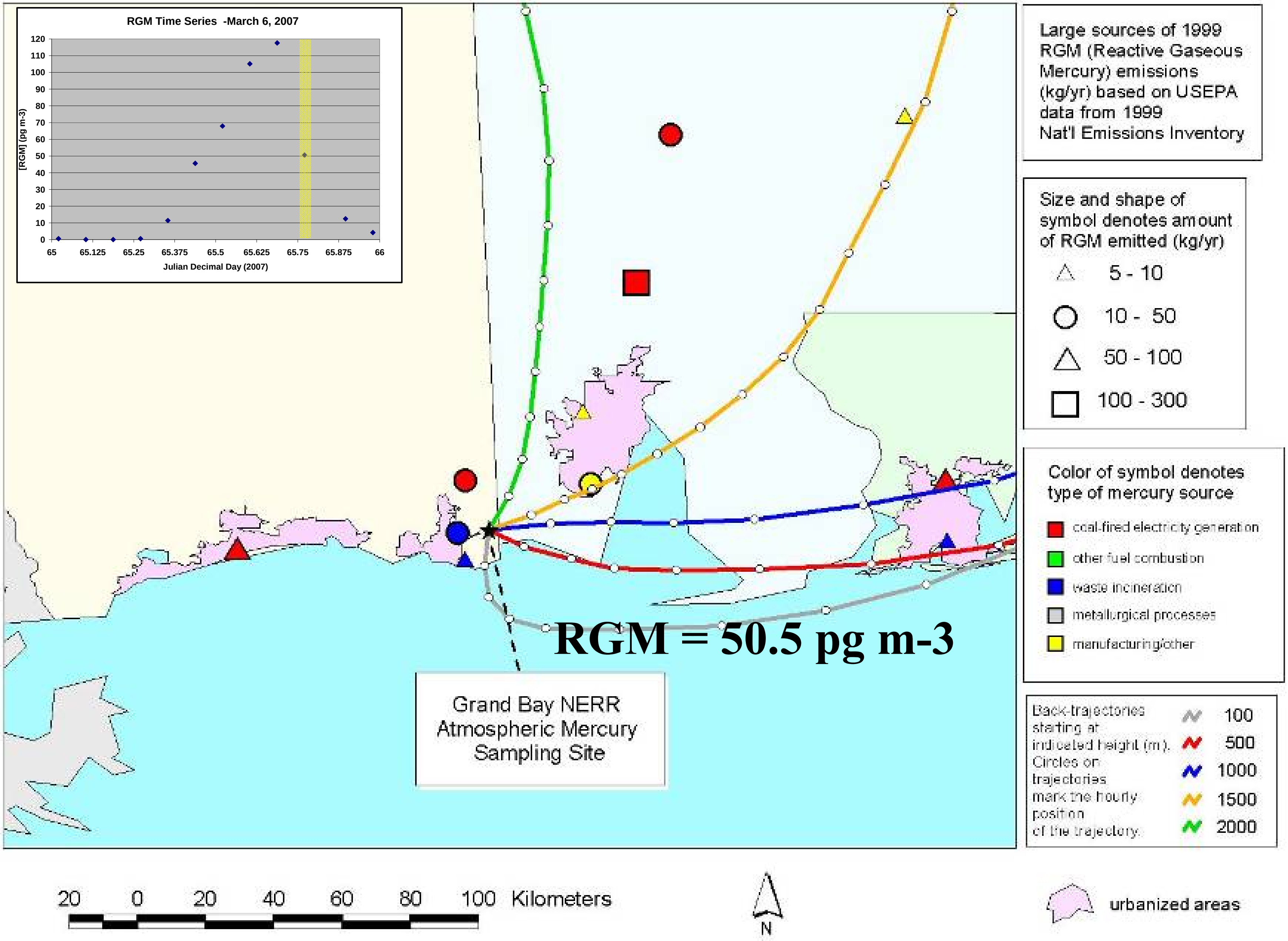
Back Trajectories Arriving at 3/06/2007 14:00 CST



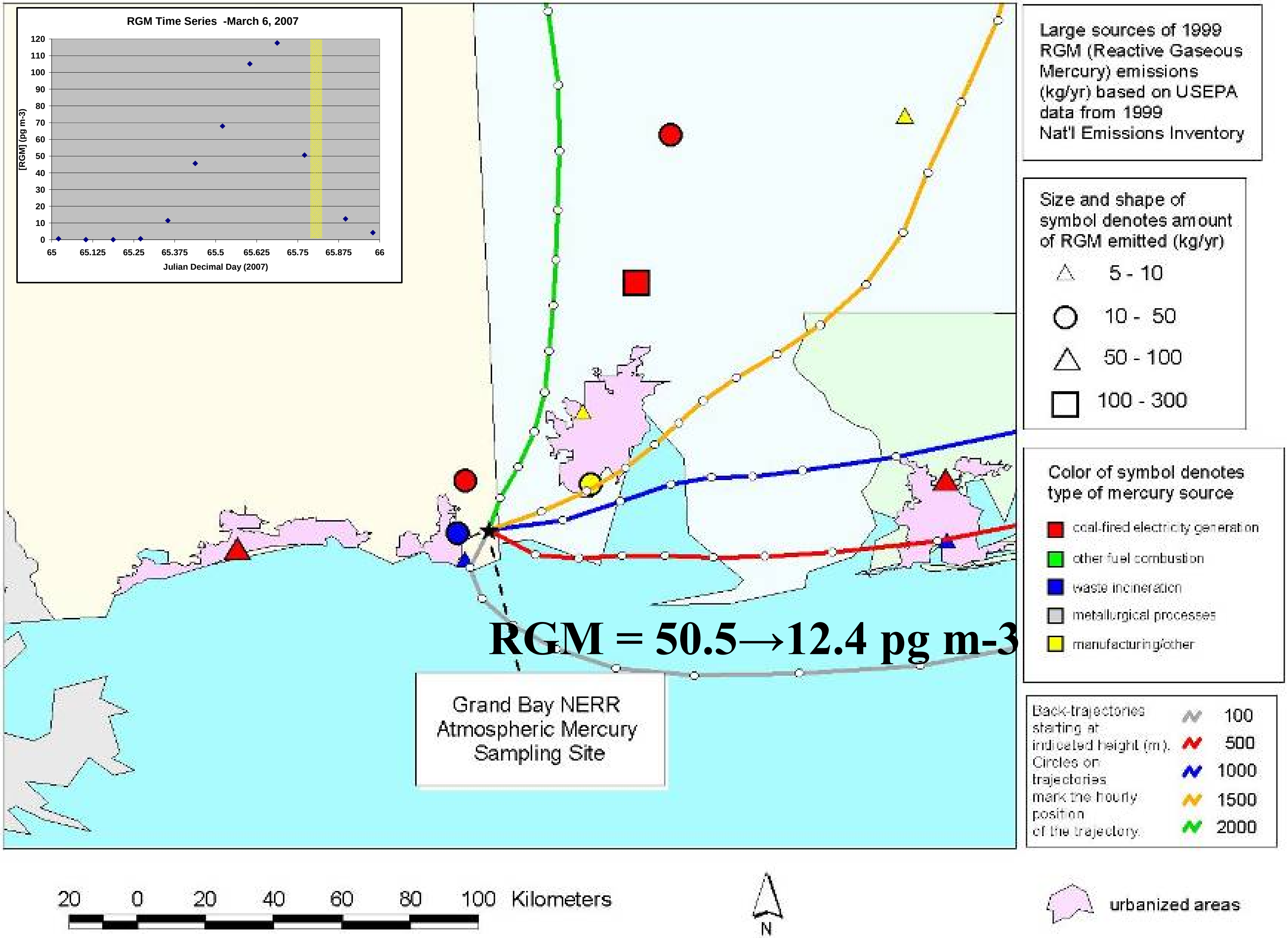
Back Trajectories Arriving at 3/06/2007 16:00 CST



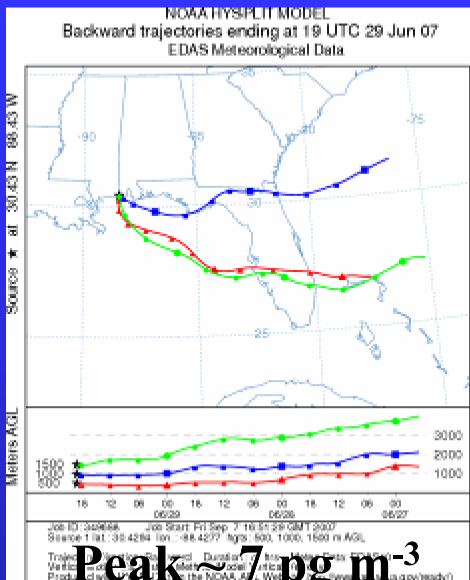
Back Trajectories Arriving at 3/06/2007 17:00 CST



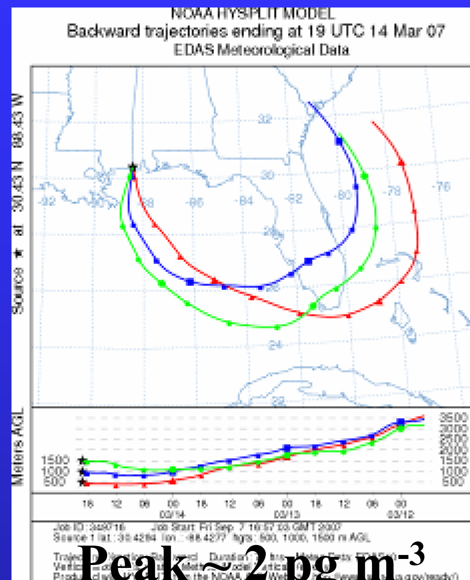
Back Trajectories Arriving at 3/06/2007 19:00 CST



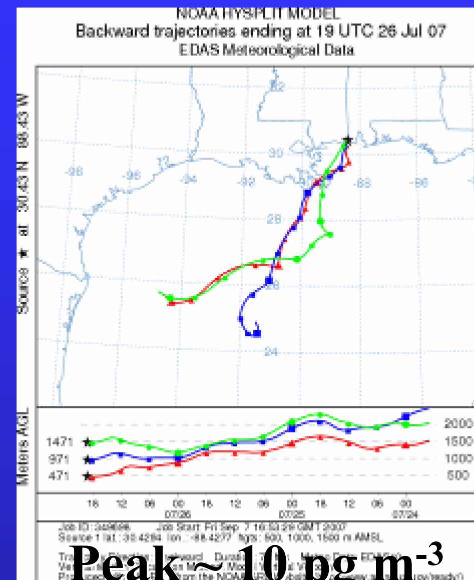
Lower RGM in Maritime trajectories



Peak ~7 pg m^{-3}

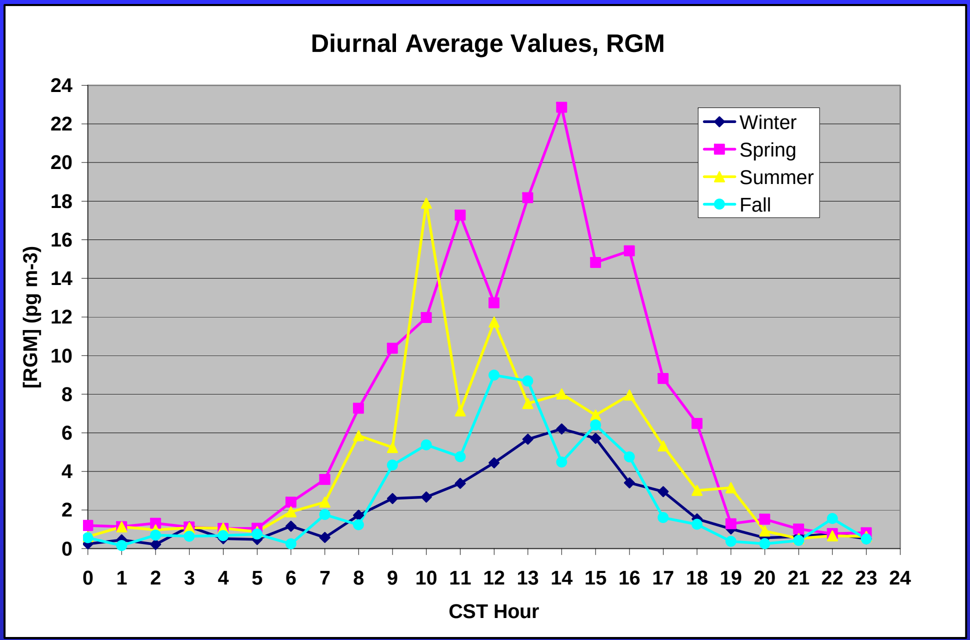


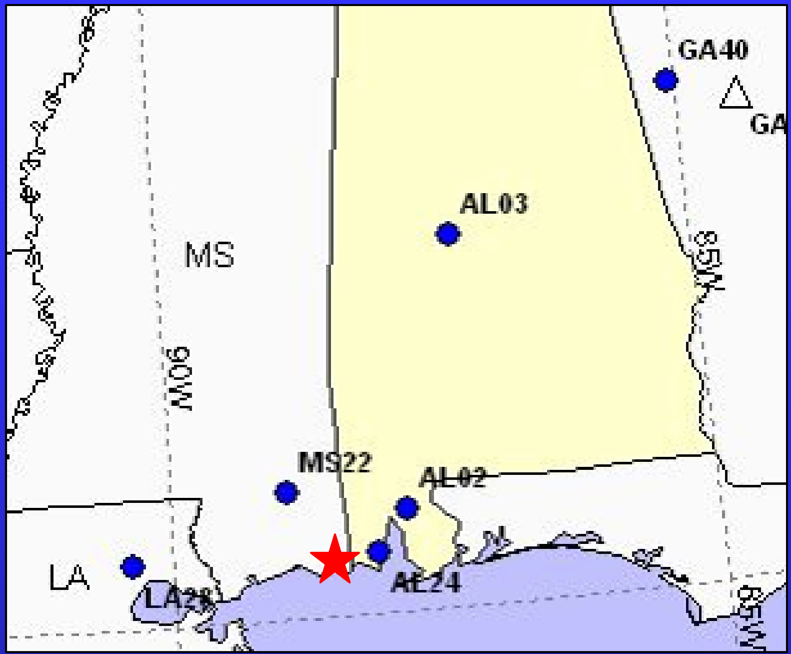
Peak ~2 pg m^{-3}



Peak ~10 pg m^{-3}

Deposition Estimates





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

	Fall	Winter	Spring	Summer
Dry Dep, Grand Bay (2006-2007)	5.4	4.3	14.2	8.6
Wet Dep, AL24 (2005-2006)	13.5	24.8	31.6	34.6
Wet Dep, MS22 (2005-2006)	11.9	28.2	28.5	65.3
Wet Dep, AL02 (2005-2006)	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_3 and SO_2 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_3 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_Y 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.