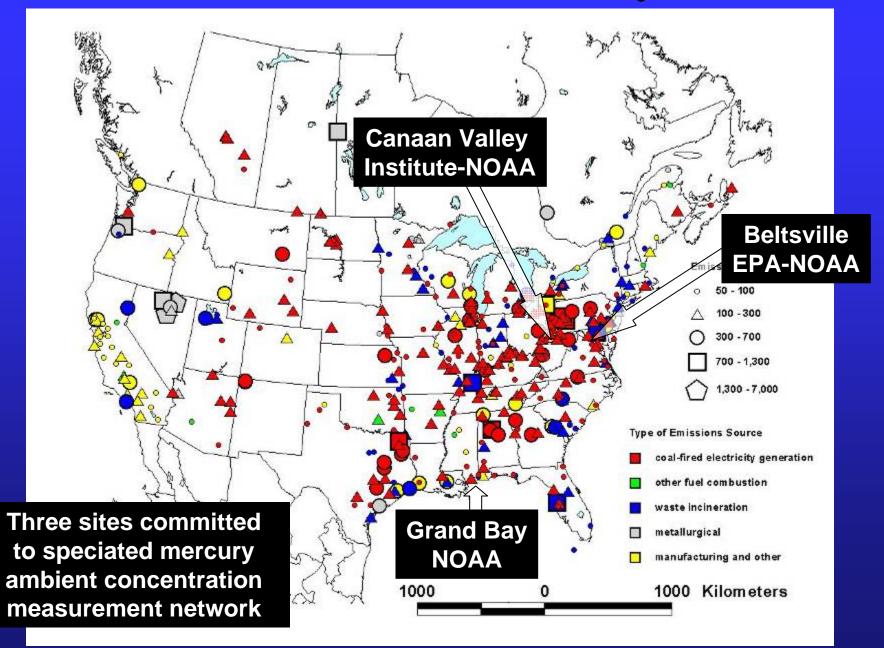
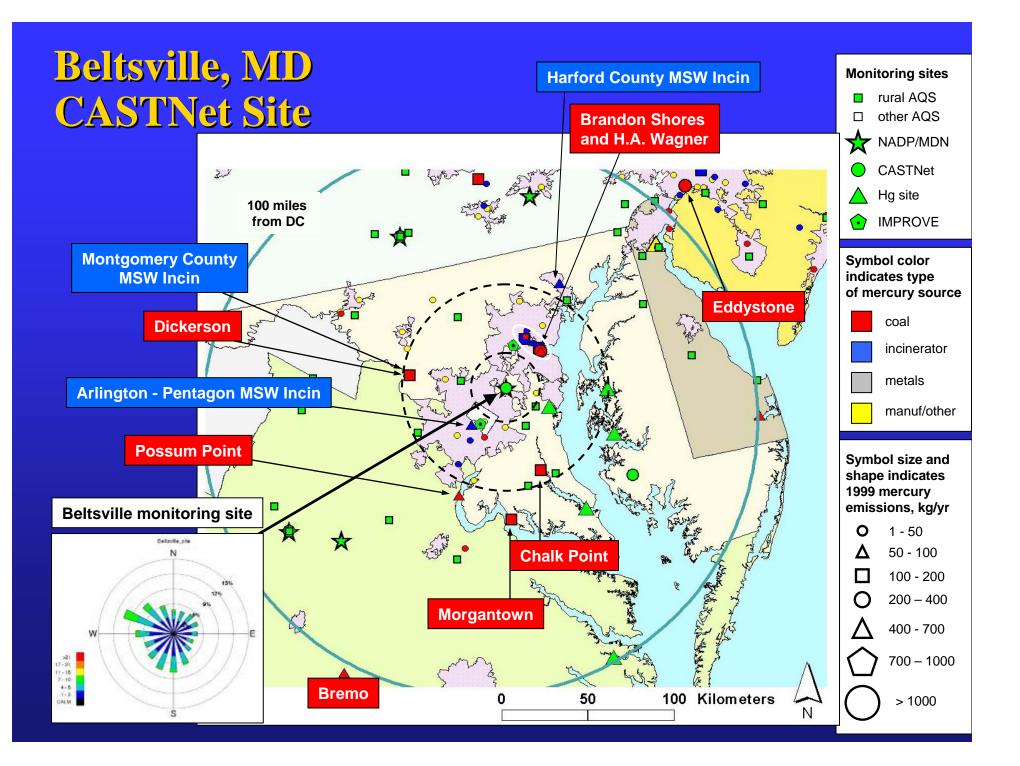
NOAA Collaborative Mercury Sites





Coal-fired power plants in MD, 500 200 VA, PA, and DE with the largest 50 100 Kilometers 0 **Beltsville** projected differences between monitoring site 2010 base and 2010 Clean Air Brandon Shores Interstate Rule (CAIR) emissions Ś H. A. Wagner Dickersor **Brandon Shores** 600 Morgantown - CAIR (kg/year) Chalk Point 500 Hg(0) Morgantown Hg(2) Sam 400 Hg(p) **Chalk Point** 300 Dickerson H.A. Wagner 2010: BASE 200 100 0 ЪЪ AES WARRIOR RUN MD READING ANTHRACITE PA Brandon Shores MD ð ΡA HATFIELDS FERRY PA BRUCE MANSFIELD PA CHALK POINT MD Wagner Station MD COGENTRIX RICHMOND VA PAUL SMITH MD ΡA DICKERSON MD MARTINS CREEK PA JOHN B RICH PA CHESTERFIELD VA Ϋ́ HUNLOCK CREEK PA CAMBRIA COGEN PA EBENSBURG COGEN PA GEN PA HOMER CITY PA ЪÀ SHAWVILLE PA EDDYSTONE PA NORTHAMPTON PA NESQUEHONING PA ЪЪ CHESWICK PA PORTLAND PA COLVER PA SUNBURY PA ARMSTRONG PA MITCHELL PA KEYSTONE PA TITUS PA CROMBY PA POTTER PA ELRAMA PA BRUNNER ISLAND FOSTER WHEELER MT CA POTOMAC RIVER Morgantown KENNERDELL CONEMAUGH MONTOUR MCADOO CO



Status of Atmospheric Measurements at Beltsville, MD CASTNet Site

Measurement

Elementa	l mercury

Fine particulate mercury

Reactive gaseous mercury

Sulfur dioxide

Ozone

Carbon Monoxide

Nitrogen Oxides (NO, NOy)

Wind speed

Wind Direction

Relative Humidity

Temperature

Precipitation

SO₄²⁻, NO₃⁻, NH₄⁺, HNO₃, SO₂ (Weekly)

Total mercury in precipitation (weekly)

Major ions in precipitation (weekly)





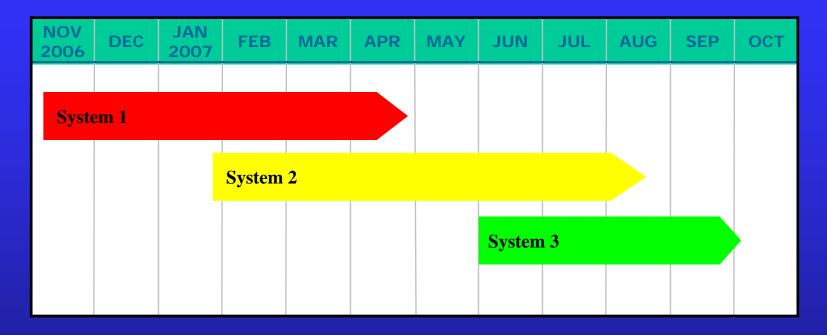
- Installed System 1 (NOAA) Nov. 7, 2006 Height of Inlet: 3.75 m above ground 0.5 m above trailer
- Installed second system (System 2-NOAA) Jan 26, 2007

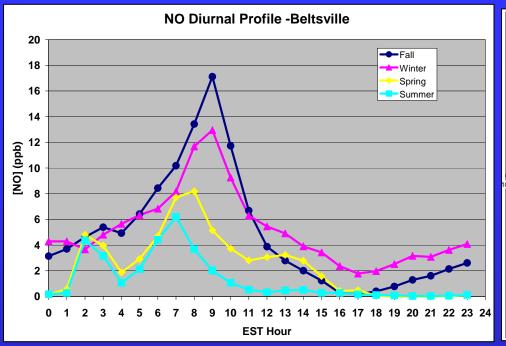


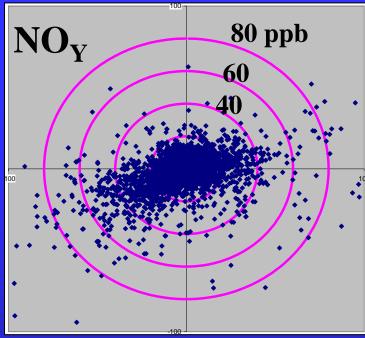
- Install System 3 (EPA) June 1, 2007
- Remove System 2 August 17, 2007

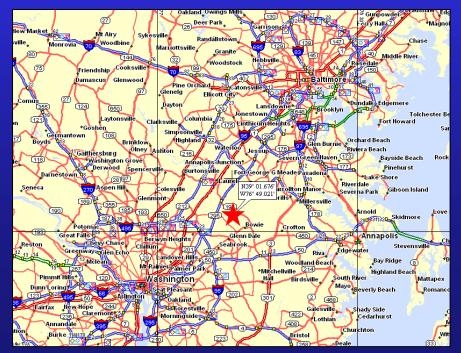


Tekran Deployment Timeline -Beltsville

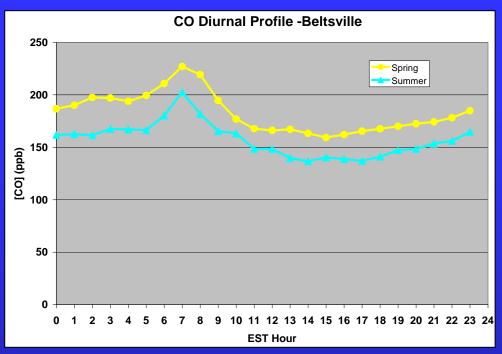




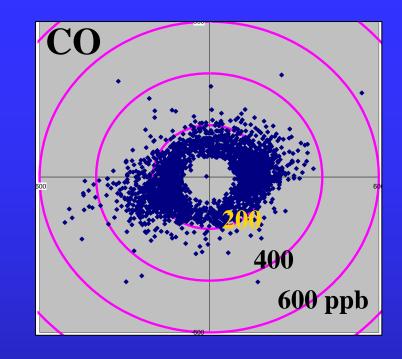




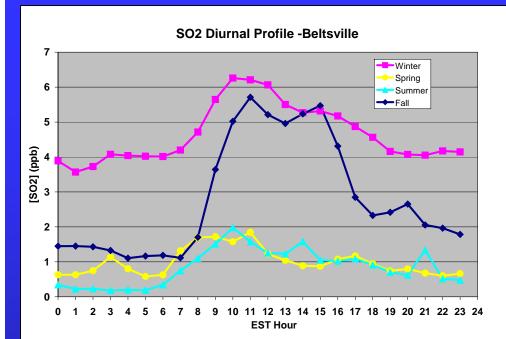
Site is influenced by vehicular traffic in Washington Metropolitan area, particularly pronounced during the morning rush hour. Higher boundary layer in the afternoon/evening dilutes vehicular emissions.



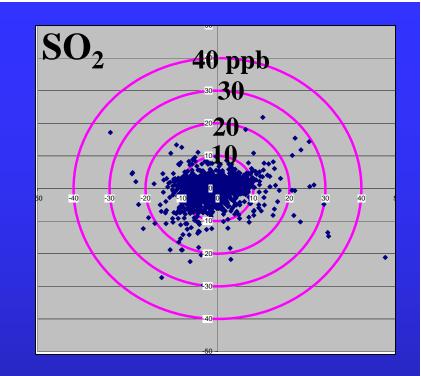




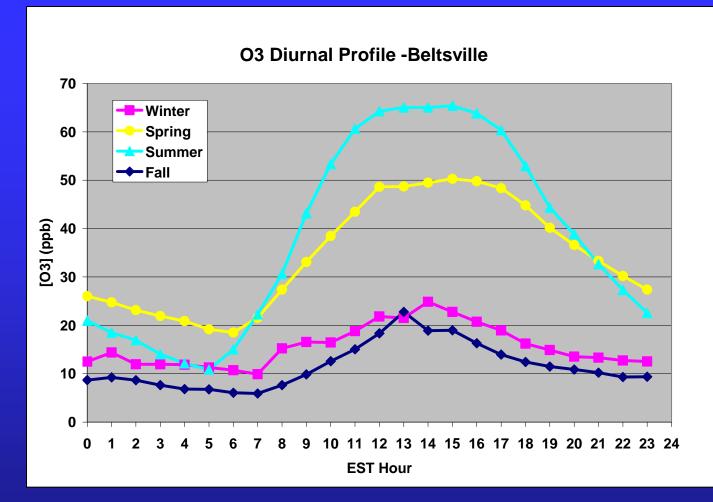
Concentrations of CO at the site also reflect the impact of vehicular emissions, but the efficacy of emission controls in the past decade have reduced the strength of this signal.





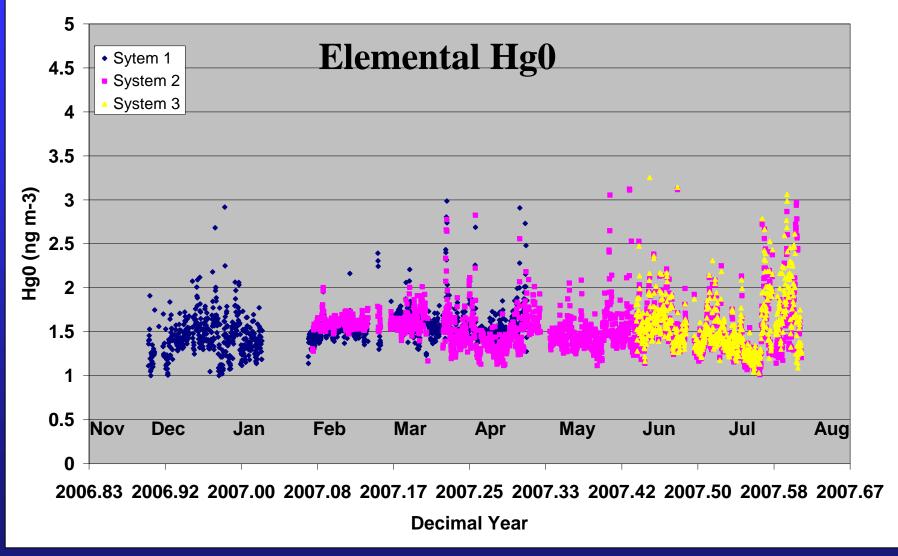


Site is also influenced by point-source emitters in the region. Higher concentrations in Fall and Winter reflect lower boundary layer heights, slower conversion of SO_2 to SO_4^{2-}

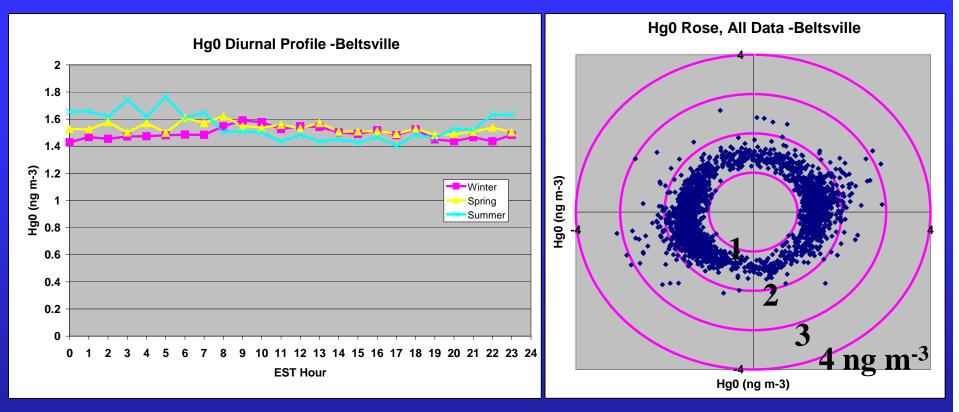


Photochemical ozone generation in the Spring and Summer leads to elevated concentrations in mid-day. Note the later time of boundary layer breakup in Fall and Winter, as evidenced by later onset of daytime increase.

Beltsville Time Series

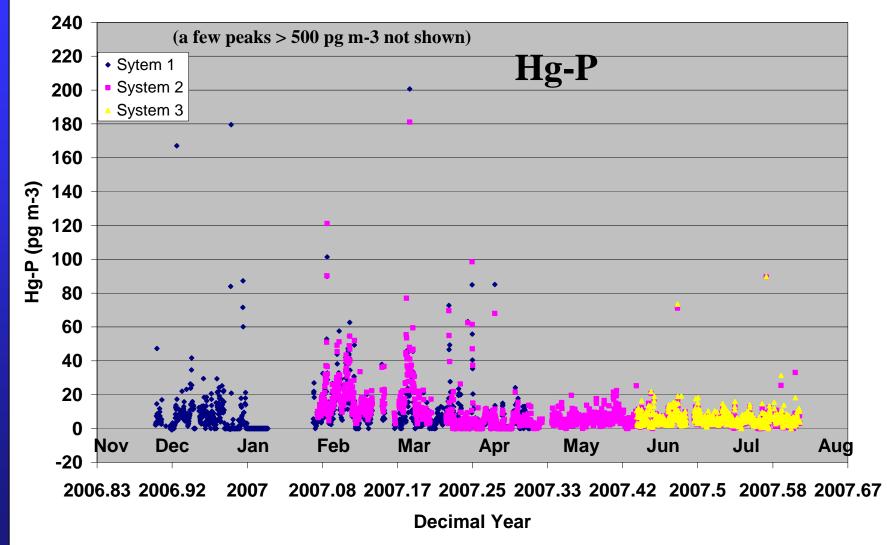


Elemental Mercury (Hg⁰) at Beltsville

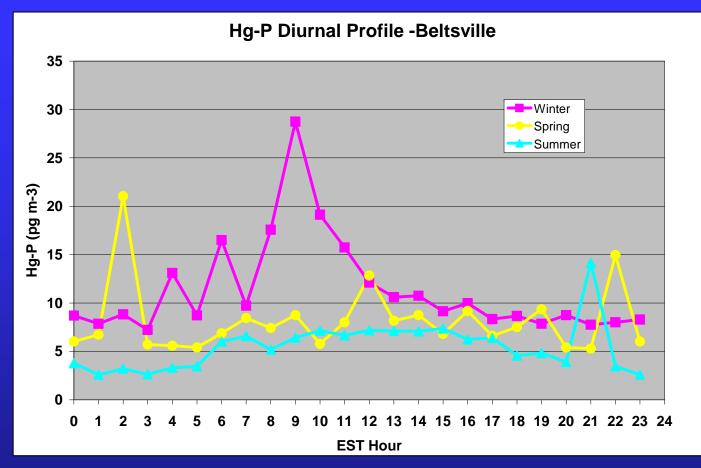


As expected, Hg0 at Beltsville shows no diurnal pattern, little dependence on WD, consistent with a long-lived, ubiquitous, and well mixed trace species. Note that emission source regions match those for SO_2 , NO_Y , CO

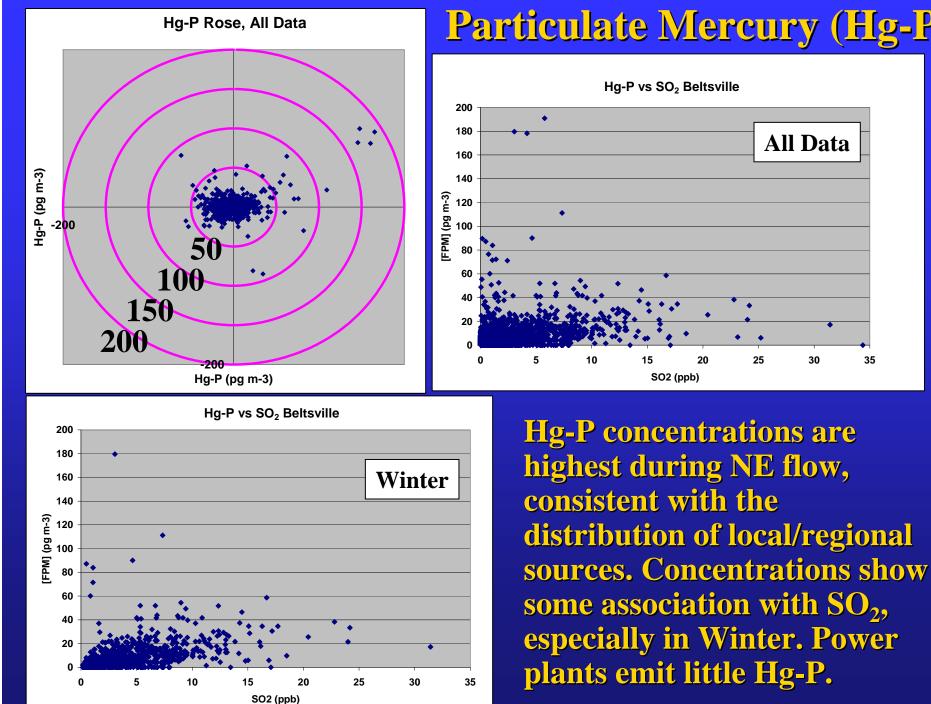
Beltsville Time Series



Particulate Mercury (Hg-P)

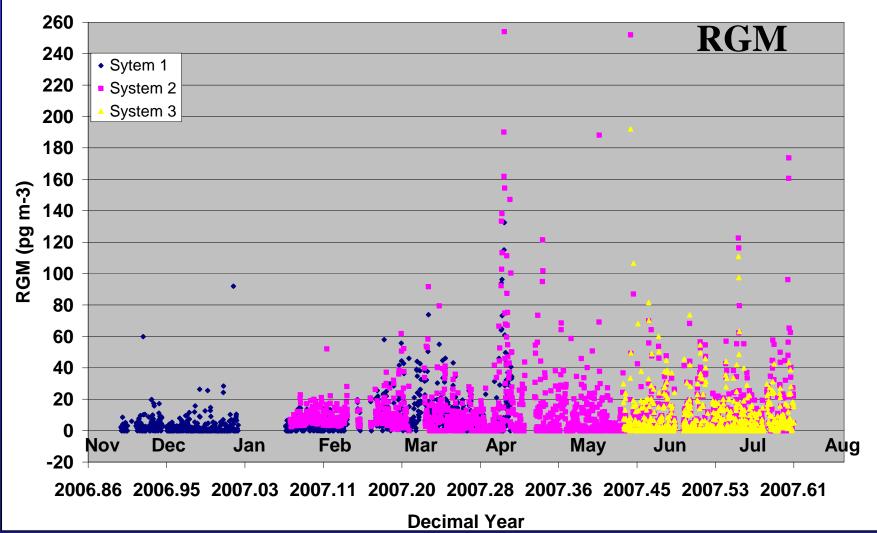


Little diurnal variation in Hg-P concentrations, with some evidence of entrainment of higher concentrations aloft beginning in the morning, after the breakup of the nocturnal inversion. Spikes due to influence of a few highconcentration events.



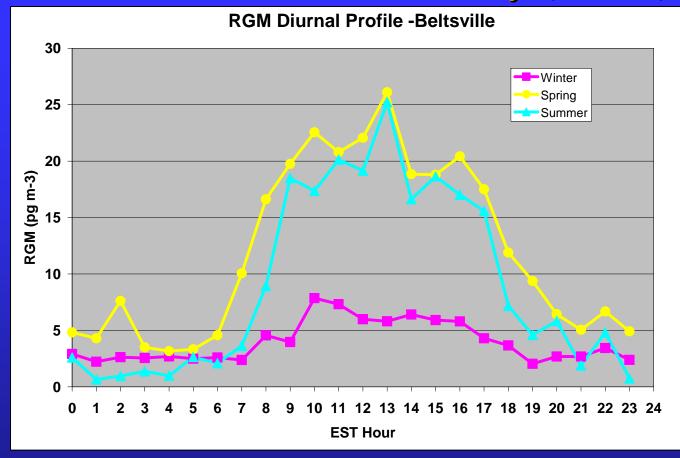
Particulate Mercury (Hg-P)

Beltsville Time Series

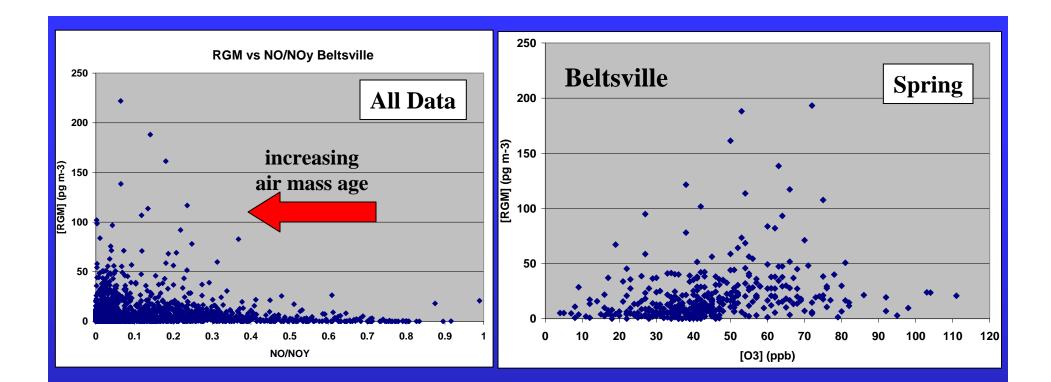


RGM concentrations generally < 20 pg m⁻³, with more frequent peaks in concentration than was seen for Hg-P

Reactive Gaseous Mercury (RGM)

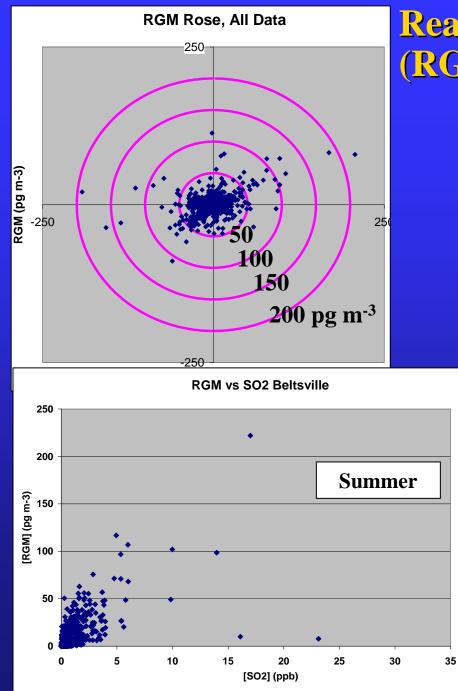


More pronounced diurnal variation in RGM concentrations, again showing evidence of entrainment of higher concentrations aloft with the breakup of the nocturnal inversion. Large seasonal differences may point to secondary (photochemical) source of RGM as well.



Association of high RGM with high O_3 and aged air masses (low NO/NO_Y ratios) suggests that secondary production of RGM may be occurring.

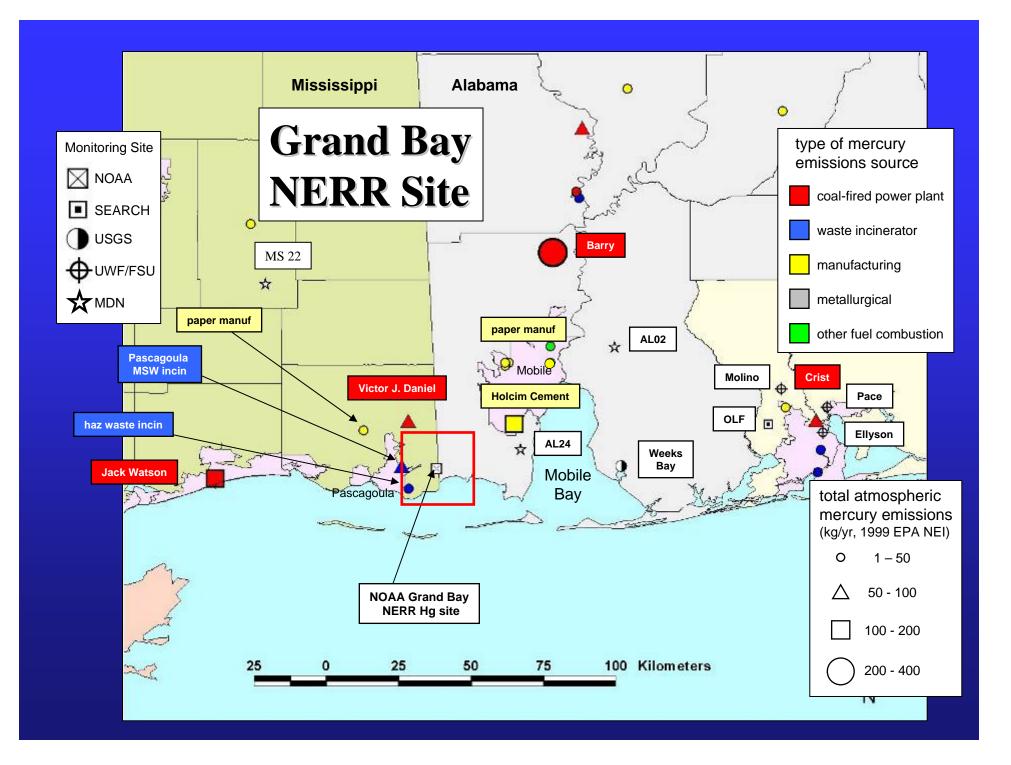
However, high concentrations of RGM may arise from primary emissions from sources a few hours away – and the air masses are somewhat aged on arrival at the site.



Reactive Gaseous Mercury (RGM)

Directionality of [RGM] shows lobes to the SW and NE, coincident with known local sources of mercury and other primary trace species.

RGM is most closely associated with SO₂ at Beltsville (Summer) suggesting that pointsource emissions also play an important role in influencing RGM concentrations at the site



Status of Atmospheric Measurements <u>at Grand Bay NERR, Mississippi</u>

4 m sampling height

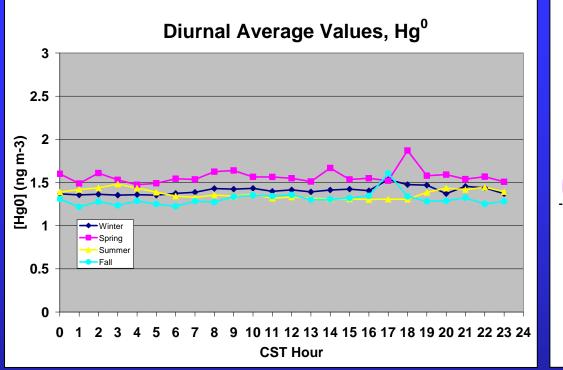


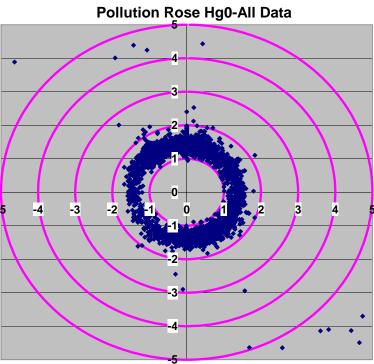
Measurement	Туре	Start Date	
Elemental mercury	A	Sept 2006	
Fine particulate mercury	A	Sept 2006	
Reactive gaseous mercury	A Sept 2006		
Sulfur dioxide	A	Oct 2006	
Ozone	A	Oct 2006	
Carbon Monoxide	A	Oct 2006	
Nitrogen Oxides (NO, NOy)	A	*	
Wind speed	С	Feb 2007	
Wind Direction	С	Feb 2007	
Relative Humidity	С	Feb 2007	
Temperature	С	Feb 2007	
Precipitation	С	Feb 2007	
Total mercury in precipitation	В	*	
Major ions in precipitation	В	*	

Type of Measurement: A = concentration in ambient air B = concentration in precipitation C = meteorological parameter

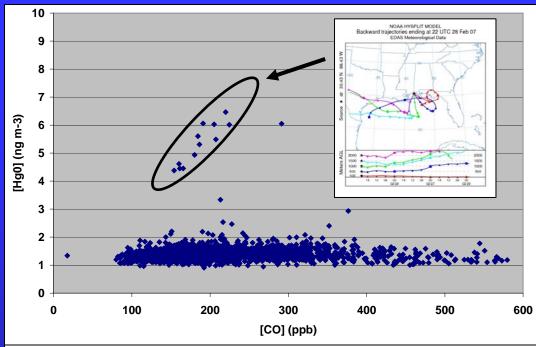
* to be established

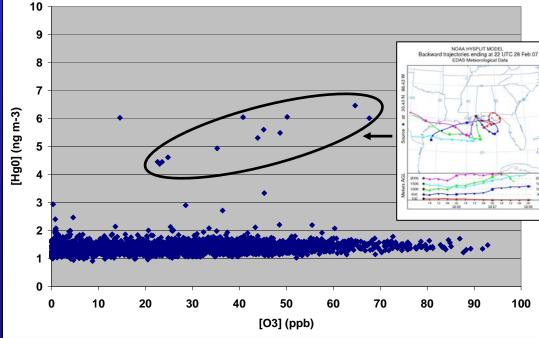
Elemental Mercury (Hg⁰) at Grand Bay





As expected, with a few exceptions Hg⁰ concentrations show little or no diurnal variation or dependence on wind direction

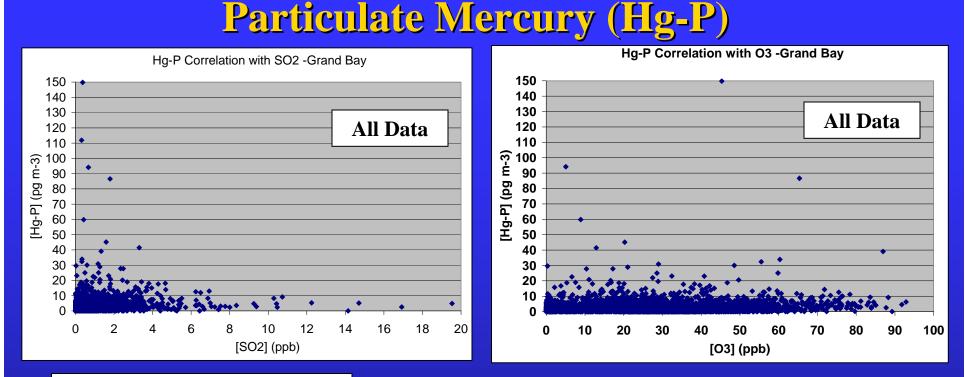


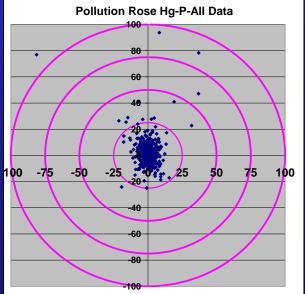


Overnight Event Feb. 28-March 1

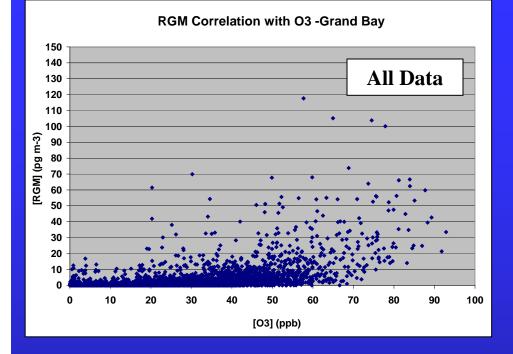
Strong correlation between Hg⁰ and CO, O₃.

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

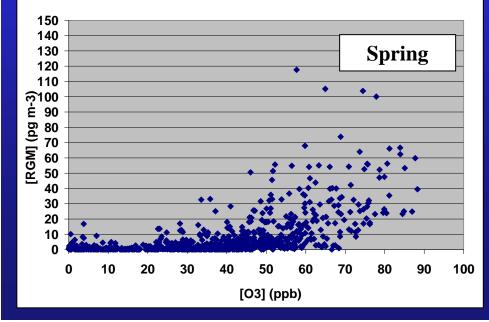




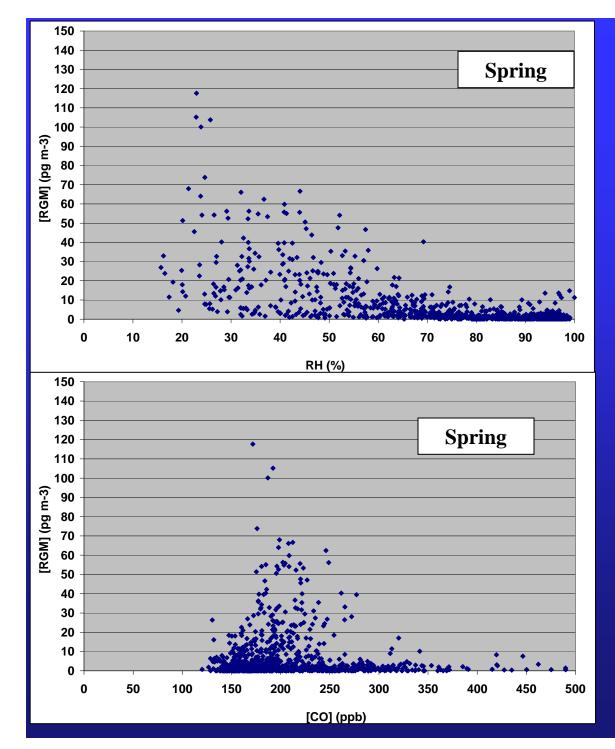
With the exception of a few well-defined transport events, Hg-P displays no consistent relationship with wind direction, and exhibits little or no correlation with other trace species



RGM Correlation with O3 - Spring

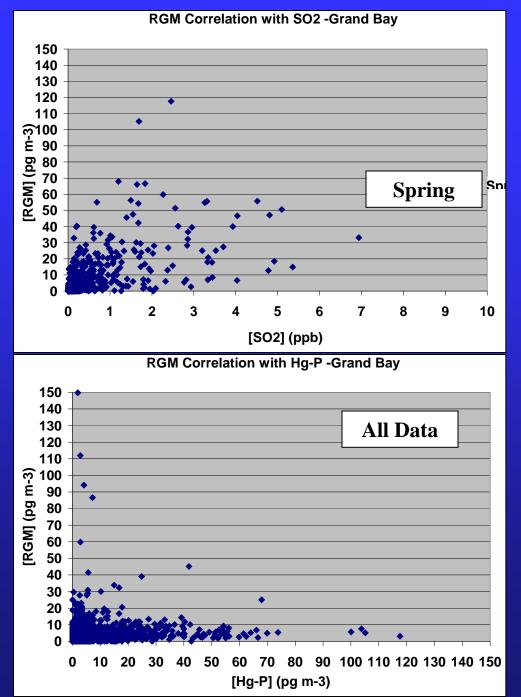


Strongest correlations seen between RGM and O_3 , most of which is driven by seasonal dependence –RGM concentrations are highest, relationship with O_3 is strongest in Spring.



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

What is the role of downward mixing of upper-tropospheric air, which contains elevated RGM, O₃, and lower CO and RH ?



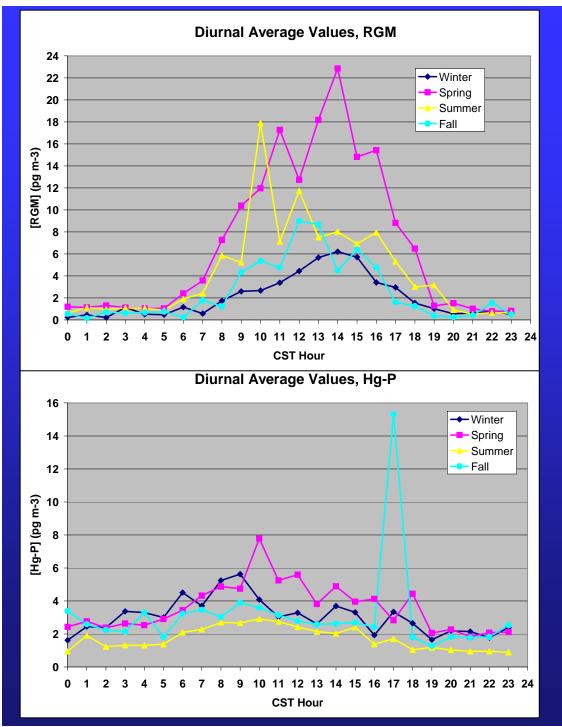
Weaker RGM – SO_2 correlation at Grand Bay than at Beltsville suggests:

A mix of primary sources with varying emission characteristics

A mix of primary and secondary sources of RGM

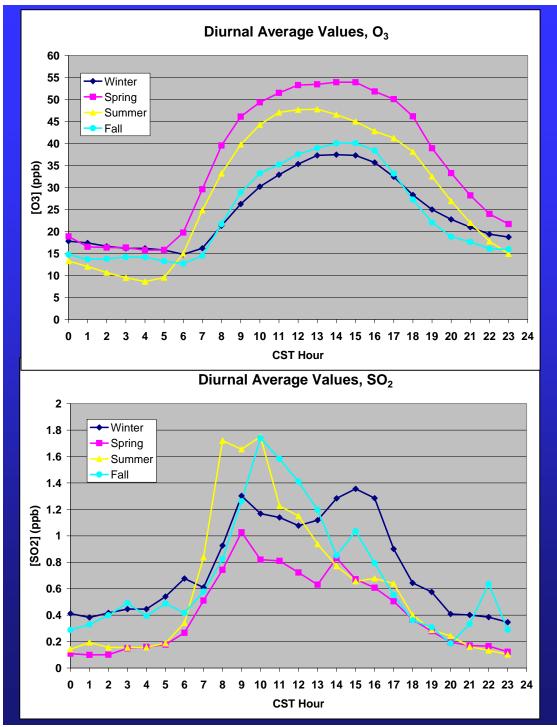
Different chemical processing and removal rates of SO₂ and RGM during transport

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



As at Beltsville, significant diurnal patterns seen in RGM, but amplitude of diurnal Hg-P profile is much smaller.

Highest RGM and Hg-P concentrations seen in Spring. At Beltsville, Hg-P peaks in the winter, and Spring-Summer differences between RGM and Hg-P are small



Similarity to O_3 and SO_2 diurnal profiles confirms the importance of downward mixing in the development of the daytime boundary layer, but photochemical (secondary) production of RGM is also possible

Summary and Conclusions – Interpretation of Ambient Measurements

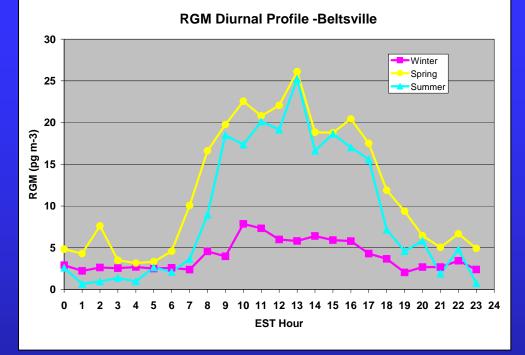
- Beltsville site is semi-urban and is ringed by emission sources of mercury and other primary trace species, with frequent peaks in RGM (less for Hg-P) concentrations due to transport from nearby sources. Grand Bay NERR Site exhibits characteristics of a rural/remote site with low concentrations of all species but occasional transport related episodes of higher concentrations.
- At both sites, RGM exhibits a more pronounced diurnal profile than Hg-P, but both profiles are coincident with O₃ and SO₂ peaks, suggesting downward mixing of an aloft reservoir upon the breakup of the nocturnal boundary layer. In situ production of RGM may also be contributing. RGM peaks in the Spring at Grand Bay, in Spring and Summer at Beltsville. Hg-P is higher in Winter at Beltsville.
- At Beltsville, RGM correlates most closely with SO₂ in Summer, suggesting the dominance of nearby (primary) emissions. However, RGM is also associated with elevated O₃ and low NO/NOy ratios, suggesting that secondary production may also be important

Summary and Conclusions – Interpretation of Ambient Measurements (continued....)

- At Grand Bay, RGM is associated with O₃ 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.

Deposition Estimates

Preliminary Deposition <u>Estimates</u> -Beltsville

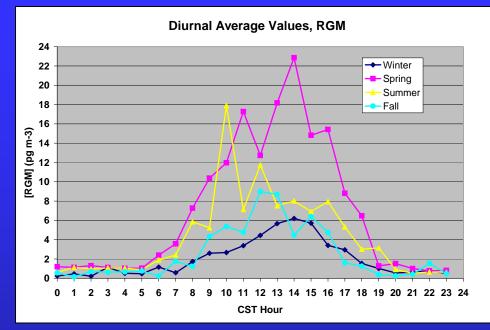


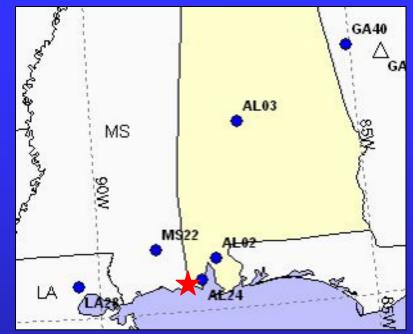
NDN84

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

Fluxes (ng m-2 day-1)FallWinterSpringSummerDry Dep, Beltsville (2006-2007)7.822.318.2Wet Dep, Beltsville (2005-2006)35.413.913.054.8

Preliminary Deposition <u>Estimates</u> - Grand Bay





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

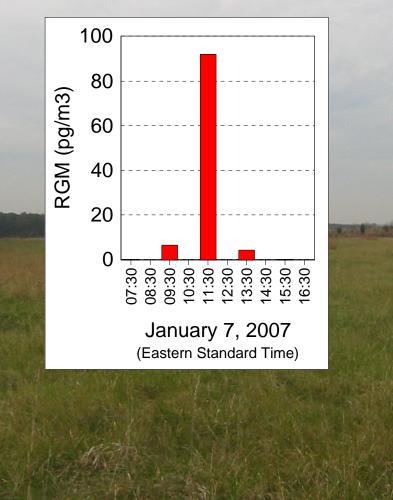
	Fluxes (ng m-2 day-1)			
	Fall	Winter	Spring	Summer
Dry Dep, Grand Bay (2006-2007)	5.4	4.3	14.2	<mark>8.6</mark>
Wet Dep, AL24 (2005-2006)	13.5	24.8	31.6	34.6
Wet Dep, MS22 (2005-2006)	11.9	28.2	28.5	65.3
Wet Dep, AL02 (2005-2006)	24.7	21.6	31.3	34.6

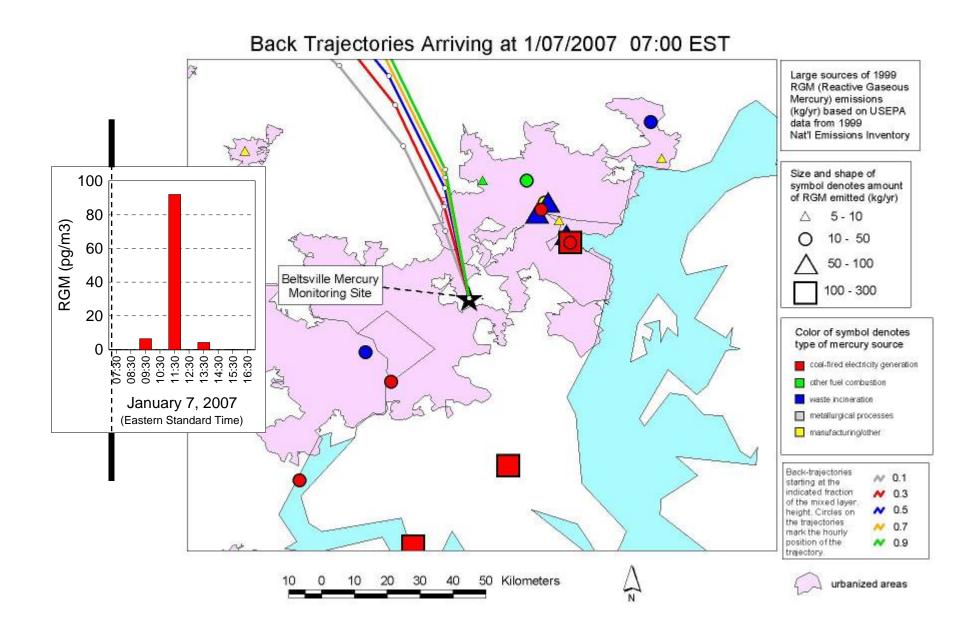
Summary and Conclusions - Deposition

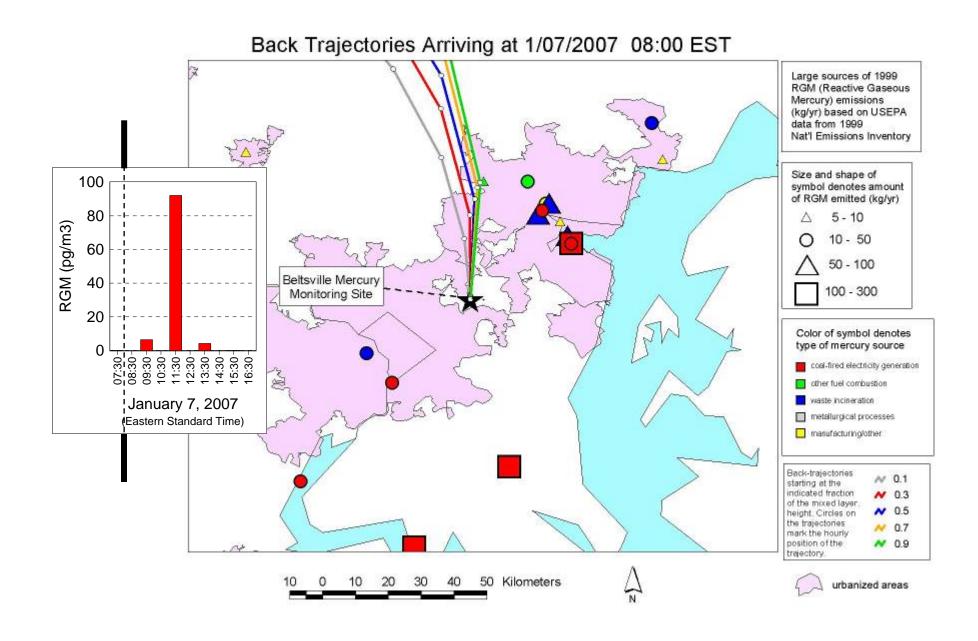
- Preliminary estimates of dry deposition have been made based on measured RGM and Hg-P concentrations. More sophisticated estimates will be made in the future.
- Dry deposition estimates, when compared with nearby MDN deposition records, suggest that dry deposition sometimes dominates at the Beltsville site, depending on season.
- At Grand Bay, wet deposition dominates the removal of reactive mercury species, especially in Winter.
- If substantial Hg exists in the coarse aerosol fraction, however, the reported dry deposition fluxes are under-estimated.

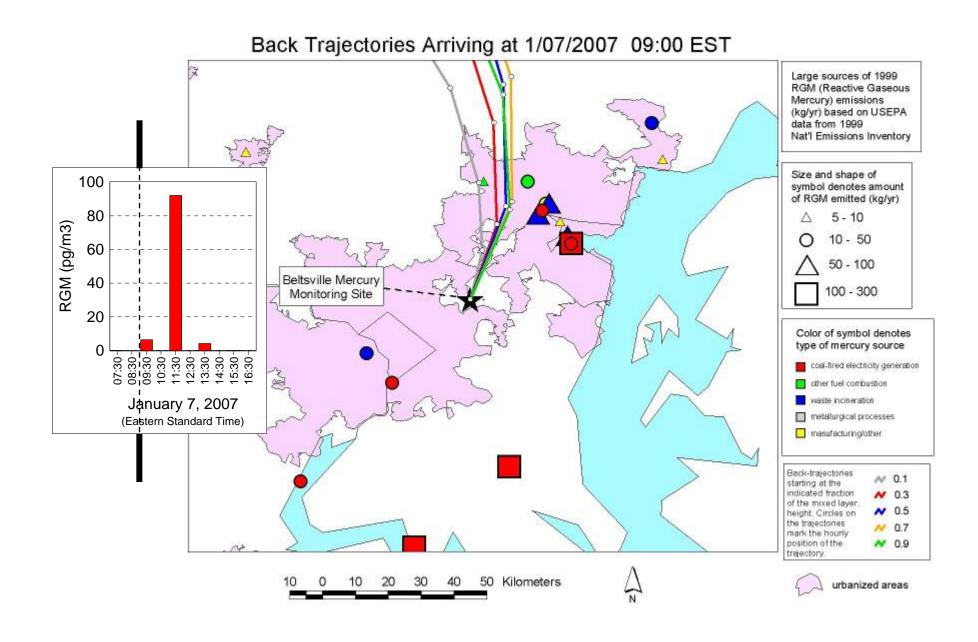
Trajectory Analysis Examples: Beltsville

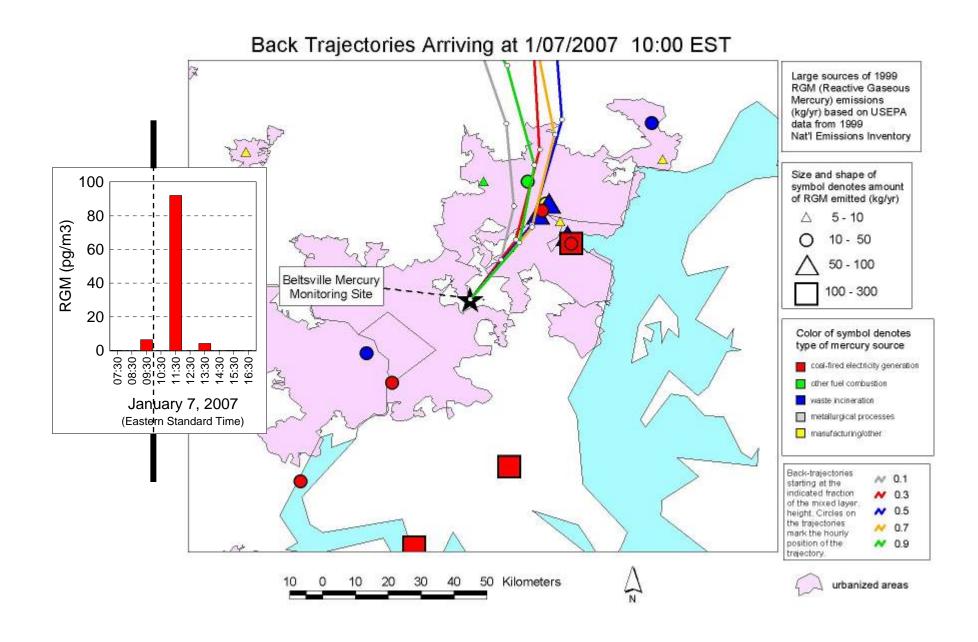
Beltsville Episode January 7, 2007

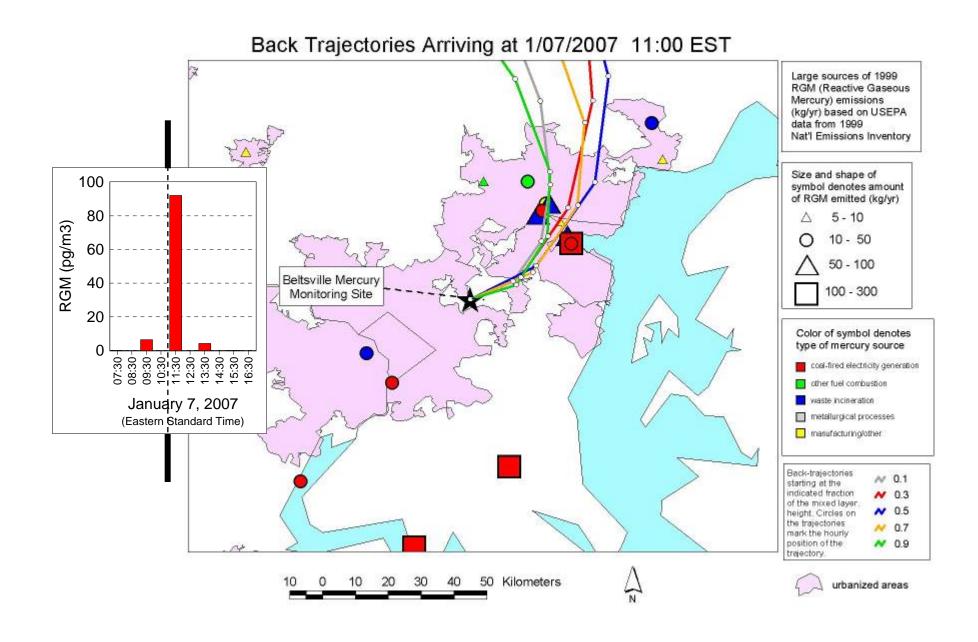


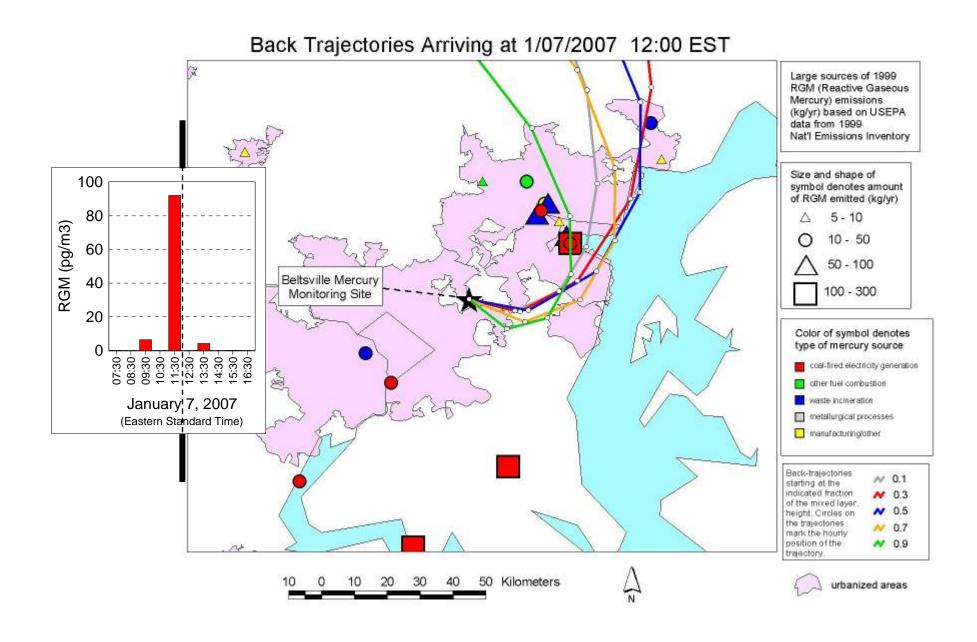


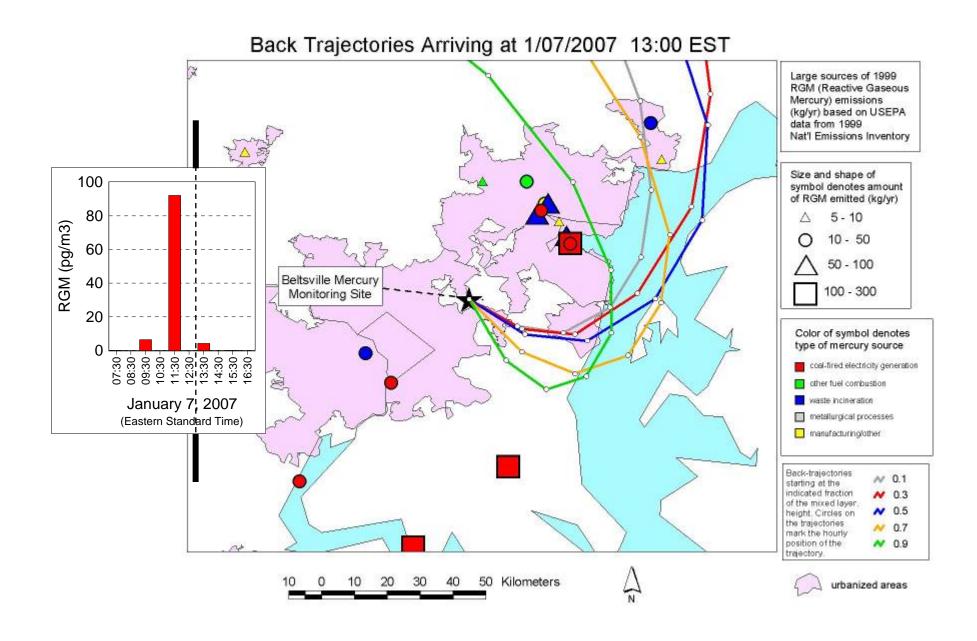


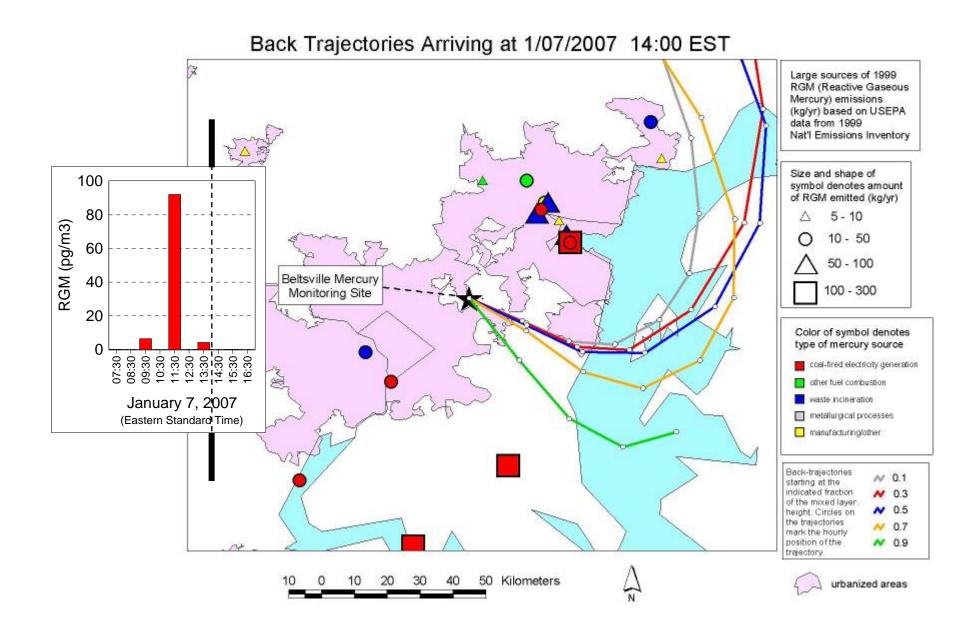


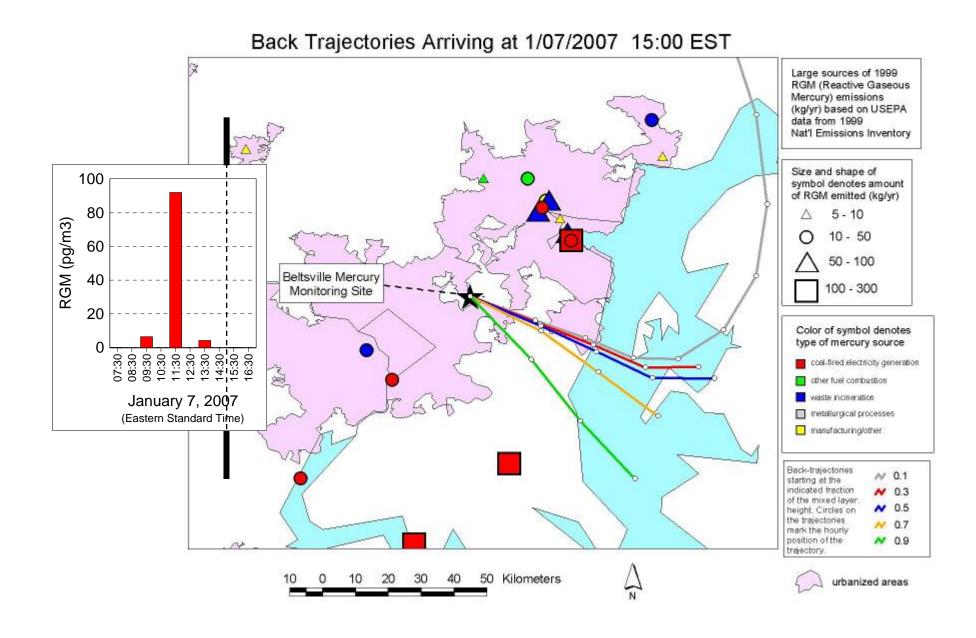


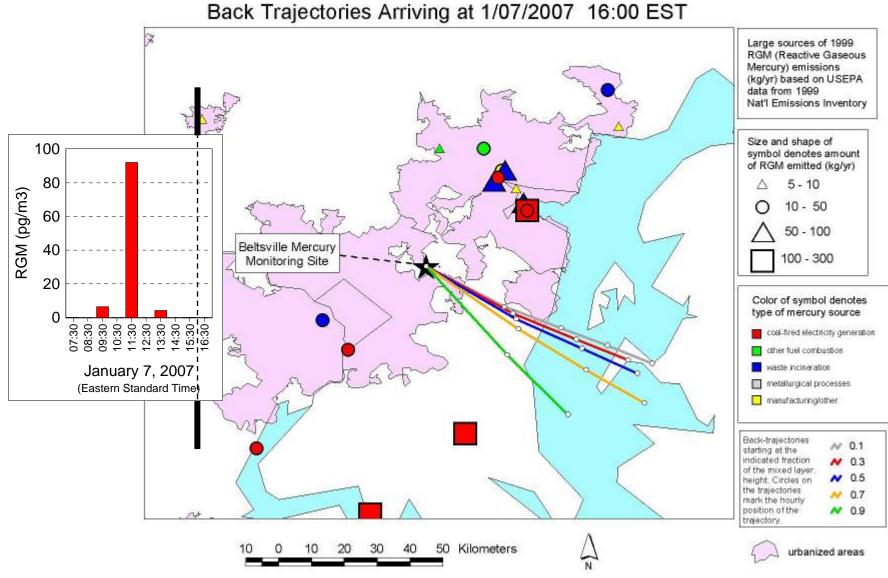




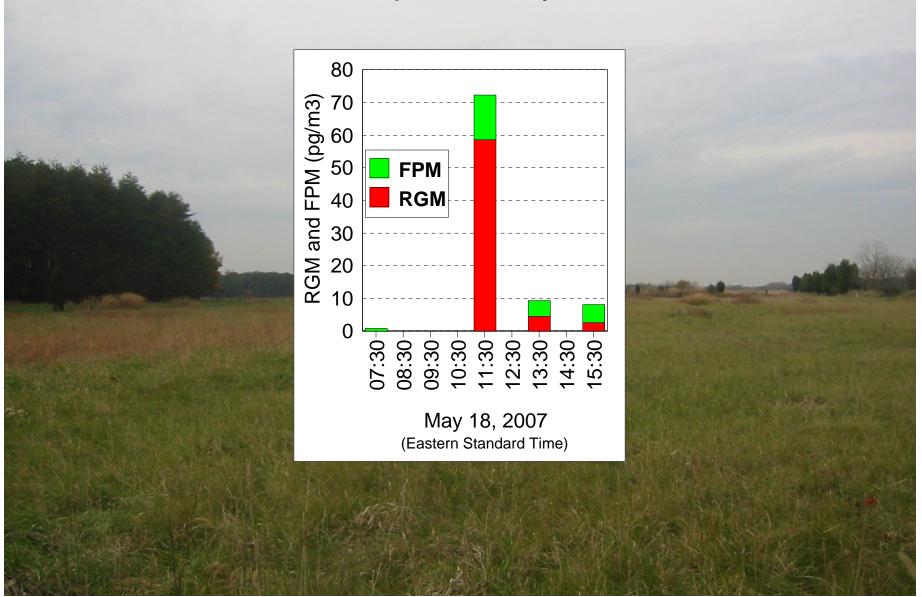


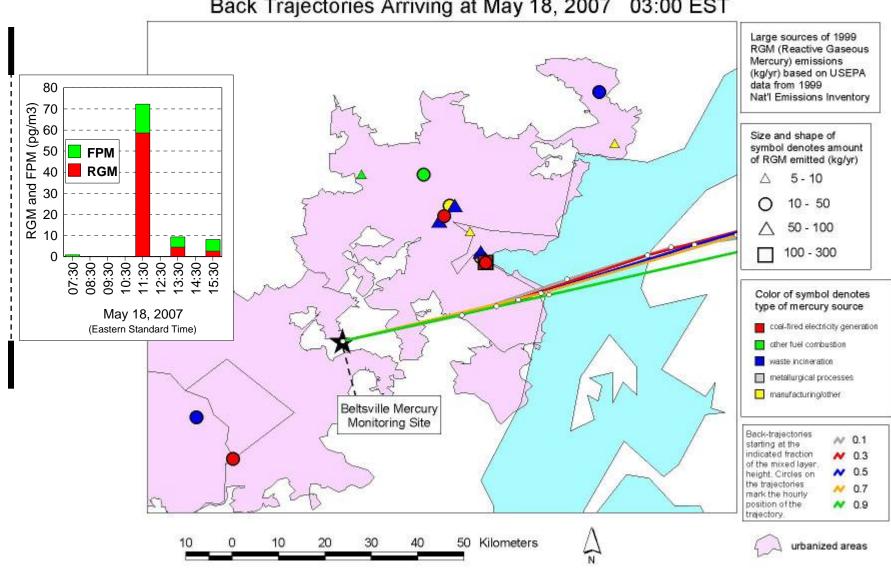




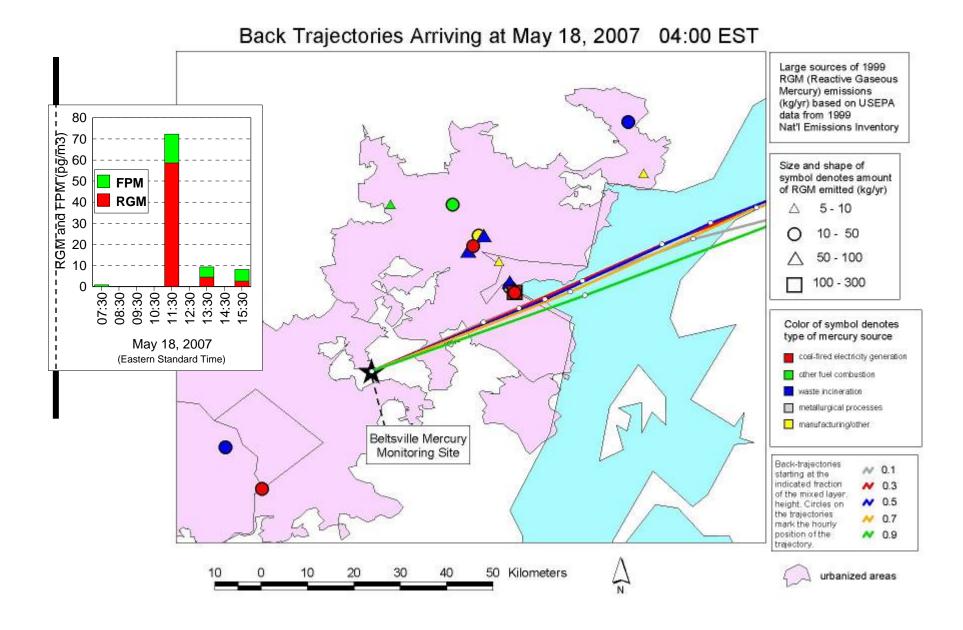


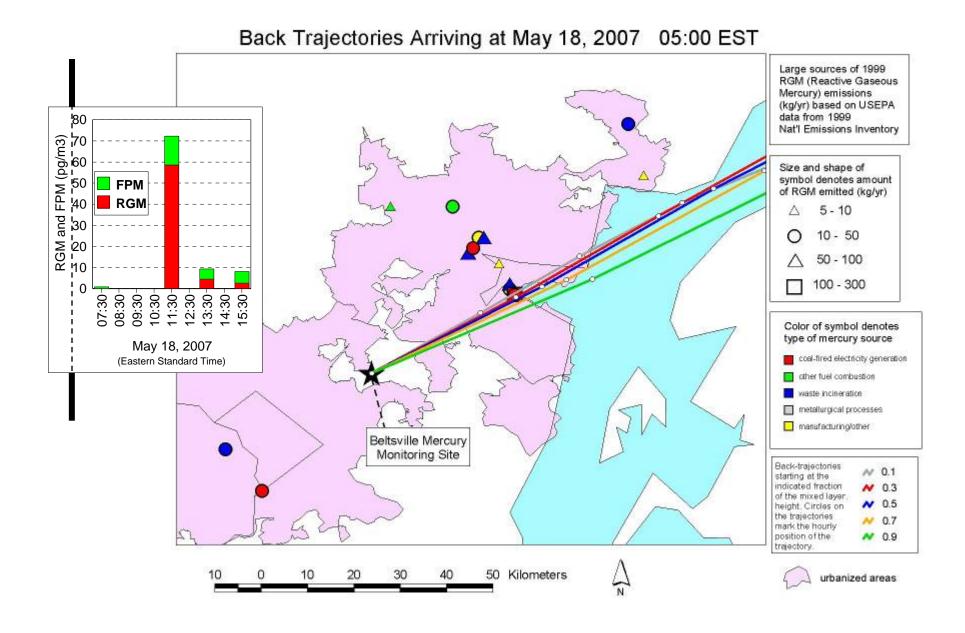
Beltsville Episode May 18, 2007

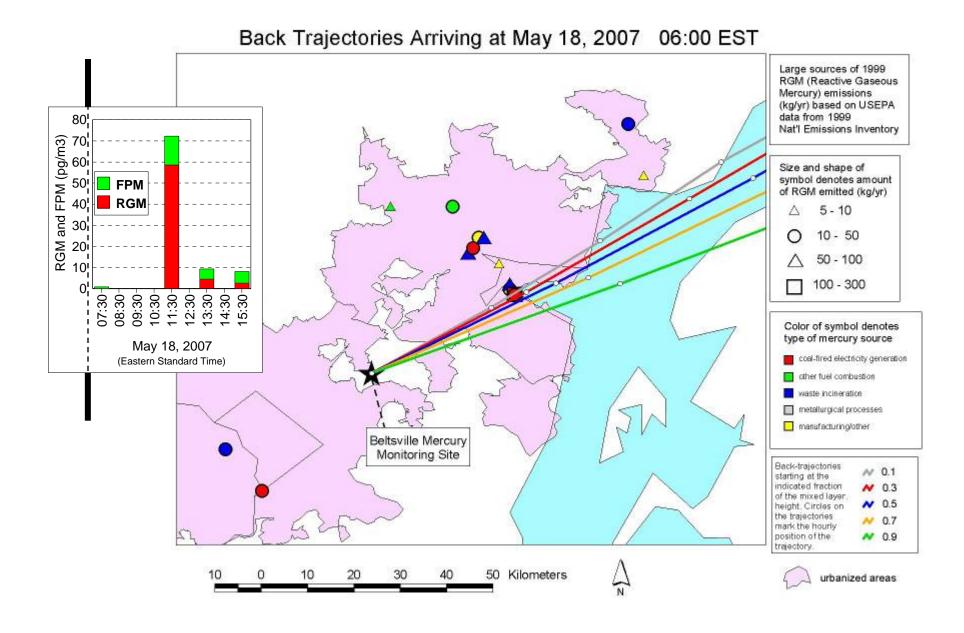


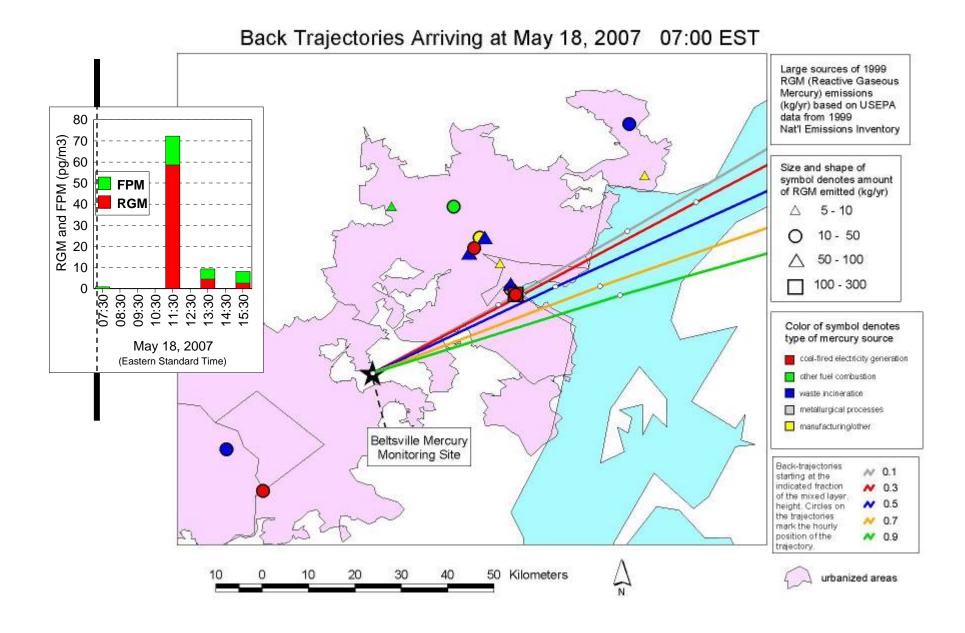


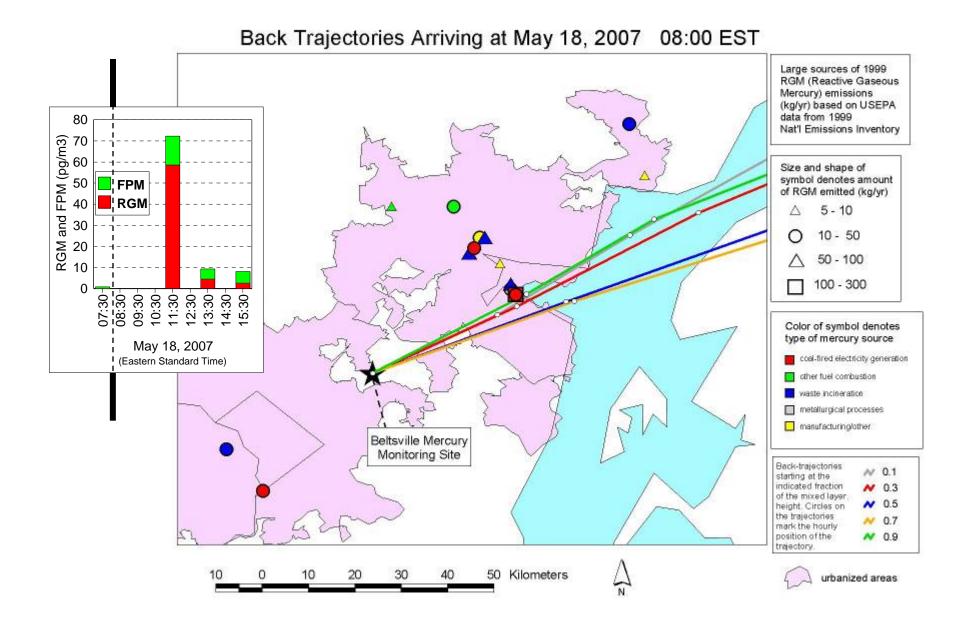
Back Trajectories Arriving at May 18, 2007 03:00 EST

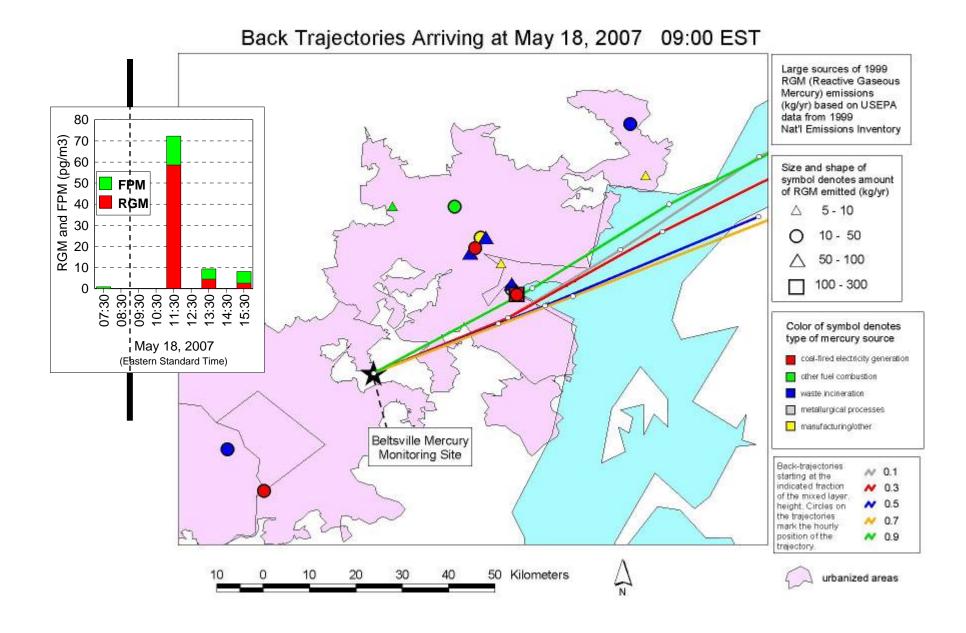


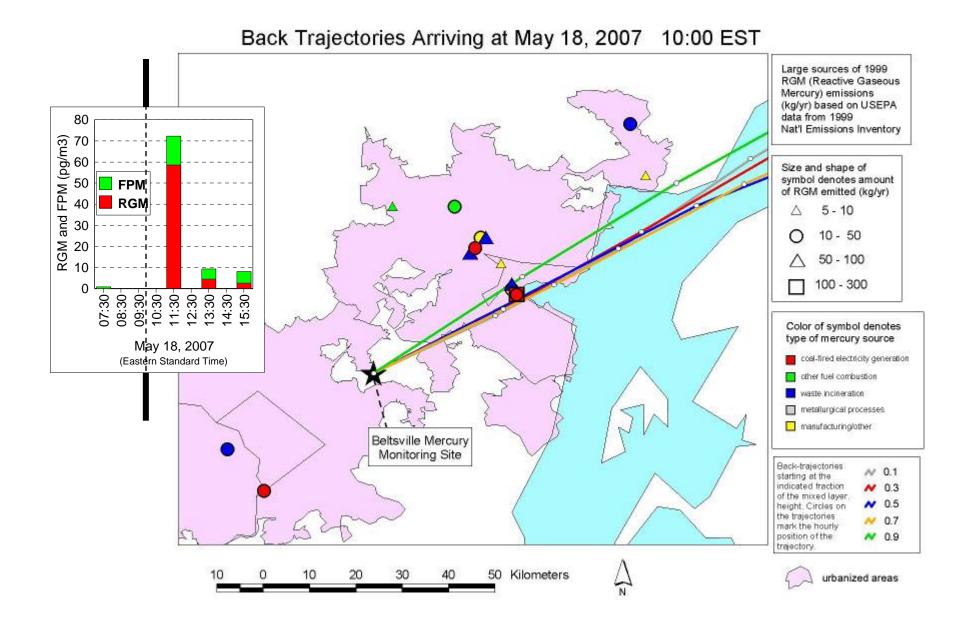


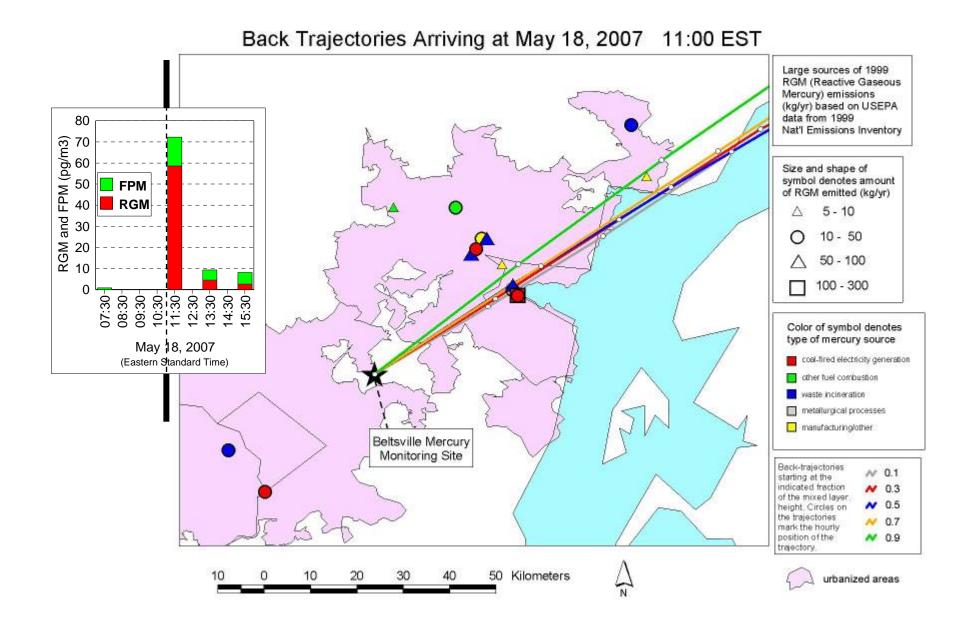


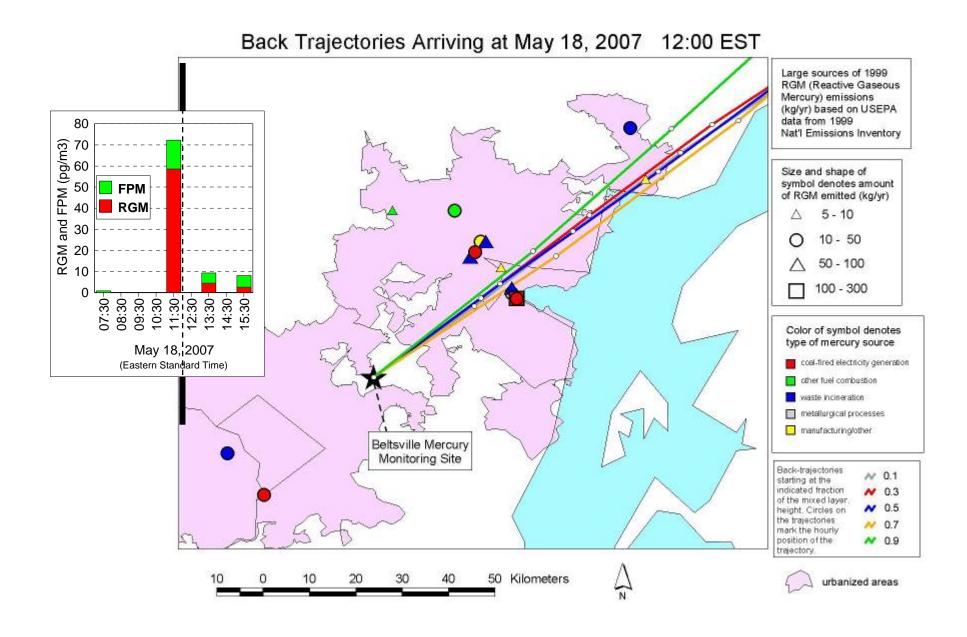


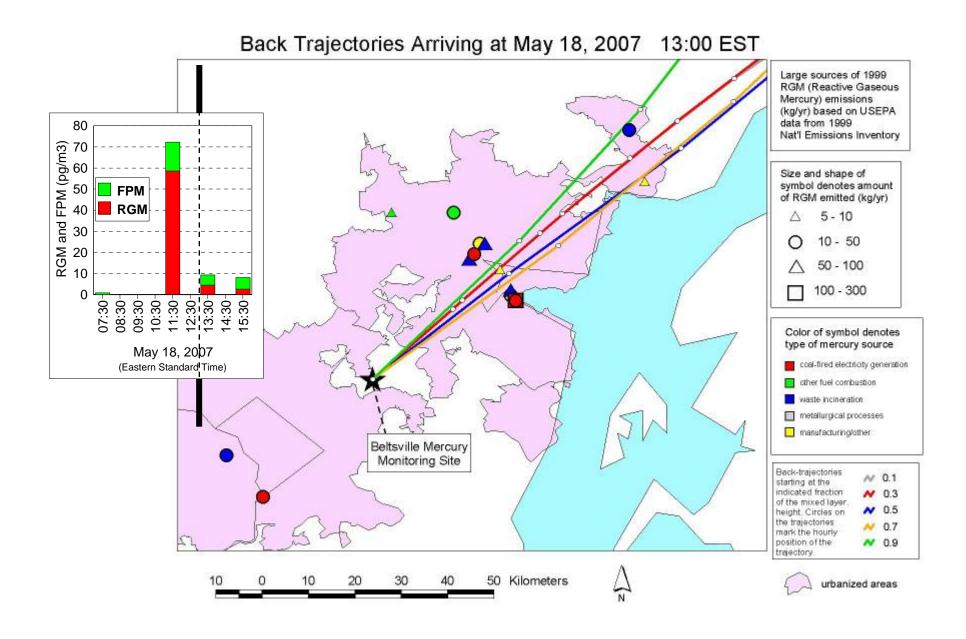


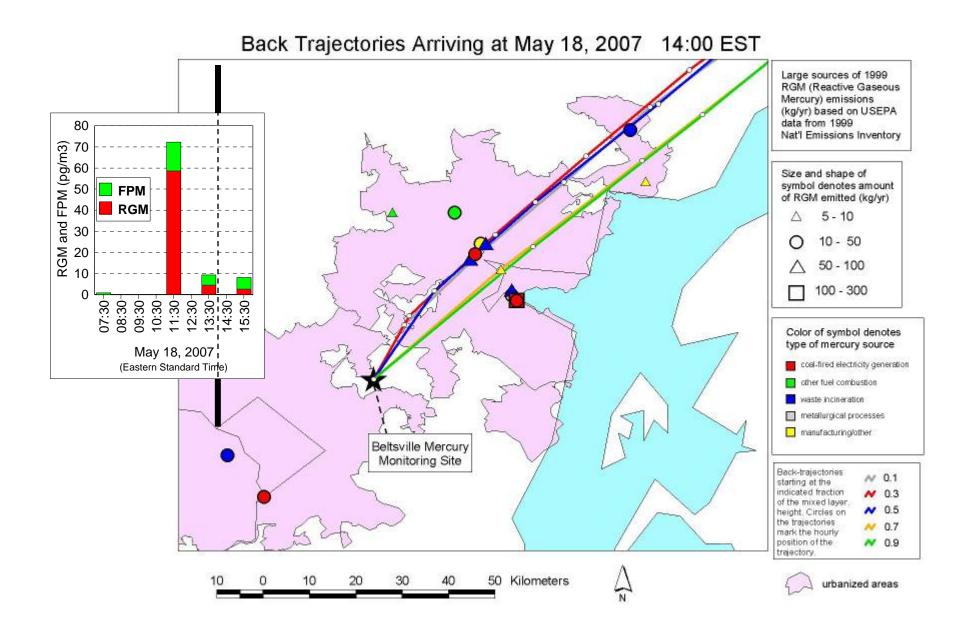


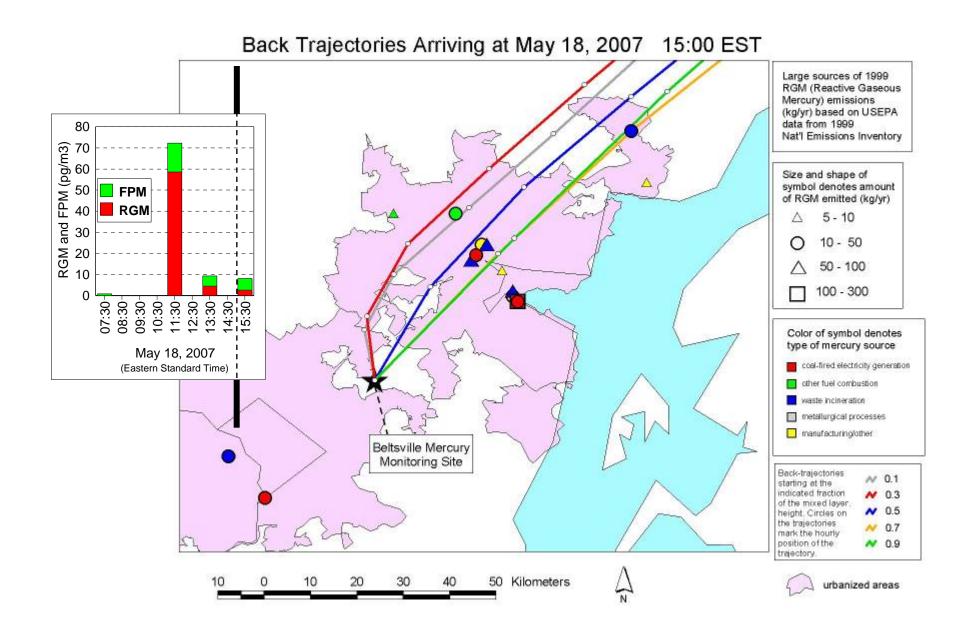


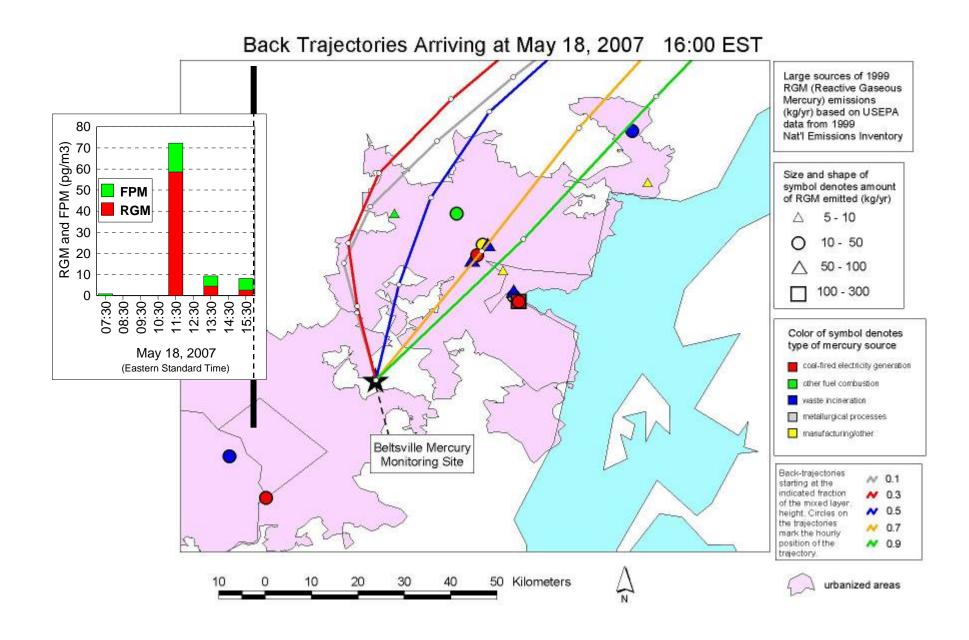


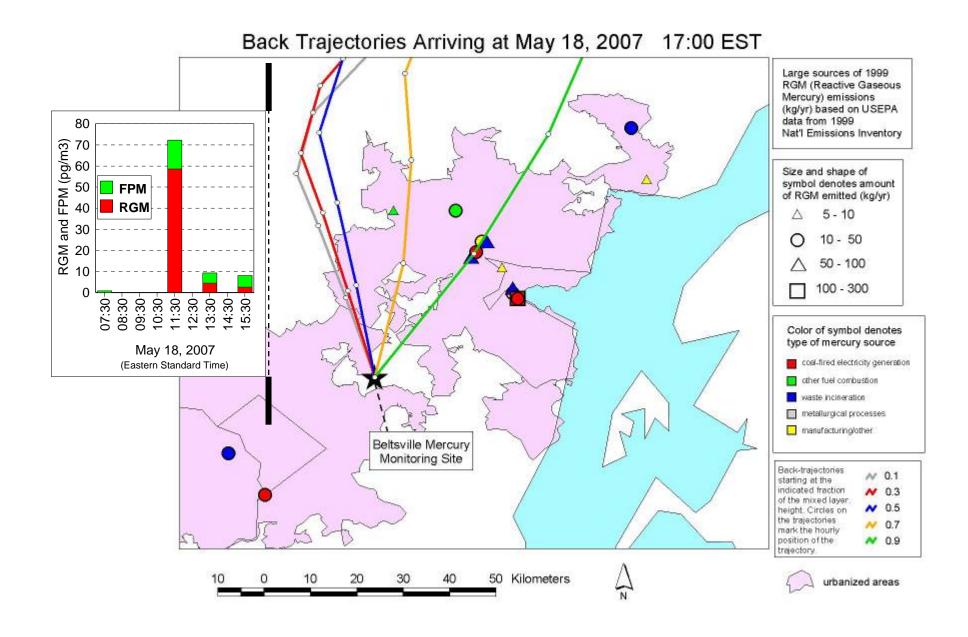


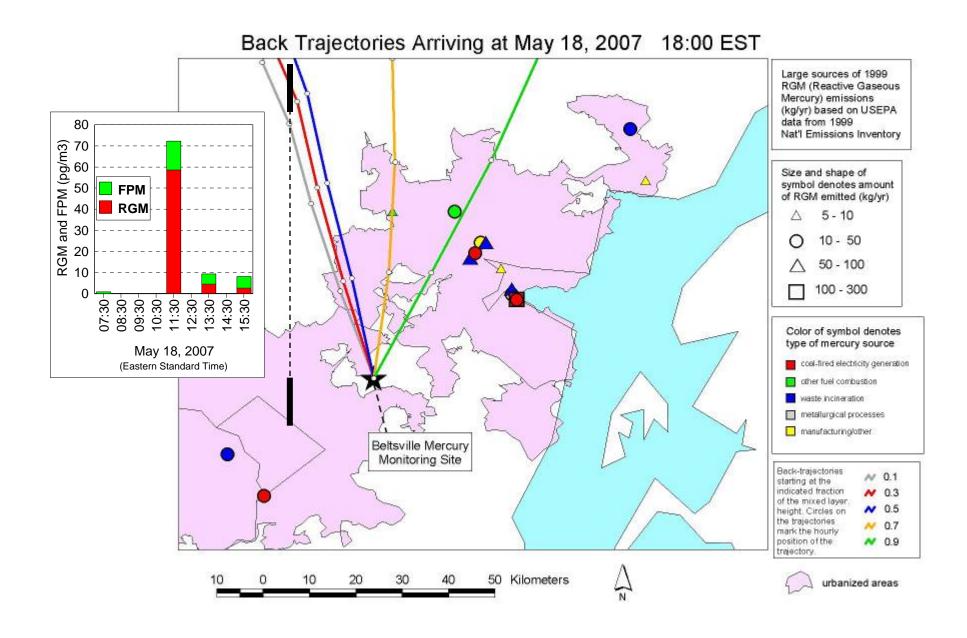












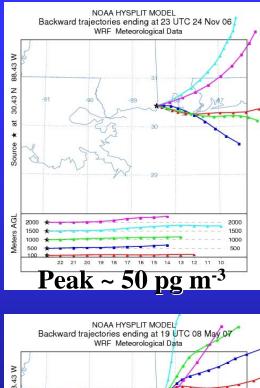
Trajectory Analysis Examples: Grand Bay

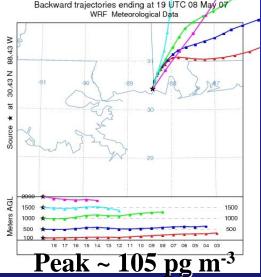
Higher RGM Associated with N-E trajectories

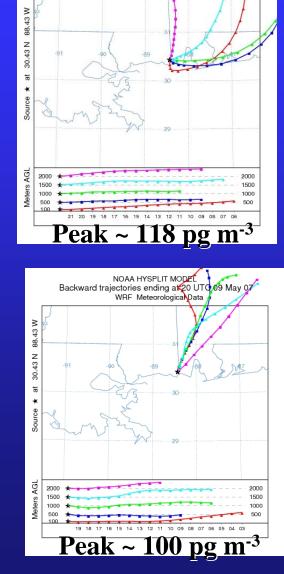
NOAA HYSPLIT MODEL

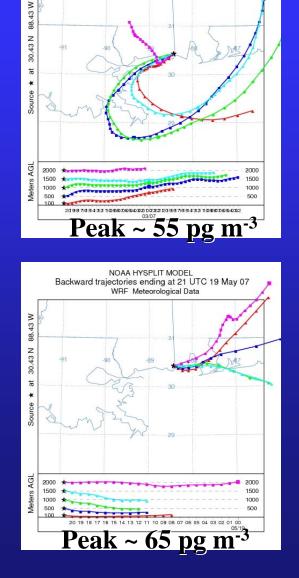
Backward trajectories ending at 22 UTC 06 Mar 07t

WRF Meteorological Data







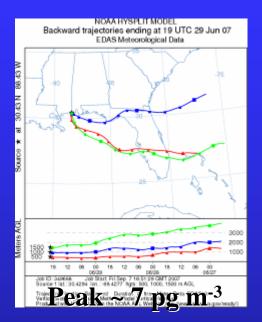


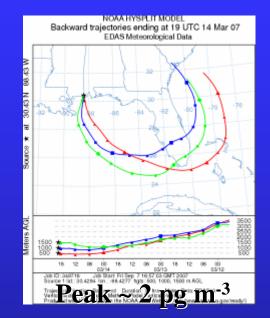
NOAA HYSPLIT MODEL

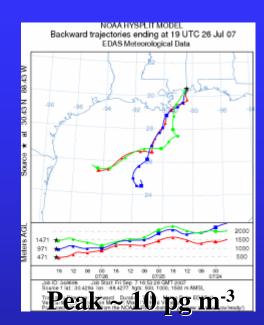
Backward trajectories ending at 21 UTC 07 Mar 07

WRF Meteorological Data

Lower RGM in Maritime trajectories



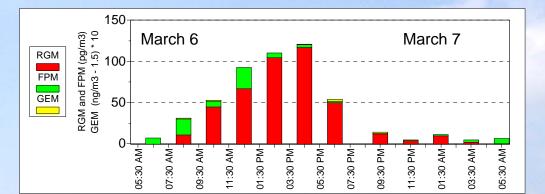




Grand Bay Episode March 6, 2007

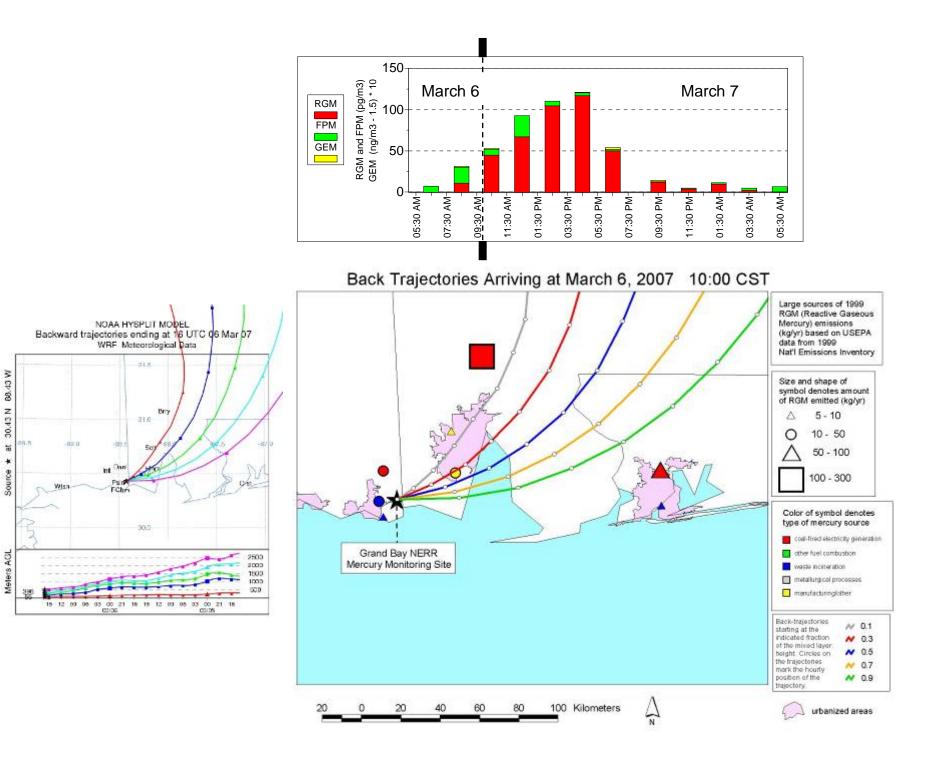
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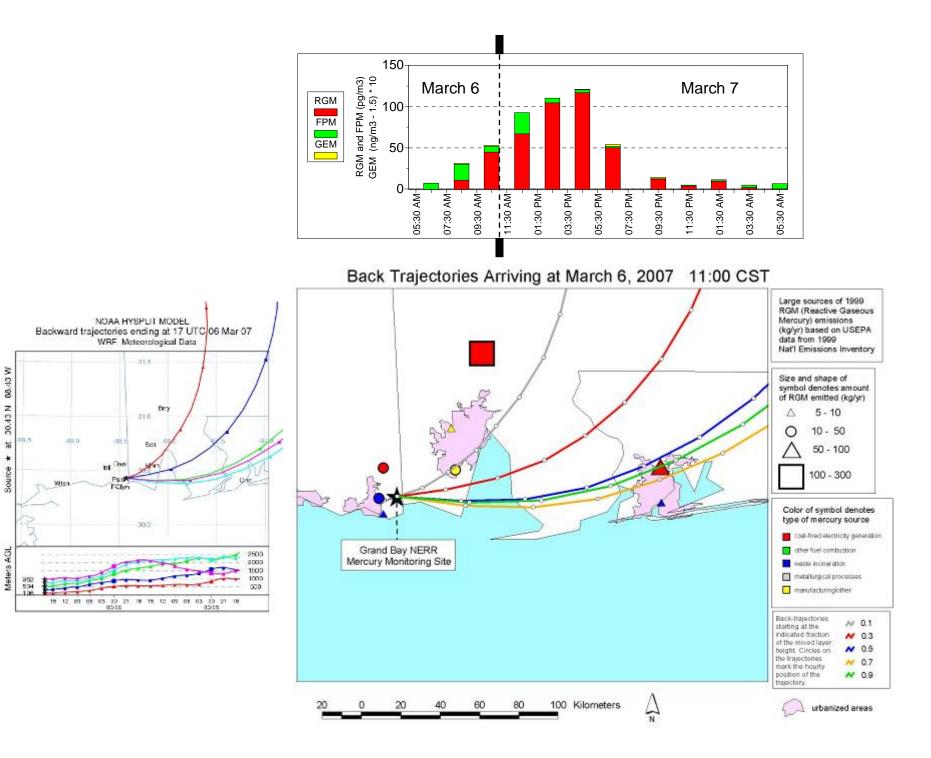
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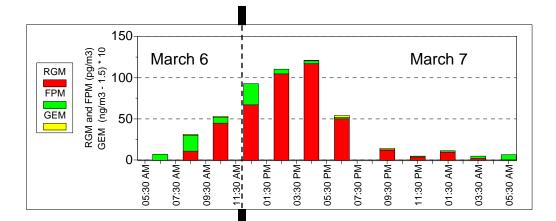


PETTERNER CONTRACTOR

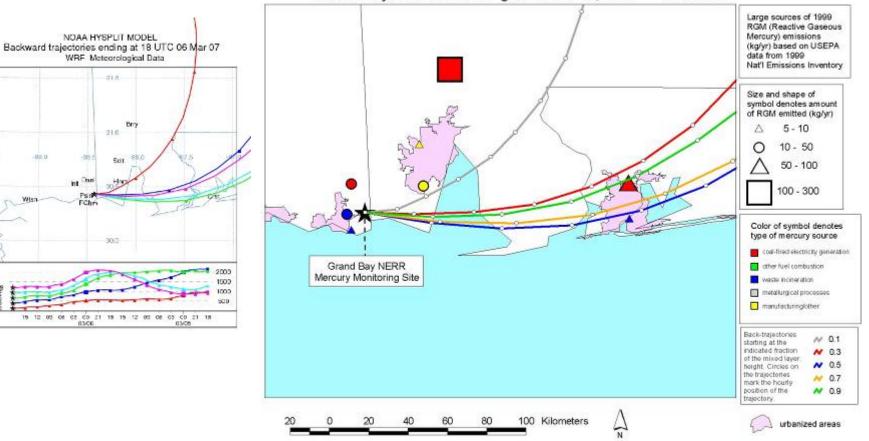
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Back Trajectories Arriving at March 6, 2007 12:00 CST



00.43 W

30.43 N

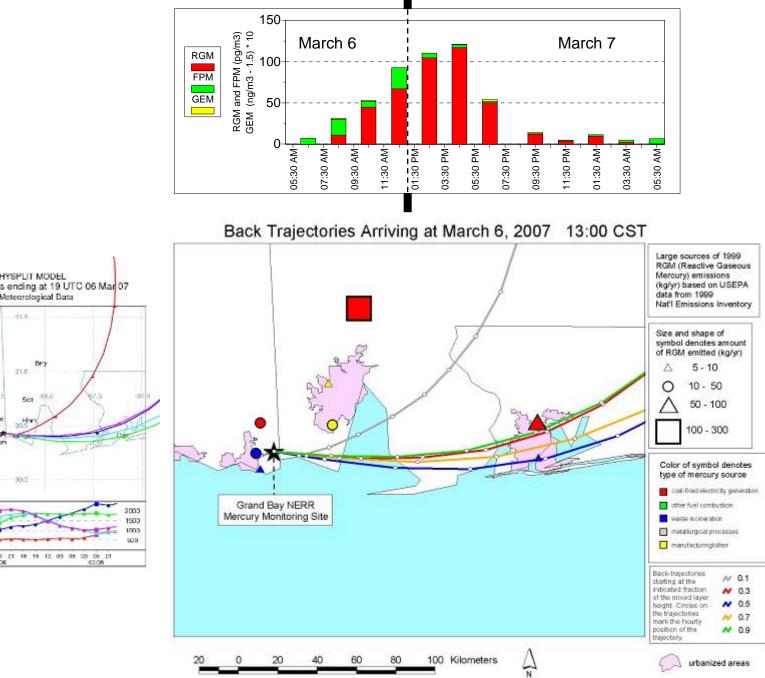
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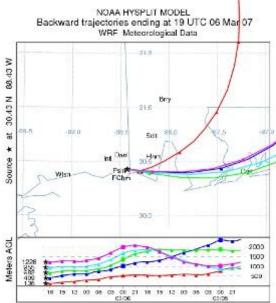
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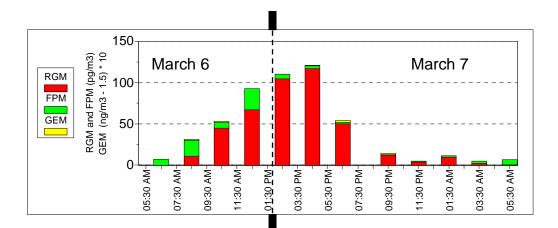
Source

Meters AGL

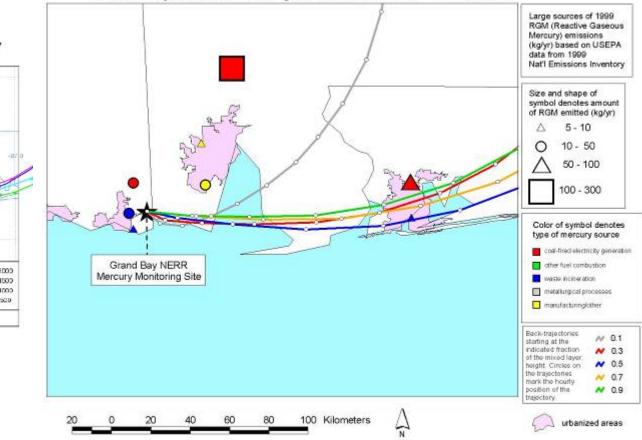
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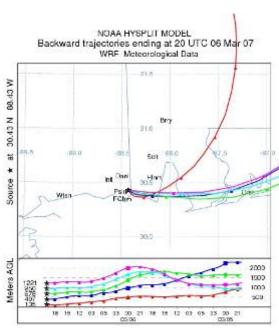


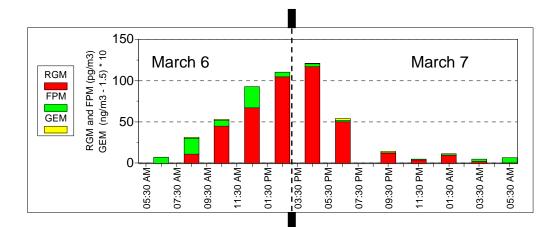




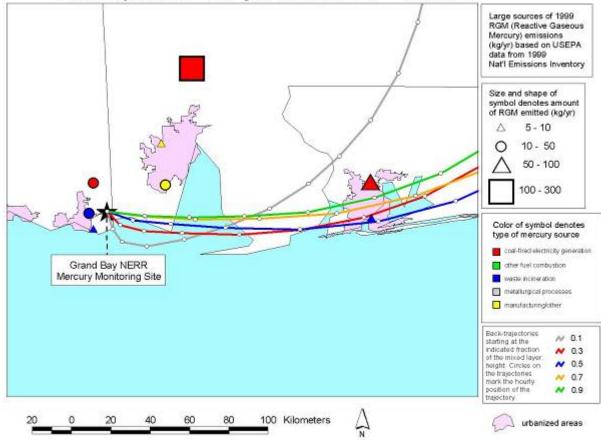
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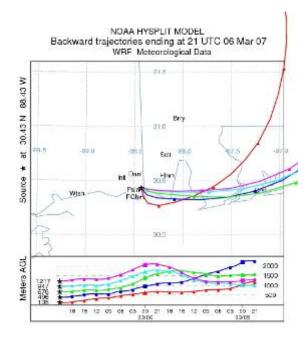


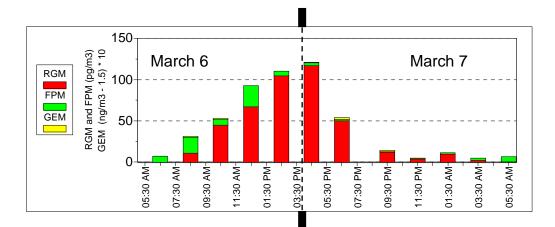




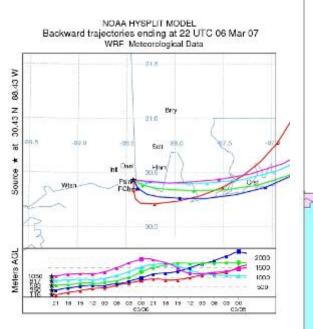
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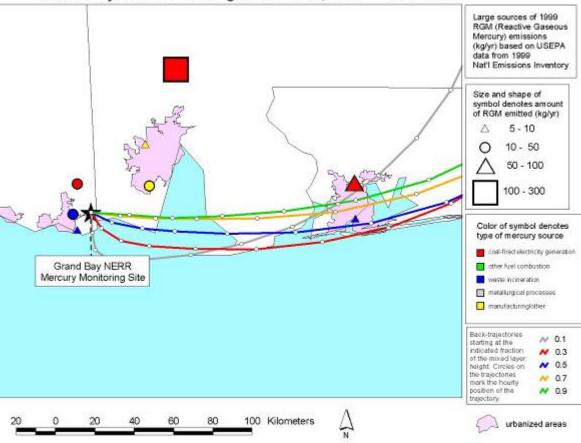


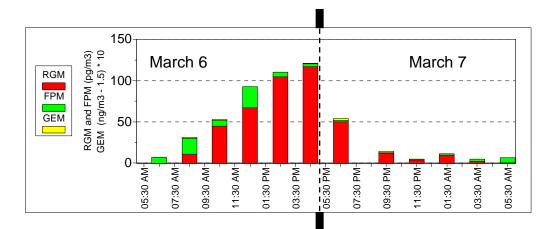




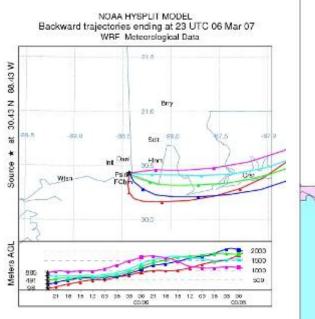
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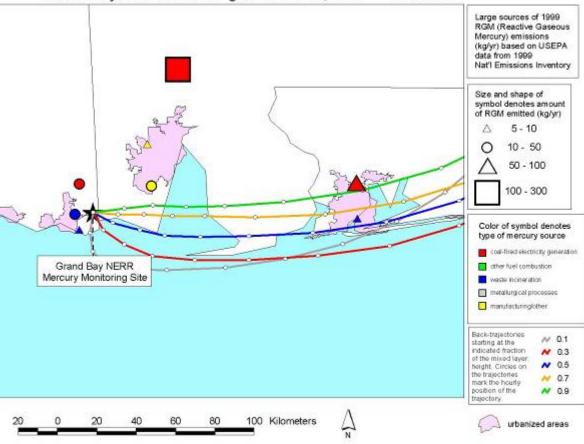


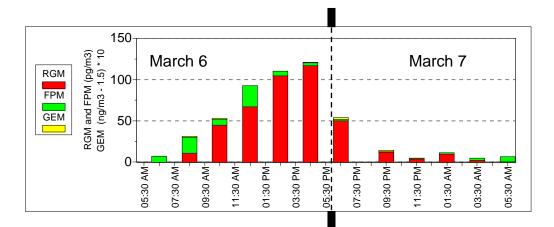




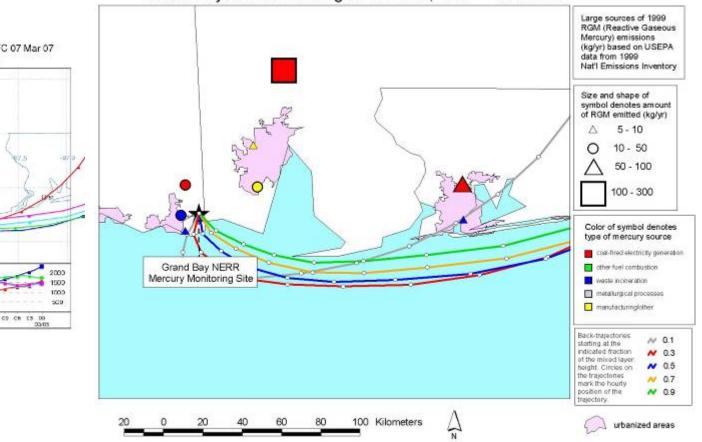
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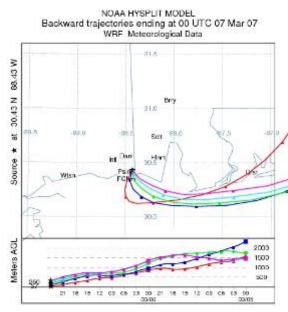


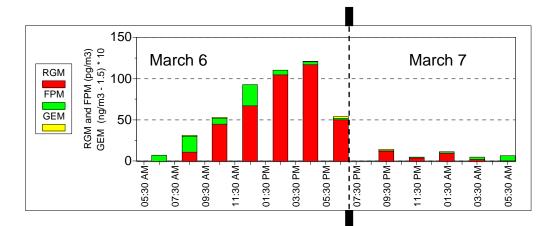




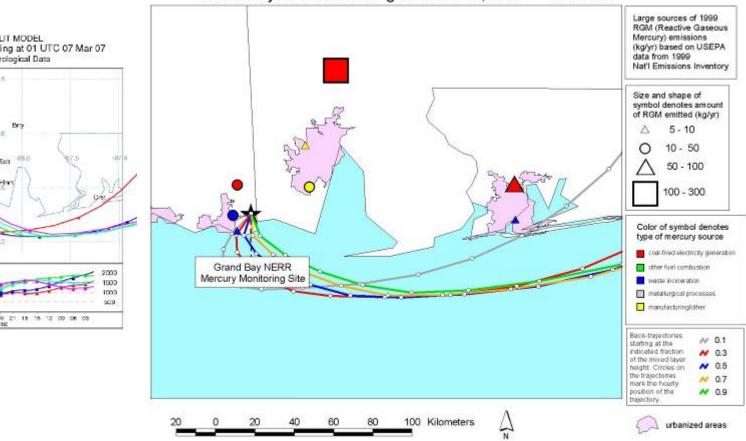
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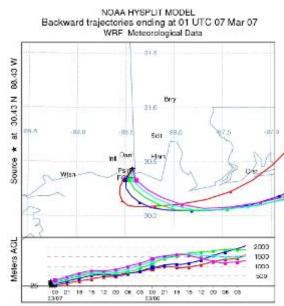


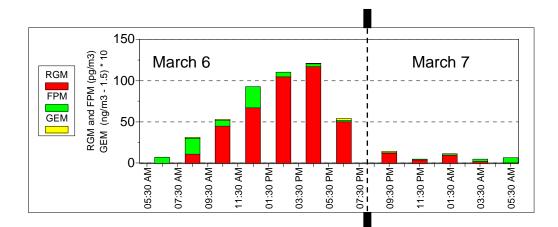




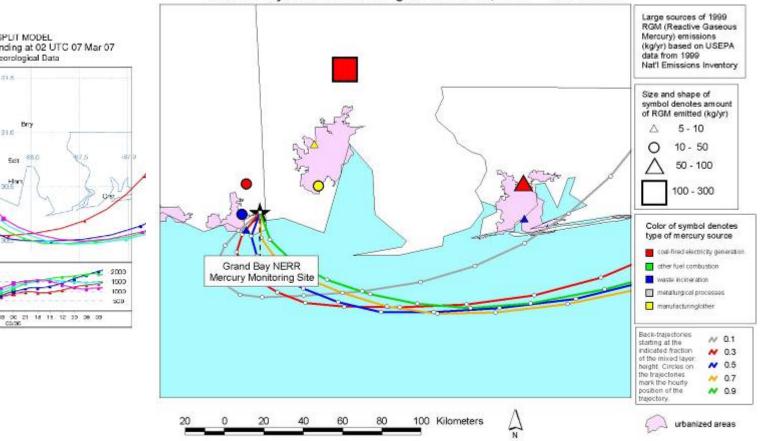
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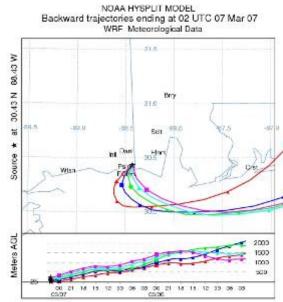


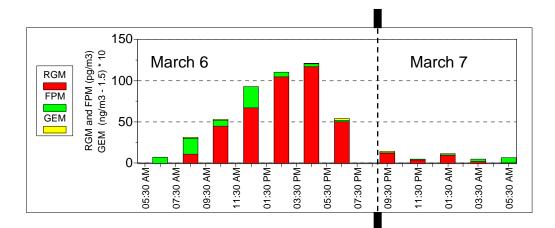




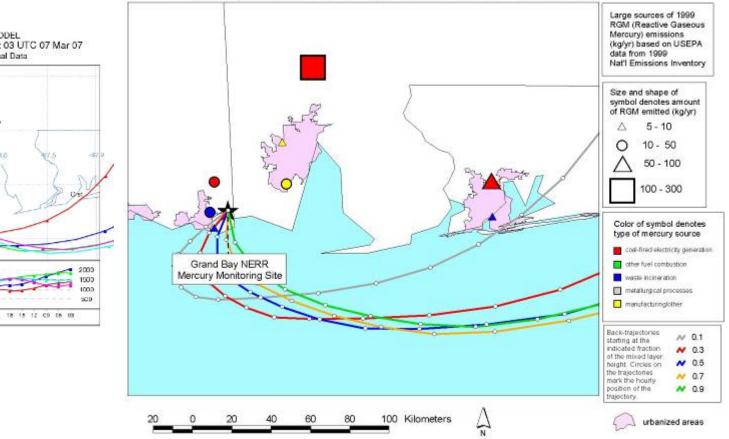
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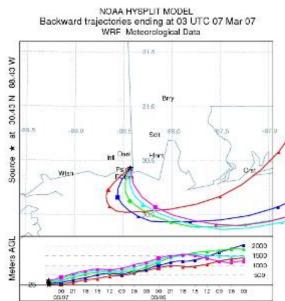


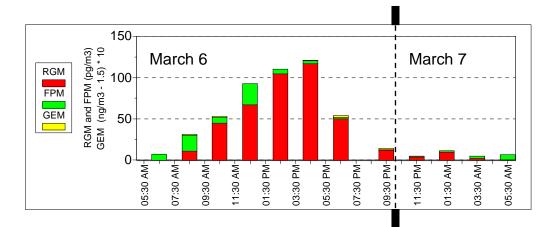




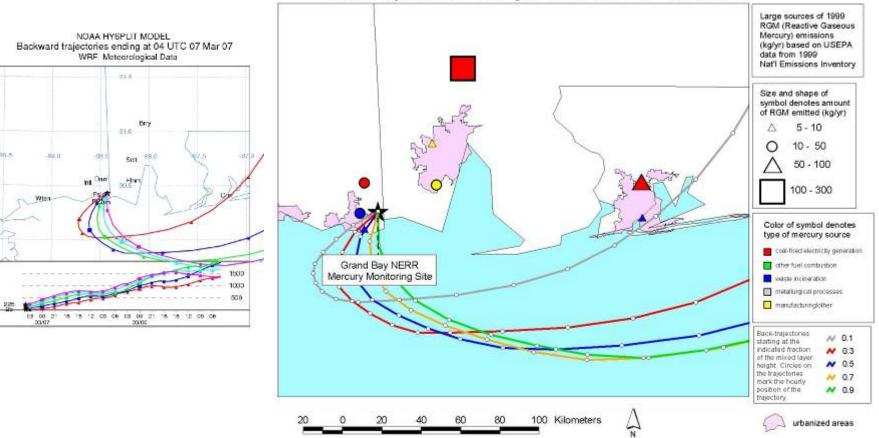
Back Trajectories Arriving at March 6, 2007 21:00 CST







Back Trajectories Arriving at March 6, 2007 22:00 CST



00.43 W

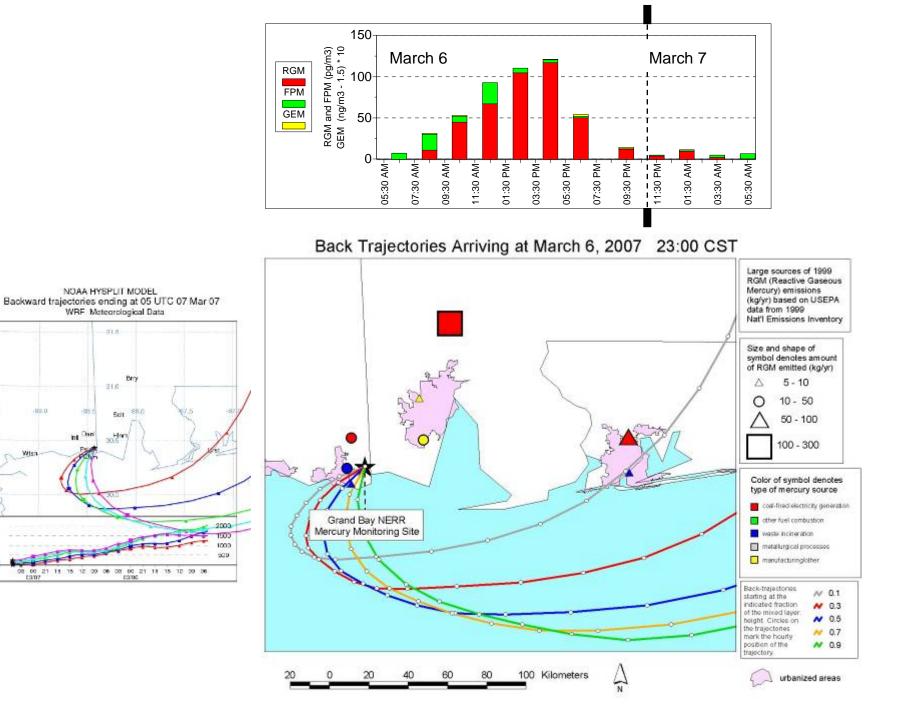
30.43 N

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Source

Meters AGL



00.43 W

30.43 N

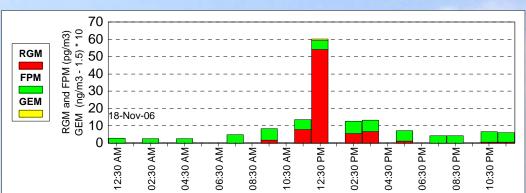
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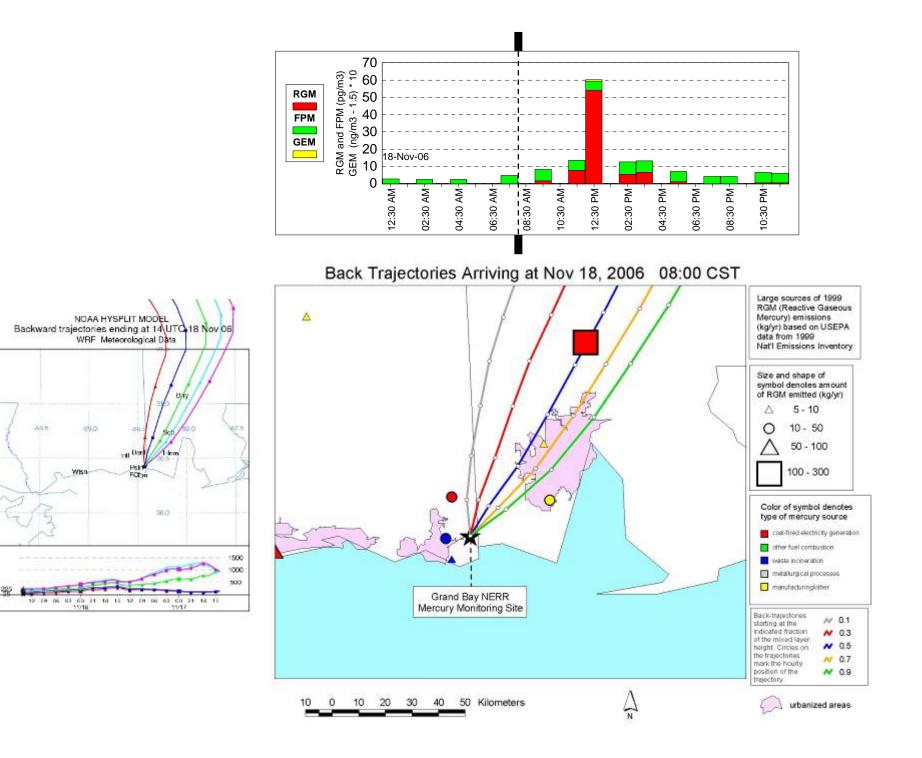
Source

Meters AGL

Grand Bay Episode Nov 18, 2006







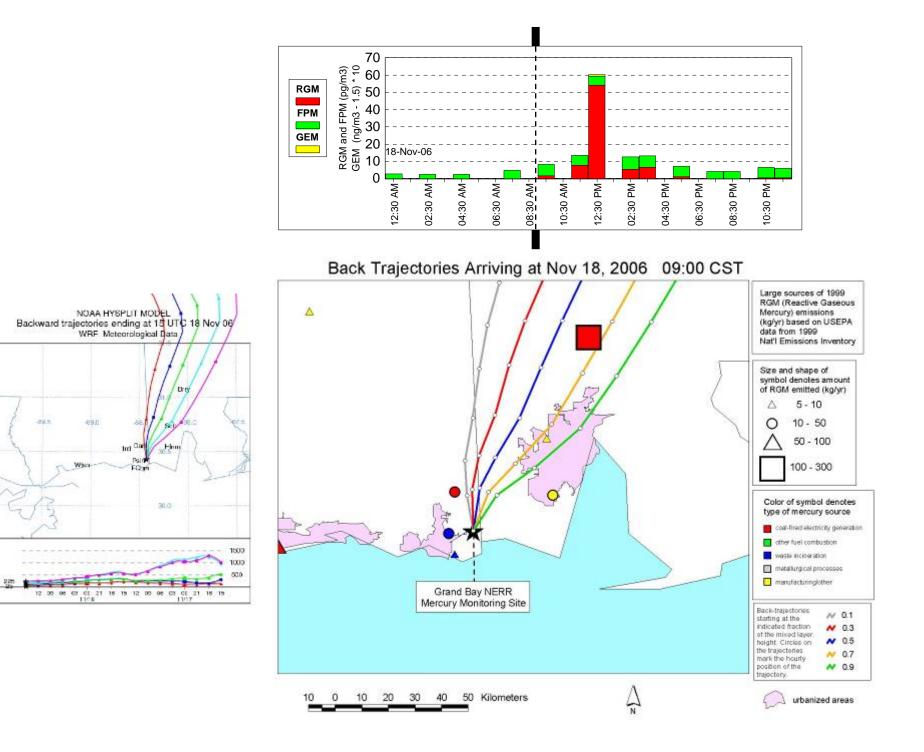
88.43 W

30.43 N

75

Source *

Meters AGL



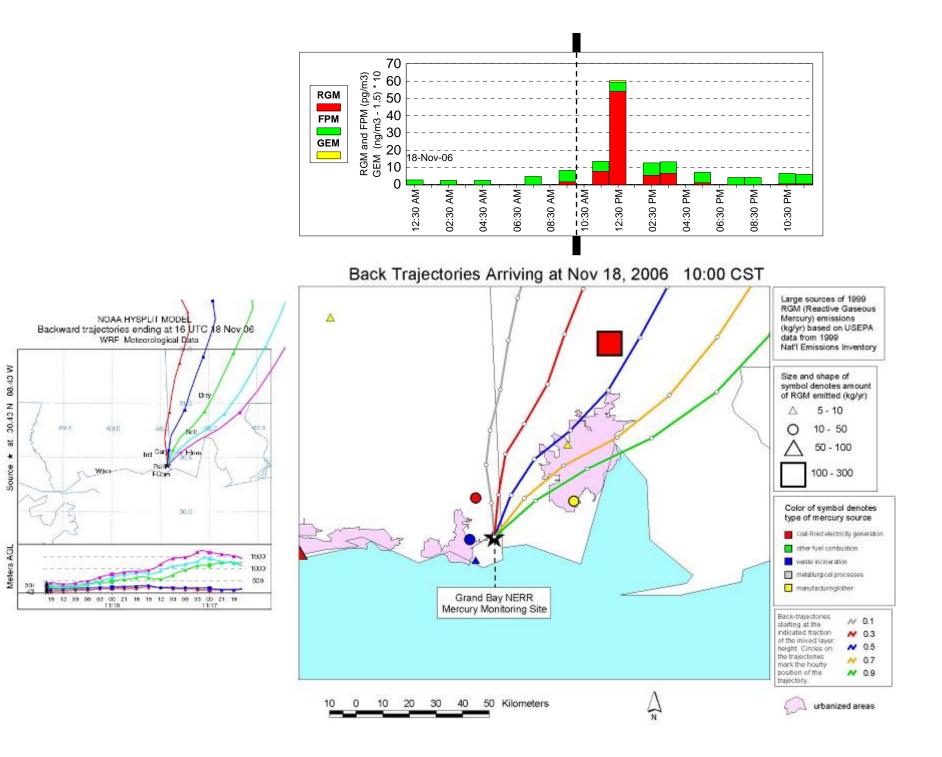
00.43 W

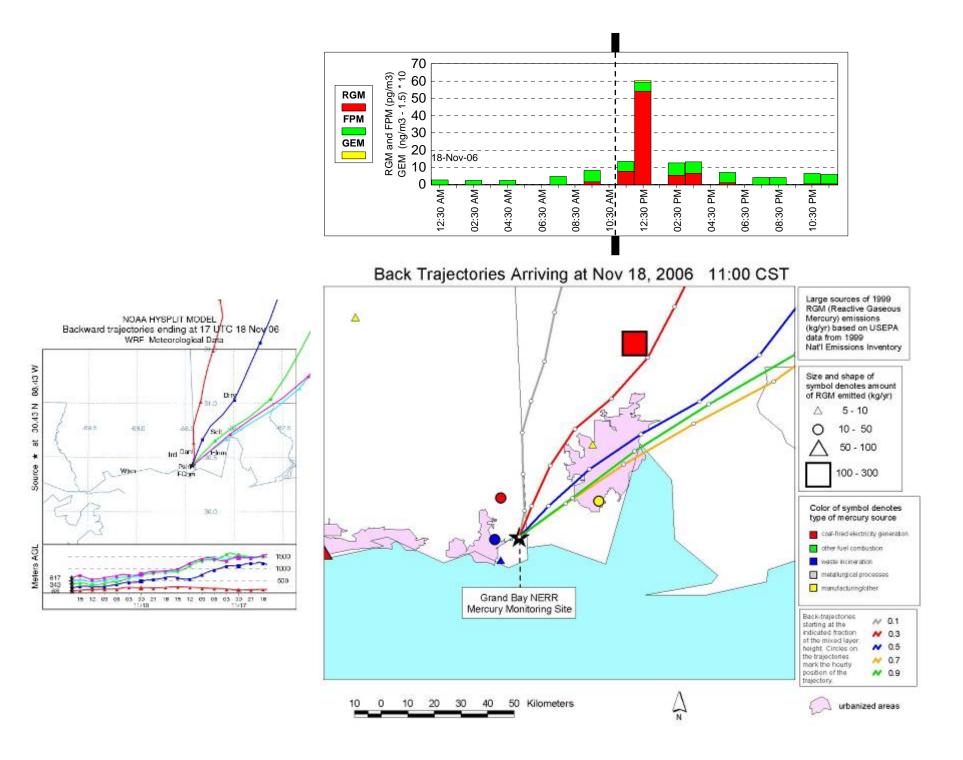
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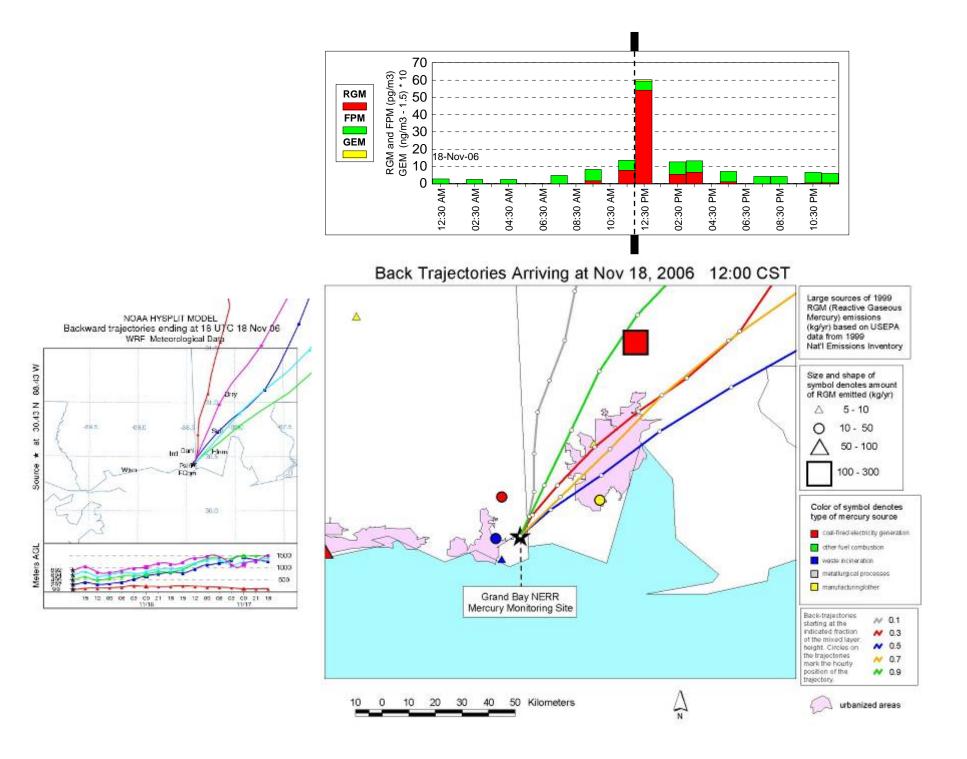
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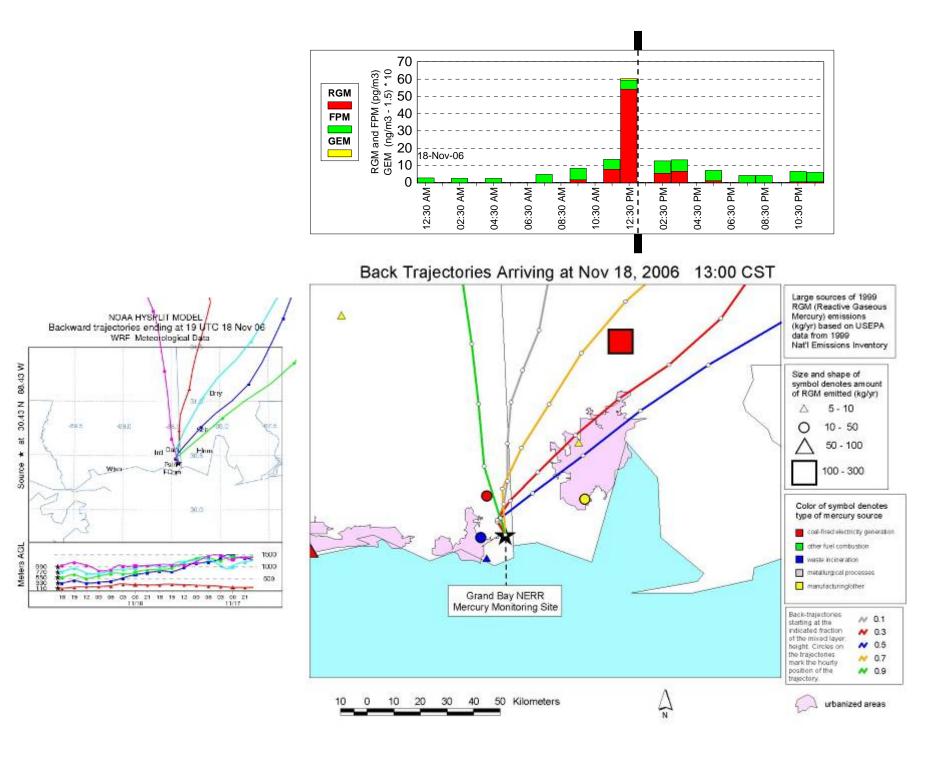
Source +

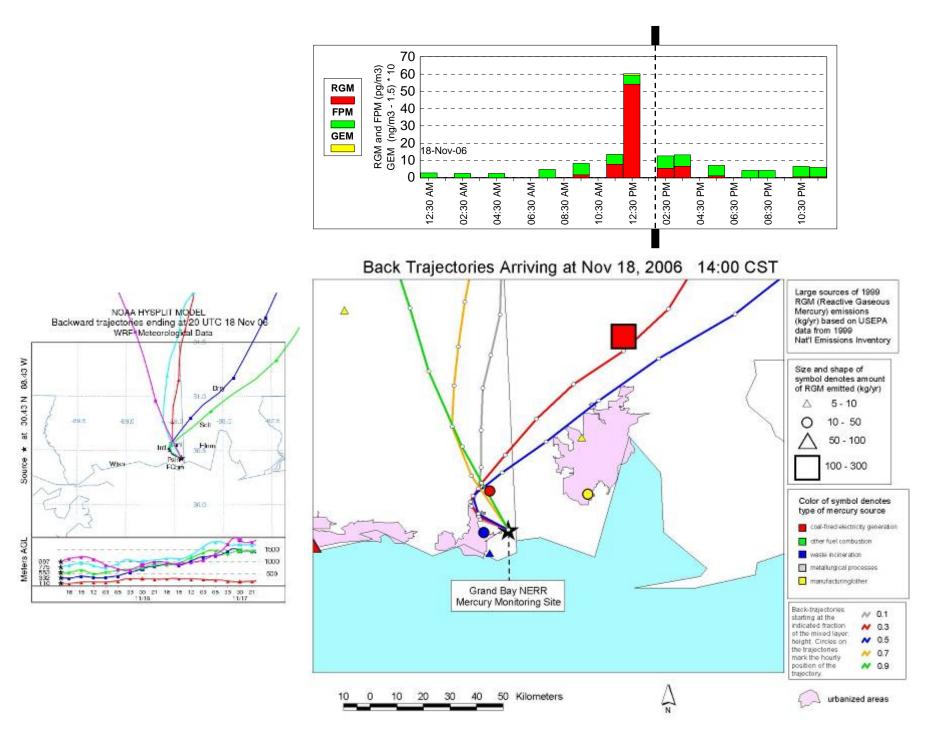
Meters AGL

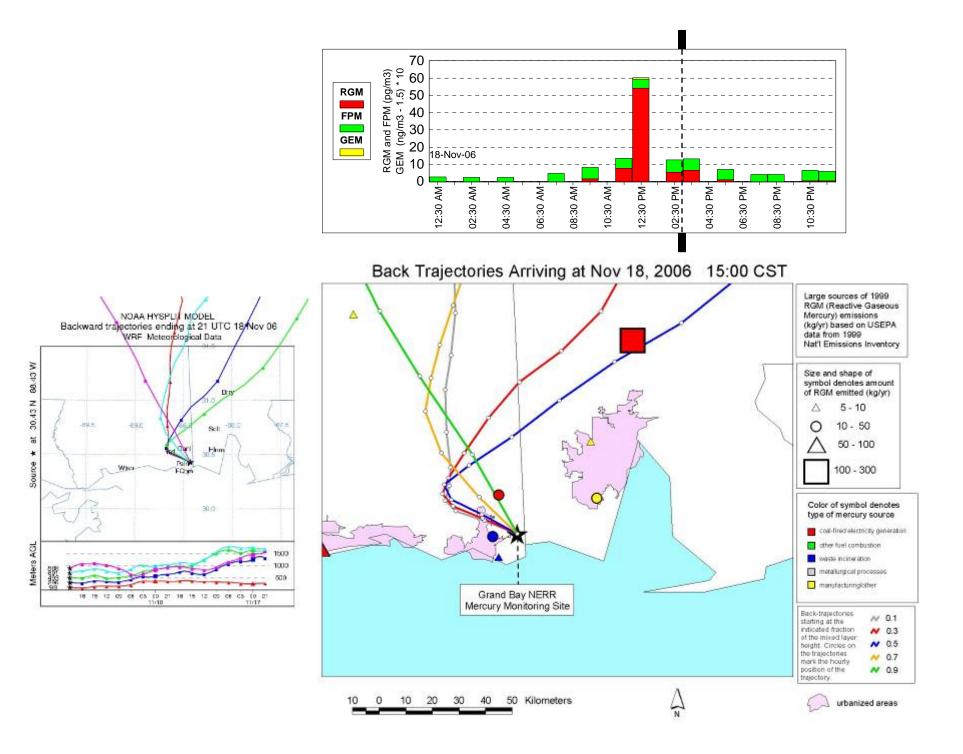


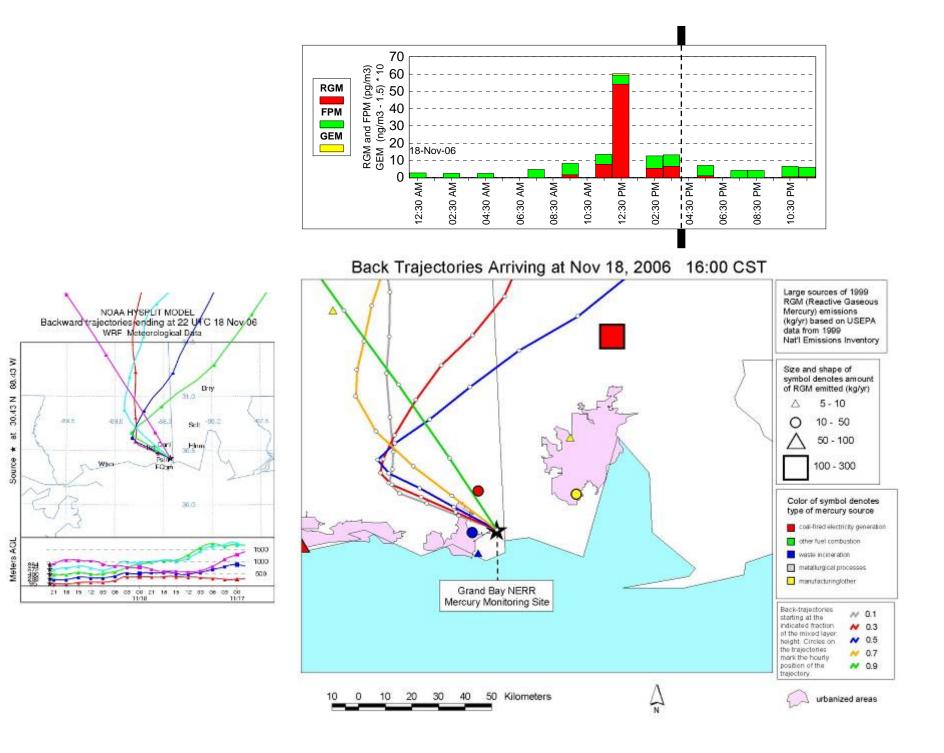


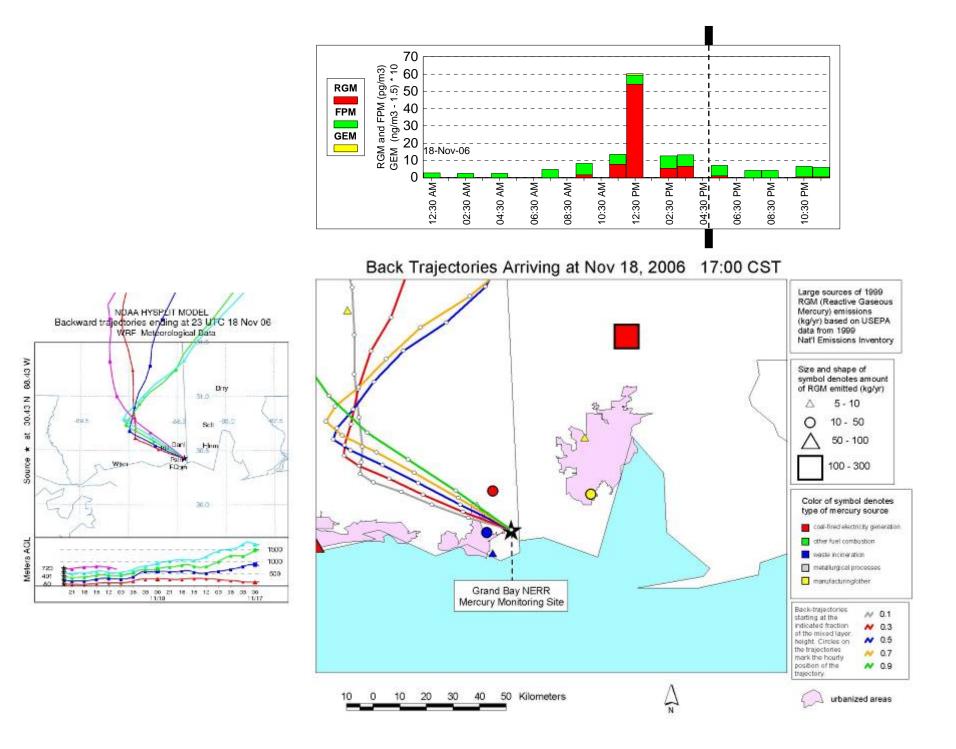












Precision, QA/QC Studies





- Installed System 1 (NOAA) Nov. 7, 2006 Height of Inlet: 3.75 m above ground 0.5 m above trailer
- Installed second system (System 2-NOAA) Jan 26, 2007



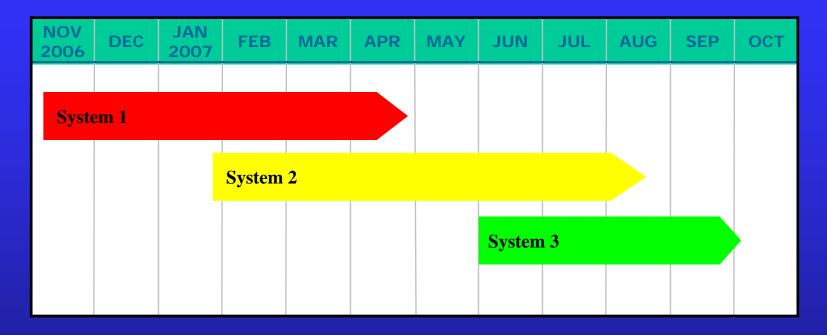
- System 1 removed April 27, 2007
- Install System 3 (EPA) June 1, 2007
- Remove System 2 August 17, 2007



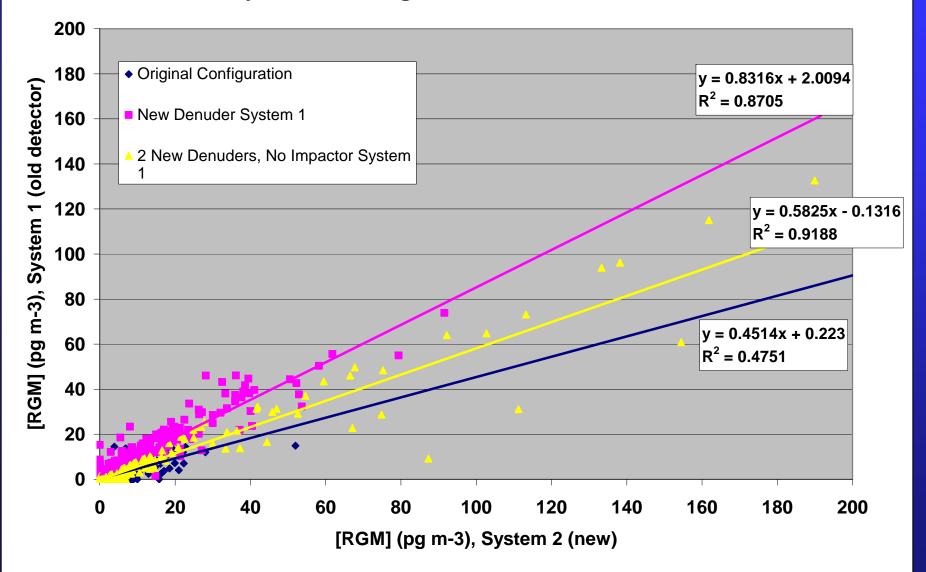
Tekran Speciation Systems QA/QC Studies

- Periodic deployment of duplicate systems Jan. 26-Apr. 27, 2007 June 1-Aug. 17, 2007
- Precision and accuracy of independent systems
- Investigation of aerosol size segregation of Hg-P

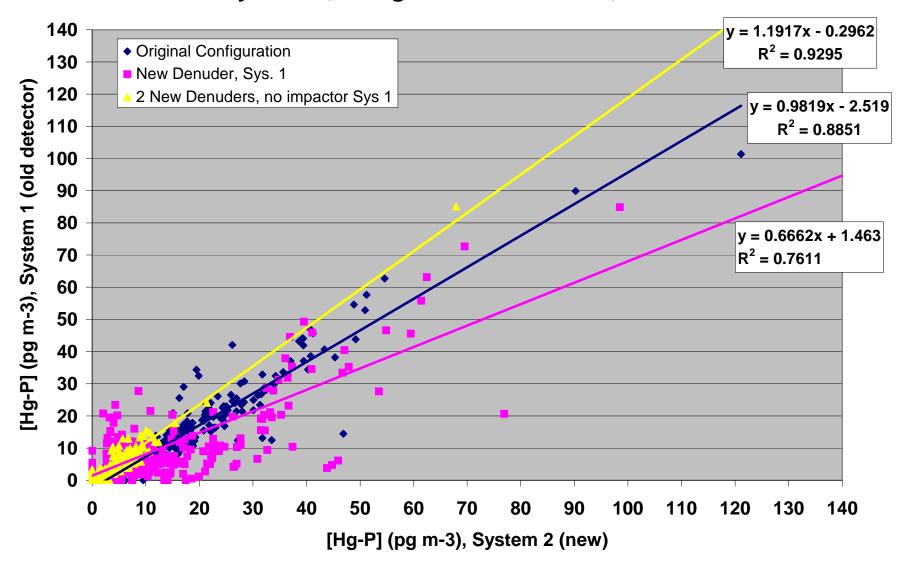
Tekran Deployment Timeline -Beltsville



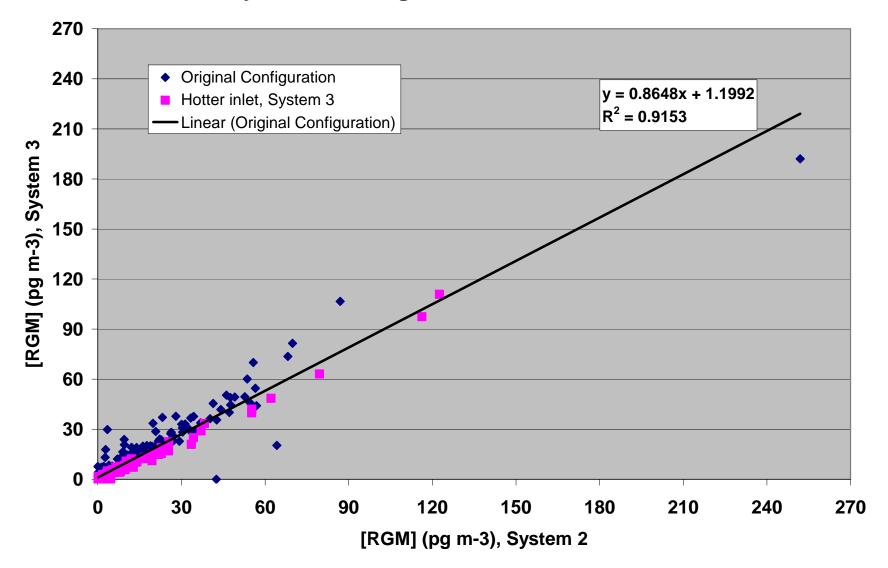
System 1, 2 Regression -Beltsville, 2007



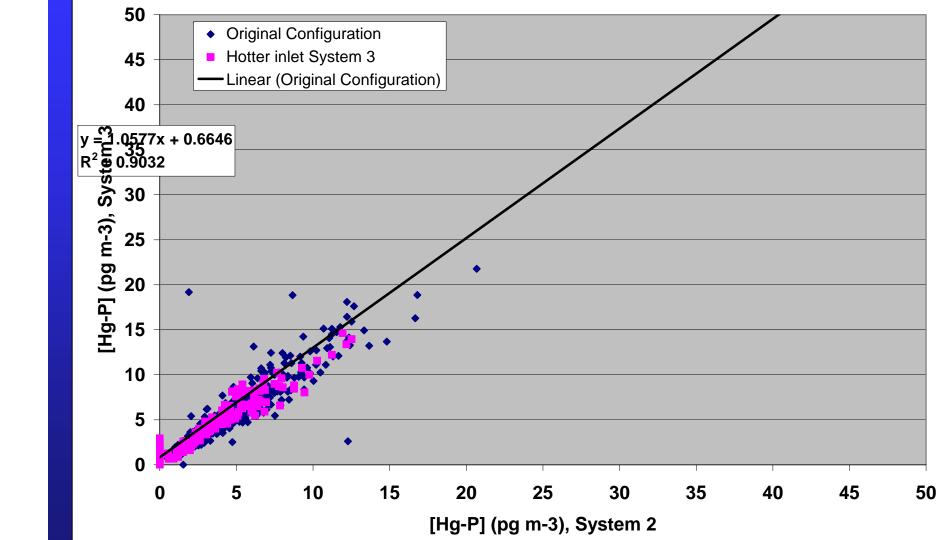
System 1, 2 Regression -Beltsville, 2007



System 2, 3 Regression -Beltsville, 2007



System 2, 3 Regression -Beltsville, 2007



Monitoring Sites: Next Steps



Beltsville

- Addition of 10 m walk up scaffold
- Migration to new shelter?
- Acquisition of second Tekran system

Synchronous sampling –precision, QA/QC studies, etc.

Asynchronous sampling for true continuous measurements



Grand Bay

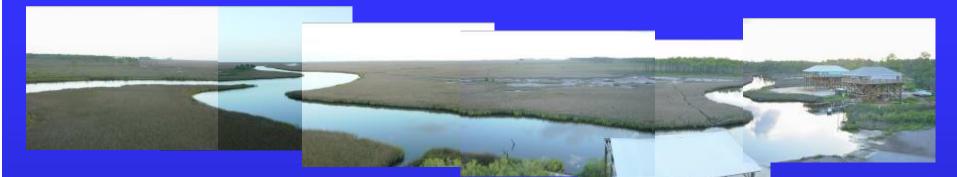
- Migration from old trailer and site to new trailer at permanent site (water's edge, 2 miles distant)
- Addition of 10m walk-up scaffold
- Addition of second Tekran System

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 – Grand Bay



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



Model Evaluation and Improvement



- improve atmospheric models, emissions inventories must be:
- Accurate for each individual source (especially for large sources), including variations
- For the same time periods as measurements used for evaluation
 - For all forms of mercury

Atmospheric Monitoring

Emissions Inventories

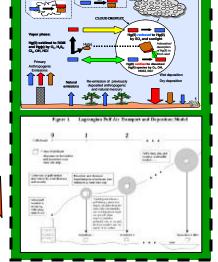
Mercury Deposition Network (MDN) (wet deposition only) 125

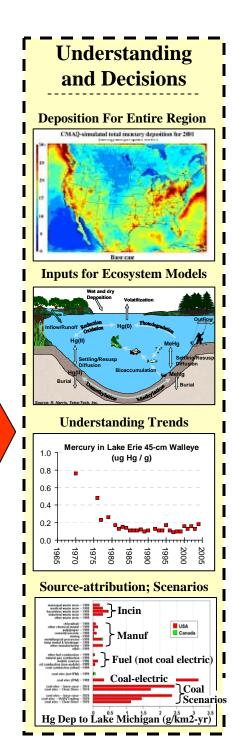
Air Concentration Network

To evaluate and improve atmospheric models, atmospheric monitoring must be:

- For air concentrations (not just wet deposition)
- For all forms of mercury
- For sites impacted by sources (not just background sites)
- At elevations in the atmosphere (not just at ground level)

Atmospheric Models





Why do we need atmospheric mercury models?

to get comprehensive source attribution information ...we don't just want to know how much is depositing at any given

location, we also want to know where it came from:

- different source regions (local, regional, national, continental, global)
- different jurisdictions (different states and provinces)
- anthropogenic vs. natural emissions
- different anthropogenic source types (power plants, waste incin., etc)

to estimate deposition over large regions

... because deposition fields are highly spatially variable, and one can't measure everywhere all the time...

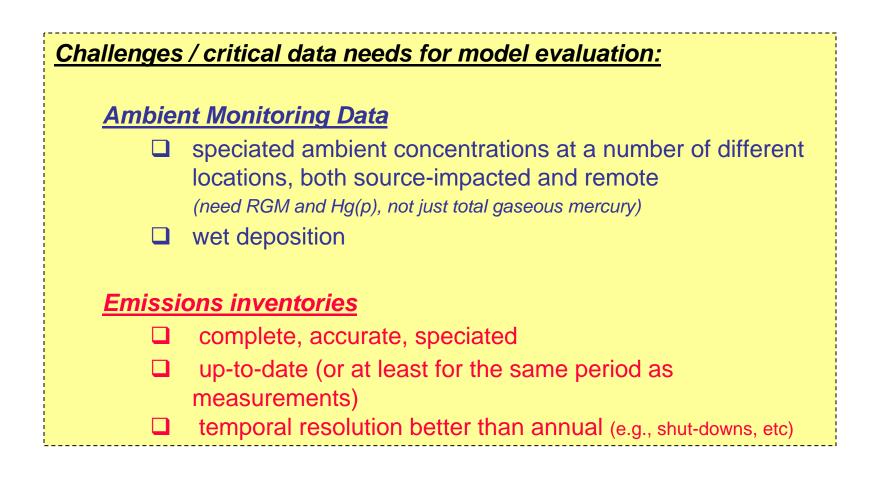
➤ to estimate dry deposition

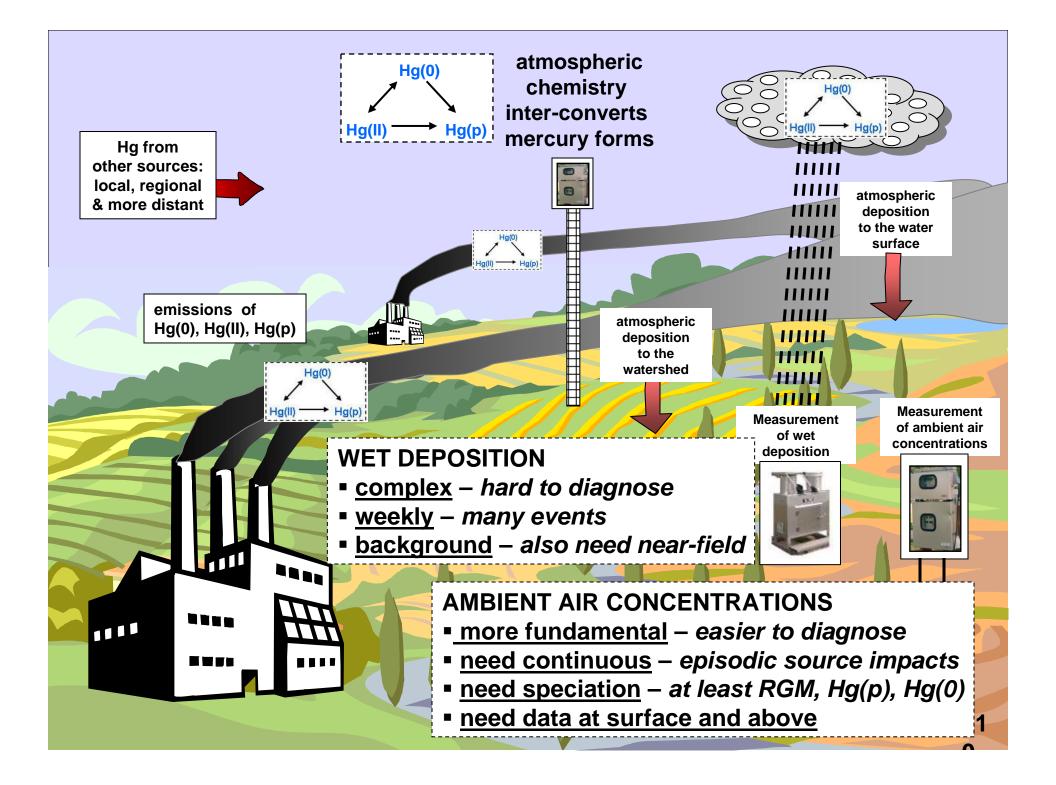
... presently, dry deposition can only be estimated via models

to evaluate *potential consequences* of alternative future emissions scenarios

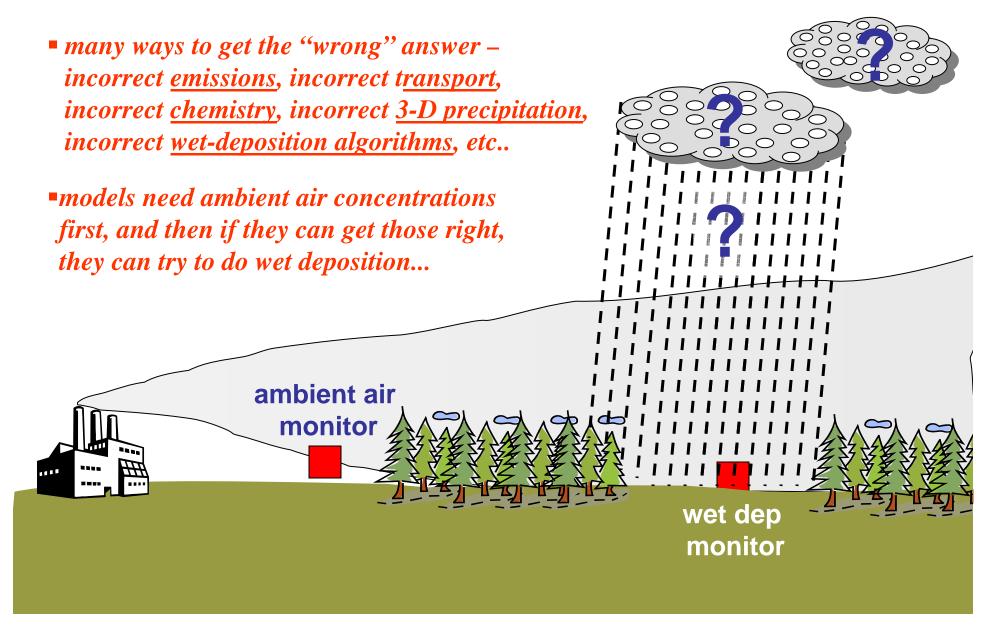
Atmospheric models can potentially provide valuable deposition and source-attribution information.

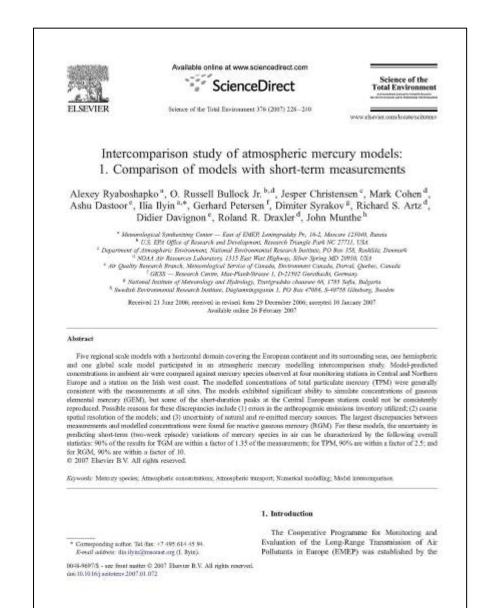
But... models have not been adequately evaluated, so we don't really know very well how good or bad they are...





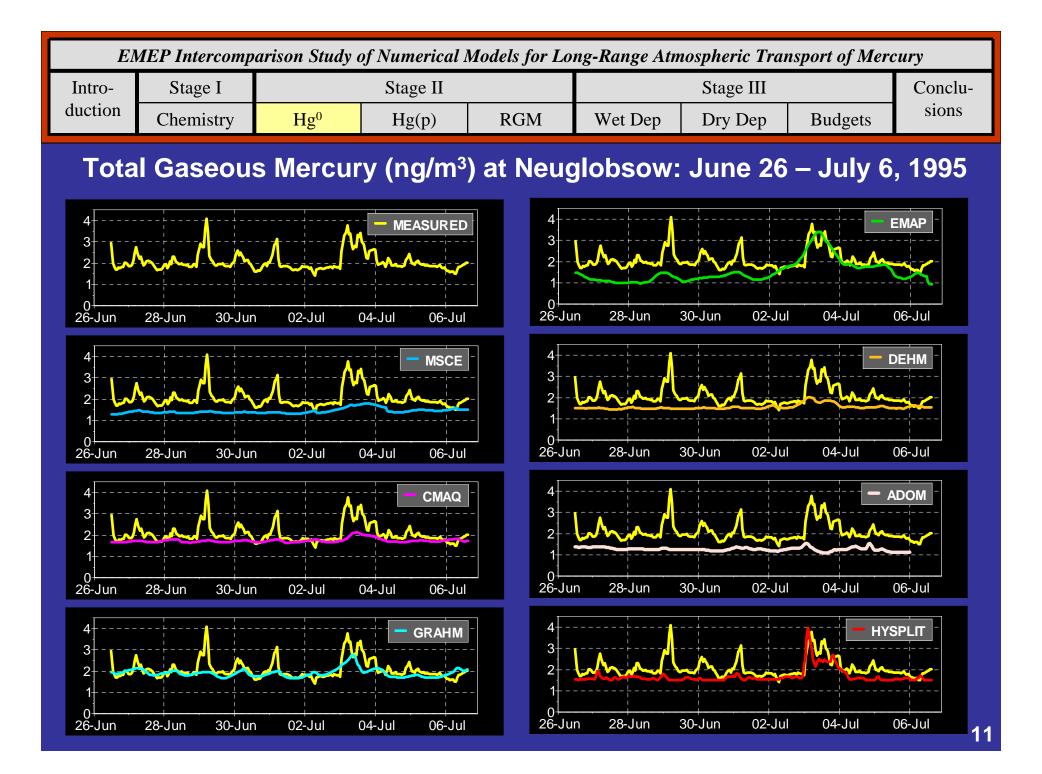
<u>Wet deposition is a very complicated multi-stage phenomena...</u> <u>not ideal for atmospheric mercury model evaluation purposes</u>

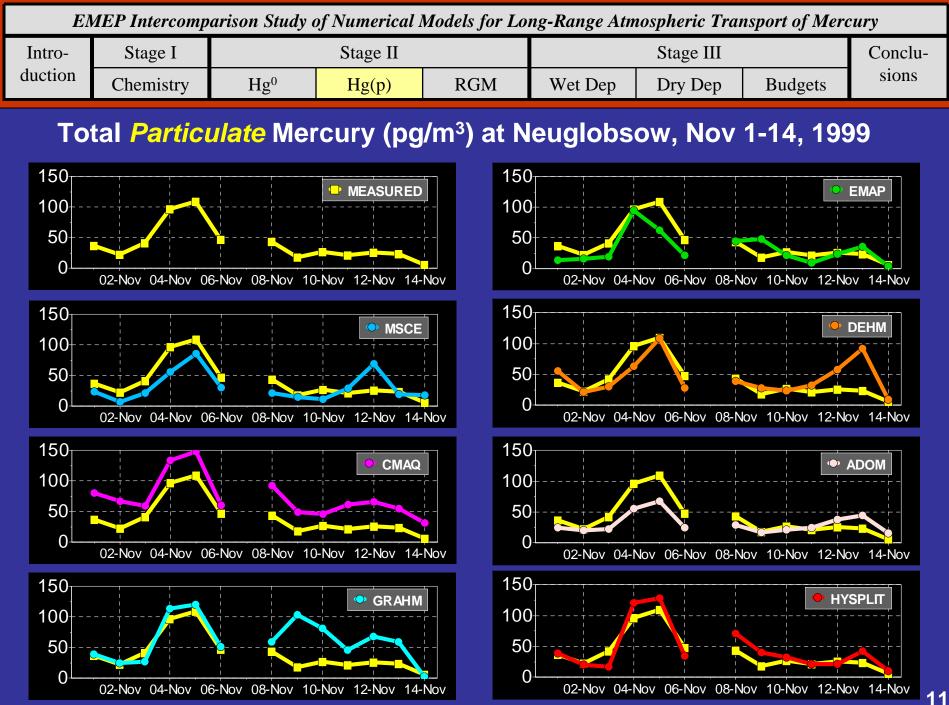


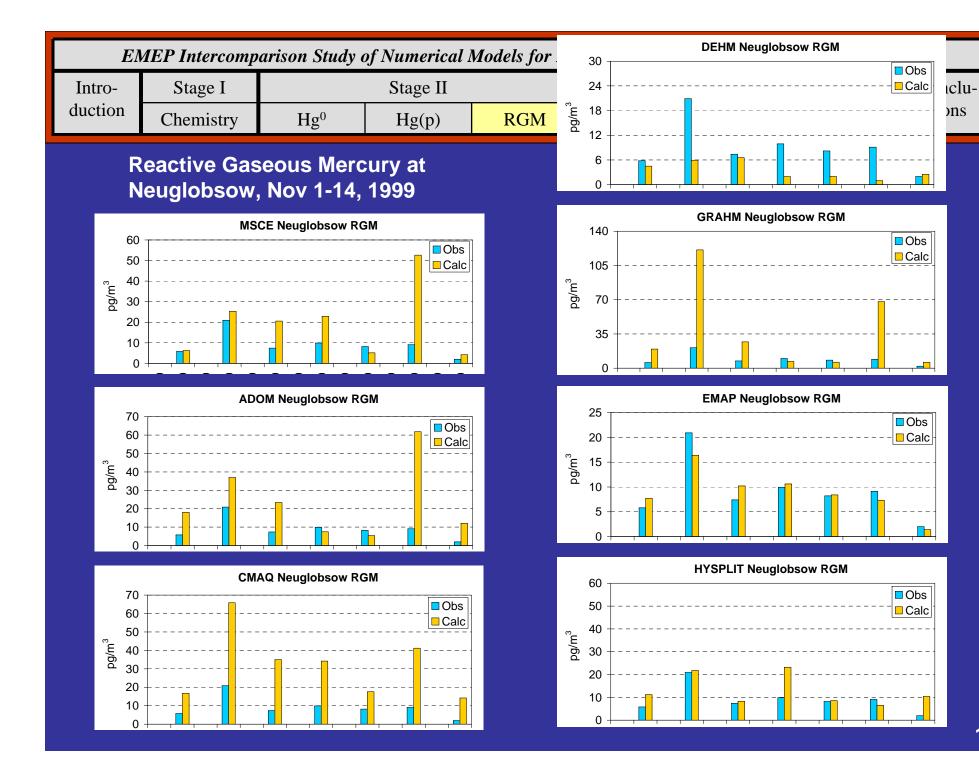


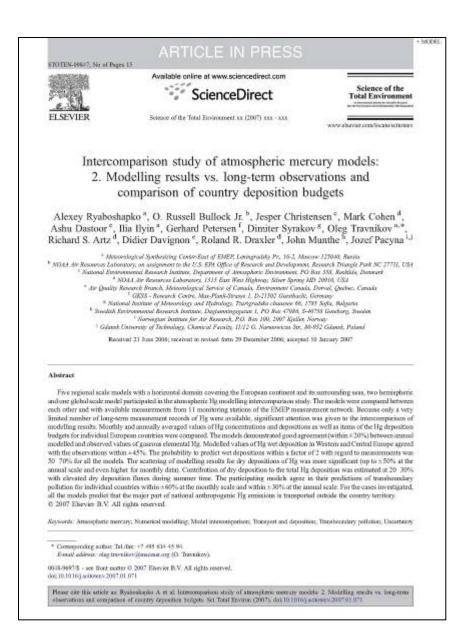
Ryaboshapko, A., *et al.* (2007). Intercomparison study of atmospheric mercury models: 1. Comparison of models with short-term measurements. *Science of the Total Environment* **376**: 228–240.

http://www.arl.noaa.gov/data/web/reports/cohen/49_EMEP_paper_2.pdf 11









Ryaboshapko, A., *et al.* (2007). Intercomparison study of atmospheric mercury models: 2. Modelling results vs. longterm observations and comparison of country deposition budgets. *Science of the Total Environment* **377:** *319-333*.

http://www.arl.noaa.gov/data/web/reports/cohen/49_EMEP_paper_2.pdf

Overall Summary

- Three long-term monitoring sites Beltsville, Grand Bay, and CVI -measuring speciated ambient concentrations of mercury, related trace species, and meteorological parameters form the core of an emerging national ambient mercury measurement network.
- The different sites provide the opportunity to investigate the effects of differences in regional source distribution, atmospheric processes, geographic characteristics, etc. on the fate and transport of atmospheric mercury. However, additional sites are needed to provide a wider range of conditions.
- Ancillary trace gas, aerosol, and meteorological measurements are critically needed to interpret mercury measurements.
- Substantial progress is being made on the development of Standard Operating Procedures (SOP) and Best Measurement Practices (BMP), as well as QA/QC protocols.
- A draft SOP / BMP document will be discussed and ratified later this week at a meeting in Chicago

Overall Summary... continued

- Initial back-trajectory analysis of peak-measurement events suggest that concentrations at the sites are influenced episodically by local/regional sources.
- Atmospheric mercury models are needed to provide source-attribution information and estimated impacts of alternative future scenarios, but models have not been adequately evaluated due to a lack of speciated ambient concentration data.
- The emerging ambient monitoring network discussed today will provide this critically needed measurement data.
- With these data, models will be able to systematically evaluated -- and improved if necessary -- allowing their results to be used with more confidence.
- Moreover, the datasets will be available on an ongoing basis for groundtruthing model results generated for policy analysis purposes.