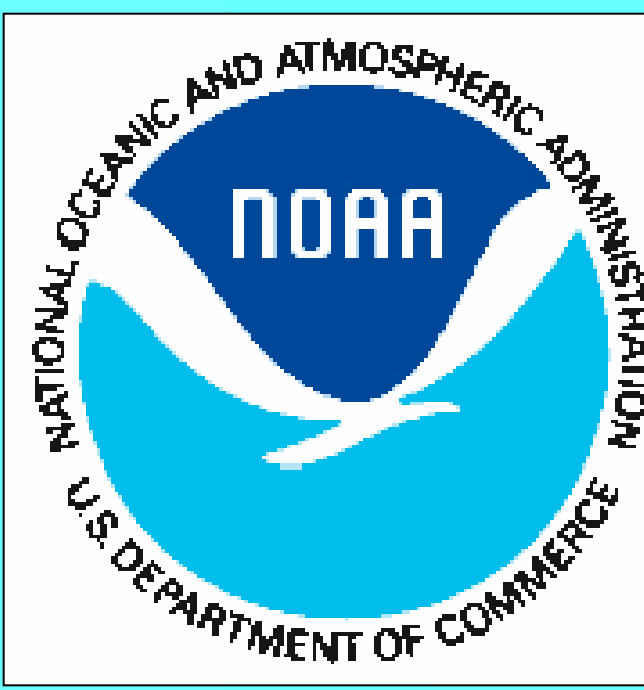




Atmospheric Mercury Measurements in the Mid-Atlantic: Trends in Concentrations and Estimated Deposition



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Introduction

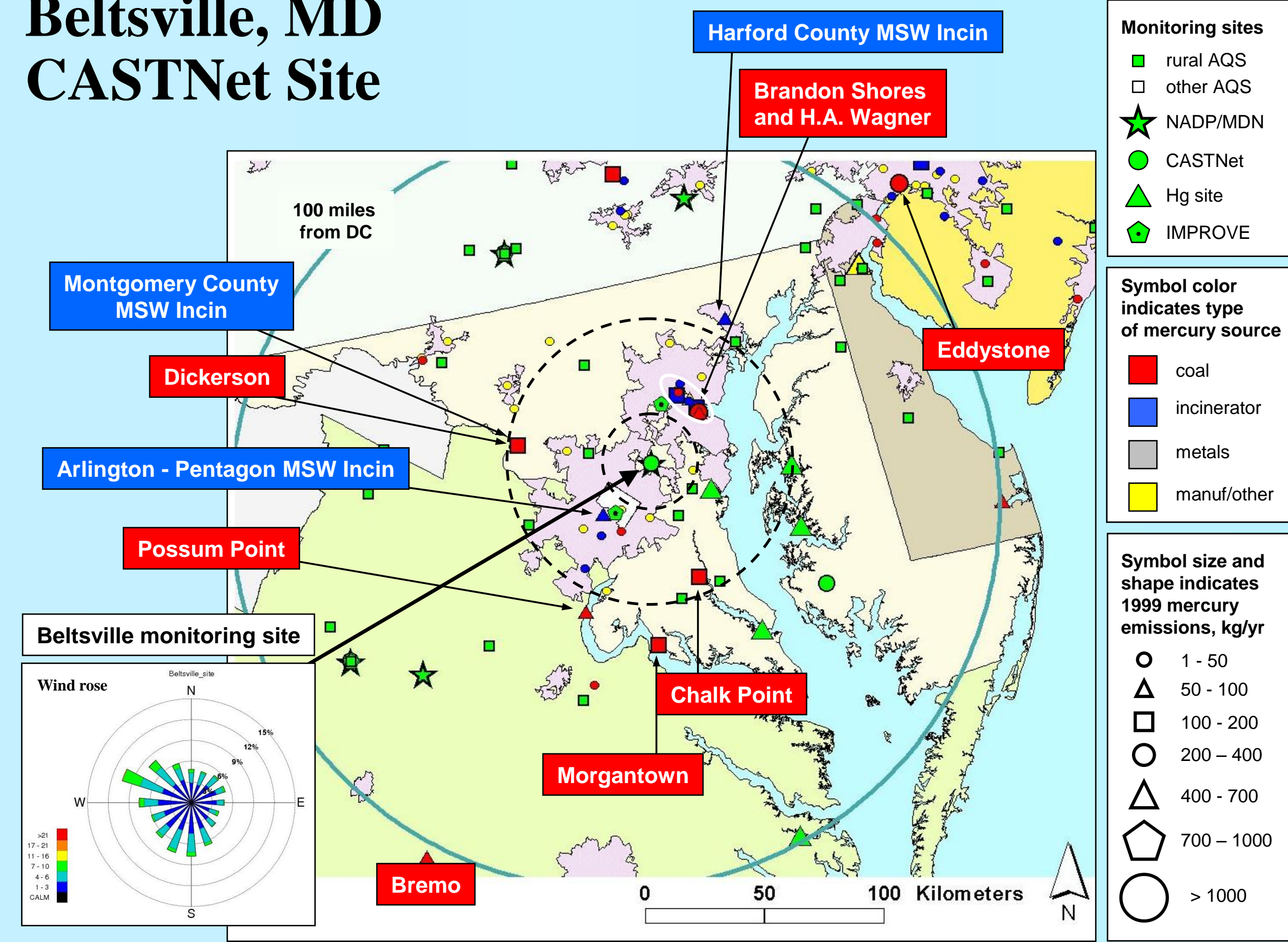
Mercury is being increasingly recognized as a significant public health threat; fish consumption is the most important route of exposure. Atmospheric deposition is a significant loading pathway for mercury, and modeling studies have suggested that the Chesapeake Bay region is subject to relatively high mercury deposition due to the prevalence of large mercury sources in the region. It is believed that estuaries (as well as coastal wetlands and salt marshes) can be significant producers of methylmercury as conditions in these locations facilitate methylation by anaerobic bacteria, a key process in the bioaccumulation of mercury. Finally, there are few atmospheric measurement data in the Chesapeake Region which can be used for model evaluation and improvement. The overall goal of this study is to further our understanding of the type and magnitude of sources of atmospheric mercury deposition to the Bay watershed, and their potential changes due to mercury emission reductions.

In November, 2006 EPA's Clean Air Markets Division partnered with NOAA's Air Resources Laboratory to initiate continuous measurements of atmospheric mercury species at the BEL116 CASTNet site (39.0284° N, -76.8172° W) on the premises of USDA's Beltsville Agricultural Research Center in Beltsville, MD. The site is now part of MercNet, NADP's emerging national mercury monitoring program.

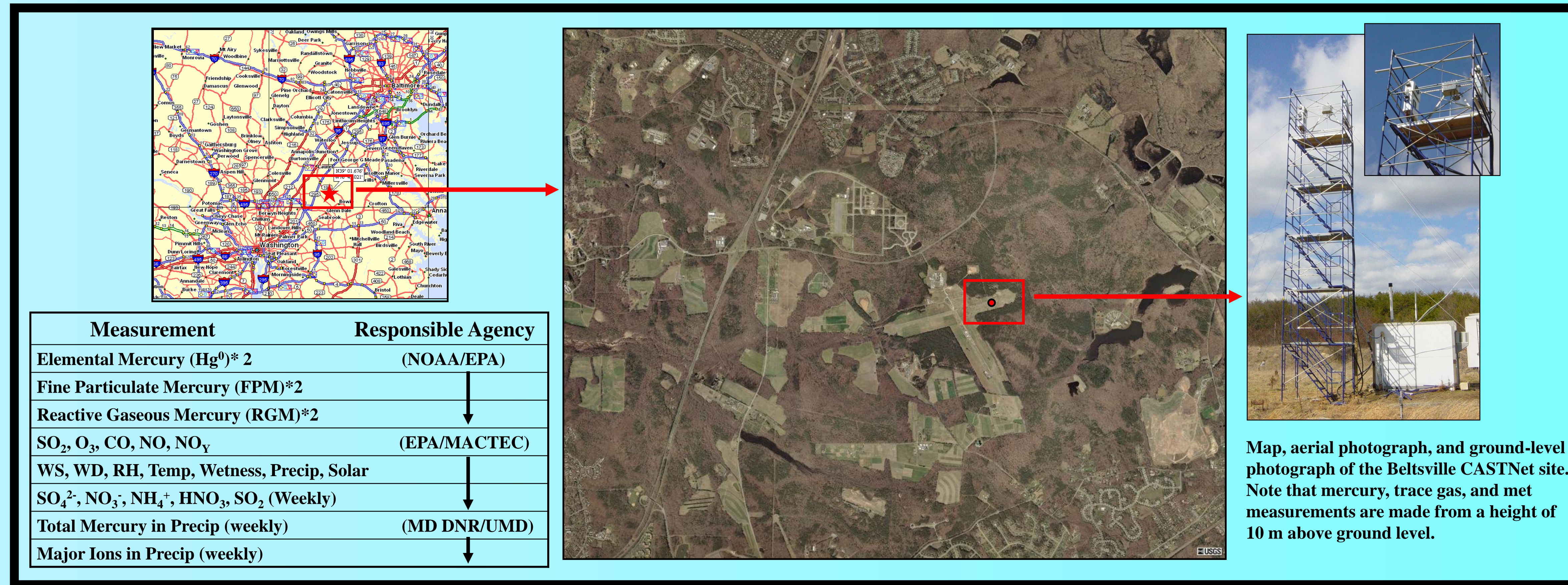
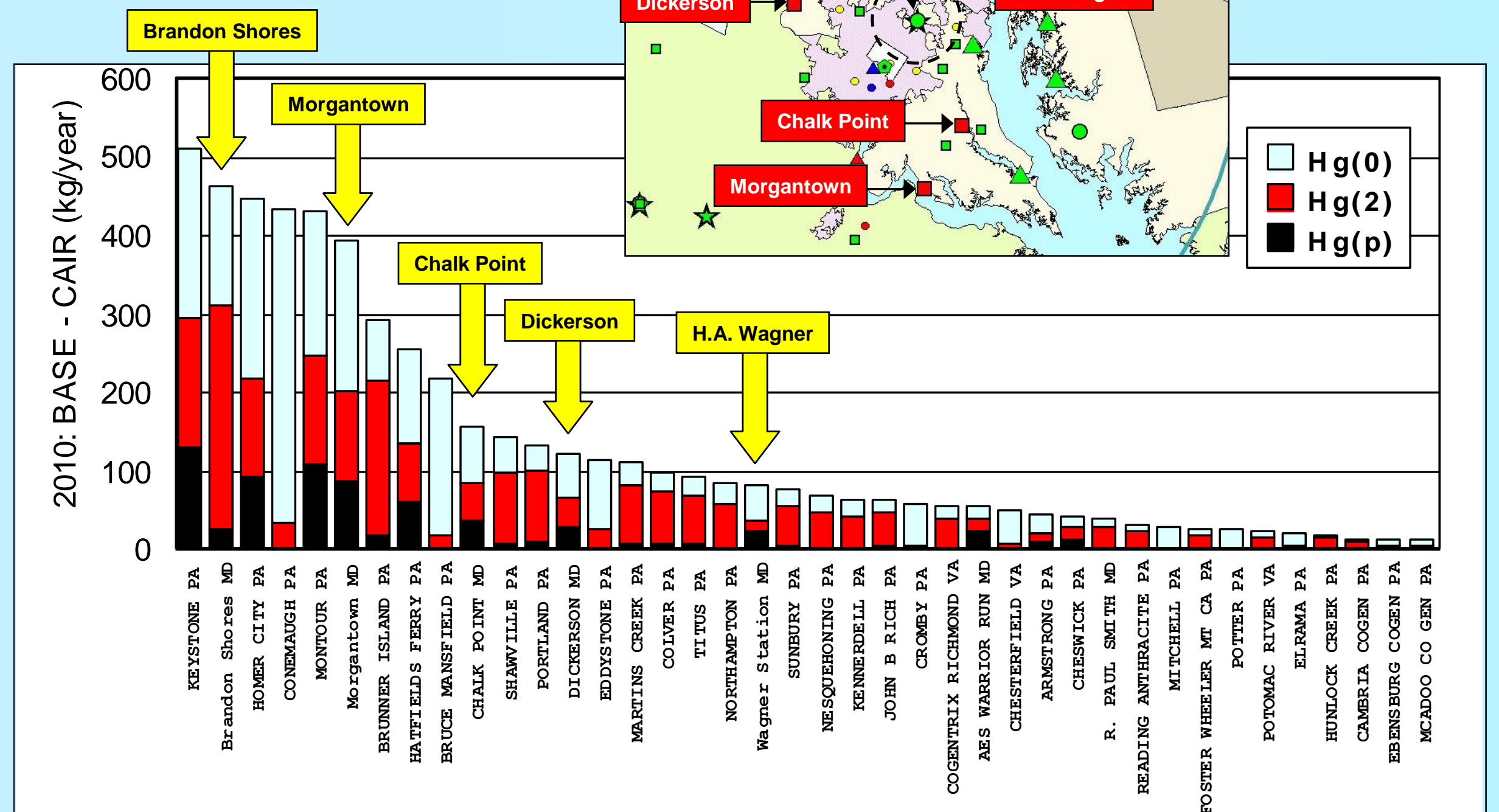
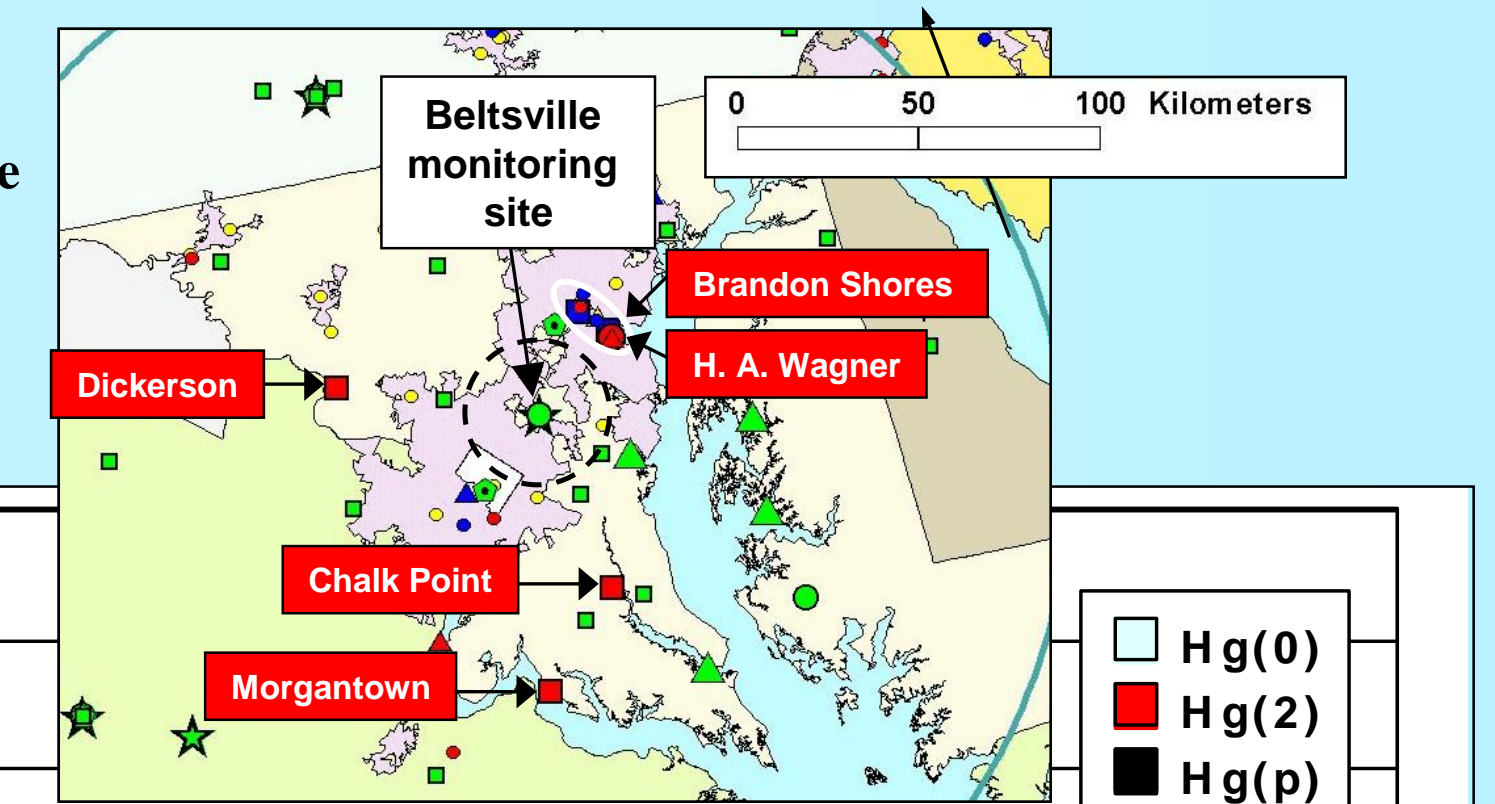
The location was chosen because the site:

- is home to extensive, existing collocated measurements (trace gases, meteorology, precip chemistry);
- is useful for understanding both background and source-impacted concentrations;
- is characterized by relatively simple terrain and a good "fetch", facilitating the estimation or direct measurement of dry deposition fluxes;
- is likely impacted by point sources targeted for significant emissions reduction under the (now defunct) Clean Air Interstate Rule, facilitating an investigation of source-receptor relationships and producing a measurable change in atmospheric signal.

Beltsville, MD CASTNet Site



Mercury sources in MD, VA, PA, and DE in the proximity of the Beltsville site (above), along with the projected differences between 2010 base and (now defunct) 2010 Clean Air Interstate Rule (CAIR) emissions for coal-fired power plants in the region (below).



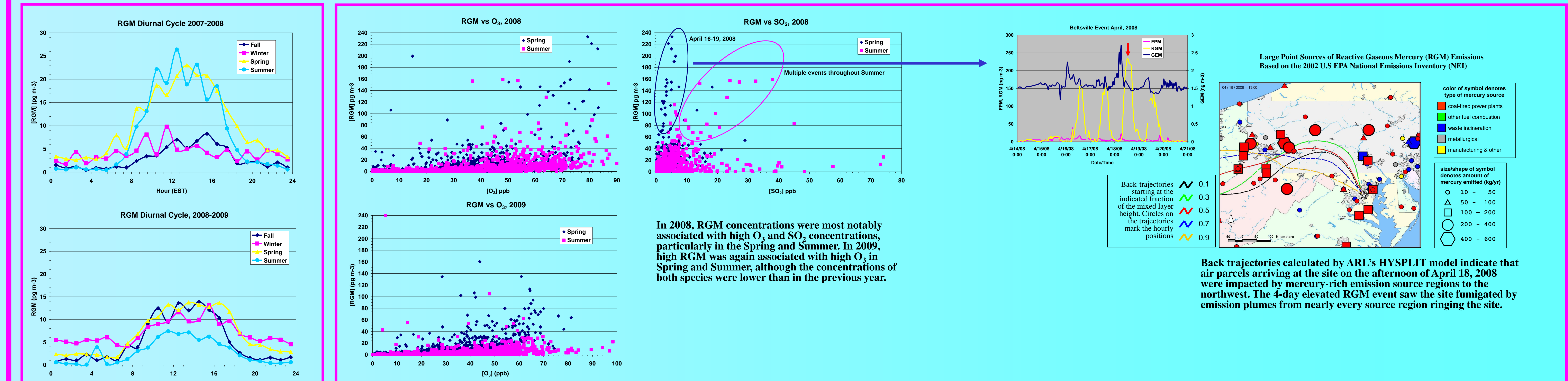
Summary and Next Steps

- The Beltsville site is well-positioned to be impacted by a variety of mercury sources with differing emission profiles, distributed in differing directions from the site.
- High RGM is typically associated with high O₃ in Spring and Summer, and with dryer air characteristic of aged continental emissions (moderate CO levels of 140-300 ppb, NO/NO_y ratios < 0.3), suggesting transport from regionally distributed, not localized, emission sources, consistent with known emission sources around the site.
- In 2008-2009, diurnal RGM profiles were similar throughout Fall, Winter, and Spring. Summer 2009 RGM levels were lower, however, contrary to typical conditions observed at Beltsville and at the Grand Bay NERR site in coastal Mississippi.
- Low concentrations of elemental mercury are occasionally noted in the overnight hours at the site, particularly in Summer. Initial tests have ruled out instrument artifact as an explanation of these depleted concentrations. Heterogeneous oxidation and loss of Hg⁰ in fog or dew events may play a role, and this phenomenon will be investigated further.

Acknowledgments

We would like to thank the staff of EPA's Clean Air Markets Division for their ongoing support of mercury monitoring at Beltsville, and Chris Rogers and the entire MACTEC staff for collecting and providing ancillary chemistry and meteorological data at the site.

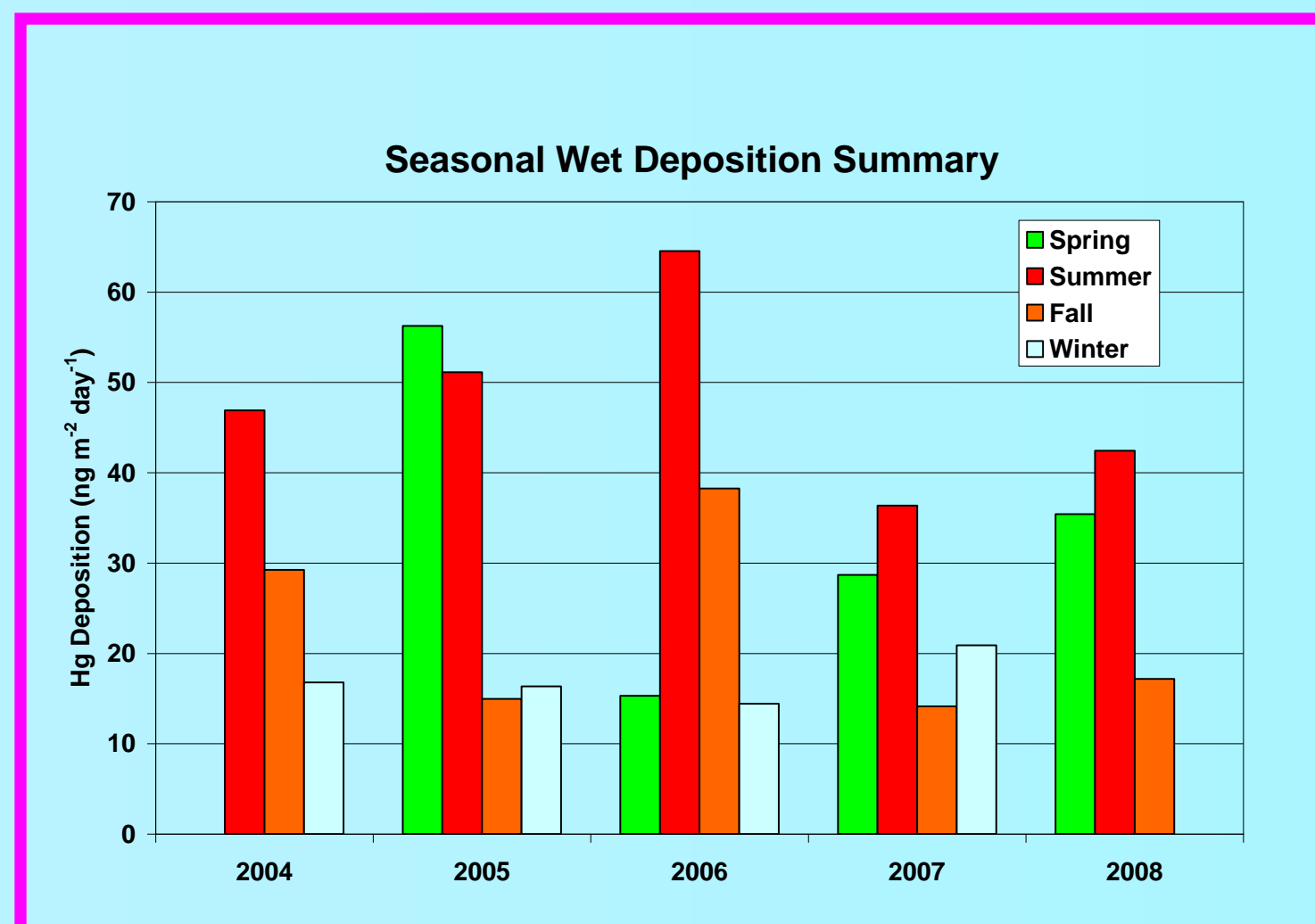
Preliminary Results



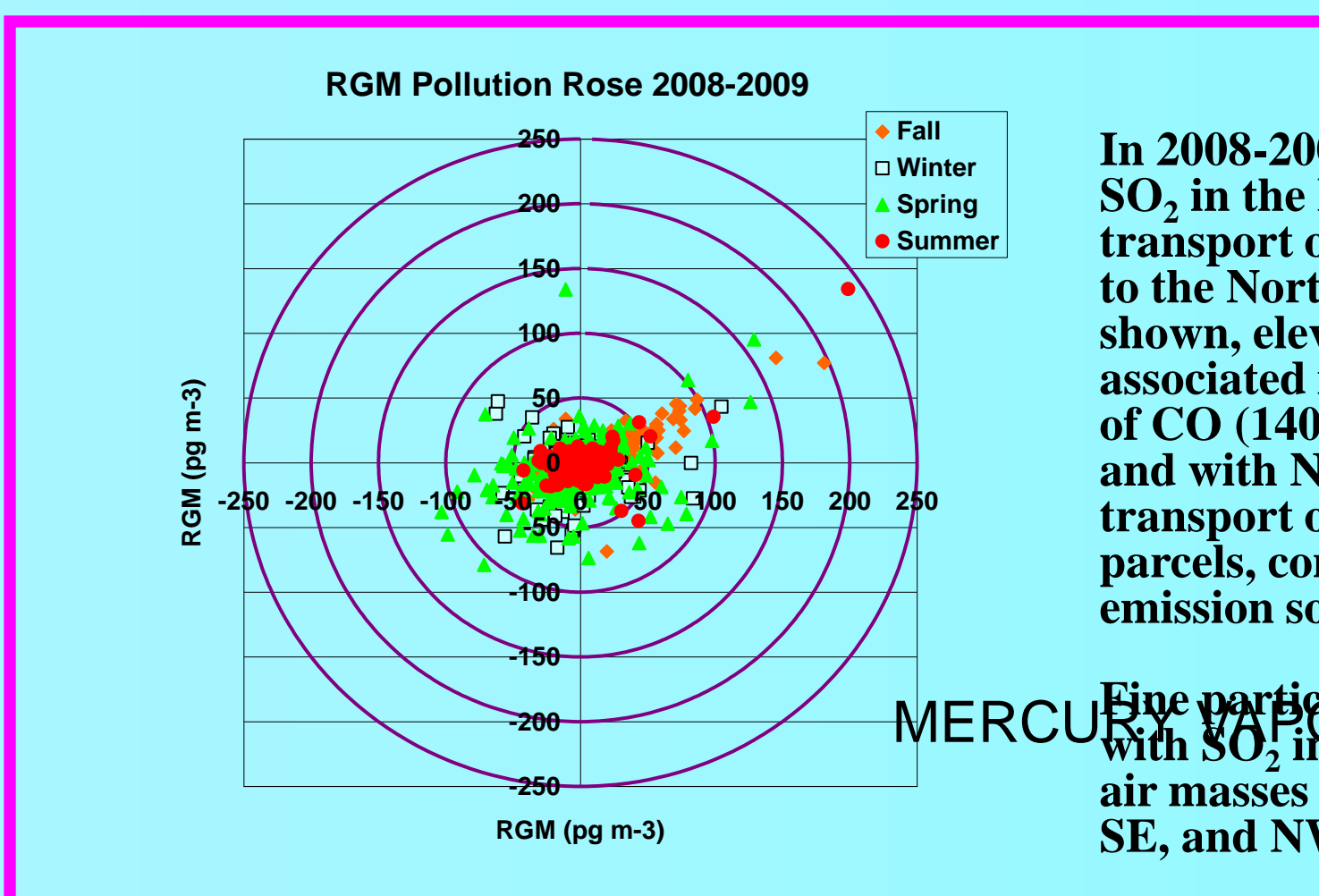
In 2008, RGM concentrations were most notably associated with high O₃ and SO₂ concentrations, particularly in the Spring and Summer. In 2009, high RGM was again associated with high O₃ in Spring and Summer, although the concentrations of both species were lower than in the previous year.

Back trajectories calculated by ARL's HYSPLIT model indicate that air parcels arriving at the site on the afternoon of April 18, 2008 were impacted by mercury-rich emission source regions to the northwest. The 4-day elevated RGM event saw the site fumigated by emission plumes from nearly every source region ringing the site.

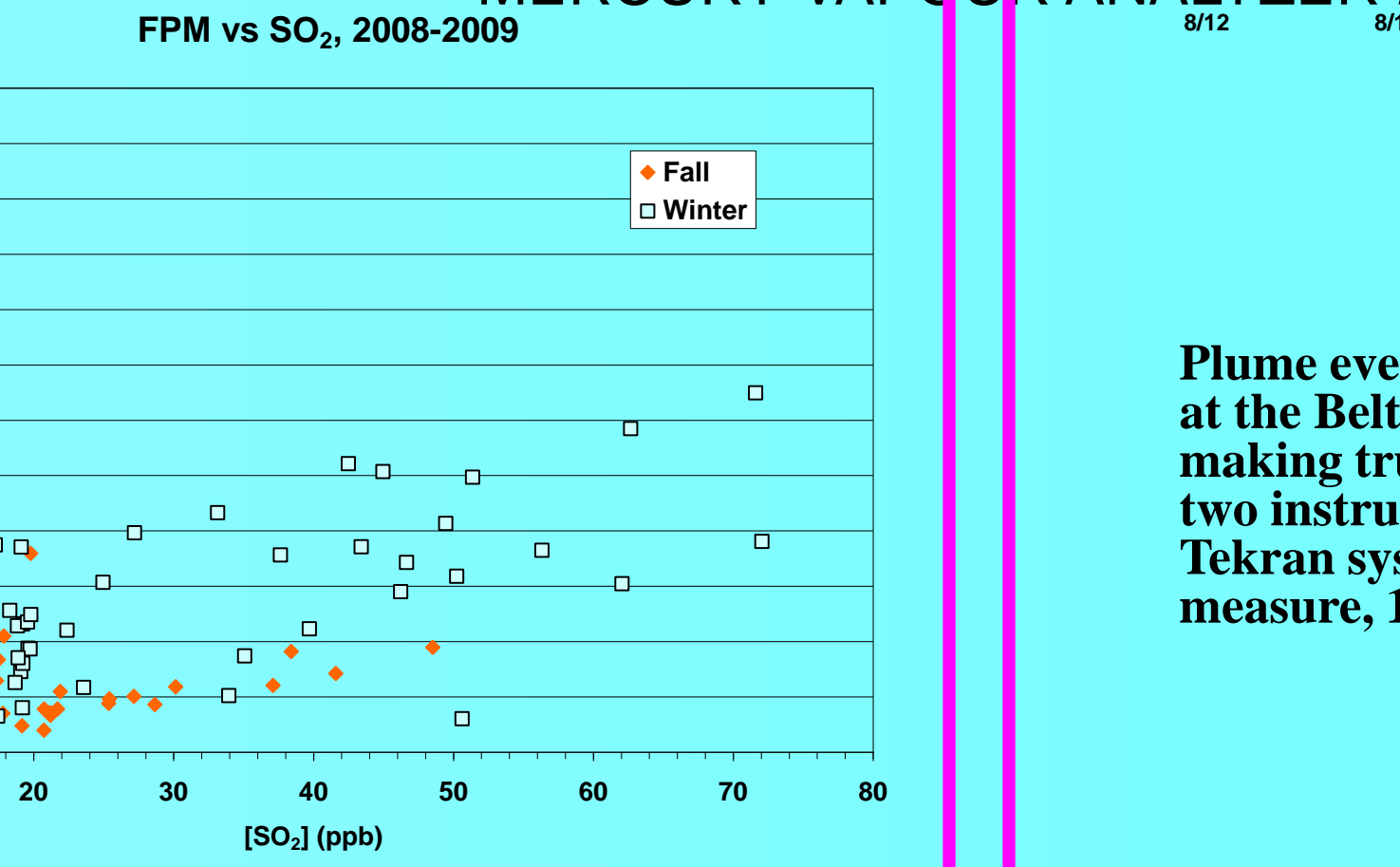
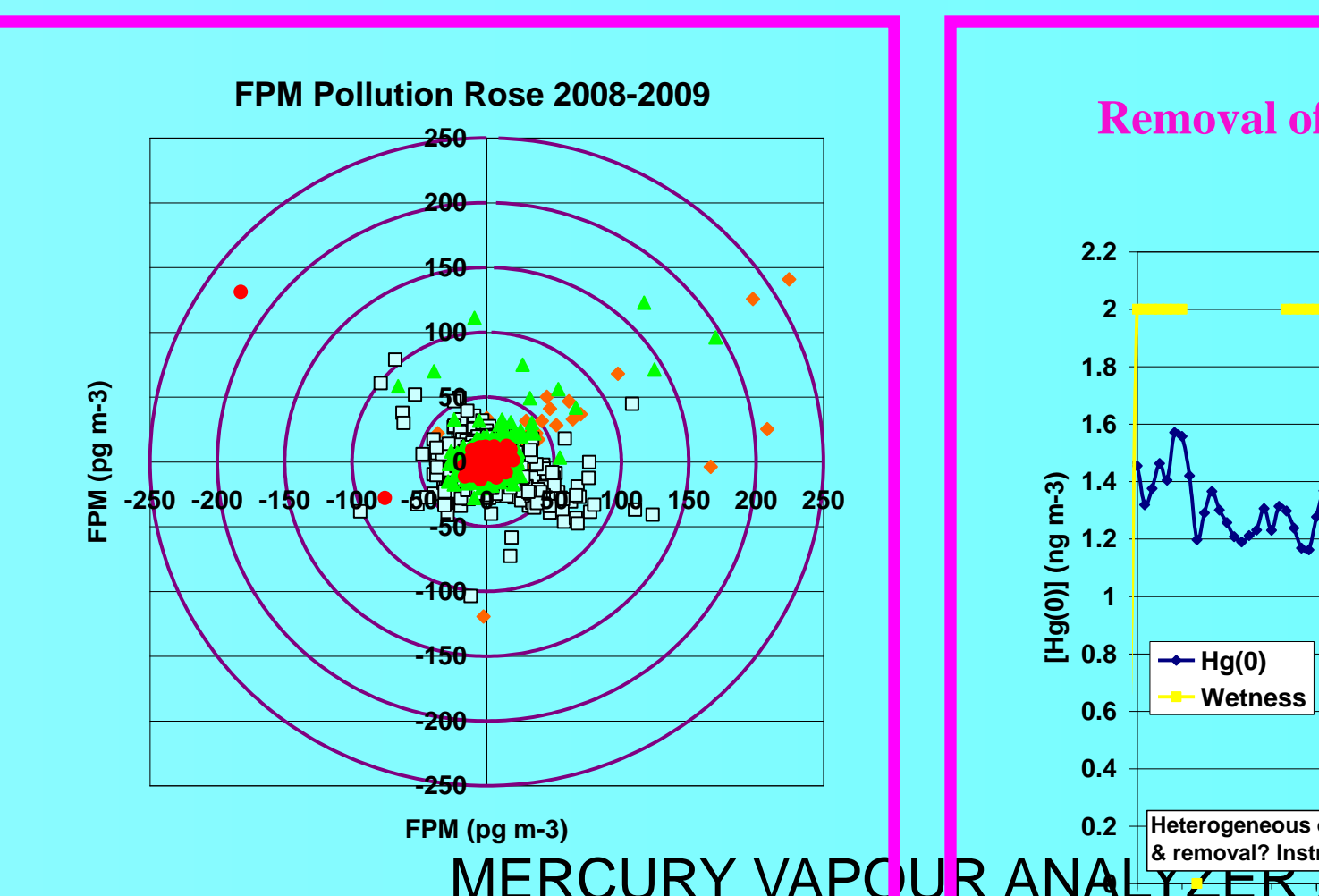
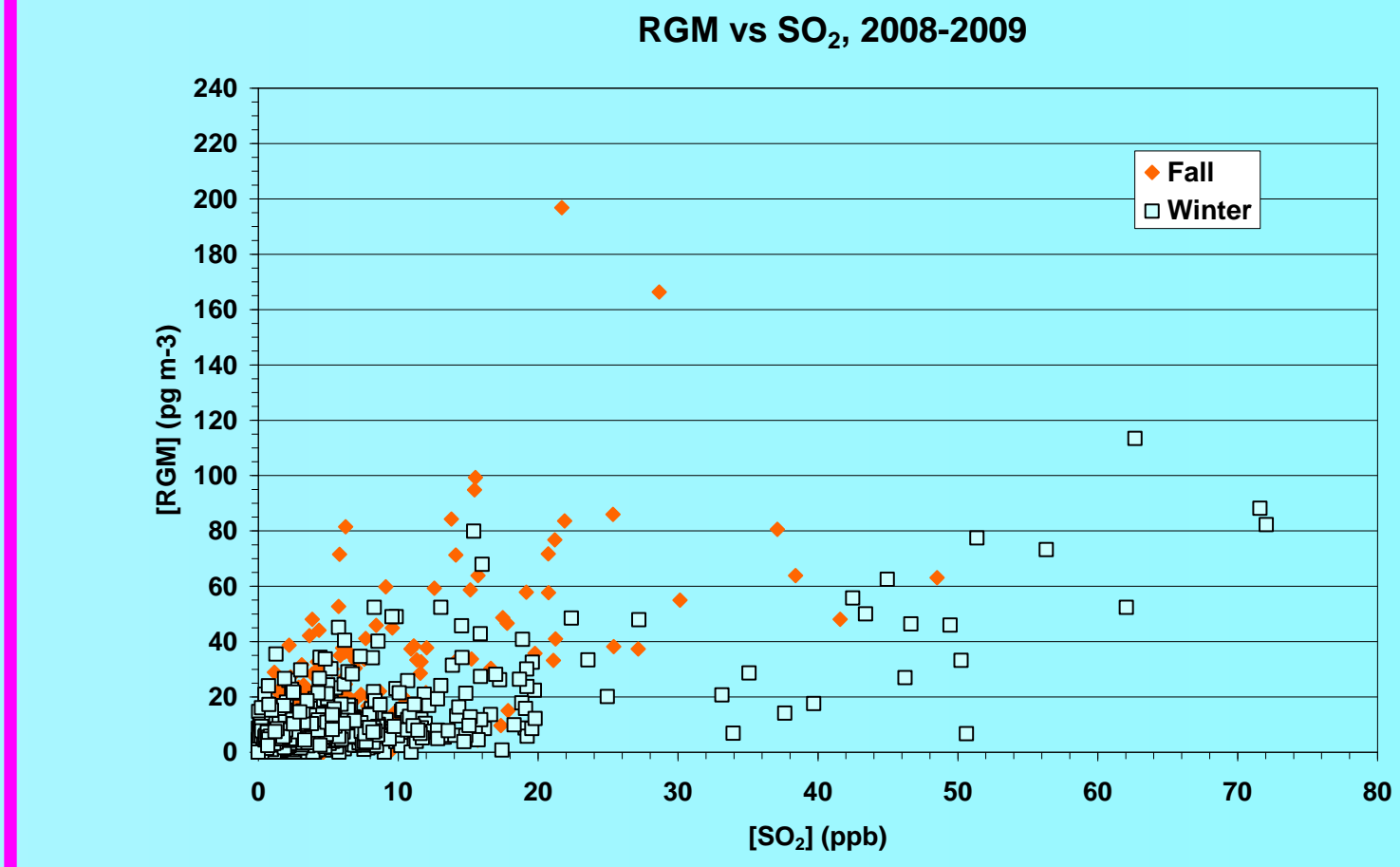
On average, RGM concentrations were lower in 2008-2009 than in the previous year. Primary pollutant concentrations (NO_x, SO₂), however, were higher in 2008-2009. In general, seasonal ozone concentrations were similar between the two years of comparison; however, summertime concentrations were considerably lower in 2009 than in 2008, consistent with cooler temperatures and fewer ozone exceedances in the region.



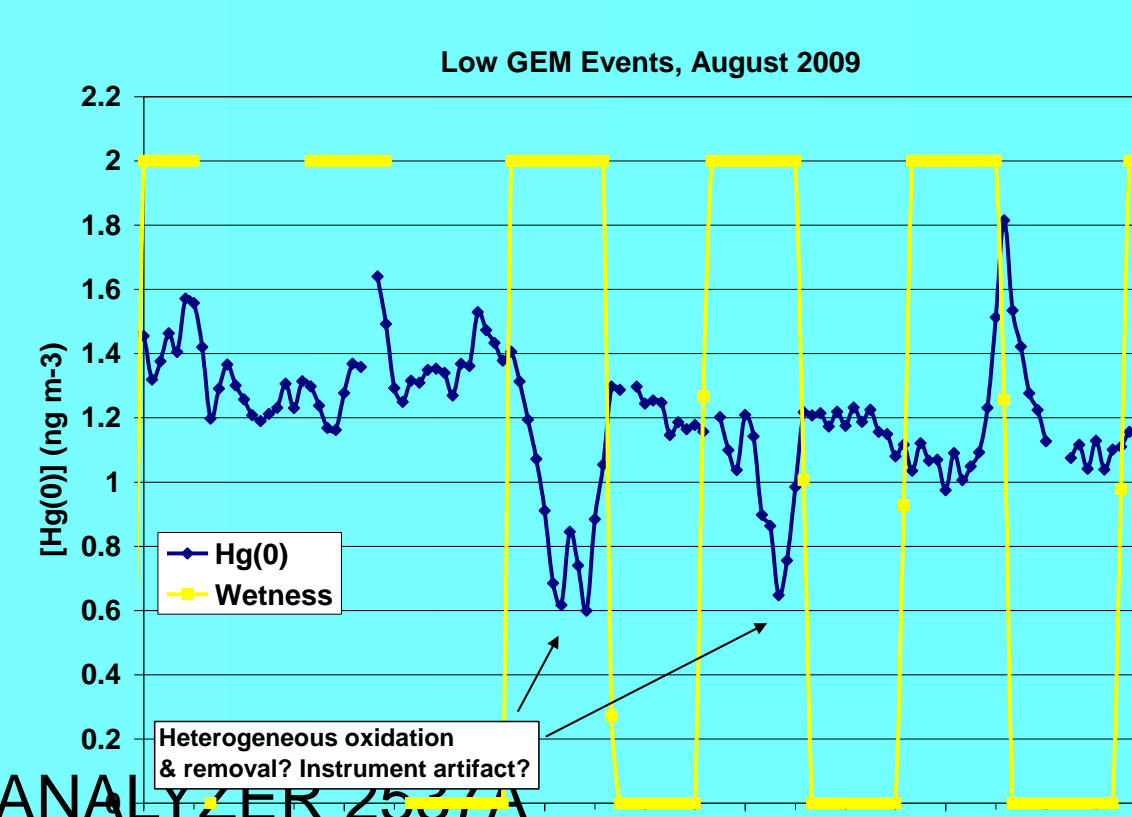
Wet deposition of total mercury in precipitation at the site, 2004-2008. Note that high deposition in Spring 2005 was produced by a single event with exceedingly high mercury concentrations and may be anomalous.



In 2008-2009 RGM was correlated with high SO₂ in the Fall and Winter; Fall saw the transport of air masses impacted by sources to the Northeast of the site. Although not shown, elevated RGM was commonly associated in both years with moderate levels of CO (140-300 ppb) and NO_x (3-15 ppb), and with NO/NO_y ratios < 0.3, suggesting transport or chemical formation in aged air parcels, consistent with the distribution of emission sources around the site.



Removal of Hg⁰ by Heterogeneous Chemistry?



Low Hg⁰ concentrations in the overnight hours are occasionally observed at Beltsville, particularly in Summer, when vegetative surfaces are coated in dew. However, not all instances of dew formation are associated with low Hg⁰. Standard additions of Hg⁰ at the time of the observations rule out loss of mercury in the analytical system.

Heterogeneous oxidation and loss of Hg⁰ on dew-covered surfaces has been hypothesized (e.g., Lindberg et al., *Atmos. Environ.*, 1998), but observational data have been conflicting. Fog formation may play a role, and this phenomenon will be investigated further.

Short Duration Plume Events

Plume events of 1 hour duration are occasionally noted at the Beltsville site, highlighting the importance of making truly continuous mercury measurements with two instruments running asynchronously. A single Tekran system operating on a 2 hour duty cycle (1 hour measure, 1 hour desorption) can miss these events.

