

Passive Monitoring of Ambient Reactive Gaseous Mercury in the Four Corners Area and Eastern Oklahoma

**Presented at the 2010 NADP Annual Meeting and Scientific Symposium,
Lake Tahoe, California, October 21, 2010.**

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First – Important Thanks to Monitoring Site Hosts and Operators!

- **Cherokee Nation** – Collocated Tekran/Passive site at Stilwell, OK; Ryan Callison, Jacque Adam, April Hathcoat, Larry Scrapper, Philip Ketcher, Dani Keese
- **New Mexico Environment Department** – Substation, Farmington Airport and Navajo Lake sites; Joe Cotie, Terry Hertel
- **National Park Service** – Mesa Verde National Park site; George San Miguel, Paul Bohmann
- **USFS/BLM** – Molas Pass site; Kelly Palmer, Brian Parker
- **Jemez Pueblo and Valles Caldera Trust** – Valles Caldera National Preserve site; Tammy Belone, Bob Parmenter

Introduction

- This presentation will summarize the first year of a two year monitoring project estimating reactive gaseous mercury (RGM, a.k.a. gaseous oxidized mercury, GOM) dry deposition in the Four Corners area and eastern Oklahoma.
- RGM of interest because of its chemical reactivity/water solubility; RGM readily deposits to water, soils and vegetation by both dry and wet processes; atmospheric lifetime = 0.5-2 days versus 0.5-2 years for elemental mercury which is mildly reactive and sparingly soluble in water.
- Two year effort funded by U.S. EPA ORD Regional Applied Research Effort (RARE) program.
- Project Collaborators: U.S. EPA Region 6, U.S. EPA ORD, Frontier Geosciences/Global Sciences, Alion, NMED, NPS, USFS/BLM, Jemez Pueblo/Valles Caldera Trust, Cherokee Nation.
- Ambient monitoring began in August, 2009, and will run through the first part of August, 2011.

Project Objectives

- To gather first-time RGM dry deposition estimates for 24 consecutive months at six sites in the Four Corners area to set a valuable ambient RGM dry deposition estimate baseline with proper assessment of: (a) the effectiveness of the Frontier Atmospheric Dry Deposition (FADD) surrogate surface devices in providing reliable RGM dry deposition estimates and (b) the inter-annual RGM dry deposition estimate variability.
- (a) to be accomplished by comparing FADD RGM data to Tekran RGM data at the Stilwell, OK site, and by assessing relative percent difference (RPD) statistics for field duplicate samples.
- Five of the seven total project sites are collocated with wet deposition mercury measurements so wet mercury + dry RGM data will be evaluated for the first time at those sites.
- The baseline data can be used to assess future success of upcoming new mercury emission reduction regulations for the power sector.

Work Done by NADP MDN Hg Analytical Laboratory - Frontier Geosciences/Frontier Global Sciences

- Input and help with study design and sampling & analysis plan
- Field sampling systems set-up and training for each site operator
- Field sampling media shipped with weekly MDN wet dep. gear
- MDN site liaison and technical support following MDN model
- Digestion, analysis, and reporting of each Passive 2-week sample
- A Quality Assurance Project Plan (QAPP) and Field Standard Operating Procedures (SOPs) document have been completed

Method Description



- “Ion Exchange” Membranes are used as surrogate surfaces for adsorption of Mercury
- The membranes collect trace amounts of mercury, mostly in the form of gaseous Hg^{2+} species
- After exposure to the atmosphere, they are collected, digested with bromine monochloride, and analyzed using cold vapor atomic fluorescence spectroscopy (Principles Of US EPA 1631)

- Mercury depositional flux (D) to the Dry Deposition membranes is calculated in $\text{ng}/\text{m}^2/\text{hr}$ as:

- $D = [(S - B)/A]/T$, where

S = total mercury recovered from a deployed sample in ng,

B = average total mercury in ng recovered from the site specific running average of the blanks

A = the exposed membrane area in m^2

T = the deployment time in hours.

Previous Studies With Method

- Caldwell, C.A., Swartzendruber, P. and Prestbo, E. (2006) **Concentration and Dry Deposition of Mercury Species in Arid South Central New Mexico (2001-2002)**, *ES&T*
- Lyman, S.N., Gustin, M.S., Prestbo, E.M. and Marsik, F.J. (2007) **Estimation of Dry Deposition of Atmospheric Mercury in Nevada by Direct and Indirect Methods**, *ES&T*
- Kindziarski, W., Brunette, R., Van der Jagt, G., Nelson, R., Kilner, P., Prestbo, E.(2008), **Spatial Dry Deposition of Reactive Gaseous Mercury In West Central Alberta**, NADP 2008 Annual Meeting and Scientific Symposium, Oct 14-16, 2008, Madison Wisconsin (Oral Presentation)
- Lyman, S.N., Gustin, M.S., Prestbo, E.M., Kilner, P.I., Edgerton, E. and Hartsell, B. (2009) **Testing and Application of Surrogate Surfaces for Understanding Potential Gaseous Oxidized Mercury Dry Deposition**, *ES&T*

Study Areas Background

- The Four Corners area of the southwest U.S. contains many protected National Parks and Monuments amidst growing oil/gas production and some of the largest coal-fired power plants in the U.S. Some of the fish tissue samples previously taken in the Four Corners Area have exceeded EPA's criterion concentration for human health consumption of fish (0.3 mg/kg methylmercury fish tissue).
- Ambient ozone and nitrogen oxides have been extensively monitored in the Four Corners area, but other pollutants of concern, such as ambient RGM, have not been monitored in the past because of cost and other considerations.
- To address cost concerns, and for ease of operations, this project is using passive sampling devices for RGM from Frontier Geosciences. A great benefit of passive sampling is that it enables more pollutant sites to be deployed for the same cost as a single continuous monitoring station.
- It was desired for confidence purposes to be able to compare the passive data to a recognized continuous method for RGM. Fortunately in Region 6, the Cherokee Nation hosts the operations of a Tekran continuous instrument in Eastern Oklahoma that monitors for elemental, particle bound, and reactive gaseous, mercury.

Study Sites

- A variety of site types was desired, including:
- **Regional Background** - Mesa Verde National Park for the Four Corners Area and Stilwell for Eastern Oklahoma.
- **Power Plant Impacted** (i.e. in close proximity to the Plants) – Substation, located about 2.5 miles west of San Juan Power Plant and about 8 miles north of Four Corners Power Plant.
- **Rural** – Navajo Lake and Valles Caldera National Preserve.
- **Urban** – Farmington Airport.
- **Elevated Mountain** – Molas Pass.

Pictures of Substation Site passive reactive gaseous mercury stand (left),
and San Juan (top right) and Four Corners (bottom right) Power Plants



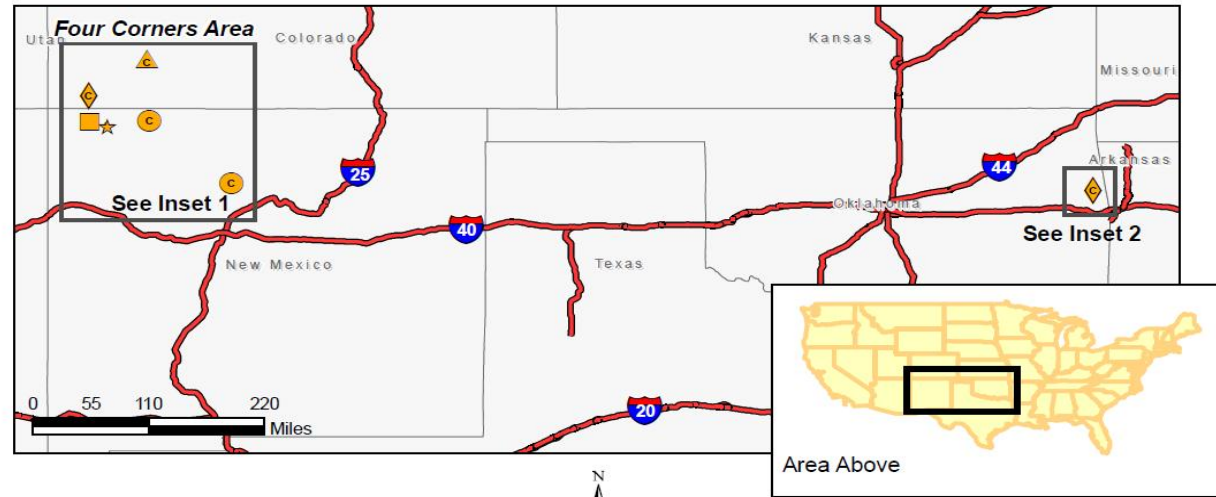
Pictures of Valles Caldera (Left) and Navajo Lake (Right) Sites



Pictures of Molas Pass site (upper left), Mesa Verde NP site (upper right), and Farmington Airport site (bottom two pictures)

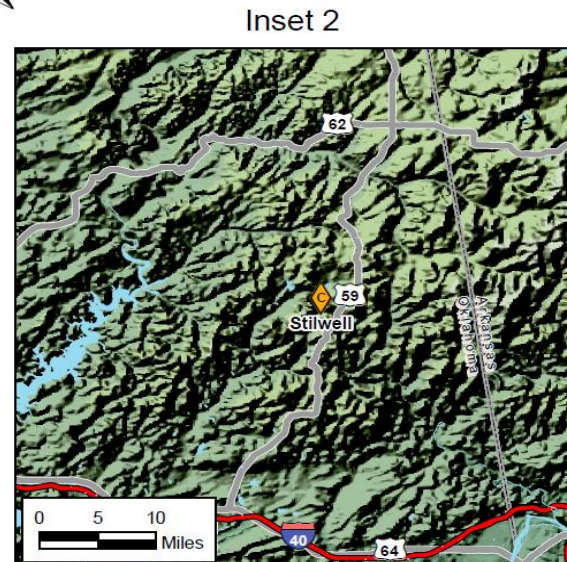
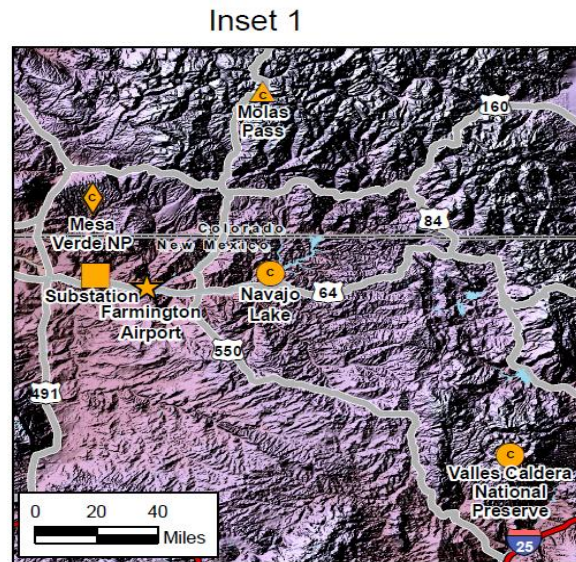


Map of the 8/2009 - 8/2011 passive mercury dry deposition monitoring sites in the Four Corners Area and Eastern Oklahoma



Monitoring Site Elevations:

- Molas Pass – 10,659 ft asl
- Valles Caldera – 8,717 ft asl
- Mesa Verde NP – 7,126 ft asl
- Navajo Lake – 6,470 ft asl
- Substation – 5,505 ft asl
- Farmington Airport – 5,492 ft asl
- Stilwell, OK – 997 ft asl



- Elevated Mountain Site
- Power Plant Impacted Site
- Regional Background Site
- Rural Site
- Urban Site
- Interstate
- US Highways
- State Boundary
- C - collocated with mercury wet deposition monitoring equipment

Sources:
U.S. EPA AQS Database, NADP,
USGS NED Data, and U.S. EPA Region 6.

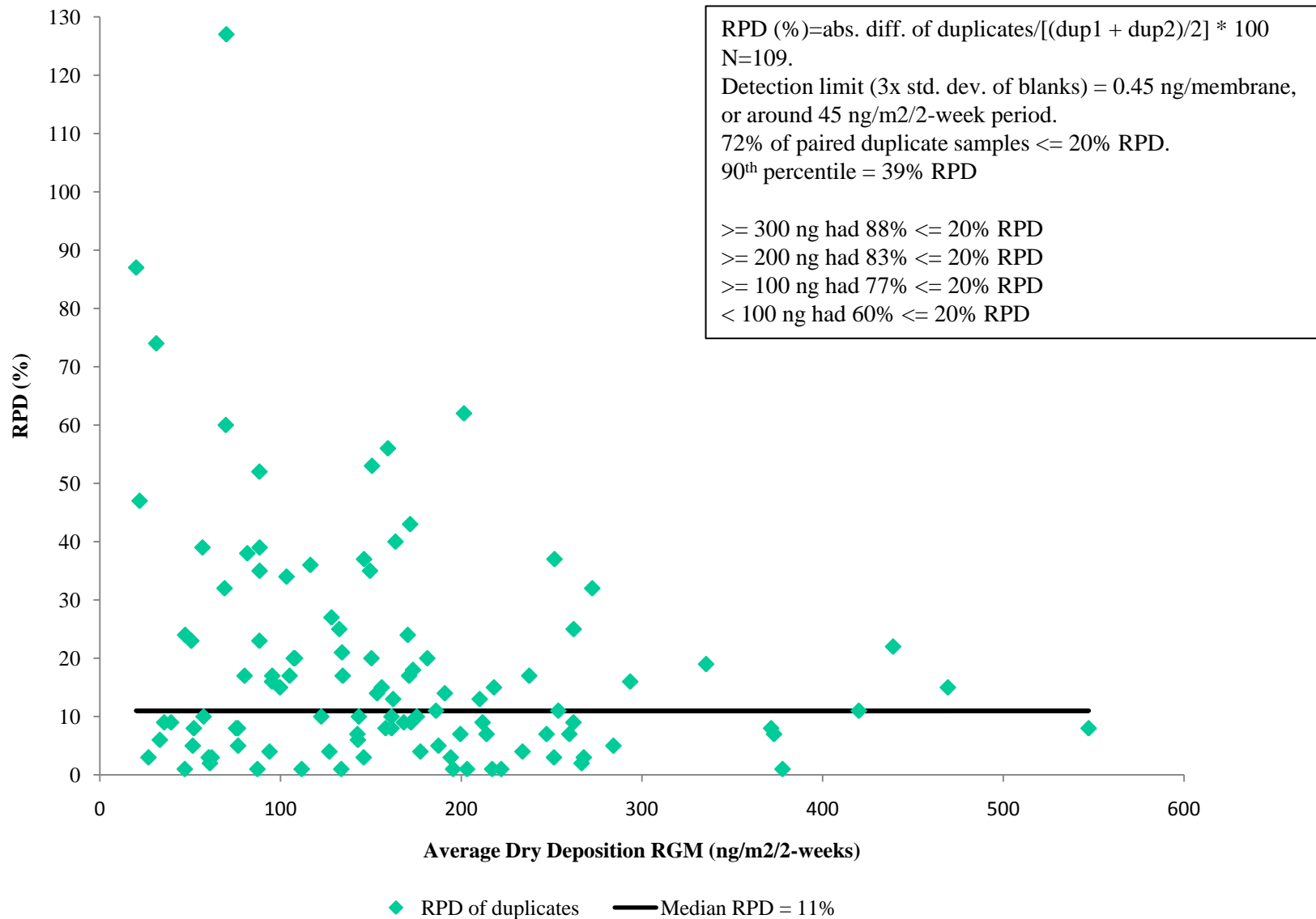


EPA Region 6
GIS Support Team
Dallas, TX
September 3, 2010

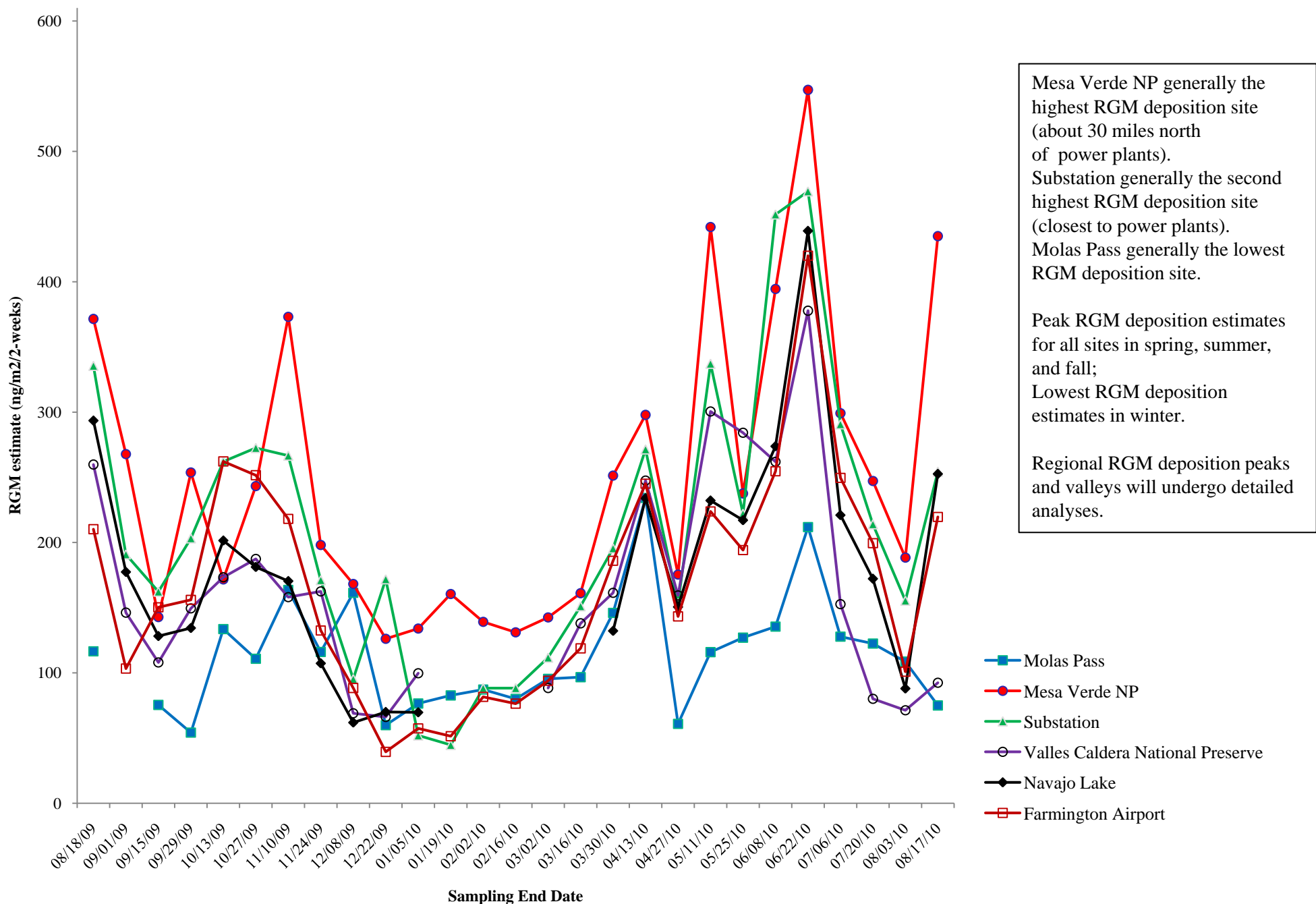
Passive Sampling

- FADD surrogate surface (Ion Exchange Membrane) samples deployed for two-week integrated periods, every other Tuesday in conjunction with national weekly wet MDN efforts.
- Duplicate field samples deployed every other sampling period and duplicate field blanks taken every four sampling periods.
- Each sample includes ultra-clean FADD filter preparation and packaging, digestion with ultra low level mercury reagents, laboratory analysis QA following the principles of U.S. EPA Method 1631.
- All sample receipt, analysis, data management and reporting follows the current existing national mercury deposition network (MDN) protocols and SOPs.
- Laboratory FADD membrane blanks are analyzed with each sample analysis set and the analysis QA consists of same-day analysis spike recoveries, reagent blanks, calibration curves, and calibration verification and system blanks. All field samples are analyzed the same week they are received at Frontier.

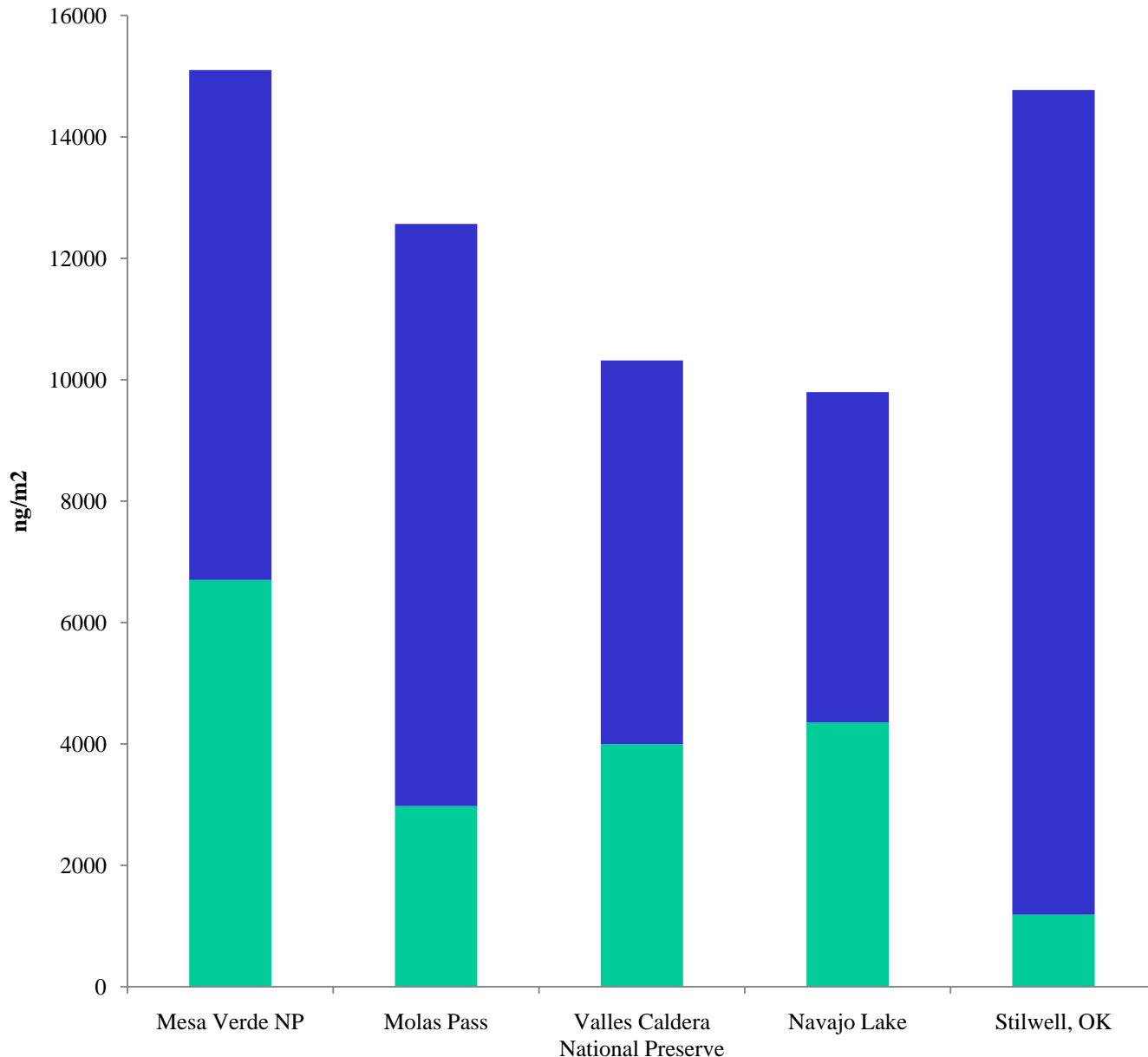
Relative Percent Difference (RPD) Analysis of Field Duplicates



Four Corners Area Estimated RGM Dry Deposition Data Time Series



Estimated Dry RGM + Wet Deposition Hg (8/09-8/10 total ng/m²)



-Stilwell, OK dominated by wet deposition (wet = 92%, dry=8%)
-Four Corners dry RGM a significant part of total deposition, ranging from:
-24% at Molas Pass
-39% at Valles Caldera National Preserve to 44% at Navajo Lake and Mesa Verde National Park.

■ wet Hg
■ dry RGM



Tekran data very limited in western U.S. The only active Tekran site in EPA Region 6 is at the Stilwell site in Oklahoma.

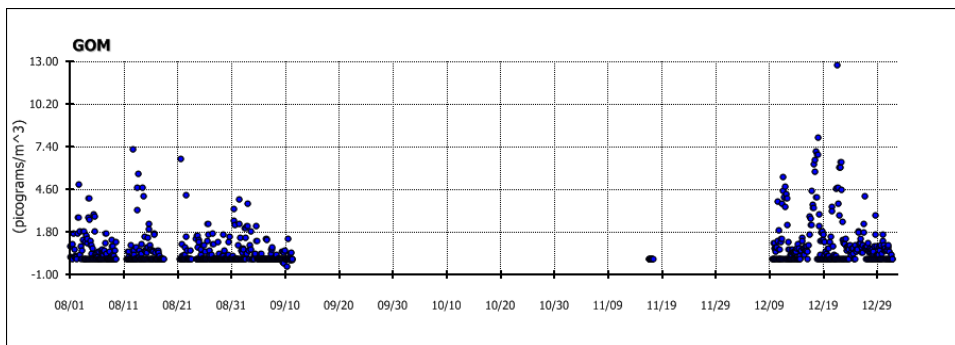
Collocated Tekran/Passive RGM Monitoring Site at Stilwell, OK.



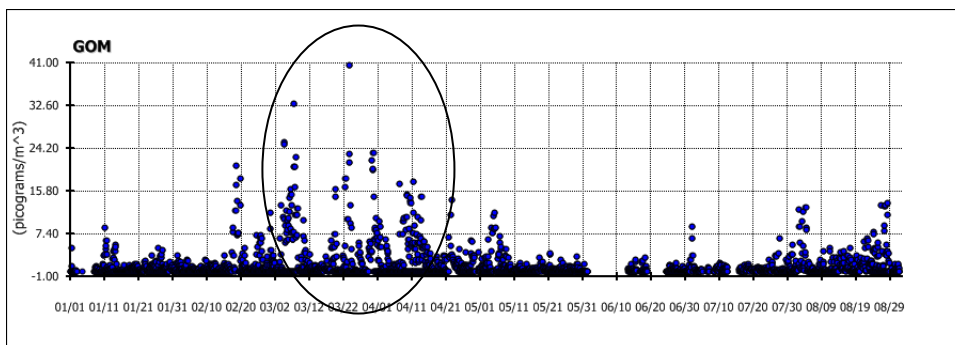
Stilwell, OK RGM Tekran and Estimated Passive RGM Data (8/2009 – 8/2010)

The higher Tekran values recorded from around 3/2/2010 to around 4/13/2010 correspond to the highest estimated passive RGM (a.k.a. GOM) data values seen so far at Stilwell.

Tekran RGM Data

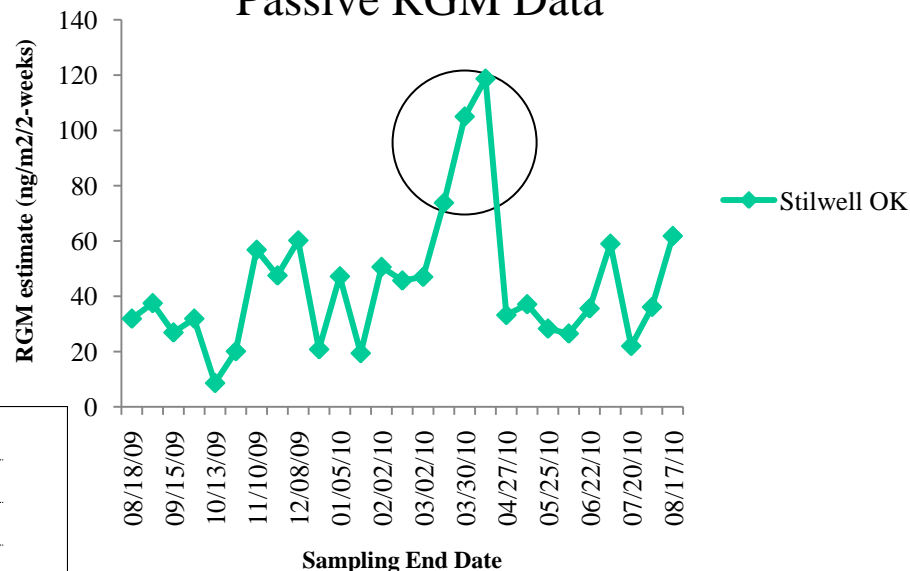


2009



2010

Passive RGM Data



Upcoming Work

- Continue second year of sampling (through the first part of August, 2011) at all seven sites.
- Conduct analysis of collocated real-time RGM/passive estimated RGM data from Stilwell site; Data from 8/2009-8/2010 had been obtained and Frontier is in process of developing a method to compare the real-time to the passive data.
- Conduct detailed analyses of the two year dataset, including merging site specific meteorological data (wind speed, wind direction, temperature) with the mercury data.
- After second year of data collection, will work with Alion on some spatial analyses of the complete two year dataset, and begin construction of journal article documenting results from the two year study.

Questions?

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