Gaseous Oxidized Mercury Dry Deposition Measurements in the Four Corners Area and Eastern Oklahoma, U.S.A.

Mark E. Sather*
Air Quality Analysis Section, U.S. Environmental Protection Agency (EPA) Region 6, 1445 Ross Avenue, Dallas, Texas 75202

Shaibal Mukerjee
National Exposure Research Laboratory, U.S. EPA (E205-03), Research Triangle Park, North Carolina 27711

Luther Smith
Alion Science and Technology, Inc., POB 12313, Research Triangle Park, North Carolina 27709

Johnson Mathew and Clarence Jackson
Houston Laboratory, U.S. EPA Region 6, 10625 Fallstone Road, Houston, Texas 77099

Ryan Callison, Larry Scrapper, April Hathcoat, Jacque Adam, Danielle Keese and Philip Ketcher
Cherokee Nation Environmental Programs, 208 E. Allen Road, Tahlequah, Oklahoma 74464

Robert Brunette, Jason Karlstrom and Gerard Van der Jagt
Frontier Global Sciences, 11720 North Creek Parkway North, Suite 400, Bothell, Washington 98011

ABSTRACT

Gaseous oxidized mercury (GOM) dry deposition measurements using surrogate surface passive samplers were collected in the Four Corners area and eastern Oklahoma from August, 2009-August, 2011. Using data from a six site area network, a characterization of the magnitude and spatial extent of ambient mercury pollution in the arid Four Corners area was accomplished, which included the observation of a strong regional signature in the GOM dry deposition data set. GOM dry deposition rate estimates ranged from 0.4-1.0 ng/m^{2}h at the six Four Corners area monitoring sites, while the GOM dry deposition rate estimate at the eastern Oklahoma monitoring site was lower at 0.2 ng/m^{2}h. The highest GOM dry deposition estimates were recorded during the spring and summer while the lowest GOM dry deposition estimates were

recorded during the fall and winter. During the second year of this study the highest annual GOM dry deposition estimate so far measured in the United States (U.S.) with smooth-edge surrogate surface passive samplers, 10 889 ng/m^2, was recorded at the Mesa Verde National Park site, a site at which the two-year cumulative GOM dry deposition estimate exceeded the mercury wet deposition estimate. GOM dry deposition estimates during the second year of the study were statistically significantly higher than the first year of the study at six of the seven sites. The data from this study provide a two-year baseline of GOM dry deposition data in the Four Corners area and eastern Oklahoma immediately before the current implementation of new U.S. power plant and boiler mercury control regulations which will significantly reduce mercury emissions from those two sectors of local and regional anthropogenic mercury emission sources.

Keywords: Air Pollution, Arid Area, Surrogate Surface Passive Sampling.

1. Introduction

Ambient mercury pollution is a global concern (Kim et al., 2005; Lindberg et al., 2007; Slemr et al., 2003) and deposits to the earth in wet and dry processes. Wet deposition mercury measurements and core mercury measurements such as from ice and sediments have been collected for many years in North America (Mast et al., 2005; Mast et al., 2010; National Atmospheric Deposition Program, 2011a; Prestbo and Gay, 2009; Schuster et al., 2002), but there is a current dearth of dry deposition mercury measurements.

GOM consists of multiple oxidized mercury compounds such as $HgCl_2$ and $HgBr_2$ (Gustin and Jaffe, 2010). GOM has a short atmospheric life time and in part is associated with local/regional mercury emission sources (Schroeder and Munthe, 1998; Skov et al., 2007), such as from coal-fired power plants, boilers, and cities. It should be noted though that some of the

GOM released from coal-fired power plant and other boiler plumes may also undergo reduction in the atmosphere downwind from the release points (Electric Power Research Institute, 2010). GOM is also formed through oxidation reactions of gaseous elemental mercury, especially in warmer seasons with higher photochemical activity (Lin et al., 2012). A significant amount of total dry deposition of mercury consists of GOM (Lin et al., 2012), and GOM, along with particle bound mercury, deposits faster to water, soils, and vegetation and is more water soluble than gaseous elemental mercury (Zhang et al., 2009). Surrogate surface sampling of mercury dry deposition, including GOM dry deposition, has been recently evaluated (Huang et al., 2011; Lai et al., 2011; Lyman et al., 2009), and also used to better understand spatial distributions of ambient mercury dry deposition (Huang et al., 2012). This paper discusses estimates of total mercury deposition in terms of mercury wet deposition estimates plus GOM dry deposition estimates only; gaseous elemental mercury dry deposition estimates or particle bound mercury dry deposition estimates are not included here. Thus, total mercury deposition estimates discussed in this paper should be viewed as conservative estimates (i.e. probably underestimating the "true" totals). There have only been a few published GOM dry deposition measurement studies of extended length in the U.S. (Caldwell et al., 2006; Castro et al., 2012; Huang et al., 2012; Lyman et al., 2007; Lyman et al., 2009; Peterson et al., 2012), and none outside of the U.S. This paper provides new information on GOM dry deposition estimates in two new areas in the south central U.S.

The Four Corners area of the U.S. consists of the region where four U.S. States (New Mexico, Colorado, Utah, and Arizona) come together (Figure 1, Inset 1). Two of the largest coal-fired power plants in the U.S. are located in the Four Corners area, and coal-fired power plants are the largest anthropogenic mercury emission source in the U.S., contributing about 50%

of all stationary source mercury emissions (U.S. EPA, 2011a). Measurements from the Mercury Deposition Network (MDN) of the National Atmospheric Deposition Program (NADP) for 2010 showed elevated wet mercury deposition levels at Mesa Verde National Park (National Atmospheric Deposition Program, 2011a), and given the arid nature of this region, dry mercury deposition has been hypothesized to be a significant portion of the total mercury deposition in the Four Corners area (Huang and Gustin, 2012; Lyman et al., 2007; Mountain Studies Institute, 2010). Thus, a two year study to collect dry deposition mercury measurements in the Four Corners area was begun in August, 2009, to test the hypothesis that significant amounts of total mercury deposition in the Four Corners area are from dry atmospheric processes. Multiple air monitoring sites were established to study the spatial distribution of dry mercury deposition. This was the first attempt at such an effort in this area. An additional objective of the study was to estimate a dry mercury deposition baseline before mercury emission controls are implemented due to the U.S. 2011 Boiler/Incinerator (U.S. EPA, 2011b) and U.S. 2012 Power Plant (U.S. EPA, 2012) mercury rules. Only one of the power plants considered here (San Juan; see Figure S1 in Supporting Material) had installed mercury emission controls before the latter rule was issued. Both rules require affected industrial sources to install mercury emission controls during the 2012-2016 time-frame.

In addition to the Four Corners area, first time extended length GOM dry deposition data were collected at the Stilwell site in eastern Oklahoma (site OK99; Figure 1, Inset 2). The eastern Oklahoma area, like the Four Corners area, contains notable coal-fired power plant mercury emissions (see Figure S1 in Supporting Material).

2. Materials and Methods

2.1 Study sites

Dry deposition of GOM was monitored from six sites in the Four Corners area (Figure 1, Inset 1). The sites were identified by their names and NADP two letter/two number codes. The sites were located in rural areas (Mesa Verde National Park – CO99, Valles Caldera National Preserve – NM97, Navajo Lake – NM98), a city (Farmington Airport – NM99), nearby the largest power plants (Substation – NM95), and at a high elevation mountain area (Molas Pass – CO96). Measurements at high elevation mountain sites (defined as above 3 000 m) are difficult for several reasons, including very remote site access, lower temperatures, and usually a higher percentage of precipitation in frozen forms like snow or ice (Latysh and Wetherbee, 2012). Despite these challenges, almost 100% data capture was achieved during the two year study at the Molas Pass site (CO96). The Substation site (NM95) was situated only 4 kilometers (km) west of the San Juan Power Plant and about 12 km north of the Four Corners Power Plant (see Figure S1 in Supporting Material). The San Juan Power Plant had installed mercury emission controls in 2009 before this study began (approximate 80% mercury control with activated carbon injection).

Also shown in Figure 1 is the Stilwell site (OK99; Figure 1, Inset 2) in eastern Oklahoma, a rural site different from the Four Corners sites because of its much lower elevation and much higher precipitation amounts. The Stilwell site (OK99) housed both the surrogate surface GOM dry deposition passive samplers and a continuous instrument which provided measurements of ambient GOM concentrations. The Stilwell site (OK99) was chosen for this study because it housed a continuous GOM concentration instrument (i.e., the standard Tekran monitor) which enabled a collocated intercomparison with the GOM dry deposition surrogate surface passive samplers. The Stilwell site (OK99) continuous GOM concentration instrument is part of the

Atmospheric Mercury Network (AMNet) of the NADP (National Atmospheric Deposition Program, 2011a). Detailed GOM monitoring site characteristics, including latitude/longitude coordinates, summary meteorological information, and distances to the largest coal-fired power plants (Four Corners Power Plant for the Four Corners area and Muskogee Power Plant for eastern Oklahoma), are found in Table S1 in the Supporting Material.

2.2 Field instrumentation for data acquisition

For cost efficiency and technical manpower considerations, smooth-edge surrogate surface passive sampling was employed to measure GOM dry deposition during contiguous two-week integrated time periods from August 4, 2009-August 2, 2011. Deployment of surrogate surface passive sampling for GOM dry deposition estimation, including use of the smooth-edge surrogate surface passive sampler, has been discussed in detail in previous published studies (Castro et al., 2012; Gustin et al., 2012; Lyman et al., 2007; Lyman et al., 2009; Peterson and Gustin, 2008; Peterson et al., 2012). Two-week sampling integrals were used in this study based on prior analyses that indicated this particular sampling integral achieved both high precision and measurements above method detection limits (Lyman et al., 2010a).

The surrogate surface passive sampling conducted in this two year study used the Frontier Atmospheric Dry Deposition (FADD) device (Frontier Global Sciences, Bothell, Washington) which utilizes a negatively charged polysulfone impregnated cation exchange filter membrane (Pall Corporation, ICE 450; 0.45 micron pore size, 140 micron thickness on a non-woven polymer backing). The FADD device was earlier developed by scientists at the University of Nevada (Lyman et al., 2009; Peterson and Gustin, 2008). Before commencement of any field sampling a quality assurance project plan was completed (on file with both U.S. EPA

and Frontier Global Sciences). The quality assurance project plan in part referenced the Frontier Laboratory's quality assurance plan (Spadafora and Strickland, 2008) and the MDN quality assurance plan (Gay et al., 2006), where details of standard preparations and calibrations are discussed. The FADD cation exchange filter membrane has been tested and shown to selectively and efficiently capture GOM (Lyman et al., 2009). However, recent literature has mentioned that some particle bound mercury could be collected by the surrogate surfaces since they are still open to the air, even pointing down (Huang et al., 2012), and that heterogeneous oxidation and reduction reactions of gaseous elemental mercury and GOM could occur on the filter membrane surfaces (Gustin et al., 2012). The captured GOM is held on the filter membrane surface and not released until laboratory immersion in oxidizing acid. Each filter membrane was mounted into a specially designed polyurethane aerodynamic filter holder (also known as an aerohead) facing down for protection from overhead solar radiation and precipitation. Each aerohead filter holder was attached to a T-shaped stand in the field, where the filter membranes could be raised to approximately 3 meters above ground level and be directly exposed to the atmosphere (reference Figure S2 in the Supporting Material).

In addition to the surrogate surface passive sampling, a continuous monitor was operated at the Stilwell site (OK99) in eastern Oklahoma by the Cherokee Nation as a part of the NADP's AMNet program. Specifically, a Tekran model 1135 particulate mercury unit was used with a model 1130 speciation unit and a model 2537A mercury analyzer (Tekran Instruments Corp., Toronto, Canada) to simultaneously monitor particle bound mercury, elemental mercury, and GOM concentrations. All Tekran data were collected using quality assurance and calibration procedures developed by the NADP (National Acid Deposition Program, 2011b). The Tekran instrument at Stilwell (OK99) used a 2-hour sampling period and a 1-hour desorption period,

sampling GOM for 67% of each 3-hour period. Current known limitations of the Tekran instrument include: (a) the underestimation of GOM concentrations using KCl-coated denuders in the presence of ozone (Lyman et al., 2010b), (b) the variability between co-located Tekran instruments for GOM concentrations recently being reported in a wide range of 9-40% (Gustin et al., 2012), and (c) the uncertainty in the sampling of all of the different chemical forms of GOM (Gustin et al., 2012).

Hourly meteorological data, including ambient temperature, wind speed, and wind direction, were collected at five of the seven sites (Figure 1). The meteorological data were collected by the National Park Service (Mesa Verde National Park site – CO99), the New Mexico Environment Department (Substation (NM95) and Navajo Lake (NM98) sites), the Valles Caldera National Preserve (for site NM97), and the Cherokee Nation (Stilwell site – OK99). Weekly wet mercury deposition measurements, courtesy of the NADP's MDN network, were collected at five of the seven sites (Figure 1), enabling conservative estimates of total mercury deposition at those five sites.

2.3 Laboratory procedures

Sample preparation and handling. The chemically treated FADD filter membranes were cut into 5 3/8th inches diameter discs using ultra clean techniques and shipped to the site operators every two weeks in tape-sealed Petri dishes, which were each sealed in plastic bags. The total field sampling budget was allocated between collecting field samples to cover two years, collecting precision data (duplicate field sampling), and finally collecting field blank data (also done in duplicate). Field blanks travelled to each site. At each of the seven sites duplicate field sampling was conducted every other sampling period to measure sampling precision (50% of the

study), and duplicate field blank sampling was conducted at the initial sampling period and every four sampling periods thereafter (~ 27% of the study). Field blank data were tracked throughout the study and field blank data were subtracted from the field sample data at each site on an up to date basis. For example, the field blank data used for sampling period 1 came from the average of the two field blank samples run during sampling period 1 (done for each individual site). Then, for sampling periods 2 through 4, field blank data were comprised of the average of the field blank samples from both sampling period 1 and sampling period 5 (since field blanks were conducted every four sampling periods, i.e. for sampling periods 1, 5, 9, 13, 17, 21 and 25 in year 1). For sampling period 5 the field blank data came from the average of the two field blank samples run during sampling period 5. Then, for sampling periods 6 through 8, field blank data were comprised of the average of the field blanks from both sampling period 5 and sampling period 9, and this procedure repeated throughout the two year study for each individual site. For each sampling period with duplicate field sampling, the final GOM dry deposition estimate was the arithmetic mean of the two duplicate field samples. At each site, installation procedures and sample change-out training were done with all of the operators for consistency and contamination mitigation. Powder-free disposable gloves were used by all monitoring site operators and laboratory chemists.

Chemical analyses. After each two-week sampling period the FADD filter membranes were returned to Frontier Global Sciences (Frontier) for chemical analysis. Each filter membrane was digested with bromine monochloride before GOM analysis using cold vapor atomic fluorescence spectroscopy (CVAFS). An aliquot of each FADD filter membrane digest was analyzed using $SnCl_2$ reduction, dual gold amalgamation, and CVAFS detection following Frontier Standard Operating Procedure (SOP) FGS-069, based on the principles of U.S. EPA Method 1631 revision

E (U.S. EPA, 2002) and additional experimental quality assurance procedures for mercury analysis (Brown et al., 2011; Pandey et al., 2011). The CVAFS instrumental detection limit (idl) is 0.08 ng/l and the method detection limit (mdl) for dry deposition filter analysis is 0.016 ng/filter. The mdl for dry deposition filter analysis is extrapolated from the following equation:

Mdl for dry deposition filter analysis = Idl for CVAFS instrument (0.08 ng/l) x minimum dilution of 2 x sample digest volume (0.1 l) x 1 /filter = (0.08 ng/l) x 2 x 0.1 l x 1 / filter = 0.016 ng/filter

2.4 Statistical analyses

Since the data were all collected as a time series, the monitored values were investigated for autocorrelation before any of the statistical testing mentioned below was conducted. Other than for temperature (as mentioned below), the autocorrelations were low (generally < 30%), and the data entered the testing "as is."

Annual mean GOM deposition estimates were compared on a site-by-site basis by examining their 95% confidence intervals (equivalent to t-tests). Similarly, the two-year deposition estimates were compared between sites using the 95% confidence intervals. In comparing between sites, no adjustment was made for the fact that multiple comparisons were being conducted.

Temperature data exhibited significant autocorrelation and therefore were averaged over six week time periods. These six week averages were then used to calculate annual means at each site. The annual means were compared via their 95% confidence intervals.

To examine temporal trend across the two year period, the seasonal Kendall test (Hirsch et al., 1982) was employed at each site. The monitoring years were divided into quarters (August-October, November-January, February-April, and May-July), and quarterly means were calculated. Because only two years of data were available, the exact form of the test was used.

2.5 Back trajectory analyses

To obtain initial information regarding mercury source impacts on the Four Corners area monitoring sites, back trajectory analyses were conducted for the highest three and lowest three GOM dry deposition two-week sampling periods at the Mesa Verde National Park site (CO99), the highest GOM dry deposition site in the two-year study. The National Oceanic and Atmospheric Administration (NOAA) HYSPLIT model (Draxler and Rolph, 2012) was employed to produce seven 48-hour back trajectories encompassing each two-week sampling period. Each back trajectory used the Eta Data Assimilation System (EDAS) meteorological data resident in the HYSPLIT model, and was conducted at a starting height of 500 meters above ground level, a height referenced in recent literature (Gustin et al., 2012).

3. Results and Discussion

3.1 Detection limit, precision, and comparison of surrogate surface passive sampling

The detection limit for the surrogate surface passive GOM dry deposition sampling using the FADD filter membranes, calculated from three times the standard deviation of the field blanks, was 0.42 ng/filter membrane (0.12 ng/m^2h based upon an 0.0102 m^2 exposure area of the surrogate surfaces) for two-week deployments averaged over all seven sites, compared to the 0.05 ng/m^2h detection limit reported in Lyman et al., 2009. All field samples collected by the

surrogate surface passive samplers were at or above the detection limit. The average field blank GOM loading for both years was 0.3 ng/filter membrane, compared to an average laboratory blank GOM loading of 0.23 ng/filter membrane for both years. The 0.07 ng/filter membrane increase in the field blanks was probably attributed to use of the Petri dish. The average field sample GOM loadings were 1.2 ng/filter membrane at the Stilwell site (OK99) and 4.85 ng/filter membrane at the Mesa Verde National Park site (CO99) for year 2 of the study, representing the lowest and highest GOM dry deposition sites respectively. For data validation purposes, data screening and outlier analysis was conducted for the complete two year dataset, with data not used due to (a) known contamination issues identified by either the site operators or laboratory chemists, (b) duplicate field samples with numerical differences greater than 200 ng/m^2 (or with dry deposition rate differences greater than 0.6 ng/m^2h) or (c) field blank or field sample values greater than 10 standard deviations from the overall study field blank or site specific field sample arithmetic means. Based on Pukelsheim (1994), this last criterion would reject valid samples no more than 1% of the time, and probably no more than 0.4% or less of the time. Few data points were excluded from analysis, with 98% data completeness for field blanks and 98%-100% data completeness for field samples for all sites except for site NM97 (Valles Caldera National Preserve), which registered a 92% data completeness rate for field samples. All final two-week GOM dry deposition estimates were derived by subtracting field blank estimate data from field sample estimate data for each specific site.

The precision for the two year study was reviewed by conducting relative percent difference (RPD) analyses of all FADD filter membrane field sample duplicates. RPD was defined as RPD = [absolute difference of field sample duplicates/average of field sample duplicates]*100%. For all of the field duplicate samples (N=194), 78% had RPDs <= 20%, with

RPD increasing for lower GOM dry deposition estimates (reference Figure S3 in the Supporting Material). The median RPD for the two year study was 10%, comparing favorably with Peterson et al., 2012. On a site by site basis, the highest GOM dry deposition estimate site (CO99-Mesa Verde National Park, N=27) had 93% of all field duplicate sample RPDs <= 20% , while the lowest GOM dry deposition estimate site (OK99-Stilwell, N=25; OK99 also a lower GOM concentration site) had 60% of all field duplicate sample RPDs <=20%.

For data confidence purposes, the surrogate surface passive GOM sampling using the FADD filter membranes was evaluated by comparing collocated GOM FADD dry deposition rate estimates with Tekran GOM ambient concentrations at the Stilwell (OK99) site (Figure 2). As a reminder, even at 75% or greater data completeness for each two week comparison period, the Tekran instrument records data for 50%-67% of the time, versus the passive surrogate surface which collects data for 100% of the time during each two week comparison period. This is due to the Tekran instrument only being able to measure the atmosphere for each two out of every three hours. Despite the low GOM ambient concentrations at the Stilwell site (OK99) recorded by the Tekran, the GOM dry deposition rate estimate data was correlated to the GOM ambient concentration data with a correlation coefficient r of 0.60, similar to correlations at other low GOM ambient concentration sites reported in previous peer-reviewed published literature (Castro et al., 2012; Lyman et al., 2009; Peterson et al., 2012). GOM ambient concentrations at the Stilwell site (OK99) were low, less than 7 picograms (pg)/m^3 for two week average time periods.

The GOM concentration estimates from the Tekran at the Stilwell, OK site (OK99) were modeled to GOM deposition estimates using an annual average deposition velocity (V_d) of 0.9 cm/s as per Zhang et al. 2012. The results are shown in Figure S4 in the Supporting Material,

comparing the modeled estimates with the measured GOM deposition estimates from the passive surrogate surfaces. The Tekran modeled estimates using the V_d of 0.9 cm/s were lower than the measured estimates by a factor of 2.6 (i.e. sum of Tekran modeled estimates = 756 ng/m^2 while the sum of the measured estimates with the passive surrogate surfaces = 1993 ng/m^2 for the period of collocated comparison). The paper by Zhang et al. 2012 cites Lyman et al. 2007 where modeled GOM dry deposition estimates were a factor of two or more less than comparison surrogate surface measurements. In addition, uncertainties in V_d can generally be within a factor of two (Lyman et al., 2007). Figure S4 in the Supporting Material also shows modeled GOM deposition estimates using a higher V_d of 2.4 cm/s at the Stilwell (OK99) site, which provide for a closer total comparison to the measured data from the surrogate surfaces for the period of collocated comparison.

3.2 GOM dry deposition estimates

Time series analysis. The GOM dry deposition estimates data time series in the Four Corners area followed a similar regional pattern at all sites for both years except for the high elevation mountain Molas Pass (CO96) site (Figure 3). Comparing the data across all sites revealed medium to high correlation coefficients across all of the Four Corners sites except for the Molas Pass site (CO96), where lower correlation coefficients were recorded (Table 1). Note the particularly high correlation coefficients (r^2 = 0.92 or 0.93) recorded between the three central Four Corners area sites at Substation (NM95), Farmington Airport (NM99) and Navajo Lake (NM98). Year one and year two data time series are compared in Figure 4. Each year of time series in Figure 4 begins on the left in the summer/fall season and progresses to the right through the fall/winter, winter/spring, and spring/summer seasons. From the north (Mesa Verde National Park – CO99) to the central (Substation (NM95), Farmington Airport (NM99), Navajo Lake

(NM98)) and to the south (Valles Caldera National Preserve (NM97)) of the Four Corners area, five sites exhibited similar time series traces for GOM dry deposition for both years, showing peak GOM dry deposition estimates in the spring and summer, and the lowest GOM dry deposition estimates in the winter. Note also how in general year 2 tracks similarly to year 1, with year 2 being generally higher. The only site that does not follow the regional pattern is the high elevation mountain Molas Pass site (CO96), the most northern site in the study and the highest site in terms of elevation (3 249 m asl). The higher precipitation amounts in the mountains versus the surrounding lowlands likely contributes to the lower dry deposition of GOM at this site. The weekly NADP rain gage data from the Molas Pass site (CO96) over the course of the two year study (66 total inches (1 676 mm)) was higher than the hourly precipitation totals over the course of the two year study at the Valles Caldera National Preserve (NM97) site (38 total inches (965 mm)) and the Mesa Verde National Park (CO99) site (29 total inches (737 mm)). GOM dry deposition is strongly affected by precipitation, so a different precipitation regime in the mountains versus the surrounding lowlands could result in more scrubbing out of the GOM dry deposition in the air at a mountain site.

The Mesa Verde National Park (CO99) site (2 172 m asl) was usually the highest GOM dry deposition site, with the Substation (NM95) site (1 678 m asl) generally the second highest GOM dry deposition site. Looking at both years of data, the Mesa Verde National Park site (CO99) recorded the highest bi-weekly GOM dry deposition estimate 75% of the time (39/52), with the Substation site (NM95) recording the second highest bi-weekly GOM dry deposition estimate 56% of the time (29/52). For both years the Mesa Verde National Park site (CO99) recorded either the highest or second highest bi-weekly GOM dry deposition estimates 94% of the time (49/52), while the Substation site (NM95) recorded either the highest or second highest

bi-weekly GOM dry deposition estimates 69% of the time (36/52). Analysis of hourly wind direction data revealed that the Mesa Verde National Park site (CO99) was downwind of the Four Corners Power Plant, the largest power plant with no mercury controls versus the 80% controlled San Juan Power Plant, a higher percentage of time than the Substation site (NM95). The Mesa Verde National Park site (CO99) was downwind (using compass degrees between 135 degrees and 225 degrees) of the Four Corners Power Plant 22% of the time during the two year study while the Substation site (NM95) was downwind of the Four Corners Power Plant 12% of the time during the two year study.

Mean GOM dry deposition estimates were calculated for each of the seven sites for the entire two year period. Using 95% confidence intervals, the 2-year mean GOM dry deposition estimate for the Mesa Verde National Park site (CO99) was statistically significantly higher than all of the other sites except for the Substation site (NM95), although the 2-year total GOM dry deposition estimate for the Mesa Verde National Park site (CO99) was still 3 417 ng/m^2 higher than the Substation site (NM95). The 2-year means for the Substation (NM95), Valles Caldera National Preserve (NM97), Farmington Airport (NM99) and Navajo Lake (NM98) sites were not statistically significantly different, although the 2-year total GOM dry deposition estimate for the Substation site (NM95) was still 2 398 ng/m^2 higher than the Farmington Airport site (NM99) and 3 085 ng/m^2 and 3 129 ng/m^2 higher than the Valles Caldera National Preserve (NM97) and Navajo Lake (NM98) sites, respectively. The Molas Pass site (CO96) 2-year mean GOM dry deposition estimate was statistically significantly lower than all of the other Four Corners area sites.

The two year time series GOM dry deposition data for the Stilwell site (OK99) was considerably lower than all sites in the Four Corners area, including the Molas Pass (CO96) site

(Figure 3). The Stilwell site (OK99) recorded over 110 inches of precipitation over the two year study versus the under 40 inches of precipitation recorded at the Valles Caldera National Preserve site (NM97) and the under 30 inches of precipitation recorded at the Mesa Verde National Park site (CO99). Thus, as mentioned earlier for the Molas Pass site (CO96), GOM dry deposition is strongly affected by precipitation, so more precipitation at Stilwell (OK99) could result in more scrubbing out of the GOM dry deposition in the air at the Stilwell site (OK99). For all sites except the high elevation mountain Molas Pass site (CO96), the year 2 GOM dry deposition estimates were statistically significantly higher compared to the year 1 GOM dry deposition estimates. A likely contributing factor to the higher year 2 GOM dry deposition estimates at six of the seven sites was the statistically significantly higher ambient temperature found at all of the meteorological data sites in year 2 versus year 1, especially for the three quarters from August, 2010 to April, 2011. Higher ambient temperatures can lead to increased oxidation of elemental mercury to GOM (Lin et al., 2012). The higher GOM dry deposition estimates recorded in the May-July period of the second year (vs. the first year) in the Four Corners area may also have resulted in part from two additional factors: (1) increased mercury emissions from stationary sources as indicated by statistically significantly higher ambient sulfur dioxide concentrations recorded at the Substation site (NM95) in May-July of year 2 (0.5 ppb mean) versus May-July of year 1 (0.2 ppb mean); and (2) increased mercury emissions downwind of the large Wallow (Arizona/New Mexico) and Las Conchas (Northcentral New Mexico) Fires, which occurred beginning May 29, 2011 (Wallow) and June 26, 2011 (Las Conchas), during year 2 of our study. There were no reported large fires of this magnitude during year 1 of our study. Smoke plumes from fires primarily output mercury in elemental form, with some output also in particle form (Friedli et al., 2003) and reactive gaseous form

(Wang et al, 2010). GOM output is minimal within fire smoke plumes (Obrist et al., 2008); however, as the plumes move farther downwind some of the increased elemental mercury from the plumes could convert to GOM, especially during a period of warm temperatures such as observed during the fourth quarter of the second year of this study.

As noted above, the monitoring data suggests a significantly higher level of GOM dry deposition in the second year of the study. To examine this in more detail, the data were tested for a time trend using the exact form of the seasonal Kendall test on quarterly means at each site. The results showed that mean GOM dry deposition estimates increased within each quarter at every site except the Molas Pass site (CO96). Thus, a statistically significant ($p=.0625$) increase in GOM dry deposition was observed at the Stilwell, Oklahoma site (OK99) and across the Four Corners region in year 2 (except at Molas Pass – CO96).

Back trajectory analysis. To obtain some initial information regarding mercury source impacts on the Four Corners area monitoring sites, a back trajectory analysis was conducted for the highest three and lowest three GOM dry deposition two-week sampling periods at the Mesa Verde National Park site (CO99), the highest GOM dry deposition site in the two-year study. The highest two-week GOM dry deposition measurement at the Mesa Verde National Park site (CO99) occurred from March 29 – April 12, 2011 with an estimate of 1 107 ng/m^2 (Figure 4). For this example, the National Oceanic and Atmospheric Administration (NOAA) HYSPLIT model (Draxler and Rolph, 2012) was employed to produce seven 48-hour back trajectories encompassing the two-week period March 29-April 12, 2011. All seven back trajectories along with the locations of the four coal-fired power plants in the Four Corners area are plotted in Figure 5. Three of the back trajectories pass almost directly over the two largest Four Corners area power plants, the largest anthropogenic mercury emissions source sector in the area. But

other arriving air masses were not as proximal to the Four Corners power plants. This suggests multiple mercury emission sources (e. g., local and regional, including coal-fired power plants; natural and global, including subsiding air containing mercury from the free troposphere) may be impacting the mercury deposition monitoring sites. The back trajectory maps for the second and third highest GOM dry deposition two-week sampling periods at the Mesa Verde National Park site (CO99) similarly indicate arriving air masses passing over the areas containing the Four Corners area power plants, as well as other trajectories not as proximal to the Four Corners power plants. These additional two maps can be viewed in the Supporting Material (see Figures S5 and S6). Interestingly for these top three GOM dry deposition two-week sampling periods at the Mesa Verde National Park site (CO99), which all occurred in the spring months, all back trajectories pass over the Four Corners area or other areas in the western U.S., not other areas in the central or eastern U.S. These southwest and northwest back trajectories for high mercury deposition events have also been reported in Oregon (Weiss-Penzias et al., 2007), in Utah (Peterson and Gustin, 2008), and in Nevada (Huang and Gustin, 2012).

Back trajectories were also conducted for the three lowest GOM dry deposition two-week sampling periods at the Mesa Verde National Park (CO99) site, which all occurred in the winter months, and all three plots can be viewed in the Supporting Material (Figures S7, S8 and S9). For the two-week period December 22, 2009 – January 5, 2010 (Figure S8), none of the seven plotted two-week back trajectories passed proximal to the largest Four Corners power plants. The other two low deposition back trajectory plots did contain some air masses passing proximal to the two largest Four Corners area power plants (Figures S7 and S9). However, each of the back trajectory air masses passing over the largest Four Corners power plants in Figures S7 and S9 were also associated with precipitation being measured at the time of pass-over at the Mesa

Verde National Park site (CO99), unlike the three highest GOM dry deposition two-week sampling periods analyzed above, where the back trajectory air masses passing over the largest Four Corners power plants were not associated with any precipitation being measured at the time of pass-over at the Mesa Verde National Park site (CO99). Precipitation occurring as the air masses pass over the power plants would tend to lower the GOM deposited downwind of the power plant plumes.

Comparison with other extended length U.S. studies. Annual and 2-year cumulative data summaries for GOM dry deposition, mercury wet deposition, and conservative total mercury deposition estimates are found in Tables 2 and 3. Seasonal data summaries are presented in the Supporting Material (Table S2). For comparison purposes, Table 2 also presents annual data summaries from previous extended length GOM dry deposition studies conducted in the U.S. in Nevada, Georgia, Florida, and Maryland (Castro et al., 2012; Lyman et al., 2009; Peterson et al., 2012). The second year GOM dry deposition estimate for the Mesa Verde National Park site (CO99) was the highest annual GOM dry deposition estimate reported in the U.S. to date using the smooth-edge surrogate surface passive samplers. Also, note how dry deposition comprises a significant portion of the total mercury estimates in the arid Four Corners area, up to 51% for the two year period August, 2009-August, 2011 (Table 3). The annual GOM dry deposition estimates at all six Four Corners area sites were higher than the annual GOM dry deposition estimates recorded at eastern U.S. sites in Georgia, Florida and Maryland. In contrast to the more arid Four Corners and Reno, Nevada areas, the more humid eastern Oklahoma site at Stilwell (OK99) was dominated by wet deposition, with the dry deposition averaging a lower percentage of 11% of the total estimated mercury deposition for the two year period August, 2009-August, 2011. However, when combining the dry deposition GOM estimates and wet

deposition mercury estimates to get a conservative total mercury deposition estimate, the Stilwell site (OK99) is the second highest total mercury deposition site in the two year study, below only the Mesa Verde National Park (CO99) total mercury deposition site estimate for the two year study (Table 3, and Figure S1 in the Supporting Material). In year 1 of the study the Stilwell site (OK99) had the highest total mercury deposition estimate for all seven sites (Table 2), indicating how wet mercury deposition strongly dominates at the Stilwell site (OK99). This wet deposition domination is also seen at many eastern U.S. sites such as in Georgia, Florida and New England (Lombard et al., 2011; Lyman et al., 2009; Peterson et al., 2012).

Study Implications. Further monitoring of these two areas is planned in about four years after completion of the implementation of the mercury controls required by the new power plant and boiler rules recently promulgated by the U.S. EPA. The power plant rule projects a 90% mercury control rate, so GOM dry deposition is expected to dramatically decrease in the future from this significant mercury emission source in the U.S. However, there are other local/regional/global/natural sources of GOM dry deposition beyond power plants and boilers, which could be contributing more or less GOM dry deposition to the atmosphere than the power plants and boilers. A significant amount of the air masses in the back trajectories tracked back through both the Four Corners region and high elevations of the western U.S. Thus, it is important that this study has set a credible GOM dry deposition estimate baseline for the Four Corners area and eastern Oklahoma which can be compared to future monitoring results to help assess the effectiveness of the new mercury pollution controls on power plants and boilers at significantly decreasing total amounts of atmospheric GOM dry deposition recorded at certain monitoring sites. In light of this study which found statistically significant differences between

year 1 and year 2, it is recommended that at least two years of data be collected in the future to adequately account for inter-annual variability in both emissions and meteorology.

4. Conclusions

This two year study has provided the first extended length gaseous oxidized mercury (GOM) dry deposition monitoring data in two areas of the U.S. not previously sampled, the Four Corners area and eastern Oklahoma. The Four Corners area was hypothesized to have a significant portion of its total mercury deposited to the earth in dry processes, and indeed dry mercury deposition (conservatively represented by the GOM dry deposition measurements) ranged from 40%-51% of total mercury deposition at the Four Corners area monitoring sites. Interestingly, at the highest elevation site in the Four Corners area (3 249 m asl), the estimated dry deposition contribution to the total mercury deposition was notably lower for the two year period at 24%. The more humid and lower elevation Stilwell (OK99) site (304 m asl) in eastern Oklahoma was dominated by wet mercury deposition, with the GOM dry deposition estimate contributing a lower percentage of 11% to the two year mercury deposition total estimate at that site. To reiterate, since only GOM dry deposition is estimated in this paper, the dry mercury deposition estimates discussed are conservative (i.e., probably underestimates) because they do not include complete dry deposition inputs from particle bound mercury and gaseous elemental mercury. However, in arid areas with less vegetative cover, deposition of gaseous elemental mercury is lower (Hartman et al., 2009), and it is unknown what size particles and fraction of particles might be collected on the down facing smooth-edge surrogate surface passive sampler. The smooth-edge surrogate surface passive sampler has been shown to adequately operate at different wind speeds (Huang et al., 2011; Lyman et al., 2010a), such as experienced during our

two year study, and the down-facing orientation protects the collecting filter membranes from absorbing large amounts of precipitation and dew.

The data produced here for the Four Corners area showed a similar regional GOM dry deposition data pattern for all sites except for the high elevation mountain site, and consistently showed the highest or second highest GOM dry deposition estimates at Mesa Verde National Park (CO99). The similar regional data pattern recorded at five of the six sites supports the premise that those sites were significantly impacted by the same regional/natural/global mercury emission sources. Variations in the underlying regional data pattern at five of the Four Corners monitoring sites probably occurred due to: (a) different distances of local/regional mercury emission sources, such as coal-fired power plants, to the monitoring sites; and (b) different percentages of time the monitoring sites were downwind of local/regional mercury emission sources. For example, the Mesa Verde National Park site (CO99) was further away from the large non-mercury emission controlled Four Corners coal-fired power plant than the Substation site (NM95), but was downwind of the Four Corners coal-fired power plant a higher percentage of time than the Substation site (NM95). Data from this study, and planned future monitoring after the completion of mercury emissions control on U.S. coal-fired power plants and boilers, will help in hypothesizing how much mercury (whether it be high or low amounts) is contributed from regulated U.S. coal-fired power plants and boilers to total atmospheric mercury emissions, which also include other local, regional, natural and global mercury emissions.

Acknowledgements and Disclaimer

The authors are grateful to the following managers and field operators involved in careful ambient data collection, including Terry Hertel and Joseph Cotie of the New Mexico

Environment Department, Kelly Palmer and Brian Parker of the U.S. Forest Service (USFS)/Bureau of Land Management (BLM), George San Miguel and Paul Bohmann of the National Park Service (NPS-Mesa Verde National Park), Tammy Belone of the Pueblo of Jemez, and Robert Parmenter of the Valles Caldera National Preserve. The authors are also grateful to Diana Greiner of the U.S. EPA Region 6 for her detailed GIS map work. The U.S. EPA through its Office of Research and Development funded and managed the research described here under contracts EPD05065 to Alion and EP09D000391 and EP10D000659 to Frontier Global Sciences. This paper has been subjected to Agency review and approved for publication.

Supporting Material Available

Additional Detailed Information Regarding GOM Monitoring Sites and Seasonal GOM Data; GOM dry deposition monitoring sites locational and meteorological characteristics (Table S1); Seasonal GOM dry deposition and mercury wet deposition estimates for Four Corners and Eastern Oklahoma sites (Table S2); Elevation, mercury deposition estimates from the 2009-2011 Four Corners/Eastern Oklahoma GOM dry deposition monitoring study, and locations of coal-fired power plants within 100 km of the mercury deposition monitoring sites with coal-generated electricity capacity greater than or equal to 100 megawatts (MW)(Figure S1); GOM Dry Deposition Monitoring Stand at the Valles Caldera National Preserve site and detailed schematic of the aerodynamic sampler head (Figure S2); Precision in terms of relative percent difference (RPD) of the Frontier Atmospheric Dry Deposition (FADD) filter membrane field sample duplicates for the 2009-2011 Four Corners Area and Eastern Oklahoma GOM Dry Deposition Monitoring Study (Figure S3); Modeled Tekran GOM deposition estimates (Figure S4); Back Trajectory Analysis at Mesa Verde National Park site (CO99) April 26 – May 10, 2011 (Figure S5); Back Trajectory Analysis at Mesa Verde National Park site (CO99) June 7 – June 21, 2011

(Figure S6); Back Trajectory Analysis at Mesa Verde National Park site (CO99) December 9 – December 22, 2009 (Figure S7); Back Trajectory Analysis at Mesa Verde National Park site (CO99) December 22, 2009 – January 5, 2010 (Figure S8); Back Trajectory Analysis at Mesa Verde National Park site (CO99) February 2 – February 16, 2010 (Figure S9); This information is available free of charge via Internet at http://www.atmospolres.com.

References

Brown, R.J.C., Kumar, Y., Brown, A.S., Kim, K-H., 2011. Memory Effects on Adsorption Tubes for Mercury Vapor Measurement in Ambient Air: Elucidation, Quantification, and Strategies for Mitigation of Analytical Bias, *Environmental Science & Technology*, 45, 7812-7818.

Caldwell, C.A., Swartzendruber, P., Prestbo, E., 2006. Concentration and Dry Deposition of Mercury Species in Arid South Central New Mexico (2001-2002), *Environmental Science & Technology*, 40, 7535-7540.

Castro, M.S., Moore, C., Sherwell, J., Brooks, S.B., 2012. Dry deposition of gaseous oxidized mercury in Western Maryland, *Science of the Total Environment*, 417-418, 232-240.

Draxler, R.R. and Rolph, G.D., 2012. HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website (http://ready.arl.noaa.gov/HYSPLIT.php). NOAA Air Resources Laboratory, Silver Spring, MD.

Electric Power Research Institute, 2010. Measuring Mercury's Chemistry in Power Plant Plumes, Product ID 1022188, September, 2010. Available at: http://www.epri.com/search/Pages/results.aspx?k=Measuring%20Mercury's%20Chemistry%20in%20Power%20Plant%20Plumes

Friedli, H.R., Radke, L.F., Lu, J.Y., Banic, C.M., Leaitch, W.R., MacPherson, J.I., 2003. Mercury emissions from burning of biomass from temperate North American forests: laboratory and airborne measurements, *Atmospheric Environment*, 37, 253-267.

Gay, D., Van der Jagt, G., Spadafora, K., Rhodes, M., 2006. Quality Assurance Plan, Mercury Analytical Laboratory, National Atmospheric Deposition Program.

Gustin, M. and Jaffe, D., 2010. Reducing the Uncertainty in Measurement and Understanding of Mercury in the Atmosphere, *Environmental Science & Technology*, 44, 2222-2227.

Gustin, M.S., Weiss-Penzias, P.S., Peterson, C., 2012. Investigating sources of gaseous oxidized mercury in dry deposition at three sites across Florida, USA, *Atmospheric Chemistry and Physics*, 12, 9201-9219.

Hartman, J.S., Weisberg, P.J., Pillai, R., Ericksen, J.A., Kuiken, T., Lindberg, S.E., Zhang, H., Rytuba, J.J., Gustin, M., 2009. Application of a Rule-Based Model to Estimate Mercury Exchange for Three Background Biomes in the Continental United States, *Environmental Science & Technology*, 43, 4989-4994.

Hirsch, R.M., Slack, J.R., Smith, R.A., 1982. Techniques of Trend Analysis for Monthly Water Quality Data, *Water Resources Research*, 18, 107-121.

Huang, J., Liu, Y., Holsen, T.M., 2011. Comparison between knife-edge and frisbee-shaped surrogate surfaces for making dry deposition measurements: Wind tunnel experiments and computational fluid dynamics (CFD) modeling, *Atmospheric Environment*, 45, 4213-4219.

Huang, J., Choi, H-D., Landis, M.S., Holsen, T.M, 2012. An application of passive samplers to understand atmospheric mercury concentration and dry deposition spatial distributions, *Journal of Environmental Monitoring*, 14(11), 2976-2982.

Huang, J. and Gustin, M.S., 2012. Evidence for a Free Troposphere Source of Mercury in Wet Deposition in the Western United States, *Environmental Science & Technol*ogy, 46, 6621-6629.

Kim, K.H., Ebinghaus, R., Schroeder, W.H., 2005. Atmospheric mercury concentrations from several observatory sites in the Northern Hemisphere, *Journal of Atmospheric Chemistry*, 50, 1-24.

Lai, S-O., Huang, J., Hopke, P.K., Holsen, T.M., 2011. An evaluation of direct measurement techniques for mercury dry deposition, *Science of the Total Environment*, 409, 1320-1327.

Latysh, N.E. and Wetherbee, G.A., 2012. Improved mapping of National Atmospheric Deposition Program wet-deposition in complex terrain using PRISM-gridded data sets, *Environmental Monitoring and Assessment*, 184, 913-928.

Lin, C-J., Shetty, S.K., Pan, L., Pongprueksa, P., Jang, C., Chu, H-W., 2012. Source attribution for mercury deposition in the contiguous United States: Regional difference

and seasonal variation, *Journal of the Air & Waste Management Association*, 62(1), 52-63.

Lindberg, S., Bullock, R., Ebinghaus, R., Engstrom, D., Feng, X., Fitzgerald, W., Pirrone, N., Prestbo, E., Seigneur, C., 2007. A Synthesis of Progress and Uncertainties in Attributing the Sources of Mercury in Deposition, *Ambio*, 36, 19-32.

Lombard, M.A.S., Bryce, J.G., Mao, H., Talbot, R., 2011. Mercury deposition in Southern New Hampshire, 2006-2009, *Atmospheric Chemistry and Physics*, 11, 7657-7668.

Lyman, S.N., Gustin, M.S., Prestbo, E.M., Marsik, F.J., 2007. Estimation of Dry Deposition of Atmospheric Mercury in Nevada by Direct and Indirect Methods, *Environmental Science & Technology*, 41, 1970-1976.

Lyman, S.N., Gustin, M.S., Prestbo, E.M., Kilner, P.I., Edgerton, E., Hartsell, B., 2009. Testing and Application of Surrogate Surfaces for Understanding Potential Gaseous Oxidized Mercury Dry Deposition, *Environmental Science & Technology*, 43, 6235-6241.

Lyman, S.N., Gustin, M.S., Prestbo, E.M., 2010a. A passive sampler for ambient gaseous oxidized mercury concentrations, *Atmospheric Environment*, 44, 246-252.

Lyman, S.N., Jaffe, D.A., Gustin, M.S., 2010b. Release of mercury halides from KCl denuders in the presence of ozone, *Atmospheric Chemistry and Physics*, 10, 8197-8204.

Mast, M.A., Campbell, D.H., Krabbenhoft, D.P., Taylor, H.E., 2005. Mercury Transport in a High-Elevation Watershed in Rocky Mountain National Park, Colorado, *Water, Air, and Soil Pollution*, 164, 21-42.

Mast, M.A., Manthorne, D.J., Roth, D.A., 2010. Historical deposition of mercury and selected trace elements to high-elevation National Parks in the Western U.S. inferred from lake-sediment cores, *Atmospheric Environment*, 44, 2577-2586.

Mountain Studies Institute, 2010. Sources of Atmospheric Mercury Concentrations and Wet Deposition at Mesa Verde National Park, Southwestern Colorado, 2002-08. Mountain Studies Institute Report 2010-03 by Wright, W.G. and Nydick, K. Available at: http://www.mountainstudies.org/sites/default/files/pdf/research/mercury/MesaVerde_Hg_Sources_FINAL_Sept29_2010.pdf

National Atmospheric Deposition Program, 2011a. *National Atmospheric Deposition Program 2010 Annual Summary*. NADP Data Report 2011-01, pp 18-20. Illinois State Water Survey, University of Illinois at Urbana-Champaign, IL.

National Acid Deposition Program, 2011b. AMNet Operations Manual 2011-05, Version 1.0. Available at: http://nadp.sws.uiuc.edu/amn/docs/AMNet_Operations_Manual.pdf

Obrist, D., Moosmuller, H., Schurmann, R., Antony Chen, L-W., Kreidenweis, S.M., 2008. Particulate-Phase and Gaseous Elemental Mercury Emissions During Biomass Combustion: Controlling Factors and Correlation with Particulate Matter Emissions, *Environmental Science & Technology*, 42, 721-727.

Pandey, S., Kim, K-H., Brown, R.J.C., 2011. Measurement techniques for mercury species in ambient air, *Trends in Analytical Chemistry*, 30(6), 899-917.

Peterson, C. and Gustin, M., 2008. Mercury in the air, water and biota at the Great Salt Lake (Utah, USA), *Science of the Total Environment*, 405, 255-268.

Peterson, C., Alishahi, M., Gustin, M.S., 2012. Testing the use of passive sampling systems for understanding air mercury concentrations and dry deposition across Florida, USA, *Science of the Total Environment*, 424, 297-307.

Prestbo, E.M. and Gay, D.A., 2009. Wet deposition of mercury in the U.S. and Canada, 1996-2005: Results and analysis of the NADP mercury deposition network (MDN), *Atmospheric Environment*, 43, 4223-4233.

Pukelsheim, F., 1994. The Three Sigma Rule, *The American Statistician*, 48(2), 88-91.

Schroeder, W.H. and Munthe, J., 1998. Atmospheric Mercury – An Overview, *Atmospheric Environment*, 32, 809-822.

Schuster, P.F., Krabbenhoft, D.P., Naftz, D.L., Cecil, L.D., Olson, M.L., Dewild, J.F., Susong, D.D., Green, J.R., Abbott, M.L., 2002. Atmospheric Mercury Deposition during the Last 270 Years: A Glacial Ice Core Record of Natural and Anthropogenic Sources, *Environmental Science & Technology*, 36, 2303-2310.

Skov, H., Sorensen, B.T., Landis, M.S., Johnson, M.S., Sacco, P., Goodsite, M.E., Lohse, C., Christiansen, K.S., 2007. Performance of a new diffusive sampler for Hg^0 determination in the troposphere, *Environmental Chemistry*, 4, 75-80.

Slemr, F., Brunke, E-G., Ebinghaus, R., Temme, C., Munthe, J., Wangberg, I., Schroeder, W., Steffen, A., Berg, T., 2003. Worldwide trend of atmospheric mercury since 1977, *Geophysical Research Letters*, 30, 1516, 4 pp.

Spadafora, K. and Strickland, P.G., 2008. Quality Assurance Plan, Frontier Geosciences, Inc.

U.S. EPA, 2002. Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry, EPA-821-R-02-019, August, 2002. Available at: http://water.epa.gov/scitech/methods/cwa/metals/mercury/upload/2007_07_10_methods_method_mercury_1631.pdf

U.S. EPA, 2011a. Memorandum: Emissions Overview: Hazardous Air Pollutants in Support of the Final Mercury and Air Toxics Standard; U.S. EPA; EPA-454/R-11-014, November, 2011. Available at: http://www.epa.gov/mats/pdfs/20111216EmissionsOverviewMemo.pdf

U.S. EPA, 2011b. The reconsideration proposals for the Boiler major source Maximum Achievable Control Technology (MACT), boiler area source, and commercial and industrial solid waste incinerator rules are available at 76 Federal Register 80598, 76 Federal Register 80532, and 76 Federal Register 80452 (all dated December 23, 2011), respectively, and online at www.epa.gov/airquality/combustion/.

U.S. EPA, 2012. Final Mercury and Air Toxics Standards (MATS) rule available at 77 Federal Register 9304 (dated February 16, 2012) and online at www.epa.gov/mats.

Wang, Y., Huang, J., Zananski, T.J., Hopke, P.K., Holsen, T.M., 2010. Impacts of the Canadian Forest Fires on Atmospheric Mercury and Carbonaceous Particles in Northern New York, *Environmental Science & Technology*, 44, 8435-8440.

Weiss-Penzias, P., Jaffe, D., Swartzendruber, P., Hafner, W., Chand, D., Prestbo, E., 2007. Quantifying Asian and biomass burning sources of mercury using the Hg/CO ratio in pollution plumes observed at the Mount Bachelor observatory, *Atmospheric Environment*, 41, 4366-4379.

Zhang, L., Wright, L.P., Blanchard, P., 2009. A review of current knowledge concerning dry deposition of atmospheric mercury, *Atmospheric Environment*, 43, 5853-5864.

Zhang, L., Blanchard, P., Gay, D.A., Prestbo, E.M., Risch, M.R., Johnson, D., Naravan, J., Zsolway, R., Holsen, T.M., Miller, E.K., Castro, M.S., Graydon, J.A., St. Louis, V.L., Dalziel, J., Estimation of speciated and total mercury dry deposition at monitoring locations in Eastern and Central North America, *Atmospheric Chemistry and Physics Discussions*, 2012, 12, 2783-2815.

Figure Captions

Figure 1. Monitoring sites for the August, 2009-August, 2011 Four Corners/Eastern Oklahoma GOM Dry Deposition Monitoring Study.

Figure 2. Collocated GOM concentration and GOM deposition to surfaces rate estimates at the Stilwell (OK99) site; 2-week off dates 1/19/10-6/7/11; GOM concentration data from Tekran instrument and GOM concentration data capture > 75% for each 2-week comparison period; N=27.

Figure 3. GOM dry deposition data two year time series for the Four Corners area and Stilwell, Oklahoma sites; August 4, 2009-August 2, 2011.

Figure 4. GOM dry deposition data time series for the Four Corners area and Stilwell, Oklahoma sites comparing years 1 and 2; year 1 = August 4, 2009-August 3, 2010; year 2 = August 3, 2010-August 2, 2011. The 26 two-week sampling periods are ordered as follows left to right: 1-6 (August-October), 7-13 (November-January), 14-19 (February-April), and 20-26 (May-July).

Figure 5. Back trajectory analysis for the Mesa Verde National Park site (CO99) for March 29 – April 12, 2011. Seven contiguous 48-hour back trajectories ending at 1000 LST on April 12, 2011. End date of each 48-hour back trajectory plotted for each trajectory trace (e.g. 3/31 represents 48-hour back trajectory for 3/29 – 3/31); Four Corners area coal-fired power plant locations are located at center of open circles.

Figure 1

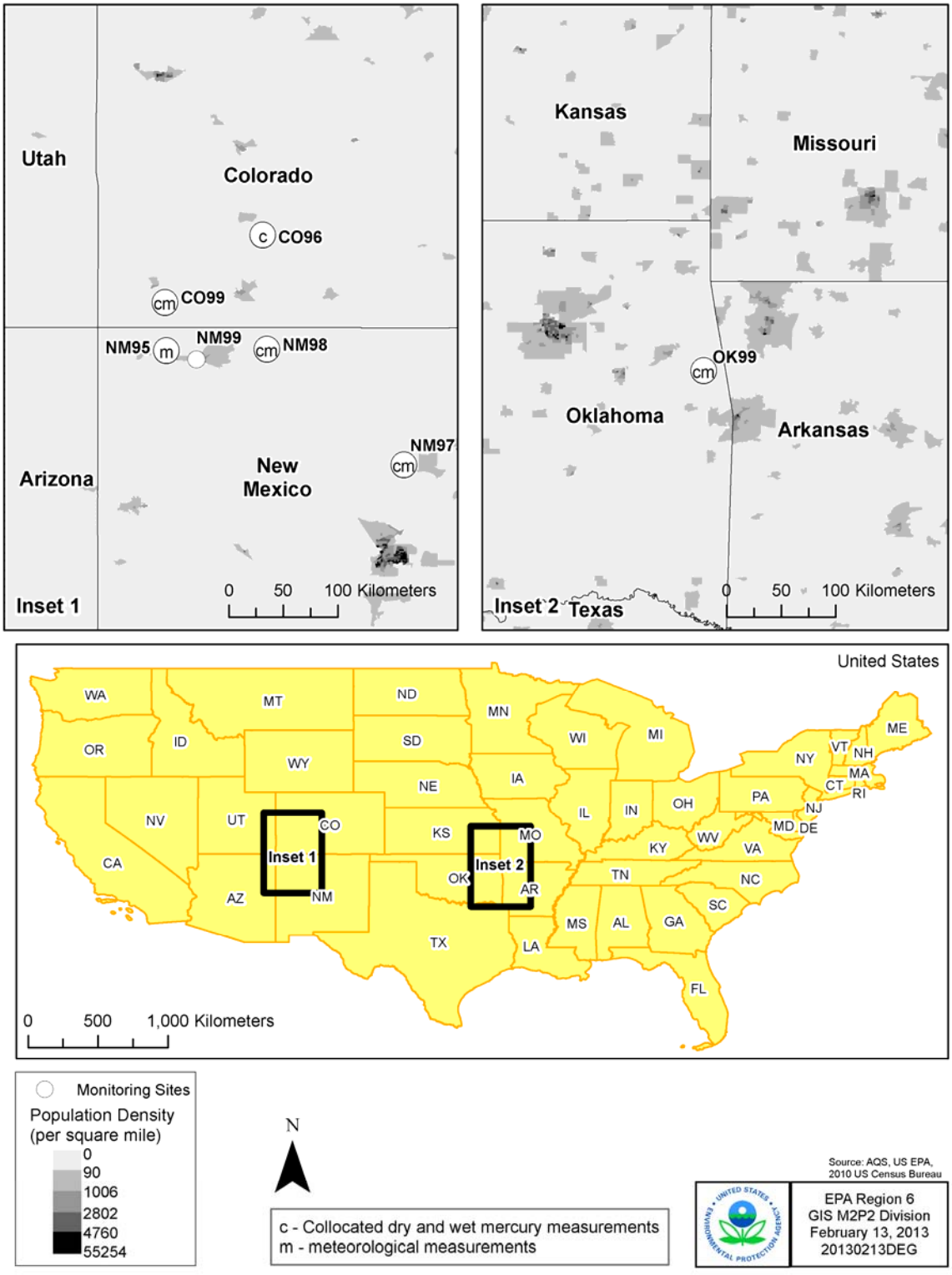

Utah
Colorado
CO96
CO99
NM95
NM99
NM98
Arizona
New Mexico
NM97
Inset 1
0 50 100 Kilometers
Kansas
Missouri
OK99
Oklahoma
Arkansas
Inset 2
Texas
0 50 100 Kilometers
United States
WA
OR
CA
ID
NV
MT
WY
UT
AZ
CO
NM
ND
SD
NE
KS
OK
TX
MN
IA
MO
AR
LA
WI
IL
MS
MI
IN
KY
TN
AL
OH
WV
GA
FL
SC
NC
VA
PA
NY
MD
DE
NJ
CT
RI
MA
VT
NH
ME
Inset 1
Inset 2
0 500 1,000 Kilometers
Monitoring Sites
Population Density
(per square mile)
0
90
1006
2802
4760
55254
N
c - Collocated dry and wet mercury measurements
m - meteorological measurements
Source: AQS, US EPA,
2010 US Census Bureau
EPA Region 6
GIS M2P2 Division
February 13, 2013
20130213DEG

Figure 2

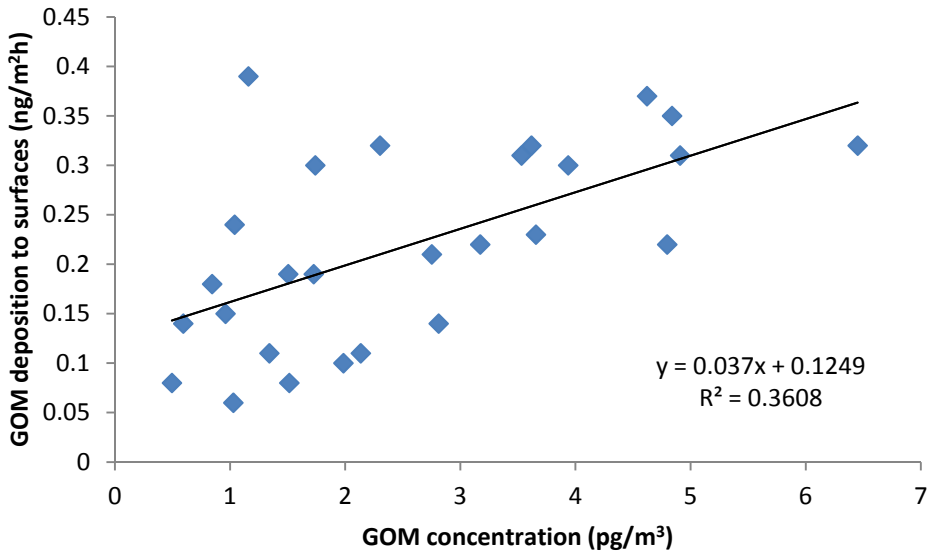

GOM deposition to surfaces (ng/m²h)
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
0
1
2
3
4
5
6
7
GOM concentration (pg/m³)
y = 0.037x + 0.1249
R² = 0.3608

Figure 3

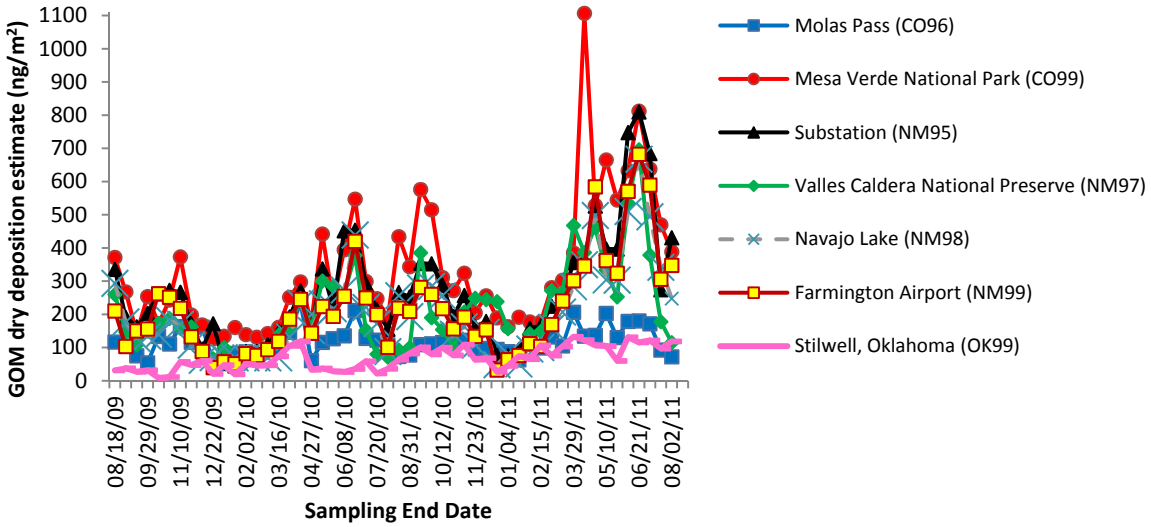
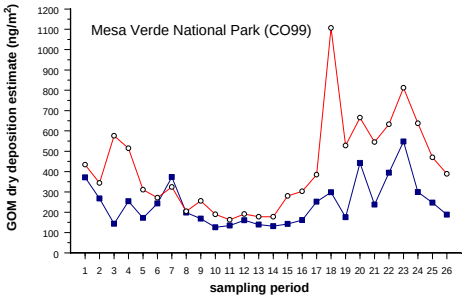
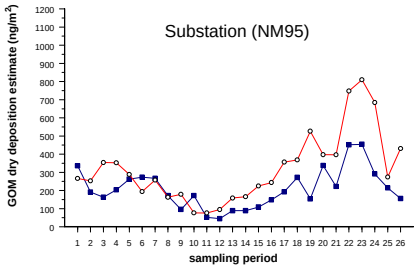
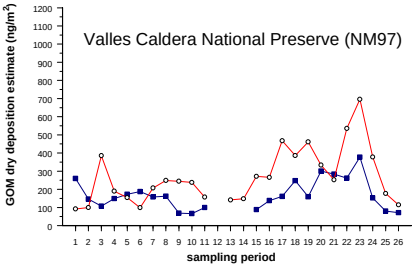
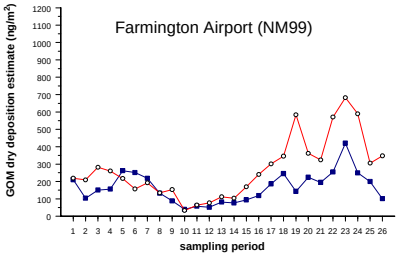

GOM dry deposition estimate (ng/m²)
1100
1000
900
800
700
600
500
400
300
200
100
0
08/18/09
09/29/09
11/10/09
12/22/09
02/02/10
03/16/10
04/27/10
06/08/10
07/20/10
08/31/10
10/12/10
11/23/10
01/04/11
02/15/11
03/29/11
05/10/11
06/21/11
08/02/11
Sampling End Date
Molas Pass (CO96)
Mesa Verde National Park (CO99)
Substation (NM95)
Valles Caldera National Preserve (NM97)
Navajo Lake (NM98)
Farmington Airport (NM99)
Stilwell, Oklahoma (OK99)

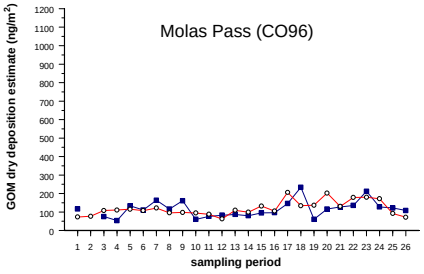
Figure 4

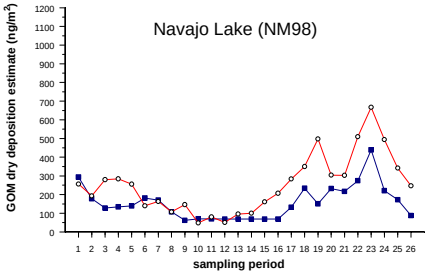

Mesa Verde National Park (CO99)
GOM dry deposition estimate (ng/m²)
sampling period


Substation (NM95)
GOM dry deposition estimate (ng/m²)
sampling period


Valles Caldera National Preserve (NM97)
GOM dry deposition estimate (ng/m²)
sampling period


Farmington Airport (NM99)
GOM dry deposition estimate (ng/m²)
sampling period


Molas Pass (CO96)
GOM dry deposition estimate (ng/m²)
sampling period


Navajo Lake (NM98)
GOM dry deposition estimate (ng/m²)
sampling period

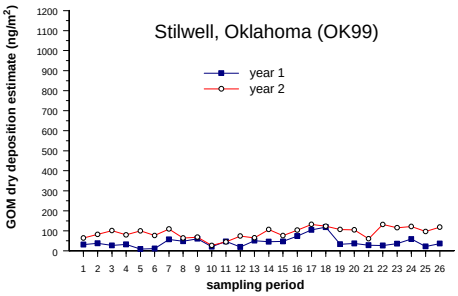

Stilwell, Oklahoma (OK99)
year 1
year 2
GOM dry deposition estimate (ng/m²)
sampling period

Figure 5

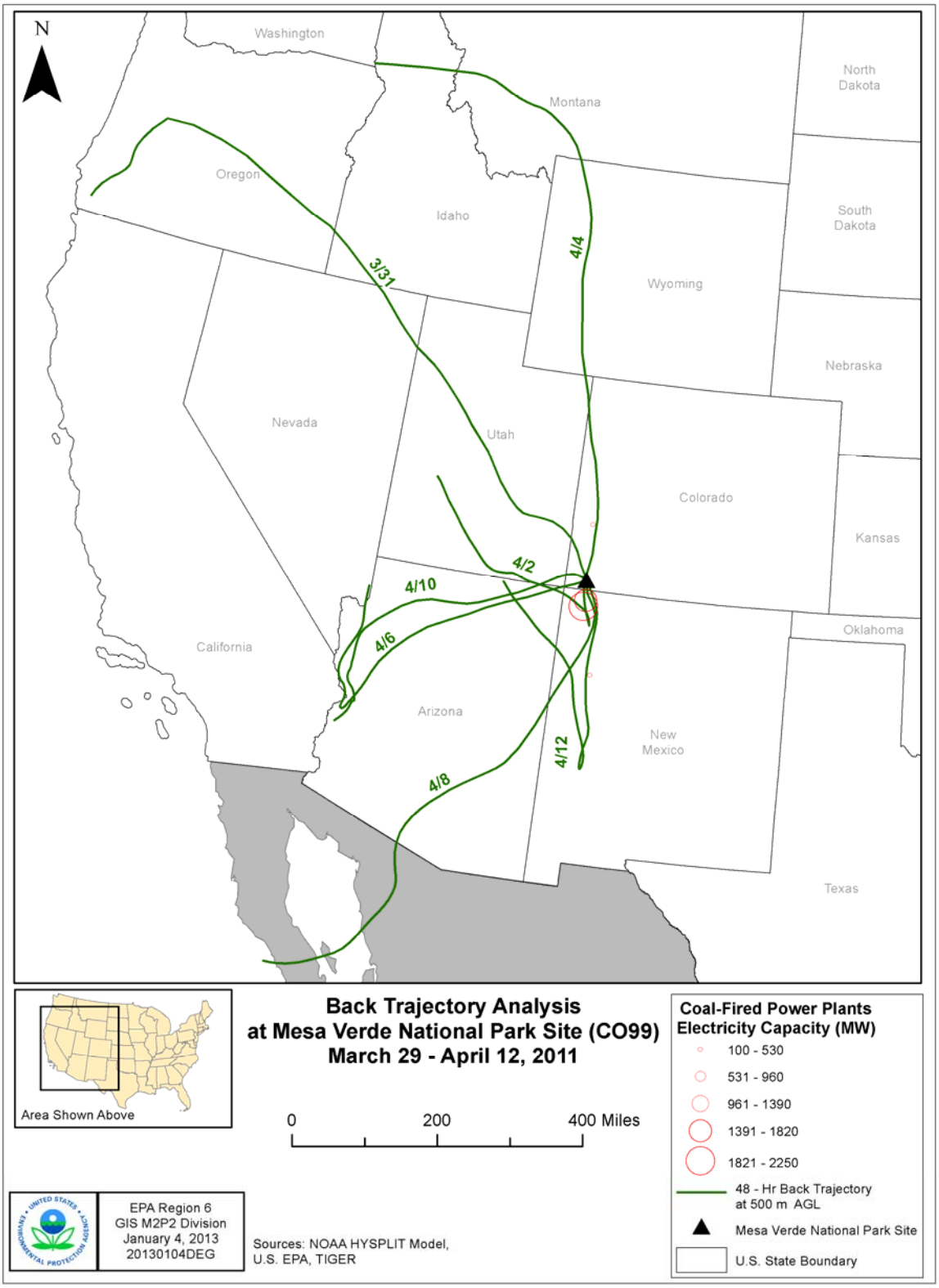

N
Washington
Montana
North Dakota
Oregon
Idaho
South Dakota
Wyoming
Nebraska
Nevada
Utah
Colorado
Kansas
California
Oklahoma
Arizona
New Mexico
Texas
3/31
4/4
4/2
4/10
4/6
4/12
4/8
Area Shown Above
Back Trajectory Analysis
at Mesa Verde National Park Site (CO99)
March 29 - April 12, 2011
0
200
400 Miles
Coal-Fired Power Plants
Electricity Capacity (MW)
100 - 530
531 - 960
961 - 1390
1391 - 1820
1821 - 2250
48 - Hr Back Trajectory
at 500 m AGL
Mesa Verde National Park Site
U.S. State Boundary
EPA Region 6
GIS M2P2 Division
January 4, 2013
20130104DEG
Sources: NOAA HYSPLIT Model,
U.S. EPA, TIGER

Table 1. Regression coefficients (r^2) for Four Corners and Stilwell, Oklahoma GOM smooth-edge surrogate surface passive sampling sites compared site to site.

Site (across and down)	Mesa Verde National Park (CO99)	Substation (NM95)	Farmington Airport (NM99)	Navajo Lake (NM98)	Valles Caldera National Preserve (NM97)	Molas Pass (CO96)	Stilwell, Oklahoma (OK99)
Mesa Verde National Park (CO99)	-----	0.63	0.64	0.71	0.52	0.24	0.32
Substation (NM95)	0.63	-----	0.92	0.90	0.64	0.33	0.27
Farmington Airport (NM99)	0.64	0.92	-----	0.93	0.64	0.36	0.31
Navajo Lake (NM98)	0.71	0.9	0.93	-----	0.68	0.33	0.27
Valles Caldera National Preserve (NM97)	0.52	0.64	0.64	0.68	-----	0.36	0.25
Molas Pass (CO96)	0.24	0.33	0.36	0.33	0.36	-----	0.18
Stilwell, Oklahoma (OK99)	0.32	~~.027~~0.27	0.31	0.27	0.25	0.18	-----

Table 2. Annual GOM dry deposition (dep.) and mercury wet deposition estimates for Four Corners, Eastern Oklahoma, and other comparison U.S. sites. For Four Corners and Eastern Oklahoma sites Year 1 = August 4, 2009 – August 3, 2010, and Year 2 = August 3, 2010 – August 2, 2011; na = not available; total mercury deposition estimates = GOM dry deposition estimates + mercury wet deposition estimates; Comparison GOM data for 10/06-10/08 sites could be higher by 0.2 ng/m^2h.

Site		GOM dry dep. estimate (ng/m^2)	Mercury wet dep. estimate (ng/m^2)	GOM dry dep. + mercury wet dep. estimates (ng/m^2)	GOM dry dep. % of total mercury dep. estimate
Mesa Verde National Park (CO99)	Year 1	6 266	8 293	14 559	43
	Year 2	10 889	8 289	19 178	57
Substation (NM95)	Year 1	5 404	na	na	na
	Year 2	8 334	na	na	na
Farmington Airport (NM99)	Year 1	4 308	na	na	na
	Year 2	7 032	na	na	na
Valles Caldera National Preserve (NM97)	Year 1	3 903	9 133	13 036	30
	Year 2	6 750	6 952	13 702	49
Navajo Lake (NM98)	Year 1	4 039	5 886	9 925	41
	Year 2	6 570	6 323	12 893	51
Molas Pass (CO96)	Year 1	2 900	7 805	10 705	27
	Year 2	3 107	11 438	14 545	21
Stilwell (OK99)	Year 1	1 118	13 452	14 570	8
	Year 2	2 350	13 263	15 613	15

Annual U.S. Comparison Sites					
Reno, Nevada (10/06-10/08; Lyman et al. 2009)		6 800	1 500	8 300	82
Yorkville, Georgia (10/06-10/08; Lyman et al. 2009)		1 900	10 700	12 600	15
Pensacola, Florida (10/06-10/08; Lyman et al. 2009)		700	13 600	14 300	5
Pensacola, Florida (7/09-7/10; Peterson et al. 2012)		1 869	16 118	17 987	10
Tampa, Florida (7/09-7/10; Peterson et al. 2012)		2 949	18 217	21 166	14
Fort Lauderdale, Florida (7/09-7/10; Peterson et al. 2012)		2 781	21 420	24 201	12
Western Maryland (9/09-9/10; Castro et al. 2012)		2 530	7 700	10 230	25

Table 3. Two year cumulative totals for GOM dry deposition (dep.) and mercury wet deposition estimates for Four Corners and Eastern Oklahoma sites; August 4, 2009-August 2, 2011; asl = above sea level; na = not available; h=hour; total mercury deposition estimates = GOM dry deposition estimates + mercury wet deposition estimates.

Site	Elevation (asl)	Surrogate surface dep. rate estimate (ng/m^2h) $\pm$ standard deviation	GOM dry dep. estimate (ng/m^2)	Mercury wet dep. estimate (ng/m^2)	GOM dry dep. + mercury wet dep. estimates (ng/m^2)	GOM dry dep. % of total mercury dep. estimate
Mesa Verde National Park (CO99)	2 172 m	1.0 $\pm$ 0.6	17 155	16 582	33 737	51
Substation (NM95)	1 678 m	0.8 $\pm$ 0.5	13 738	na	na	na
Farmington Airport (NM99)	1 674 m	0.6 $\pm$ 0.4	11 340	na	na	na
Valles Caldera National Preserve (NM97)	2 657 m	0.7 $\pm$ 0.4	10 653	16 085	26 738	40
Navajo Lake (NM98)	1 972 m	0.6 $\pm$ 0.4	10 609	12 209	22 818	46
Molas Pass (CO96)	3 249 m	0.4 $\pm$ 0.1	6 007	19 243	25 250	24
Stilwell (OK99)	304 m	0.2 $\pm$ 0.1	3 468	26 715	30 183	11