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Atmospheric wet deposition of mercury and other trace elements in Pensacola, Florida

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Abstract

To understand and quantify the impact of local, regional, and distant atmospheric mercury sources to rainfall mercury deposition in the Pensacola, Florida watershed, a program of event-based rainfall sampling was started in late 2004. Modified Aerochem-Metrics wet/dry rainfall samplers were deployed at three sites in the region around the Crist coal-fired power plant and event-based samples were collected continuously for three years. Samples were analyzed for total mercury, volatile elements As, Se, and Sn, and a suite of trace elements including Al, Bi, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ho, Ga, Gd, La, Li, Lu, Mg, Mn, Na, Nb, Nd, Ni, P, Pb, Pr, Rb, Sb, Sc, Si, Sm, Sr, Tb, Th, Ti, Tm, U, V, Y, Yb, and Zn. Nutrients and major ions were also measured on each sample.

Multivariate statistical methods are used to sort these tracers into factors that represent potential source components that contribute to the rainfall chemistry. Hg, As, Se, Sn, Sb, and non sea-salt sulfate were all significantly correlated with one anthropogenic factor. Using various Hg/element ratios, we can estimate that 22–33% of the rainfall mercury in the region results from coal combustion.

1 Introduction

Atmospheric mercury deposition is a cause for great concern for human health in the United States as well as all other parts of the world due to atmospheric mercury incorporation as methyl mercury into fish. Current emissions to the atmosphere are estimated to be more than three times the pre-industrial amount. Anthropogenic mercury released to the atmosphere is estimated to be 3.4×10^9 g/yr (Selin et al., 2008 and references therein). Gaseous elemental mercury (GEM) is known to have a half-life of 1/2 to 2 years in the troposphere before it is oxidized and washed out of the atmosphere. Atmospheric emissions of GEM from industrial point-sources therefore are widely dispersed throughout the atmosphere before finally becoming oxidized to reac-

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tive gaseous mercury (RGM) and conversions to aerosol (particulate) mercury (HgP) after which they will deposit through wet and dry deposition.

Several studies have been conducted in the state of Florida in an effort to determine the influence of regional and global sources of mercury to the watersheds but few have been conducted to determine the effects of known point-source emitters to the local watersheds. One such study was conducted in 1993 over a three-week period in Broward County, Florida (Dvonch, et al., 1998). Daily rain event samples were collected and analyzed for total mercury and other trace elements. The samples collected nearest the point source had elevated mercury levels as compared to a control site, suggesting the importance of a local point-source. During the same period, Guentzel et al. (2001) concluded that local sources of atmospheric mercury could only account for about 30% of the rainfall deposition of Hg to the Florida Everglades.

Our study was originally commissioned to evaluate the impact of one particular coal-fired power plant (Gulf Power Company's Crist plant) on rainfall mercury deposition in Pensacola. By sampling individual rain events at three sites over three full years, we have identified some important characteristics of the trace element concentrations, including mercury, from local and regional emissions, and long-range transport, of atmospheric mercury to the Pensacola Bay watershed. The Crist plant is estimated to release on the order of 200 lbs of mercury per year to the atmosphere, with about 25% as reactive gaseous mercury (RGM) that may have some local impact. Other sources of mercury to the Pensacola Bay watershed include automobiles, a medical waste incinerator, a paper mill, chemical plants and other manufacturing companies. The paper mill burns coal and releases about 1.9 lbs/year; the other sources combined account for less than 0.06 lbs/year. There are significant regional sources of atmospheric mercury in Alabama and Georgia (and farther north), mostly the result of coal combustion for electricity generation.

This study looks at several different aspects of local rainfall deposition chemistry. Characteristics identified include seasonal variation and uniformity of deposition to the watershed. In addition to mercury concentrations in each rain sample, we analyzed a

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suite of trace elements including the alkali metals and alkaline earth elements, all three rows of the transition metals, and the rare earth elements. By using multi-element factor analysis we were able to identify at least three significant factors that can explain the variance in the data. Those factors include mineral dust, sea-salt aerosols, and at least one significant anthropogenic factor that explains much of the variance for Hg, As, Se, Sb, Sn, and non sea-salt sulfate (nss-SO_4); species that are commonly associated with coal combustion. Thus, a major source of mercury to rainfall in the Pensacola area appears to be via local and regional combustion of coal. Our data demonstrate that coal combustion in the southeastern US pollutes the regional airshed with volatile elements such as mercury, arsenic, antimony, selenium, tin, and non-sea salt sulfate (nss-SO_4), but that a significant fraction of the rainfall mercury appears to be the result of long-range transport.

2 Study area

This research was conducted as part of the Partnership for Environmental Research and Community Health (PERCH) in order to quantify the atmospheric deposition (in rainfall) of mercury and trace elements to the Pensacola Bay watershed. There are numerous potential local, regional, and distant sources for mercury and other trace elements in rainfall. It was shown by Fu and Winchester (1994) that the entire southeastern US airshed is affected by NOx emissions, primarily from coal-fired power plants. Thus we would expect to find mercury and trace elements associated with coal combustion in Pensacola rainfall. NO_x and SO_2 emissions are dominated by power generation, although significant NO_x emissions are also the result of motor vehicle activity in the region. According to the 2002 EPA air emissions inventory, two nearby counties in Alabama (Mobile and Escambia) were responsible for 780 and 880 lbs. of atmospheric mercury emission. From a 2005 emissions inventory, a coal-fired electricity generating plant (Plant Crist) was the largest local source of atmospheric mercury in Escambia County, Florida, estimated to release approximately 191 lbs. per year. A

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coal-fired industrial boiler at the International Paper Plant (1.9 lbs), a medical waste incinerator (0.002 lbs) and landfills (0.04 lbs) were also identified as minor sources of mercury emissions (T. Rogers, Florida Department of Environmental Protection, personal communication, 2009). A significant natural source of atmospheric mercury and trace elements is wild fires, which occur frequently in the region.

Rain collectors were installed at three sites between November and December 2004 (Fig. 1) and maintained through December 2007 for event based collection of rain samples using AerochemMetrics model 301 and equivalent Loda model 2001 rain samplers (Fig. 2a). The first collection site is at the Florida Department of Environmental Protection (FDEP) site at the Ellyson Industrial Park located off Scenic Highway in Pensacola. This site was chosen for its close proximity (about 4.7 km southeast) to the Crist coal fired power plant. The sampler is set on an open raised platform on fenced FDEP property. Event rain collection began at this site in November 2004. The second site is located on the fenced property of Pace Water Systems in Santa Rosa County. The sampler is set in a remote open area near a small wetland pond. Access to this site is limited to employees of Pace Water Systems and those with permission to enter the site. This site is approximately 5.5 km east-northeast of the power plant. Event rain collection began in December 2004 at this site. The third collection site is about 24.2 km northwest of the power plant on private property in the city of Molino. This site is remote with very little human disturbance. The sampler is set in an open field with no obstructions within at least 50 feet. Event rain sample collection at this site began in mid-December 2004. This site was chosen because it is often upwind of the Crist power plant, and is impacted by air masses coming out of the continental (southeastern) US.

A Plexiglas "splash guard" was attached to the leading edge of the retractable roofs to minimize rain splash contamination of the sample bottles when the roof is retracting. The "wet" buckets were modified to hold 3 bottles with Teflon collars and polycarbonate funnels (Fig. 2b) as in the Florida Atmospheric Mercury Study (Landing et al., 1998). Duplicate 1 liter FEP Teflon bottles for mercury and trace element analyses were de-

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ployed along with a single 1 liter polyethylene bottle for pH and major ions analysis. About 10% of the deployments had a single Teflon bottle and duplicate polyethylene bottles for pH and major ions in order to acquire some replicate samples for QA/QC purposes. Results for pH, major ions, and nutrients are reported in Caffrey et al. (2009). To avoid damage to the rain samplers, sampling was suspended from 9–26 July 2005 due to Hurricane Dennis. Rain samples were collected within 24 h of 0.5 cm rain events and shipped back to FSU for processing and multi-element analysis. The funnel/collar combination is removed from the receiving bottle, and the receiving bottles are capped, and replaced with freshly cleaned bottles. The funnel/collar combinations are changed about every 6 months, or when they appear to have been soiled by birds or other debris.

3 Methods

3.1 Mercury analysis

Rain samples (in FEP Teflon bottles) were acidified after return to the FSU clean lab to 0.045 M HCl plus 0.048 M HNO_3, using ultra-pure acids (Optima, Fisher Scientific) then placed in a low wattage UV digestion box (730 µwatts/cm^2; 254 nm) for at least 48 h to completely solubilize the collected Hg (Landing et al., 1998). The digested samples were analyzed by CVAFS using EPA method 1631 using a Tekran 2600 Mercury Analyzer. We use ultra-pure HCl and HNO_3 for sample acidification and UV digestion because the standard oxidant for total dissolved mercury analysis (bromine monochloride; BrCl) is not clean enough for the other trace elements we wish to analyze. Landing et al. (1998) showed that the HCl/HNO_3/UV treatment is as effective as BrCl for the analysis of 100% of the total dissolved mercury from rain and freshwater samples. FEP Teflon bottles are about 50% transparent to UVA (254 nm) radiation, as is obtained from low pressure mercury vapor lamps.

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3.2 ICPMS analysis

A multi-element analytical program was set up using a Thermo-Finnigan "Element-I" high-resolution magnetic sector ICP-MS. We identified 44 elements that are significantly enriched in rain samples relative to the method blank, including the alkali metals and alkaline earth elements, all three rows of the transition metals, and the rare earth elements (Al, Bi, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ho, Ga, Gd, La, Li, Lu, Mg, Mn, Na, Nb, Nd, Ni, P, Pb, Pr, Rb, Sb, Sc, Si, Sm, Sr, Tb, Th, Ti, Tm, U, V, Y, Yb, and Zn). An Agilent 7500cs quadrupole ICP-MS equipped with an octopole reaction-collision cell (ORC) was used to measure As, Se, and Sn. All analyses were conducted using external standard solutions (in the same $HCl+HNO_3$ matrix as the samples), and the analytical sensitivities were compared to spiked samples (standard additions) to confirm that there was no signal suppression or enhancement due to slight matrix differences between samples and standards.

Analytical results from duplicate rain samples in the FEP Teflon bottles are shown in Fig. 3 for Hg, As, Se, and Ba. When the concentrations are well above the detection limits, one finds excellent agreement between the "A" and "B" bottles (arbitrarily defined), as is seen for Hg, As, and Se. When the concentrations approach the detection limit, one sees significantly greater scatter about a 1:1 line passing through the data, as is seen for Ba (also for Zr, Hf, and Ta).

4 Results

A total of 225 separate rain events were sampled from 19 November 2004 through 2 January 2008, yielding 565 rain samples from the three sites. We observed generally higher rainfall amounts in the Spring (March-May), although the annual amount of precipitation was not significantly different among the 3 sites, nor between years.

Seasonally segregated rainfall fluxes for Hg, Zn, and Fe for the entire 3 year sampling period are shown for example in Fig. 4. While we see significantly higher rainfall Hg

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fluxes in Spring and Summer (Fig. 4a), the Hg fluxes are not significantly different between the three sampling sites, despite the much closer proximity to the Crist power plant of the Ellyson site (4.7 km) relative to the Molino site (24.2 km). Rainfall Hg fluxes were also not significantly different between years at the three sites, nor between our three sites and nearby sites that are part of the NADP/Mercury Deposition Network (see Caffrey et al., 2009).

Rainfall fluxes of Zn were significantly higher at the Ellyson site, which is likely from Zn enriched aerosols due to its heavily urbanized location and the amount of vehicular traffic on the surrounding interstate (I-10) and highways (Fig. 4b). The rainfall fluxes of Fe are shown as an example of the impact of mineral dust aerosols (Fig. 4c). During the Spring and Summer months, mineral dust from arid regions in Africa is uplifted into the dry Saharan Air Layer and makes its way within 7–10 days across the North Atlantic where it impacts Florida and the eastern Gulf of Mexico (e.g. Prospero, 1999) . During those months, we see significantly higher rainfall fluxes of Fe (and other trace elements associated with mineral dust; Si, Al, Mn, Cs, La, Ce, (and the other rare earth elements), Th, and U). We also see no significant differences between the three sites, indicating that the mineral dust is more likely the result of long-range transport rather than locally-generated soil dust from agricultural practices. A very similar pattern of summertime mineral dust deposition was reported for wet deposition rain samples from the Florida Everglades (Landing et al., 1995) and more recently by Trapp et al. (2009).

There are significant inter-element relationships in our dataset that appear to reflect source categories for various aerosol types. Supporting the previous conclusions regarding mineral dust transport and deposition, Fig. 5a show the very strong correlation between the wet deposition of Fe and Al (R^2=0.92). Correlation coefficients (R^2) greater than 0.7 were also found between Al and Ce, Cs, La, Si, and Th. Figure 5b shows the excellent correlation between Sr and Mg (R^2=0.85). Strong correlations were found between Na, Mg, and Sr since these are all indicators of the input of sea-salt aerosols.

Multi-element data of this type are often evaluated using multi-variate statistical

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methods such as factor analysis or positive matrix factorization. We used SPSS Statistics 17.0 to analyze the data using factor analysis (with varimax rotation). We used the flux database rather than the concentration database since small volume rain events often have high concentrations of many elements and this can skew the analysis. Converting concentrations to fluxes tends to produce more normally distributed data. The analysis showed 6 components with eigenvalues greater than 1.0 (Table 1). Component 1 is clearly related to the mineral dust flux, since we see high R^2 values (greater than 0.6) for Al, Ba, Ce, Cs, Fe, La, Mn, Nb, Si, Th, and U. Component 2 is related to anthropogenic pollution and shows high R^2 values for Hg, As, Se, Sb, H+, and nss-SO_4. We interpret this component to reflect input from atmospheric emissions during coal combustion (to be discussed later). Component 3 shows high correlations with Bi, Li, and Pb and probably also reflects an anthropogenic component. Component 4 obviously reflects the input of sea-salt aerosols, with high correlations between Na, Mg, and Sr. Component 5 has high correlations with Cd, P, and Zn. This component may reflect an anthropogenic term, however we cannot explain why P would be correlated with Cd and Pb. There has been speculation that this component may reflect biomass burning, since northwest Florida experienced numerous wildfires during our study period. We are currently investigating this possibility by analyzing aerosol samples collected during large-scale controlled burns conducted by the Florida Department of Agriculture. Component 6 has high correlations with Co, Cr, and Ni. This component may also represent an anthropogenic input term, since these three elements are all associated with steel manufacturing. Because of the small amount of variance accounted for by Components 4, 5, and 6, we re-ran the factor analysis while reducing the number of components from 6, to 5, to 4 and finally to 3 (Table 2). The first three components (which appear to reflect mineral dust, sea-salt, and anthropogenic Hg) were maintained in all of these analyses and accounted for 65% of the variance in the data. The next three components accounted for less than 5% (each) of the variance in the data.

Figure 6 shows scatter plots of Cr vs. Ni, Cd vs. Zn, Bi vs. Pb, and non sea-salt sulfate (nss-SO_4) vs. Hg that support the findings from the factor analysis. In all cases

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the correlations are very significant, with R^2 values greater than 0.5. Figure 7 shows scatter plots of Sb vs. Hg, Sn vs. Hg, As vs. Hg, and Se vs. Hg. The correlations are all significant, however the correlation coefficients (R^2) are between 0.26 and 0.5.

5 Discussion

Because of the negative human health effects from mercury exposure, the various states and the US EPA are all working on reducing anthropogenic mercury emissions within the US with the goal of reducing atmospheric mercury deposition. Unfortunately, a recent comprehensive model analysis of the global mercury cycle (Selin et al., 2008) suggests that only 20% of the mercury deposition over the USA is due to North American (primarily USA) industrial emissions, while 31% is due to sources outside the USA. They also concluded that 32% of the mercury deposition was due to the natural mercury cycle and that 16% was the result of legacy anthropogenic mercury accumulated in soils and the oceans. The recent REMSAD analysis conducted by the EPA (REMSAD, 2008) reaches a similar conclusion, that greater than 50% of the atmospheric mercury deposition across the USA is due to Hg emissions outside the USA. Using a very conservative approach, Guentzel et al. (2001) concluded that only 30–46% of the rainfall Hg in the Florida Everglades was due to local and regional emissions, and that over 50% was due to long range transport. Guentzel et al. (2001) further showed that their data was consistent with long-range mercury transport in the northeast trade winds, which sweep across southern Florida and up into the northeastern Gulf of Mexico during the period from June through September. Our observation of higher than average rainfall Hg deposition in Spring and Summer (Fig. 4a) suggests that long-range transport of mercury may dominate rainfall mercury deposition during those months.

We can use the data from this study to estimate the fraction of rainfall mercury that results from various anthropogenic activities, namely coal combustion. The data from the Florida Atmospheric Mercury Study in the mid-1990s, the more recent NADP/MDN data, and the recent modeling studies all suggest that there is a significant long-range

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transport component to rainfall mercury deposition in Florida and along the coast in the northeastern Gulf of Mexico during the summer months. Because the gaseous elemental mercury species is the form that undergoes this long-range transport (before oxidizing to reactive gaseous mercury to be scavenged to particles and by rainfall), it becomes de-coupled from other tracers in its original source emissions profiles. Thus, we expect a significant amount of rainfall Hg in our study to not reflect any associations with other chemical tracers of anthropogenic activity. On the other hand, the fraction of the rainfall mercury that results from local and regional sources within the southeastern USA should be deposited along with other chemical tracers reflecting the various emissions profiles.

For this evaluation, we assert that any given rain sample from our study includes Hg from long-range transport in addition to what is contributed from local and regional sources, but that other chemical tracers such as volatile elements emitted during coal combustion (As, Sb, Se, Sn, and nss-SO_4) will predominantly reflect the local and regional emissions of those trace elements. If so, then the ratio of Hg to the other volatile tracers in any given rain sample will reflect a balance between the long-range transport term (leading to higher Hg/volatile ratios) and the local plus regional term (leading to lower Hg/volatile ratios). Our assumption that the volatile trace elements (As, Sb, Se, Sn, and nss-SO_4) are due almost completely to coal combustion is supported by the EPA mercury emissions inventory, which shows that we have almost no metal ore smelting in the southeastern US that would also contribute to volatile trace element emissions.

We evaluated the Hg/volatile ratios in our data set, searching for the lowest ratios. For Hg/As, Hg/Se, Hg/Sn and Hg/nss-SO_4 the lowest ratios were found in the November–March period, not coincidentally when long-range mercury transport associated with the northeast trade winds would be at its minimum and when continental air masses (winter cold fronts) frequently sweep across the region. If we further assume that the rainfall deposition of these volatile tracers is due exclusively to local and regional emissions from coal combustion, then we can use the deposition of these volatile tracers to

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constrain the fraction of rainfall Hg that is also due to local and regional emissions from coal combustion:

$$\%\text{Hg from coal} = \frac{\text{Annual TE deposition} \cdot (\text{Hg/TE})\ \text{minimum} \cdot 100}{\text{Annual Hg deposition}} \quad (1)$$

Using Eq. (1), the average of the ten lowest Hg/volatile ratios was used to constrain the (Hg/TE)minimum value, and the annual TE and Hg deposition values were calculated from our data. Table 3 shows the results of these calculations, which suggest that from 22–33% of the rainfall Hg deposition at our sites in the Pensacola region is due to local and regional coal combustion. These estimates are consistent with the REMSAD modeling results (using the 2001 EPA mercury emissions inventory) which showed that 78% of the total atmospheric (wet plus dry) Hg deposition in the Pensacola area was due to long-range transport, with 22% from local and regional sources (Dwight Atkinson, US EPA, personal communication, 2009).

In conclusion, our data support a conceptual model that while long-range transport of atmospheric Hg dominates the rainfall deposition of mercury in the Pensacola region, we can demonstrate the impact from local and regional coal combustion. We cannot identify any particular emissions source with our data analysis, however we can identify source categories for the atmospheric tracers we measured.

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Table 1. Rotated component matrix from Factor Analysis (with varimax rotation) of the rainfall flux data using SPSS Statistics 17.0. Six components with eigenvalues greater than 1.0 were allowed in this analysis. Yellow highlighted cells reflect R^2 values greater than 0.6.

Rotated Component Matrix						
	Component (R^2)					
	1	2	3	4	5	6
Hg	.070	.620	.062	.008	.002	.003
As	.000	.317	.229	.103	.040	.007
Se	.010	.718	.002	.009	.016	.004
Sb	.115	.405	.228	.010	.075	.003
Sn	.002	.162	.206	.057	.022	.000
H+	.030	.608	.134	.002	.001	.000
Na	.000	.053	.039	.821	.001	.001
NH_3	.116	.235	.337	.030	.009	.002
NO_3	.129	.207	.177	.046	.010	.001
Cl	.022	.019	.004	.319	.006	.002
SO_4	.021	.762	.013	.083	.004	.000
$nssSO_4$	.018	.816	.014	.026	.003	.000
Al	.817	.006	.045	.002	.001	.003
Ba	.412	.082	.281	.001	.002	.072
Bi	.070	.082	.556	.004	.113	.005
Cd	.001	.007	.002	.000	.783	.001
Ce	.824	.033	.041	.000	.005	.006
Co	.347	.014	.037	.007	.000	.484
Cr	.126	.000	.004	.000	.026	.769
Cs	.844	.021	.024	.005	.026	.002
Cu	.092	.213	.034	.011	.190	.110
Fe	.891	.014	.038	.001	.001	.007
Ga	.304	.170	.060	.053	.032	.033

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Table 1. Continued.

Rotated Component Matrix						
	Component (R^2)					
	1	2	3	4	5	6
La	.802	.056	.074	.001	.005	.006
Li	.235	.025	.402	.069	.015	.015
Mg	.014	.008	.000	.883	.007	.001
Mn	.768	.048	.083	.004	.011	.017
Nb	.596	.098	.004	.008	.029	.011
Ni	.004	.003	.004	.009	.000	.934
P	.066	.062	.002	.007	.415	.001
Pb	.112	.114	.523	.008	.002	.028
Si	.859	.003	.000	.000	.000	.004
Sr	.161	.029	.009	.657	.027	.003
Th	.834	.000	.010	.000	.002	.001
U	.621	.075	.033	.036	.021	.002
V	.225	.170	.111	.090	.000	.023
Zn	.012	.001	.030	.001	.774	.005

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Table 2. Rotated component matrix from Factor Analysis (with varimax rotation) of the rainfall flux data using SPSS Statistics 17.0. This analysis was limited to three components.

Rotated Component Matrix			
	Component (R^2)		
	1	2	3
Hg	.060	.583	.031
As	.003	.542	.132
Se	.004	.556	.030
Sb	.129	.687	.019
Sn	.000	.339	.067
H+	.025	.669	.002
Na	.000	.064	.819
NH_3	.140	.476	.049
NO_3	.130	.351	.058
Cl	.022	.008	.341
SO_4	.009	.589	.135
$nssSO_4$	.007	.635	.062
Al	.827	.028	.001
Ba	.520	.240	.002
Bi	.121	.491	.003
Cd	.000	.154	.016
Ce	.826	.068	.001
Co	.527	.028	.042
Cr	.283	.004	.013
Cs	.831	.057	.004
Cu	.129	.358	.018
Fe	.899	.036	.000
Ga	.328	.246	.071

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Table 2. Continued.

Rotated Component Matrix			
	Component (R^2)		
	1	2	3
La	.811	.114	.002
Li	.306	.137	.103
Mg	.010	.003	.826
Mn	.804	.116	.007
Nb	.575	.112	.010
Ni	.019	.003	.067
P	.059	.193	.000
Pb	.178	.388	.024
Si	.835	.003	.000
Sr	.153	.041	.612
Th	.775	.000	.001
U	.605	.119	.038
V	.248	.230	.129
Zn	.025	.166	.008

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Table 3. Minimum Hg /trace element ratios used to estimate the fraction of rainfall Hg due to local and regional coal combustion in the Pensacola area (±1 SD).

Volatile Tracer	Minimum Hg/TE ratio	%Hg from Coal Combustion
As	28±8	31±9
Sb	96±21	27±6
Se	22±5	33±8
Sn	58±5	22±2
nss-SO_4	3.1±0.9	31±9

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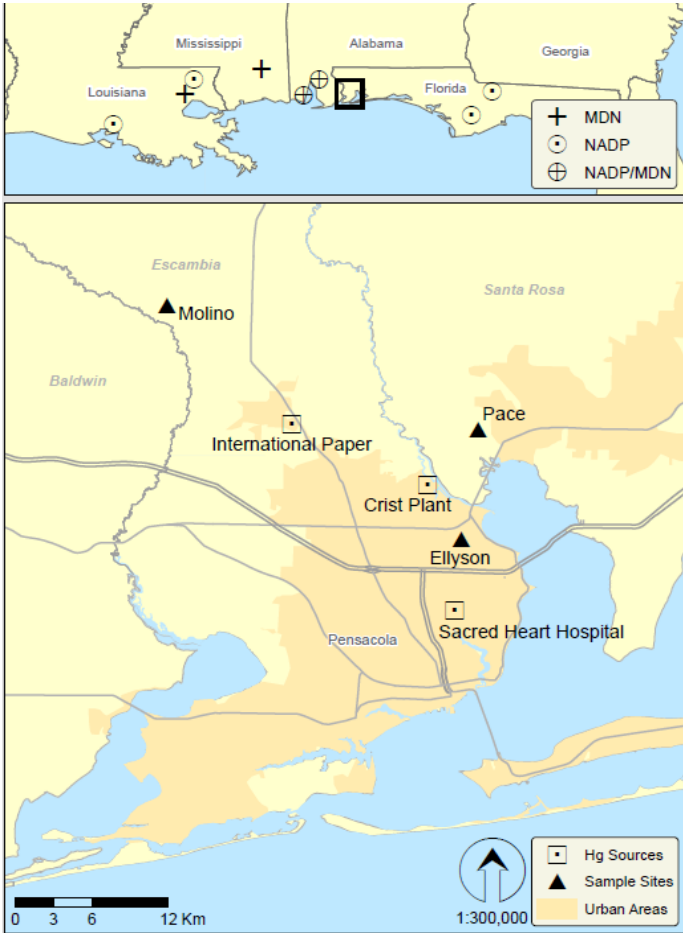

Fig. 1. Rainfall sampling sites and atmospheric mercury sources in the Pensacola, Florida area.

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Fig. 2. Automated rainfall collector with a Plexiglas splash guard on the leading edge of the roof to avoid splash contamination during roof retraction **(a)**. Modified receiving bucket with three nested receiving bottles connected to polycarbonate funnels using PTFE-Teflon collars.

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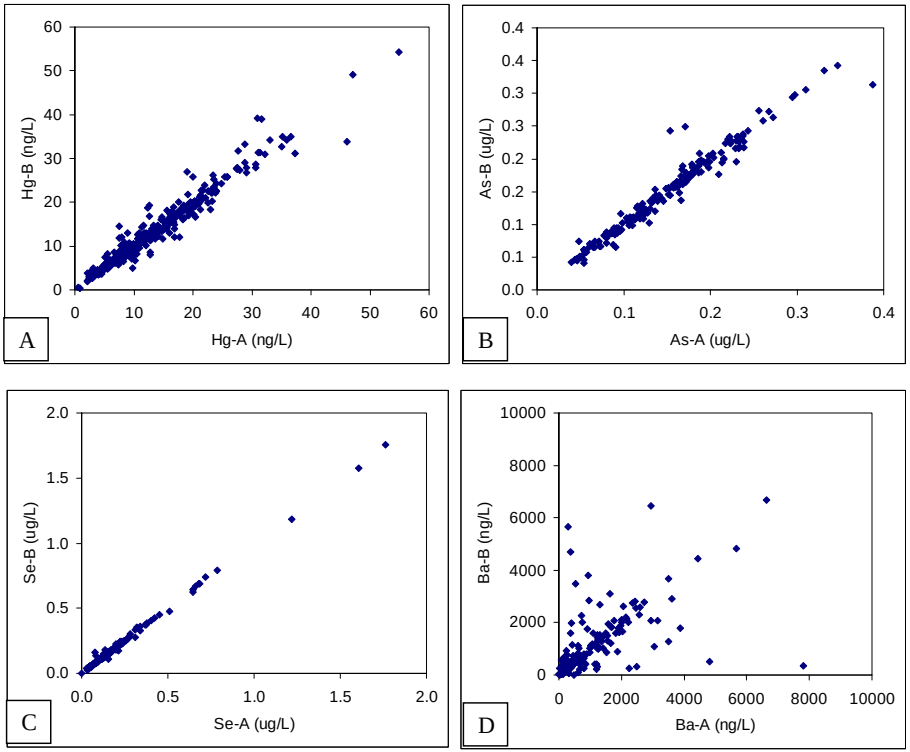

Fig. 3. Comparison of analyses of duplicate (A vs. B) rain samples. Mercury **(A)**, arsenic **(B)**, and selenium **(C)** all show excellent agreement with data well above the detection limits. Barium **(D)** shows significant scatter due to concentrations near the detection limit.

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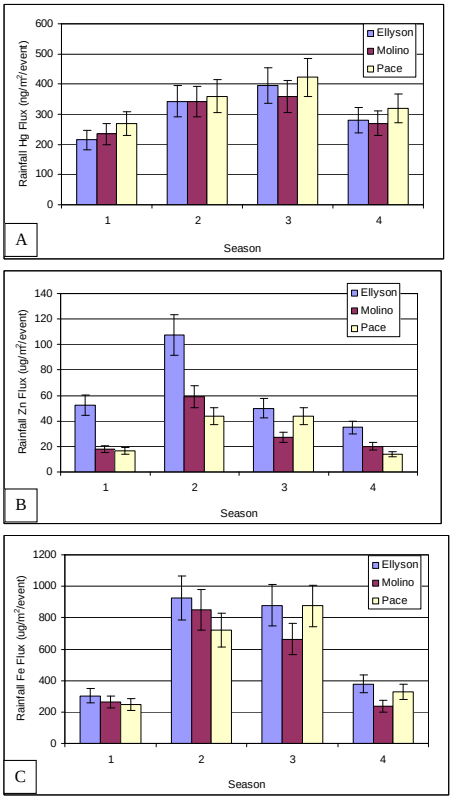

Fig. 4. Seasonal comparisons of rainfall fluxes at the three sampling sites in the Pensacola area for Hg **(A)**, Zn **(B)**, and Fe **(C)**. Season 1 represents December–February. Season 2 represents March–May. Season 3 represents June–August. Season 4 represents September–November.

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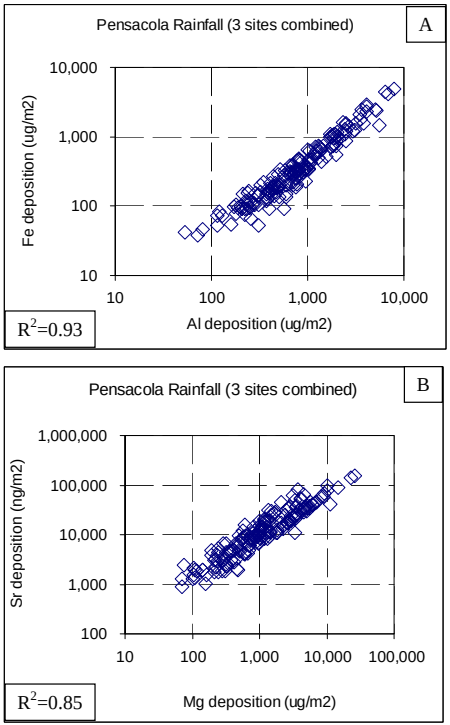

Fig. 5. Scatter plots of the rainfall deposition data for Fe vs. Al, reflecting the contribution from mineral dust **(A)**, and Sr vs. Mg, reflecting the contribution from sea salt aerosols **(B)**. Correlation coefficients (R^2) are from linear regression analysis.

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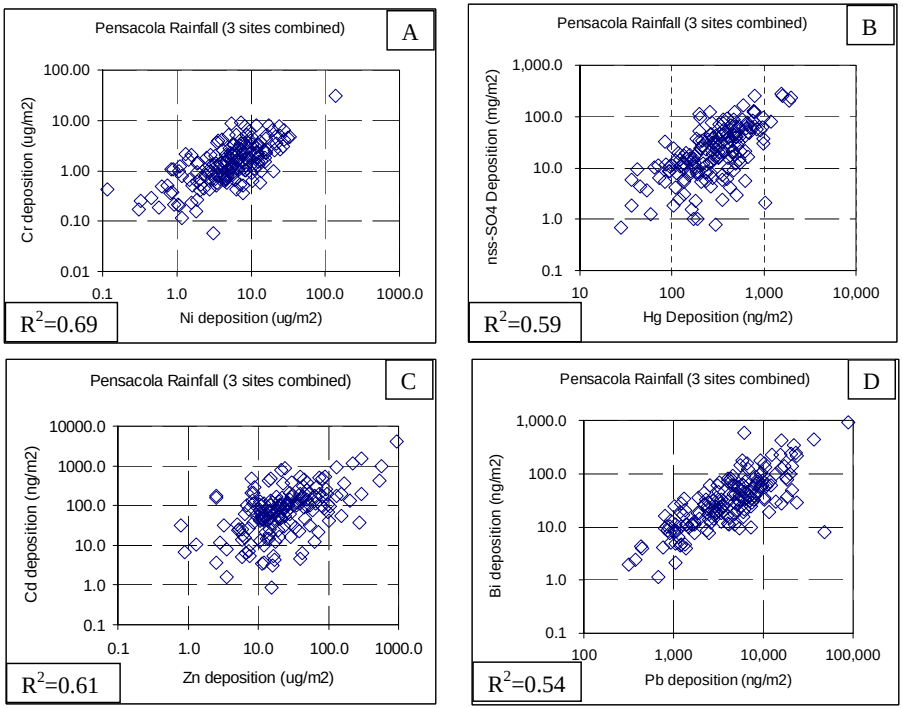

Fig. 6. Scatter plots of the rainfall deposition data for Cr vs. Ni **(A)**, nss-SO_4 vs. Hg **(B)**, Cd vs. Zn **(C)**, and Bi vs. Pb **(D)** all reflecting various contributions from anthropogenic emissions. Correlation coefficients (R^2) are from linear regression analysis.

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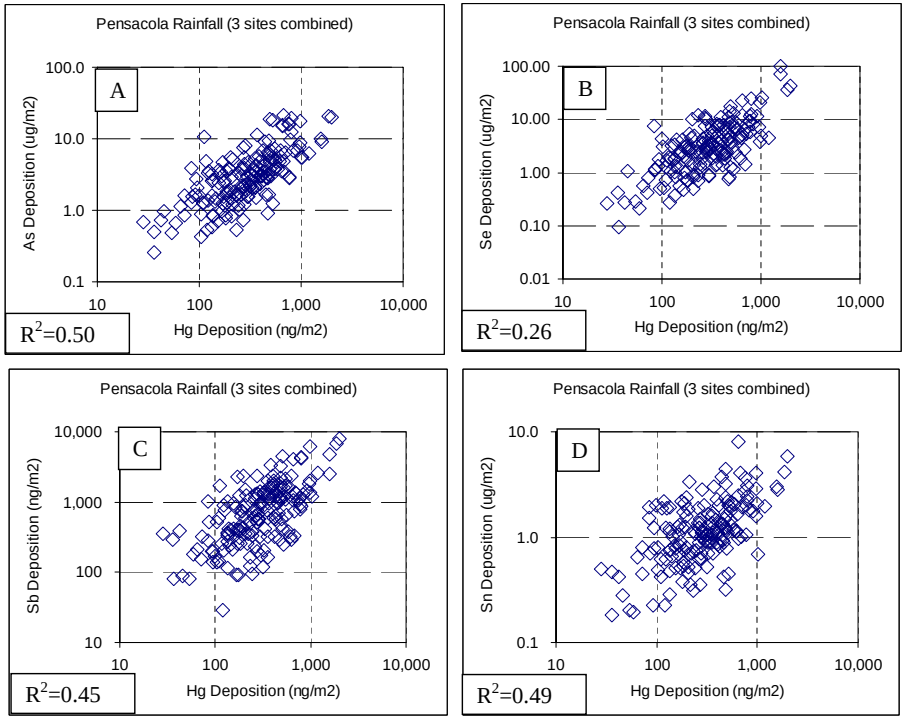

Fig. 7. Scatter plots of the rainfall deposition data for **(A)** As vs. Hg, **(B)** Se vs. Hg, **(C)** Sb vs. Hg, and **(D)** Sn vs. Hg. All reflecting contributions from coal combustion. Correlation coefficients (R^2) are from linear regression analysis.

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