

Progress report

Submitted to the U.S. Environmental Protection Agency, Region 4

Atmospheric Deposition of Mercury and Trace Metals to the Pensacola Bay Watershed

Jane M. Caffrey

William M. Landing

February 15, 2006

## Introduction

Atmospheric deposition represents a significant source of nutrients and other contaminants in many watersheds (Valigura et al 2001). Contaminants come from both local emissions and emissions hundreds of kilometers away. Our primary objective is to provide measurements of mercury, trace metals and major ions in rainfall over an annual cycle. We evaluate the temporal and spatial patterns in atmospheric deposition by comparing the results among 3 sites in the Pensacola Bay watershed and comparing them with data collected at MDN and NADP sites in the Southeast Region along the Gulf Coast.

We have been measuring the concentrations of mercury, trace metals and major ions at 3 sites in the Pensacola Bay watershed. The first site was established at Ellyson Field on November 19, 2004. This site is located on the Florida Department of Environmental Protection (FDEP) property. FDEP is monitoring ozone, SO<sub>2</sub>, PM<sub>2.5</sub>, wind speed and direction at this location. The Pace site was installed on Dec 9<sup>th</sup> on the Pace Water Systems property on Woodbine Road. Part of this property is used as a treatment wetlands and the rest is a nature preserve. The collector was installed away from the treatment wetlands in an open field. The Molino site was installed on December 15<sup>th</sup> in an open field at a private residence. The collector at the Ellyson site is being powered by AC, while the Pace and Molino sites are being powered by 12V batteries.

## Methods

Rain samples were collected within 24 hours of 0.5 cm rain events. Standard EPA protocols for data collection and analysis were used during this study. Duplicate bottles for major ion analysis were collected for 10% of the deployments. For the rest of the deployments (90%), duplicate bottles for trace metal and Hg analysis were collected.

### Mercury Analysis

Rain samples (in FEP Teflon bottles) were acidified after collection to 0.48 M HCl plus 0.24M HNO<sub>3</sub>, then placed in a low wattage UV digestion box for at least 48 hours to completely solubilize the collected Hg. The digested samples were analyzed by CVAFS using EPA method 1631.

### Trace metal analyses

Rain samples in the replicate Teflon bottles (acidified to 0.048M HCl plus 0.024M HNO<sub>3</sub>) were used for the trace element analyses. Samples were analyzed for total metal concentrations using a Finnegan Element-I high resolution magnetic sector ICP-MS.

### Major ions and pH

The pH of the samples was measured in the laboratory immediately following collection. The major ions,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ , and  $\text{K}^+$  were measured in polyethylene sample bottles. Major ion analyses were measured on Dionex DX500 ion chromatograph using EPA method 300.0 for anions and Dionex protocols (Application Note 141, [http://www1.dionex.com/en-us/webdocs/application/industry/chempetro/AN141\\_V15.pdf](http://www1.dionex.com/en-us/webdocs/application/industry/chempetro/AN141_V15.pdf)) for cations.

A subset of samples (49) were analyzed for total organic carbon and total nitrogen by the USEPA, NHEERL, Gulf Ecology Division laboratory in Gulf Breeze, FL. These samples, collected between November 2004 and May 2005, had already been analyzed for all major ions.

### Calculations and statistics

The bi-weekly, monthly, seasonal, or annual average rainfall mercury concentrations can be calculated from the individual rain event data by volume weighting the data prior to summing over the desired time interval. For example, since we generally collect duplicate samples for Hg determinations at each site (sample A and B), we calculate the volume-weighted mean by multiplying the measured Hg concentrations ( $C_A$  and  $C_B$ ) by the volume of rain collected in the bottles ( $V_A$  and  $V_B$ ), then summing both the A bottle and B bottle fluxes over the desired time interval, then dividing by the total amount of rain collected in both bottles (A+B). This incorporates the concentration and rain volume data from the duplicate samples without calculating simple arithmetic means:

$$\text{Volume-weighted mean} = \frac{[\text{SUM}(C_A V_A) + \text{SUM}(C_B V_B)]}{[\text{SUM}(V_A) + \text{SUM}(V_B)]} \quad \text{Eqn. 1}$$

To obtain an estimate of the precision of these volume-weighted mean concentrations, and because the “standard deviation” of two values is not a statistically useful error estimate, we use the volume-weighted average absolute deviation of the duplicate Hg fluxes from each rain event expressed as a percentage:

Volume-weighted absolute deviation (%) =

$$\frac{\text{SUM} \left[ \frac{(100 * \text{ABS}(F_A - F_B)) * (V_A + V_B)}{\text{AVERAGE}(F_A, F_B)} \right]}{\text{[SUM}(V_A) + \text{SUM}(V_B)]} \quad \text{Eqn. 2}$$

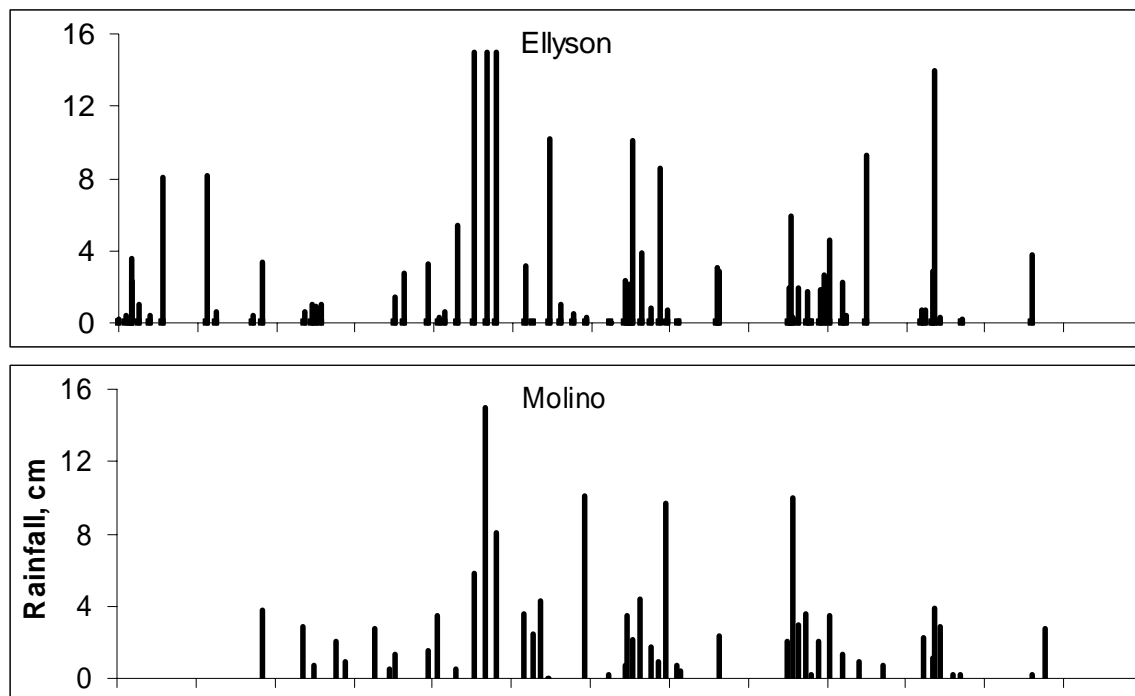
where  $F_A = C_A V_A$  and  $F_B = C_B V_B$ . In both equations, the  $\text{SUM}()$  expressions refer to the summation of the values over the desired time interval (bi-weekly, monthly, seasonal or annual). In Eqn. 2, we incorporate the rain volumes from both of the duplicate samples rather than using the arithmetic mean.

Mercury, sulfate and nitrate deposition rates were calculated by multiplying rainfall amount and concentration. In order to compare our results with MDN network

results, we integrated our samples over the same period as the MDN. We performed correlation analysis on the data analyzed to date. Correlation coefficients ( $r$ ) and significance levels ( $\alpha$ ) are reported in text.

## Results

Peak rainfall occurred during April 2005 when we collected over 15 cm of rain in individual rain events at the different sites (Figure 1). There is site to site variation in rainfall amounts, associated with the patchy nature of thunderstorm activity. Some breaks in rain collection at Pace and Molino occurred in December and January because of a loss in battery power. There is also a gap during February at the Ellyson site when the motor for the collector was in for repair. The collectors were not deployed during Hurricanes Dennis and Katrina, so there were gaps in collections between July 9 - July 26 and August 28 - 31. Collectors were deployed for Hurricane Arlene which came ashore on June 11. To facilitate collecting samples during tropical storms and moderate hurricanes, we are securing Pace and Molino collectors to posts which have been fixed in cement.



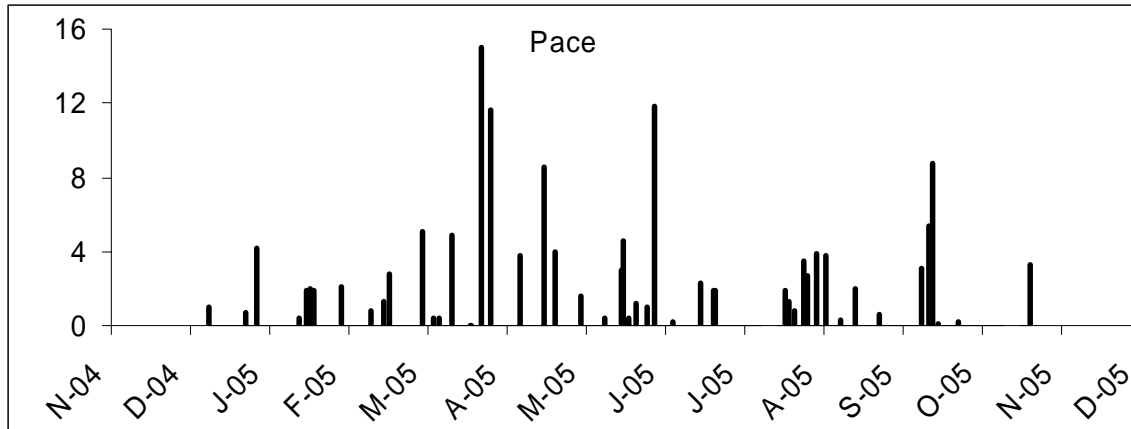


Figure 1 – Rainfall amounts (cm) collected at Ellyson, Molino and Pace sampling locations.

pH values at the three sites ranged from 3.4 to 6.7 (Figure 2). There were no consistent differences among the different sites. Small rain events had lower pH values and higher ion and trace metal concentrations than large rain events (pH vs rain amount  $r = 0.49$ ,  $\alpha = 0.001$ ). Rain events with low pH values had high mercury concentrations ( $r = -0.58$ ,  $\alpha = 0.001$ ). Sulfate concentrations and pH values were negatively correlated ( $r = -0.72$ ,  $\alpha = 0.001$ ) as were nitrate and pH ( $r = -0.50$ ,  $\alpha = 0.001$ ).

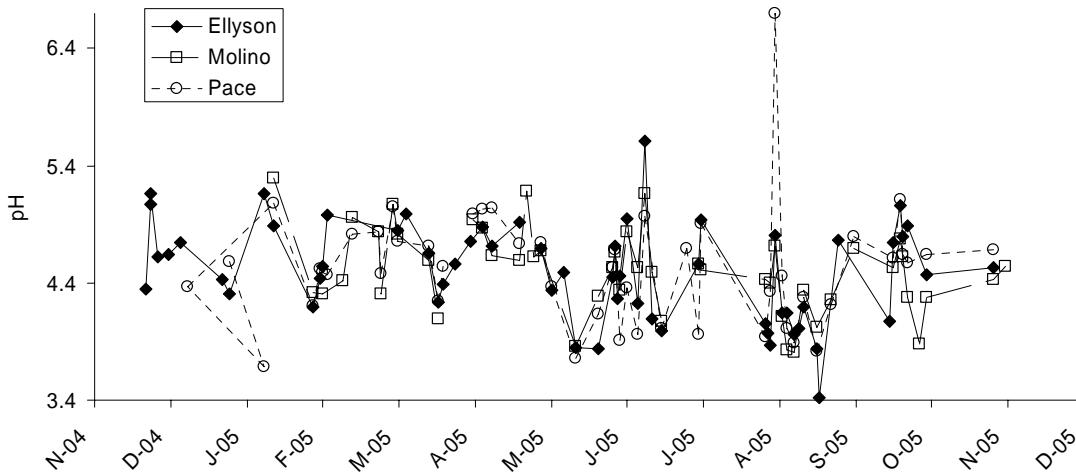


Figure 2 – pH values in rain collected at Ellyson, Molino and Pace.

Mercury concentrations ranged from 2 to 40 ng/L at the collection sites. There were no consistent differences among sites (Table 1, Figure 3). We examined how mercury deposition at our sites compared with nearby MDN sites in Alabama (Figure 3). Weekly deposition at the Pensacola sites was similar to the deposition measured at Baldwin County, Alabama (AL02) and Mobile County, Alabama (AL24).

Table 1 – Average concentration of mercury (in ng/L), major ions (in mg/L), other trace metals (in ppb), total organic carbon (TOC) and total nitrogen (TN) at Ellyson, Molino and Pace. Absolute deviation (in %) is reported for mercury concentration,  $\pm$  SD are reported for the other constituents.

Trace metal or ion concentration	Ellyson	Molino	Pace
Hg	9.50 (3.16%)	9.35 (2.96%)	8.89 (5.56%)
SO <sub>4</sub> <sup>2-</sup>	1.77 $\pm$ 1.02	1.81 $\pm$ 1.25	1.88 $\pm$ 1.18
NO <sub>3</sub> <sup>-</sup> as N	0.25 $\pm$ 0.16	0.28 $\pm$ 0.20	0.23 $\pm$ 0.11
Cl <sup>-</sup>	2.63 $\pm$ 2.48	1.79 $\pm$ 0.69	2.02 $\pm$ 1.40
Na <sup>+</sup>	1.55 $\pm$ 1.39	0.50 $\pm$ 0.34	1.24 $\pm$ 1.13
Cd	0.031 $\pm$ 0.025	0.029 $\pm$ 0.029	0.042 $\pm$ 0.076
Pb	0.48 $\pm$ 0.46	0.60 $\pm$ 0.91	0.35 $\pm$ 0.24
Al	60.0 $\pm$ 67.1	63.4 $\pm$ 132	44.9 $\pm$ 39.8
V	0.66 $\pm$ 0.5	0.56 $\pm$ 0.49	0.61 $\pm$ 0.49
Mn	1.45 $\pm$ 1.24	1.80 $\pm$ 3.0	1.23 $\pm$ 0.84
Fe	29.5 $\pm$ 28.4	28.1 $\pm$ 41.3	23.8 $\pm$ 19.4
Co	0.14 $\pm$ 0.26	0.08 $\pm$ 0.12	0.11 $\pm$ 0.25
Ni	2.64 $\pm$ 5.79	1.22 $\pm$ 2.00	1.78 $\pm$ 3.88
Cu	0.98 $\pm$ 1.37	0.44 $\pm$ 0.56	0.61 $\pm$ 1.01
Zn	2.24 $\pm$ 1.75	2.14 $\pm$ 3.03	1.60 $\pm$ 0.99
TOC	0.71 $\pm$ 0.51	0.73 $\pm$ 0.33	0.89 $\pm$ 0.59
TN	0.38 $\pm$ 0.28	0.41 $\pm$ 0.19	0.41 $\pm$ 0.25

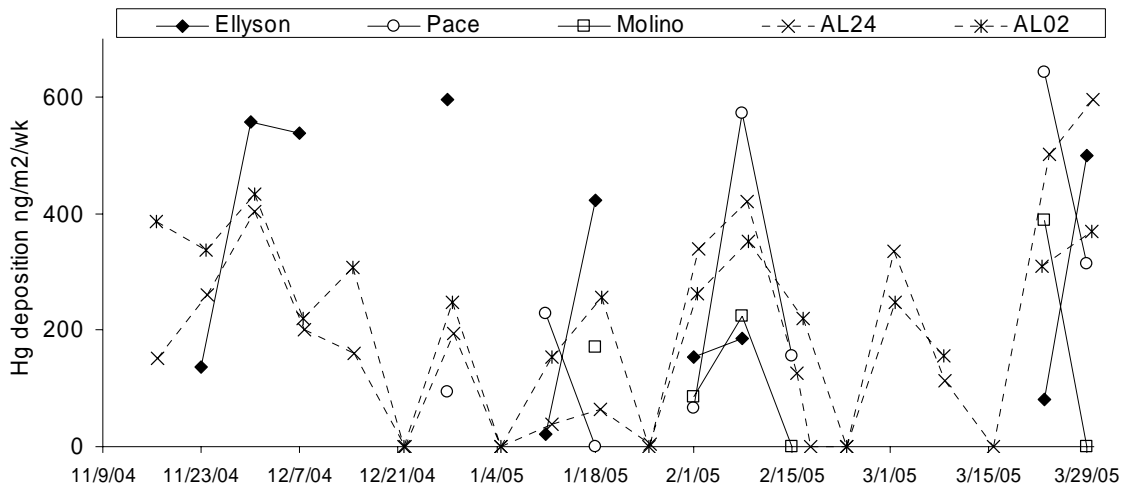


Figure 3 – Weekly mercury deposition (ng/m<sup>2</sup>/wk) at Ellyson, Pace, Molino and Alabama MDN sites, AL02 and AL 24.

Average values for major ions and trace metals are included in Table 1. The marine influence is evident at the Ellyson and Pace sites, which had higher chloride and sodium concentrations than the Molino site. Chloride and sodium concentration were significantly positively correlated ( $r = 0.88$ ,  $\alpha = 0.01$ ). Nickel and zinc concentrations

were the highest at Ellyson, which may be influenced by nearby industrial operations and commercial businesses. However, concentrations at Ellyson were not significantly different than those at the other two sites. When we compared sample dates where all three analyses nitrate, ammonium and total nitrogen analyses were performed, inorganic (nitrate and ammonium) nitrogen comprised over 85% of the total nitrogen.

As we observed with the mercury deposition, there were no consistent differences among the sites in sulfate and nitrate deposition (Figure 4). Future analyses will incorporate weather data such as wind speed and direction from the Pensacola regional airport and HYSPLIT modeling in order to evaluate the importance of local versus regional sources.

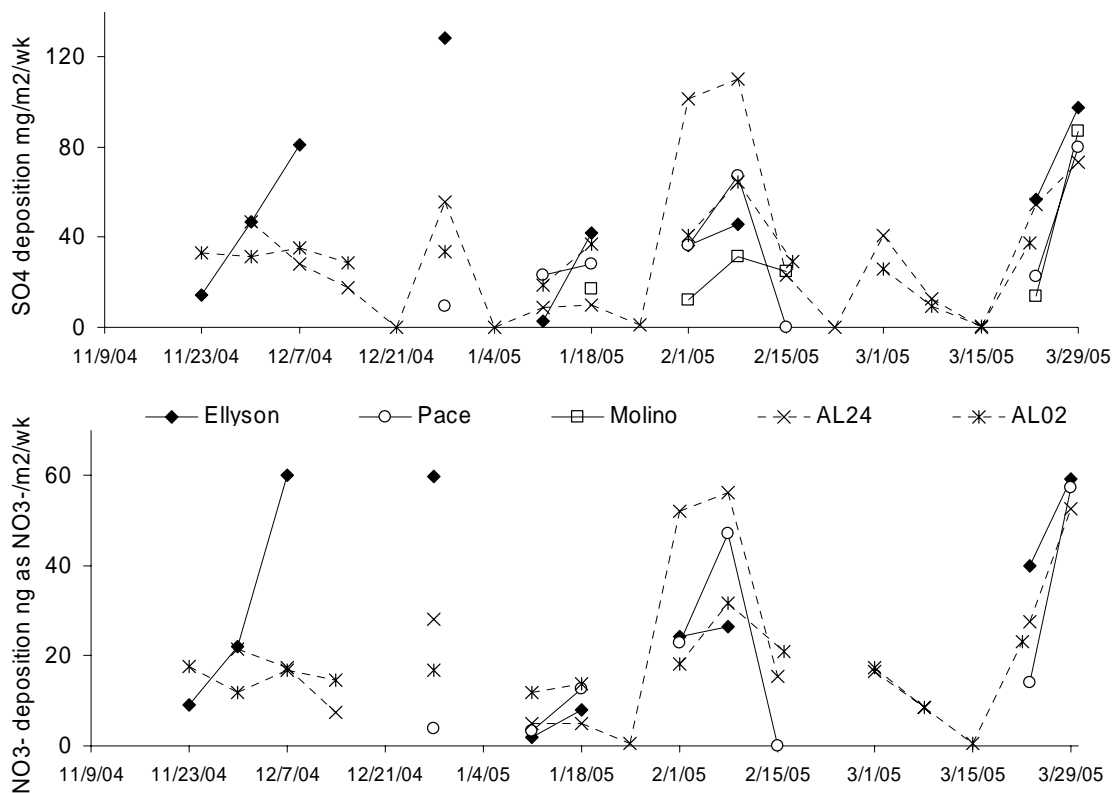


Figure 4 – Weekly sulfate and nitrate deposition (mg/m<sup>2</sup>/wk) at Ellyson, Pace, Molino and Alabama MDN sites, AL02 and AL 24.

A total gaseous mercury analyzer was installed at Ellyson Field on February 9, 2005. Readings were integrated over 5 minute intervals. The instrument was calibrated on June 3. The results of the calibration indicated that the instrument was reading about 18% low, so all values prior to June 3, were corrected. February and March were characterized by periodic afternoon spikes of mercury exceeding 10 ng/m<sup>3</sup> (Figure 5). These spikes were less common in April and May and concentrations greater than 10 ng/m<sup>3</sup> did not appear in June or July. Between August and the end of November, the instrument was undergoing repairs. Total gaseous mercury concentrations in December averaged 1.68 ng/m<sup>3</sup> with maximum concentrations of 3.3 ng/m<sup>3</sup> (Figure 5).

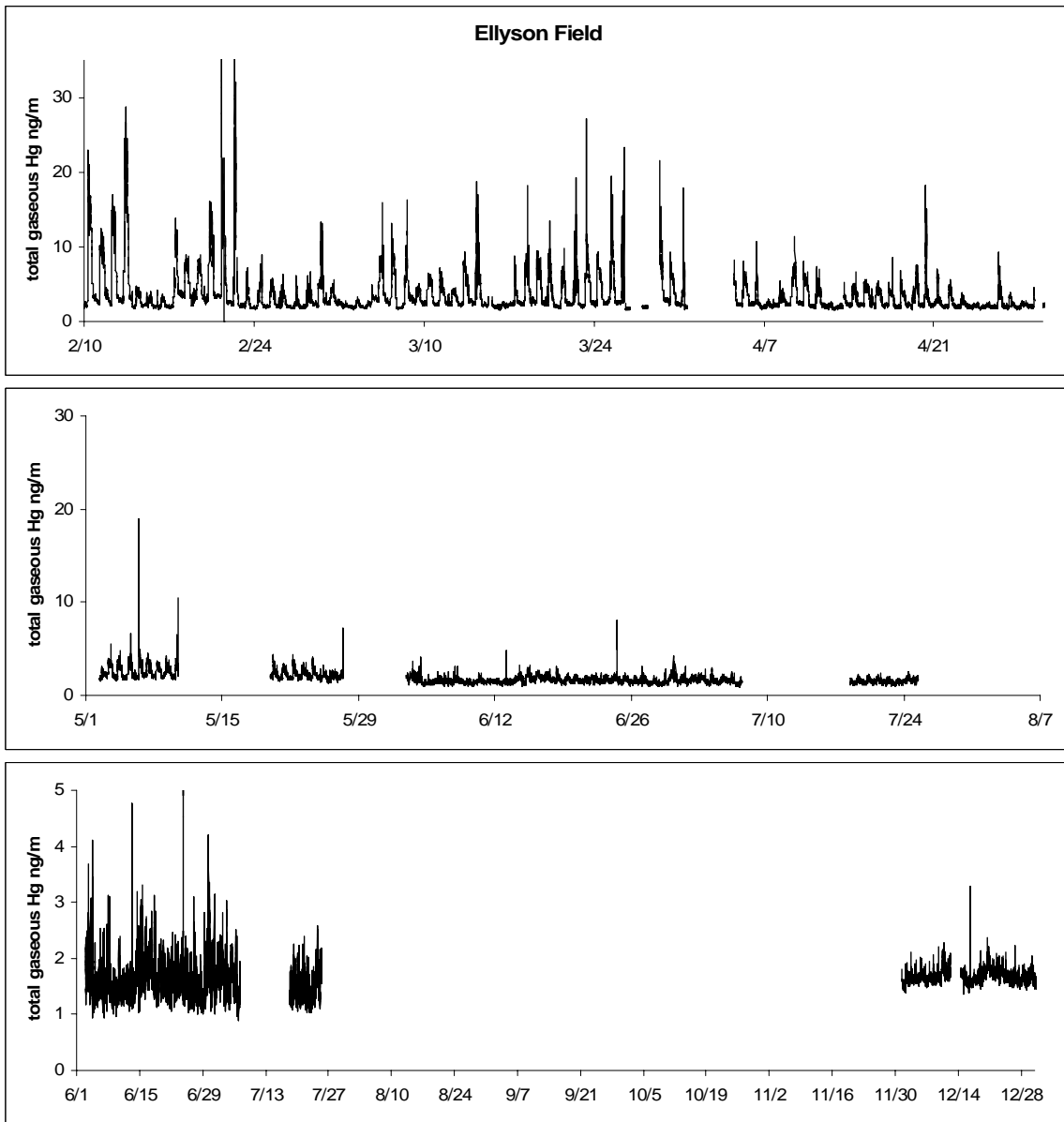


Figure 5- Concentrations (ng/m<sup>3</sup>) of total gaseous mercury at Ellyson Field in 2005. Note the change in scale in the lowest panel.

There appear to be two patterns in the concentrations; the February through May period which showed afternoon peaks in total gaseous mercury and the June through December period which generally showed concentrations less than 5 ng/m<sup>3</sup>, with maximum concentrations occurring at any time during day (Figure 6).



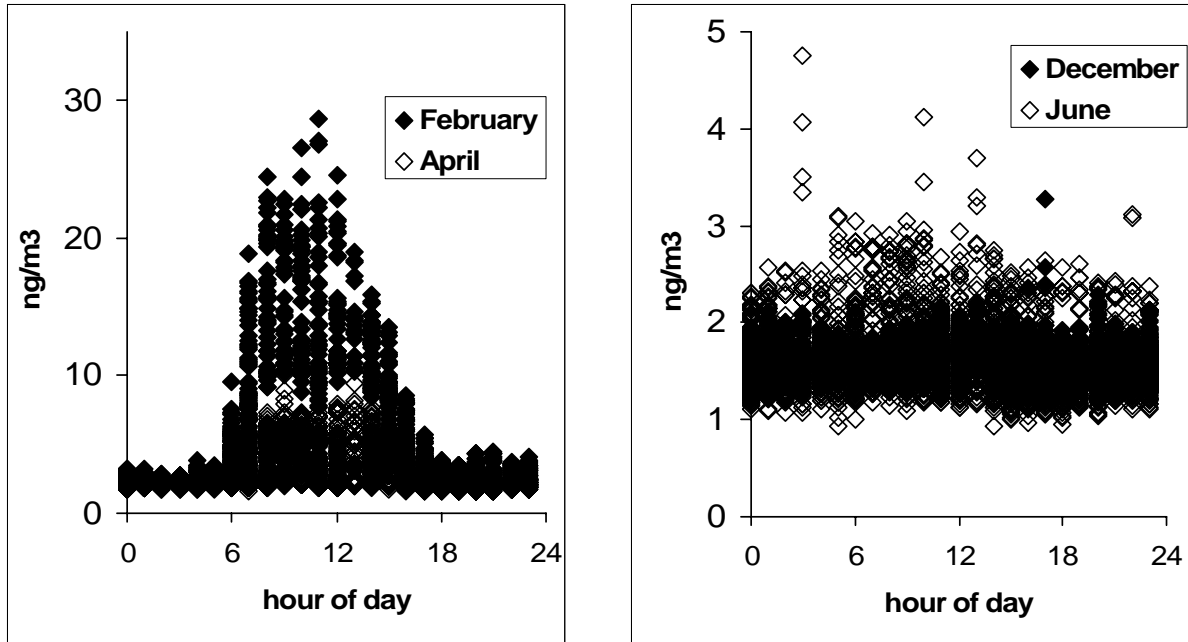


Figure 6. Hourly concentration (ng/m<sup>3</sup>) of total gaseous mercury in February and April (left panel) and June and December 2005 (right panel). Note the change in scale between panels.

In future analyses, we will evaluate Hg-trace element-major ion ratios, principal components factor analysis, and air mass back trajectory analysis in an effort to identify emission sources. Further analysis of the data on gaseous mercury emissions will also be conducted to see how peaks in total gaseous mercury relate to SO<sub>2</sub>, NO<sub>x</sub> and weather patterns. Understanding the magnitude and relative importance of different sources is critical information necessary to target the most effective reduction in atmospheric deposition of mercury, trace metals, and nitrogen.

#### References

Valigura, R.A. 2001. An introduction to the first assessment of nitrogen loads to US estuaries with an atmospheric perspective. pp. 1-10. In R.A. Valigura, R.B. Alexander, M.S. Castro, T.P. Meyers, H.W. Paerl, P.E. Stacey and R.E. Turner (eds.) Nitrogen loading in coastal water bodies: an atmospheric perspective. AGU. Washington, D.C.