

# Rainfall mercury deposition and trace element correlations in the Pensacola Bay watershed

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## Introduction

This project examines rainfall input of mercury and other trace elements to the Pensacola Bay watershed. According to the EPA, 1% of the mercury emissions to the atmosphere are from US coal fired power plants. The largest potential source in the Pensacola Bay area is the Crist coal fired power plant. By sampling at 3 sites around the Crist coal fired power plant and comparing with data collected by the Mercury Deposition Network (MDN), we can see if a known point source has a direct impact in the local environment. Comparing trace elements of interest to Al is a traditional way to estimate "excess" trace element input from anthropogenic sources. Trace elements identified by Principal Component Factor Analysis (PCFA) which cluster with Hg have been studied in more detail by this method.

## Sampling design

Three sampling sites were set up around the Pensacola Bay area (Fig. 1). Modified Aerochem Metrics model 301 wet/dry deposition samplers were used to collect three samples for each rain event. Two samples were collected in 1 L L FEP Teflon bottles for Hg and trace element analyses and a third sample was collected in a 1 L polyethylene bottle for pH, major ions and nitrogen species analyses. The sampling set up is shown in Figure 2a and 2b.



Figure 1. Topographic map of Pensacola Bay showing sampling locations. 1 – Ellyson Field, 2 – Pace site, 3 – Molino site, 4 – Crist Plant, 5 – Pensacola airport (PNS)



Figure 2a. Aerochem sampler at the Pace sampling site showing the in field setup and b. the bottle and funnel setup.

## Sample analyses

Samples were prepared for analysis by addition of acids to produce a dilute aqua regia solution (final concentration of 0.045M HCl and 0.048M HNO<sub>3</sub>), then UV oxidized for 24 hours to break up any organics that may have Hg bound to them. The prepared samples were analyzed for total Hg by using a Tekran 2600 Cold Vapor Atomic Fluorescence Spectrometer (CVAFS). Trace elements were analyzed on the samples by using a Thermo-Finnigan "Element" high-resolution ICP-MS. 46 elements were identified as significantly enriched in rain samples relative to the method blank.

## Results and discussion

Monthly (and annual) mercury deposition was calculated by summing the product of the concentration of mercury and the average sample volume in each rain event for each month (full year). The results are compared to area MDN sites AL24 (in southwestern Alabama) and AL02 (in southeastern Alabama). Table 1 shows good agreement for the annual wet deposition of Hg among the various sites. Figure 3 shows that the monthly integrated wet deposition of Hg at the five sites compares very well, showing higher deposition during the summer months (April through September) and lower deposition for the winter months (October through March). Our data for July are artificially low since the rain samplers were pulled from the field to avoid hurricane damage.

|         | VWM Hg (ng/L) | Hg flux (ng/m <sup>2</sup> ) |
|---------|---------------|------------------------------|
| AL24    | 8.43          | 18128                        |
| AL02    | 9.82          | 18346                        |
| Ellyson | 9.77          | 17057                        |
| Pace    | 9.19          | 14906                        |
| Molino  | 9.58          | 13823                        |

Table 1. This table shows a comparison of the annual 2005 volume weighted mean (VWM) Hg concentrations and the mercury flux for each site. The MDN sites only include data from January through August for the VWM (MDN, 2006). Flux data includes all months in 2005 for all sites. Our data does not include all of July since the samplers were not deployed for much of the month to avoid hurricane damage.

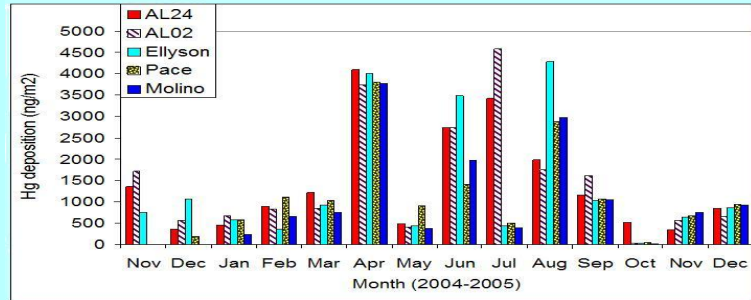


Figure 3. The monthly Hg flux for 5 rain event sampling sites in the Pensacola Bay region collected during 2005 are shown here. Data include our three sampling sites and MDN sampling sites AL24 and AL02.

PCFA revealed four factors associated with the mercury and trace element deposition: the Al-Si (crustal abundance) factor, the sea-salt factor, the "P" factor (linking phosphorus with copper and zinc, possibly from agriculture or area mining?) and the Hg factor. The Hg factor clusters Hg with five trace elements: Ga, Bi, Sb, Pb and V. Bi and Sb are volatiles that we assume come from coal combustion. Ga, V and Pb may also come from coal combustion. We used the crustal trace element to Al ratios to calculate the excess trace elements of interest (Ga, Bi, Sb, Pb and V). If we assume that 100% of the excess for these trace elements in the rain samples comes from atmospheric pollution from local and regional coal combustion, then excess trace element to excess Hg ratio can be used to calculate the Hg input from coal combustion. Three methods were used to calculate the trace element/Hg ratio in rainfall resulting from the impact of coal-fired power plants: The highest observed TE/Hg ratio, the average of the top 10 highest TE/Hg ratios, and the average TE/Hg ratio from samples with the ten highest TE/Al ratios. The calculation for the annual percentage of Hg associated with coal burning is shown in the following equation:

$$\text{annual \% of Hg associated with coal burning} = \frac{\sum_{2005} [\text{TE flux} / \text{TE}/\text{Hg}_{\text{coal}}]}{\sum_{2005} [\text{Hg flux}]} \times 100$$

| ratio   | Annual % of Mercury from Coal |                             |                             |
|---------|-------------------------------|-----------------------------|-----------------------------|
|         | highest TE/Hg                 | Average of 10 highest TE/Hg | Average of 10 highest TE/Al |
| Ga/Hg   | 20.69                         | 30.65                       | 43.39                       |
| Bi/Hg   | 20.26                         | 27.47                       | 51.50                       |
| Sb/Hg   | 12.30                         | 23.98                       | 39.25                       |
| Pb/Hg   | 11.93                         | 22.18                       | 68.59                       |
| V/Hg    | 10.06                         | 20.22                       | 31.23                       |
| average | 15.05                         | 24.90                       | 46.79                       |
| SD      | 5.03                          | 4.18                        | 14.21                       |

Table 2. Overall annual percentages of Hg associated with each trace element calculated using the highest ratio, the average of the trace element to Hg ratio from the highest 10 trace element to Al ratios and the average of the 10 highest trace element to Hg ratios.

Trace element to Al ratios were compared to the back trajectories created for each rain event (shown in Figure 4a-f). No temporal pattern emerged by clustering by trajectory type (marine, continental or stagnant). Back trajectories which show high TE/Al (due to low [Al]) are often associated with marine trajectories, suggesting that pollutant metals have become widely dispersed in the regional atmosphere, so that even "marine" air masses are affected. Though these comparisons do not show any significant pattern, we will continue to investigate the use of meteorological models to explain the data.

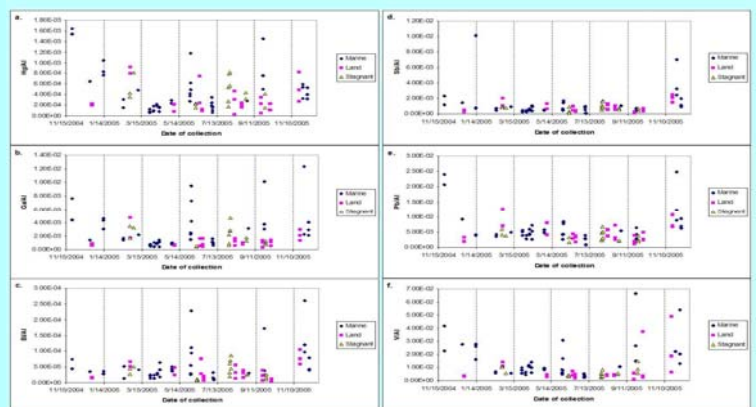


Figure 4a-f NOAA Hysplit 24 hour back trajectory models were clustered by whether the origin of the air parcel was continental, marine or relatively stagnant. The trajectories that were the most characteristic of these three types were compared to the trace element to Al ratios to determine if any pattern could be discerned: a. Hg/Al, b. Ga/Al, c. Bi/Al, d. Sb/Al, e. Pb/Al and f. V/Al. No significant pattern emerges for any of the categories.

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