

## Trace Element Analysis of Rainfall Samples from the Pensacola Airshed

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### Introduction

This continuing project focuses on the use of rainfall chemistry to identify and “fingerprint” emission sources of trace elements in rainfall. The primary trace element of interest is mercury; emitted by coal-fired power plants and deposited by rainfall. The goal of the project is to determine the extent to which the Crist power plant near Pensacola contributes to local rainfall Hg deposition. Event-based rain samples have been collected from three sites surrounding the power plant since November 2004. Each sample has already been analyzed for total dissolved Hg; subsamples were taken for analysis of additional trace elements in an effort to identify transport and deposition from local, regional, and long-range sources. These samples were analyzed using the Finnigan Element-I high resolution ICPMS and the Agilent 7500cs quadrupole ICPMS with an octopole collision cell in the Geochemistry group at the NHMFL

### Experimental

Duplicate event-based rain samples are collected from three sites around the Crist power plant in Pensacola in 1 liter FEP Teflon bottles attached to polycarbonate funnels and nested into an AerochemMetrics automated wet/dry collector. The samples are recovered after each rain event (within 24 hours) and shipped to FSU where they are acidified to 0.045M HCl and 0.048M HNO<sub>3</sub> with ultrapure acids. The bottles are placed in a UV-flux for 24 hours to solubilize 100% of the dissolved mercury that might have adsorbed to the bottle walls. The samples are analyzed for total dissolved Hg and a subsample is taken for ICPMS analysis at the NHMFL. A method using the octopole collision cell (He mode) with the Agilent ICPMS was developed to analyze samples for total dissolved As. Use of H<sub>2</sub> gas in the collision cell enabled the analysis of total dissolved Se. From 40-50 other elements are analyzed using the Element-I ICPMS.

### Results and Discussion

While many samples remain to be analyzed, we have found significant relationships among the many trace elements that have been analyzed thus far. Significant correlations were found between As-Hg; As-Sn; As-Sb; and Sb-Sn. Factor analysis was used to identify four factors that can explain 90% of the variance in the data set;

1. Al/Si factor: explains the variance for many elements that are generally expected to reflect “crustal abundance”.
2. Sea-salt factor explains Na, Mg, Li, and Sr variance.
3. “Hg” factor: explains Hg, Sb, Pb, and Bi variance, and sometimes includes V and Ga. Possible indicator of coal combustion due to presence of volatile metalloid elements.
4. “P” Factor: explains P, Cu, and Zn variance, and is currently unexplained. This factor may be associated with controlled burning and wildfires in the region. We are arranging to collect aerosol samples from controlled burns to check for these elements.

When the analyses have been completed, we will continue to apply multi-variate statistical methods to explain the data variance. In an effort to identify local vs. regional and long-range sources, we will study the chemistry of individual rain events with respect to their atmospheric origin using meteorological back-trajectory analysis.

### Conclusions

Our conclusions are still being developed, and several journal articles are anticipated after the sample analysis has been completed in 2008. As a result of our success thus far, we have been funded for another full year of sample collection by the Electric Power Research Institute (EPRI) to continue sampling at our existing sites, and to add one new “background” site at the EPA-Gulf Breeze lab near the coast.

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