Data Analysis of Fly Ash Impacts in Delaware River Sediments and Surface Water

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Background

On August 23, 2005, failure in a discharge control structure resulted in the release of approximately 100 million gallons of a mixture of water and fly ash from an ash basin at PPL's Martins Creek Steam Electric Station (Plant), in Martins Creek, Pennsylvania. The release deposited ash onto PPL-owned land, onto the dry creek bed and into the Delaware River. PPL responded proactively to the fly ash release with an aggressive emergency cleanup to remove bulk fly ash deposits, as well as concurrent investigations of the nature and extent of fly ash in the Delaware River. More than 60 miles and 200 locations were sampled or observed. These studies included evaluating metals concentrations in sediment (both river bank and in-river), surface water, fish and mussel tissue, as well as conducting aquatic surveys of fish, benthic macroinvertebrate, mussels and periphyton. This poster focuses on methods used to distinguish contributions to sediment and water quality resulting from fly ash and other natural and anthropogenic sources.

Setting

The Delaware River consists of a non-tidal, freshwater portion that extends approximately 200 miles to the tidal limit at Trenton, New Jersey (Figure 1). Downstream the river transitions to saline Delaware Bay, which contains over 133.5 miles of tidal estuary. The fly ash investigation focused on the lower non-tidal portion from river miles 194.2 (fly ash release location) to Trenton. The Lehigh River is a major tributary entering at Easton, approximately 8 miles downstream of the release.

The August release occurred after a near record low-flow period (late-April thru early October). Major localized precipitation events between October 7 and 15 caused two high-flow events that exceeded 43,000 cfs. The release was bracketed by the two largest floods in 50 years (Figure 2).

Figure 1. Site location within Delaware River watershed

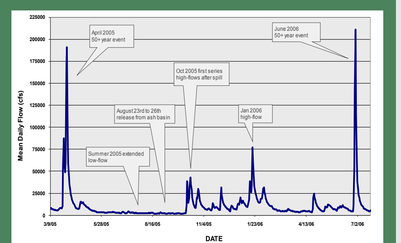


Figure 2. Hydrograph for Delaware River at Belvidere March 2005 to July 2006

Chemistry

Fly ash is a mineral residue from coal combustion consisting mostly of silicon dioxide, aluminum oxide and iron oxide. Fly ash also contains heavy metals, such as arsenic, copper, lead, mercury and zinc. Typically, fly ash consists of glassy spheres that effectively bind the metals, thereby limiting its bioavailability in aquatic systems.

Arsenic (As) as surrogate

As was selected as a chemical surrogate for the presence of fly ash. Data indicated the solids stored in Ash Basin 4 and in-river deposits had nearly identical chemical composition, as noted in Figure 3. For the Martins Creek Site, As concentration in material from Ash Basin 4 was approximately 120 mg/kg; by comparison, As concentrations in upstream sediments averaged 2.7 mg/kg. The ratio of 45:1 for As is the highest among the metals (Figure 4). Other elements with an elevated "ratio" greater than 10 compared to background were barium, beryllium and mercury. Elevated concentrations of other metals with low ratios without corresponding As increases would indicate a non-fly ash-related source.

Aluminum (Al) normalization

Al was selected as the conservative element for normalization of trace metal concentrations to correct for natural variability because:

- Local anthropogenic inputs of Al are minimal
- Al is non-reactive in a sediment environment
- Al concentrations in Ash Basin 4 are similar to Delaware River sediments
- Linear relation between Al and other metals in the Delaware River sediments has no significant intercept
- Al concentrations were strongly correlated with fine-grained sediment

Figure 3. Pool I and II similar to ash basin material

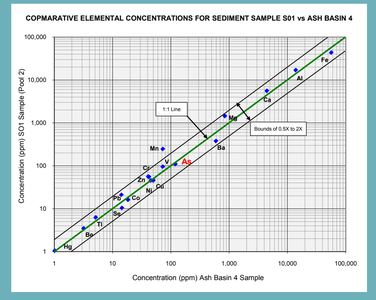


Figure 4. As selected as chemical surrogate for fly ash contribution to riverbank and sediment

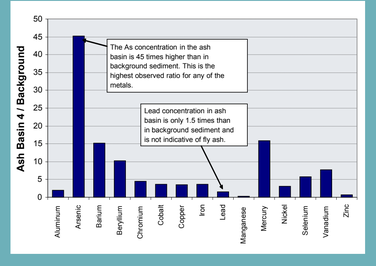
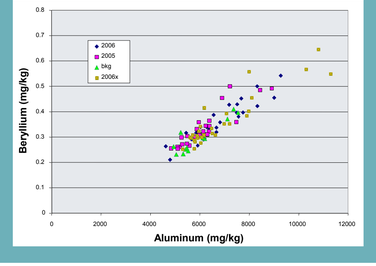


Figure 5. Beryllium as a function of sediment Al content



Other Geochemical Comparisons

Metals concentrations in sediments and bank soils were compared to various regional natural soils levels. Sediment As concentrations were compared to temporal and spatial patterns in elements not related to fly ash. Similarities in the patterns indicate that variations in As may not be related to fly ash (Figure 6).

Residual Analysis

Residual analysis is an alternative to aluminum normalization as a means of adjusting data to account for natural variability in sediment metals concentrations. Regression analysis using multiple variables that effect metals concentration, such as grain size, TOC and aluminum are the independent variables, while metals concentration is the dependent variable. The residuals values are the difference between the observed and predicted (from the regression analysis) metals concentrations. Patterns in residuals are then examined for potential correlations once natural variability has been suppressed. In Figure 7, a correlation between Vanadium (V) and As is shown, while Figure 8 shows no correlation between Zn and As.

Surface Water Concentrations

In the four months after the release, more than 2,200 surface water samples were collected. Initially, high concentrations declined with both distance and time, until a temporary increase during the first high-flow event in October (Figure 9). Strong geochemical evidence, using the Al:As ratio, indicated exhaustion of a majority of deposited materials. Subsequent high-flows indicated a return to the background Al:As ratio. After the first major high-flow event, less than 1percent of surface water samples had detectable As.

Figure 6. In-river sediment sampling – June 2006 relation of As and Zn to percent fines

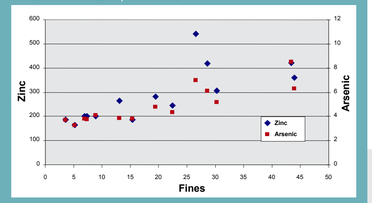


Figure 7. Vanadium residual vs. As residuals for riverbank samples

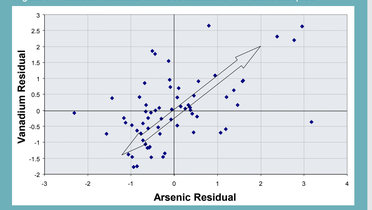


Figure 8. Zn residuals vs. As residuals for riverbank samples

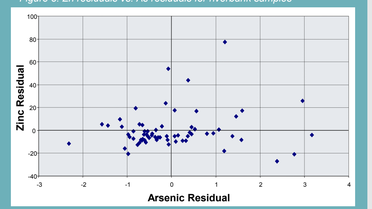
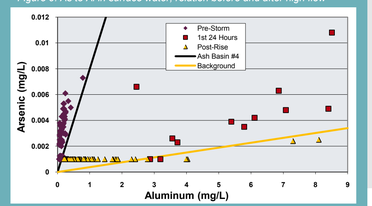


Figure 9. As to Al in surface water, relation before and after high flow



Lehigh River Considerations

Various methods, including radar plots (Figure 10), residual analysis and principal component analysis (Figure 11) were used to demonstrate the dominant contribution of metals from the Lehigh River. In addition, the ΣSEM (simultaneously extractable metals) in the Lehigh River was much greater than in the Delaware River immediately downstream of the release. These results helped focus studies of potential impacts to the first 8 miles.

Figure 10. Radar plot (spider plot)

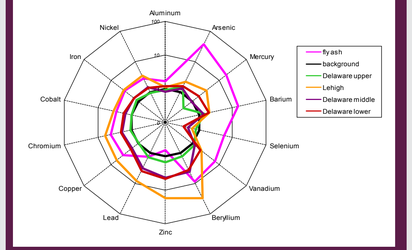
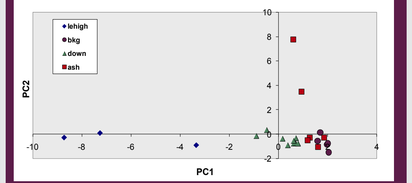


Figure 11. Principle component analysis



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