Abstracts

TVA-Kingston Fly Ash Release Environmental Research Symposium

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Integrated Ecological Research - TVA Kingston Ash Recovery Project

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The Kingston fly ash spill deposited several million cubic yards of ash into portions of Watts Bar reservoir. Most of the ash has been removed from the Emory River, but about 300,000 cubic yards remains that may be impossible to remove without causing more environmental damages than benefits.

Recognizing the potential for adverse environmental effects from both the initial spill and the ash that may remain in the rivers, TVA has developed an integrated research program that draws on its own technical expertise, nationally-recognized third-party researchers, and academic institutions to assess effects of ash-related contaminants on ecological receptors at multiple trophic levels. Primary objectives of this program are to 1) accurately assess immediate and intermediate-term effects of the spill on the aquatic ecology of the system, 2) develop information necessary to predict long-term system responses to ash that may remain in the river, and 3) identify potential problems for which innovative solutions must be developed.

This research spans multiple disciplines (e.g., environmental geochemistry, toxicology, and ecology), and examines ecological effects at cellular, organ, organism, and population levels. For key contaminants such as arsenic and selenium, it includes characterizing chemical speciation, bioaccumulation, and biogeochemical transformation rates, and the effects of environmental conditions on those rates.

This poster describes the different components of this research program and uses results to date to illustrate linkages among the different research components.

Assessment of Mercury and Methylmercury in the Emory and Clinch River System after the December 2008 Coal Ash Spill at the Kingston Fossil Plant, TN

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The coal ash released from the TVA Kingston Plant into the Emory River is enriched in mercury (Hg) (~0.15 mg/kg) relative to background levels in the sediment of the Emory River. As the coal ash accumulates and re-mobilizes within the river system, leaching of Hg and other materials from the ash could stimulate the production of methylmercury (MeHg), a bioaccumulative neurotoxin, in river sediments. The objective of this study was to evaluate surface water and sediment quality with respect to Hg and MeHg. Sediment and surface water samples were collected from August 2009 to August 2010 at sites upstream and downstream of the spill site, and further downstream in the Clinch River. Hg concentrations in surface water were generally low (< 12 ng/L) while Hg concentrations in sediments appeared to increase in the Emory near the spill site (0.11 ± 0.03 mg/kg) relative to upstream (0.06 ± 0.03 mg/kg). Further downstream in the Clinch River, however, average Hg content in the sediment (0.86 ± 0.36 mg/kg) was greater than average values in the Emory River. Contamination of the Clinch River was most likely due to historical releases of mercury from the Y-12 facility at Oak Ridge, TN. While Hg contamination exists in the rivers near the ash spill site, the conversion of this Hg to MeHg by anaerobic bacteria (such as sulfate reducers) in river sediments is a concern due to the toxicity of MeHg. MeHg concentrations in the river sediments varied spatially and temporally and did not correlate to total Hg content. The percentage of mercury as MeHg was largest at locations in the Emory River at locations near the spill site, and lowest in the historically contaminated Clinch River, indicating that conditions in the Emory River were amenable to MeHg production. Hg isotope data suggest that much of the mercury near the spill site in the Emory River was derived from coal ash. Thus, higher relative MeHg levels could be due to stimulation of biomethylation from coal ash in sediments or conditions in the Emory River that favor MeHg production. The coal ash was a source of leachable sulfate to river sediments and may have stimulated growth of sulfate-reducing bacteria that produce MeHg. Additional experiments to investigate the environmental fate of coal ash include: (1) anaerobic incubation studies using river sediments spiked with coal ash to evaluate whether coal ash can enhance MeHg production; (2) sequential extraction leaching experiments to identify the Hg species are present in the ash; (3) leaching experiments using dissolved organic matter to determine if the presence of organic matter can facilitate leaching of Hg from coal ash. Overall, our results suggest that mercury methylation potential and the bioavailability of coal ash leachates to MeHg-producing bacteria should be considered when evaluating the hazards of coal combustion products with respect to mercury.

Tracing Multiple Sources of Mercury in River Sediments near the TVA Kingston Site using Hg Stable Isotope Ratios

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Following the December 22, 2008 ash spill at the Tennessee Valley Authority's (TVA) Kingston coal-burning power plant, elevated levels of mercury (Hg) were detected in the river system's sediments. However, there are other sources of Hg in the system, including known releases from the U.S. Dept. of Energy Y-12 plant near Oak Ridge, regional atmospheric Hg, and natural background. Variations in Hg stable isotope abundances may provide a means of tracing the Hg from various sources as it moves through the system.

Sediment samples from the Clinch River (both upstream and downstream of the Kingston power plant), and the Emory River upstream from the plant were digested overnight in aqua regia to release Hg, which was separated from other elements via ion exchange and analyzed using a Nu Instruments multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS). The $^{202}Hg/^{198}Hg$ abundance ratio was measured with a precision of approximately 0.12 parts per thousand (per mil, or ‰). Results are expressed as $\delta^{202}Hg$ values, which are per mil deviations from NIST SRM-3133, an accepted interlaboratory standard. Odd isotope (^{199}Hg and ^{201}Hg) anomalies were also measured and are reported as $\Delta^{199}Hg$ and $\Delta^{201}Hg$.

Our results suggest three distinct $\delta^{202}Hg$ "signatures" for the three most likely sources influencing the system. Average $\delta^{202}Hg$ values for the Clinch River, Kingston fly-ash, and the natural background (represented by Emory River Mile Marker 12 samples) are -0.26 ± 0.16‰, -1.71 ± 0.42‰, and -1.17 ± 0.13‰, respectively. The data suggest that the upstream Clinch River is dominated by near-zero $\delta^{202}Hg$ values. This source may be the Y-12 plant near Oak Ridge, which is known to discharge Hg into the Clinch River system. Sediment samples around the Kingston TVA plant, on both the Emory (up to Emory River Mile 4 – where ash has been found) and Clinch rivers, are fully consistent with a three end-member mixing model. This model enables us to estimate the contributions of the three regional Hg sources to the total Hg inventory in each sediment sample.

The data also show that the Clinch River has $\Delta^{199}Hg$ and $\Delta^{201}Hg$ values distinct from the fly-ash and Emory River. The average ^{199}Hg and ^{201}Hg anomalies in the Clinch River samples are -0.10 ± 0.04‰ and -0.08 ± 0.02‰, respectively. The Emory River ($\Delta^{199}Hg$ and $\Delta^{201}Hg$ values of -0.21 ± 0.06‰ and -0.15 ± 0.03‰, respectively) and fly-ash ($\Delta^{199}Hg$ and $\Delta^{201}Hg$ values of -0.22 ± 0.01‰ and -0.16 ± 0.02‰, respectively) are indistinguishable from each other.

We infer from the data that Hg isotope ratios in river sediments really are semi-permanent "signatures" that do not change much with time. The range of values of Clinch River Mile 5.5 is 0.40‰ over an 11 month timescale, with no trend. The narrow overall range for these upstream samples suggests a lack of strong shifts as the Hg ages in the river system. However, it would be risky to simply assume that the Hg is completely chemically inert in the system.

Baseline Ecological Risk Assessment for the TVA Kingston Fly Ash Recovery Project

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The release of fly ash at the Tennessee Valley Authority (TVA) Kingston Fossil Plant on December 22, 2008 discharged approximately 5.4 million cubic yards of coal ash slurry into the adjacent aquatic and terrestrial systems. The initial response focused on public protection and stabilization of the released ash, but rapidly evolved to include comprehensive monitoring of ambient media and ecological receptors. Metals and metalloids are the primary constituents of potential concern for fly ash. A Conceptual Site Model (CSM) was developed to summarize and illustrate the ecological receptors and potential exposure pathways associated with the release.

The Screening Level Ecological Risk Assessment (SLERA) indicated that a Baseline Ecological Risk Assessment (BERA) is warranted for the River System. The direct exposure pathways being evaluated for the River System include exposures to ash as sediment, sediment porewater, groundwater discharging to surface water, surface water, and seasonally-exposed sediment. Dietary exposures are also a concern for some ash-related constituents, including arsenic and selenium. The ecological receptors for which bioaccumulation and food web pathways are being studied at this site include fish, benthos, emergent insects, piscivorous birds and mammals, aerial-feeding insectivores, herbivorous birds, omnivorous mammals, amphibians, reptiles, and others. The BERA strategy presented in this poster was used to develop data quality objectives for the River System Investigation and identify additional data needs. The CSM and BERA Strategy were then used to refine the numerous field and laboratory studies being performed or supported by TVA, many of which are presented in this poster session.

Porewater in Sediment at Kingston Ash Recovery

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Measurements of porewater concentrations of arsenic, selenium, mercury, boron, and barium are compared to ash concentration at sites on the Emory River near the site of the Kingston ash spill and Clinch River downstream of the Emory.

Characterization of Coal Fly Ash Associated with a Release of Fly Ash at TVA's Kingston Fossil Plant

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Keywords: Kingston, Fly Ash, Physical Properties, Chemical Properties

The composition and characteristics of fly ash depend on the source of coal and the types of burners and pollution control devices. The Tennessee Valley Authority Kingston Fossil Plant burns mostly eastern bituminous coal, but has also used coal from Illinois, and blends low-sulfur Western coal to reduce emissions. This results in some heterogeneity of the ash as different sources or combinations of coal were burned. KIF produces about 80% fly ash and 20% bottom ash. For ease of handling, water is used to flush fly ash and bottom ash to an onsite ash pond for settling. Settled ash has been hydraulically dredged to dredge cells for de-watering and long-term storage.

TVA has evaluated the characteristics of KIF coal ash following the release that occurred in December, 2008. KIF ash has been tested for chemical, radiological, and physical properties using EPA methods for total metals, TCLP metals, BTEX, radionuclides, polynuclear aromatic hydrocarbons, grain size, acid volatile sulfides and simultaneously extractable metals, standard toxicity tests, and polarized light microscopy to evaluate the degree of mixing with native sediment.

The initial assumption following the ash release was that mixing of the various layers of ash during the release resulted in a relatively homogeneous material in the river. However, closer analysis shows a reasonable amount of heterogeneity in the ash deposited in the river due to less mixing of the initially deposited ash than was assumed, particle size sorting as storm flows re-suspend and transport ash downstream, and mixing with native sediment.

The Geochemical and Isotopic Characterization of the Environmental Impacts of the TVA Coal Ash Spill: A 30 month investigation

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Our investigation of the largest coal ash spill in US history at the Tennessee Valley Authority (TVA) coal-fired power plant in Kingston, TN has revealed several conclusions about the impacts of the coal combustion residues (CCRs) released into the environment and the effects of remediation at the different phases of the clean up effort. Our initial research immediately after the spill showed that CCRs could leach contaminants into the environment [1], where mobilization of leachable coal ash contaminants (LCACs) such as boron, arsenic, selenium, strontium, and barium depend on ash composition and environmental factors such as pH and redox conditions. Initially, the surface water in areas of restricted water exchange near the spill revealed high levels of LCACs (e.g., As: 9- 95 µg/L), but remediation and removal of ash from this area combined with diversion of surface water has led to a reduction of the LCAC concentrations with time. Throughout the Phase 1 clean up, systematic sampling of the water and sediments revealed that the Clinch and Emory rivers downstream of the spill had low LCAC concentrations below the EPA maximum contaminant level (As=10 µg/L), but with levels (e.g., As ~4 µg/L) above the baseline of the upstream rivers. Dredging activities had little impact on the concentration of LCACs in the surface water, while reservoir level (dilution effect) played a much larger role in the concentration of LCACs measured [2]. Pore water extracted from bottom sediments of the downstream rivers contained significantly higher LCAC levels (e.g., As 9-2010 µg/L), which are associated with both CCRs contents and some degree of anoxic conditions that enhance mobilization of some LCACs, particularly uncharged arsenic species from the spilled CCRs [2]. A follow up investigation, about 30 months after the spill, is currently undertaken to determine the remaining effects after the Phase 1 clean up was completed.

Field data and independent laboratory leaching experiments of CCRs indicate that boron is a sensitive indicator for CCR leaching, with boron content up to 1518 µg/L in pore water relative to upstream river water (6 to 9 µg/L). Boron mobilizes from CCRs has a distinctive isotope fingerprint that is significantly different from that of meteoric boron in the upstream rivers. Pore water and surface water (sampled downstream of the spill) revealed a $\delta^{11}B$ value of -11‰ and -12‰ respectively (relative to the standard NIST951), while most natural waters and other potential contaminants (e.g., domestic waste water) have a much more positive $\delta^{11}B$ value.

Currently our research group examines CCRs (e.g., bottom ash, combustion by-products, effluents) from other TVA plants. We are conducting leaching experiments in CCRs in order to simulate various environmental conditions and to test their different effects. The leachates are analyzed for its trace metal distribution, geochemical and isotopic signatures. The results from this investigation will allow for better environmental management practices and better monitoring the potential impacts CCRs on the environment.

[1] Ruhl, et al. (2009) *Env. Sci. Tech* **43**, 6326–6333.
[2] Ruhl, et al. (2010) *Env. Sci. Tech* **44**, 9272–9278.

Stratigraphy and Magnetic Susceptibility of Ash Deposits Two Years after the Release

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A second phase of characterization of the ash distribution was completed early this year, 2 years after the release. In the Emory River, coarse grained deposits including sand and gravel beds bury ash and beds of an ash/sediment mixture. Burial of the ash by post-release high-energy flow deposits indicate that although ash may no longer be at the sediment-water interface is it still present at depth within the channel cross section. Ash beds also occur beneath beds rich in organic matter that includes leaves, pine needles and twigs. This waterlogged vegetation could have been deposited during periods of low flow or slack water. Both cohesive organic beds and gravel deposits reduce the possibility for remobilization of the buried ash beds during typical flow velocities.

Previous studies documented percent ash in the alluvial sediment using point counting of ash spherules on smear slides. This method is effective however it requires a large time investment. We are investigating the use of mass specific magnetic susceptibility (MS) to estimate ash content in alluvial deposits within the river systems. This technique was chosen because it is rapid, nondestructive and some fly ash spherules are known to be coated with iron. Preliminary results show a correlation between MS and percent ash measured by point counting. There is variability in the correlation between the three different river systems. This may be explained by bedrock geology differences within the drainage basins. Metal concentrations were also compared to MS for the same samples. Elevated elemental concentrations occurred in samples with MS values between $2x10^{-6}$ and $6x10^{-6}$ m^3/kg. We are exploring the possibility that this observation indicates that ash spherules within this range of MS values contain higher concentrations of metals.

Future research includes comparing soil chemistry and ash content with MS values measured on samples recently collected to increase the coverage of the data set. In addition we plan to classify ash spherules by point counting Fe coated vs. other types. We hope to establish MS as a method for rapid identification of ash content in alluvial sediment within the river systems.

Evaluation of Human Health Risk from Potential Exposures to Fly Ash at the TVA Kingston Fly Ash Recovery Project

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Keywords: Kingston, Human Health, Risk Assessment, non-cancer, cancer

The release of fly ash at the Tennessee Valley Authority (TVA) Kingston Fossil Plant (KIF) on December 22, 2008 discharged approximately 5.4 million cubic yards of coal ash slurry into the adjacent terrestrial and aquatic systems. The initial response focused on public protection and stabilization of the released ash, but rapidly evolved to include comprehensive monitoring of ambient media and ecological receptors.

The objective of the human health risk assessment for the TVA Kingston Fly Ash Recovery Project was to develop quantitative and qualitative estimates of potential cancer risks and non-cancer hazards for human receptors potentially exposed to the ash. These estimates were developed to support remediation decision making. Risks to both current (or near-term) and potential future receptors were evaluated. Potential receptors were distinguished as on-site and off-site. Onsite receptors are those who reside, work, or play on the ash, whereas, offsite receptors are those whose activities occur in areas where ash is not present. The risk analysis was based on analytical data collected from ash in the failed dredge cell and surrounding land, surface water from the Swan Pond Embayment, and shallow and bedrock groundwater beneath the dredge cell. Metals including arsenic and selenium are the primary constituents of potential concern for human exposures to fly ash.

Evaluation of Impacts on Surface Water Quality Associated with a Release of Fly Ash at TVA's Kingston Fossil Plant

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Keywords: Kingston, Fly Ash, Surface Water, Monitoring

In response to the coal ash spill at the Tennessee Valley Authority's (TVA) Kingston Fossil Plant (KIF), TVA, the Tennessee Department of Environment and Conservation (TDEC) and the Environmental Protection Agency (EPA) have collected surface water samples from the Emory, Clinch, and Tennessee Rivers. The objective of the surface water monitoring was to determine whether there was any immediate down-river migration of ash-related constituents posing an imminent public health or environmental threat.

Sampling was conducted at five Emory River, four Clinch River, and two Tennessee River locations. TVA sampled these locations two days per week and analyzed the samples for a 24 total and dissolved metals and total suspended solids. To monitor the effectiveness of best management practices to reduce ash migration during dredging, TVA performed daily monitoring of dredge plumes in the Emory River. TVA has collected more than 2,500 surface water samples since the spill.

During the time-critical removal action, total arsenic in four Emory River surface water samples exceeded its Tennessee Domestic Water Supply Standard (TDWS) and Tennessee Water Quality Criterion (TWQC) of 0.01 mg/L. Dissolved copper exceeded the fish and aquatic life criterion in one sample at ERM 1.75. Total lead exceeded its TDWS in two Emory River samples at ERM 1.75. Thallium was detected in 64 samples, all of which exceeded its TWQC. This poster summarizes the results of TVA water quality monitoring a KIF during the period in which dredging of ash from the river was occurring.

So What Does It Mean? What Ecological Effects Has the Kingston Ash Spill Caused?

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Immediately following the TVA Kingston fly ash spill, on the basis of a few hastily-collected samples several researchers predicted calamitous effects on the aquatic ecology in the Emory, Clinch, and Tennessee Rivers as a result of bioaccumulation of ash-related constituents.

This poster describes the extent of ecological effects observed during the first two years following the ash spill and possible relationships with bioaccumulation results that are presented in a companion poster. Information is presented on observations of ecological effects at the cellular, organ, organism, and population levels. Results are presented on species abundance and diversity, reproductive success, early life stage effects and survival, and other potential ecological effects.

Because selenium is a significant contaminant in fly ash that in other studies has been shown to have adverse effects on animal reproduction, particular emphasis has been placed on evaluating potential reproductive effects that could have cascading effects on populations of the affected organisms and their predators.

Using Raman Spectroscopy for Analyzing Fly Ashes

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Keywords: Fly Ash; Raman spectroscopy; Characterization; Hydration; Reactivity

This study focused on determining the chemical composition and mineral phase of various fly ashes and Portland cement. Six fly ashes were studied, three of which were from TVA and three were from local concrete material suppliers. Using the Raman spectroscopy technique, the amorphous and crystalline phases in the dry cementitious materials and wet pastes were investigated, and the results were correlated with those from XRD/XRF analyses as well as with those from the ASTM strength index tests. It is found that Raman spectroscopy is an effective technique in characterizing fly ashes and estimating their pozzolanic reactivity. Proper use of this technique may help power plants, including the Kingston fossil plant, and the concrete industry in more effective characterization and enhanced usage of fly ashes.

Increasing Use of Fly Ash in Concrete through Nanomaterial Modification, Multiscale Characterization, and Improved Processing

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Keywords: Fly ash, pozzolanic reactivity, heat of hydration, nano-materials, clays

The present poster will summarize the research activities performed in the first year of a project sponsored by Oak Ridge Associated Universities (ORAU). The project is aimed at increasing use of fly ash in concrete. This objective is approached through modifying fly ash mortar and concrete with various commercially available nano-materials and clays. The fly ashes used in the project are mainly from the Tennessee Valley Authority (TVA), and some are from local concrete material suppliers. The investigation has been centered at the characterization of cementitious materials (fly ashes, nano-materials, and clays) at multiple scales (from nano- to neso-/macro-scales). It includes evaluating pozzolanic reactivity of fly ashes and examining the effects of clays, nano-silica, and nano-limestone on paste/mortar compressive strength, heat of hydration, air content, and flow ability (or rheology). It was found that the fly ashes received from TVA plants had comparable pozzolanic reactivity and general properties (strength, heat of hydration, and flow) to the commercially available Class F fly ashes used in the present study. Some manufactured clay materials (such as Metamax) showed a significant effect on mortar strength, while others (such as Actigel, nanoclay) had a considerable effect on the rheology of mortars. Addition of nanolimestone reduced flowability of a cement-based material but substantially recovered the strength loss resulting from addition of high volume TVA fly ashes. Further research is in progress to study the interactions among cement, fly ash, and nano-materials, optimal mix design of self-consolidating concrete (SCC) consisting of high fly ash content and nano-materials, and the SCC performance. Since the research is focused on the TVA fly ashes, the results can be directly applied to the beneficial uses of the fly ashes at the Kingston fossil plant.

Fly Ash as a Potential Food Supplement? Bioaccumulation in Critters Near the Kingston Ash Spill

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Immediately following the Kingston ash spill, on the basis of a few hastily-collected samples several researchers predicted dire effects on the aquatic ecology in the region as a result of bioaccumulation of ash-related constituents.TVA developed an integrated research program to evaluate the potential for adverse environmental effects from the Kingston fly ash spill. One part of that work focuses on determining whether there has been increased bioaccumulation in fish, invertebrates, birds, and other organisms living near the site.

This poster presents information on levels of bioaccumulation observed in a wide variety of organisms that have been collected over the last two years by researchers from TVA, Oak Ridge National Laboratory, Virginia Tech, and several other institutions. These include organisms throughout the food chain from the spill area and reference sites, and include measurements of ash-related contaminant concentrations in whole organisms, as well as various types of tissues, eggs, and blood. Preliminary results show increased bioaccumulation of some ash-related contaminants. Since most of the ash has been removed from the Emory River, these results constitute a baseline for tracking further increases or decreases in bioaccumulation.

A companion poster describes investigations of potential ecological effects and efforts to establish whether there are relationships with particular bioaccumulated contaminants.

2D Sediment Transport Simulation to Support the Monitored Natural Recovery Process for Watts Bar Reservoir

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In December of 2008 an 84-acre containment berm failed on a fly ash storage facility at the TVA Kingston Fossil Plant, releasing approximately 6 million cubic yards of ash which impacted approximately 300 acres of the surrounding area, including 3 million cubic yards of ash which deposited in the Emory River. The ash completely filled the Emory River channel adjacent to the Swan Pond Embayment, with ash transporting more than 2 miles upstream in the Emory River due to the momentum of the slurry release.

After the spill, the channel thalweg was filled with ash (ash depths up to 30 feet), thus the channel capacity was significantly reduced. This in turn resulted in an immediate flood risk for the numerous properties that were located on both sides of the channel. Studies conducted by the TVA indicated that the ash deposits in the river increased the predicted flood elevation for the 100 year flood by 8 feet.

A two-dimensional sediment transport model (AdH) was developed for the Emory, Clinch, and Tennessee Rivers, from Emory River Mile 4.0 to Watts Bar dam at Tennessee River Mile 530 (45 miles). The model was used to evaluate the fate and transport of fly ash that transported downstream from the Kingston spill site on the Emory River. Model results indicated that approximately 90,000 – 120,000 cubic yards of ash transported from the site during a 70,000 cfs flow event that occurred in May 2009.

During 2010 - 2011, the model was used to evaluate the potential for native river sediments to mix with or cap post-spill ash deposits in the Emory, Clinch, and Tennessee Rivers. A two year model simulation was conducted. An average flow year (1995) and a high flow year (2003) were included in the simulation to evaluate deposition and scour throughout the system. The final bed characteristics from the initial fly ash transport simulation were utilized as the initial condition for this model scenario. Results of the study will provide guidance on long term capping effectiveness based on spatial distribution of ash and natural sediment deposits.

The Effect of Dissolved Organic Matter on the Release of Trace Elements from Coal Ash in Natural Surface Waters

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Keywords: dissolved organic matter, mercury, aromaticity, calcium, leaching

In order to understand the effect that dissolved organic matter has on metal leaching from coal fly ash, a series of batch experiments in the presence and the absence of dissolved organic matter were done using coal ash generated at the Kingston Fossil Plant. The type and concentration of the dissolved organic matter in solution was varied in order to uncover the properties of the dissolved organic matter most important for metal leaching. Major and trace metals, anions, dissolved organic carbon, UV absorbance, and pH were measured for the filtered ash leachate. Results indicate that dissolved organic matter plays an important role in the leaching of mercury from the ash.

Selenium at the Base of Aquatic Food Webs – Insights from Laboratory-Based Bioaccumulation Studies with Periphyton and the Mayfly *Centroptilum Triangulifer*

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Keywords: Selenium, periphyton, mayfly, bioconcentration, bioaccumulation, toxicity, trophic transfer, food rationing, selenite, selenate

The primary goal of this research is to assess the movement of dissolved inorganic selenium into primary producers at the base of aquatic food webs, conversion to organo-Se, and subsequent trophic transfer and toxicity to primary consumers. We have been addressing this goal by using a promising new toxicity model, the mayfly *Centroptilum triangulifer*, while explicitly considering environmentally relevant exposure pathways and chemical concentrations. We perform bioconcentration experiments and dietary selenium exposures to *C.triangulifer* using natural periphyton plates grown in a flow-through system at Stroud Water Research Center. The plates are loaded with Se using $^{75}SeO_3$ as a radiotracer for following the movement of Se through our laboratory microcosms (2L glass bottles).

Our research has shown that *C.triangulifer* is affected by dietary Se exposure in a dose-responsive manner. This contradicts prior assertions that aquatic insects are generally tolerant of dietary Se exposure, however adverse effects appear to be mediated by food rationing. Mayflies with an abundance of food do not appear to suffer adverse effects, whereas those with reduced rations (i.e., competition for resources) do. Further, we are showing that dissolved selenite is much more readily absorbed by periphyton than selenate and that selenate uptake is most likely mediated by biological reduction to selenite prior to absorption. Lastly we are seeing that elevated sulfate concentrations reduce the uptake of selenium into periphyton. Ongoing efforts are focused on the speciation of Se once incorporated into periphyton using synchrontron based XANES analysis of periphyton exposed to either selenite or selenate.

These results imply that aquatic insect communities may be adversely affected in selenium contaminated systems, however the speciation and ambient water chemistry significantly impact the ability of selenium to enter the base of aquatic food webs.

Groundwater Flow and Transport Model Development for Proposed Ash Landfill at Kingston Fossil Plant

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Three dimensional groundwater flow and transport models have been developed for a proposed ash landfill at the TVA Kingston Fossil Plant. The models have been used to predict ash-related constituent concentrations and mass loadings entering adjacent surface waters via groundwater seepage from ash sources. These predictions will subsequently be used in evaluating long-term risks to human and aquatic receptors. The constituents of concern (COCs) selected for transport model include arsenic, selenium, and radium-226. These are naturally-occurring constituents that can be concentrated in ash through the coal combustion process.

A comprehensive three-dimensional groundwater flow model that utilized the MODFLOW code was first calibrated for 2010 conditions using groundwater levels from 179 wells and piezometers. These data were supplemented by surface water level measurements at 34 locations. Revisions to the calibrated flow model were necessary to incorporate planned engineering design features for the closed ash cell. Model simulations of future conditions incorporate proposed changes in the geometry of ash fill areas, ashfill capping, perimeter stabilization walls, and surface water boundary conditions

The groundwater flow model representing future site conditions was subsequently linked to the transport model code MT3D to predict concentrations of COCs entering surface waters over a time period of 100 years. Future COC source areas include the Closed Ash Landfill, capped Ball Field, and capped Settling Basin. In addition to boundary conditions identified for the groundwater flow model, boundary conditions for the transport model include recharge concentrations (source term) for each COC to represent leachate emanating from the vadose zone of the ash landfill. Initial conditions for the transport model include constituent (COC) concentration distributions that were developed from porewater and groundwater sampling. The predicted COC mass flux to surface waters is a combination of a leaching source from the Closed Ash Landfill, existing COC concentration distributions, and COC background concentrations. Partitioning coefficients were used to represent attenuation of COCs during groundwater transport.

Surface waters recipient to groundwater discharge were subdivided into three segments due to differences in geography, hydrology and potential receptors. The segments include: Swan Pond Embayment, Emory River, and the Intake Channel (eastern portion). The model predicted spatial distributions of COC concentrations with time and mass fluxes to receiving streams are calculated and summarized. These results will be subsequently used in evaluating long-term risks to human and aquatic receptors.