Abstracts

TVA-Kingston Fly Ash Release Environmental Research Symposium

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Fish Health and Bioaccumulation studies for evaluating fly ash exposure and effects in aquatic ecosystems.

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As a major component of the comprehensive biological monitoring and assessment project related to the TVA Kingston fly ash release, we conducted a baseline fish health and bioaccumulation study for the purposes of evaluating possible effects of fly ash exposure on fish health and for determining possible relationships between levels of metals in fish and various indicators of fish health. Three species of fish, representing different trophic levels and home ranges, were sampled at sites in the immediate vicinity of the fly ash release and at sites upstream and downstream of the spill. Muscle and liver tissue for individual fish were analyzed for 25 metals and an in-depth health profile, based on the multiple bioindicator approach, was conducted for each fish including bioindicator measures of physiological function, electrolyte homeostasis, tissue damage (histopathology), bioenergetic status, organ dysfunction, and reproductive integrity. Results of these studies, conducted 2-4 months after the spill, indicate (1) no obvious patterns or relationships between levels of metals in fish and fish health, (2) for some measures of fish health and bioaccumulated metals, there is a downstream gradient of responses with some variables increasing and others decreasing along the spatial gradient of the river and, (3) based on EPA's three- tiered approach for assessing effects of selenium on wildlife, future studies will be focused at the Tier 2 level because of slightly elevated levels of selenium in some fish and in ovarian tissue. Results of this study to date have also emphasized the importance of the weight-of-evidence approach for assessing potential relationships between multiple environmental factors and the health of biological systems. Current studies are focused on assessing the relationship between reproductive competence of fish and levels of selenium in target organs such as liver and ovary.

Geochemical characterization of river sediment contaminated by fly ash from a breached containment pond, Kingston, TN

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Following the fly ash spill at TVA's Kingston Fossil Plant on December 22, 2008, we collected a series of via box, gravity, and vibra-core samples in affected reaches of the Emory, Clinch, and Tennessee Rivers to characterize both the extent of the fly ash spill and its geochemical characteristics downstream of the initial discharge. During the one-year period after the spill, fly ash was found interbedded amongst organic mats in the Emory River with ash-sediment mixtures thining to <25 cm at the confluence with the Clinch River. Within the downstream reaches of the Clinch and Tennessee Rivers, thinner (10-15 cm) deposits of ash mixed with native sediments occur. Microscopy of river sediments indicates that older ash deposits extend to depths of ≈1.5 m throughout the affected reach of the Clinch down to the Tennessee River. Selected river sediments with variable amounts of ash were analyzed for trace elements in four sequential extractable phases ranging from water-extractable to reducible (0.1 M $NH_2OH{\cdot}HCl$ dissolved in 25% acetic acid). Reducible As concentrations were generally higher in sediments containing greater levels of fly ash (2.38 – 6.56 mg kg^{-1} relatively pure ash; 0.25 – 3.00 mg kg^{-1} high ash – sediment mixtures; 0.14 – 1.53 mg kg^{-1} low ash – sediment mixtures; and 0.12 – 0.18 mg kg^{-1} predominantly native sediments). Similar trends were found for water extractable and readily exchangeable (1 M NH_4Ac, pH=7) As. Results for Cd, Cu, and Pb provide no evidence that higher ash concentrations affected metal concentrations for any of the extractable fractions. The ratio of water extractable to reducible trace elements in bottom sediments was higher for As and Cu compared to Cd and Pb, while the ratio of readily exchangeable to reducible concentrations was higher for Cu and Cd compared to Pb and As; these ratios were unaffected by ash levels. There were no discernable trends in any of the labile fractions of trace elements downstream of the spill source except that all reducible elements were higher in the Clinch River compared to the Emory and Tennessee Rivers.

The Effects of Fly Ash Release from the TVA Kingston Steam Plant on Fish and Benthic Macroinvertebrate Assemblages

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The magnitude of the TVA Kingston Steam Plant fly ash spill certainly suggests concern about the effects on aquatic organisms such as fish and macroinvertebrates. A comprehensive assessment of the ecological consequences from the ash spill was initiated soon after the incident. Included in this assessment were studies of fish and benthic macroinvertebrate assemblages. Following the ash spill, fish were sampled using TVA's Reservoir Fish Assemblage Index (RFAI) and Spring Sport Fish Survey (SSS) methodologies in the Clinch, Emory, and Tennessee Rivers. The RFAI methodology uses boat electrofishing and gill netting to collect fish from a variety of habitat types based on their proportions in the study area to ensure that species collected provide a true representation of community structure and function. Fish are collected with the SSS methodology using boat electrofishing; this method specifically focuses on monitoring long-term trends in black bass (largemouth, smallmouth and spotted bass) populations. Historical results from RFAI and SSS surveys provided baseline data for comparison. An initial assessment of the benthic macroinvertebrate assemblage was completed in January 2009, with quantitative collections at 11 locations in the Emory, Clinch, and Tennessee Rivers; at least one upstream site served as a reference for each river. Benthic invertebrate samples are collected with a Ponar grab sampler and analyzed in the laboratory for taxonomic identification and enumeration. The 2009 results indicate that the fish assemblage and sport fish population (i.e., largemouth bass) were similar to those observed prior to ash release; future sampling is required to detect any potential long-term effects.

The benthic macroinvertebrate assemblage was clearly different between reference and downstream sites in the Clinch River and Emory River, but there appeared to be little difference between Tennessee River sites. For example, two reference sites on Clinch River had significantly higher densities than other sites due to high numbers of tubificid worms and/or chironomids. The mayfly *Hexagenia* and the fingernail clam *Musculium* were most abundant in the Clinch River downstream of the Emory River and generally less abundant at reference sites. Nonmetric multidimensional scaling ordination (Bray-Curtis similarity) showed that sites within the same river and with the most similar channel morphology generally had the most similar invertebrate communities. Future monitoring should help determine whether community differences are due to natural factors, effects associated with the ash spill, or a combination of these factors.

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

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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), located in Martins Creek, Pennsylvania. The fly ash/water mixture entered the Delaware at a point adjacent to the Plant, and was transported downstream via surface water flows. PPL responded proactively to the fly ash release with an aggressive emergency cleanup action to remove bulk fly ash deposits, and concurrently implemented a series of investigations to characterize the nature and extent of fly ash in the Delaware River.

Visual observations (with divers) and chemical data indicated that bulk fly ash in the Delaware River sediment was generally limited to the 1.5 mile reach of River immediately downstream of the release. To evaluate possible downstream impacts, characterization of sediments and surface waters was conducted over a 37-mile stretch both before and after an October 2005 high flow event. Background sediment samples were collected from upstream locations and from the Lehigh River, a major downstream tributary to the Delaware River, so the relative contributions of any fly ash-related constituents could be better quantified.

This poster presents results of various data analysis techniques successfully used to evaluate the downstream distribution of fly ash in sediments and surface water, and to distinguish fly ash-related impacts from those of other sources. Key steps in the data analysis included:

- Development of enrichment factors for metal and metalloids in fly ash relative to Delaware River background
- Selection of arsenic (As) as an appropriate tracer as a result of high enrichment ratio
- Normalization of metal concentration to aluminum to account for natural variability in sediment metals concentrations prior to statistical analysis
- Using geochemical ratios to evaluate surface water data and demonstrate exhaustion of readily transportable fly ash during first major storm event, and
- Using exploratory data analysis techniques (radar plot, principal component analysis) to demonstrate influence of Lehigh River on downstream Delaware River sediment.

Similar techniques as those applied to the Delaware River fly ash spill may benefit analysis of the downstream nature and extent of fly ash in the Tennessee River.

Geochemical investigations of metals release from submerged coal fly ash using extended elutriate tests

A.J. Bednar, M.A. Chappell, J.M. Seiter, J.K. Stanley, D.E. Averett, W.T. Jones, B.A. Pettway, A.J. Kennedy, S.H. Hendrix, and J.A. Steevens

A storage pond dike failure occurred at the Tennessee Valley Authority Kingston Fossil Plant that resulted in the release of over 5 million cubic yards of fly ash. Approximately half of this material deposited in the main channel of the Emory River, 2.2 miles upstream of the confluence of the Emory and Clinch Rivers, Tennessee, USA. Remediation efforts to date have focused on targeted removal of material from the channel through hydraulic dredging, as well as mechanical excavation in some areas. The agitation of the submerged fly ash during hydraulic dredging introduces river water into the fly ash material, which could alter the redox state of metals present in the fly ash and thereby change their sorption and mobility properties. A series of extended elutriate tests were used to determine the concentration and speciation of metals released from fly ash. Solid state (XANES) and liquid state (HPLC-ICP-MS) speciation techniques were used to determine major metalloid species. The results indicated that arsenic and selenium species released from the fly ash materials during elutriate preparation were redox stable over the course of ten days, with arsenic being present as arsenate, and selenium being present as selenite. Additional selenium (organo-selenium, selenium sulfide) and arsenic (arsenite, arsenic sulfide) species were identified in the solids using XANES analyses. Concentrations of certain metals, such as arsenic, selenium, vanadium, and barium, increased in the elutriate waters over the 10 day study, whereas manganese concentrations decreased, likely due to oxidation and precipitation reactions. Our team is returning to the TVA site to collect additional samples in order to assess how dredging activities have affected As and Se speciation.

Assessing selenium dynamics at the base of aquatic food webs: Application of a novel periphyton-mayfly test system

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Coal combustion byproducts are known to contain relatively high concentrations of Se and can act as sources of this contaminant when introduced to aquatic ecosystems. Selenium contamination provides management challenges because bioaccumulation in fish and birds is largely a function of dietary exposure, yet the traditional focus has been on direct water to organism interactions. The toxic effects of Se on fish and birds have been widely studied, however Se dynamics at the base of aquatic food webs is largely not understood and may be affected by dissolved Se speciation (i.e., selenate vs. selenite). Upon entering the food web Se can potentially biomagnify and elicit adverse effects in higher trophic levels, including the invertebrate prey of many fish and birds. Here, we used ^{75}Se (as selenite) as a radiotracer to characterize Se bioaccumulation into natural periphyton biofilms and subsequent dietary and maternal transfer in the mayfly, *Centroptilum triangulifer*, in a life-cycle assay. On average periphyton biofilms bioconcentrated Se 1113 (± 430) - fold following 7-9 days of exposure to a range of environmentally relevant dissolved concentrations (2.4 – 13.9 μg L^{-1}). Mayflies grown to adulthood on these diets further biomagnified Se with trophic transfer factors averaging 2.2 (± 0.4) – fold in postpartum maternal tissues. Adults then transferred 46.5 (± 8.8) % of their body burdens to eggs with an observed reduction in fecundity for mayflies fed on diets greater than ~11 μg g^{-1}. Second generation mayflies exposed to dietary Se exhibited teratogenic defects in tibial and tarsal development. Additionally, we used XANES analysis at the Se K-edge to compare Se speciation in periphyton differentially treated with dissolved selenate or selenite, and in *C. triangulifer* larvae fed on these diets. Periphyton spectra were nearly identical following exposure to each anionic Se form, and displayed enrichment of organo-Se species. Larval speciation was different than that of periphyton, but was also characterized by a high proportion of organo-Se species. These results suggest that invertebrates, which have largely been considered tolerant to Se exposure, may be adversely affected by environmentally relevant dietary Se concentrations. Further, potential differences in the uptake kinetics of selenate and selenite at the base of aquatic food webs may determine the extent to which organic Se is incorporated into higher trophic levels. These methodologies can be directly applied to the Kinston Recovery Program to assess trends of Se incorporation (and effects) at the base of aquatic food webs. Future studies will compare uptake kinetics of selenate and selenite into primary producers, the subsequent conversion to organic Se species, and examine effects in a model mayfly system including multi-generational effects of maternal transfer of Se to eggs. Oxidative stress studies using molecular and physiological approaches are ongoing.

Kingston Ash Release--Initial water, air, & ash monitoring

Neil Carriker

The Tennessee Valley Authority's (TVA) response to the December 22, 2008 release of ash from a holding cell into the Emory River included an immediate assessment of the surface water quality effects and the extent of ash deposits that entered the river system. The surface water quality monitoring response initially necessitated a coordinated and multi-disciplined effort for sample collection, analytical support and data management, with on-site input from regulatory agencies. Although this early and immediate effort was a significant challenge, the water quality monitoring program implemented during the first week has continued with relatively few changes. Since that time, other sampling and analytical programs have been implemented for a variety of purposes (e.g., human health and ecological risk assessment and disposal purposes). Briefly, the collective programs include air monitoring, ash and sediments, waste disposal monitoring and an array of aquatic and terrestrial biota monitoring. Each of these programs required objective formulation, documented rationale and planning and execution by TVA and consulting environmental experts, analytical service providers and data management professionals. Of particular challenge was the ash and sediment monitoring since it required a more dynamic approach to evaluate redistribution by high flow events and mixing of ash with native sediments. Further complicating the ash and sediment program was the objective to separate the effects of the recent spill from effects of legacy pollutants in the system. While the collective monitoring programs since the spill have been substantial, sampling locations maps that are presented are limited to ash/sediment and surface water. Summaries of the surface water, ash and sediment analytical results generated for samples collected during the first 10 months following the release are also presented. Finally, the initial rationales for sampling design and subsequent refinements are also included.

Assessing Fish Community Health following the Kingston Fly Ash Spill

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Fly ash has been documented to affect fishes through direct mortality from alkaline shock, chronic oxidative stress, and bioaccumulation of toxic elements such as selenium. Since January 2009, our team has conducted quarterly fish community sampling to begin assessment of the long-term impact of the Kingston spill on the fish community in Watts Bar Reservoir. Sampling has been conducted by boat electrofishing for 25-minute periods at five sites on the Clinch, Emory, and Tennessee rivers. Sampled fish are identified to species and standard measures are recorded (weight and length). A subset is retained for toxicological analysis, while the remainder is released at that site. Over the past year, ERM 2.0 has ranged from 4-6 species and 6-74 individuals. Of the two upstream sites, ERM 3.5 has ranged from 5-13 species and 24-71 individuals, and CRM 5.5 has ranged from 9-10 species and 113-219 individuals. Five km downstream of the spill, CRM 3.5 has ranged from 10-13 species and 118-148 individuals, while TRM 567.6 has ranged from 11-15 species and 96-367 individuals. Externally, fishes have displayed elevated rates of lesions and anomalies, particularly gill clubbing. In addition, more than 10% of the bluegills caught at Tennessee River Mile 567.6 in January 2010 (11 km downstream of the spill site) exhibited exopthalmia (popeye). Tissue from these individuals is being screened for selenium loading. As seasonality greatly affects community structure, we plan to continue sampling until at least January 2012.

Reproductive Status of Fish Exposed to the TVA Kingston Steam Plant Fly Ash Spill

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On December 22, 2008, a dike containing fly ash at the Tennessee Valley Authority's (TVA) Kingston Steam Plant in Tennessee failed and released a large quantity of ash into the adjacent Emory River. Ash deposits extended as far as 4 miles upstream in the Emory River and downstream past the confluence of the Emory River with the Clinch River, with ash detectable as far downstream as Tennessee River mile 564 (~4 miles downstream of the Tennessee River confluence with the Clinch River). In the spring of 2009, a study was initiated to evaluate the reproductive status of sentinel fish populations effected by the ash spill. Female largemouth bass, white crappie, bluegill sunfish, and a limited number of channel catfish were collected from sites within the spill zone and from upstream reference sites in both the Emory and Clinch Rivers. Fish were examined for ovarian size and gross appearance and quantitatively scored for oocyte developmental status, including the presence or absence of atresia among vitellogenic or maturing oocytes and the abundance of vitellogenic oocytes. Batch and/or total fecundities were estimated from counts of the leading clutch of maturing oocytes or, in the case of fish that spawned prior to collection, the abundance of shed follicles in the ovaries. Samples of ovarian tissue were histologically examined for various lesions including atresia of smaller oocytes, and ovarian and other tissues were analyzed for a suite of metals. Significant reproductive dysfunction was not observed in these fish collected 3-5 months after the spill. However, selenium concentrations in ovaries were approaching levels thought to be capable of triggering reproductive failure in fish populations through effects on larval fish development. Similar studies are planned for the spring of 2010 to re-examine the reproductive condition and bioaccumulation of contaminants in fish ovaries approximately 1.5 years after the spill. In addition, a new series of studies will be initiated in the spring of 2010 to specifically examine the potential effects of the fly ash spill on the early life stages of exposed fish populations. These studies will include: (1) laboratory testing of fly ash from the spill site with fish embryos and larvae by adaptations of established EPA and ASTM protocols; (2) experimental studies of larvae obtained from the *in vivo* spawning of bluegill sunfish exposed to ash in simple indoor exposure systems; and (3) an evaluation of the developmental success of larvae obtained from fish exposed *in situ* at locations in the Emory and Clinch Rivers and spawned *in vitro* using adaptations of standard operating procedures for measuring the effects of selenium on fish early life stages (Janz and Muscatello 2008). These integrated field and laboratory studies are expected to provide a better understanding of the risks of fly ash exposure to fish populations affected by the Kingston spill.

The Application of Microscopy for the Detection and Quantification of Fly Ash in Riverbank Sediment.

The purpose of this study is to characterize fly ash source material and use this information to identify, and quantify, fly ash concentrations in unknown sediment samples.

Six samples were received by RJ Lee Group, Inc. for characterization from the Tennessee Valley Authority Kingston Recovery Project. One sample was a reference material consisting of fly and bottom ash, whereas the remaining five were portions of core samples collected at varying depths along the banks of the Emory River.

The initial step involved the characterization of the reference material. Once a representative elemental composition and particle morphology were ascertained analysts could then use this information to positively identify, and quantify, the presence of target material in a variety of unknown samples. Material characterization including that performed in field sample evaluations was conducted with the use of stereo-optical microscopy, polarized light microscopy (PLM) and scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS).

A visual estimation of particulate components indicates that no fly ash was detected in two samples, a trace amount was detected in one sample and over 50% was detected in the remaining two samples. As a complimentary technique the presence, and or absence, of fly ash was confirmed by SEM/EDS.

The results indicate that microscopy is a technique that can be used to quickly and accurately determine the presence of fly ash in unknown samples, including river sediments.

The next logical step would be to collect a series of core samples along the banks of the Emory River in a grid pattern. Portions from various core depths would be analyzed by the microscopy techniques described above for the presence and amount of fly ash. This information can then be relayed into a spatial analysis tool that could create a map illustrating ribbons and pockets of fly ash material that still require dredging.

Assessment of mercury and methylmercury in the Emory, Clinch and Tennessee 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 Fossil Plant into the Emory, Clinch and Tennessee River system has been found to be enriched in mercury (Hg) (~0.15 mg/kg1) 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 nutrients from the ash and the potential for mercury methylation in river sediments could negatively impact human health and the aquatic ecosystem. The objectives of this study were to evaluate surface water and sediment quality with respect to total Hg and methylmercury, the form of mercury that bioaccumulates in food webs. Sediment and surface water samples were collected during seven sampling events in 2009 at sites along the Emory River upstream and downstream of the ash spill site, and further downstream in the Clinch and Tennessee Rivers. In surface water samples, total Hg concentrations ranged from 0.1 to 10.3 ng/L, less than the EPA water quality guideline for surface waters. In sediments of the Emory River near the spill, total Hg in the sediments were 0.11 ± 0.03 mg/kg, greater than Hg levels in sediments upstream of the spill (0.06 ± 0.03 mg/kg). Further downstream in the Clinch River, however, average Hg content in the sediment was greater (0.86 ± 0.36 mg/kg). Contamination of the Clinch River is probably 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 metal poses a hazard if converted to methylmercury (MeHg) by anaerobic bacteria (such as sulfate-reducing bacteria) in the sediments of aquatic systems. In this river system, we observed total MeHg in the river water, but concentrations varied spatially and temporally. In September we observed higher levels of MeHg in the water column (from 0.2 to 0.4 ng/L) at sites in the Emory River near the spill. However in November, the 'hotspots' for MeHg (0.1 to 0.65 ng/L) were observed further downstream in the Clinch River. We also quantified acid volatile sulfide in the sediments of this region (0.01 to 0.50 μmol/g), indicating that anaerobic conditions (necessary for biological Hg methylation) were occurring in river sediment. The spatial and time dependence of MeHg concentration in the river suggest that methylation was limited by factors that promote growth of methylating microorganisms and biouptake of inorganic Hg to these bacteria. These factors include substrates for bacterial growth (such as sulfate and organic carbon) and speciation of bioavailable Hg in sediment porewater. Overall, our data suggests that surface water quality with respect to total Hg has not been impacted by the coal ash but river sediments should be closely monitored for MeHg production.

Mercury Stable Isotope Ratios as Tracers of Contamination at the TVA Kingston Site

Thomas M. Johnson (Lead PI), Gideon Bartov

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, the Tennessee River downstream of the Kingston power plant, and the Emory River up stream 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 0.1 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 measured but were not significant.

Initial results suggest distinct $\delta^{202}Hg$ "signatures" for the three expected Hg contributions influencing the system. Average $\delta^{202}Hg$ values for the Clinch River, Kingston fly-ash, and the natural background (represented by the Emory River sample) are -0.466‰ ±0.204, -1.974‰ ±0.463, and -1.042‰ ±0.204, respectively. The data suggest that the upstream portion of the Clinch River is dominated by a source of Hg with near-zero $\delta^{202}Hg$ values. This source may be the Y-12 plant, which is known to impact a creek that eventually flows into the Clinch River. Downstream of the confluence at Kingston, the Hg isotope ratios shift to lower values that are less than those of the nominally uncontaminated Emory River samples and closer to those measured for fly ash from the Kingston power plant.

At present, we use the word “signature” with caution. We do not know if the $\delta^{202}Hg$ values of the various forms of Hg remain constant as the Hg moves through the system. In order to fully understand the situation at the TVA Kingston site, more research is needed to characterize the different Hg sources and consider geochemical transformations that might alter Hg isotope ratios.

Kingston Ash Release: Potential Exposure Pathways and the Associated Environmental Investigations

Daniel Jones – ARCADIS, Knoxville, TN

Suzy Young – ARCADIS, Knoxville, TN

The largest unplanned release of coal ash to the environment occurred on Monday, December 22, 2008, when a dike containing the Tennessee Valley Authority (TVA) Kingston Fossil Plant (KIF) coal ash dredge cells failed, releasing approximately 5.4 million cubic yards (cy) of fly ash and bottom ash into adjacent waterways and over land. The KIF is located near the confluence of the Emory and Clinch Rivers on Watts Bar Reservoir near Kingston, Tennessee. Recovery of ash from the Emory River near the point of release via excavation and hydraulic dredging is scheduled to be complete by May 2010 under a CERCLA time-critical removal action. Disposition of any remaining ash in the River System is being addressed as a non-time-critical CERCLA action that will include extensive environmental sampling, ecological studies, and a baseline ecological risk assessment.

In cooperation with State and Federal entities, TVA's initial environmental monitoring efforts rapidly evolved to include comprehensive monitoring of potentially exposed ecological receptors and their prey and forage. These and other field studies are ongoing and in 2010 TVA is initiating additional ecotoxicological studies of the released coal ash. Several other research organizations are performing independent investigations with funding from private and public sources, including the National Science Foundation.

This poster will present a Conceptual Site Model that describes the ecological receptors and potential exposure pathways associated with the Kingston fly ash release. The direct exposure pathways being evaluated at this site include exposures to as ash sediment, sediment pore water, groundwater discharging to surface water, surface water, and seasonally exposed sediment. Dietary exposures are also a concern for some ash-related metals, 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 conceptual site model is used to organize and evaluate the numerous field and laboratory studies being performed by TVA and others at the site, many of which will be presented at this research symposium.

Ash Migration Investigation using Sub-Bottom Profiler

James Lane

1) Purpose and Objectives

Ash migration from the Kingston Fossil Plant ash spill into the Emory, Clinch, and Tennessee Rivers was a major concern following the incident that occurred on December 22, 2008. A high-flow event occurred on May 4, 2009 in which a significant amount of ash migrated from the spill site. Subsequent efforts to characterize the extent and amount of ash were marginally successful due to the logistical constraints in surveying vast areas of waterway. TVA purchased an EdgeTech 3200-XS Sub-Bottom Profiling System (SBP) to overcome these constraints. The three phases of the SBP investigation included: 1) Identification of the areal extent of ash migration from the ash spill, 2) Characterization of the depth of ash throughout the deposition area, 3) Developing maps depicting both extent and depth of ash.

2) Approach and/or Experimental Design

During Phase 1, cross-sectional profiles were collected with the SBP, a device designed to differentiate between types of sediment based on density, outside of the immediate proximity of the spill site. The profiles were used to target locations of recent sediment deposition. Sediment samples were collected, described, and used to create maps according to sediment type (ash or native sediments) and depths. During Phase 2 (in progress), SBP data was collected in a grid between the site and the extent defined in Phase 1. Several coring devices were utilized to determine ash depth and to correlate the reflective imagery. Once the profiles are ground truthed, the ash and other sediment layers will be digitized and mapped.

3) Results or Findings to Date

The extent of measurable ash was defined as mostly contiguous ash that is at least ¼ inch thick, and was identified to be located at approximately Emory River Mile 6, Clinch River Mile 5, Tennessee River Mile 568.7 (upstream), and Tennessee River Mile 562 (downstream). Sediment sampling from both phases revealed that the ash has either been covered by native sediments or has mixed with native sediments. Mixing of ash and native sediments has caused difficulties in delineating between the two using the reflective imagery.

4) Significance and Benefit of Results to Kingston Ash Recovery Program

The SBP was utilized to survey large areas of waterway in a time-efficient manner. Maps have been and will continue to be created depicting the depth and extent of ash migration.

5) Continued or Future Studies

Differentiating between ash and native sediment is a difficult problem that has not currently been solved using this method (ground truthing has not matched SBP data). Data acquisition parameters need to be fine tuned based on subsurface properties to obtain data that matches core samples. Depending on future high-flow events, portions of this investigation may be repeated.

Heavy Metal Extraction from Water using New Trianex Chelating Resins

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Coal fly ash has been shown to contain heavy metal contaminants such as arsenic, selenium, lead, mercury, chromium, and nickel which leach into the water. At TTU, we have produced new types of metal-sequestering materials that actually remove these very metal pollutants from water. The new materials have been named "Trianex®", and in preliminary studies, they exhibit high metal-uptake abilities at a wide range of pHs due to a soft/hard tridentate chelation system, which exhibits great thermodynamic and kinetic stability. We wish to continue the evaluation of these materials with a host of metal ions in water under varying conditions, develop the adsorption/desorption isotherms, and develop process models for prediction of scalability and economics. These materials should be invaluable tools in reducing and removing these heavy metal pollutants from the water drainage primarily from these storage facilities, but could also be used to reduce contamination at other sites.

The scheme below depicts the chelating action of Trianex® on a host of various metal ions in aqueous solution.

A proposed study -- Aqueous biogeochemistry for effective management of hazardous trace elements in mixed and layered ash-contaminated soil/sediment systems

Richard H. Loeppert[1], Fabio Sartori[2], Binayak P. Mohanty[3], and Greg Johnson[4]

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The potential environmental and ecological hazard of trace metals resulting from the Kingston plant release of impounded coal ashes will be impacted primarily by the ensuing trace-metal solubility and bioavailability. The actual metal solubility will be dictated by local environmental and geochemical conditions (e.g., pH, Eh and dissolved ion composition), the availability of retention sites for trace metals (e.g., on Fe and Mn oxides and particulate organic matter), and local biological processes. The mixing of ash with soil or sediment and the resulting change in mineral matrix, carbon content and biological activity can result in either increased or decreased metal solubility, depending on trace-metal characteristics and local conditions.

The objective of our proposed study is to evaluate how change in environment from isolated ash to mixed soil/ash and sediment/ash systems will impact metal (As, Se, Pb, Cr, Cd and Hg) solubility and mobility. Our experiments are based on the hypothesis that local mineralogy, environmental conditions and biology will control metal mobility and retention. Our goal is to determine the conditions that favor retention vs. dissolution of metals in mixed soil/ash and sediment/ash systems.

We will utilize soil and sediment samples either from or similar to the affected soils/sediments near Kingston Plant, Berkshire Slough, Swan Pond Slough, and the Emory and Clinch Rivers. Experiments will involve both batch and column systems to evaluate metal solubility and bonding. Column studies will be conducted using layered and mixed soil/ash and sediment/ash systems that simulate actual field conditions. The column setup includes probes for in-situ measurement of EC, pH and Eh, and collocated ports to allow sampling for determination of soil/sediment/ash solution composition. In some experiments, additives will be utilized to evaluate the influence of soil/sediment conditions, e.g., pH, fertility (N and P) and organic addition, on trace-metal biogeochemistry and metal solubility. We have previously utilized similar columns for the evaluation of solution composition and geochemistry of trace metals in mixed soil/mine tailings systems and sediment systems. Batch studies will be performed by incubation of ash materials and soil/ash and sediment/ash mixtures in both oxidized and reduced systems. Selective extractions will be used in conjunction with column and batch experiments to evaluate metal-release potential.

The information that will be obtained from the proposed study will be important to understanding the factors impacting the release/retention of metals in surface and subsurface systems at the Kingston site, and will contribute to optimized science based environmental management and site remediation. More broadly, it will improve current knowledge and methods for environmental risk assessment, environmental management, and site remediation in coal-fired production sites nationwide.

Mapping and Estimation of Phosphorus and Copper Concentrations in Fly Ash Spill Area using LANDSAT TM data

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The LANDSAT Thematic Mapper (TM) images have been used to monitor the largest coal fly ash spill in U.S. history that occurred in Tennessee on December 22, 2008. The total phosphorus (P) and copper (Cu) concentrations in the fly ash spill vicinity were mapped and determined by application of LANDSAT algorithm models, which we previously developed for monitoring the P and Cu concentration in soils amended by sewage sludge in NW Ohio. LANDSAT image analysis reveals the occurrence of elevated P and Cu concentrations on December 22, 2008 as a result of the fly ash spill a few hours before LANDSAT overpass, compared to P and Cu concentrations of bare soils in the pre-spill image of November 20, 2008. The progress in clean-up operations, through spreading of grass and straw mulch over the spilled fly ash, was evident in a February 1, 2009 image, where the P and Cu concentration values were recorded at significantly lower levels than were recorded in the December 22, 2008 image. The display of surface chemical concentrations in exposed soils and piles of fly ash demonstrates how satellite data can be used to quantitatively map certain occurrences of environmental contamination and to track surface manifestations of remediation/restoration efforts.

Establishing Effective Limits of Detection for Metals in Surface Water

Organization- TestAmerica Laboratories

Authors- J. Mitchell, J. Tuschall, R. Burrows.

- **Purpose and Objectives of the investigation:** For analysis of metals in environmental samples, the variability of instrument sensitivity over time, coupled with the limitations of the most common approach to determining Method Detection Limits (MDL), may lead to data that is qualitatively unreliable, i.e., false positives and false negatives are possible. One means of improving reliability for results near the MDL is to first establish an improved determination for MDL that can be verified over time through the use of results for method blank analysis.
- **Approach or Experimental Design**: This study investigates the use of historical data for laboratory-prepared method blanks to establish detection limits that are subsequently verified daily for precision through the analysis of MDL verification standards.
- **Results or Findings to Date**: False positive results, as determined through the ongoing evaluation of method blanks, were significantly reduced when the Detection Limit was established by the alternate procedure. A false positive result was reported in more than 90 % of the method blanks evaluated for 4 of the analytes of concern when compared to the MDL determined using the 40 CFR procedure. When reported using the alternate MDL determination, less than 10 % of the method blank analyses performed had a reported value above the detection limit. Default precision limits of 70-130 % recovery were met on average for all analytes spiked at the alternate MDL, providing verification for values reported at or near the detection limit in environmental samples. Average recoveries for verification standards spiked at the MDL as determined using the procedures outlined in 40 CFR Part 136 were outside these acceptance limits for all analytes measured.
- **Significance and Benefit of Results to Kingston Ash Recovery Program**: This approach provides a continuing verification of the precision of data at a minimum detection limit, and provides end users with an increased level of certainty beyond that typically provided by following only the procedures outlined in the 40CFR MDL requirements. This alternate procedure allows for a more precise evaluation of the risk associated with detection level concentrations of chemicals of concern through the confidence provided by analytically verified data. This alternate procedure also reduces the frequency of positive blank results, providing increased certainty in the results obtained in environmental samples.
- **Continued or Future Studies**: By applying statistically defined acceptance limits for analytical quality control to the recoveries measured in the analyses spiked at the level of detection defined through the use of historical blank data, an established level of certainty can be assigned to results reported at the detection limit. Using this procedure, future studies will measure the effects of changes in instrument and method performance over time to determine how these changes affect the alternate MDL established by this procedure.

Contaminants in Fish from the Clinch River Prior to the Kingston Fly Ash Release: An Assessment of Baseline Conditions

M.J. Peterson, T.J. Mathews, W.K. Roy, and G.R. Southworth, Oak Ridge National Laboratory, Oak Ridge, TN and T.F. Baker, Tennessee Valley Authority, Chattanooga, TN

Assessments of the impact of a point source contaminant release on lotic ecosystems often include before and after release comparisons. Post-release sampling at sites upstream of a spill can be a key reference for evaluation of contaminant accumulation and/or toxicity downstream of the release site, but care must be taken in the interpretation of these data, as sites may differ in water chemistry, contaminant bioavailiability/exposure, and ecology. Ideally, long-term trends in contaminant concentrations in fish at locations around the point source would be available to provide a baseline for post-spill comparisons. In the case of the Kingston fly ash release, Oak Ridge National Laboratory (ORNL) and the Tennessee Valley Authority (TVA) have extensive long-term fish contaminant datasets in the Clinch River system that can help define appropriate site-specific goals for fish contaminant reduction, as well as the potential human and ecological risks associated with fish near the spill (inclusive of other contaminants in fish not related to the Kingston site). Based on these historical data, the State of Tennessee has issued fish consumption advisories in the Clinch River and Watts Bar Reservoir that focus on concerns relative to PCBs and mercury. PCB concentrations in channel catfish from sites in the Clinch River have shown a steady decline over the last 20+ years, decreasing from levels in the 1.5 to 2 μg/g range in the 1980s and 1990s to levels less than 0.5 μg/g in recent years. Mercury concentrations in fish from some sites are above the 0.3 μg/g EPA guidance value, with a clear spatial pattern of decreasing concentrations with distance from point sources upstream of Kingston. Although recent data for metals (other than mercury) in fish is limited near Kingston, there are good regional historical datasets useful in defining background metal concentrations for some species, and for different tissue types (e.g., fish fillet and whole-body samples). Fish tissue obtained prior to the spill from near the Kingston Fossil Plant (KIF) discharge has been archived and may be analyzed in the future, providing additional information regarding the potential baseline conditions near the spill site.

Elemental Associations between Mercury and Selenium in Fish Collected from a Gradient of Fly Ash Exposure (and Reference) Sites

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Previous researchers have reported an inverse relationship between levels of mercury and selenium in aquatic biota where exposure to elevated trace metals has occurred. During 2007-2008, composite and individual whole body fish samples (representing a total of nine species) were collected from sites influenced by a gradient of fly ash exposure, and at reference sites, to assess elemental associations. At two locations in West Virginia (Conner Run and Little Scary Creek), fishes were collected from fly ash impoundment receiving streams where the fly ash discharge represented 95 – 100% of stream flow. A site in Kentucky (Blaine Creek) represented intermediate fly ash exposure, whereas the low exposure location was in the Ohio River adjacent to a power plant located in Lawrenceburg, IN. All power plants burn predominantly eastern bituminous (Northern Appalachian) coal. At the high- and intermediate-exposure sites, whole body selenium levels were elevated (range of concentrations 5.38 to 57.4 mg/kg dry wt.), with almost all samples exceeding U.S. EPA's draft whole body chronic criterion for selenium (7.9 mg/kg). Selenium levels in whole body samples of fish collected from low-exposure and reference sites ranged between 2.3 – 3.9 mg/kg. Levels of mercury in all fish samples were low (range 4.3 to 70.4 ng/g dry wt.). There was a significant inverse relationship between log-transformed whole body selenium and mercury concentrations (all species combined; $r^2 = 0.66$). Among each species, the ratios of molar selenium concentration to molar mercury concentration were consistently higher at high exposure sites and, to a lesser degree, at the intermediate exposure site. For all nine species combined, the selenium to mercury molar ratio increased with water selenium concentration ($r = 0.68$).

These results, consistent with previous studies, provide indirect evidence that elevated selenium in tissues of aquatic biota antagonistically regulate the bioaccumulation of mercury. These findings may have implications for fish consumption risk assessments where locally consumed fish have experienced some level of fly ash exposure.

Myxomycetes and Dictyostelids as Biological Indicators

Adam W. Rollins[1], John C. Landolt[2], and Steven L. Stephenson[3]

Myxomycetes and dictyostelids (eumycetozoans) are two groups of microscopic protists that represent normal components of the soil microflora and whose fruiting bodies superficially resemble those produced by fungi. They have been documented as occurring in virtually all terrestrial habitats, ranging from forested ecosystems to deserts, and extend geographically from the Polar Regions to the tropics, wherever detritus (i.e., dead and decaying plant material) is present. These organisms apparently play a major role in maintaining the ecological balance that exists between bacteria and other soil organisms. In fact, small amounts (1 cm^3) of soil can contain as many as 20,000 individual myxomycete cells, suggesting that eumycetozoans also are important in nutrient cycling as members of the detritus food chain. Eumycetozoans seem especially well suited to serve as biological indicators for assessing the fundamental differences that exist for the soil microbial system among selected study sites. The feasibility of utilizing eumycetozoans to assess the accumulation of heavy metals in the environment has been tested successfully, and some species have been reported to tolerate incredibly high levels of heavy metal accumulation. For example, *Fuligo septica*, a common myxomycete, has been reported to bioaccumulate zinc and survive at extremely high levels of concentration (4,000 to 20,000 ppm). Our project will utilize a series of 10 x 10 m replicated plots placed in the area affected by the 2008 fly ash spill in Kingston (Tennessee) and in comparable unaffected areas adjacent to the affected area. Samples obtained from these areas will be used to compare the microbial dynamics occurring within and between sites, and we will utilize atomic absorption spectrophotmetry to analyze various soil parameters and their correlations to fruiting bodies produced by eumycetozoans. The expected outcome of the project will be the development of methodologies utilizing these protist groups for assessing remediation efforts as well as the pathways (through the soil microbial system) of targeted analytes at spill sites. In addition, these methods could be used to monitor the conditions associated with various storage operations such as the leeching of selected analytes from fly ash buried in landfills.

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Geochemical speciation of selenium and other heavy metals in coal fly ash after prolonged submersion in the Emory River at the Kingston Fossil Plant site.

Mark A. Chappell, Jennifer M. Seiter, Anthony J. Bednar, Jacob K. Stanley, Alan J. Kennedy, Daniel E. Averett, Jeffery A .Steevens

The U.S. Army Engineer Research & Development Center (ERDC) conducted geochemical investigations of the coal fly ash spilled in the Emory River at the Kingston Fossil Plant. Commissioned by the Tennessee Valley Authority (TVA), these investigations were designed to geochemically characterize the fly ash, in order to distinguish any changes or transformations that may have occurred during its prolonged submersion in the Emory River. Fly ash and water samples were collected on site from the original ash pile that did not move during the leeve failure, from the Emory River, and from the ash recovery ditch (ARD) containing ash removed during dredging. The purpose was to perform a detailed chemical and physical characterization of the ash material, and evaluate its potential to release metals, particularly oxidized forms of selenium (e.g. selenate) into the river system. Detailed information for this work was acquired through synchrotron-based X-ray absorption studies as well as sequential extraction partitioning. C and N profiles showed the ash had accumulated humics from the Emory River. Fly ash manganese reduced to Mn (II) while Fe, As and other metals changed nominally. Arsenic was predominantly found in the oxidized (arsenate) form. Bulk XANES analysis showed that selenium in the original ash pile was composed of inorganic selenite. However, since the ash was deposited into the river, the selenium species had changed substantially; with the river-submerged ash containing about 57 % ash-bound selenite, and 27 % organic/thiol-associated selenium, containing what appears to be Se(-II), with 16 % Se sulfide. The results show that the fly ash exhibits geochemical stability, but is undergoing kinetically slow transformations while submerged in the Emory River.

Distribution and stratigraphy of fly ash deposits in the Emory and Clinch Rivers

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Fly ash from the December 2008 release filled the Emory River channel at the source area and deposited a bed of ash on the submerged river terrace to the east. A coring program was conducted to assess the distribution and characterize the stratigraphy of ash deposits in the Emory and Clinch Rivers. Box cores and Eckman dredge samples of surficial bottom sediment show that thin lenses of ash occur in isolated depositional settings throughout the study area.

A cohesive organic mat caps the bed of ash extending across the submerged terrace east of the source area. Channel deposits upstream of the release at Emory River mile (ERM) 3.5 consist of a bed of laminated ash overlain by graded traction deposits and capped with a layer of pebble-sized pieces of coal. Total ash thickness at this location is about 30 cm and our cores terminated in a bed of loamy sand with coal and organics. These deposits likely represent the upstream extent of the channel fill from the release.

Channel deposits of ash extend downstream to the Clinch River with characteristics that change with distance from the source area. Immediately downstream of the source area (ERM 1.8) two beds of ash overlie a bed of gravely mud at a depth of 30-40 cm. At ERM 1.2 deposits of an ash/sediment mixture are interbedded with three organic mat layers. A near-surface organic mat caps a thick ash/sediment mixture, which in turn, overlies a bed of laminated ash at ERM 1.0. The bed of ash/sediment mixture thins to < 25 cm at the confluence with the Clinch River. Deposits on the submerged Emory River terrace downstream of the source area are relatively thin (~20 cm) and are capped by or incorporated into an organic mat. In the Clinch River the ash is typically found in surface deposits mixed with sediment, ranging in depth from 15 cm thick at the mouth of the Emory River to ~10 cm in the lower Clinch River.

The organic mats associated with the ash deposits appear to be the result of the initial failure since they are not present upstream of the fly ash deposits and, with one exception, are not present in the older lake sediment. During the December 2008 release, a large seiche several meters in height is reported to have ripped across the submerged terrace east of the failure. This terrace is only 1-2 meters below the lake level and the seiche could have eroded organics from the terrace surface and surrounding shoreline. Flow in the Emory River was diverted across this terrace when the fly ash filled the former river channel west of the terrace. These organic mats are cohesive interwoven layers of foliage and woody debris and could protect the underlying ash deposits from erosion during future high flows in the river. The dispersed lenses of ash on the river bed and on submerged terraces are limited in volume, but could be easily transported downstream in future high flows.

A Multi-phased Toxicity Study for Evaluating Potential Risks of Kingston Fossil Plant Fly Ash Exposures to Benthic and Aquatic Biota

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TVA initiated multi-phase laboratory toxicity studies in March 2009 to evaluate potential risks to biota from exposure to fly ash from the Kingston ash release to the Emory River and subsequent dredging. The overall objective is to evaluate toxicity (survival, growth, reproduction) and metals bioaccumulation elicited by exposure of benthic and aquatic species to whole ash, elutriates, dredge plume water, and ash stilling pond effluent. Various acute and chronic test protocols were used in the first phase with (1) two 3.1-m Vibracore® ash composite samples collected March 17; (2) two 3.1-m Vibracore® ash composite samples collected June 11-12; and, (3) monthly Emory River dredge plume and stilling pond effluent samples collected April – June. Results from the March 17 ash composite samples indicated no appreciable bioaccumulation of metals in *Corbicula fluminea* exposures (28-d) to whole ash nor any toxic effects in *Ceriodaphnia dubia* (96-h), *Pimephales promelas* (96-h), or *Lampsilis siliquoidea* (10-d) exposures to ash elutriates. *Lumbriculus variegatus* exposures (4-d) to whole ash showed no effects on survival, but worms did not burrow so bioaccumulation was not assessed. No effects on survival were noted for *L. siliquoidea* 5-d exposures to whole ash, but 10-d exposures to one of the whole ash samples did result in significant effects on survival relative to laboratory control sediment. *Hyalella azteca* exposures (10-d) to both whole ash samples indicated adverse effects on survival. No effects (survival, reproduction) were observed in 7-day chronic exposures with *C. dubia* to plume or stilling pond effluent samples collected April –June. Results with identical exposures to the April and May samples by *P. promelas* (survival, growth) were invalidated due to confirmed pathogen interference. *P. promelas* chronic tests with Ultraviolet-treated plume and stilling pond effluent samples collected in June resulted in no adverse effects. The second phase of testing (96-h *C. dubia and P. promelas*) involves weekly (August – September) and bimonthly (October – present) monitoring of dredge plume and stilling pond effluent samples in response to increased dredging rates; results through mid October have shown no effects on survival. Test results from the June 11-12 ash composite samples are currently being evaluated. A third phase of this study focusing on the bioavailability of metals in ash and evaluating resin-treatment of ash to provide a suitable reference control is underway.

Accumulation of Potential Fly Ash Contaminants by Aquatic Invertebrates Downstream of the Tennessee Valley Authority Kingston Fossil Plant

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T. F. Baker, Tennessee Valley Authority, Chattanooga, TN

On December 22, 2008, a dike failure at the Tennessee Valley Authority's (TVA) Kingston Fossil Plant (KIF) released an estimated 5.4 million yd^3 of ash into the Emory River. A comprehensive assessment of the consequences of the spill to the aquatic ecosystem was initiated soon after the release. Included in this assessment was a study of contaminant (i.e., metals) exposures to aquatic invertebrates in summer 2009. Two widespread and abundant aquatic macroinvertebrate species found throughout the affected watershed were chosen as study animals. The silty horn snail, *Pleurocera canaliculatum,* is a relatively large snail that lives along the shoreline in the shallow littoral zone. Nymphs of the burrowing mayfly, *Hexagenia bilineata*, live in burrows dug in the bottom sediments in the reservoir. Each year from June through August, they emerge from the water in large numbers as non-feeding adults and are consumed by many aquatic and terrestrial predators. A core of five sampling sites was assessed: three on the Emory River (ERM 6.0 upstream of KIF; ERM 2.5 and ERM 1.0 downstream of KIF) and two on the Clinch River (CRM 6.0 and CRM 1.5, upstream and downstream of Emory River respectively), although additional sites were added based on availability of specimens. Snails were collected by hand and held for 72 hr in a laboratory to clear their digestive systems (i.e., depuration) before analysis. *Hexagenia* nymphs were collected with a Peterson dredge. A full complement of samples was analyzed without depuration, but a subset of samples was also collected from ERM 1.0 and CRM 1.5 and depurated for 48 hr before analysis. *Hexagenia* adults were collected opportunistically with a sweep net or by hand and sorted by sex and adult stage (i.e., imago and subimago) before analysis. Preliminary results showed elevated concentrations of some contaminants downstream of the ash spill that varied with species and developmental stage. For example, similar concentrations of selenium were found in nymphs and adult mayflies, and depuration had no effect on body burden. Arsenic (As) in contrast, was only slightly elevated in adult mayflies, but significantly elevated in nymphs. However, purging studies showed that ≈75 % and 47 % of the As in nymphs at CRM 1.5 and ERM 1.0, respectively, was attributable to undigested food. Higher concentrations of mercury (Hg) were found at the Clinch River sites, with the highest concentrations in mayfly nymphs (0.65 µg/g dry wt) and adults (0.39 µg/g dry wt) at CRM 6.0 located upstream of the Emory River. As for arsenic, ≈75% of the Hg burden in nymphs at CRM 1.5 was attributable to undigested food. Future studies will focus on better understanding the spatial extent of contaminant transport downstream of the KIF and clarification of the influence of sex and presence of undigested food on estimates of contaminant burdens.

Fly ash and mercury: does selenium in ash inhibit methylmercury bioaccumulation?

George Southworth, Mark Peterson, Marshall Adams, Teresa Mathews, Dick Ketelle, others?

Selenium is known to have an antagonistic effect on the mammalian toxicity of inorganic mercury, and appears to play a role in reducing the accumulation of methylmercury in fish in some aquatic ecosystems. The Biological Monitoring and Abatement Program (BMAP) at Oak Ridge National Laboratory (ORNL) has measured mercury and selenium concentrations in largemouth bass over a 20 year span in a quarry that once received direct discharges of slurried fly ash. When monitoring started in 1990, a year after ash disposal in the quarry was discontinued, mercury concentrations in fish averaged less than 0.02 ppm, and selenium exceeded concentrations in fish from regional reference sites by five-fold. Over the next 10 years, mercury concentrations in bass steadily increased to over 1 ppm before reaching an apparent steady-state, and selenium concentrations decreased but never returned to background levels. During this time, streamflow into the quarry drained a large basin that had been filled with fly ash prior to its direct discharge to the quarry. In the mid 2000's, selenium concentrations in bass began to increase rising from 1 to over 2 ppm between 2005 and 2009. Mean mercury concentration in fish decreased from 1.1 ppm to nearly 0.5 ppm over the same period.

ORNL and TVA staff sampled fish from the ash stilling pond at the Kingston steam plant in 2009, with results similar to those observed in Rogers Quarry in the mid 1990's. Average mercury concentration in bluegill from the stilling pond was 0.01 ppm and selenium was 2.4 ppm. An experimental recirculating indoor stream mesocosm system has been established at ORNL to investigate the production and bioaccumulation of methylmercury in mercury-contaminated stream ecosytems. Results to date indicate that waterborne inorganic and methylmercury concentrations to closely simulate levels typical of mercury-contaminated East Fork Poplar Creek in Oak Ridge. We have proposed to use this system to investigate whether trace additions of selenite can inhibit the production and/or bioaccumulation of methylmercury without elevating selenium concentrations in aquatic biota to unacceptable levels.

Overview of the Human Health Risk Assessment Process

TVA Kingston Fly Ash Recovery Project

Mark Stack – Jacobs Engineering

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 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 including arsenic and selenium are the primary constituents of potential concern for fly ash.

The KIF is located on the Emory River near the confluence of the Clinch and Tennessee Rivers. This portion of the Tennessee River Valley is bounded by ridges and impounded by Watts Bar Dam. The reach of Watts Bar Reservoir at the KIF transitions from the upstream riverine reaches of the Emory River and the Clinch River to the more lacustrine conditions found in the impounded portions of the Clinch River and Emory River backwaters of Watts Bar Reservoir. This multi-use reservoir supports a diversity of aquatic and terrestrial wildlife. The size and complexity of the potentially affected ecosystems necessitates a comprehensive environmental sampling and monitoring program, which TVA has implemented in cooperation with numerous federal, state, and academic organizations.

The objective of the human health risk assessment for the TVA Kingston Fly Ash Recovery Project is to develop quantitative and qualitative estimates of potential cancer risks and non-cancer hazards for human receptors exposed to environmental media impacted by the ash remaining following completion of the time-critical removal action. These estimates will be developed to support remediation decision making. Risks to both current (or near-term) and potential future receptors will be evaluated. The risk analysis will be based on analytical data collected from ash, surface water, sediment, and fish sampling.

This poster presents an overview of the human health risk assessment process as it is being applied at the TVA Kingston Fly Ash Recovery Project.

Investigating TVA Kingston coal fly ash toxicity to larval and juvenile fathead minnows using extended elutriate bioassays

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In order to assess the potential impacts to fish of coal fly ash resuspension during dredging operations at the TVA Kingston site, extended (10 d) elutriate bioassays were conducted with larval (9-d old) and juvenile (3 month old) fathead minnows. Elutriates were prepared using a greatly extended aeration time of 10-d in order to provide an extreme case scenario for metal release, dissolution and changes in speciation and a settling time of 1-h. Larval fish were exposed to elutriates created from fly ash from the Emory River and Ash Recovery Ditch, while the juvenile fish were exposed to only the Emory River fly ash elutriate. Other treatments included an Emory River reference water and a performance control (dechlorinated tap water). In the juvenile exposure, rigorous aeration was used to keep fly ash particles suspended in the water column during the bioassay. The larval fish exposure chambers were aerated less vigorously to avoid energetic stress associated with high flow conditions. Both exposures were static-renewal, renewed on days 3 and 7. Larval and juvenile fish were fed Artemia or flake food, respectively, every other day. Endpoints assessed include survival and growth in the larval bioassay and survival, growth, liver-somatic index, gill histopathology, and metal bioaccumulation in the juvenile bioassay. No significant toxic effects to larval or juvenile fathead minnows were observed. Gill histopathology results were inconclusive. Bioaccumulated metal concentrations in juvenile fish were compared to literature toxicity reference values (TRVs). Only vanadium exceeded literature TRVs, but this was likely due to vanadium associated with fly ash in the fish gut.

Evaluation of potential toxicity of fly ash released to the Emory River, TN, to benthic invertebrates in whole-sediment and elutriate exposures

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The objective of this study was to evaluate the potential toxicity of fly ash in whole-sediment or fly ash in elutriate toxicity tests conducted with benthic invertebrates. A preliminary 10-d whole-sediment toxicity test was conducted at the US Army Corps of Engineers (USACE) Engineer Research and Development Center with amphipods (*Hyalella azteca*) exposed to two ash samples collected from the Emory River and a control sediment (Browns Lake, MS). Mean 10-d survival and growth of amphipods in the ash samples were significantly reduced relative to the control. Concentrations of arsenic, copper, cadmium, and nickel in the ash samples were at or above the threshold effect levels for amphipods. Longer-term whole-sediment toxicity tests were conducted at the US Geological Survey (USGS) Columbia Environmental Research Center with amphipods (*H. azteca*) and two juvenile mussels (rainbow mussel, *Villosa iris* and wavy-rayed lampmussel, *Lampsilis fasciola*) for 28 d, and midge (*Chironomus dilutus*) for 10 d. Organisms were exposed to one ash sample and a control sediment (West Bearskin Lake, MN). Mean survival or growth of amphipods and mean growth of wavy-rayed lampmussels and mdige in the ash sample was significantly lower than the control, whereas the survival and growth of rainbow mussels were not significantly different between the control and ash samples. The concentration of arsenic in the ash sample was above the empirically based sediment probable effect concentration. Additionally, two elutriate samples were prepared to simulate an extreme re-suspension event of fly ash in the Emory River and the sluice channel during dredging to remove fly ash, and used to conduct a 10-d elutriate toxicity test with 5-month-old rainbow mussels at USGS. The elutriates contained elevated concentrations of arsenic, selenium, and barium relative to local soil and sediment. Mean 10-d survival of the mussel (based on foot movement or heartbeat) ranged from 90 to 100% and was not significantly different among reference site water (0% elutriate), 10%, 50%, and 100% elutriate concentrations for both elutriate samples. However, a significantly lower percentage of mussels moved their foot with exposure to 100% elutriate from sluice channel compared to mussels in reference site water. These results indicate that fly ash can be chronically toxic to some sediment-dwelling organisms possibly due to elevated metal concentrations. However, the short-term release of contaminants during re-suspension of fly ash may not adversely affect the survival of juvenile rainbow mussels.

Aquatic Ecosystem Assessment of the Kingston TVA Fly Ash Disaster

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An interdisciplinary and multi-institutional collaborative team from NC and TN began collecting water, sediments and fish within two weeks of the Tennessee Valley Authority's Kingston Fossil Plant spill to determine a baseline level of contaminants in sediments and fish. The initial levels will be used to measure any movements of ash from the spill site to downstream sites and possible increases in toxic element body burdens in fish which could indicate subsequent short and long-term effects of the spill on the aquatic ecosystem. Samples were collected in January, March, April and July 2009 and again on January 2010. Sediments were collected with an Ekman dredge and fish were captured by boat electroshocking at the following river mile locations (Emory - ERM 14, 3.3, 2.0, Clinch - CRM 5.5, 3.3, and Tennessee - TRM 564, 567 and 568). Analyses of ash, water, sediments, and fish tissues collected from 6 sites at 5 and 18 days following the dike failure have shown the following: 1) initially, dissolved and/or total available toxic metals (As, Cd, Cr, Cu, Ni, Pb, Se, Tl) in water immediately below the spill exceed protective aquatic life criteria levels; 2) ash and ash-laden sediments from the river have high arsenic levels; 3) fish gills exposed to waterborne ash show several histological alterations indicative of stress from toxic element exposure; 4) fish body burdens of selenium were nearing the thresholds of toxicity for reproduction and growth; and 5) chemical analysis of the surface of coal ash cenospheres from surface water samples by Energy Dispersive X-ray analysis (EDS) revealed detectable levels of arsenic (~10,000 ppm) associated with iron oxide gels. The initial collection data suggest the selenium in the fish tissues is legacy selenium, possibly from decades of unregulated release of this metal from ash settling ponds at the TVA Kingston plant. Two independent data sources have made clear that in the years just after the KIF plant was built (~1955), straight piping of ash to the river was occurring and had created a "delta" of ash in the Emory River and sediment cores collected in the Emory River indicated that fly ash deposits were regularly occurring in the Emory River. Recent fish collections have shown only slightly increasing concentrations of selenium, but there was a concurrent increase in number of fish demonstrating selenium related pathologies. Over the long-term, selenium body burdens in fish may increase significantly as the selenium released into the aquatic system from the initial spill and subsequent dredging is absorbed and bioaccumulated in the food web. Quarterly water, sediment, and fish sampling will continue to determine the changes in levels of selenium (and other ash constituents) over the next two years.

Using AF4 multi-detection to characterize aquatic colloids generated from coal fly ash

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Coal fly ash is often stored in open aquatic settling basins where potentially toxic trace elements may be leached and discharged into surface waters creating hazards to aquatic organisms. Soils may also become contaminated either through unintentional releases of fly ash from aquatic settling basins or through intentional amendment of soils with fly ash. Regulatory monitoring schemes and transport models typically focus on the operationally defined dissolved phase, the total recoverable metals, or total metal concentrations in soils and sediments. Given that fly ash is composed of nanometer to micrometer sized particles, there is also great potential for dispersal of colloids from fly ash and fly ash containing soils. I have applied a technique using asymmetrical flow field flow fractionation (AF4) with multi-angle laser light scattering (MALLS), ultraviolet-visible absorbance (UV-vis), and inductively coupled plasma mass spectrometric (ICP-MS) detection to characterize colloids generated from fly ash. This technique allows determination of particle size, interaction with organic matter, and elemental composition as a function of particle size. My preliminary results have demonstrated that the so-called dissolved fraction of aqueous leachates from coal ash amended soils contain particles ranging in size from 5-400 nm and vary in chemical composition as a function of particle size. I have also demonstrated the potential for organic amendments to aid in the dispersion of such colloidal particles. Previous studies of engineered nanoparticles have demonstrated that these particles can be taken up by organisms and bio-distributed to target tissues. Therefore, the presence of colloidal particles needs to be taken into account not only when considering the fate and transport of trace-elements, but also bioavailability and toxicity. These results demonstrate the potential of AF4-MALLS-UV-vis-ICP-MS for understanding processes governing the generation, transport and fate of coal fly-ash associated colloids.

The impact of the Tennessee Valley Authority (TVA) coal ash spill on the quality of the Emory and Clinch Rivers: the first year evaluation

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A year-long systematic monitoring of the of the environmental impacts of the largest coal ash spill in US history at the Tennessee Valley Authority (TVA) Kingston coal-burning power plant has revealed that interaction of the coal combustion products (CCPs) with natural waters mobilizes leachable coal ash contaminants (LCACs) such as boron, arsenic, selenium, strontium, and barium. Since January 2009 we have monitored the quality of water and sediments in downstream segments of the Emory and Clinch Rivers near the spill site. We reveal three distinctive patterns (1) surface waters in areas of restricted water exchange (the "Cove"/East Embayment) show high LCACs levels (e.g., As: 9- 95 µg/L). Removal of ash from this area and diversion of surface water has led to a reduction of the LCAC's concentrations with time; (2) downstream Emory and Clinch Rivers show low LCACs concentrations below the EPA maximum contaminant level (As=10 µg/L) and Tennessee Fish and Aquatic Life Criterion for Continuous Arsenic Concentration (As= 150 µg/L) thresholds, but with levels (e.g., As ~4 µg/L) above the baseline of the upstream rivers; and (3) pore water extracted from bottom sediments of the downstream Emory and Clinch rivers with significantly high LCACs levels (e.g., As 9-285 µg/L). We show that boron is one of the sensitive indicators for contaminants' leaching from CCPs, with boron content up to 1276 µg/L in pore water relative to the upstream river water (6 to 9 µg/L). The high correlation between boron and arsenic clearly indicates that boron can be used as a sensitive proxy for detection of CCPs' contaminants in aquatic systems. The boron isotope composition of CCP's leachates measured in both leaching experiments and in surface waters at areas of limited water exchange is significantly different from that of upstream Emory River. We therefore use the boron isotope data as additional constraints for quantifying the relative contribution of LCACs in the environment. Overall, we show that while significant dilution reduces the LCAC's impact in the Emory and Clinch Rivers, leaching continues to occur at the bottom sediments and mobilizes LCACs to the underlying pore water.

Differential leaching of trace metals and their isotopes from coal combustion products

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Investigation of the environmental impacts of the December 2008 Tennessee Valley Authority (TVA) coal ash spill in Kingston, TN has indicated that trace elements from coal combustion products (CCPs) can be mobilized into the environment. We have conducted laboratory leaching experiments on bulk, fly, and bottom ashes from the TVA Kingston plant and lime-treated ash samples from Duke University. Leaching experiments were simulated reactions of CCPs with strong acid (HCl in 0.5N), weak acid (HCl in 0.02N), strong-basic (NaOH in 0.2N), weak-basic (NaOH in 0.00063N), deionized water under two S/L ratios, and Toxicity Characteristic Leaching Procedure (TCLP; EPA method 1311). Leaching conditions varied over a wide range of acidity (pH of 0.4 to 12). Preliminary results from the leaching experiments have revealed several distinctive patterns: (1) the CCPs composition and acidity control the pH of the leachates and magnitude of contaminants leaching; (2) differentiation between oxyanion (B, As, Se) and cationic (Ca, Sr) species, in which the former show maximum mobilization under low and high pH conditions while the latter show progressive increase in mobilization with increasing acidity; (3) differentiation of trace elements abundances in fly ash relative to bottom ash (relative enrichment of As, Se, Pb, B); (4) systematic boron isotope ratios ($^{11}B/^{10}B$) in leachates originated from a wide pH conditions that are significantly different from the isotope ratios of natural boron; (5) preliminary strontium isotope ($^{87}Sr/^{86}Sr$) results of TVA leachates are different from that Duke ash, which could be related to the original coal source and/or lime treatment of Duke ash. Overall, the leaching experiments data indicate that combination of CCPs properties, environmental conditions such as pH, and speciation of oxyanion species would control mobilization of contaminants from CCPs. Boron isotopes can be used to predict species distribution of oxyanion species while strontium isotopes can be applied as a surrogate for the origin of cationic species. Consequently, modeling of the mobilization of metals and metalloids from coal ash requires an in-depth understanding of the metal behavior under different geochemical constraints such as acidity, salinity, water composition (e.g., ion-pair formation for boron species), and the characteristics (e.g., acidity) of the ash itself.

Producing Defensible Environmental Data using Modified and Non-Standard Methodology

Organization- TestAmerica Laboratories

Authors- A.F Vicinie, L. Matko, M. Matrozza, T. Martz, N. Derubeis, P. McIsaac.

Purpose and Objective: To demonstrate the need in project design to establish data quality objectives to ensure that environmental data generated is defensible and able to support the needs of the data user community.

Approach or Experimental Design- Identify fundamental aspects of environmental laboratory quality systems. We will also identify potential gaps that may exist in standard quality systems when performing modified or non-standard methodology that should be considered in experimental design and execution. Discussion on how these systems and considerations are being applied to evaluate coal ash and Kingston specific studies to provide data of known quality to the user community. .

Results or Findings to date- Utilizing a Kinston coal ash project specific sequential extraction method for metals, we will provide examples of how quality systems were adapted to conform to industry standards and what supplemental information should be considered in project design.

Significance or Benefit to Kingston Ash Recovery Program

Data generated from this program will have many uses and users. It will be utilized for a variety of purposes. Significant decisions will be made from data generated to investigate this site and incident. The data underlying these decisions must be of known quality and able to provide support to assist in appropriate evaluation and decision making.

Future Studies- Continued emphasis to increase awareness of project communication in advance during project design to ensure that all appropriate measures are considered and in place prior to data generation.

Regulatory Framework--Kingston Ash Recovery Project

Craig Zeller

On May 11, 2009, the Tennessee Valley Authority (TVA) entered into an Administrative Order on Consent (AOC) with the Region 4 Office of the United States Environmental Protection Agency (EPA), under the regulatory authority of the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA), to address the approximate 5.4 million cubic yards (CY) of coal ash released to the environment on December 22, 2008. The Superfund program was selected as the preferred regulatory framework due to its comprehensive human health and ecological risk assessment process and its proven ability to actively engage and involve multiple stakeholders in large, complex environmental cleanup projects. A series of phased Time Critical and Non-Time Critical Superfund Removal Actions are underway to address coal ash that was released to area waters, including the Emory River, tributaries, embayments, and sloughs. Time Critical Removal Actions involve wet excavation, mechanical and hydraulic dredging, rapid materials handling and disposal of an estimated 3 million cubic yards of ash from the Emory River to mitigate further downstream transport. Ash removed from the river is dewatered on-site and loaded onto rail cars for disposal at an approved landfill in Perry County, Alabama. Under the direction of the Superfund Removal Program, river removal production has increased from an average of 2500 CY/day to nearly 15,000 CY/day with the potential of 20,000 CY/day. River removal is expected to be complete by May of 2010. Non-Time Critical Removal Actions will be utilized to address the 2.5 million CY of ash in the embayments and sloughs, and to assess the environmental risks posed to ecological receptors by residual ash in the river system. This poster will provide an overview of the regulatory framework, and short- and long-term removal actions employed by EPA to protect human health and the environment.

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