

Porewater Studies Subsequent to the Kingston Ash Event

Presented at World of Coal Ash, April 22-25, 2013, Lexington Kentucky

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ABSTRACT

The 2008 TVA Kingston Fossil Plant fly ash release into the Emory River near Kingston, Tennessee, provided a unique opportunity to study the impacts of coal ash on the environment. TVA, in conjunction with university researchers, sampled porewater from the top few inches of sediment at various locations on the Emory and Clinch Rivers on several occasions from November 2009 through June 2011.

Three different sampling techniques were used to collect porewaters in these investigations:

(A) In 2010, a series of porewater samples were collected using a Geoprobe™ to insert well screens into the top meter of groundwater at several points in the relic ash cell and active ash processing areas of the Kingston ash recovery project. Porewater samples were collected by pumping water from the well-points using peristaltic pumps, followed by vacuum-filtering through 0.45-micron filters.

(B) Earlier sampling events utilized on-boat filtration of well-mixed river sediments using a battery-operated vacuum pump and 0.45-micron filters. Most of these samples were obtained with a box corer, but a few were sampled with VibeCore™ samplers.

(C) In 2011, river sediment was sampled in a box corer, brought to the surface with the overlying water trapped in the sampler, then the collected sediments were sub-sampled into short coring tubes that were quickly capped to protect the sediment from exposure to air. Porewaters were subsequently extracted from these samples by centrifugation and filtration in an inert atmosphere in a laboratory.

Porewater concentrations of arsenic and selenium were substantially lower for the 2011 samples that were carefully protected from exposure to the atmosphere. Temporal and spatial information for arsenic, selenium and various other elements in the porewater are presented and compared to solid-phase concentrations.

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I. INTRODUCTION

Background

On December 22, 2008, a coal ash spill occurred at the Tennessee Valley Authority's (TVA) Kingston Fossil Plant in Roane County, Tennessee. The plant is located at the confluence of the Emory and Clinch Rivers, approximately four miles upstream from the confluence of the Clinch and Tennessee Rivers on Watts Bar Reservoir in Roane County, Tennessee.

The Kingston Fossil Plant has operated since 1955, producing approximately 1000 cubic yards of coal ash per week. For several years the plant operated with no air pollution controls on stack emissions. Over time various air pollution abatement systems were added as regulations evolved. Reports by the U. S. EPA have observed that it is possible for particulates from stack emissions from the period preceding air pollution controls to show up in sediment profiles near coal-burning power plants (U. S. EPA 2003).

The spill allowed 5.4 million cubic yards of coal ash to escape from a dredge cell into the Swan Pond Embayment and the adjoining Emory River. Approximately 2.4 million cubic yards of ash filled the Swan Pond Embayment; the remaining 3.0 million cubic yards entered the Emory River at approximately Emory River Mile (ERM) 2.1. The initial ash release traveled upriver as far as ERM 5.75, and ash eventually was transported downstream into the Clinch River and as far downriver as Tennessee River Mile 564 by subsequent high-river flow events. (Arcadis 2012)

Hydraulic dredging to remove the released coal ash from the Emory River began March 20, 2009, and continued until May 29, 2010. Limited mechanical dredging of pockets of ash continued until August 2010. Because of legacy contaminants in Clinch River and lower Emory River sediments from former U. S. Department of Energy operations at Oak Ridge and the potential undesirable aspects of resuspension of those contaminants, dredging was constrained to areas upstream of ERM 1.75. Consequently, approximately 500,000 cubic yards of ash are estimated to remain in the lower portion of the Emory River and the Clinch River (Jacobs 2010).

Coal ash is an aluminosilicate glass material with substantial fractions of iron and calcium. Research by universities and studies internal to the Kingston ash recovery project have focused on arsenic (average ~65 mg/kg in Kingston ash) and selenium (average ~6.7 mg/kg) since these two elements pose potentially significant long-term ecological risks (Arcadis 2012, Jacobs 2010, TVA 2012). Ash differs from surrounding soils and geologic media in boron (average ~99 mg/kg) and strontium (average ~202 mg/kg) concentrations.

While regional soils may approximate arsenic concentrations in the ash (Kopp 2001), local soils contain less arsenic than the ash: 6 to 8 mg/kg (Rogers et al. 2010). The underlying geologic units (Knox Group Conasauga Group and Rome Formation) appear to be enriched in arsenic relative to local soils. Core samples with depths to 65 feet into underlying geology in areas adjacent to the plant that were collected by TVA in 2010 were found to contain 52 mg/kg arsenic (ranging from 3 to 101 mg/kg), 13 mg/kg boron (11 to 15 mg/kg), and 2.7 mg/kg selenium (2.3 to 3.9 mg/kg). These core samples were similar to ash in arsenic concentration, but differed significantly from ash in boron concentration. The core samples had roughly one half the selenium of ash.

Arsenic biogeochemistry

Arsenic (As) in the aquatic environment exists in two stable valences, As (3+) and As (5+). In well-oxygenated water bodies, arsenic is present predominantly as the As (5+) oxyanion, arsenate (AsO_4^{3-}) (U. S. EPA 2003).

Metabolism of arsenate follows the same biochemical process as its chemical analog, phosphate, which accounts for arsenic's toxicity to living organisms (ATSDR 2007). Microbial-mediated reduction of

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arsenate to arsenite has been observed and is postulated to be a protective mechanism, since arsenite is much less like phosphate metabolically than is arsenate (U. S. EPA 2003).

Arsenate is less mobile than the As (3+) oxyanion, arsenite (AsO_3^{3-}) (U. S. EPA 2003). Microbial reduction can mobilize otherwise stable and sparingly soluble arsenate complexes (Lloyd and Oremland 2006). Depending on solution pH, arsenate and arsenite may be present in water as several different hydrated ion complexes of varying solubility (Komárek et al. 2013, Streat et al. 2008, Magalhães 2002). The literature is rich with reference to interactions of arsenic with hydroxyanions of aluminum and iron and the decreased lability of those ion complexes relative to the hydrated arsenate and arsenite ions (Komárek et al. 2013, Streat et al. 2008). It also may be environmentally significant that the solubility of barium arsenate, a very insoluble arsenate salt, is increased by the presence of carbon dioxide (Robins 1981, Robins 1985, Robins et al. 2001).

Selenium biogeochemistry

Selenium (Se) in the aquatic environment exists in four valences: elemental selenium (Se (0)), selenide (Se (2-)), selenite (Se (4+)), and selenate (Se(6+)). Thermodynamically, selenium should be present in oxygenated waters as selenate; however, there are kinetic barriers that significantly impair that oxidation, thus selenium often is predominantly present as selenite in the aquatic environment (Catalano et al. 2012, Wang et al. 2007). Recent work on the dynamic nature of selenium valence inter-conversions suggests that selenite in the aquatic environment may be oxidized to selenate by exposure to ultraviolet light (Bednar et al. 2010, Chappell 2013, Steevens et al. 2011).

Selenium does not develop the strong aluminum and iron hydroxyanion complexes that arsenic and several other elements exhibit. Instead, selenium chemistry in coal combustion and air pollution control systems follows that of sulfur, its chemical homolog (Catalano et al. 2012, ATSDR 2003).

Selenium is an essential element for living organisms over a very narrow concentration range, above which it interferes with reproduction and can cause a variety of skeletal deformities when it substitutes for sulfur in amino acids. Similar to its combustion chemistry, selenium appears to substitute for sulfur in various enzyme systems (ATSDR 2003). Another interesting and sometimes confounding aspect of biomonitoring is that selenium and mercury appear to have an antagonistic relationship in living organisms, with increased bioaccumulation of selenium inhibiting mercury uptake, and vice-versa (Khan and Wang. 2009, Yang et al. 2008, Southworth et al. 2000 and 1994, Pelletier 1986).

II. STUDY TECHNIQUES

Leaching of arsenic, selenium, and other contaminants from ash particles into porewater is the presumed initial release point of ash-related contaminants into the aquatic environment and subsequent incorporation into the food chain. Consequently, several TVA-funded research investigations have focused on characterizing the processes by which leaching takes place, factors affecting those processes, and the extent of leaching that occurs. Some of those investigations include porewater studies to assess the potential for mobilization of arsenic and selenium from ash to the aqueous phase.

A. Ash Storage Cell Saturation Zone

In September 2010, TVA staff sampled the remnant ash cell, ash processing area, and ash flow area for *in situ* porewater in the top meter of saturated ash. A truck-mounted Geoprobe™ was pushed into the body of ash to determine the depth to groundwater. The equipment was then offset by two feet and a separate probe was pushed to one meter below the measured groundwater level. A screen was inserted and the top layer of the interstitial groundwater was sampled using a peristaltic pump and inert tubing. The collected water was filtered through a 0.45-micron filter and was considered to be a sample of the porewater in the saturated ash. All porewater samples were assumed to be in 100 percent previously buried coal ash. Samples were collected in this manner from the portion of the dredge cell that did not fail (“the relic”),

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the 1960s-era initial ash storage area (“ballfield”), the portion of the dredge cell from which ash spilled on December 22, 2008, and from the active ash handling and de-watering areas.

B. River Sediments Open to Atmosphere

B1. River Sediment Box Corer Samples – Homogenization Open to the Atmosphere

Duke University researchers utilized a box corer device that penetrated to as much as 20 centimeters into the sediment to collect sediments at various locations in the Emory and Clinch Rivers (Ruhl et al. 2010). The sediment samples collected by this technique were lifted to the surface and manually mixed in clean polymer tubs on the deck of the sampling vessel using inert polymer stirrers. The homogenized sediments were vacuum-filtered through 0.45-micron filters to obtain porewater samples. In most cases, TVA scientists collected co-located samples or field splits of the Duke University samples during these Duke University sampling events.

B2. River Sediment VibeCore™ Samples - Homogenization Open to the Atmosphere

On April 28, 2010, Duke University researchers used lined VibeCore™ tubes to penetrate into sediments at ERM 1.0 and ERM 2.0 and at Clinch River Mile 4.0 (CRM 4.0) at locations sampled the day previous with a box corer. Penetration depths ranged from 82 to 158 centimeters. Duplicate cores were collected at each location with one archived at Duke University and one selected for porewater extraction. After retrieval, cores were described in field notes by visual characteristic or color. At ERM 2.0, the 109 cm core was divided into two equal segments which were homogenized and filtered in a similar manner as the box corer samples collected by these researchers. CRM 4.0 did not yield sufficient porewater for analysis due to a high proportion of fines, and at ERM 1.0 the core selected for porewater extraction was taken to Duke University for an attempt at extraction in the laboratory. TVA scientists received split porewater samples from two portions of the single Vibecore™ sample from ERM 2.0.

C. River Sediment - Capped Four-Inch Cores Maintained in an Inert Atmosphere

Subsequent to the box corer sampling by Duke University, TVA researchers developed a technique to collect sediment samples and extract porewater in an inert atmosphere that would be more representative of conditions at the bottom of the reservoir and that would protect the sediments from atmospheric oxidation during handling. A box corer was deployed, then was retrieved with a sediment sample and overlying water. On board the vessel several 1.5-inch diameter by 4-inch long acrylic sample tubes equipped with vented caps were carefully pressed vertically into the intact sediments in the box corer, allowing the overlying water to escape through a pre-drilled hole in the cap until the tube was completely inserted to the top of the sediment. After all tubes were inserted, a gloved finger was then placed over the vent hole to temporarily seal it, and each four-inch core tube was slowly pulled from the box corer sediment sample, thereby collecting undisturbed sediment core samples with minimal overlying water. The bottom of each tube was quickly capped and the vented cap at the top was either sealed with electrical tape or replaced with a solid cap. This extraction of core samples from each box corer required only a few seconds, thus minimizing sediment exposure to the atmosphere. The sealed samples were stored upright on wet ice, and within 24 hours were delivered to a contract laboratory where porewater was extracted from each companion sediment core by centrifugation in a glove box containing an inert (nitrogen) atmosphere.

Percent ash was determined using optical microscopy and a point-counting technique. Arsenic, boron, selenium, and strontium in sediment and porewater were determined by Inductively Coupled Plasma/Mass Spectroscopy (ICP/MS). Liquid chromatography (anion exchange) coupled with ICP/MS or with Hydride-Generation Quartz Furnace Atomic Absorption Spectroscopy was used to separate and quantify arsenate, arsenite, selenate, and selenite in samples taken in 2011.

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III. RESULTS

A. Ash Storage Cell/Ash Processing/Ash Flow Area - Top Meter of Groundwater

The assumption in examining the top meter of groundwater in these areas was that it would represent geochemical near-equilibrium concentrations of arsenic and selenium since the stored ash had been in contact with groundwater (or process water) for decades in the “ballfield” area and intact “relic” cell, and for years or months in the other areas. From that perspective, arsenic was found to be lower in the “ballfield” samples, but no real distinction can be made between the intact relic cell and ash flow areas (see Table 1).

Table 1 - Relic Cell Saturated Zone Sampling

| Location | Arsenic (µg/L) | Boron (µg/L) | Selenium (µg/L) | Strontium (µg/L) |
|---------------------------------------|---------------------------|-------------------------|----------------------------|-----------------------------|
| GP07 “ballfield” - 1960s-era ash cell | 110 | 1400 | <0.33 | 2060 |
| GP08 “ballfield” | 66.6 | 1200 | 0.35 | 3810 |
| GP09 “ballfield” | 48.1 | 1920 | <0.33 | 3120 |
| GP10 “ballfield” | 43.5 | 2235 | <0.33 | 2285 |
| GP11 Intact Relic | 382 | 3090 | 0.53 | 2350 |
| GP12 Intact Relic | 915 | 3880 | 0.97 | 1840 |
| GP13 Intact Relic | 463 | 5060 | 16.5 | 1980 |
| GP14 Disturbed Relic “ash flow” | 905 | 4250 | <0.33 | 5460 |
| GP15 Disturbed Relic “ash flow” | 339 | 7800 | 0.4 | 5860 |
| GP16 Lateral Expansion Cell | 8.87 | 3920 | 0.92 | 3620 |
| GP18 Dewatering Area | 3.9 | 12200 | 19.6 | 15800 |

For comparison to the other data, arsenic ranged from 339 to 915 µg/L in porewaters from the areas representative of the ash that was spilled. Selenium ranged from non-detect (for example, <0.33 µg/L) to 16.5 µg/L in the same porewaters. Boron and strontium have been noted to be excellent tracers for the presence of ash when compared to sediment and underlying geology. The high concentrations of boron and strontium found in the top meter of groundwater collected from the dewatering area indicates the rapid solubility and accumulation of these two species while the lower arsenic value (3.9 µg/L) may indicate a slower dissolution from the surface of the ash. Consequently, while elevated solid-phase boron and strontium have proven to be useful as indicators of the presence of ash; they may be lost from aqueous phases, depending on the nature of ash processing.

B. River Sediment Box Corer Samples - Concentrations as a Function of Percent Ash

The box corer samples split with Duke University researchers chronologically preceded the September 2010 relic cell saturation zone study. Selenium concentrations in the porewater appeared to be fairly independent of ash concentration (Figure 1), with one exception at ERM 2.0 (8.4 µg/L). None approached the 16.5 µg/L seen in the relic cell samples. Not shown is a porewater selenium measurement of 7.7 µg/L upstream at ERM 12.2. In the solid phase, selenium exhibited a generally linear relationship to percent ash (Figure 2).

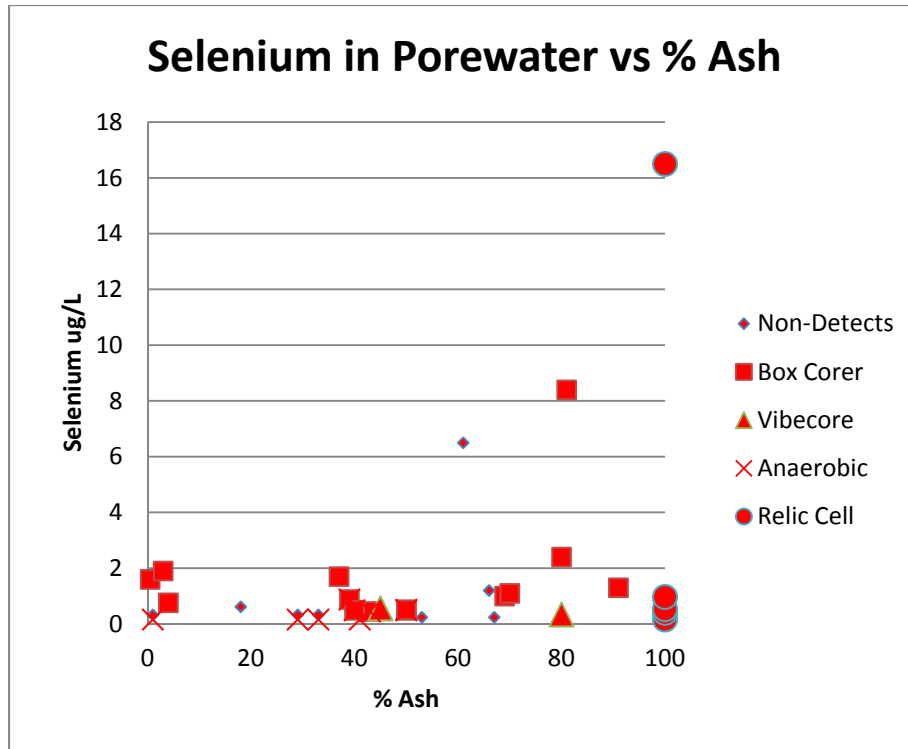


Figure 1 - Selenium in Porewater vs. Percent Ash

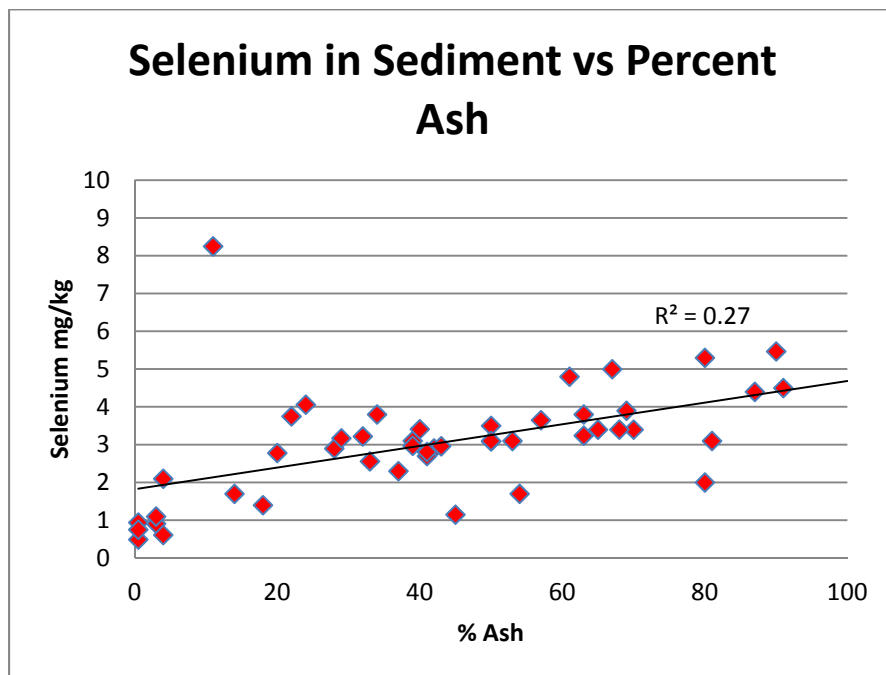


Figure 2 - Selenium in Sediment vs. Percent Ash

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Porewater arsenic concentrations for the box corer samples were roughly proportional to percent ash starting at 40 percent ash (Figure 3). In one box corer sample at ERM 4.0, arsenic was present in higher concentrations than was observed in the top meter of water in the relic cell. Two other higher values were found at ERM 2.0 in the VibeCore™ sample.

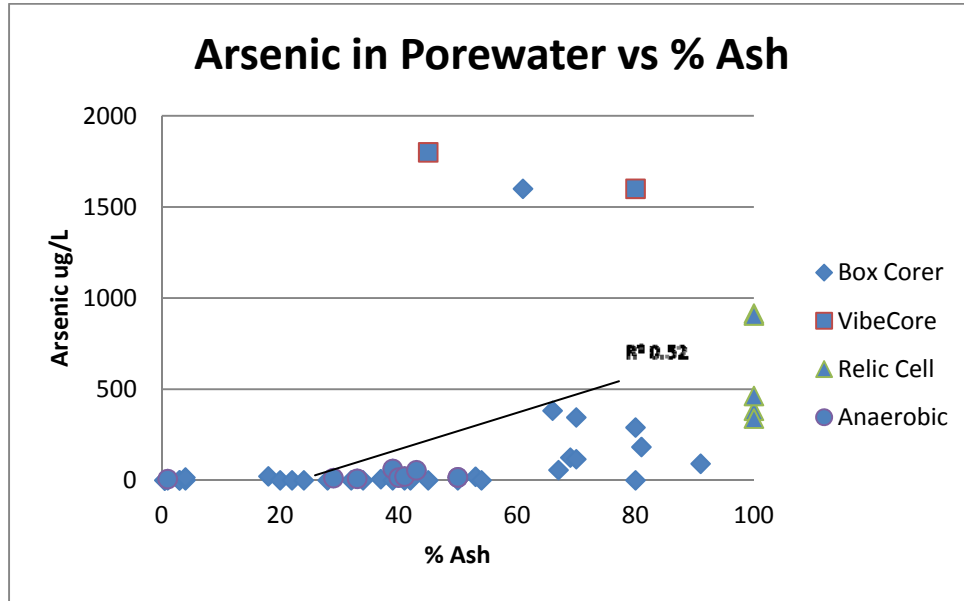


Figure 3 - Arsenic in Porewater vs. Percent Ash

As expected, arsenic in sediment appears to exhibit a linear relationship to the percent ash (Figure 4).

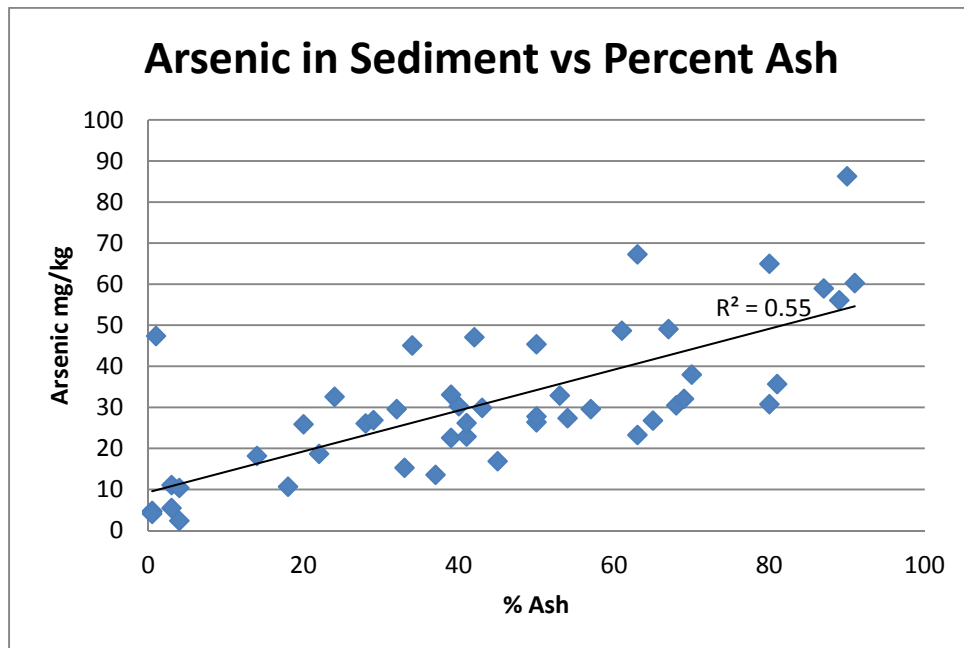


Figure 4 - Arsenic in Sediment vs. Percent Ash

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An upstream selenium value at ERM 12.2 of 7.7 $\mu\text{g/L}$ was also measured in porewater, but percent ash was not determined for that sample. It must be cautioned in interpreting selenium data that no unusually high selenium porewater concentrations are noted compared to the ERM 12.2 value or to the relic cell value of 16.5 $\mu\text{g/L}$.

Two samples with solid phase concentration selenium values greater than 8 mg/kg were found at ERM 4.0, but are not plotted in Figure 2 because percent ash was not measured for all samples.

Porewater Time Series

When plotted as a time series, selenium appears to increase with time in the porewater (Figure 5) even though no inordinately high values were observed for all Duke University-TVA split samples, especially at ERM 2.0, which is at the spill site and also at CRM 2.0 and CRM 0.0. The high value at ERM 12.2 (coupled with low arsenic values in the same sample) hints at an upstream source for this element. Upstream on the Clinch River, no unusually large values were observed. The point labeled PLNTEFF is the discharge point for the Kingston cooling water channel flowing into the Clinch River near CRM 1.7 and had two values below 2 $\mu\text{g/L}$. It appears that selenium is ubiquitous, but variable in the environment, and while some influence on porewater from ash is observed, values appeared to fall within bounds of background samples.

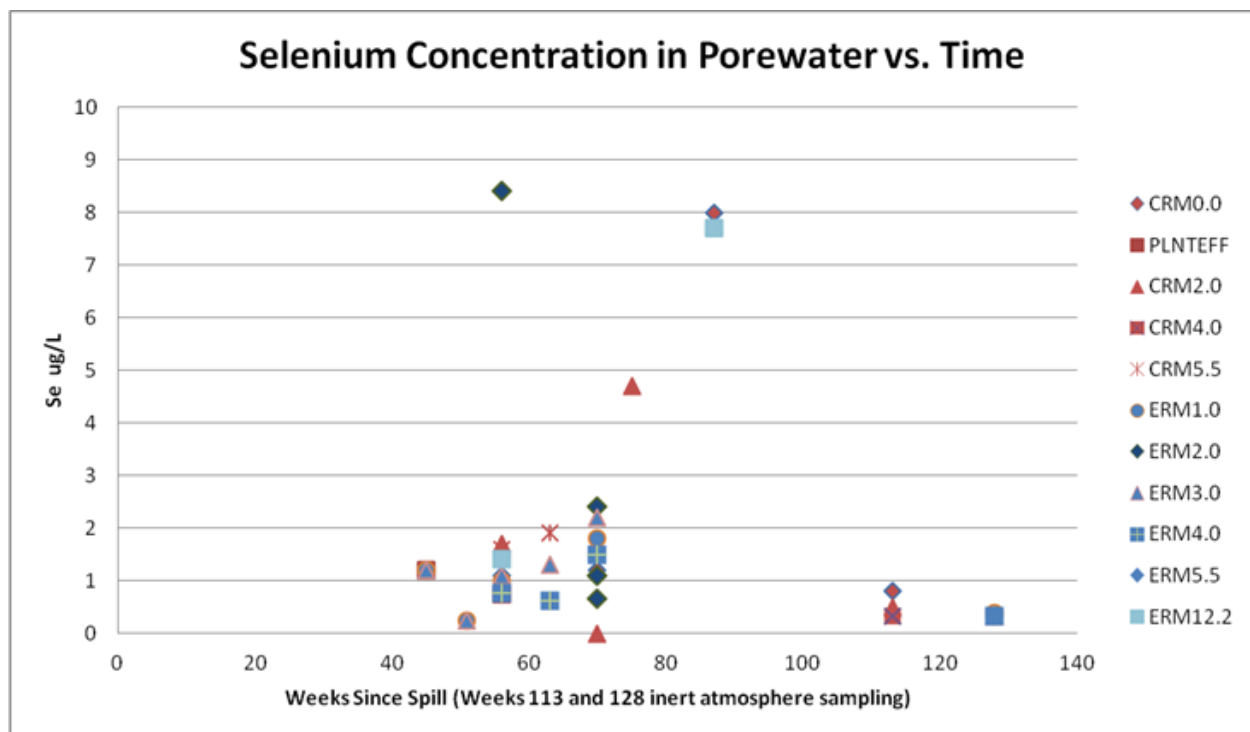


Figure 5 - Selenium in Porewater - Time Series

Time-series plots of arsenic in porewater in the Clinch and Emory Rivers are somewhat more difficult to interpret (Figure 6). While Duke University researchers concluded there was an increasing trend over time in porewater arsenic (Ruhl et.al. 2010), that published work only included data through June 2010 (week 75). The TVA data set on split samples which continued through August 2010 may indicate the beginnings of natural attenuation of arsenic in sediments porewater at ERM 2.0 and 3.0, although values at ERM 1.0 appeared to continue to increase through the period covered by the Duke University-TVA split sample study (week 87).

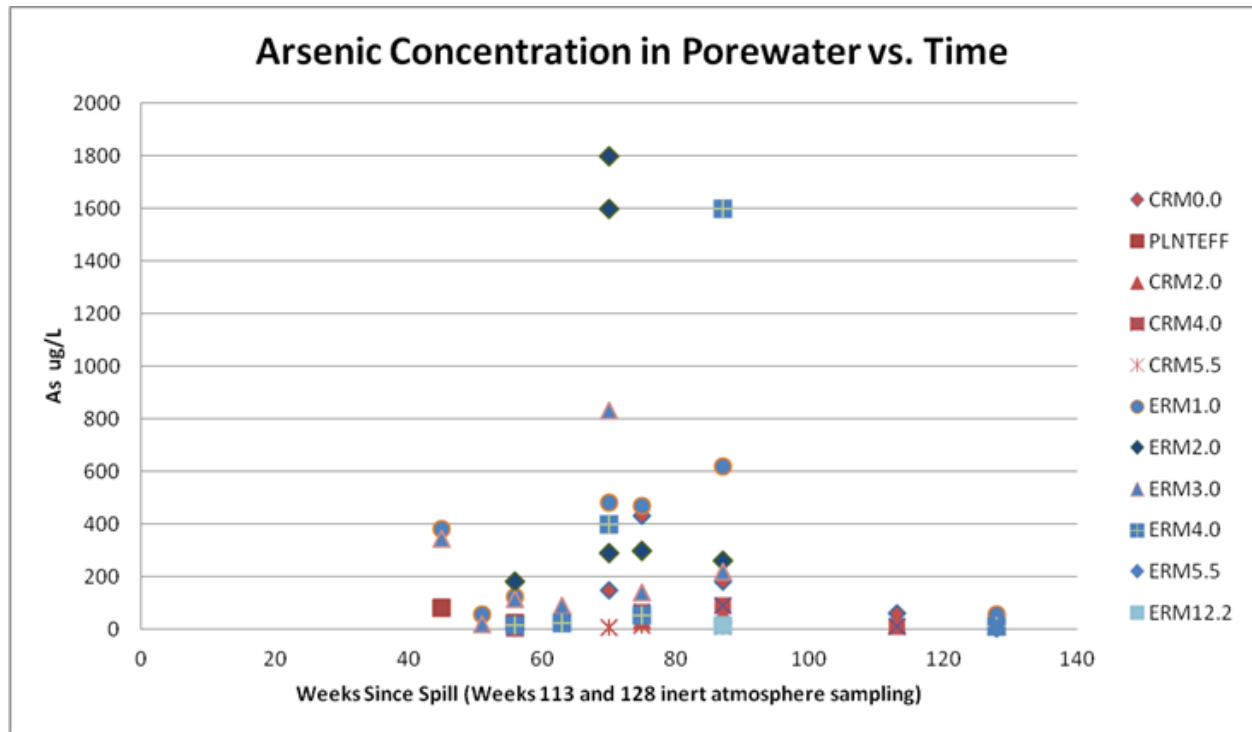


Figure 6 - Arsenic in Porewater - Time Series

The reported value of 1600 µg/L arsenic at ERM 4.0 was higher than the largest value observed in the relic cell. A reanalysis confirmed the concentration. Since the sample itself was 61 percent ash, not the highest value for which corresponding porewater data were available, TVA researchers began to question whether the open-air homogenization technique for preparing porewater may have affected the results. Researchers conducting porewater and sediment sampling are increasingly emphasizing the need for taking great care to exclude atmospheric influences during sediment sampling (Manheim 1976, Adams 1991, Burone et al. 2005, Loudrino-Cabana et al. 2012).

Box corer samples which were taken to a maximum of 20 centimeters depth comprised most of the sampling effort by both TVA and Duke University; however, the Duke University deep corer (VibeCore™) river porewater samples collected April 28, 2010, at ERM 2.0 were a focus of the published data analysis by Ruhl et al. (2010). The VibeCore™ porewater samples yielded the highest values for porewater arsenic of all the sampling events except for the ERM 4.0 box corer sample discussed above. In Table 2, the two Duke University porewater samples taken from the deep sediment cores (0 to 55 and 55 to 109 centimeters) are compared to results from a box corer sample taken the previous day at the same river location.

Table 2 - VibeCore™ and Box Corer Porewater Results at ERM 2.0

| Depth (cm) | % Ash | Arsenic µg/L | Boron µg/L | Selenium µg/L | Strontium µg/L |
|------------------|-------|--------------|------------|---------------|----------------|
| 0 - 55 | 45 | 1800 | 1800 | <1.1 | 470 |
| 55 - 109 | 80 | 1600 | 1800 | <0.67 | 1100 |
| 0-10 (box corer) | 80 | 290 | 1400 | 2.4 | 970 |

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Arsenic concentrations in the VibeCore™ segment porewater samples were much higher than in the shallower box corer porewater. Porewater strontium and boron from the box corer sample were similar to the deep-core segment values, but not as high as those in the relic cell (refer to Table 1). Selenium was actually higher in the box corer porewater sample than in the VibeCore™ porewater samples. This unusual array of concentrations raised a concern that the open-air homogenization and filtration process may have solubilized arsenic in some fashion. Simple oxidation does not appear to be the mechanism since arsenite, the reduced species, is more mobile than the arsenate. In addition, carbon dioxide affects re-dissolution of barium arsenate only above pH 8 (Robins 1981, Robins 1985, Robins et al. 2001) whereas field measurements of sediment pH rarely went above 7.5. Loudrino-Cabana et al. (2012) reference literature indicating that oxygen only penetrates a few millimeters into certain river sediments. In their study, reducing conditions would be expected to predominate in any samples encountered. Given the complex redox- and pH-sensitive chemistry of arsenic oxy-anions with iron, aluminum, and calcium, it becomes very difficult to hypothesize a mechanism.

C. River Sediment - Capped Four-inch Cores Maintained in an Inert Atmosphere

Based on concerns that open-air homogenization could have influenced the porewater results, TVA collected additional sediment samples in February 2011 and again in June 2011, carefully protecting them from exposure to the atmosphere during sample collection. At the laboratory, porewater was extracted under an inert atmosphere. Following extraction, the porewater samples were preserved and analyzed for dissolved metals/metalloids and for arsenic and selenium species (selenate, selenite, arsenate, arsenite, total arsenic, total selenium and organic selenium, and organic arsenic calculated by difference). When the inert-atmosphere samples are included in the time series graphs (see Figures 5 and 6), they indicate that either the open-air homogenization solubilizes arsenic species in some way or that natural attenuation proceeds rapidly.

As observed in Table 3, arsenic is present as a mixture of arsenate and arsenite with some organic arsenic indicated on Clinch River samples. The more mobile reduced species, arsenite, predominates in most samples. Selenium, when detected, is also present as the reduced form. This is very similar to the results found by Turner (1981).

Table 3 - Results of Porewater Arsenic and Selenium Speciation (µg/L) - Extracted in Inert Atmosphere

| | Arsenate | Arsenite | Organic Arsenic | Arsenic | Selenate | Selenite | Organic Selenium | Selenium |
|---------|----------|----------|-----------------|---------|----------|----------|------------------|----------|
| CRM_REF | 1.19 | 5.84 | 1.59 | 8.62 | <0.16 | <0.29 | 0.429 | 0.429 |
| ERM4.0 | 5.41 | 7.81 | <1.5 | 12.8 | <0.16 | <0.29 | <0.16 | <0.39 |
| ERM3.0 | 4.07 | 9.12 | <1.5 | 14.6 | <0.16 | <0.29 | <0.16 | <0.39 |
| ERM2.5 | 135 | 654 | <45 | 543 | <0.16 | <0.29 | 0.861 | 0.861 |
| ERM1.0 | 13 | 86.1 | <1.5 | 60.6 | <0.16 | <0.29 | 0.817 | 0.817 |
| ERM0.5 | 48 | 99.2 | <3.0 | 112 | <0.16 | <0.29 | 0.546 | 0.546 |
| CRM4.5 | 5.93 | 11.8 | 1.55 | 19.3 | <0.16 | <0.29 | 0.572 | 0.572 |
| CRM4.0 | 1.63 | 11.8 | 2.38 | 15.8 | <0.16 | <0.29 | 0.571 | 0.571 |
| CRM3.5 | 1.62 | 18.8 | 5.49 | 25.9 | <0.16 | <0.29 | <0.16 | <0.39 |
| CRM3.0 | 11.9 | 57.9 | 5.81 | 75.1 | <0.16 | <0.29 | <0.16 | <0.39 |
| CRM2.5 | 5.52 | 12.9 | 1.96 | 20.4 | <0.16 | 0.356 | <0.16 | 0.574 |
| CRM2.0 | 10.2 | 8.06 | 1.4 | 19.7 | <0.16 | 0.388 | <0.16 | 0.553 |
| CRM1.5 | 3.54 | 7.47 | <0.90 | 11 | <0.16 | <0.29 | <0.16 | <0.39 |
| CRM0.0 | 30.6 | 13.9 | 27.2 | 71 | <0.16 | <0.29 | <0.16 | <3.9 |

After porewater was extracted, the remaining sediment was subjected to a strong hydrochloric acid leach. The leachate was analyzed for arsenic and selenium species. Data are presented in Table 4. Figures 7 through 12 show the concentrations of the various species in porewater and solid phase and for arsenic as

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their relative percentages. It is interesting that organic arsenic is not observed in porewaters in the highest impact zone (ERM 3.0 down to ERM 0.0). This suggests microbial uptake or periphyton uptake is not occurring there, or that there is little organic detritus depositing which might be available for transformation to organic arsenic. However, Clinch River samples do contain some organic arsenic. On the other hand, organic selenium accounts for most of the observed porewater selenium in the Emory River samples. Since there is little relationship between selenium in porewater and percent ash, there may be no sorptive mechanisms for organo-selenium, but good sites for the inorganic arsenite (or mineralization of arsenic species) in the Emory River samples with 40 percent ash being related to the binding capacity of the ash/sediment mixture for arsenic. In addition, selenium concentrations are much lower than arsenic concentrations, so that any inorganic selenium dissolved from the ash quickly gets taken up again by whatever sorptive mechanism is present.

In the solid phase, arsenate can be present in greater concentrations than the more mobile arsenite while selenium is present as selenite and “organic selenium”.

Table 4 - Results of Solid Phase Extraction and Speciation (mg/kg) - Inert Atmosphere

| | Arsenate | Arsenite | Organic Arsenic | Arsenic | Selenate | Selenite | Organic Selenium | Selenium |
|----------------|----------|----------|--------------------|---------|----------|----------|---------------------|----------|
| CRM_REF | 17.4 | 7.19 | <2.6 | 18.9 | <0.31 | <0.39 | <0.31 | <0.47 |
| ERM5.5 | 1.58 | 0.195 | <0.44 | 1.65 | <0.30 | <0.38 | 0.651 | 0.651 |
| ERM4.0 | <2.7 | 4.48 | 4.29 | 9.76 | <0.43 | <0.54 | 1.83 | 1.83 |
| ERM3.0 | 2.71 | 1.59 | <2.1 | 5.82 | <0.31 | <0.39 | 1.12 | 1.12 |
| ERM2.5 | 68.3 | 8.11 | <8.5 | 75.6 | <0.23 | 4.31 | <0.23 | 4.62 |
| ERM1.0 | 12.6 | 12.7 | <24. | 24.9 | <0.44 | 1.1 | 3.04 | 3.06 |
| ERM0.8 | 15.9 | 16.1 | <14. | 28.9 | <0.50 | 0.824 | 2.25 | 3.07 |
| ERM0.5 | 20.9 | 5.53 | <11. | 20.9 | <0.27 | 1.09 | 2.24 | 3.34 |
| CRM4.5 | 8.86 | 5.59 | <2.9 | 14 | <0.29 | <0.50 | 1.34 | 1.83 |
| CRM4.0 | 12.9 | 9.06 | <3.2 | 17.6 | <0.41 | <1.0 | 1.34 | 2.37 |
| CRM3.5 | 10.3 | 11.4 | <3.0 | 22.5 | <0.38 | <0.90 | 2 | 2.9 |
| CRM3.0 | 16.1 | 14.6 | <3.9 | 25.8 | <0.43 | <0.94 | 2.07 | 3.01 |
| CRM2.5 | 8.69 | 10.1 | <3.3 | 20.2 | <0.36 | <1.2 | 1.37 | 2.54 |
| CRM2.0 | 21.3 | 2.74 | <2.6 | 21.4 | <0.28 | <0.62 | 1.38 | 1.99 |
| CRM1.5 | 7.82 | 3.78 | <1.7 | 12.4 | <0.36 | <0.81 | <0.36 | 1.33 |
| CRM0.0 | 10.4 | 14 | 3.77 | 28.2 | <0.51 | <1.1 | 2.03 | 3.13 |

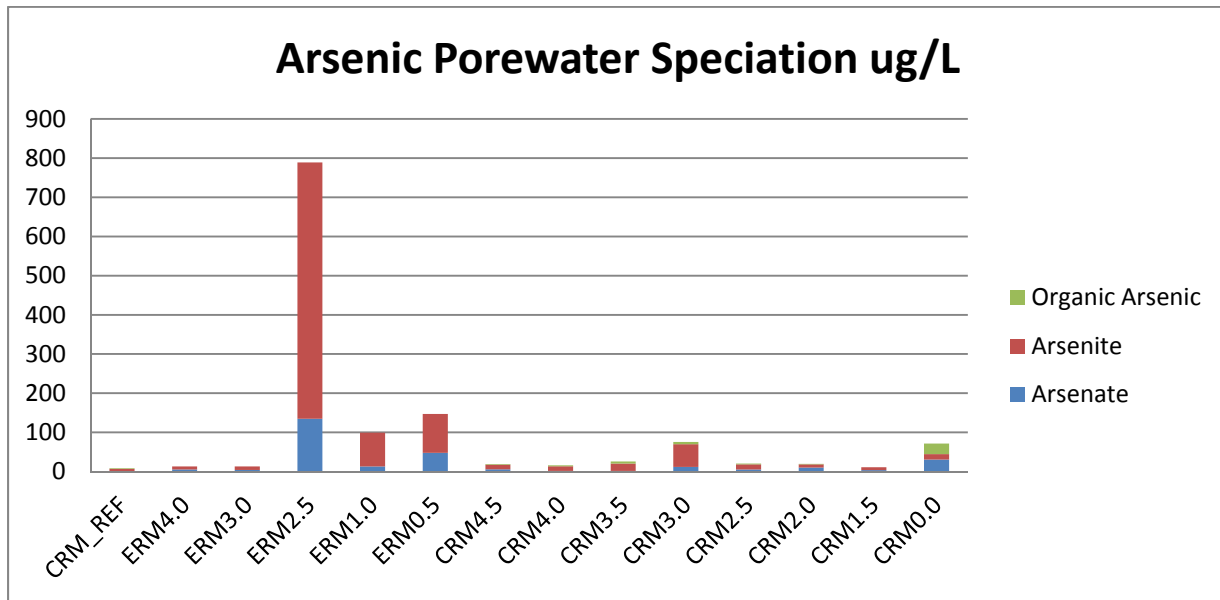


Figure 7 - Arsenic Speciation in Porewater

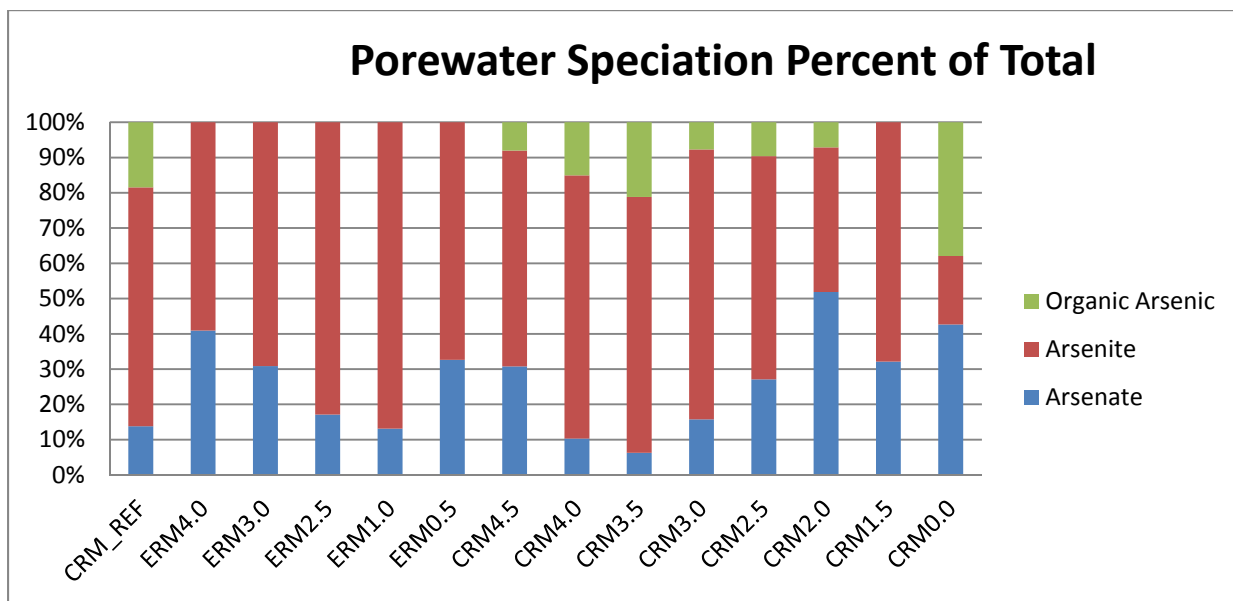


Figure 8 - Arsenic Speciation in Porewater (Percentages)

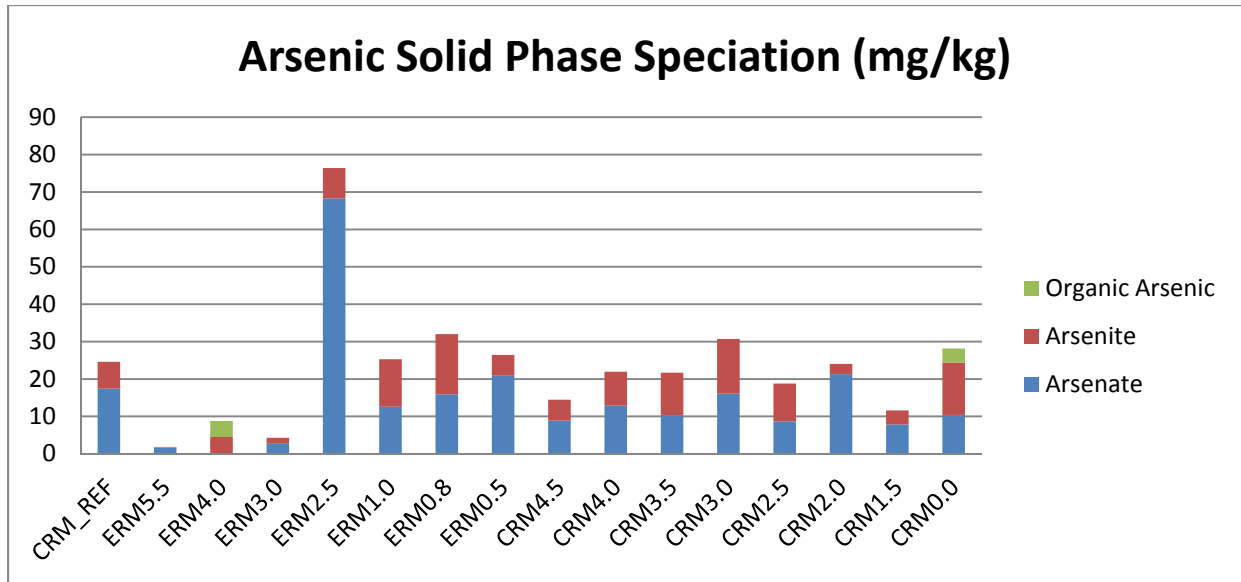


Figure 9 - Arsenic Speciation in Solid Phase

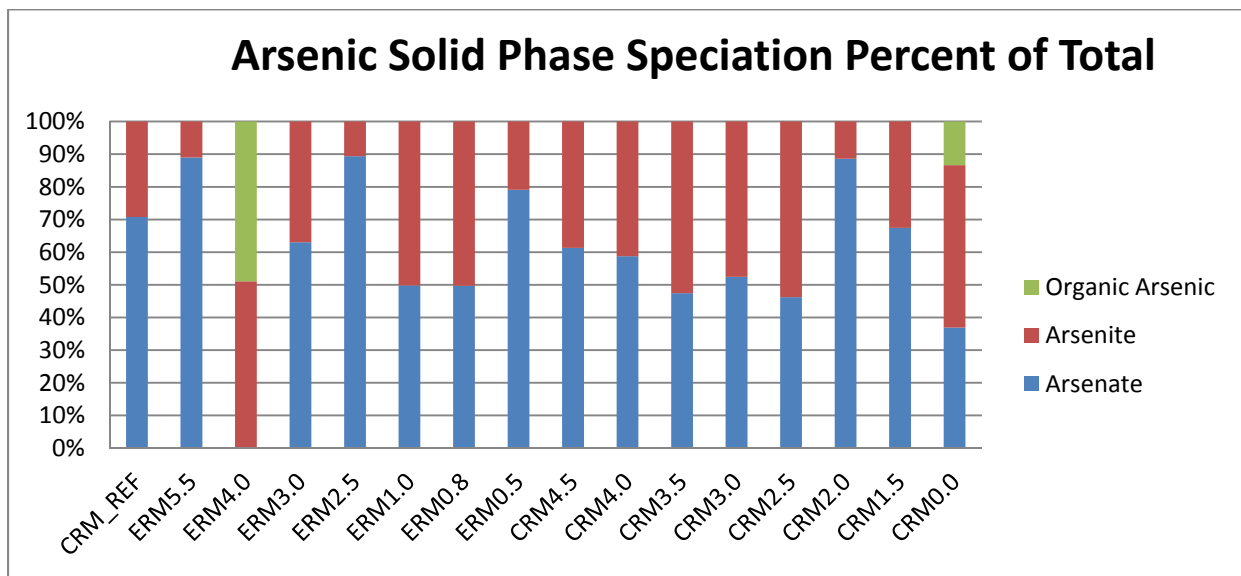


Figure 10 - Arsenic Speciation in Solid Phase (Percentages)

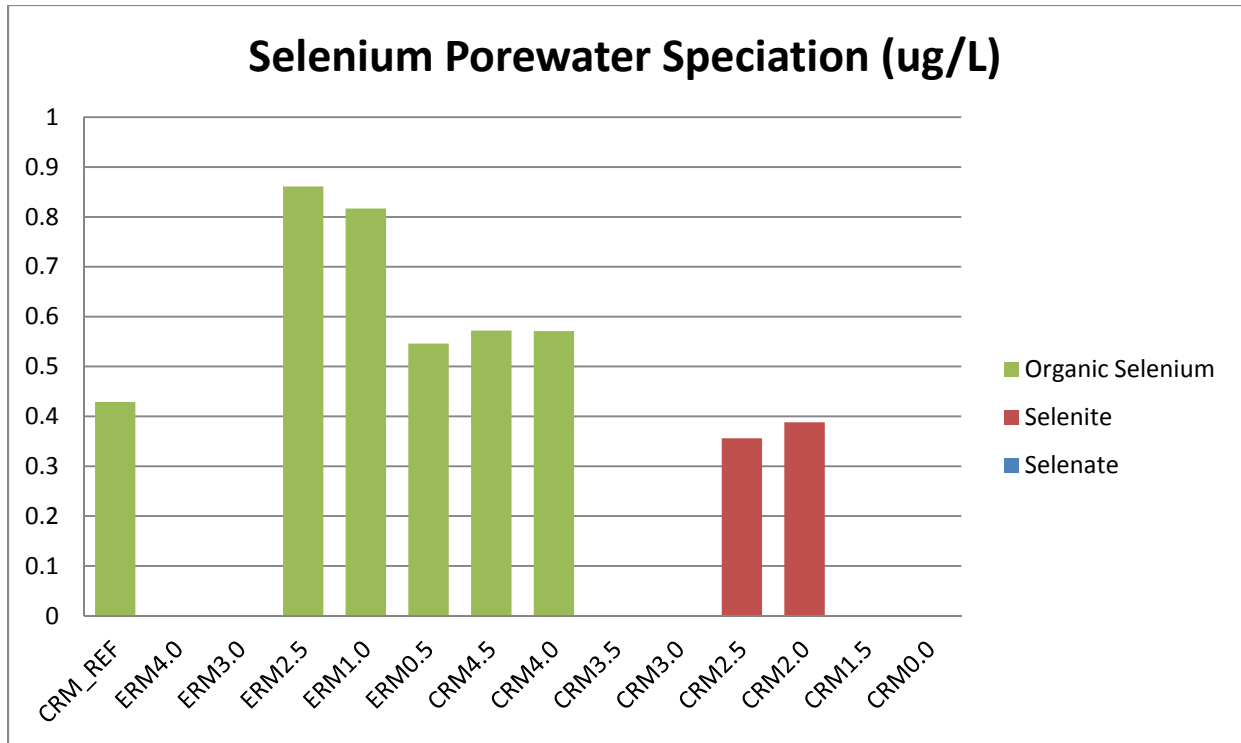


Figure 11 - Selenium Speciation in Porewater

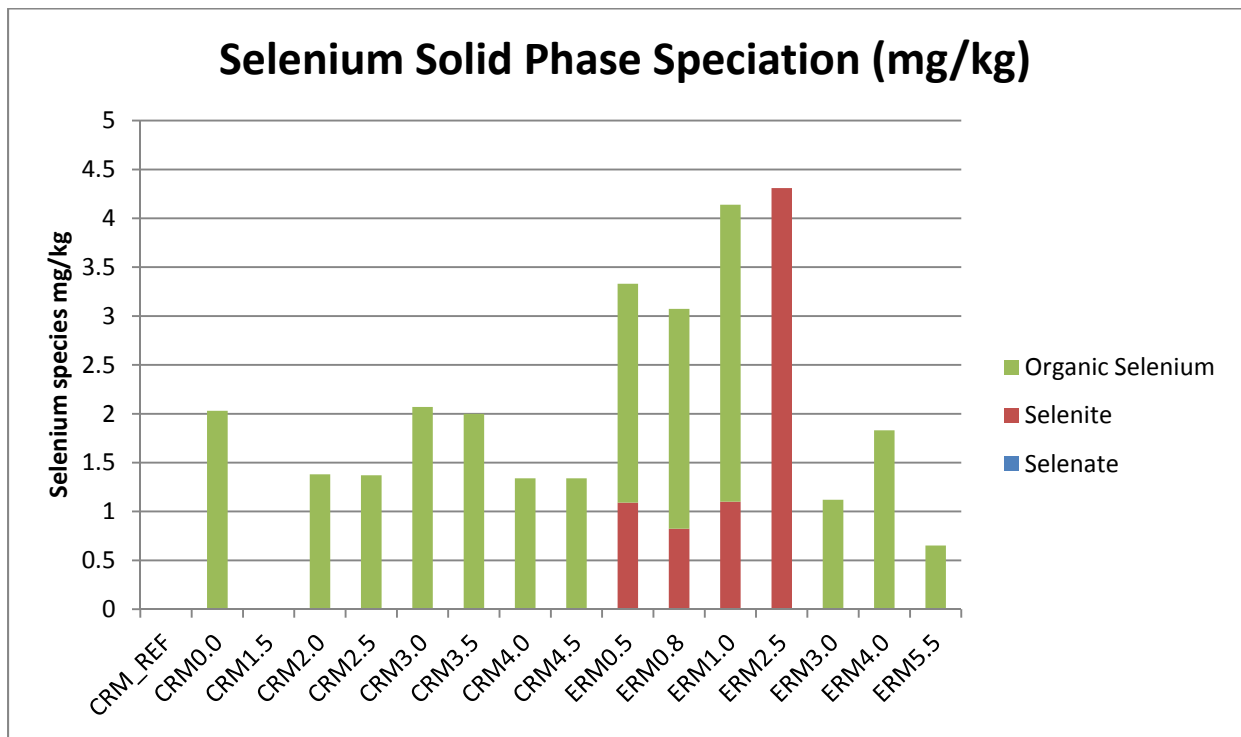


Figure 12 - Selenium Speciation in Solid Phase

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IV. DISCUSSION / CONCLUSIONS

On the basis of the multiple, albeit limited, sampling trials for the sediment and porewater collection activities, it appears that exposure of sediments to the atmosphere during sampling and processing may introduce a confounding and substantially positive bias for arsenic concentrations. When sampling porewater in sediment, care should be taken to preserve the sediments and extract the porewater in an inert atmosphere. Whatever the confounding effect, a clear time series for arsenic is difficult to observe, and data shown here may indicate the maximum concentration in porewater has passed.

Selenium in porewater never appeared to differ markedly from the surrounding sediment. Selenite seems to predominate in the porewater, and a mixture of selenite and organic selenium is found in the solid phase.

Arsenic exists largely as the mobile arsenite in the porewater while the more insoluble arsenate appears to predominate in the solid phase.

Given the rapid solubility of boron and strontium discussed above, it would appear that after two years, porewater concentrations of these species do not remain a good tracer for the presence of ash in disturbed surface sediments.

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