

Evolution of Dissolved Arsenic in Groundwater Downgradient of a Coal Ash Impoundment

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ABSTRACT

An investigation was performed to evaluate the origin and evolution of dissolved arsenic concentrations beneath and downgradient of a coal ash impoundment. More than 500 sediment, ash, groundwater, and leachate samples were collected and analyzed for arsenic and other parameters. Samples were collected along twelve background and downgradient transects. These samples were collected from monitoring wells near the impoundment, and using direct-push methods downgradient of the impoundment and in background locations. In addition, direct-push vertical profile samples were collected at selected locations, including the edge of a lake immediately downgradient of the impoundments.

Total arsenic concentrations in the sediments were within regional ranges, which reflect historic arsenic contamination in this region; however, there was no apparent correlation between sediment concentrations and groundwater concentrations. Dissolved arsenic in the ash leachate was predominantly the less-mobile arsenate species, while dissolved arsenic in groundwater was predominantly the more-mobile arsenite species. Dissolved arsenic concentrations downgradient of the impoundment varied by distance from the impoundment and by depth, and did not correlate with the distribution of ash indicator parameters. These observations, combined with measurements of redox indicator parameters, led to the determination that arsenic concentrations in downgradient groundwater decrease and increase as the water passes through specific redox zones, with much of the arsenic precipitating or coprecipitating as groundwater discharges to surface water. Concentrations in sediment porewater are relatively high beyond the zone of active groundwater flow, where groundwater is stagnant and a methanogenic zone has developed.

INTRODUCTION

Elevated arsenic concentrations in groundwater downgradient of two coal ash impoundments prompted an investigation into the origin and evolution of this arsenic as it migrates toward a lake. This presentation focuses on the geochemical results of a larger investigation that was performed under a regulatory context.

Site History and Setting

The power plant and impoundments are located next to a large river, where it discharges into a lake (Figure 1). Impoundment A covers an area of more than 150 acres, and was constructed in the early 1950's by building dikes from the shoreline into the lake to enclose a portion of the shallow submerged lake bottom, which had been deeded by the State to the company. The dikes were built using native soils, mostly composed of clay and silty clay. Impoundment B covers an area of more than 200 acres, and was constructed in stages over former lake bottom and adjacent marshland. Filling operations began in 1940. The currently active cell at Impoundment B was constructed in the early 1970's.

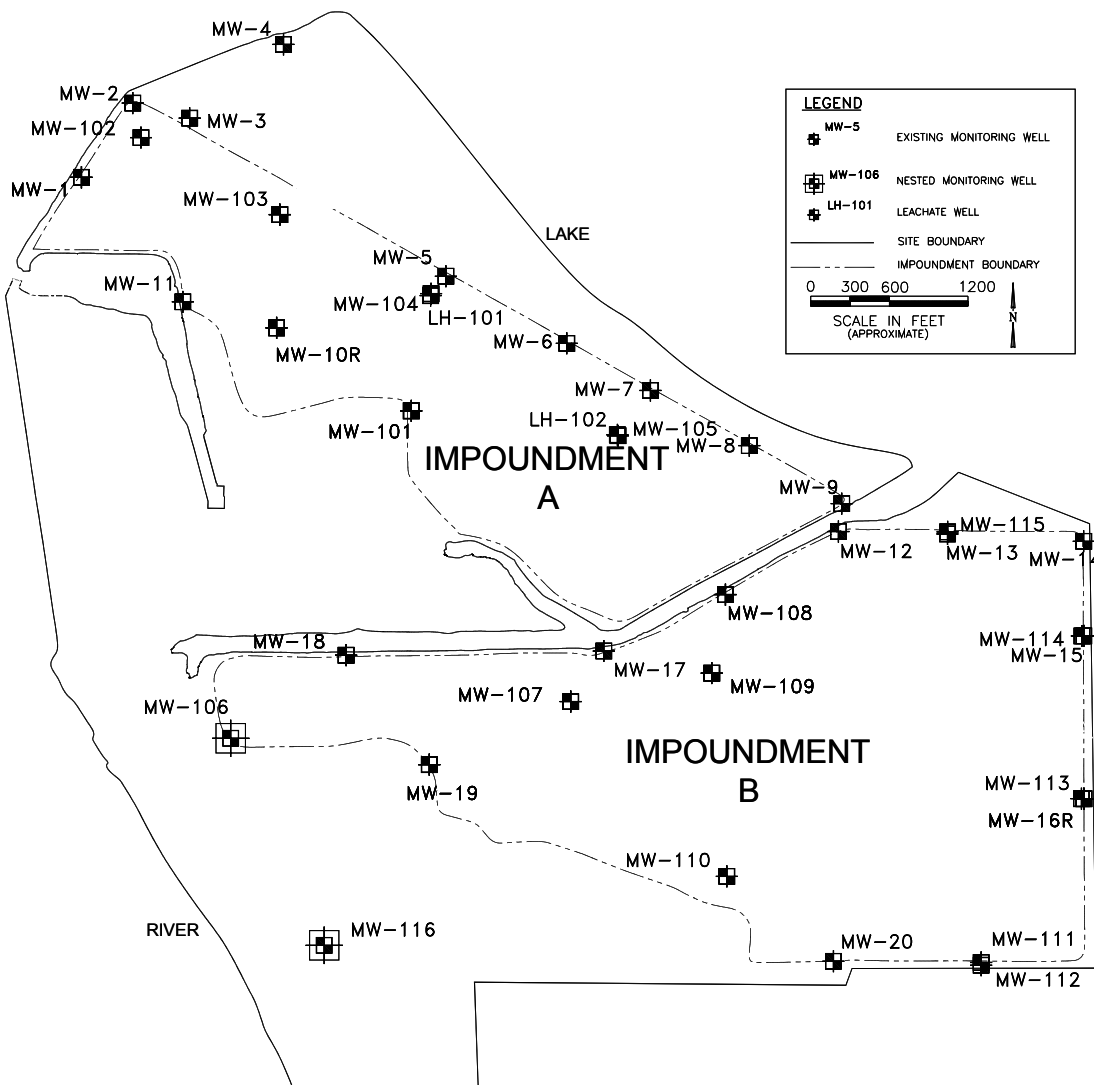


Figure 1. Site Map

The generating units associated with these impoundments burned bituminous coal until 2002, when all units were switched to a bituminous/subbituminous blend. Electrostatic precipitators are used to remove fly ash from the flue gas. Collected fly ash and bottom ash are hydraulically transported (sluiced) to the impoundments.

The site is located in an area that has been industrialized for the last century. Discharges from multiple upstream sources have resulted in contamination of river and lake bottom sediments with organic and inorganic constituents, including arsenic. High concentrations of total arsenic have been recorded in the river sediments upstream of the plant and in lake sediments.

Surficial geologic units at the site include alluvium near the river, and alluvial fan deposits along the former lake shore. The surficial units are underlain by a clay-rich diamicton unit that is more than 50 feet thick beneath the impoundments. Groundwater monitoring is performed in the sand-rich alluvial fan deposits that underlie much of the impoundment areas. The sand deposits range in thickness from 3 feet distant from the river to more than 30 feet next to the river, and are 6 to 10 feet thick throughout most of the study area.

Groundwater monitoring was historically performed at 20 locations around the two impoundments. Arsenic concentrations have varied both areally and temporally (Figure 2). Concentrations tend to be relatively low (~5 to 30 µg/L) near the river (MW1, MW2, and MW3), and have been as high as 1,200 µg/L in other locations. Twelve of the 20 monitoring wells have yielded groundwater samples with arsenic concentrations exceeding 100 µg/L on multiple occasions.

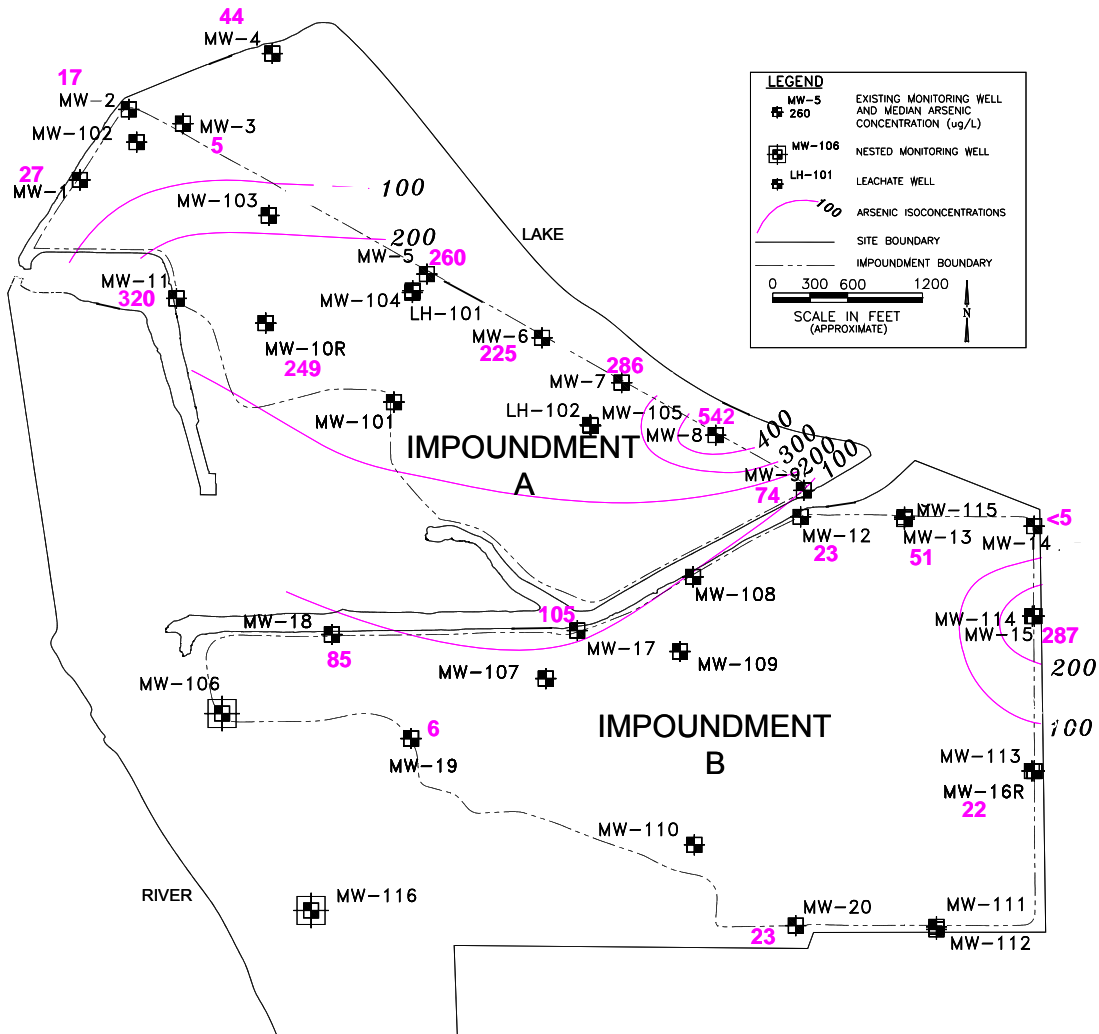


Figure 2. Median Arsenic Concentrations in Site Monitoring Wells

A Literature-Based Model of the Relationship between Arsenic Concentrations in Groundwater and Redox Zones

Arsenic concentrations in natural groundwater are typically lower than 10 µg/L; although relatively high concentrations can be found under certain conditions, notably when pH is high under oxidizing environments and under strongly reducing environments.^[1] Furthermore, high-profile cases (e.g., the Bengal Basin) of groundwater with high arsenic concentrations can be associated with reducing conditions, particularly in deltaic and alluvial environments.^[1] Cases of naturally-occurring elevated arsenic concentrations in groundwater, associated with strong reducing conditions, have also been documented in the United States.^[2]

Figure 3 illustrates the conceptual relationship of arsenic, sulfate, ferrous iron (Fe^{2+}), and methane concentrations under the redox regimes that may occur in a deltaic environment similar to that found at the impoundments.

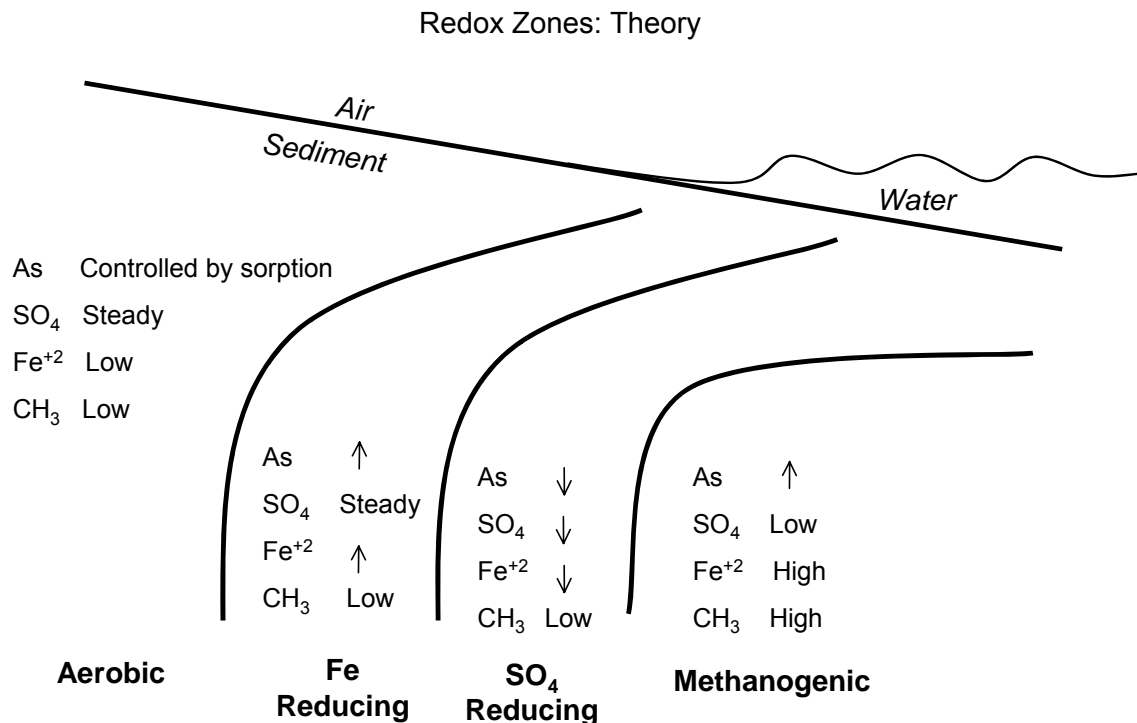


Figure 3. Effect of Redox Zones on Arsenic Concentration in Groundwater

- Under oxic or aerobic conditions, arsenic concentration is controlled by sorption, which is pH-dependent, sulfate concentration is based on natural and anthropogenic sources, Fe²⁺ concentrations are low because iron is in the oxidized ferric iron (solid) state, and methane concentrations are very low.
- As oxygen is depleted, nitrate reducing and then manganese reducing zones develop; however, these zones have negligible effect on the constituents of interest to this investigation and are not illustrated in Figure 3.
- When nitrate and manganese oxides are depleted, an iron reducing zone develops where dissolved iron concentrations (mostly Fe⁺²) increase as iron oxides are consumed. Arsenic bound to the iron oxides is also released to solution during this reaction and dissolved arsenic concentrations in groundwater increase. The iron-reducing bacteria that predominate in this redox zone are also present in the sulfate reducing and methanogenic zones, resulting in continued release of dissolved arsenic from iron oxides; however, as noted below, arsenic concentrations increase only if allowed to accumulate.^[2] Sulfate concentrations are not affected, and methane concentrations remain low in the iron reducing zone.

- As reducing conditions become stronger, a sulfate reducing zone develops, where sulfate is reduced to sulfide, which precipitates with Fe^{2+} to form iron sulfide, decreasing Fe^{+2} concentrations. Arsenic concentrations decrease in sulfate reducing zones due to precipitation with sulfide species or coprecipitation with other sulfide minerals.^[2]
- After sulfate is depleted, a methanogenic zone develops where sulfate concentrations are very low and methane accumulates. Because sulfide is not being produced, Fe^{2+} also accumulates and high concentrations are typical. In addition, because sulfide minerals are not precipitating, arsenic does not precipitate or coprecipitate, and dissolved arsenic accumulates, resulting in relatively high concentrations.^[2]

The model above is highly simplified, and it is possible that individual zones may not always be present or may overlap. For example, if ferric minerals are limited, then the rate of iron reduction may be slowed to the point that iron and sulfate reduction proceed at the same time.^[2] Furthermore, these zones may occur in a highly compressed, reverse order as groundwater discharges to surface water. In this case, dissolved iron precipitates as oxic conditions are encountered near the sediment interface, and arsenic is adsorbed to or coprecipitates with the iron.

Objective

The portion of the investigation described here was performed to evaluate the relationship of the high arsenic concentrations in groundwater beneath the impoundments to the coal ash leachate, historic sediment contamination, and the local redox environment.

INVESTIGATION

Twelve sampling transects were established: three background transects, six transects at Impoundment A, and three at Impoundment B (Figure 4). The impoundment transects extended as much as 500 feet from the toe of the dikes out into the lake. Sediment samples and water samples were obtained at 100-foot intervals, beginning at the toe of the dike. Sediment samples were collected once and water samples were collected three times over a 13-month period.

Sediment samples were obtained near the surface and the base of the sand unit at dry locations along the transects and analyzed for total composition. Groundwater samples were obtained from multiple depths within the sand at locations along the transects that were either dry or submerged under shallow water. Surface water samples were collected as close to the sediment interface as possible at submerged locations. Vertical profile samples, consisting of five water samples at depths ranging from the base of the sand to the surficial six inches, were obtained at the water's edge. Groundwater samples along the transects were collected using hand-driven direct-push methods.

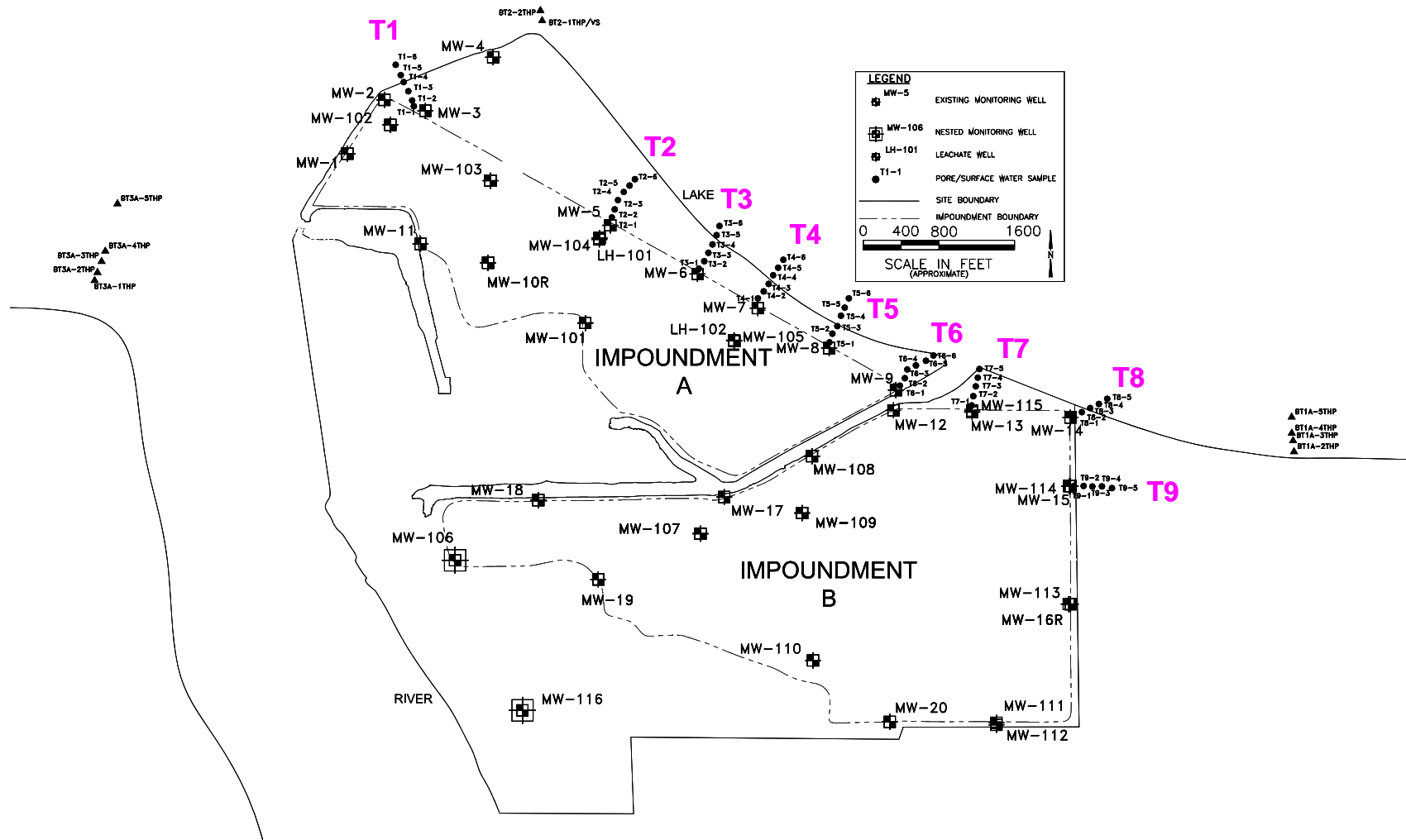


Figure 4. Sampling Transects

In addition, two leachate monitoring wells were installed and sampled, and existing monitoring wells that were located on the impoundment dikes were sampled if they were in line with the transects.

In total, more than 500 sediment and water samples were collected and analyzed. Key constituents analyzed during this investigation were arsenic, which historically had concentrations greater than 1,000 µg/L in some site monitoring wells, boron, and sulfate. Boron and sulfate are often indicator parameters for coal ash leachate; however, sulfate proved to be a poor indicator at this site because it is reduced to sulfide in many locations and concentrations were often below detection limits. Boron is non-reactive and is highly mobile in sand, and was the key site-specific indicator parameter for delineating the zone of influence of coal ash leachate.

RESULTS AND DISCUSSION

Sediment Samples

Total arsenic concentrations in the downgradient sediment samples were consistent with those from the background samples (mostly lower than 5 mg/kg). Overall, concentrations were lower than the average total arsenic concentration compiled by other researchers for the entire lake bottom.

Water Samples

The median dissolved boron concentration in background groundwater was 80 µg/L. Background boron concentrations were fairly consistent between 30 and 130 µg/L. Sulfate concentrations in background groundwater ranged from non-detect (<500 µg/L) to 155,000 µg/L, with a median concentration below detection limits. In contrast, the median background concentration of sulfate in surface water samples was 44,000 µg/L.

Arsenic, boron, and sulfate concentrations in lake water samples taken at the far (downgradient) ends of the transects were essentially the same as background lake water samples. The remainder of this discussion focuses on groundwater samples.

Boron concentrations indicated that the ash leachate plume extended 100 to 500 feet beyond the dikes. This distance fluctuated by about 100 feet at some transects over the three sample events. The ash leachate plume delineates the zone of active groundwater flow in the thin sand unit. Methanogenic conditions were typically found beyond the extent of the ash leachate plume.

Data from most transects at the two impoundments suggested two separate zones of elevated dissolved arsenic concentration. The first zone (iron reducing) occurred beneath the impoundment and dikes, where arsenic can be released to groundwater as iron oxide minerals are dissolved. Concentrations within the iron-reducing zone were greater than 1,000 µg/L at some sample points. Concentrations then decreased in a sulfate reducing zone as arsenic precipitated with sulfide or coprecipitated with other

sulfide minerals. The second zone of increased arsenic concentrations was the methanogenic zone. Dissolved arsenic concentrations as high as 500 µg/L were observed in the methanogenic zone. Because the high dissolved arsenic concentrations in the methanogenic zone occurred in areas beyond the extent of the ash leachate plume, these concentrations were not attributed to migration of ash leachate, nor could they be attributed to diffusion from the leachate plume since arsenic concentrations at the lakeward edge of the plume were typically lower than those in the methanogenic zone. Three specific examples from Impoundment A, and one from Impoundment B are provided below to illustrate this sequence.

Transect T3, Impoundment A

During both sample events, dissolved arsenic concentrations were greater than 200 µg/L beneath and near the dike, then decreased to less than 100 µg/L before increasing to more than 200 µg/L at the end points of the transect (Figure 5).

Boron concentrations decreased to near background concentrations at T3-3 in 2003 and T3-4 in 2004, and remained low to the end of the transect, while arsenic concentration increased in the groundwater samples at the end of the transect. Because boron is non-reactive, and only minimally sorbs in sand formations, the low concentrations at the far end of the transect indicated that groundwater carrying coal ash leachate had not migrated to that point. This area appears to be a stagnation zone where hydraulic head in the sand is the same as the lake level. These observations suggest that arsenic concentrations are increasing beyond the limits of the ash leachate plume due to bacterially-mediated reactions with the sediment.

Sulfate concentrations decreased to non-detect levels by T3-4, indicating that sulfate reduction had occurred. The decreasing dissolved arsenic concentrations in the middle of the transect were then due to reactions with iron sulfide minerals forming in this zone. As the sulfate is depleted, iron sulfide is no-longer formed, and arsenic accumulates in the methanogenic zone at T3-4 and beyond.

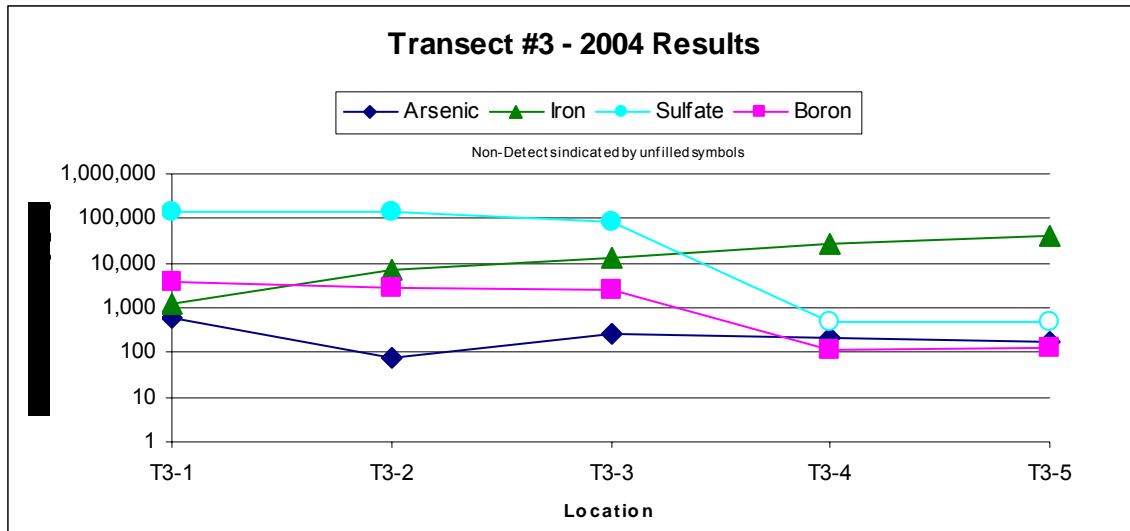


Figure 5. Dissolved Arsenic, Iron, Sulfate, and Boron Concentrations at Transect T3. All samples were collected outside of the dike.

Transect T4, Impoundment A

In 2003 and 2004, dissolved arsenic concentrations were greater than 200 µg/L inside and beneath the dike, decreased at T4-2, and then increased to more than 300 µg/L in the farthest groundwater sample of the transect (Figure 6). The pattern of increasing arsenic concentration with distance was similar in 2005, except that the lowest arsenic concentration was observed at T4-1 rather than at T4-2.

Boron concentrations for all three sample events decreased to near-background concentrations at T4-3, indicating the extent of the ash leachate plume. Similar to transect T3, dissolved arsenic concentrations increased significantly beyond the limits of the ash leachate plume, indicating a bacterially-mediated sediment source rather than transport from the ash impoundment.

Sulfate concentrations decreased to levels lower than background at T4-4, while iron concentrations increased. These relationships indicated that a methanogenic zone exists beyond this point where iron sulfides cannot form, and arsenic concentrations are not controlled by reactions with the iron sulfide. Methane concentrations were measured along this transect in 2005, and concentrations increased sharply beginning at T4-3, confirming that a methanogenic zone existed in groundwater at the far end of the transect.

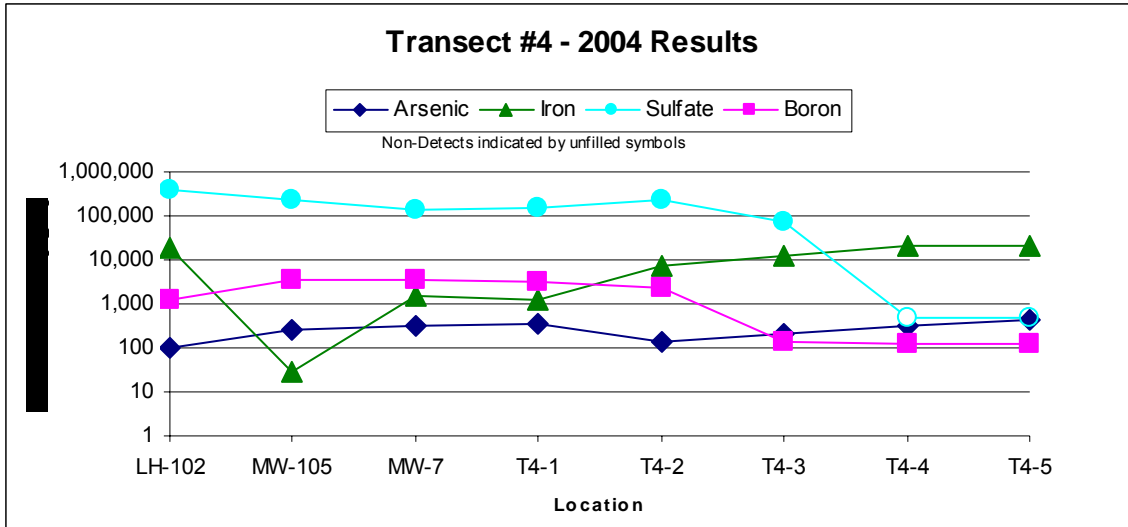


Figure 6. Dissolved Arsenic, Iron, Sulfate, and Boron Concentrations at Transect T4. Note that LH-102 is screened in coal ash, MW-105 is nested with LH-102 and is screened in the sand unit inside the dike, MW-7 is screened in sand beneath the dike, and the T4 samples were collected outside the dike.

Transect T6, Impoundment A

Dissolved arsenic concentrations in groundwater were relatively low, less than 100 µg/L, at the sample points nearest to the impoundment, and exceeded 100 µg/L at the far end of the transect (Figure 7).

Boron concentrations were higher than background, although low compared to the other Impoundment A transects, through T6-2 in 2003 and T6-3 in 2004. Boron concentrations decreased to background levels between these points and the end of the transect.

Abundant sulfate concentrations and increasing iron concentrations from T6-1 through T6-3 suggested an iron reducing zone, enabling dissolution of arsenic. Low sulfate concentrations and decreasing iron concentrations from T6-4 through T6-6 in 2003 suggested a well-defined sulfate reducing zone, and arsenic concentrations were at background levels in these samples. In 2004, the sulfate-reducing zone was not evident, and non-detectable sulfate concentrations indicated the presence of a methanogenic zone. Correspondingly, arsenic concentrations accumulated over the far points of this transect in 2004.

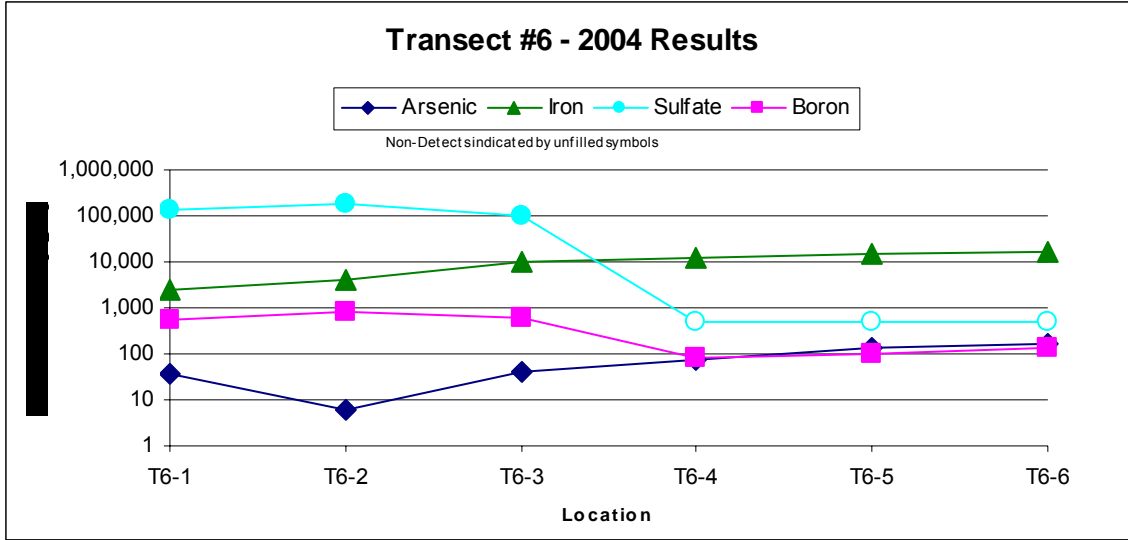


Figure 7. Dissolved Arsenic, Iron, Sulfate, and Boron Concentrations at Transect T6. All samples were collected outside of the dike.

Transect T8, Impoundment B

Moderate iron concentrations and slightly decreasing sulfate concentrations at T8-1 and T8-2 indicated that the limited concentrations of arsenic migrating from beneath the dike were removed from solution in the sulfate reducing zone (Figure 8). Non-detectable sulfate concentrations at T8-3 and beyond indicated the presence of a methanogenic zone, and associated accumulation of arsenic and iron.

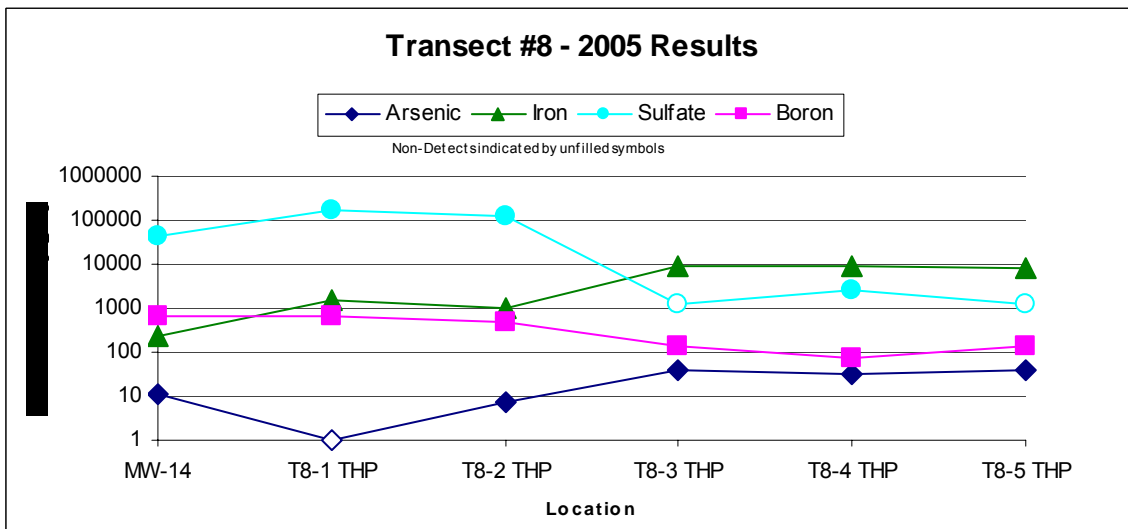


Figure 8. Dissolved Arsenic, Iron, Sulfate, and Boron Concentrations at Transect T8. MW-14 was collected from the sand unit beneath the dike, the other samples were collected outside of the dike.

Vertical Profiles of Arsenic Concentrations at Water's Edge

Vertical profile sampling consistently demonstrated decreasing arsenic concentrations with decreasing depth in samples taken at the water's edge (Figure 9), while boron concentrations showed no trend with depth. These samples were typically obtained at points along the transect interpreted to be within the sulfate reducing zone, where, as noted previously, arsenic precipitates and coprecipitates with iron sulfides. As a result, dissolved arsenic concentrations in the shallow samples at most vertical profile locations were less than 50 $\mu\text{g/L}$.

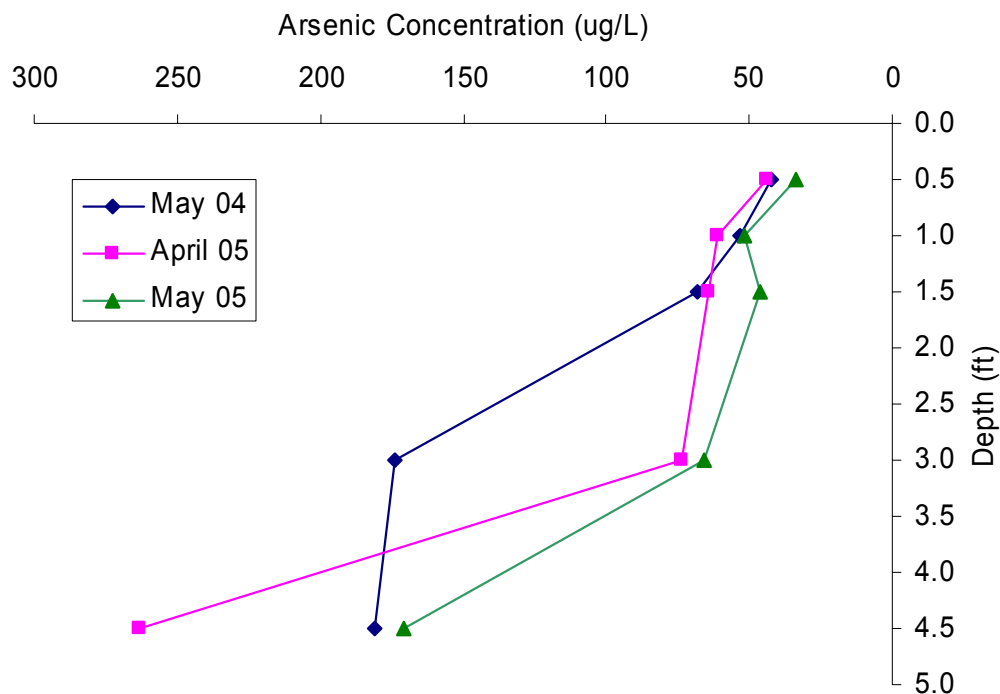


Figure 9. Dissolved Arsenic Concentrations in Three Vertical Profile Samples along Transect T4. The samples were collected at the water's edge during three different events, and because lake levels were variable, each sample was collected at a different location along the transect.

Arsenic Speciation

Speciation was performed on a surface water sample from the impoundment, and selected leachate and groundwater samples collected along transects T2, T4, and T5. Results indicated that surface water in the impoundment had abundant dissolved oxygen and relatively high ORP, indicative of oxidizing conditions. Correspondingly,

arsenic concentration in the surface water sample was dominated by the oxidized species, arsenate [As(V)] (Figure 10).

Dissolved oxygen concentrations were lower in the ash leachate samples than in the pond water, although ORP values were still relatively high, and arsenic was still dominated by the arsenate species. Arsenic concentrations in the ash leachate were higher than in the pond due to leaching as water percolated through the ash column.

Groundwater in the sand unit immediately beneath the ash had similar dissolved oxygen and ORP levels as the ash leachate, and arsenic concentrations in the groundwater were higher than in the ash leachate. The reduced species was dominant along one transect, and the oxidized species along the other.

By the time groundwater migrated to the dikes, the dissolved oxygen was mostly depleted and ORP levels were low, indicative of reducing conditions. Correspondingly, arsenic concentrations were dominated by arsenite [As(III)], although the water also contained significant amounts of As(V). Reducing conditions and arsenite dominance were also observed in samples obtained from the sand unit outside of the dike. The persistence of reducing conditions suggested little mixing with oxidized surface waters.

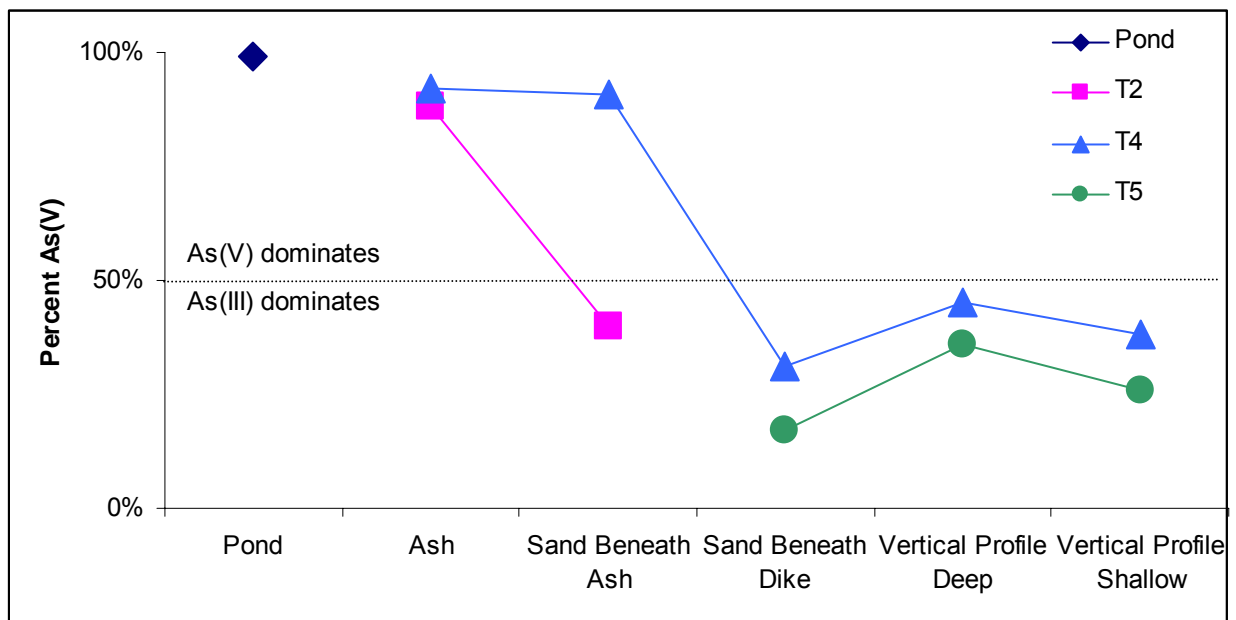


Figure 10. Plot Showing the Dominant Arsenic Species Along the Flow Path of Three Transects.

CONCLUSIONS

Sampling and analysis of sediment and water samples for arsenic, coal ash leachate indicator parameters, and redox indicator parameters yielded the following observations:

- Total arsenic concentrations in the sediments were within regional ranges, which reflect historic arsenic contamination in this region; however, there was no apparent correlation between sediment concentrations and groundwater concentrations.
- Dissolved arsenic in the ash leachate was predominantly the less-mobile arsenate species, while dissolved arsenic in groundwater was predominantly the more-mobile arsenite species.
- The zone of active groundwater flow, as indicated by higher-than-background ash indicator concentrations, extended 100 to 500 feet beyond the impoundment dikes.
- Dissolved arsenic concentrations downgradient of the impoundment varied by distance from the impoundment and by depth, and high concentrations extended beyond the limits of the ash leachate plume and zone of active groundwater flow.

These observations, combined with measurements of redox indicator parameters, led to the determination that arsenic concentrations in downgradient groundwater decrease and increase as the water passes through specific redox zones, with much of the arsenic precipitating or coprecipitating as groundwater discharges to surface water. Arsenic concentrations in sediment porewater are relatively high beyond the zone of active groundwater flow, where groundwater is stagnant and a methanogenic zone has developed.

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