

# Trace Element Partitioning in Ground Water at an Abandoned Mine-Land Site Reclaimed with Coal Combustion Products

**Tracy D. Branam<sup>1</sup>, Ronald T. Smith<sup>1</sup>, Margaret V. Ennis<sup>1</sup>, James P. Rybarczyk<sup>2</sup>, and John B. Comer<sup>1</sup>**

<sup>1</sup>Indiana Geological Survey, 611 North Walnut Grove, Bloomington, IN 47405;

<sup>2</sup>Department of Chemistry, Ball State University, Muncie, IN 47306

KEYWORDS: coal combustion products, trace elements, water quality

## ABSTRACT

In Pike County, Indiana, an abandoned mine-land site generating acid-mine drainage was reclaimed using coal-combustion products as fill and cap material. Concentrations of several trace elements were monitored in ground water on a quarterly basis over a period of four years. Pre-reclamation monitoring established that the trace elements arsenic, cadmium, chromium, copper, lead, nickel, and zinc occurred in higher concentrations in acidic waters (pH < 4) than in waters more nearly neutral. The trace element boron occurred in low concentrations (<1 mg/L) throughout the study area while barium, mercury, and molybdenum were at or below detection limits in all water samples.

Only arsenic, boron, and molybdenum increased in concentration after reclamation.

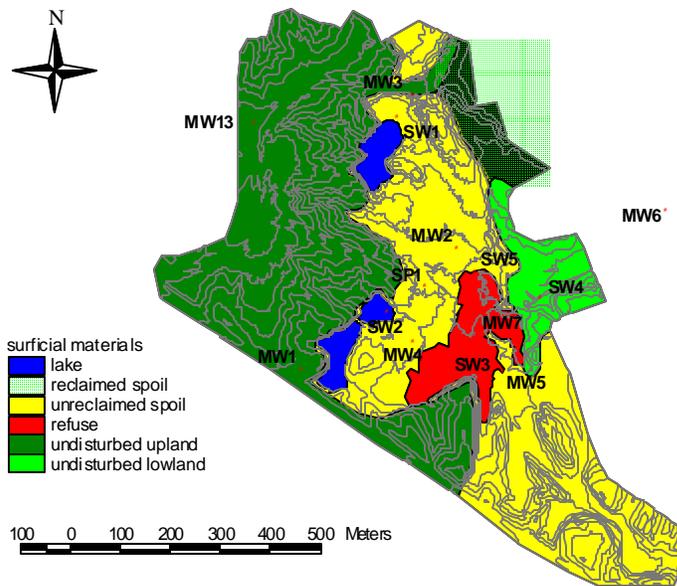
Arsenic levels remain highest in acidic ground water, but also occur above pre-reclamation levels in some monitoring wells in close proximity to coal-combustion products. The highest boron and molybdenum levels occur in wells screened in fill material close to a fixated scrubber sludge cap. High concentrations of iron limit molybdenum solubility due to co-precipitation, inhibiting dispersion of molybdenum through the ground water. Boron mobility does not appear to be constrained like molybdenum and is more widely dispersed in ground water.

## INTRODUCTION

The use of coal-combustion products (CCPs) to reclaim abandoned mine-lands is a relatively new activity in the state of Indiana. Persistent concerns about impacts on the southwestern Indiana environment warranted a closely monitored demonstration project. The demonstration

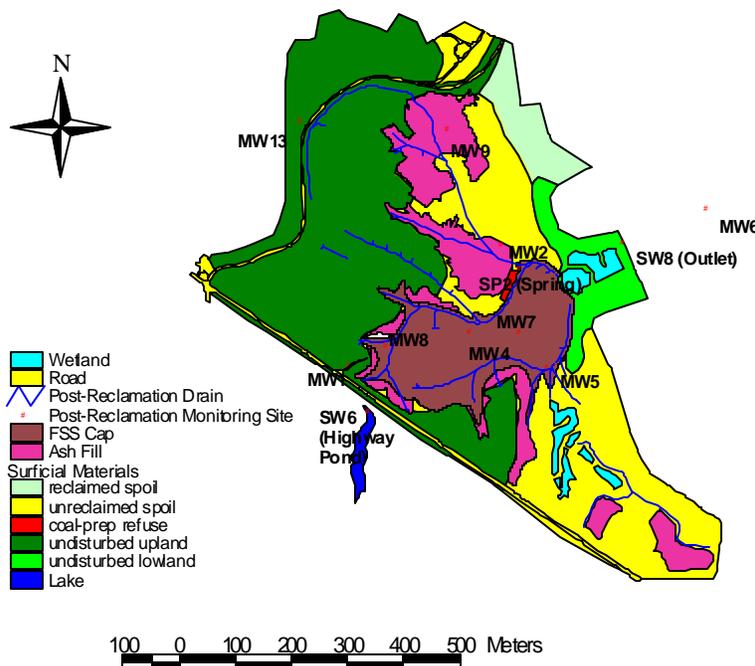


**Figure 1. Map of Indiana showing location of study area in Pike County.**



**Figure 2. Pre-reclamation surficial materials and monitoring sites.** Modified from map provided by ATEC Associates, Inc.

with fly ash and lime, called fixated scrubber sludge (FSS), was used as a capping material<sup>1</sup>.



**Figure 3. Post-reclamation distribution of coal combustion products and monitoring sites.** Modified from map provided by ATEC Associates, Inc.

reclamation at locations that documented the effects of CCP leaching on water quality at

documented the effects of CCPs on water quality at the Midwestern Site in Pike County (Figure 1). Acidic, metal-rich runoff had prevented vegetation and contributed to uncontrolled erosion and deep gulying at this site. Reclamation was designed to reduce acidity and re-establish vegetation to minimize erosion. The absence of low-permeability soil in the study area and the close proximity to a coal-powered generating station afforded the opportunity to use CCPs in reclaiming the site. A blend of bottom ash and fly ash, called ponded ash, was used as fill material, and a mixture of flue-gas desulfurization sludge filter cake

Pre-reclamation conditions in the study area have been described in previous reports<sup>1,2</sup>. Highwall lakes and a coal-processing refuse deposit (Figure 2) were the major sources contributing trace elements to ground water. Bryenton and Gasper<sup>1</sup> described reclamation plans intended to reduce acid and trace element concentrations by filling the high-wall lakes with ponded ash, and capping a large portion of the central area with FSS (Figure 3).

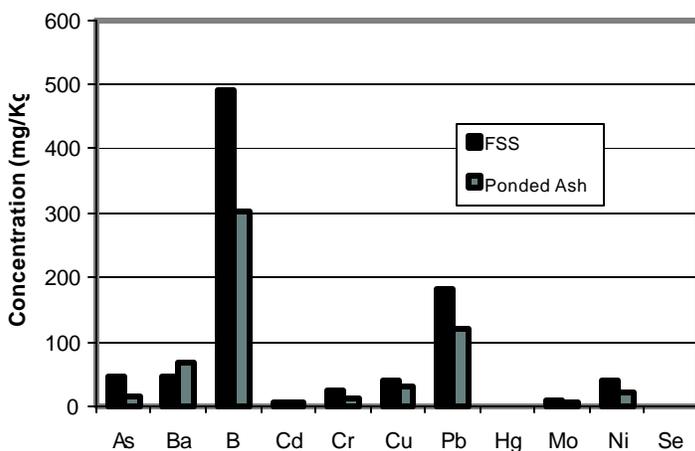
Inorganic parameters in the ground water were monitored before and after

the site (*Figures 2 and 3*). The water-quality monitoring program was designed and implemented by the Indiana Geological Survey (IGS)<sup>2</sup> in April 1995 and reclamation construction commenced in the fall of 1995. Water-quality monitoring continued at the periphery of the site during the construction phase. In the fall of 1996, monitoring sites were re-established within the project area and post-reclamation monitoring continued through January of 1999. Post-reclamation monitoring sites were either the same as those used during pre-reclamation monitoring or were located as close as possible to pre-reclamation sites that were destroyed during construction (*Figure 3*). *Table 1* lists the depth and material in which each well was screened for both pre- and post-reclamation monitoring. Branam *et al*<sup>3</sup> described the sampling procedures and parameters analyzed. The success of the project in reducing acid runoff and altering recharge patterns has been reported elsewhere<sup>3,4</sup>. The purpose of this paper is to document changes in trace element concentrations in ground water at the site and to determine if CCPs are a source.

## RESULTS

### *Laboratory Studies*

ATEC Associates analyzed the CCP materials used to produce FSS and ponded ash for



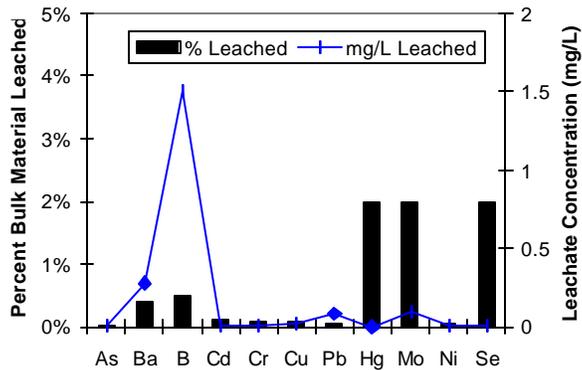
**Figure 4. Concentrations of trace elements in fixated scrubber sludge and ponded ash.**

major inorganic components and selected trace elements and conducted standard 18-hour and 30-day leaching tests<sup>5</sup>. For the trace elements tested, concentrations in FSS generally exceeded those in ponded ash (*Figure 4*). Boron was by far the most abundant trace element. Lead was present in significant amounts. Of the remaining trace elements determined, mercury and selenium had the lowest concentrations with values near detection limits.

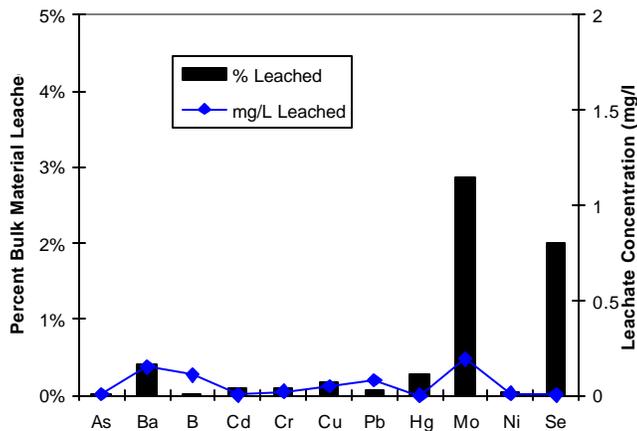
During the leaching tests, few trace elements were mobilized in measurable quantities from the CCP materials used at the Midwestern Reclamation Site. The most concentrated component in the 30-day leachate from ponded ash is boron (*Figure 5*). The 30-day leach for FSS extracted lower amounts of trace elements than ponded ash (*Figure 6*). Although molybdenum was consistently the most completely leached component, the percentage leached was less than 4% for all CCP materials tested. The leaching studies suggest that trace elements in the CCPs used at the Midwestern Site are relatively immobile in aqueous solutions. However, behavior of CCPs at the site may be somewhat different because ambient conditions cannot be precisely duplicated in the laboratory.

## Site Characteristics

At the Midwestern Site the highest levels of arsenic, cadmium, chromium, copper, lead, and nickel occurred in acidic, highly mineralized water taken from monitoring wells screened in and near the coal refuse. Lesser amounts were found in acidic ground water



**Figure 5. 30-day leach results for ponded ash. Percent bulk material leached is compared to leachate concentrations for trace elements.**



**Figure 6. 30-day leach of fixated scrubber sludge (FSS) comparing percent of bulk material leached to leachate concentrations for trace elements.**

collected from monitoring wells screened in unreclaimed spoil near the refuse. Ground water concentrations for these elements were near or below detection limits at the peripheral wells.

Boron and molybdenum concentrations increased dramatically after reclamation indicating that they are leached from CCPs (Figure 7). Boron levels increased significantly in seven of eight wells located within the reclaimed area, but not in the three peripheral wells. Increases in molybdenum were found in four of the eight central wells and none of the peripheral wells.

The maximum concentration for arsenic does not increase following reclamation (Figure 7), yet increases occurred in three of the eight central wells. This is sufficient evidence to suggest that some arsenic was leached from the CCPs.

## DISCUSSION

### *Boron in ground water*

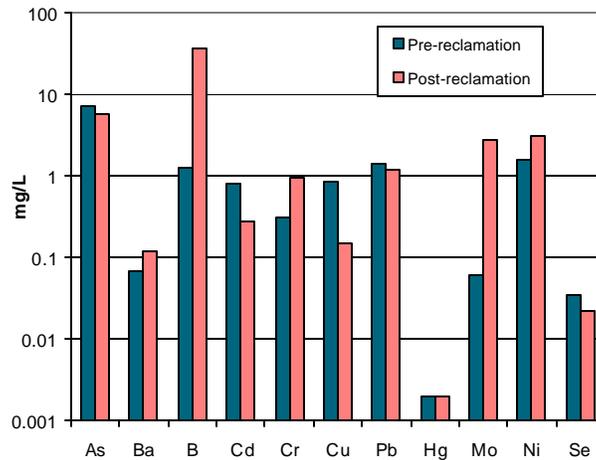
Boron increased in ground water after reclamation more than any other trace element. This, plus the absence of significant sorption of boron by solid phases, makes boron the

optimum indicator for CCP leaching and leachate plume migration. Following the last construction activities at the site, there was a general decrease in the concentration of boron as a function of time, with minor fluctuations. This generally decreasing boron concentration trend has been observed at all monitoring sites that experienced an initial post-reclamation boron increase. The overall decline suggests that progressively lesser amounts of boron are leached from CCPs and the periodic

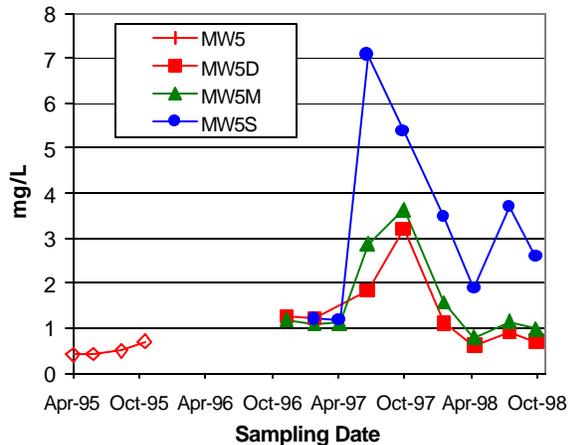
reversals are consistent with the interpretation that seasonal variations in rainfall may account for boron concentration fluctuations<sup>3</sup>. Furthermore, the cluster of monitoring wells at site MW5 (MW5S, MW5M, and MW5D) produced an attenuation pattern consistent with dilution effects (*Figure 8*). Post-reclamation levels of boron did not decrease to pre-reclamation levels in the deeper monitoring wells. This is more indicative of dilution effects rather than sorptive removal of boron from solution because concentrations in the deeper wells respond to the same fluctuations seen in the shallow well, only at lower concentrations.

#### *Molybdenum in ground water*

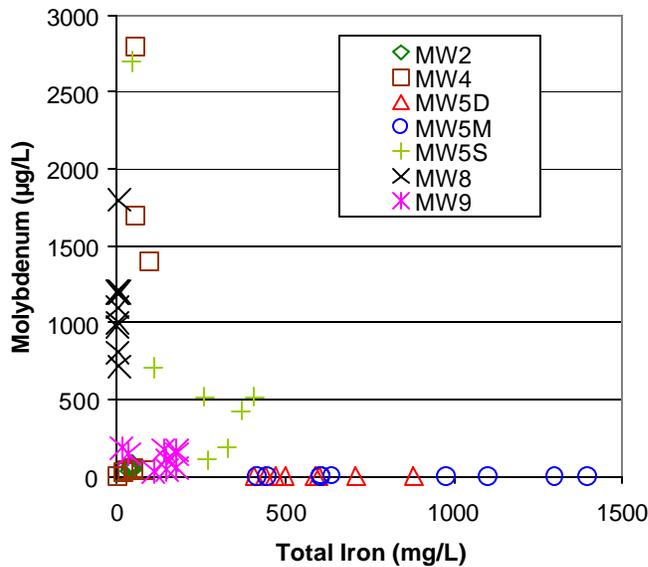
Molybdenum concentrations in ground water experienced the greatest proportionate increase (nearly two orders of magnitude) from pre- to post-reclamation (*Figure 7*). This suggests that CCPs contribute most of molybdenum to the ground water system. However, molybdenum concentration rapidly attenuates and is not a good indicator of the extent of a CCP-leachate plume in this abandoned mine-land setting. Molybdenum, like arsenic and boron, typically forms oxyanion complexes in aqueous solutions. In the presence of abundant iron, relatively insoluble ferrous molybdate scavenges molybdenum from aqueous solutions and thus exerts a significant control on



**Figure 7. Maximum concentrations of trace elements in ground water at the Midwestern Site.**



**Figure 8. Boron concentrations at site MW5 for pre- and post-reclamation well cluster. MW5S is screened 2 meters below FSS cap.**



**Figure 9. Molybdenum and iron concentrations in ground water from post-reclamation wells screened in or near CCP.**

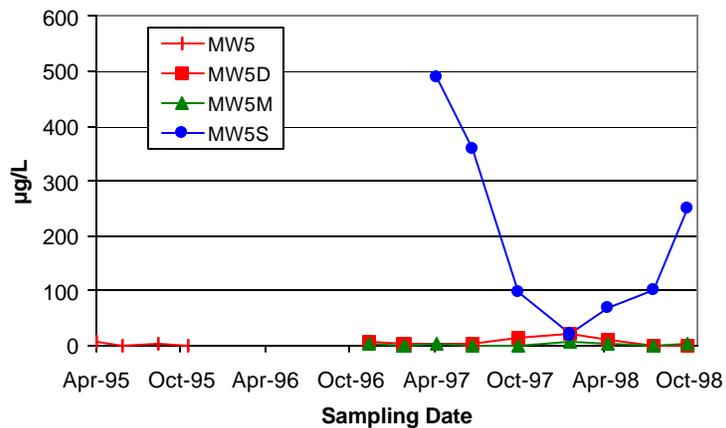
molybdenum concentration<sup>6</sup>. This attenuation mechanism appears to operate at monitoring wells screened either in CCPs or within close proximity (*Figure 9*). Ground water in these wells contained elevated amounts of boron, indicating a CCP source; whereas molybdenum concentrations appear to be inversely related to the amount of iron present in the water. MW5M is screened in spoil 2 meters below MW5S and contained virtually no molybdenum illustrating that molybdenum is removed from solution over a very short vertical distance. Concentrations as high as 2,700 µg/L in MW5S decreased to near the detection limit of 1 µg/L within a vertical distance of 2 meters.

Such rapid attenuation limits the use of molybdenum as a CCP-leachate tracking tool.

*Arsenic in ground water*

Arsenic levels in ground water are normally quite low in natural settings because arsenic-bearing solid phases are uncommon and natural waters typically are not sufficiently aggressive to mobilize the arsenic.

However, in acid-mine drainage environments arsenic occurs in natural sulfide minerals that are concentrated in the waste piles from coal processing. Upon exposure to surface and near-surface conditions these minerals oxidize, producing sulfuric acid and increasing total dissolved solids (TDS) in water. In acidic, oxidized water, arsenic can occur in very high concentrations. Such is the case for ground water in and near coal refuse at the Midwestern Site where arsenic concentrations were high and essentially the same before and after reclamation (*Figure 7*). At first glance these data suggest that arsenic was not noticeably impacted by the addition of CCPs to the site. However, ground water from the shallow post-reclamation monitoring well at site MW5 contained significantly higher levels of arsenic than both the deeper wells at this location and the pre-reclamation



**Figure 10. Arsenic concentrations at site MW5 showing concentration changes through time. MW5S is nearest FSS cap.**

ground water (*Figure 10*). Although the TDS is similar to that in the deeper wells, the pH (> 6 compared to < 4 for both deeper wells) and boron (*Figure 8*) were both significantly higher, suggesting that these, along with arsenic, were derived from the FSS cap. However, arsenic concentration, like that of molybdenum, rapidly attenuates and is not a good indicator of leachate plume migration in this setting. Unlike molybdenum, arsenic mobility is little affected by inorganic solubility controls in oxygenated waters<sup>6</sup>. Therefore, the most likely explanation is that the level of arsenic leached from the FSS cap is rapidly diluted or sorbed to concentrations near the detection limit within a vertical distance of two meters.

## CONCLUSION

Trace elements leached from CCPs that are likely to appear in ground water are those that can remain soluble under a wide range of conditions. Cation-forming trace elements such as cadmium, lead, and nickel would be expected to leach and remain in solution under the low pH, oxidizing conditions found in acid mine-drainage (AMD). However, the solubility for these metal cations is limited to low pH solutions and a primary effect of CCPs is to raise the pH of ground water. It is, therefore, highly unlikely that a significant proportion of these elements would have a CCP source. High levels of these metals that exist in AMD before emplacement of CCPs result primarily from the oxidation of sulfide minerals in coal refuse.

In contrast, arsenic, boron, and molybdenum form oxyanions in oxidizing aqueous solutions and remain soluble over a wide range of pH conditions. Boron and molybdenum are not appreciably leached from coal refuse by acidic solutions, but arsenic is. The fact that arsenic can be leached from coal-refuse sulfide minerals limits its use as a CCP-leachate indicator. Where derived from CCPs, the observation that arsenic concentrations decrease within a short distance from the source due to dilution and sorption further limits arsenic as a CCP-leachate indicator. Similarly, where derived from CCPs, molybdenum concentration decreases rapidly away from the source, thus limiting molybdenum as a CCP-leachate indicator. In this case, molybdenum co-precipitates with iron, one of the major components in the AMD at this site. Boron is not co-precipitated or sorbed, is more concentrated in CCPs than it is in acid generating coal refuse and spoil, and is soluble over a wide pH range. Therefore monitoring the concentration of boron is the most practical method to document CCP leachate formation and migration when CCPs are used in reclaiming abandoned mine lands.

## REFERENCES

- 1 Bryenton, D. L., and Gasper, J. H. Paper presented at the Coal Combustion By-Products Associated with Coal Mining-Interactive Forum, Carbondale, Illinois, 29-31, October, 1996.
- 2 Harper, D., Olyphant, G. A., and Branam, T. D. Paper presented at the 17<sup>th</sup> Annual Conference of Abandoned Mine Lands, French Lick, Indiana, October, 1995.

- 3 Branam, T. D., Ennis, M. V., and Smith, R. T. Paper presented at the 13<sup>th</sup> International Symposium on Management and Use of Coal Combustion Products, Orlando, Florida, 11-14, January 1999.
- 4 Spindler, K. M., Olyphant, G. A., and Haper, D. Paper presented at the 15<sup>th</sup> Annual Meeting of the American Society for Surface Mine Reclamation, St. Louis, Missouri, May 1998.
- 5 American Society for Testing and Materials, Annual Book of ASTM Standards. Section 11: Water and Environmental Technology, Vol. 11.04: Waste Disposal, 1985.
- 6 Hem, J. D. *Geochimica et Cosmochimica Acta*, 1977, **41**.

**Table 1**

**Depth and screened interval of monitoring wells. ( ) indicates approximate depth.**

PRE-RECLAMATION MONITORING WELLS			POST-RECLAMATION MONITORING WELLS		
Well	Depth (m)	Material	Well	Depth (m)	Material
MW1	15.2	Unmined Coal	MW1	15.2	Unmined Coal
MW2S	5.5	Spoil	MW2	5.5	Spoil
MW2D	7.9	Bedrock	MW4S	1.0	Soil/FSS Interface
MW3	11.6	Bedrock	MW4M	2.4	FSS/Spoil Interface
MW4S	2.7	Refuse	MW4D	4.6	Spoil
MW4D	5.8	Refuse	MW5S	(4.4)	Spoil
MW5	5.5	Refuse	MW5M	(6.4)	Spoil
MW6	2.4	Alluvium	MW5D	(10)	Spoil
MW7	3.7	Refuse	MW6	2.4	Alluvium
MW13	30.5	Mine	MW7S	1.2	Soil/FSS Interface
			MW7D	4.1	Refuse
			MW8	6.1	Ponded Ash/Lakebed Interface
			MW9	11.3	Ponded Ash
			MW13	30.5	Mine