

Metals in Leachates of Soil, Biosolids, and Fly Ash

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ABSTRACT

Although laboratory and field studies show that addition of fly ash may increase carbon sequestration in reclaimed mine soils, the use of such amendments must overcome public concerns about possible release of toxic metals before the practice is generally accepted. Towards this end, we conducted experiments to examine the leaching of metals from soil mixed with several fly ashes (both class F and class C) and biosolids under mild environmentally relevant extraction procedures (dilute CaCl₂). Both biosolids and fly ash appeared to contribute to leaching of some metals in these small scale short term column leaching studies. Fly ash appeared to increase the amounts of B and As observed in the leachate. When fly ash was combined with soil, and biosolids, significant decreases in the leachable amounts of Cr, Li, Pb, and Cd were seen, often to levels below our detection limits, when compared to leachates from fly ash or biosolids alone. Thus, application of fly ash together with other amendments such as biosolids to soils results in minimal leaching of metals. However, application rates must be carefully considered.

INTRODUCTION

The reclamation of mine soils may benefit from a program of carbon sequestration in soils to offsite CO₂ emissions. Additions of coal combustion byproducts might be useful in this effort to reclaim mine soils and promote carbon sequestration due to potential beneficial effects on soil. For example, fly ash can be useful in improving soil texture and water holding capacity¹². Based on our preliminary field and laboratory studies it appears that fly ash amendments may also increase carbon sequestration in reclaimed mine soils¹¹. There are concerns,^{1,4,6} especially when applying high rates of ash², for potential deleterious effects such as metal leaching, effects on plant germination,¹⁴ and phosphorous availability.⁹

Various treatments of ash have been examined to reduce the potential for release of metals from ash. In utilization as an amendment, fly ash can be added in conjunction with organic material such as biosolids.¹⁹ The biosolids may reduce leaching of some metals or potentially increase leaching of others. For example, Seferinoglu et al. have examined acid leaching of ash.¹³ Others have examined chemical precipitation of potentially toxic metals²⁰ or use of novel burners.¹⁸

Our experiments were designed to examine the changes in leaching of fly ash under relatively mild extraction procedures that would be more relevant to environmental applications than standard EPA methods. The experiments were also designed to determine if leaching of potentially toxic materials was influenced by mixing of the fly ash with soil and biosolids and if the biosolids could be a concern for release of metals.

MATERIALS AND METHODS

Sources of Fly ash, biosolids, and soil

Two series of experiments were designed to address release of toxic metals from fly ash and biosolid amendments. We tested class F and class C fly ash from western and eastern sources with a range of pH values (Table 1) in batch and column tests. The classes of fly ash are based on their chemical compositions and origins (specified in ASTM C618).¹⁶ Selected fly ash samples were used in column leaching tests where dilute CaCl₂ was run through small columns packed with mixtures of fly ash, biosolids, and soil.

Three of the western fly ash sources (Martin Lake, Cherokee Unit 2, and Hayden) were F type

Table 1. Characteristics of materials used in leaching experiments.

<i>Sample</i>	<i>Class</i>	<i>pH</i>	<i>Other</i>
Paradise Soil	NA	7.03	
Paradise Soil	NA	7.75	
Biosolid	NA	8.04	
TVA Fly Ash	F	7.67	
Martin Lake Fly Ash	F	11.65	LowNox
Hayden Fly Ash	F	12.82	+FGD
Cherokee Fly Ash	F	11.04	
Harrington Fly Ash	C	12.85	

ash and one was a type C. The Martin Lake fly ash is an F type ash from burning 7400 Btu lignite, mined locally near the plant. The ash was sampled from a 1000-ton truck silo. This silo receives fly ash from two separate units (840MW each) with LoNox burners. The Cherokee Unit 2 fly ash is also an F type ash. This plant burns Colorado bituminous coal (11,350 Btu) from the Twenty-Mile mine. The carbon content is typical for that unit, which normally runs 3 to 7%. The ash was collected from a dry ash truck. It is a pulverized coal top fired B&W boiler from a 110 MW unit. The final western F ash was from the Hayden plant but it was mixed with flue-gas desulfurization (FGD) materials. The ash is from Hayden Station, Unit 1 (190 MW), which is a pulverized coal-fired unit with LoNox burners. The unit is front fired and takes its coal from the Seneca Mine in Routt County, Colorado. This bituminous coal burned in the unit has a typical Btu rating of 10,400. The final western ash was from Harrington Station Unit 3 and it is a C ash. The unit is a pulverized coal unit (rated at 360MW) that burns PRB coal from Black Thunder Mine in Wyoming (8800 Btu).

The TVA power plant in Paradise, KY was the source for the final F class ash tested. The Paradise plant burns eastern bituminous coal, (about 12,500 Btu/lb average). The soil used in the column leaching study was also from the TVA power plant in Paradise Kentucky.

The biosolid material used in the column leaching study was collected from the Oak Ridge Waste Treatment Plant. The biosolids are processed with a vacuum filter press drying system (Ken Glass, personal communication). Before the anaerobically treated sludge is sent to the process, it is treated w/ ferric chloride and lime to aid in dewatering in the first stage of the press operation. In the overall process, the sludge is changed from about 2% total solids to upwards of 95%.

Column experiments

Two sets of experiments were set up with small columns (small syringes) containing 10 g of soil, biosolid and fly ash mixtures (Table 2). In experiment 1, each treatment (T1-T5) is replicated for 5 sources of fly ash and duplicates for each treatment were run with each source of fly ash. In experiment 2, two sources of fly ash (Martin Lake and Harrington) were used and triplicates for each treatment were run with each of the two sources of fly ash. Additional treatments were run in experiment two but are not presented here. The bottom of each column was lined with glass wool to prevent loss of the soil mixtures. After set up, the columns were leached in a flow through manner with 100 ml of 5 mM CaCl₂. The leaching solution was pulled through the columns with a syringe. The collected effluent was

Table 2. Design for the two column experiments.

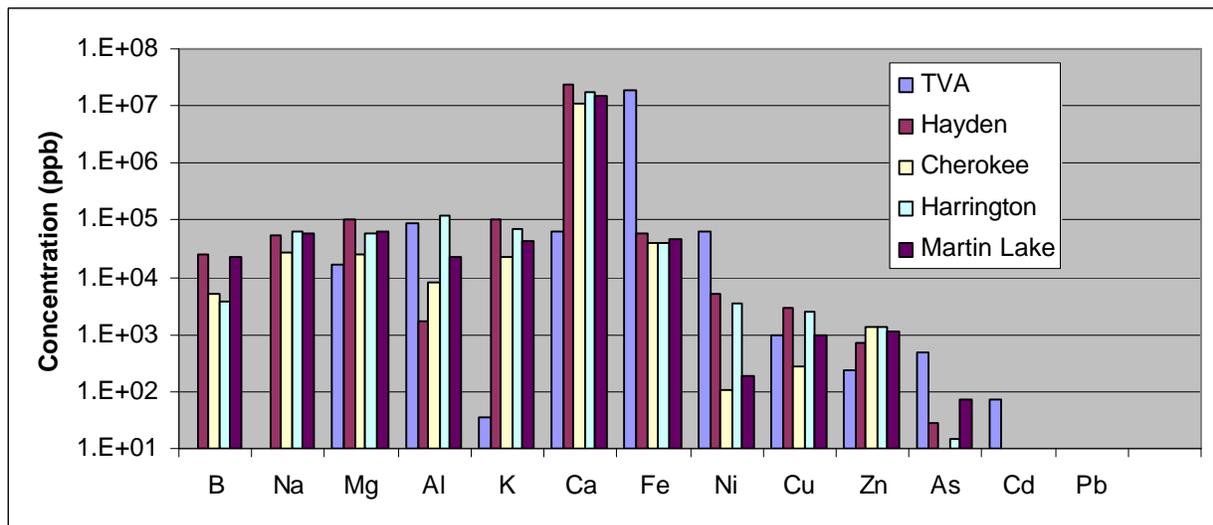
	Treatment	Fly Ash Amt. (g)	Biosolid Amt. (g)	Soil Amt. (g)
Experiment 1	T1	0	5	5
	T2	1	4	5
	T3	0	4	6
	T4	2	3	5
	T5	0	0	10
Experiment 2	T1	1	0	9
	T2	1	2	7
	T3	1	4	5
	T4	0	0	10
	T5	10	0	0
	T6	0	10	0

filtered through a 0.2um acrodisc filter and placed in vials for analysis on a Perkin Elmer 9000 Elan ICP-MS.

RESULTS AND DISCUSSION

The variability in extraction of metals with CaCl_2 from the several sources of fly ash and was highly dependent on the element (Figure 1). In general, the extraction of the heaviest and lightest elements was most different among the fly ash samples when mixed with soil.

Figure 1. CaCl_2 leaching of elements (log 10 ppb) in experiment 1 from different sources (as listed in the figure legend) of fly ash (at 10 and 20%), biosolids (at 30 and 40%) and Paradise soil (at 50%). Each bar is the mean of 4 measurements (2 replicates at 2 fly ash concentrations).

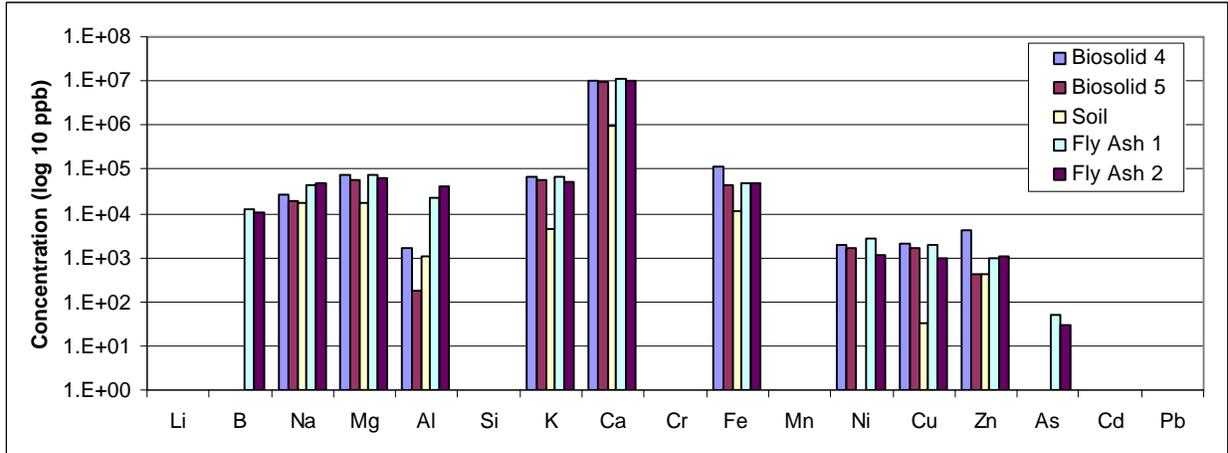


Arsenic leached in highest concentration from the TVA and Martin Lake sample mixture (Figure 1) and Cd was only seen in the leachate from the TVA sample. Pb was not seen in any of the leachates. Arsenic was not seen in Cherokee sample and Ni and Cu were lowest in the Cherokee sample (Figure 1). However, Zn was relatively high in both the Cherokee and Harrington samples. Of the light elements, B and Na were not seen in the mixture with the TVA fly ash and other light elements (e.g., Al and Mg) tended to be for the TVA samples. The Hayden sample, which was mixed with FGD, leached the greatest concentration of many light elements from B to Ca. It has been previously observed that B leaching is enhanced when fly ash is combined with FGD gypsum.⁷ The Harrington sample was intermediate in extraction of some of the light elements (e.g., B TVA). There were also a few differences among the samples in extraction of K and Ca. There were relatively small differences among the samples in extraction of Fe or Zn.

Data from the same experiment indicates the contributions of fly ash, soil, and biosolids to leaching of the metals (e.g., Figure 2). In this experiment, the columns were set up with 40% biosolids with 60% soil (Biosolid 4), 50% biosolid with 50% soil (Biosolid 5), 100% soil (Soil), 10% fly ash with 40% biosolids and 50% soil (Fly Ash 1), and 20% fly ash with 30% biosolids and 50% soil (Fly ash 2). Results presented are means of 10 replicates for soil and biosolid treatments. For the fly ash treatments, the 10 measurements for each treatment are duplicates from each of the five fly ash sources. There was little evidence for substantial leaching of metals in any treatment. At the high loading rates used, both biosolids and fly ash appeared to contribute

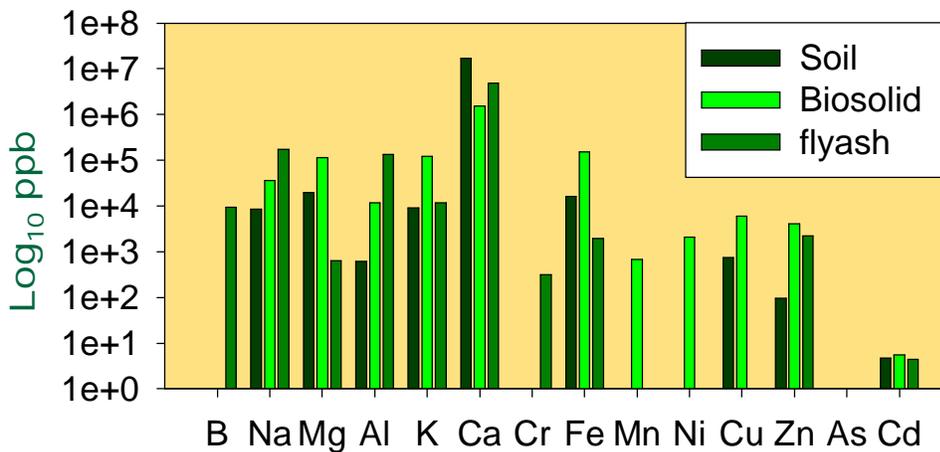
to the limited leaching observed for some metals such as Ni (e.g., Figure 2). Ni was detected in very low amounts in field leaching experiments with fly ash mixed with soil that indicated minimal potential for adverse effects.⁶ Only fly ash contributed to the leaching of B and As. No Cr, Cd, or Pb was observed in any of the treatments.

Figure 2. Leaching of elements from columns in experiment 1



Differences in the presence and concentrations of the metals in the leachates between samples from columns containing mixtures of fly ash, soil, and biosolids and columns containing only one of the materials indicates some synergistic effects. For example, Cr was detectable in leachates from columns packed only with fly ash (Figure 3), and in both hot water and acid extracts of the fly ash.¹¹ However, Cr was not detected in leachates from treatments where the fly ash was combined with soil and biosolids (Figures 1 and 2). Although Si was detected in the hot water extracts of the fly ash¹¹ it was not evident in the extracts from experiments where the fly ash was combined with soil and biosolids (Figure 2). In addition, although Pb, and Cd were

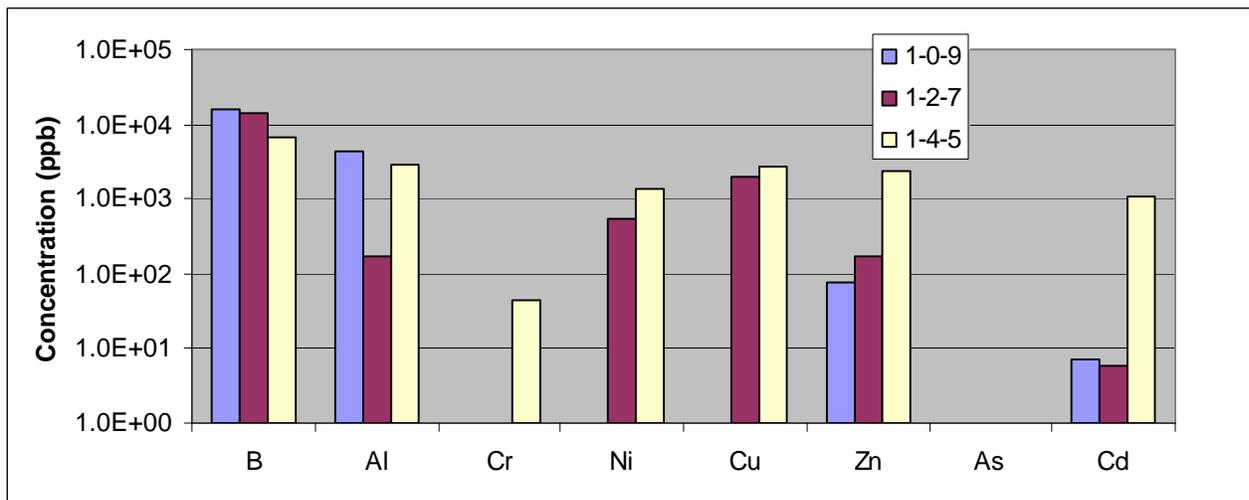
Figure 3. Concentrations of elements in CaCl₂ leachates from columns of individual materials.



present in acid extracts of the fly ash¹¹ they also were not evident in the extracts from the columns with fly ash, soil, and biosolids. Cu and Zn were leached from all the samples including the soil. Ariese et al. found that in mixtures of soil and fly ash many ions leached from fly ash are retained by the soil.³ Chaudhuri et al. have shown through sequential extraction procedures that many increases in metal concentration of soil that occurred with alkaline fly ash and sludge application were of insoluble forms except for cadmium.⁵ The ability to maintain optimum soil pH can be enhanced by coal ash if care is taken to avoid over application.⁸ High rates of application can be used although there are transitory effects on soil salinity.²

Changes in leaching of specific metals with changing proportions of fly ash and biosolids (Figure 4) may have been due to differences in the amounts of metals in the parent material and to chemical effects such as chelation or competition for sorption sites. Many of the metals are clearly present in the biosolids (e.g., see figure 2) thus the increasing amounts of leached Cu, Zn, and nickel with greater amounts of biosolids is consistent. All the data clearly indicates that boron is only coming from the fly ash thus the decrease in boron with increasing amounts of biosolids is likely due to chemical effects. Only at the highest levels of biosolids is Cr seen and at that level Cd takes a jump in concentration.

Figure 4. Concentrations of selected elements in CaCl₂ leachates from columns with increasing amounts of biosolids added to a fly ash and soil mixture. Legend indicates the number of grams of fly ash, biosolids, and soil in the column.



Although potentially toxic metals can be leached from the fly ash, for many of the most toxic elements leached the concentrations were very low. These results are consistent with those of Pathan et al. who found that potential releases from Australian fly ash were below regulatory levels.¹² Fly ash in Australia has shown to be beneficial in increasing plant biomass.¹⁷ It was also evident from the extraction studies that the TVA fly ash was considerably different than the western fly ash in that the pH was much lower (Table 1). Additional differences in composition of extracts from the fly ash samples (data not shown) are likely due to the class of the fly ash and additional materials placed with the fly ash (e.g., FGD). The low concentrations of the light elements in the TVA fly ash may have been due to natural leaching of the fly ash pile. It has

been suggested that pre-leach of B and soluble salts would be beneficial before utilization on corn crops.¹⁵

From our leaching data, we were able to determine that there are differences among fly ash sources. However, all leach very small amounts of metals when mixed with soil even under these conditions of high loadings of fly ash and biosolids and the use of CaCl₂ rather than groundwater that may represent a worst-case scenario.

ACKNOWLEDGMENTS

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