

## **ENHANCING CARBON SEQUESTRATION AND RECLAMATION OF DEGRADED LANDS WITH FOSSIL-FUEL COMBUSTION BYPRODUCTS**

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### **INTRODUCTION**

This joint ORNL and PNNL project examines the potential use of lands that have been disturbed by mining, highway construction, or poor management practices for terrestrial carbon sequestration. The approach includes examination of the effects of amendments with solid byproducts from fossil-fuel combustion, paper production, and biological waste-treatment facilities for enhancing carbon sequestration. The primary goals are to identify and quantify the key factors leading to successful C sequestration and reclamation of degraded lands, examine potential problems with application of fly ash for land reclamation, and to communicate this information to the community. Results from the available literature are combined with laboratory analysis. Specific tasks have focused on the accumulation of carbon in soil over time (including carbon sequestered in deep soil horizons) and the impact of environmental conditions on the rate of accumulation, assaying for populations of denitrifying bacteria that can effect emissions of greenhouse gases, assessing potential environmental health impacts (accomplished through a series of column leaching and toxicity experiments), comparing the results to DOE/CSiTE measurements, and evaluating management practices to optimize this sequestration strategy. Technology transfer workshops, presentations at academic and industrial meetings, and publications (e.g., Martin et al. 2003, Palumbo et al. 2004, and Palumbo et al. In press) are employed to engage industry and create working partnerships. Due to progress in these areas and funding limitations the emphasis of the project has shifted to concerns regarding the use of fly ash in reclamation and the impacts of pollution control technologies which heavily load the fly ash with ammonia (e.g., NO<sub>x</sub> removal) on the leaching properties of the fly ash.

### **BACKGROUND**

During the next several decades, a program focused on terrestrial C sequestration processes can make a significant contribution to abating the anticipated CO<sub>2</sub> increase, and easing the transition to other renewable energy sources. Within this context, the restoration of degraded soils represents an opportunity to couple carbon sequestration with the utilization of fossil fuel

and energy byproducts and other waste material (e.g., industrial sludges, municipal biosolids, mulch) while achieving ecological and aesthetic benefits for society in improved soil quality, biodiversity, and ecosystem services.

The potential of energy byproducts such as fly ash as soil amendments to enhance C sequestration in degraded lands can be most fully realized if these inorganic byproducts are applied in conjunction with organic amendments, including both mulch from biomass productivity, as well as process waste materials such as biosolids, and pulp and sludge from paper production. These organic amendments can have beneficial effects that complement and extend those of the inorganic fly ash material, including: (1) improving soil structure and moisture retention capacity of soil; (2) releasing nutrient elements within the organic structure, adding pH buffering capacity, and acting as a metal-ion buffer in soil to make micronutrients available to plants; (3) stabilizing toxic metals in soil, thereby reducing their migration to groundwater and reducing their uptake and toxic effects in plant.

The goal of this project is to study the use of fossil fuel byproducts to foster carbon sequestration in degraded lands. This has the triple benefits of carbon storage, byproduct utilization and land reclamation. This research will be conducted in conjunction with the DOE Center for Research on Enhancing Carbon Sequestration in Terrestrial Ecosystems (CSiTE), which will allow DOE to leverage existing CSiTE activities by expanding its research and partnerships to degraded lands and the use of fossil energy byproducts to stimulate carbon sequestration in those terrestrial ecosystems.

## **GOALS AND TECHNICAL APPROACH**

The **goals of this project** encompass both scientific and technology transfer components:

*Scientific Goal:* Identify optimal selection and delivery strategies to maximize the contribution of amendments to carbon sequestration.

*Technology Transfer Goal:* Foster interactions between the scientific and user communities to maximize the application of new knowledge and approaches for enhancing terrestrial C sequestration through optimal utilization of fossil energy byproducts and management of degraded lands.

Our **research strategy** to achieve the Scientific Goal of optimizing C sequestration has had three parts. Current research focuses on the 3<sup>rd</sup> of these tasks due to progress in the other areas and due to funding limitations.

1. *Evaluate Existing Experimental Sites:* Because of the diversity and extent of previous amendment studies and the long times needed to determine success or failure from a

C-sequestration perspective; we are evaluating a number of existing sites where fly ash and biosolids amendments have already been applied. Data obtained from these experimental manipulations includes parameters such as the depth distribution of carbon, amounts of carbon, types of organic and inorganic C present, emission of greenhouse gases, and changes in nitrogen cycling microbial communities.

2. *Conduct Laboratory Experiments to Identify Key Amendment Types and Potential Management Strategies:* A set of laboratory experiments to assess the relative impacts of different environmental conditions such that enhance the accumulation of C by soils are being conducted at PNNL. In addition, we are examining the potential for release of toxic metals and other greenhouse gases. This work examined nitrous oxide emissions as a result of nitrogen input via the amendments.
3. *Conduct Laboratory Experiments to Assess the Environmental Implications of Coal Combustion Byproducts and Biosolid Amendment Utilization:* A series of experiments designed to address public concern over the release of toxic metals from fly ash and biosolid amendments are being conducted through laboratory column leaching procedures. We are examining ammonia release (which could be converted by microbial processes to nitrous oxide), leaching of metals, and toxicity of the leachate. Results taken from this simulated weathering or leaching will be examined for toxicity testing of water and soil.

Our current efforts to achieve the *Technology Transfer* goal are focused on communication. Plans to expand the focus to include policy studies are on hold due to funding limitations.

1. *Communication:* The Regional Partnerships in Terrestrial Carbon Sequestration Workshop conference was sponsored by the U.S. Department of Energy and National Energy Technology Laboratory (NETL) and The DOE Consortium for Research on Enhancing Carbon Sequestration in Terrestrial Ecosystems (CSiTE) in November, 2001 in Lexington, KY. Presentations from the meeting and summaries of the breakout sessions can be found at: [http://www.netl.doe.gov/publications/proceedings/01/carbon\\_seq\\_terr/cseq-terr01.html](http://www.netl.doe.gov/publications/proceedings/01/carbon_seq_terr/cseq-terr01.html). We have published numerous other papers and abstracts based on this work.

## **TECHNICAL PROGRESS**

### **Summary from previous years:**

#### **Soil Carbon in Reclaimed Mine Soils**

In previous years, samples were taken from sites in the eastern United States, including West Virginia and Virginia (Lee Daniels) and from sites in the Midwest including several sites in Ohio

(Rattan Lal) have shown that fly ash additions appeared to consistently increase soil C in the reclaimed mine soils.

### **Microbial Analysis**

In previous years, we examined the carbon content of reclaimed mine soils treated with soil amendments using several molecular techniques. PLFA data indicated viable biomass for bacterial and fungal communities varied among amendment treatment, depth, and sites. The highest bacterial biomass was present in an A1 soil horizon containing the fly ash and sawdust amendment. Ordination techniques used to assess relationships among the sites in terms of fungal community structure revealed little consistency among samples from the same treatment (data not shown).

### **Application of Innovative Carbon and Nitrogen Analysis Methods**

We have been testing the application of newer more rapid methods for carbon analysis to mine soils and have evaluated the use of laser-induced breakdown spectroscopy (LIBS) for determination of the total concentration of carbon and nitrogen in soils. We found that to achieve good results with the LIBS technique, it is advisable to make a large number of measurements. For example, although the range can be substantial, approaching 50% of the mean for some samples the standard error of the measurement is quite small (approximately 3%) when 20 measurements are made on a soil sample.

### **Recent Technical Progress**

#### **Metals in Leachates of Soil, Biosolids, and Fly Ash**

To determine the leaching potential and influence of coal-source derived fly ash, we ran batch and column leaching experiments and analyzed the leachate composition. We tested the variability in leaching of metals from various sources of fly ash in batch experiments with hot water and mild acid extraction and compared these results to dilute  $\text{CaCl}_2$  leaching from mixtures of fly ash, soil and biosolids. Finally, we examined the influence of added phosphate containing fertilizer on leachate quality in column experiments. 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). Selected fly ash samples were used in column leaching tests where dilute  $\text{CaCl}_2$  was run through small columns packed with mixtures of fly ash, biosolids, and soil.

The soil used in the column leaching study was also from the TVA power plant in Paradise Kentucky. A high phosphate fertilizer (Schultz, Bloom Builder, Bridgtown MO) with a 10-50-10

composition was used for phosphate additions. Both ammonia and nitrate were present as nitrogen sources.

The biosolid material used in the 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%

There were major differences between hot water and acid extraction in terms of resulting elemental concentrations (Figure 1). The hot water technique was least effective in leaching out the heaviest of metals. For example, the hot water did not

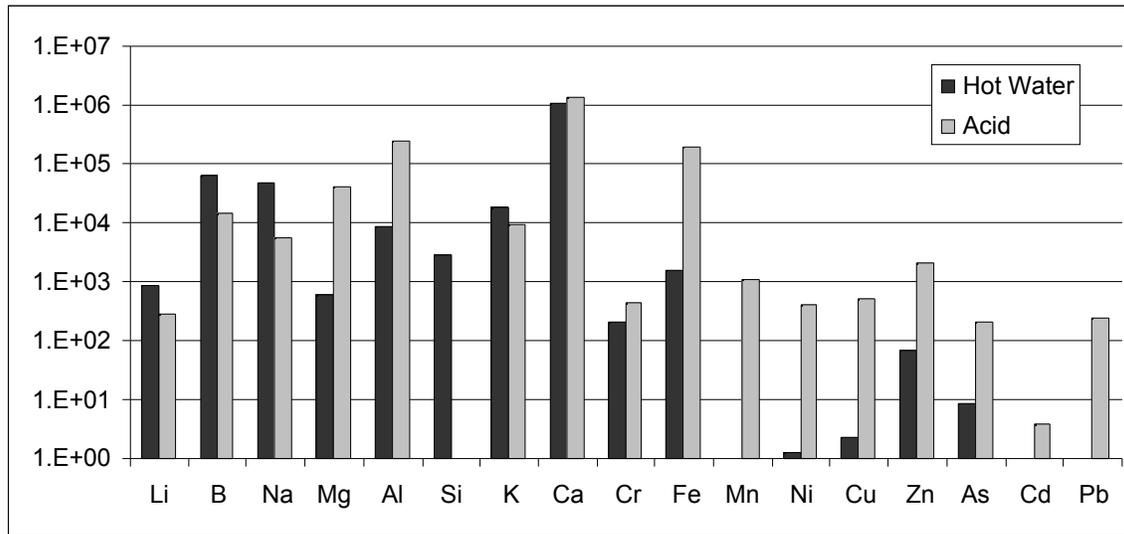
**Table 1. Characteristics of materials used in leaching experiments.**

<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	

extract Cd or Pd from any of the fly ash samples. Zn, As, Cu, Ni, Mn, Fe, Al, and Mg, were extracted in significantly higher amounts using the acid extraction. In contrast, Li, B, and Na were extracted in higher amounts with the hot water. Hot water extraction is a relatively common method for determination of B in soil (e.g., Stouraiti, et al). In general, acid was least effective in leaching out the lightest elements (Li, B, Na) and Si. Ca appeared to be leached effectively with both acid and hot water. The short term potential leaching in a field environment is more likely similar to the hot water extraction as opposed to the acid extraction. Short term column leaching experiments with the five fly ash sources and a dilute CaCl<sub>2</sub> solution in a flow through mode tended to reflect a composition more like than that of the hot water batch extraction (Sharma et al 2001). The acid extraction may represent a longer-term potential for leaching and indicate a largely insoluble reservoir of the heavier metals.

In general for both the hot water and acid extractions, the greatest variability among the sources of fly ash was in the extraction of the heaviest (e.g., Cr, Pb, As, Ni) and lightest (e.g., Li, B, Na, Si, Mg, Ca) elements (data not shown). In the hot water extraction, As was only extracted from the TVA sample and the Paradise soil (crushed mine spoil) from the site of the TVA fossil plant. Ni was only extracted from the Hayden sample. Cr was extracted from three of the five fly ash samples in the hot water extraction, but not from the soil sample. Of the light elements, Li, B, and Na extraction were low for the TVA fly ash and Paradise soil samples. The Hayden sample,

which was mixed with FGD, leached the greatest concentration of B in the hot water extraction.



**Figure 1. A comparison of hot water and acid extraction of the five fly ash samples.**

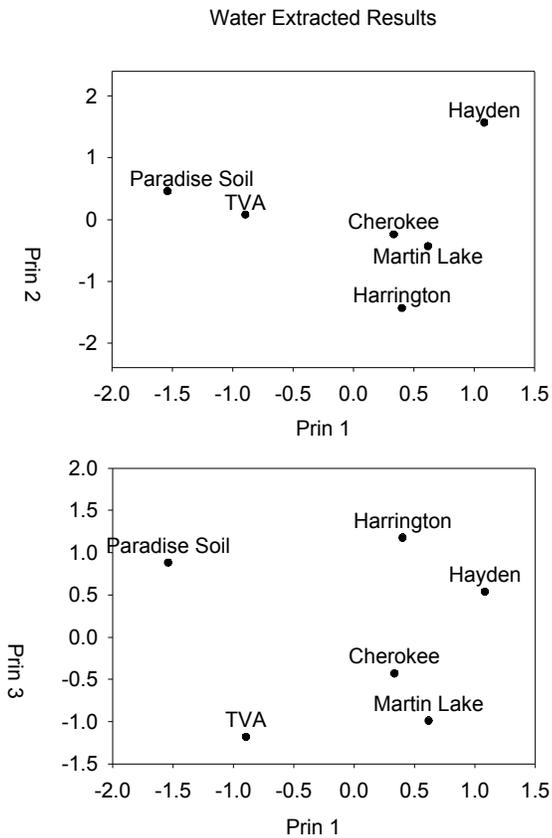
A principle component analysis (PCA) was used to summarize and reduce the leachate composition data from the hot water and acid leaching experiments (Table 2). The PCA analysis was successful in representing a large proportion of the variability of the leachate composition data for both the hot water leached experiment (85.3 %) and the acid leached experiment (0.989) in three principal components (Table 2).

The plots of the principal component values from the hot water extraction for each of the samples (Figure 2) and the plots of the loadings of the leachate composition data on the principal components (Figure 3) illustrate patterns in the leachate composition with respect to the source of mined material. Plots with very similar relationships among the samples were generated for the acid extraction leachate data (data not shown).

**Table 2. Percent variability accounted for with the first three principal components for the elemental leaching data from the water and acid extractions.**

	PCA 1	PCA 2	PCA 3	Cumulative
Water Leached	0.433	0.290	0.130	0.853
Acid Leached	0.641	0.232	0.116	0.989

The first principal component (PC-1) serves to separate the fly ash and soil samples from the TVA Paradise fossil plant (the two eastern samples) from the four western samples. B, Li, Na, and K load heavily positive on PC-1 (Figure 3). It is clear that Li, B, Na, and K are all lower in

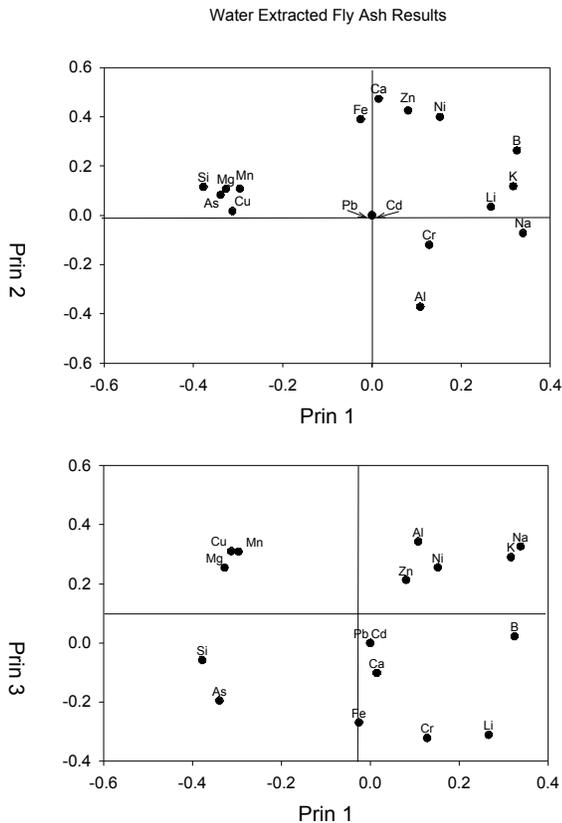


**Figure 2.** Characteristics of the leachates from different sources of fly ash or soil plotted in principal component space. Closely grouped points have similar leachate compositions.

Harrington, the one western class C fly ash, separates in leaching characteristics from the class F western ashes primarily on PC-3 (Figure 2). Again, Fe, Cr, and Li load heavily (negative) on PC-3 and Al loads heavily positive (Figure 3).

Examination of the concentration data does indicate that the Harrington sample has the lowest Li and B and highest Al among the four western ashes. Thus, leaching components likely separate this class C

these eastern samples. Also, some of the toxic metals (e.g., As, Cu) load heavily negative on PC-1 and these tend to be present in the eastern samples to a greater degree than in the western samples. Thus, the low B but high As and Cu will give the eastern leachates considerably different potentials for toxicity. The Paradise soil and the FGD fly ash separate to some degree on PC-1, while they separate significantly on PC-3. The lack of B in the soil sample (data not shown) probably is the greatest influence on PC-1. The heavy positive loading of Cu, Mg, and MN on PC-3 (Figure 3) seems to be the factor separating the samples, as concentrations of these elements are all higher in the leachates from the soil sample (Figure 2).



**Figure 3.** Loadings of element values of the three principal components. The points for Pb and Cd overlap on both plots. Elements loading at near 0 on one axis (e.g., Ca at near 0 on PC 1) are

material from the Class F ashes in leaching characteristics.

### Mercury Content

There was modest variability in the mercury concentration leached from the different sources of fly ash (Table 1). Mercury is a growing concern in fossil plant operations (Pavlish et al. 2003). However, the highest concentration of mercury measured in our study was in the biosolids. Thus, it appears that leaching of mercury to the soil may be more likely to come from biosolids amendments, than fly ash amendments. In fact, some of the fly ash samples were lower in mercury content than the Paradise soil (crushed mine spoil) sample.

### Effects of Fertilizer Addition in Column Experiments

Some elements present in the phosphate fertilizer were significantly increased in the column leachate to which the fertilizer had been added (Figure 4). For example, Fe and Zn increased significantly, likely as a direct result of their presence in the fertilizer. There was also an increase in Mn (Figure 4), but due to the variability the observed increase was not significant.

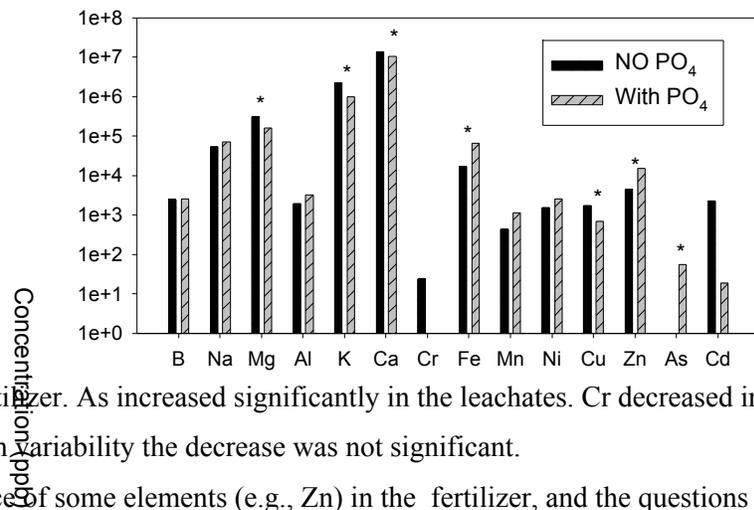
Other changes in leachate concentration were more likely due

to chemical effects such as precipitation or changes in adsorption and desorption with the increase in competing ions. Cu significantly decreased in the leachate as did Mg, K, and Ca (Figure 4). A decrease in K was noted, despite its presence

as a major component in the fertilizer. As increased significantly in the leachates. Cr decreased in the leachates, but due to the high variability the decrease was not significant.

The high variability, the presence of some elements (e.g., Zn) in the fertilizer, and the questions as to the source of some elements in the leachates from the phosphate added columns (e.g., did the arsenic come from the fertilizer or the fly ash ?) complicates interpretation of these results. Thus, future experiments are planned using liquid fertilizer applications in an effort to reduce variability by providing a more uniform distribution of the fertilizer in the columns. Additional analysis of the fertilizer to determine presence of trace elements (e.g., As) will be done. Also

Figure 4. Comparison of leachate concentrations with and without added phosphate.



additional control treatments of phosphate addition to soil rather than just to the mixed (soil, fly ash, biosolid) columns will be examined. Finally, the effects when using more normal soils than the crushed mine spoil considered here should be examined.

## **Conclusions**

Our leaching results with dilute acid and hot water extraction indicated the potential for leaching of toxic metals from fly ash and also indicate that similar sources and types of fly ash have similar leachate characteristics. These characteristics can apparently be influenced by other factors, such as mixing with FGD products and weathering. However for many of the most toxic elements leached, the concentrations were very low. Additionally, the column leaching tests were conducted under more realistic leaching solutions ( $\text{CaCl}_2$  matched to typical groundwater osmotic strength) and the leaching potential was shown to be even lower. Finally when mixed with soil and biosolids, concentrations of potentially toxic materials were often at or below detection limits. Variability in leaching from the different fly ash sources was evident as well. Most notably, the TVA fly ash was considerably different than the western fly ash in that the concentrations of many light elements in the leachates were much lower. Additional differences in the composition of extracts from the fly ash samples are evident in the PCA plots and 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. This potential loss of light elements due to natural leaching mimics deliberate pre-leach of B and soluble salts that has been beneficial before utilization of fly ash on crops. The generally low toxicity potential of the leachates is supported by Microtox™ data (not shown) that indicates no toxicity for the leachates. If B leaching and fly ash application rates are controlled, the apparent low potential for leaching of toxic concentrations of heavy metals and the apparent benefits of fly ash in soil carbon sequestration indicate that fly ash amendments should be considered when planning mine reclamation activities that also have a goal of increasing carbon sequestration in soil.

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