Issues with the Use of Fly Ash for Carbon Sequestration

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Abstract

As part of a study of the potential for carbon sequestration in degraded mine lands, we have found that based on laboratory and field experiments, fly ash and biosolid amendments can increase soil carbon. Although it appears that geochemistry plays a large part in this effect, it is not clear if there is also an effect on the microbial community and its influence on carbon sequestration. Also, addition of fly ash to soil, while generally considered safe, does cause some concern to the public. Nitrogen is an additional concern due to the potential release of nitrous oxide from microbial activity following the addition of biosolids. We examined the relationships among some aspects of the nitrogen cycling, carbon content, and microbial community structure in reclaimed mine soils. Using a variety of molecular approaches, we were able to detect large differences in microbial communities among the sites. We have started to apply an oligonucleotide-based array on the soil samples to examine genes involved in nitrogen cycling. Experiments with fly ash from several sources mixed with soil have shown diminemus amounts of toxic metals in column leachate studies. Assays of toxicity with the leachates conducted using the Microtox system have been negative for all samples tested. Thus, it appears that fly ash amendments would have little potential for toxic effects, that there is potential to further reduce metals in leachates with other amendments.

Introduction

To determine the potential for carbon sequestration in degraded mine lands, we have been examining the carbon content of reclaimed mine soil at > ten years post reclamation. Samples

were collected from land that had previously been mined and had received a variety of soil amendments in Wise County, Virginia, and Morgantown, West Virginia. These amendments included varying combinations of sawdust, fly ash from fossil fuel combustion, and biosolids. Carbon and nitrogen accumulation was analyzed from the research plots and we found (data not shown)that the fly ash and biosolid amendments used during reclamation resulted in higher carbon levels. Because of the potential dual benefits for using fossil-fuel combustion byproducts while sequestering carbon and reclaiming degraded lands, we felt it was important to address some issues associated with the use of these amendments.

The three issues addressed in this paper include studies of the microbial community structure and the environmental health impacts associated with potential leaching of metals from the fly ash and biosolid amendments used. Specifically, we are interested in whether there are distinct microbial communities associated with higher carbon accumulation and if there could be a potential release of other greenhouse gases associated with microbial activity (e.g., nitrous oxide resulting from denitrification). We were also interested in testing other amendments that could be used to reduce potential problems associated with leaching and with other greenhouse gases.

Methods

Sample sites - Controlled Overburden Placement Experiment (CP) plots received biosolid, sawdust, and fertilizer treatments beginning in 1982Control plots consisted of 2:1 sandstone:siltstone, amended with 1120 kg/ha of 15-30-15 fertilizer. Plots amended with sawdust consisted of 112 Mg/ha sawdust + 1120 kg/ha 15-30-15 fertilizer + 336 kg/ha N fertilizer. Local municipal biosolid material was used to amend plots for organic biosolid application. A separate location receiving biosolid amendments in 1989 was the Powell River Biosolids (PRP) Project. This area consisted of 70 ha of mine soil amended with biosolids known as “Philadelphia mine mix.” Amendments were applied in a ratio of 1:1 biosolid:composted wood chips.

Fly ash amendments were applied to two separate areas known as, Jenkins Farm and Walls Farm. Research plots from the Jenkins farm area, established in 1989, are located in Preston County, West Virginia. Walls farm researches plots, located in northern West Virginia, were established 30+ years ago. These plots were amended with 12 in. of fly ash. Both A1 and A2 horizons were sampled from two separate research areas; in addition, the lower C2 horizon was sampled from site 1 of Walls farm. For the DNA microarray testing, we chose samples from the previously mined land in Virginia. One site consisted of material taken from the A horizon soil of

the biosolid, wet treatment (known as site 2). A sample of A horizon soil was also taken from a control site (site 7).

Microbial Methods -

Because the cloning and sequencing results compared to the TRLFP data indicated a higher diversity of fungi than expected, we decided to use this information in the construction of microarrays. Microarray technology allows the use of a high throughput system with the capability of gathering large amounts of data (Schena and Davis, 2000). The array used in our sets of experiments included the list of functional genes shown in Table 1 and additional genes included in Table 2. DNA was extracted from 2g soil samples (Hurt et al., 2001) and the 2µg bulk community DNA was labeled with Cy3 or Cy5 and hybridized on the arrays.

Table 1: Functional genes used on array for microbial community assessment of degraded lands

Genes	# of unique genes isolated in our lab	Total # of genes (the remainder are from the database)	% of genes with < 85% similarity	Total # of probes on array
amoA	65	275	15%	43
pmoA	10	99	5%	5
nirK	621	1020	37%	375
nirS	407	472	33%	156
nifH	483	662	41%	274
dsrAB	0	663	35%	233
Total	1587	3191	34%	1086

Table 2: List of other genes used on the array

Gene Category	# of Genes	Justification
18s Genes	32	Fungal identification
16s Genes	10	Positive controls
Yeast Genes	5	Negative Controls

Laboratory Leaching of Soil Amendments for Enhancing Carbon Sequestration

A series of experiments was designed to address public concern over the release of toxic metals from fly ash and biosolid amendments through laboratory column leaching procedures. We tested both type F and type C ash with a range of pH values (Table 3). The classes of fly ash are based on their chemical compositions and origins (specified in ASTM C618) (Stouraiti et al., 2001). Class F is produced from burning anthracite or bituminous coal and class C is produced from burning subbituminous coal and lignite. Class C also has cementitious properties and pozzolanic properties from the free lime (Stouraiti et al., 2001). Three of the western fly ash sources (Martin Lake, Cherokee #2, and Hayden) yielded F type ash and a source of eastern fly ash (TVA Paradise) was also a class F. One sample, Harrington consisted of Class

C. The soil used in the column leaching study was also from the TVA power plant in Paradise Kentucky (Table 3).

Table 3. Characteristics of materials used in leaching experiments.

Sample	***Class***	***pH***	***Other***
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	

The biosolid material used in the column leaching study was collected May 24, 2002 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 end, the sludge is near 95% solids.

Procedure for Hot Water Extraction s

An aliquot of 50 g of soil, fly ash material, and biosolids was added to 100 ml of de-ionized water in acid washed glassware. Each sample was covered with a watch glass and placed on a hot plate until boiling occurred. Samples were allowed to boil for 10 minutes and then removed. After five minutes of cooling, the samples were re-measured and the loss of weight from boiling was made up by adding de-ionized water (*Procedures based upon Gupta, 1967 and 1993; Gestring and Soltanpour, 1981; Odom 1980; and Soltanpur et al., 1995). Samples were then filtered with No. 42 Whatman filters and placed in appropriate vials for ICP-MS analysis on a Perkin Elmer Elan series.

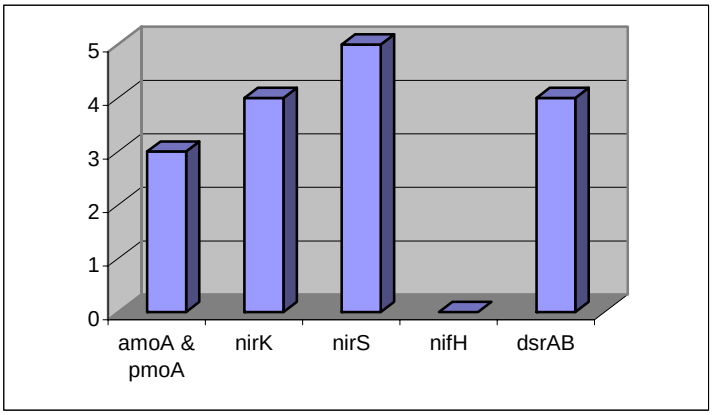
Soil Leaching Procedure

Columns were set up on ring stands (Figure 1). The bottom of the column was lined with glass wool to prevent sample loss. Soil, biosolids, and fly ash and mixtures of the materials were added to the columns. 100ml of 5mM $CaCl_2$ was slowly added and allowed to flow through the column Effluent was collected filtered through a 0.2um acrodisc filter and placed in vials for analysis on a Perkin Elmer 9000 Elan ICP-MS. All treatments included duplicate samples for each part of the leaching

Results

Community Data

Figure 1. Overlap between the 2 sites of the most dominate 5 genes in the class.



The array indicated both similarities and differences between the two sites based on the dominant types of the different functional genes (Figure 1). For example, none of the five most dominate types of nifH genes (nitrogen fixation) at the two sites were the same. However, all of the 5 most dominant nirS genes (nitrite reductase)at the two sites were the same. The other genes including the other type of nitrite reductase (nirK), sulfite reductase (dsrAB) and the combined amoA (ammonia monooxygenase) and pmoA (particulate methane monooxygenase) fell between these extremes.

The relative abundance of fungal communities determined by the array varied. However, information gathered from the sites was much more similar than the limited clone data indicated. For instance, from data gathered from the control site (100 clones) few of the 32 clones were observed (Table 4), while data gathered from the biosolid treated site (50 clones) determined that only 6 of the 32 clones were observed. However, for both sites, 32 of the 32 clones were observed on the microarray. We are examining cross reactivity issues but it also should be noted that the microarray method will potentially sample millions of genomes while the cloning technique only sampled 50-100 genomes per sample. This preliminary data indicates that it is feasible to detect functional genes (e.g., those associated with the potential for nitrous oxide emissions) and phylogenetic (fungi) genes on the same array.

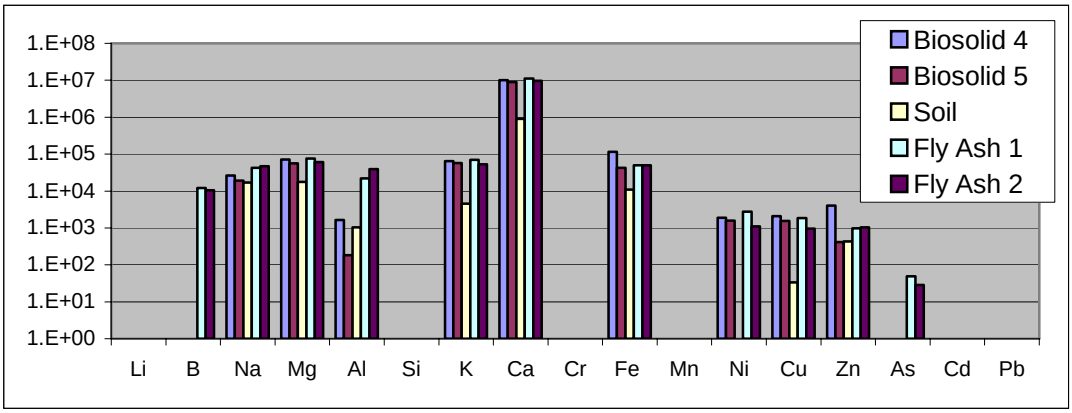
Table 4. Number of the 32 fungal clones on the array detected at the two sites using the cloning and sequencing method and the microarray method.

	Control site	Biosolid site
Cloning and Sequencing	12	6
Microarray analysis	32	32

Leaching Results

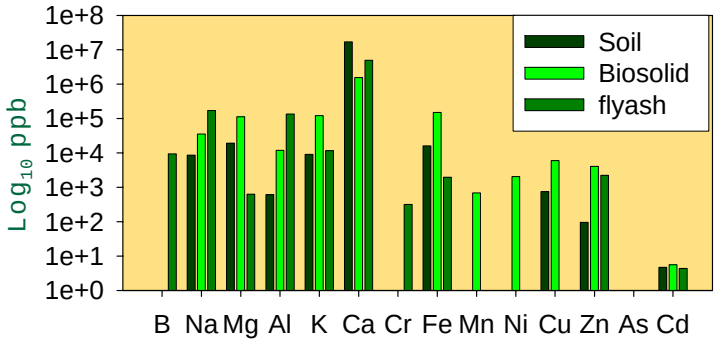
Several rounds of leaching experiments (e.g., Figure 2) were done on combinations of fly ash, biosolids, and mine soil and all indicated little evidence for substantial leaching of metals. At the high loading rates used, both biosolids and fly ash appeared to contribute to leaching of some metals such as Ni and (e.g., Figure 2). Only fly ash contributed to the leaching of B and As. No Cr, Cd or Pb were observed in any of the treatments.

Figure 2. Leaching of columns 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).



Differences in the presence and concentrations of the metals in the extracts between those from the column experiments and from the fly ash extractions (e.g., Figure 3) may indicate the influence of the soil and biosolids in adsorption of specific elements. For example, Cr was detectable in column extracts (Figure 3), and in both hot water and acid extracts of the fly ash (data not shown) but were not detected in

Figure 3. Concentrations of elements in leachates from column extractions of individual materials.



experiments where the fly ash was combined with soil and biosolids. Although Si was detected in the hot water extracts of the fly ash it was not evident in the extracts from experiments where the fly ash was combined with soil and biosolids. Also, although Pb, and Cd were present in the acid extracts of the fly ash they also were not evident in the extracts from the columns with fly ash, soil, and biosolids.

It was also determined that the addition of the phosphate fertilizer (light blue) mixed with the fly ash and soil resulted in a shift in the composition of leachates, most notably B, Al, Cr, Cu, and Cd (data not show). Results from the time course experiment showed that leachate from the column samples that were allowed to sit for two weeks contained higher amounts of B, As, and Cd (data not shown).

Table 5. Concentrations of light elements in extracts of different fly ash samples.

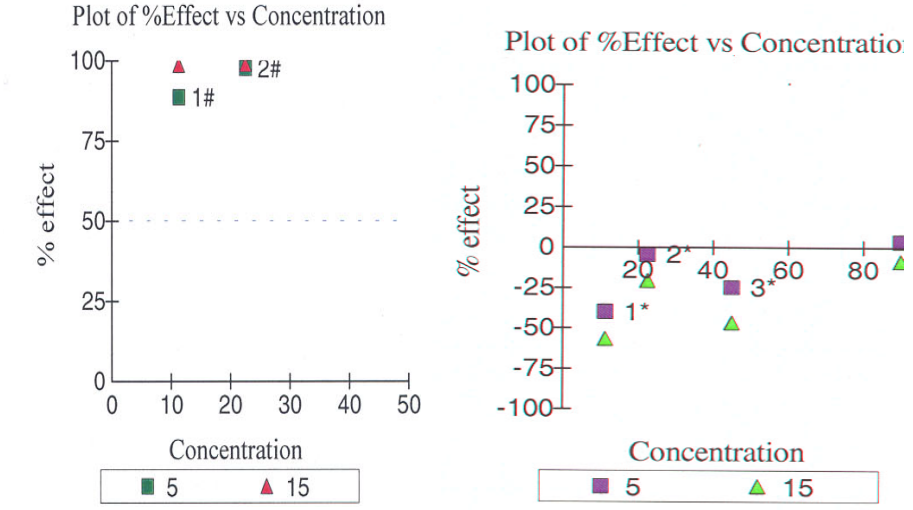
Sample	B (ppb)	Na (ppb)	Al (ppb)
TVA	0	16,521	36
Hayden	25,042	57,183	1,740
Cherokee	5,085	27,488	8,491
Harrington	3,794	63,832	120,189
Martin Lake	22,335	57,941	23,756

Although potentially toxic metals can be leached from the fly ash, for many of the most toxic elements leached the concentrations were very low. It was also evident from the extraction studies that the TVA fly ash was considerably different that the western fly ash in that the pH was much lower (Table 1) and the concentrations of light elements was also lower (Table 5). 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).

Microtox Results

Results taken from the simulated weathering or leaching were examined using the Microtox system, a standard biosensor-based measurement technique for toxicity testing of

Figure 4: Results from positive control (0.11 ppb multi-element standard) to the 40% biosolid treatment indicate 0% toxicity effect for 5 and 15 minute microtox readings.



water and soil. Replicate samples taken from the column-leaching experiments, fly ash blanks from all 5 sources, and a biosolid blank were run to determine the toxicity response *of Vibrio fischeri*, a luminescent bacteria. Additionally, positive controls including a multi-element standard (Perkin Elmer, Shelton, CT) containing Al, As, Ba, Be, Bi, Cd, Co, Cr, Cs, Cu, Fe, Ga, Li, Ni, Pb, Rb, Se, Ag, Si, Ti, V, Zn and a biosolid blank were run. Results from the column-leaching experiment did not result in any detectable toxicity (Figure 4).

Summary and Conclusions

Data acquired from the developed microarray yielded both phylogenetic and functional information that may help us establish the relationships among the microbial community and the prospect for carbon sequestration. The microarray techniques appeared to represent significantly more of the community than did cloning. In the next stage of the microbial community study, we plan to run arrays on more of the samples collected from the previously mined sites located in Virginia and West Virginia. We also plan to include an array designed to measure functional aspects of carbon metabolism.

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 $CaCl_2$ rather than groundwater that may represent a worst case scenario. Toxicity testing indicated that any toxic response resulting from exposure to the leachate was below detection limits, as measured by the Microtox© system.

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Acknowledgements

This research is sponsored by the U.S. Department of Energy, Office of Fossil Energy and DOE National Energy Technology Laboratory (NETL). Oak Ridge National Laboratory is managed by the University of Tennessee-Battelle, LLC, for the U.S. Department of Energy under contract DE-AC05-00OR22725.