Issues With the Use of Fly Ash for Carbon Sequestration

Anthony V. Palumbo, L. Suzanne Fisher, Jana R. Tarver, W. Lee Daniels, Zamin Yang, Sonia M. Tiquia, Lee Wu, Jizhong Zhou, and Jim Amonette

Environmental Sciences Division,
Oak Ridge National Laboratory,
Oak Ridge, TN

Introduction:

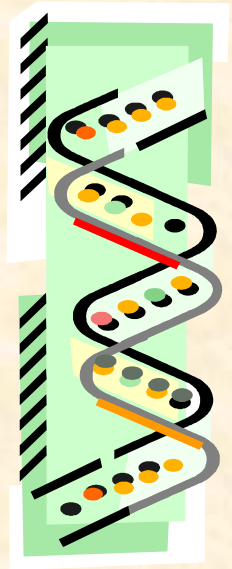
- To determine the potential for carbon sequestration in degraded mine lands, we have been examining carbon content of reclaimed mine soils at > 15 years post reclamation.
- We have found that fly ash and biosolids amendments during reclamation appear to result in higher carbon levels
- What are the issues associated with the use of these amendments?

Issues Addressed

- Are specific microbial communities associated with higher C sequestration or potential release of other greenhouse gases e.g., nitrous oxide as a result of the amendments?
- Is there potential for leaching of metals from the amendments?
- Are there other amendments that could be used to reduce the potential for problems with other greenhouse gases or leaching?
- Are there toxicity indications from the leachate?

Microbial communities, Sequestration, and Potential Nitrous Oxide Emissions

- Low Specificity Methods (will not present details)
  - TRLFP – indicates much lower diversity of fungal species that would be expected of bacterial species
  - PLFA – indicates that at some sites high microbial biomass is associated with high C and N in the soil
- High Specificity Methods
  - Cloning and sequencing – indicates higher diversity of fungi than expected based on TRLFP and ***gives information used in construction of microarrays***
  - Microarrays – preliminary indicates that is feasible to detect functional genes (e.g, those associated with the potential for nitrous oxide emissions) and phylogenetic (fungi) genes on same array



Array used in these experiments

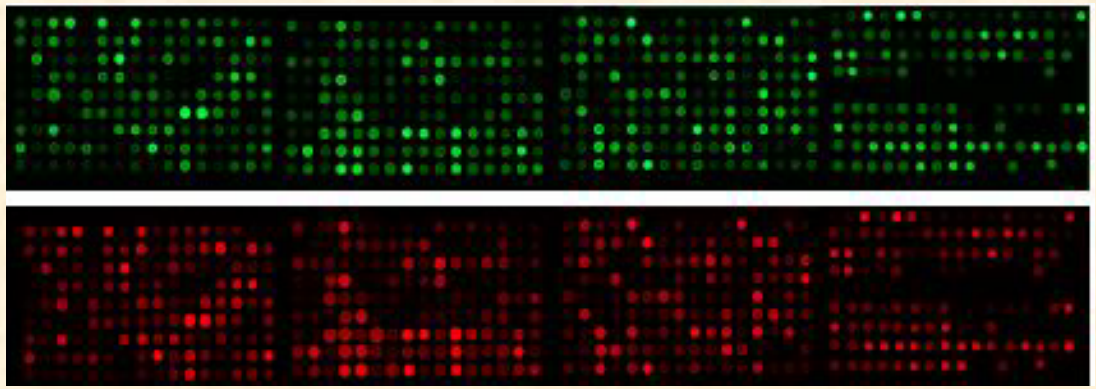
- 1086 - 50 mer oligos for functional genes
  - Based on the analysis of 3191 gene sequences
  - primarily nitrogen cycle genes
    - e.g., nirS genes, nirK genes, amoA genes, nifH,
    - High and diverse nirS and nirK could indicate potential for nitrous oxide generation via denitrification
  - Other funcitonal gens - dsrAB, pmoA , genes
- 16S genes:
  - 10, positive controls
- Yeast genes:
  - 5, negative controls
- 18S genes: 32 specific fungal species
  - Many of the most prevalent and randomly selected representatives of the least prevalent based on cloning

DNA Microarray Testing

- **Array used on**
  - **Site 2 - A horizon, Biosolids, Wet treatment**
  - **Site 7 - A horizon, Control**
- **DNA was extracted from 2 g soil sample**
- **2 µg bulk community DNA was labeled with Cy3 or Cy5 and hybridized on the arrays**

Cy3

Cy5



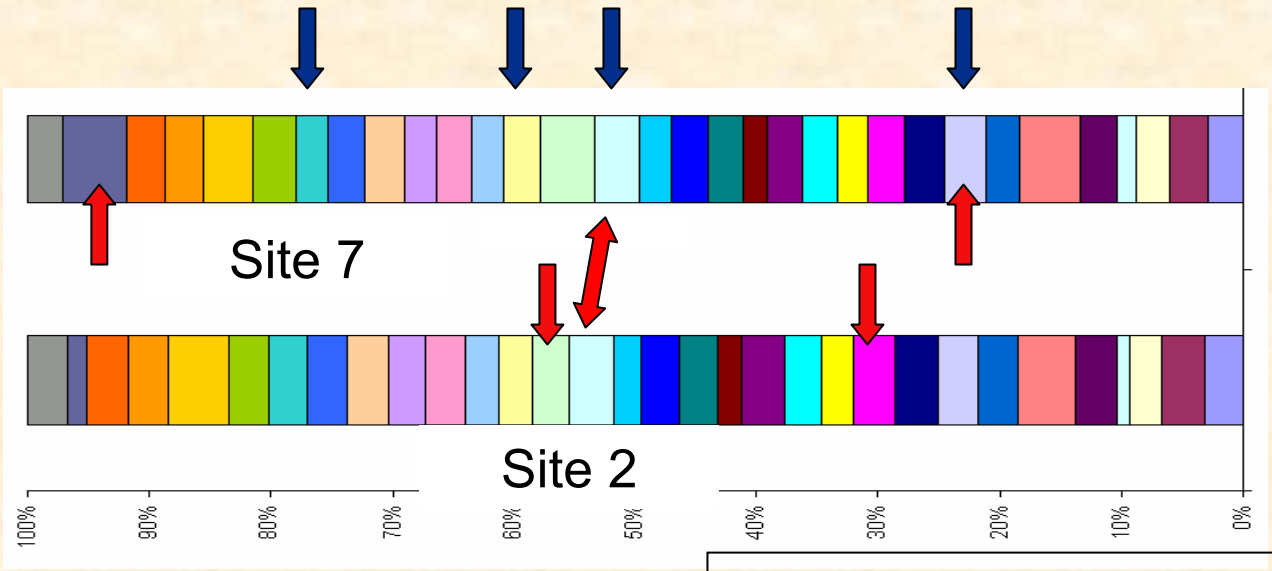
- A portion of two arrays showing reproducibility with the different dyes

Functional Genes on Array

Genes	# of unique genes isolated in our lab	Total # of genes (the remainder are from the database)	% genes with < 85% similarity	Total # of probes	Number of probes (of the top 5 in abundance) in common at 2 site
*amo*A	65	275	15%	43	3
*pmo*A	10	99	5%	5	
*nir*K	621	1020	37%	375	4
*nir*S	407	472	33%	156	5
*nif*H	483	662	41%	274	0
*dsr*AB	0	663	35%	233	4
Total	1587	3191	34%	1086	

Phylogentic Indicators on the Array

- Variations in abundance are evident
- But sites are much more similar than limited clone data indicated
  - For site 7 (100 clones) only 12 of these 32 clones were observed
  - For site 2 (50 clones) only 6 of these 32 clones were observed
- **For both sites 32 of 32 were observed on the array**
  - **Cross reactivity is being characterized**



4 most common clones across all sites

most common clones at these two sites

Each color represents the signal intensity for one of the 32 species – data normalized to 100% for each sample

Leaching Studies

- Column and batch leaching experiments were designed to examine
  - variation in leaching from different sources of fly ash
  - the leaching of metals under mild environmentally relevant conditions
  - variability of leaching with regard mixtures and amendments amendments
- Treatment combinations were added to a 10 in^3 volume column and 100ml of 5mM calcium chloride was slowly added to dried material
- Leachate from all tests were collected, filtered, and analyzed on a Perkin Elmer 9000 Elan ICP-MS

Leaching columns were set up on ring stands and the bottom of the column was lined with glass wool to prevent sample loss. Elution time ~5-10 minutes.

Leaching Treatments

Mixtures of Fly ash, soil, and biosolids

Several Rounds of Leaching experiments

- Separate components
  - Soil – TVA paradise site
  - Fly Ash
    - 5 sources
  - Biosolids
    - Oak Ridge Sewage Treatment plant
- Mixtures
  - Fly ash (0-20%)
  - Biosolids (20-30%)
  - Soil (50% - 90%)
- Mixtures with high phosphate fertilizer

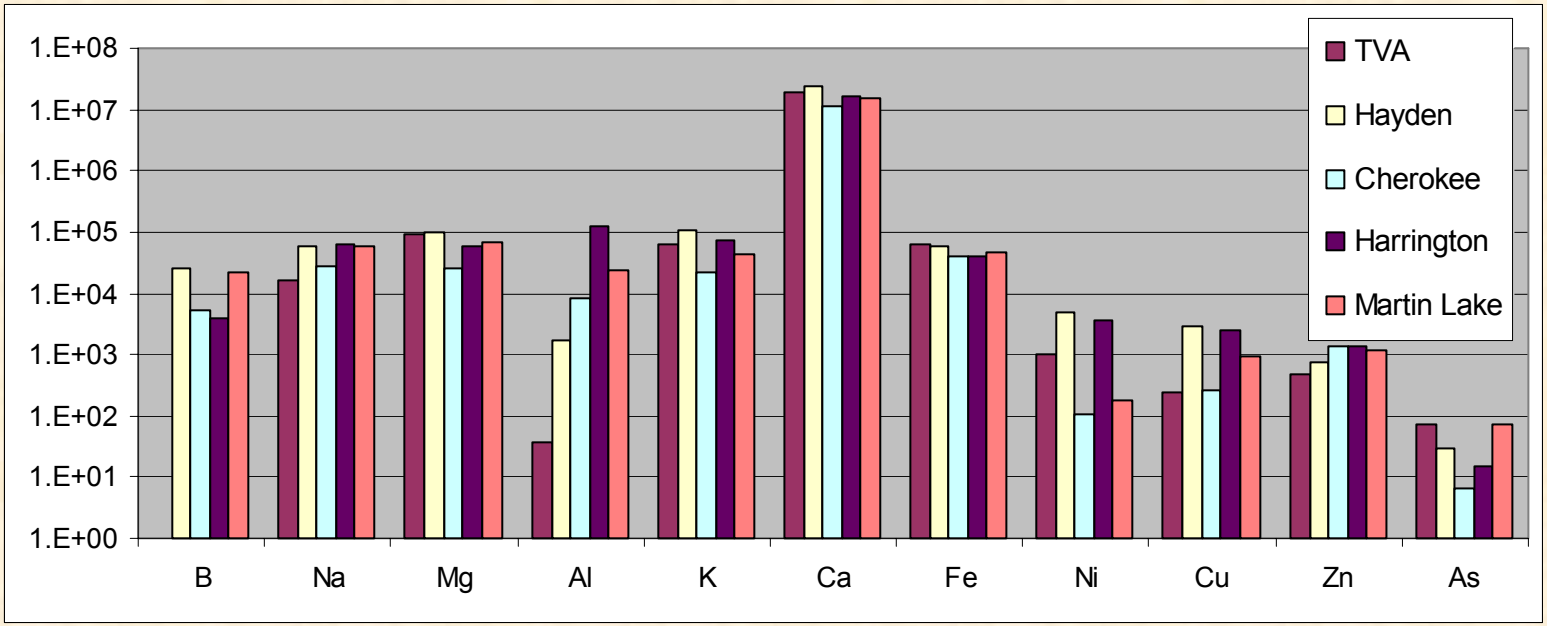
Leaching Studies - Cautions

In many ways the conditions in the experiments e.g.,

- **Loading rates of fly ash and biosolids**
- **Use of $CaCl_2$ instead of natural groundwater**
- **Poor starting soil**

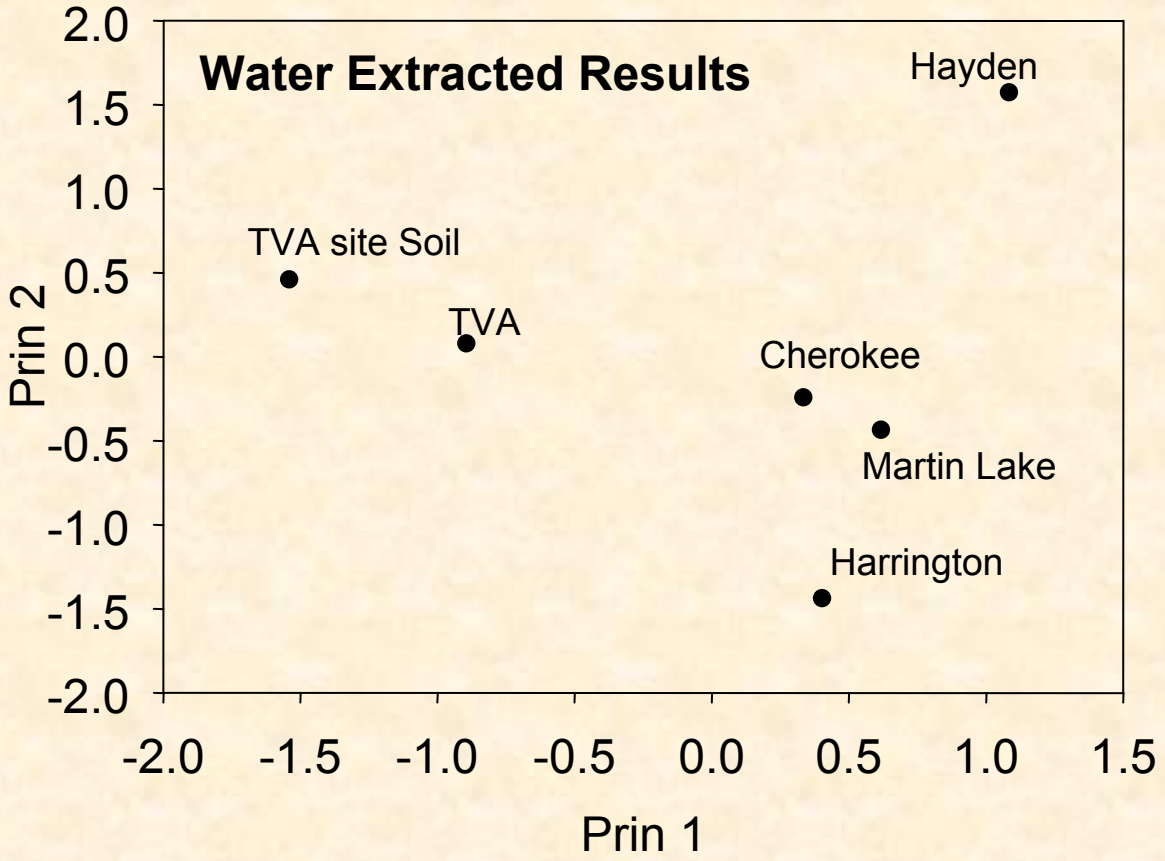
Will tend to maximize leaching thus these can be considered worst case scenarios

Different Sources of Fly Ash (hot water extraction)



- TVA – little leaching of B & other light elements
- Cherokee less leaching of many metals (Ni, Cu,As)
- In General - Similarities? Differences? → PCA

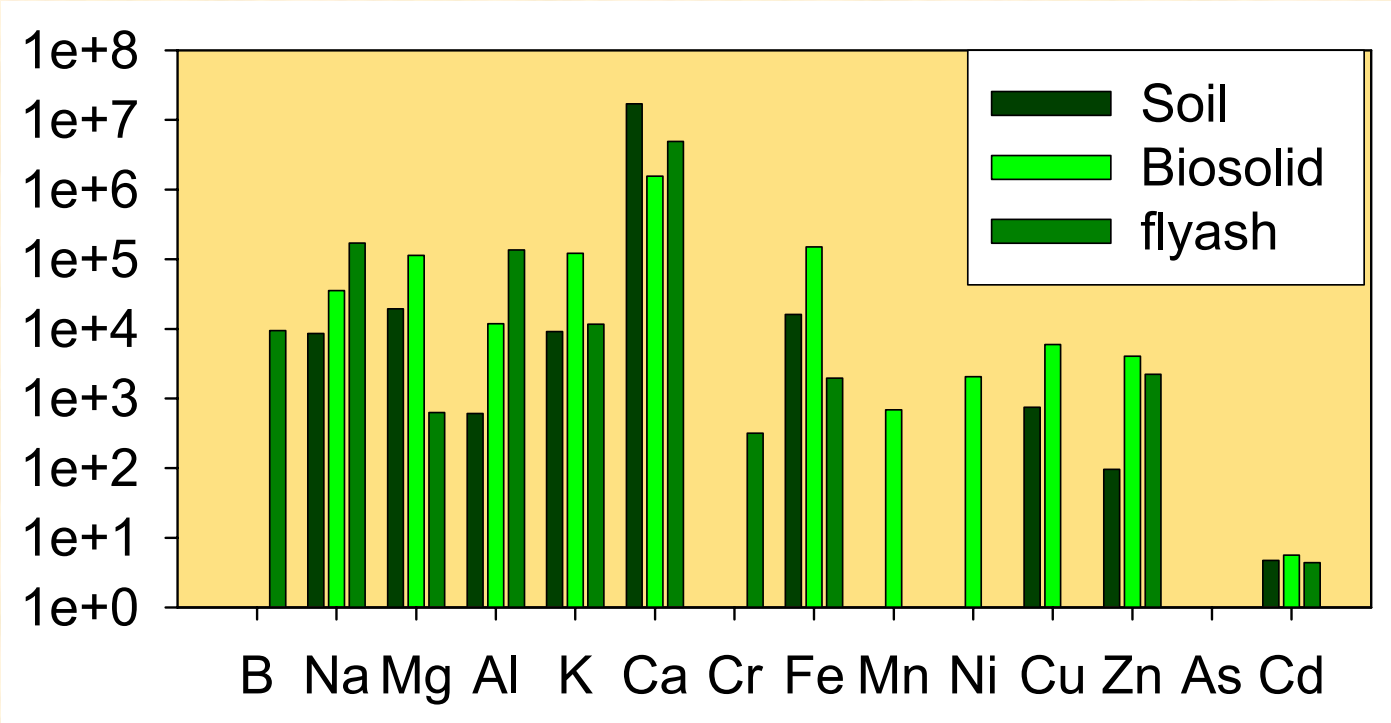
Differences in Patterns of Leaching of Fly Ash from Different Sources as Indicated by PCA analysis



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	

Fly ash class, pH and mixing with FGD all appear to influence patterns of composition of leachates

Comparison of leaching from fly ash to biosolids and soil

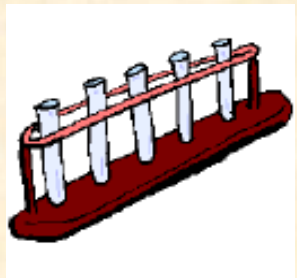


- **Biosolids – Zn,Cu,Ni,Mn,Cd**
- **Fly Ash* – B, Al, Cr, Zn**
- **Soil – Zn, Cd,**

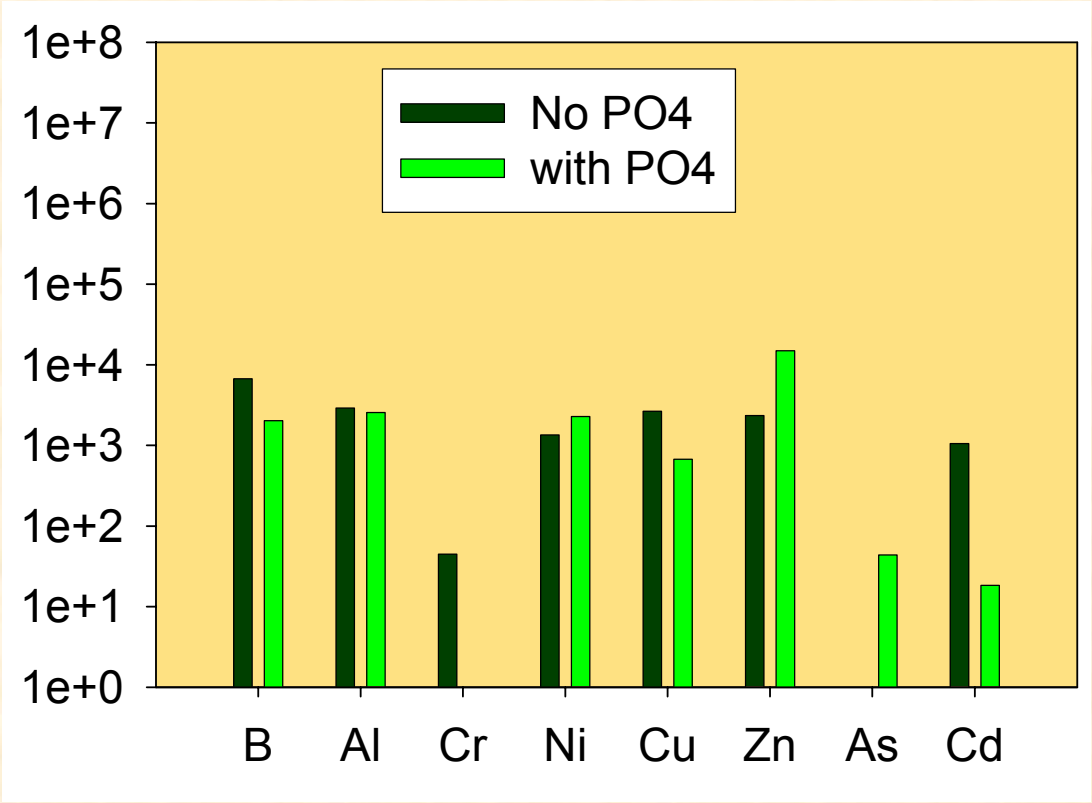
Is addition of biosolids worthwhile given their contribution to metal leaching?

Effects of Other Amendments (phosphate)

- Phosphate can form very insoluble compounds with many metals thus it could potentially reduce leaching of metals from applications of fly ash and biosolids
- A third round of testing included a time course leaching experiment, incorporating treatment 6 (10% fly ash, 40% biosolid, 50% soil, and 3.3% phosphate fertilizer)
- 20ml of millipore water was added to the 1st set of duplicate samples and allowed to sit over night before leachate collection. The solid material was refrigerated and after a period of two weeks re-ran on the leaching column
- The second duplicate was mixed with 20ml of millipore water, refrigerated, and allowed to sit over the two week period before leaching



Leaching* – Effect of Phosphate



* Data shown is limited to potentially toxic elements - 10% fly ash, 40% biosolids, 50% soils

- **Both declines and increases observed with dry phosphate fertilizer application**
- **Need more studies with application of dissolved PO4 and different concentrations of PO4**

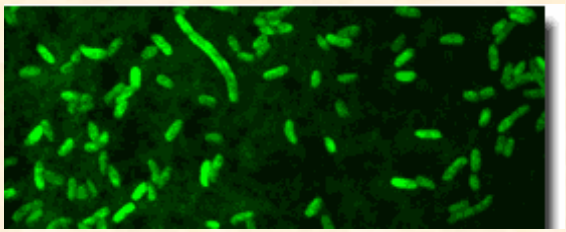
Toxicity Measurement Methods

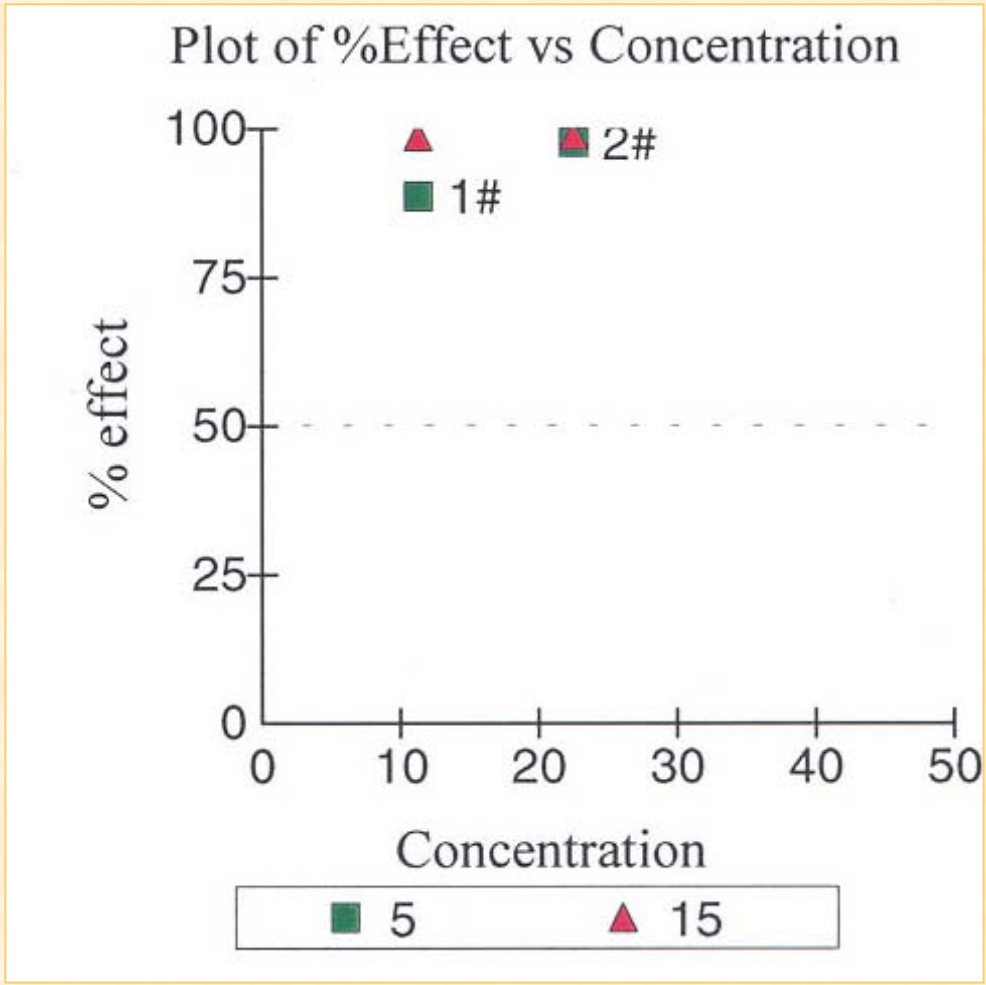
- Microtox-standard biosensor-based measurement technique for toxicity testing of water, soil, and sediments
- Luminescent bacteria *Vibrio fischeri* NRRL-11177 exposed to samples, toxicity is measured by the decreased rate of luminescence
- Treatments included
  - **Positive control**
  - **Replicate samples from treatments 1-5 of column leaching experiment (mixtures)**
  - **Leachate from 100% fly ash, and**
  - **Leachate from 100% biosolids**

Fly Ash from five different sources were tested (TVA Paradise, Hayden, Cherokee, Harrington, and Martin Lake).

Positive Control

- 0.11 ppb 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
- Toxicity (EC50) demonstrated

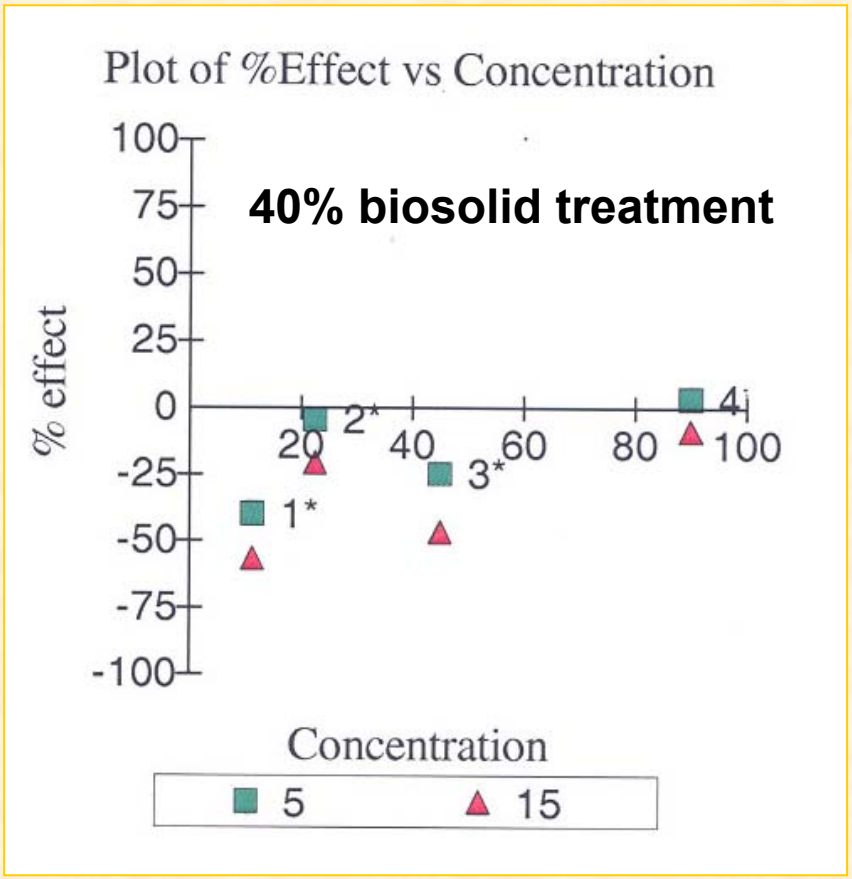


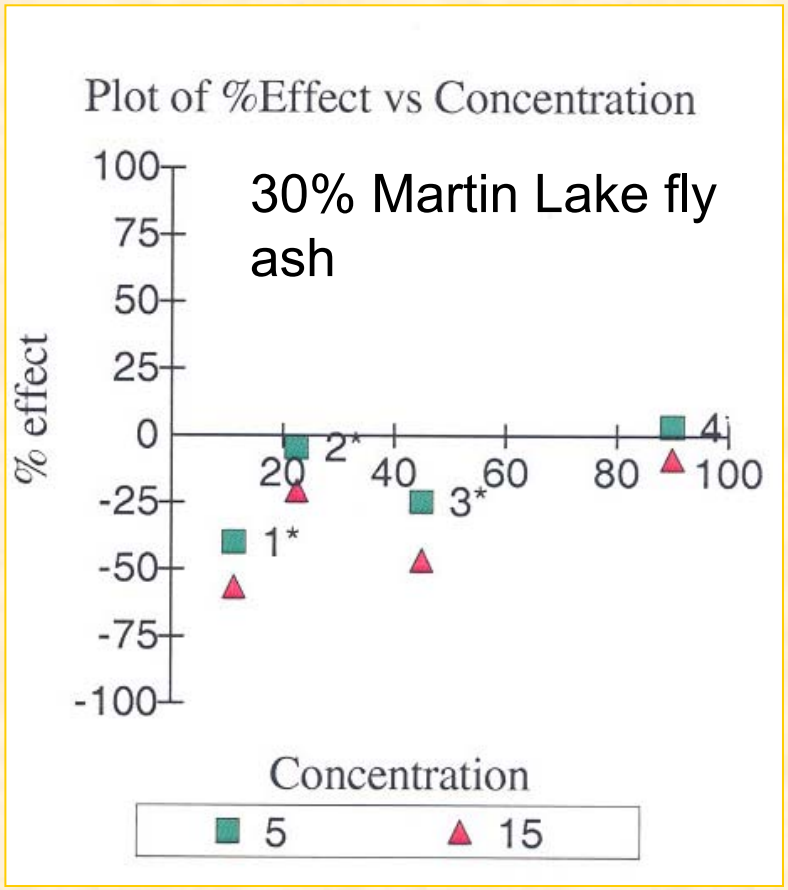


No Toxicity Detected in Leachates

Typical results from the column leaching experimental treatments (two treatments shown)

→NO detectable levels of toxicity (as measured by Microtox)





Summary

- **Microarrays**
  - **yield both phylogenetic and functional information that may help us better establish the relationships among the microbial community and the carbon sequestration – appeared to represent significantly more of the community than did the cloning**
  - **In the next stage of the study, we will run arrays on more of the sites, and include an array designed to measure functional aspects of carbon metabolism.**
- **Leaching**
  - **There are differences among fly ash samples but all leach very small amounts of metals when mixed with soil**
- **Toxicity**
  - **Any toxicity in the leachates is below detection limits as measured by the microtox system**

Acknowledgments

We thank the DOE Office of Fossil Energy through the National Energy Technology Laboratory (Program manager - Lynn Brickett) for providing funding for this project.

Kickapoo State Park today illustrates the recreation potential of mine reclamation areas*.

Kickapoo strip mine in the early 20th century*.

*Illinois State Geological Survey