Fifth Annual Conference on Carbon Capture & Sequestration

Steps Toward Deployment

Terrestrial Sequestration

Fly Ash Characteristics and Carbon Sequestration Potential

Anthony V. Palumbo (presenter), James E. Amonette*, Jana R. Tarver,

Lisa A. Fagan and Meghan S. McNeilly

Oak Ridge National Laboratory, *Pacific Northwest National Laboratory

May 8-11, 2006 • Hilton Alexandria Mark Center • Alexandria, Virginia

Introduction:

The overall goal of the project was to examine the use of fly ash in promoting carbon sequestration in association with coal mine reclamation

Approach

- **Retrospective studies of carbon accumulation on reclaimed mine lands**
    - **Leaching studies of fly ash**
    - **Carbon Sorption studies of fly ash**

Associated project by Jim Amonette at PNNL

- **Mechanisms of carbon sequestration**

Kickapoo strip mine in the early 20th Century *Illinois State Geological Survey

Summary of Previous Results

- **Our previous studies have shown that**
  - **fly ash may increase carbon sequestration in reclaimed mine soils with**
  - **minimum potential for leaching of toxic metals**
  - **Toxicity of leachates is very low**
- **Summaries of these results are presented below**
- **New Results**
  - **Additional leachate data on high vs low ammonia fly ash**
  - **Carbon sorption properties of fly ash**

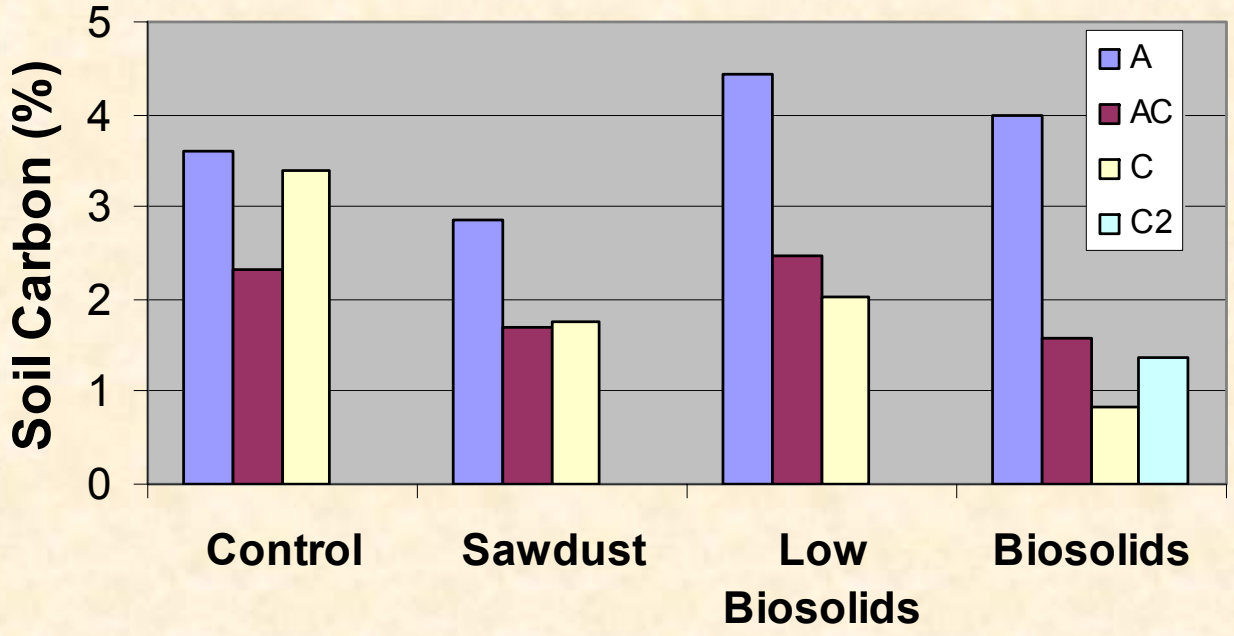
Sites of Retrospective Studies

- Wise County, VA
  - Control
  - Sawdust
  - Biosolids
- Morgantown, WVA - Jenkins and Walls Farm
  - Control
  - Sawdust and Fly Ash
  - Fly Ash
- Studies done with Lee Daniels of Va. Tech

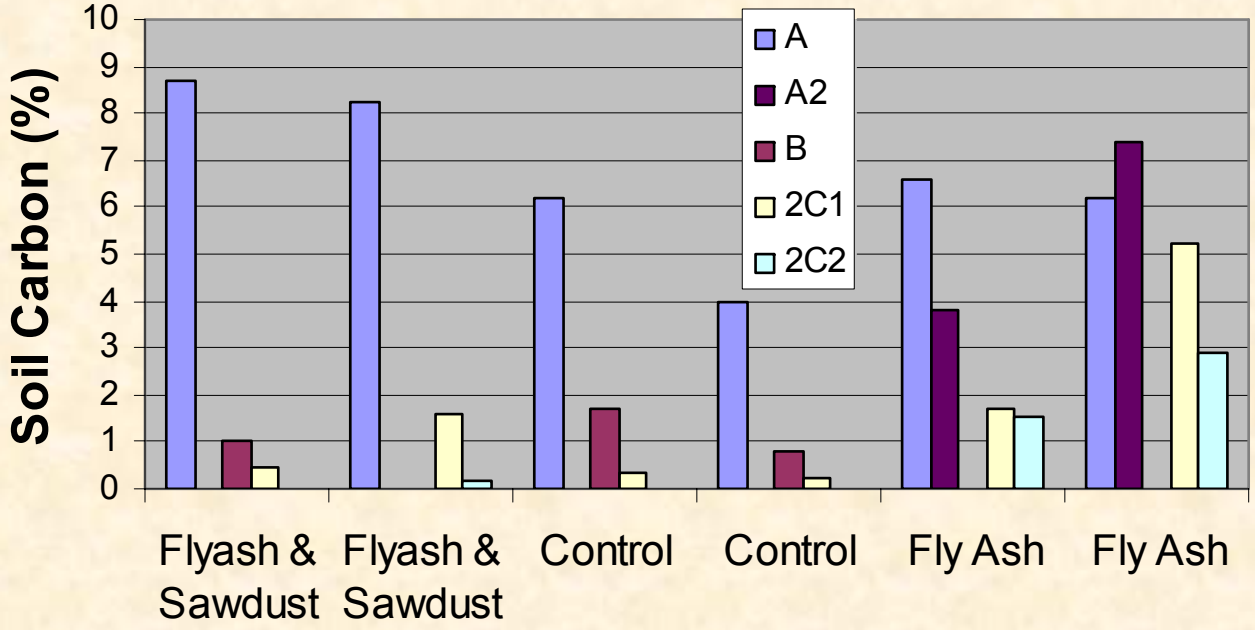
An example of a soil profile showing development of carbon rich layers

Effect of Organic Amendments on Soil Carbon – Wise County

- **The control and the low biosolid treatments increased over time in the A horizon**
- **Also, no apparent lasting effect of sawdust**



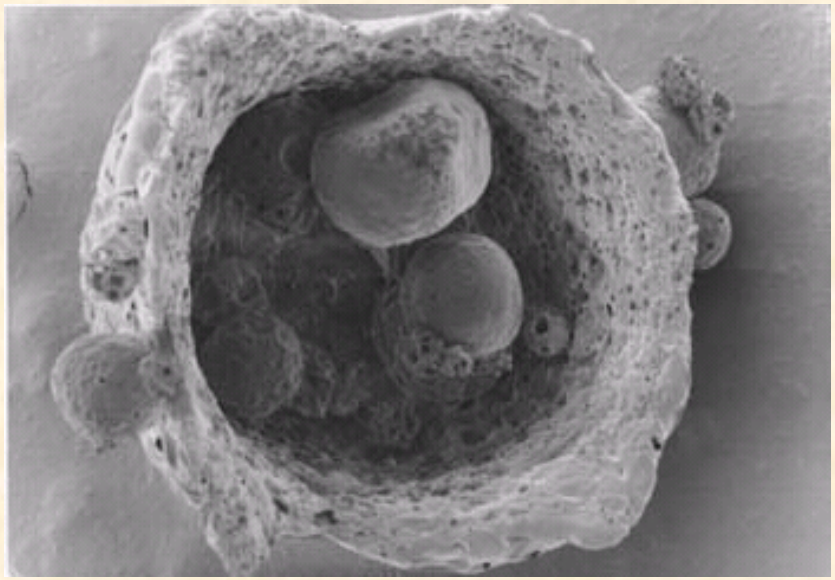
Effect of Fly Ash Amendments on Soil Carbon -Morgantown, WVA



- **Greater accumulating in fly ash amended soils**
- **In 12 years significant soil carbon developed in these "new" surface soils**

Leaching Issues

- **What is the potential for leaching of heavy metals from fly ash?**
- **Does the potential for leaching of metals change with ammonia content, pH, fly ash class?**
- **Are there indications of toxicity from the leachate?**
- **Does leaching vary with high ammonia content?**



SEM of Fly Ash

Leaching Experiments

- **Column Experiments**
  - **100ml of 5mM calcium chloride was slowly added to dried material**
- **Batch Experiments**
  - **fly ash types and two soils**
  - **10 g of fly ash was mixed with 100 ml of 5mM $CaCl_2$**
- **Acid Extraction (data not shown)**
  - **fly ash types and three soils**
- **Leachate from all tests was collected, filtered, and analyzed on a Perkin Elmer 9000 Elan ICP-MS**

Leaching Summary and Example

- **With respect to metal leaching characteristics, we observed that mixing fly ash with soil and phosphate fertilizer significantly decreased Cr, Li, Pb, and Cd in the leachate.**
- **Example with High ammonia fly ash mixed with soil**

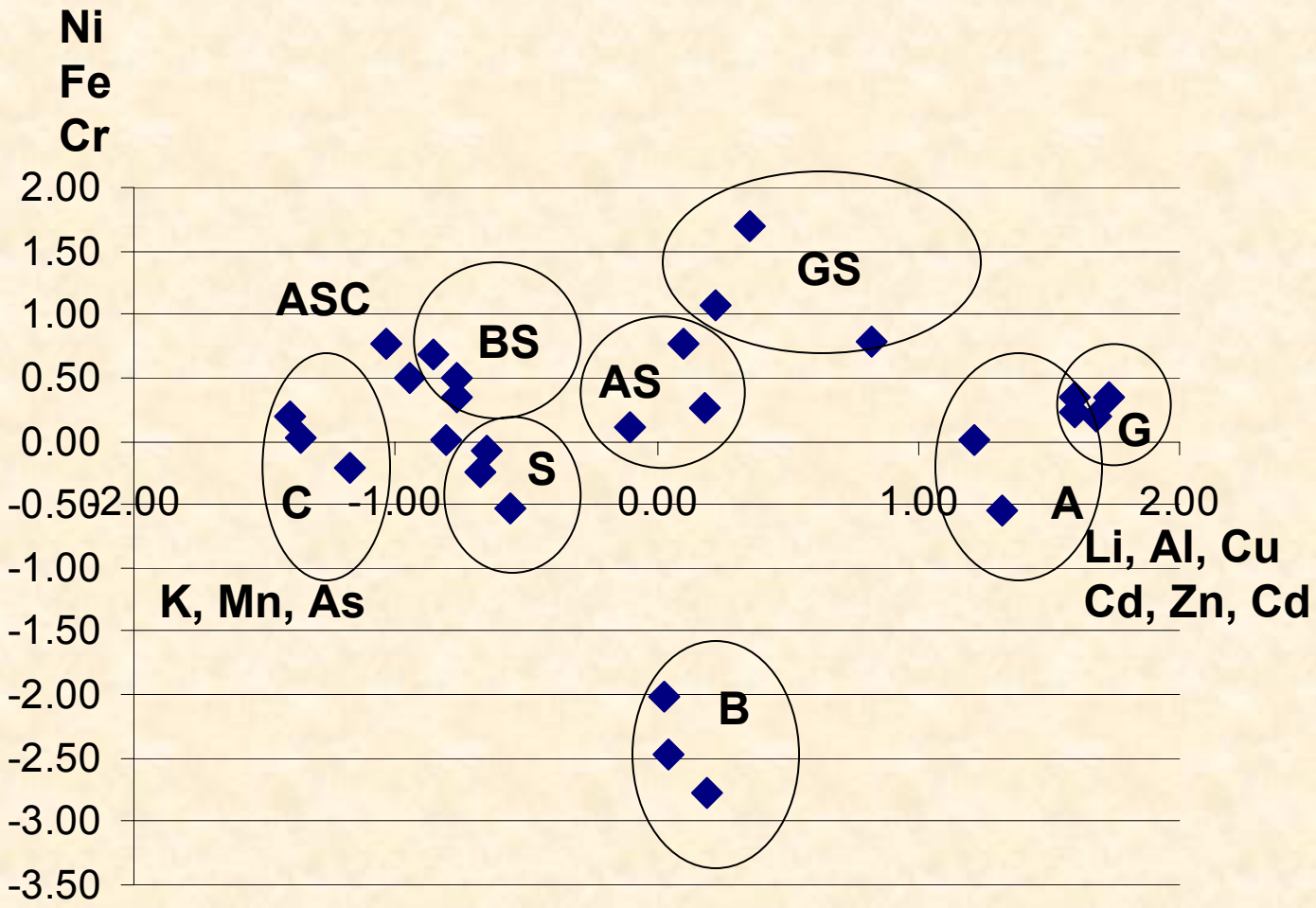
Fly Ash	Ammonia	pH
B	22.5	10
G	8.69	4.72
A	3.12	4.3
Soil		6.55

Leaching of High Ammonia Fly Ash Mixed with Soil

Treat	Fly Ash	Soil	Coal
A	10.0	0.0	0.0
A + S	7.5	2.5	
A + S +C	5.0	2.5	2.5
B	10.0		
B + S	7.5	2.5	
C	10.0		
G	10.0		
G + S	7.5	2.5	
S			10.0

PCA Results

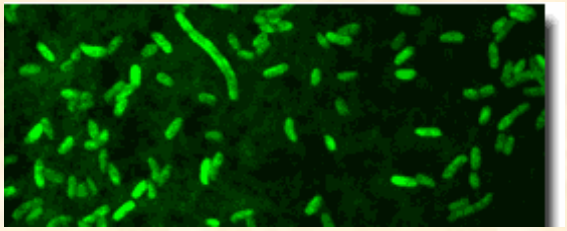
- **Samples clustered by Fly Ash type**
- **Mixtures have less leaching of Cd, Zn, etc**



Toxicity Measurement Methods

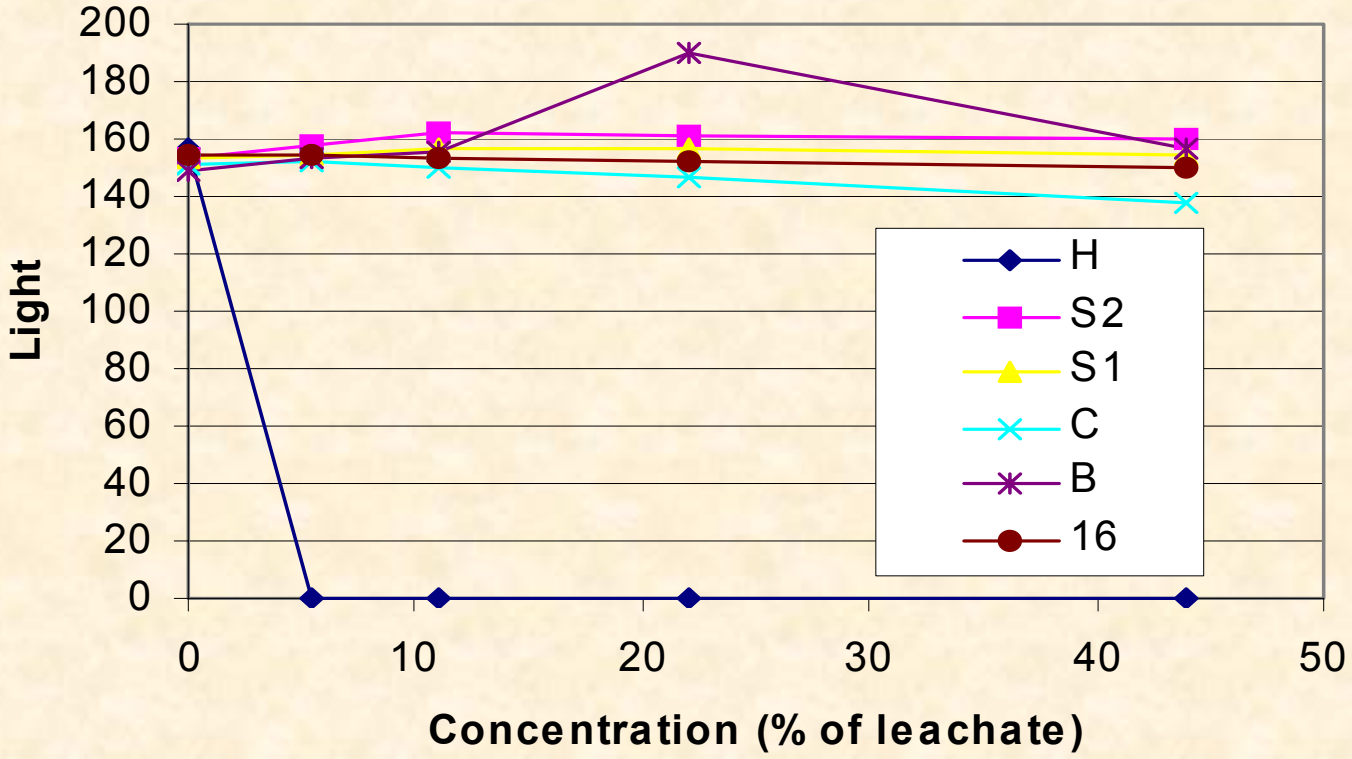
- **Microtox-standard biosensor-based measurement technique for toxicity testing of water, soil, and sediments**
- **Luminescent bacteria *Vibrio fischeri* NRRL-11177 exposed to samples, toxicity is measured by the decreased rate of luminescence**
- **Treatments included**
  - **Positive control**
  - **Leachate from 100% fly ash**

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



No Toxicity Detected in Batch Leachates except highest pH sample

- **Only toxicity is in highest pH sample (H)**
- **No toxicity in highest Ammonia sample (C)**
- **Neutralization of the leachate from this fly ash eliminated the toxicity**

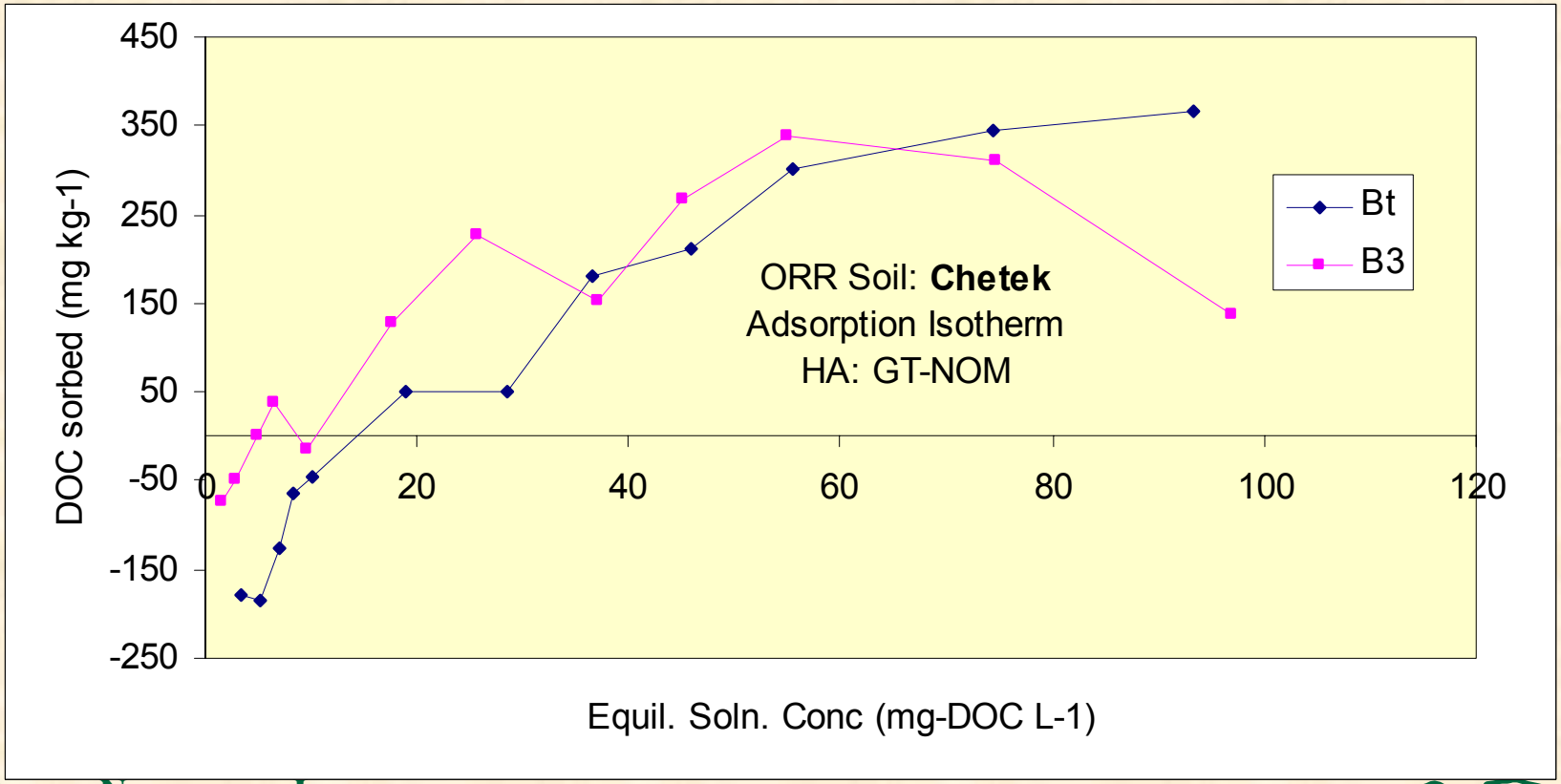


Carbon Sorption Studies

- **Equilibrium Isotherms in Batch**
- **These fly ashes originated from systems with NOx removal equipment and had pHs ranging from 3.7 to 12.4.**
- **Added humic acid (0 to 100 mg C/L)**
  - **30 ml solution**
- **0.5 g soil**

DOC Sorption to Soil

- **Examination of over 60 soils collected for other projects (P. Jardine, J. Tarver) gave peak sorption of**
  - **no greater than 2000 mg/kg and**
  - **most between 200 and 1000 mg/kg**

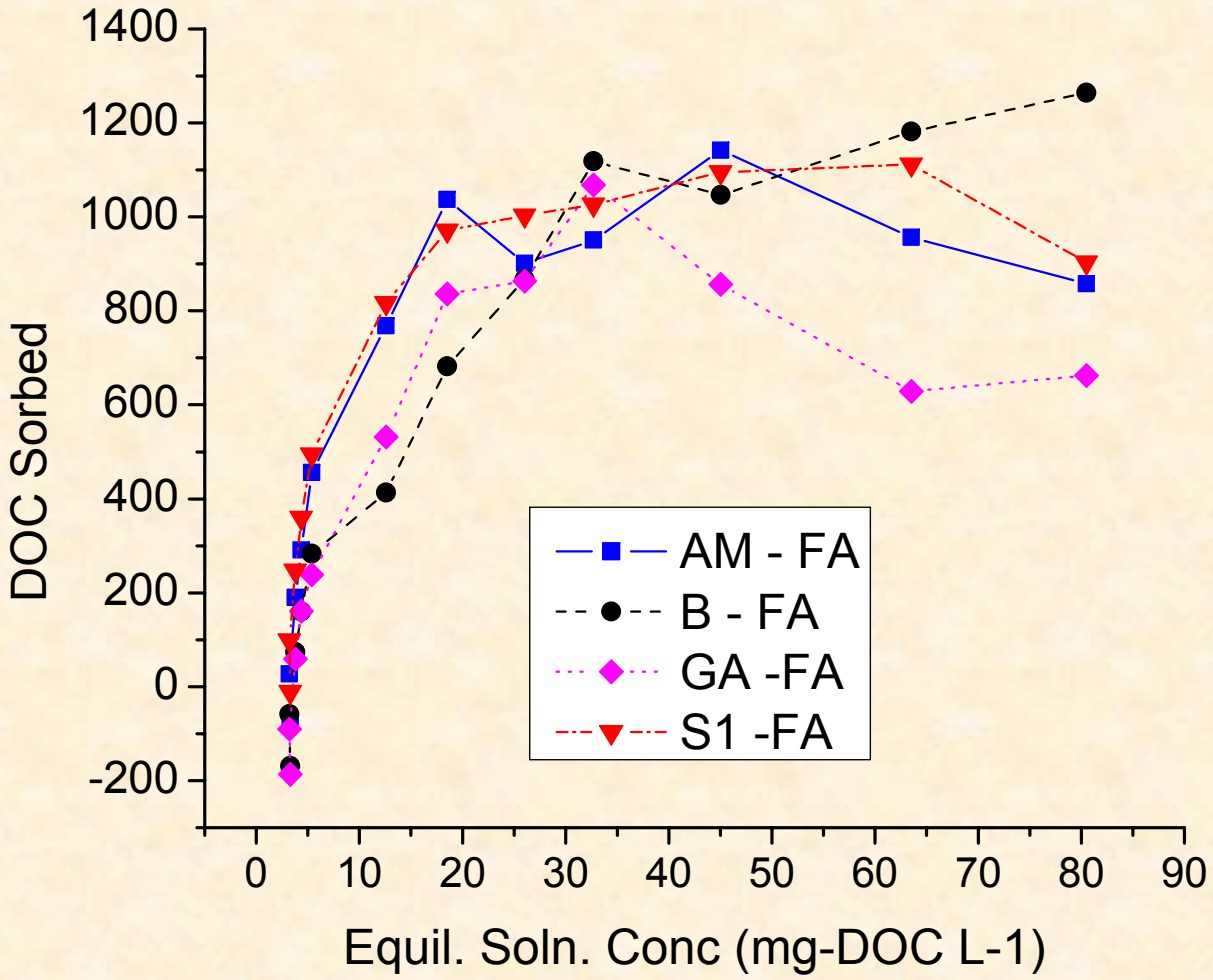


Fly Ash Samples for Carbon Sorption Studies

Sample	pH	LOI	Final pH
S2	4.13	10	5.50
Co	4.24	10	7.70
Am	4.48	2.3	6.25
S1	4.53	10	6.99
Ga	4.76	2.3	8.08
T	7.03	3	7.80
Bo	8.37	2	8.73
Ch	11.04	7.5	8.71
Ma	11.65	0.5	9.33
Ha	12.37	3.3	10.32

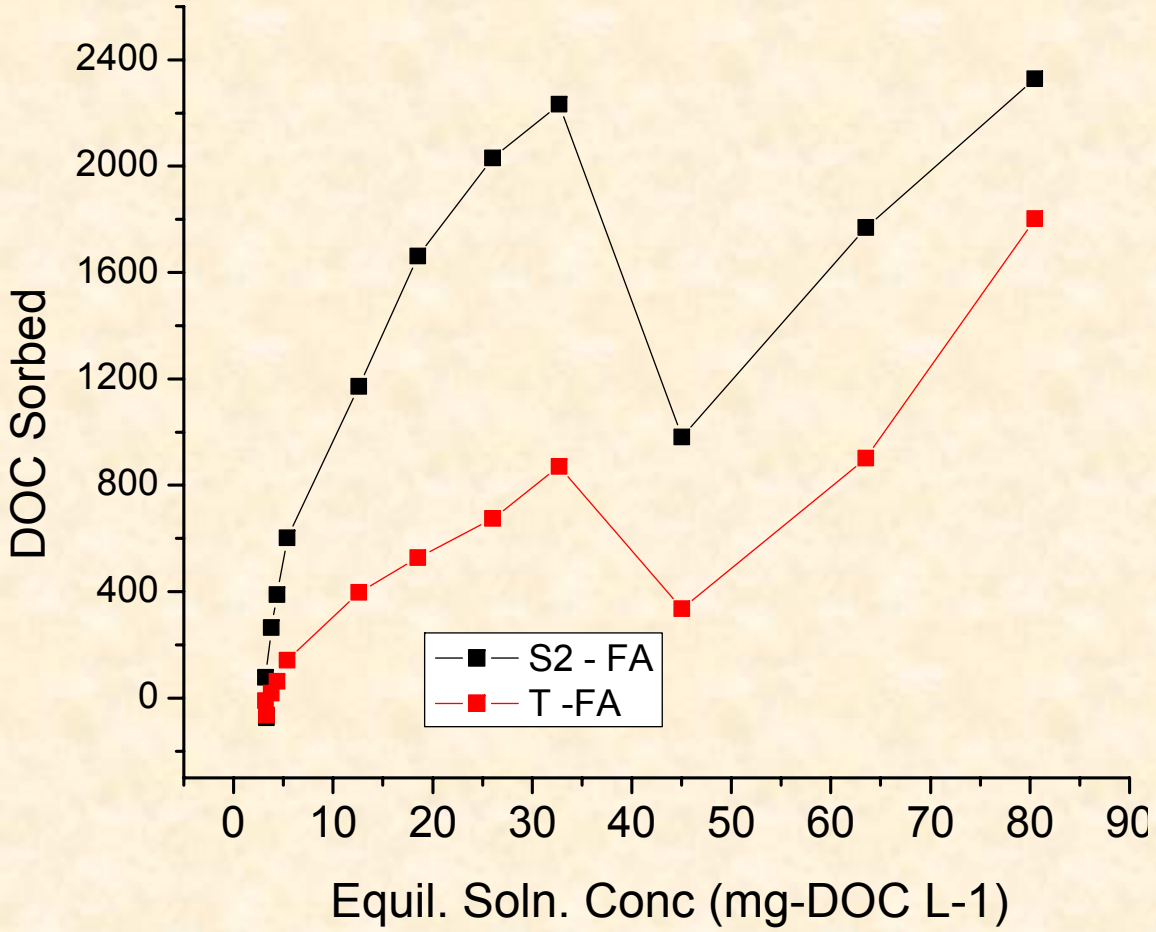
Low Sorption Fly Ash

- **Mean Peak sorption is 1146 mg/C kg^{-1}**
- **Mean pH is 5.53**
- **Mean LOI is 4.15 %**



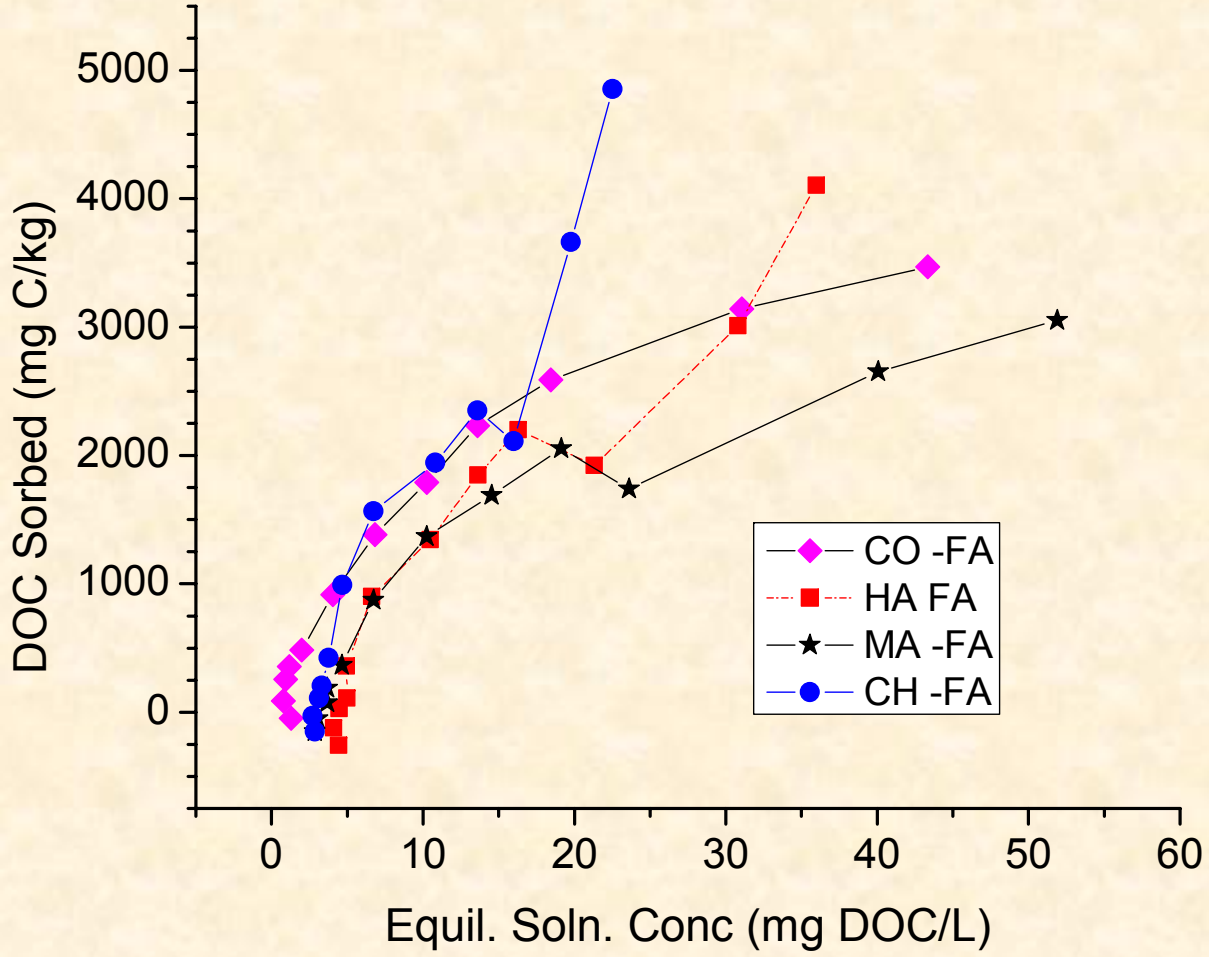
Medium Sorption Fly Ash

- **Mean Peak sorption is 2065 mg-C kg^{-1}**
- **Mean pH is 5.58**
- **Mean LOI is 6.5%**



High Sorption Fly Ash

- **Mean Peak sorption is 3870 mg-C kg^{-1}**
- **Mean pH 9.825**
- **Mean LOI 5.325**

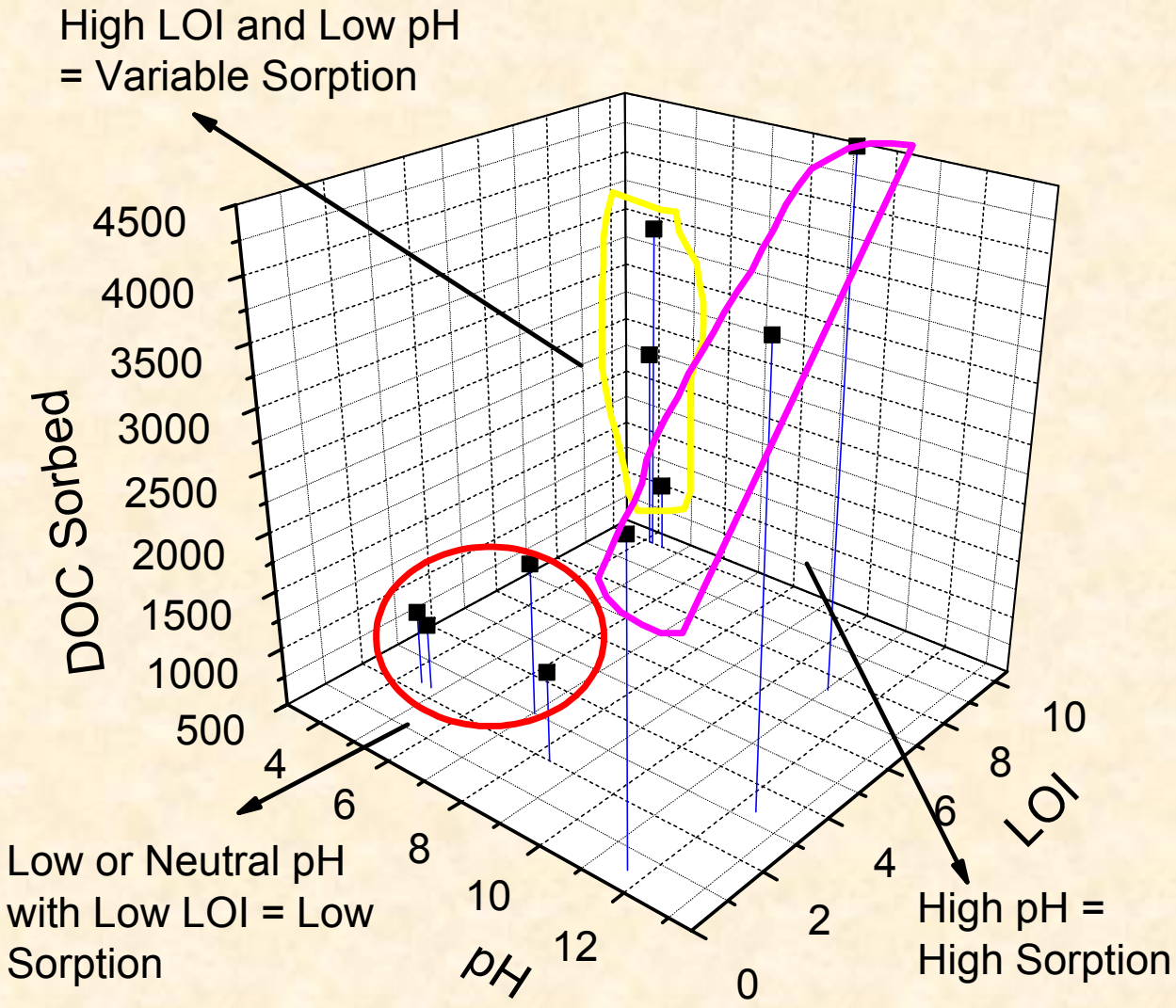


Carbon Sorption Summary Table

Sample	pH	Mean LOI %	Final pH	Sorption at 20 mg	Max Sorption
S2	4.13	10	5.50	1172	2329
CO	4.24	10	7.70	914	3468
AM	4.48	2.3	6.25	768	1141
S1	4.53	10	6.99	817	1111
GA	4.76	2.3	8.08	531	1067
T	7.03	3	7.80	397	1802
BO	8.37	2	8.73	413	1264
CH	11.04	7.5	8.71	990	4855
MA	11.65	0.5	9.33	871	3053
HW	12.37	3.3	10.32	900	4103

LOI, pH, and Sorption

- **ANOVA indicates that there are relationships among pH, LOI and Sorption**



LOI, pH, and Sorption - Analysis of Variance

ANOVA – All 10 samples

- $R^2 = 0.749$
- Degrees of Freedom = 2, 7
- No significant pH*LOI interaction

	F (or t)	Probability
Model	10.46	0.0079
pH	4.42	0.003
LOI	3.02	0.019

ANOVA – 9 samples

- $R^2 = 0.897$
- Degrees of Freedom = 2, 6
- No significant pH*LOI interaction

	F (or t)	Probability
Model	25.966	0.0011
pH	4.42	0.0007
LOI	3.02	0.0015

Carbon Sorption Conclusions

- **We found large differences in the ability of the different fly ashes to adsorb carbon in the form of humic acids.**
- **Typical results could be explained by the Langmuir isotherm equation and showed a maximum adsorption capacity of 800-1200 mg/kg.**
- **The capability to adsorb carbon appeared to be related to high pH and/or high LOI**

Summary

- **Fly Ash can be beneficial in carbon sequestration in soil**
- **Careful selection of fly ash can maximize potential for carbon sequestration and minimize chances for toxicity.**
- **Further, some fly ash material may be well suited to land application while others may be better suited to other uses.**

Acknowledgments

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.