# Soil Amendments and Carbon Sequestration

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#### For

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#### Why are we here?



- The concern for the potential global warming consequences of increasing atmospheric CO<sub>2</sub> has prompted interest in the development of mechanisms to reduce or stabilize atmospheric CO<sub>2</sub>
- During the next several decades, a program focused on terrestrial sequestration processes can make a significant contribution to abating the increase, and easing the transition to other renewable energy sources
- Within this context, it is useful to consider the restoration of degraded soils for C sequestration



## **Benefits for reclamation of degraded lands**

- Reclamation of degraded and disturbed lands, such as mine- spoil materials, highway rights of way, and poorly managed lands, through the addition of beneficiating amendments has a long history of research.
- Much is known about the methods to improve these soils, however funding for implementation is often limited.
- Consideration of Carbon sequestration could improve funding



# Potential ecological benefits from linking C sequestration and reclamation of degraded lands

- Potential for achieving ecological and aesthetic benefits for society in improved soil quality. For example,
  - Wildlife habitat
  - Recreational sites
  - Reduction in land fill space







#### Potential byproduct utilization benefits from linking C sequestration and reclamation of degraded lands

- Potential for the utilization of fossil fuel and energy byproducts in reclamations
- Potential for the utilization of other waste material (e.g., sludge, biosolids, mulch)





#### **Degraded land characteristics and the utility of amendments**

- Degraded lands are often characterized by acidic pH, low levels of key nutrients, poor soil structure, and limited moisture retention capacity.
- Addition of energy-related products can address these adverse conditions through a variety of mechanisms and enhance plant growth and carbon production.





# Why amendments for carbon sequestration?

- Soil fertility can significantly impact the level of carbon sequestered and degraded land can be deficient in nutrients
- Soil structure must support growth and there are often problems in this area





# Why couple reclamation and carbon sequestration?

- Concern for C sequestration may change the economics of degraded land reclamation.
- Carbon credits may supply funding for continued attention to degraded sites
  - "Carbon boards of trade have set up shop in the United States, Canada, and New Zealand – although not yet at the Chicago Board of Trade – and no credits have been traded. But carbon prices have been set initially at \$6 to \$8 a ton."\*





### **Concerns with reclamation and carbon sequestration**



Before these methods can be implemented on a significant scale questions that still must be addressed that are related to

- toxicity of amendments
- stability of the carbon
- Unintended consequences
  - e.g. emissions of other greenhouse gases





#### What amendments?

- Coal Combustion by products
  - Fly ash
  - Bottom ash
  - FGD byproducts
- Organic additions
  - Biosolids etc.
- Fertilizers
  - will not consider as the greatest potential for cost effectiveness is the use of the waste type materials
- Toxic materials are often present in these amendments and this must be considered
- Potential for synergistic effects with addition of organic matter and CC byproducts (e.g., in reduction of toxicity)



#### **Optimal amendments?**

- The literature suggests the great potential for the addition of a suite of amendments containing organic and inorganic energyrelated byproducts to improve degraded land increase sequestration of C, and utilize energy byproducts.
- However, the optimal strategy for rapid enhancement of C sequestration is not currently known.
- As yet, there are still unknowns related to
  - appropriate materials to be added,
  - the method of addition,
  - and the management of the sites.





# Fossil-fuel combustion byproducts as amendments

- The two major coal combustion products that have potential for use in prompting C sequestration are fly ash and FGD byproducts.
- Fly ash is a coal combustion residue with a matrix that is comparable to soil (Adriano et al., 1980; El- Mogazi et al.,1988;

Qafoku et al., 1999; Dick et al., in press).

 Unburned C is present with quartz, mullite, hematite, magnetite, and the majority of the fly ash consists of glassy spheres (Qafoku et al., 1999).





#### **FGD Byproducts**

- FGD byproducts, which are produced by new SO<sub>2</sub> scrubbing technologies such as
  - pressurized fluidized bed combustion (PFBC) and
  - lime injection multistage burners (LIMB)
- Primarily composed of alkaline materials consisting of
  - excess sorbent (calcite or dolomitic limestone, calcium oxide, calcium hydroxide, and magnesium oxide),
  - S- bearing compounds (calcium sulfate, calcium sulfite, and magnesium sulfate), and
  - fly ash (Crews and Dick, 1998).
- 22 Mg of FGD byproducts produced in the U.S.
  - <7% for was reused (American Coal Ash Association, 1997).</p>
- FGD byproducts are of interest mainly as liming agents and sources of divalent cations for improvement of soil pH and aggregation.



### **Fly Ash**

- Quantity
  - 54 Mg of fly ash and
- Use
  - less than 25% was reused (American Coal Ash Association, 1997).
  - The remainder was disposed in landfills.
  - fly ash finds use mainly for engineering purposes, to modify texture in soils, and as a source of trace nutrients for plants,





#### **Macronutrients with CC residues**

- Coal combustion residues can contribute Ca to improve soil structure and increase the pH of acidic soils.
  - Low pH appears to be a major negative in revegetation of surface-mined coal beds (Skousen et al., 1994).
  - FGD has been able to supply base cations and trace elements for growth of commercially important tree species (Crews and Dick, 1998).
- The sulfur present in FGD byproducts can often add nutritional value for plants.



#### **Micronutrients**

#### In areas limited by specific elements, these products can supply micronutrients

- Micronutrient amendment from coal fly ash with sewage sludge was applied to an acid boron deficient loamy soil in China with resulting higher yield for cucumber and corn than either the control treatment or a boron-containing fertilizer (Jiang et al., 1999).
- Increases in barley production have been observed with fly ash addition in Se-deficient soil (Sale et al., 1996).
- FGD has been able to supply base cations and trace elements for growth of commercially important tree species (Crews and Dick, 1998)





#### **Soil Structure of the use of CC residues**

Benefits to soil structure as a result of fly ash incorporation are clear.

- Ash additions to an easily clodded clay loam soil increased bulk density and desirable aggregates and decreased the modulus of rupture (Sale et al., 1997).
- Fly ash has been shown to increase porosity, water holding capacity, pH, conductivity, sulfate, carbonate, bicarbonate, chloride and metals, although the effect is reduced in high clay soils (Matsi and Keramidas, 1999).
- While surface soil P and Mn were also important, soil depth appears to be a positive factor in establishing white pine on mine spoil (Andrews et al., 1998). Thus, fly ash incorporation to increase depth of soil could be beneficial.



#### **CC** byproduct effects on plant growth

- At low levels of application to barley (Hordeum vulgare L. var. Leduc), fly ash resulted in increased plant heights and grain yields (Sale et al., 1996).
- With addition to wheat, 50% fly ash applied to soil resulted in increased growth and yield, with comparable effects to soil + compost + NPK (Tripathy and Sahu, 1997).
- Increased growth of wheat was seen with addition of fly ash and fly ash leachate (Karpate and Choudhary, 1997).
- With tomatoes, an increased yield was observed in loam soil (Kahn and Khan, 1996) with up to 60% v/v additions of coal fly ash.
- The addition of low boron fly ash increased biomass of rye grass (*Lolium perenne L.*) up to 80% over controls in Red Mediterranean acid soils (Matsi and Keramidas, 1999).



#### **Organic amendments**

- Organic matter additions could include
  - mulch from biomass productivity
  - process waste materials such as biosolids
  - pulp and sludge from paper production
- These organic amendments can have beneficial effects that complement and extend those of the inorganic fly ash material.







#### **Potential benefits of organic amendments**

- Improving soil fertility nutrients
  - Nitrogen and others
- May decrease effects of toxic metals
- Improving soil structure and moisture retention capacity,
  - "Biosolids are "especially beneficial when applied to soils that have been subject to soil erosion or excavated. It has about 65% organic matter which loosens heavy clay soils so common in our county and helps water infiltration which helps minimize soil erosion"

http://lancaster.unl.edu/enviro/biosolids/overvew.htm



# **Organic additions and nutrients**

- Biosolids and other organic amendments can supply macro and micronutrients
- Microbial mineralization of organic matter releases nutrient elements within the organic structure to soil solution for plant uptake
  - "Many area farmers use it for its phosphorus and zinc because these two elements are deficient on many area soils."

http://lancaster.unl.edu/enviro/biosolids/overvew.htm

- In addition, organic matter can bind essential metal nutrients, acting as a metal-ion buffer in soil to make micronutrients available to plants.
  - For example, organic matter can complex soil-phase Fe and make it available for uptake by plants.





### **Sources of organic matter and carbon mineralization**

- Biosolids, organic waste from treatment facilities, and similar waste material (swine manure, chicken litter) provide an excellent source of organic nutrients
- However, these readily bioavailable organic amendments may be less likely to be retained in the soil over long times, and thus may contribute little to long-term C sequestration.
- More recalcitrant, lignin-rich amendments such as woody biomass, and possibly paper and pulp mill sludge, are less labile in the soil and have a higher affinity for binding to soil particles.



# **Organic additions and toxicity reduction**

- Organic matter can stabilize toxic metals in soil, thereby reducing their migration to groundwater and reducing their uptake and toxic effects in plants.
- Soil organic matter has been demonstrated to bind a variety of metals that are sometimes present in fly ash and FGD byproducts, such as Zn, Ni, Pb, Cd, Cu, and B.



# **Toxicity reductions in field studies**

- At metal-contaminated and metal-amended sites, addition of humic materials
  - reduced uptake of a suite of heavy metals (Ni, Cr, Cu and Zn) in clover by 60% and
  - decreased the concentration of metals leached into soil solution by 50-90%.
  - Biomass production also tripled in the humic-treated contaminated soil
- Even greater reductions in metal uptake and larger increases in biomass were observed in greenhouse studies (Wong, 1995; Chu and Poon, 1999).



### **Organic mater and toxicity reduction field studies with fly ash**

- Fine fly ash from the DOE Savannah River Site (SRS)
  - mixed with sandy loam soil at a 1:3 ratio and further amended with composted lawn clippings resulted in high yields that were correlated with higher K, Ca, and N levels and lower B levels (Menon et al., 1992).
  - Mixing composted lawn clippings and fine fly ash (20%) from SRS increased mustard and collard green yields, but depressed yields of string beans, bell pepper, and eggplant as a result of boron accumulation (Menon et al., 1993).



#### **Tilth – CC byproducts and organic additions**

- Inorganic and organic amendments both contribute to soil tilth, and act in a complementary fashion
- The Ca<sup>2+</sup> from fly ash promotes coagulation between soil particles and stabilizes soil structure through cation bridging
- Organic matter can sorb to mineral surfaces and creates a more reactive network for water, air, and nutrient interactions in the soil
- The organic matter contributes pH buffering capacity.
- The interaction of organic matter with soils is enhanced by Ca<sup>2+</sup>, thus the addition of both organic and inorganic amendments would provide synergistic benefits to soil improvement



# Soil structure and organic carbon amendments

- Primary particles and clay microstructure are bound to micro-aggregates and in turn to larger macroaggregates. This process may be enhanced by growth of roots and hyphae.
- Organic matter associating with the aggregates may become physically protected from decomposition (Tisdall and Oades, 1980; Jastrow 1996).





### **Organic amendments in conjunction with fly ash in successful reclamation**

- Addition of compost and manure proved effective in increasing vegetation at a mine reclamation site in South Africa where Se levels in grass leaves may have been toxic (Van Rensburg et al., 1998).
- Application of gypsum reduced Se levels in plants grown on a coal ash landfill (Woodbury et al., 1999),
- In FGD sludge pond revegetation, growth of grasses (but not shrubs) was increased by amendments with manure, wood shavings and fly ash (Salo et al., 1999).
- Rates must be controlled
  - For example, yields of barley silage on a minespoil
  - increased at intermediate fly ash amendment rates (200 t ha<sup>-1</sup> or less)
  - but decreased at 400 t ha<sup>-1</sup>.



#### Fly ash and sewage sludge

- Sewage sludge has been mixed with alkaline industrial byproducts to make a commercial soil substitute that has beneficial effects on moisture holding capacity when applied at rates of 500 Mg/ha (Logan and Harrison, 1995).
- Fly ash mixed with poultry manure or sewage sludge (1 to1) was beneficial to growth of sudangrass at 25 tons acre<sup>-1</sup> and fly ash mixed with dairy manure increased growth at rates to 50 tons acre<sup>-1</sup> (Sajwan et al., 1996).
- These beneficial effects have been seen in other studies with varying amounts of fly ash but occasionally with a boron toxicity at high applications (Wong et al., 1998; Wong and Su, 1997; Chu and Poon 1999).
- The fly ash also provides a pH-buffering capacity to counteract the increase in acidity during the initial decomposition of organic matter.



### **Consideration of site specifics**

- Fly ash and FGD byproduct mixtures may have to be tailored to site conditions.
- In degraded lands that lack small-size soil particles, silt-size fly ash particles could contribute directly to increases in moisture retention capacity of the soil.
  - However, addition of large amounts of alkaline fly ash may increase the soil pH or boron too much for some desirable crops.



#### **Ph considerations with amendments**

- In later stages of a C-enhancement strategy, woody plants may be desirable to store biomass in both above- and below-ground C pools.
- Many of the pine trees typically grown in the Southeast require acid soils, and thus will not thrive if fly ash additions raise the pH above neutral.
- Alkaline pH promotes leaching of soil organic matter, thus potentially reducing both C sequestration and soil fertility unless C is captured in deeper soil layers



# Considerations and challenges with the use of soil amendments

Areas likely to be critical in the success of the sequestration effort include

- the effects of the coal ash,
- the composition of the organic matter, and

Specific questions to be addressed in these areas are listed below.



#### **Coal Ash Effects and Selection**

- Will coal ash will improve tilth (soil aggregate structure) and pH in weathered, clay- rich soils but have little benefits in sandy soils?
- Will Ca- rich FGD byproducts increase soil pH in highly weathered soils and promote soil C accumulation?
- Will differences in the oxidizing capability of fly ash and FGD byproducts influence rates and extent of organic C polymerization in the soil?





#### **Organic Matter Additions**

 Will chemical composition of organic matter influence the stability of the C in the soil? Lignin- rich organic matter (e.g., wood, paper sludge) is expected to promote longer- term C storage in soils. Lower molecular weight, more readily metabolized organic matter (e.g., biosolids) may promote higher respiration rates and release CO<sub>2</sub>?



• Will organic additions improve both above-and belowground productivity and C storage through beneficial effects on soil structure, water retention capacity and pH?



# **Complicating effects – other greenhouse gases?**

Will the presence of low molecular weight organic matter contribute to establishing the microbial community and stabilizing nutrient cycling without stimulating N<sub>2</sub>O production (e.g., by increasing nitrification rates)?





# Interactions of added soil carbon with nutrients and toxics

 The possible trend toward N limitation of microbial activity in soils receiving larger inputs of biomass, which may further affect the relative rates of degradation of the major components of biomass.

The concentration of toxic metals in mobile soil solution, because DOM that is not retained by soil may complex toxic metals and enhance their leaching to groundwater.



# **Quantity and Quality of Soil Organic C Accumulation.**

- The effectiveness of different treatment options to C-sequestration must be evaluated based on
  - changes in the quantity of C,
  - the quality of the C in terms of the recalcitrance of the C.
- One of the challenges that must be addressed is the difficulty in directly measuring a change in the SOM levels.



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