SOIL AMENDMENTS PROMOTE VEGETATION ESTABLISHMENT AND CONTROL ACIDITY IN COAL COMBUSTION WASTE

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1. ABSTRACT

The effects of adding various soil amendments and a pyrite oxidation inhibitor to aid in the establishment of vegetation and to reduce acid drainage (AD) from coal fly ash and coal reject (FA + CR*) were assessed in an outdoor mesocosm study. Preliminary greenhouse experiments and field observations at the U.S. Department of Energy's Savannah River Site (SRS) indicated that plants would not survive in this material without altering its physical and chemical characteristics. Samples of mixed FA + CR were obtained from a field site at the SRS. The following treatments were used: Biosolid only (Treatment A), Biosolid + Surfactant (Treatment B), Topsoil + Surfactant (Treatment C), and Biosolid + Topsoil + Surfactant (Treatment D). Leaching was induced due to inadequate rainfall. Loblolly pine seedlings (*Pinus taeda*) inoculated with ectomycorrhizal fungi - *Pisolithus tinctorius* (Pt) and *Scleroderma cepa* (Sc) - were transplanted into each mesocosm tank. Soil solution samplers were installed in each unit at 15 and 41 cm depths. Samples were taken periodically and measured for pH, EC, and other parameters.

The results indicate that the addition of amendments can aid in the revegetation of a FA + CR landfill and control AD. Pine seedlings growing in treatments with biosolid application were significantly taller than the treatment without it; however, there were no significant differences concerning diameter, biomass, and plant tissue concentrations of Al, Fe, and Mn for the pines. Biosolid addition also appears to be effective for mitigating proton generation. Sodium lauryl sulfate (SLS) and topsoil addition were not as important to plant survival and growth as biosolid addition; nonetheless, SLS and topsoil addition did not appear to be disadvantageous to growth in the treatment with biosolid addition (Treatment D). Based on leachate data, the topsoil + surfactant treatment had a much lower initial pH (pH ~ 3 or below) than the other treatments, and Al concentrations were correspondingly high. Electrical conductivity, in general, has been decreasing since the inseption of the study and appears to indicate that the addition of biosolid + surfactant

*CR = coal reject – refers to raw coal discarded due to its low combustion quality.

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(Treatment B) is the most effective treatment for inducing the lowest sulfate and metal concentrations. Preliminary results indicate that the use of amendments is essential for plant growth and establishment in pyrite enriched coal waste sites.

2. INTRODUCTION

Worldwide, coal-fired power plants burn gigatonnes of coal annually, thus producing enormous amounts of coal combustion products (CCPs). In the United States, 860 million tonnes of coal were burned during 2000, generating 98 million tonnes of CCPs[1]. The general types of CCPs are fly ash (FA), bottom ash (BA), boiler slag (BS), and flue gas desulfurization residue (FGD or synthetic gypsum)[1]. Fly ash is the primary CCP produced of which little (<30%) has been reutilized for beneficial purposes in the United States[2]. Due to a lack of utilization, the accumulating FA becomes a waste disposal problem[2]. Currently, the most widely accepted disposal methods for FA are landfilling, stockpiling, and storage in settling ponds[3].

The mineralogical, physical, and chemical properties of FA are extremely variable and depend on the nature of the parent coal, combustion conditions, emission control device efficiency, storage and handling methods, and climatic conditions[2, 3]. Certain elements (As, B, Mo, and Se) present in FA can bioaccumulate and could become critical in the food chain[4, 5]. The pH is an important factor in determining the bioavailability of FA derived metals and can vary from 4.5-12.0, being primarily dependent on the S content of the parent coal and amount of lime (i.e. for desulfurization) added to the material[6].

High levels of metals/metalloids in animals exposed to FA and CR left over from combustion activities had been reported at the U.S. Department of Energy's Savannah River Site (SRS)[7]. For example, studies at the SRS indicate that Se could cause morphological deformities in both teeth and spinal columns in bullfrog tadpoles[7]. Research concerning the problems related to FA and CR storage and disposal merits attention. By-products arising from worldwide reliance on coal as a major energy source will continue to pose serious ecological problems.

Located at the SRS, the 488 D-Area Ash Basin is an unlined, earthen basin approximately 8.5 ha in size that contains approximately 1 million tonnes of dry ash and CR[8] (Fig. 1). The CR is pyritic in nature resulting in the generation of acid drainage (AD) that has contributed to a deterioration in groundwater quality and poses a threat to the biota in down gradient wetlands[8]. Pyrite (FeS_2) is commonly associated with coal as well as metal ore deposits (including Zn, Cu, U, Au, and Ag) (e.g. from old mining sites). The exposure of pyrite and other iron sulfides to air and water oxidizes the sulfides resulting in AD. This process is complex due to the involvement of chemical, biological, and electrochemical reactions that are sensitive to various environmental conditions[9]. The general stoichiometry can be described by the reaction:

$$FeS_{2(S)} + 3.75O_2 + 3.5H_2O \quad Fe(OH)_{3(S)} + 2H_2SO_4 \qquad [Eq.\ 1]$$

where iron sulfide and other mixed-metal sulfides decompose upon exposure to the atmosphere, producing sulfuric acid and insoluble ferric iron hydroxide from hydrolysis[10]

The AD is highly acidic (pH can be <2) and is often enriched with Fe, Mn, Al, SO_4^{2-} and other trace elements[9]. The kinetics of pyrite oxidation depend on oxygen availability, abundance of iron-oxidizing bacteria, surface area of the exposed pyrite, and chemical characteristics of the influent water[11]. *Thiobacillus ferrooxidans* is the primary iron-oxidizing bacteria involved in pyrite oxidation and catalyses the reaction. Anionic

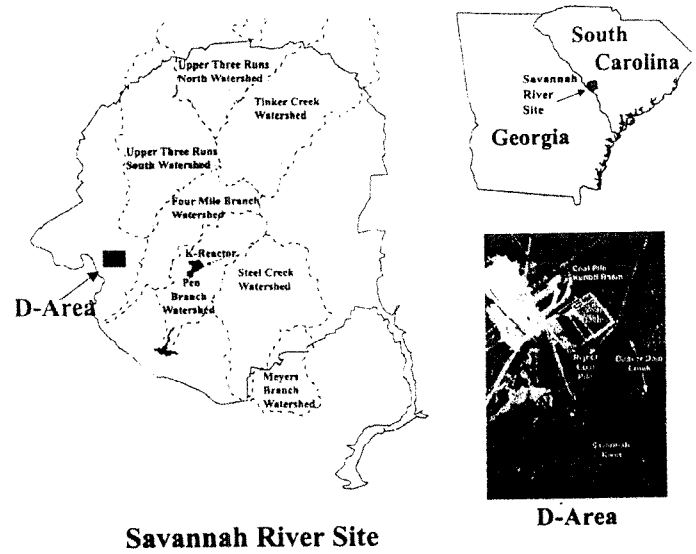


Figure 1. Location of the fly ash–coal reject landfill site (D-Area Ash Basin, DOE Savannah River Site, SC).

surfactants (e.g. sodium lauryl sulfate - SLS), applied at concentrations greater than 25 mg L^{-1} can reduce this bacterial activity consequently slowing acid production[12]. In previous studies, SLS was found to inhibit *Thiobacillus ferrooxidans* activity at lower concentrations than other generally available surfactants[11]. In essence, surfactants wash away the protective slime coating of the bacteria, breaking the surface tension of the cell wall and causing the cell to lyse[11]. However, anionic surfactants are very soluble and thus are susceptible to leaching. Accordingly, surfactant solutions may have a short period of effectiveness, generally only 2 or 3 months, but such a time frame of effectiveness may be sufficient to promote vegetative establishment on problem sites[11].

Use of a vegetative cover to control AD via enhanced evapotranspiration has been hypothesized by Barton et al.[13]. Not only would a vegetative cover influence the redox conditions and AD generation of a waste site, but enhanced buffering capacity due to organic metabolites from root exudates and plant decay could help to break the acid production cycle[11]. A healthy root system can compete with acid-producing bacteria for both oxygen and water, and organic acids can be formed by beneficial heterotrophic soil bacteria and fungi creating an unfavorable environment for *Thiobacillus ferrooxidans*[11]. Biosolids, such as municipal sewage sludge and animal waste, are an important group of soil amendments that are increasingly being used in agro-forestry and reclaimed lands[2]. As well as supplying plant nutrients, the organic matter (OM) in biosolids enhances aeration, porosity, tilth, and water retention capacity of soils[2].

The main objective of this research was to examine the use of various amendments to facilitate the establishment of vegetation and inhibit AD generation in coal combustion waste (in this case combined coal FA and CR). The study was aimed to elucidate these effects in a large–scale mesocosm study using dry FA and CR from the 488 D-Area Ash Basin on the SRS.

3. MATERIAL AND METHODS

An outdoor mesocosm study was initiated on 13 June 2000. Field samples of mixed FA + CR from the D-Area Ash Basin were used for the experiment. The material was contained in 61 x 244 cm galvanized steel cattle tanks fitted with leachate ports. About 30 cm of the mixed FA + CR was deposited in the bottom of the tanks with the amendment material (15 cm) and the topsoil added (7 cm) on the surface: Treatment A – Biosolid only, Treatment B - Biosolid + Surfactant, Treatment C - Topsoil + Surfactant, and Treatment D – Biosolid + Topsoil + Surfactant. The biosolid material consisted of sanitary sewage sludge, poultry waste, and wood chips composted for 90 days. Sodium lauryl sulfate was applied in the amount of approximately 0.24 L of a 0.6 % SLS solution to the mixed FA + CR to inhibit acid-producing bacteria. The soil type of the topsoil was Dothan sand (Fine-loamy, siliceous, thermic Plinthic Paleudults) and was collected on the SRS.

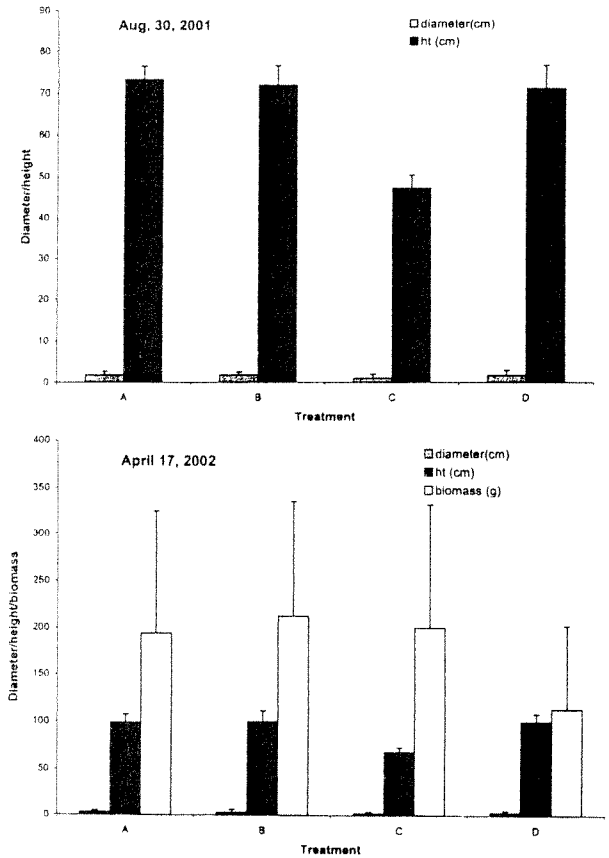


Figure 2. Height, diameter, and biomass data for pines (mean and standard deviation where n=3 for height and diameter; mean and standard deviation where n=6 for biomass)

Table 1. Chemical characteristics of substrate materials used in the mesocosm study.*[a]

Parameter	Topsoil	Biosolid/compost	FA-CR mix
pH (1:1)	5.07 (0.62)[a]	6.83 (1.03)	1.72 (0.75)
EC (1:5) (mS cm^{-1})	0.07 (0.08)	2.66 (0.53)	5.92 (1.86)
OM (%)		31.9	
NO_3-N	10.3 (3.0)	31.0 (14.7)	BDL
P†	6.8 (2.9)	BDL	BDL
K†	17.2 (10.0)	79.6 (19.2)	2.3 (1.5)
Mg†	48.7 (34.3)	146.0 (107.6)	174.3 (82.2)
Ca†	208.2 (118.3)	766.3 (64.5)	526.0 (47.0)
Al‡	4193.8 (146.3)	430	1767.9 (495)
Fe‡	3510.5 (195.5)	351	20476.4 (13827.1)
Mn‡	222.3 (8.89)	2.33	7.18 (12.3)
Zn‡	14.3 (11.1)	4.95	1.96 (6.00)
Cd‡	BDL	0.13	0.1 (0.58)
Pb‡	8.15 (1.1)		28.4 (12.4)
As‡	9.88 (0.72)	BDL	64.7 (43.0)
Se‡	BDL	BDL	8.88 (5.80)

*mg kg^{-1} except where noted otherwise.
†Mehlich-1 method (HNO_3-H_2SO_4).
‡U.S. EPA method 200.2 (HNO_3-HCl).
BDL = below detection limit
[a]Values in parentheses represent standard deviation.

These tanks were set up in a restricted access area at the Savannah River Ecology Laboratory, having a randomized order with three replicates per treatment. The treated materials were moistened and then equilibrated before planting. Loblolly pine seedlings (*Pinus taeda* L.) (9 seedlings/tank) inoculated with *Pisolithus tinctorius* (Pt) and *Scleroderma cepa* (Sc) were transplanted in mid-April 2001. An automatic sprinkler system was set up, and lysimeters (Soilmoisture Equipment Corp., Goleta, CA) were installed at two depths (15 cm and 41 cm) in mid-June 2001. After one year of growth, biomass samples of the pine seedlings were taken mid-April 2002; two seedlings were sampled, keeping disturbance of the soil to a minimum. Rainfall data taken by a weather station at the SRS showed the average rainfall per month from June 2001 to December 2001 to be 62 mm; however, there was very little rainfall for the months of October to December with the average being only 16 mm. For January 2002 to June 2002, the average was 38 mm. Rainfall averages compiled since 1952 showed an average rainfall per month of 100 mm for June through December, 76 mm for October to December, and 106 mm for January to June. Thus, drought-like conditions were indicated for much of the study period.

For periodic sampling of the soil solution, the tanks were slightly oversaturated by the sprinkler system and suction applied to the ceramic lysimeters after an overnight equilibration. The pH and EC were measured immediately after collection. Samples were taken on the following dates: 6/29/2001, 7/13/2001, 8/31/2001, 11/29/2001, 1/24/2002, 3/27/2002, 5/28/2002, and 7/31/2002. Solution samples were filtered using 0.45 µm nylon syringe filters, acidified by adding HNO_3 (1% of sample volume), and maintained in cold storage for Inductively Coupled Plasma Optical Emission Spectroscopy (ICP/OES) analysis. Ion Chromatography (IC) was used for anion analysis.

For plant biomass and analysis of plant tissue metal concentrations, plant material was oven-dried at 65°C until no further weigh loss occurred. The material was then

separated into leaves, stems, and roots and weighed to determine dry biomass. Dried plant tissue was ground using a sample mill (Thomas, Arthur H., Wiley, 2-mm mesh, Philadelphia, PA) and digested in a 5 M HNO_3 + H_2O_2 by microwave (CEM Corp. MDS-2000, Matthews, NC) in pure Teflon PFA vessels.

Analysis of variance (ANOVA), general linear models (GLMs), and PROC Univariate were calculated using SAS (SAS, 1999) to determine significant differences within the data.

4. RESULTS AND DISCUSSION

4.1 Substrate Material

The FA + CR substrate material exhibited high acidity (pH = 1.72) and high EC (5.92 mS cm^{-1}). Low pH values (pH ~ 1 or lower) had been observed in sulfide-rich tailings from impoundments and weathered mine sites[14, 15]. Since the FA + CR mix is composed of alumino-silicate and sulfide minerals, high concentrations of Fe, Al, and other trace elements were evident. The low buffering capacity and low nutrient content of the FA + CR substrate are not conducive to plant establishment or growth. On the other hand, the biosolid exhibited a high OM content (~ 32%) and should provide ample buffering capacity for the substrate. The biosolid data also indicate the presence of primary and secondary plant nutrients that, although initially low, may serve as a slow release fertilizer in addition to serving as a buffering agent. The topsoil exhibited near circumneutral pH conditions and low quantities of nutrients.

Table 1. Chemical characteristics of substrate materials.* [a]

4.2. Effect on Pine Growth

Growth measurements for the pines (4 and 12 months after transplanting) indicated that there was no significant difference in diameter induced by the treatment; however, differences in height were apparently due to the biosolid application, with the pines in treatments containing biosolid (Treatments A, B, and D) being significantly (P<0.0001) taller than the topsoil + surfactant treatment (Treatment C) (Fig. 2).

Soils with pH values below 5.5 generally contain exchangeable Al at sufficiently high concentrations to be toxic to plants[16]. In addition, the oxidation of sulfur containing compounds may result in the formation of high acidity in the soils, generally noted by pH values below 4.0, which is highly unfavorable to the growth of most plant species[17]. For the shallow samples the pH did not drop below 3.5, and no plant mortality was noted. Soil solution (i.e., leachate) data indicate that Treatment C had a much lower initial pH than the other treatments (pH ~ 3 or below), with Al concentrations being correspondingly high (Fig. 6). The potential for Al toxicity at these levels is high and may have contributed to the difference in plant height.

Although results indicated that the topsoil addition was not as important to plant survival and growth as biosolid addition, the topsoil addition did not appear to be

Table 2. Al, Fe, and Mn concentrations (mg kg^{-1}) in leaf tissue (mean and standard deviation where n=6).* [a]

Treatment	Al	Fe	Mn
A	251 (81)[a]	79 (17)	237 (100)
B	191 (85)	72 (10)	176 (120)
C	335 (108)	86 (38)	328 (139)
D	298 (114)	85 (26)	322 (178)

*Analysis of variance (ANOVA) indicates no significant difference.
[a]Values in parentheses represent standard deviation.

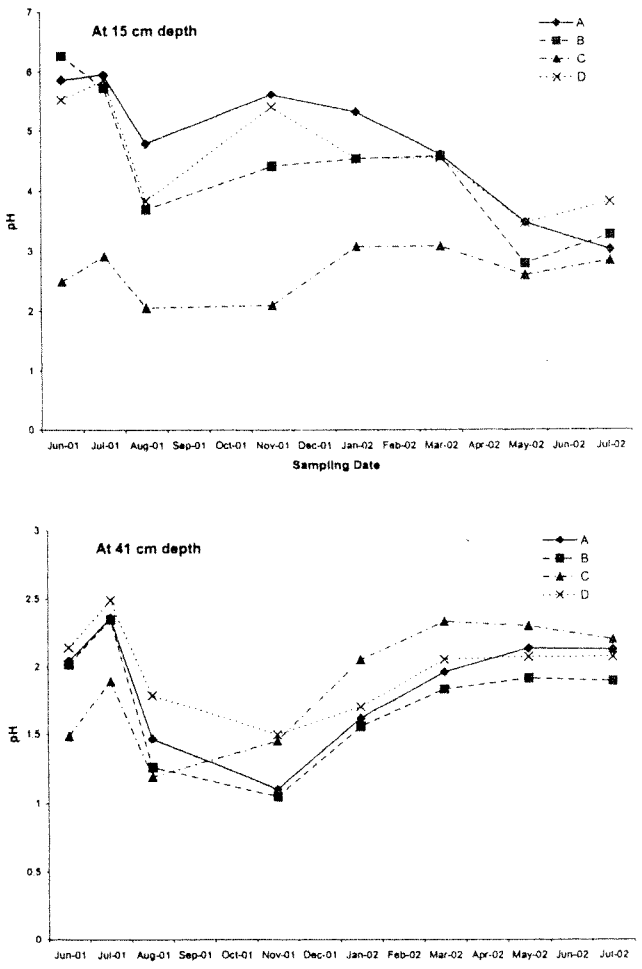


Figure 3. pH of soil solution/leachates from two sampling depths (15 and 41 cm) (mean and standard deviation where n=3)

detrimental to growth in the treatment with biosolid addition (Treatment D). In addition, height differences may be attributed to the OM content in the biosolids which supplied plant nutrients and enhanced physical soil properties[2]. Like the data for the diameter, biomass analysis showed no significant difference (P=0.4891, n=6) for the different treatments. There were also no significant differences in plant tissue concentrations of Al, Fe, and Mn for the pines (Table 2).

4.3. Effect of Treatments on pH and EC

In comparison with the initial data (Table 1) of the untreated FA + CR material, the pH was dramatically increased from 1.7 to an average pH of 5 (for the four treatments) at the shallow depth (15 cm) in the beginning of the study (6/29/2001) (Figs. 4 and 5). The pH lingered for about a month through the second sampling date (7/13/2001) and rapidly declined on the third sampling date (8/31/2001); conversely, the EC started low (5.92 mS cm^{-1}) at the inception of the study, stayed somewhat low through the second sampling date, and drastically increased on the third sampling date – exactly the opposite of pH. For the lysimeter soil solution samples collected at the 15 cm depth, pH values appear to have gradually decreased over time for Treatments A, B, and D, but not for Treatment C. Initially, the OM and/or humic compounds in the biosolid can complex Fe^{3+}, which otherwise at this state may serve as an electron acceptor that can exacerbate the oxidation of the pyrite. Over time, the OM undergoes oxidation and the buffering potential decreases eventually resulting in a lowering of the pH.

Based on the pH, the effect of the SLS on acid generation was negligible. These results may be due to the solubility and subsequent leaching and/or biodegradation of the surfactant. However, this may also suggest that the primary mechanism of the oxidation of pyrite in these materials is one of a physicochemical, rather than of a biological nature. A study by Barton et al. indicated a similar phenomenon for these substrate materials where Fe^{3+} served as the primary oxidizing agent, i.e., electron acceptor[13].

The OM content of the biosolid likely inhibited oxidation by serving as an electron donor (i.e., lowering oxidation) and complexing of Fe^{3+}. The EC of the leachates followed an inverse correlation to that of the pH. When pH values were low, EC concentrations were high. The IC data indicate that sulfate was the most dominant anion; only low concentrations of chlorides and nitrates were observed. The dominance of the sulfates was apparently due to the FeS_2 oxidation; the sulfates may serve as the main ion pair for the metals. Sulfate concentrations somewhat correspond with the EC (Fig. 4). The EC as well as the sulfate concentrations appear to be decreasing over time.

From the sulfate data (Fig. 5), the biosolid + surfactant (Treatment B) appears to have induced the lowest sulfate concentrations for the 41 cm depth samples, while the biosolid only (Treatment A) induced the lowest sulfate concentrations for the 15 cm depth samples. The peaks for the 41 cm samples occurred around the 19 November 2001 sampling date, with the leachate pH at its lowest (Fig. 3). The correspondence between the EC and sulfate concentrations was expected due to exorbitant generation of SO_4^{2-} from pyrite oxidation of the reject coal, becoming the dominant electrolyte in the soil solution/leachate. The dominating mitigating effect of the biosolid on acidity (i.e., low pH) as well as total dissolved solids (TDS), i.e., as indicated by the EC (TDS can be estimated by multiplying EC (mS cm^{-1}) by 640 for soils with EC values between 0.1 and 5.0 mS cm^{-1} and 800 for those with EC values > 5.0 mS cm^{-1}), is very obvious throughout virtually the duration of the study but especially during the initial 5 months[18]. This might be due to the time needed to equilibrate the various amendments with the substrate and to decompose the biosolid.

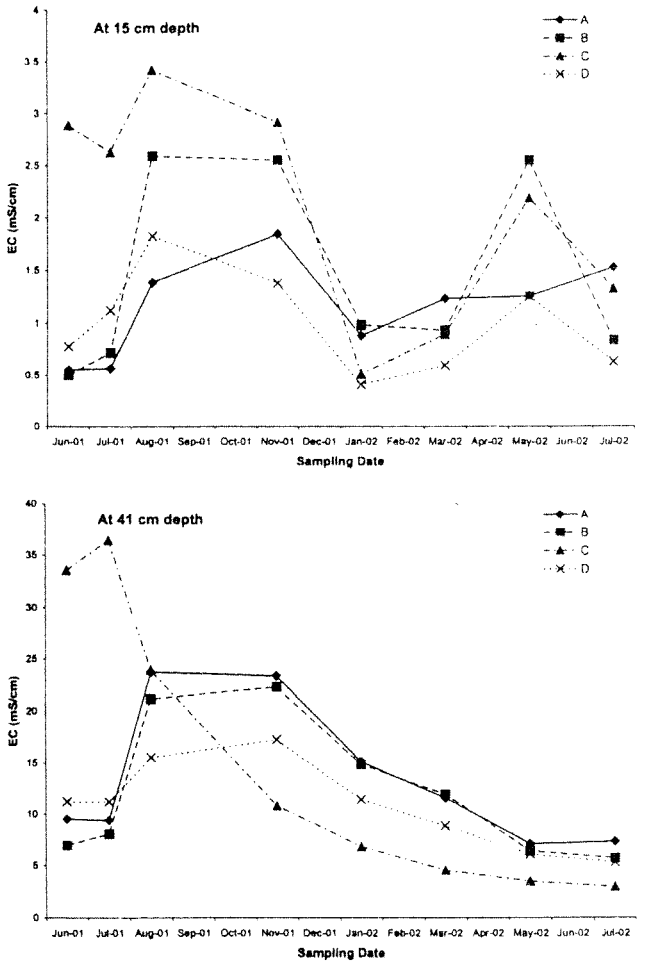


Figure 4. EC (mS cm^{-1}) of soil solution/leachates from two sampling depths (15 and 41 cm) (mean and standard deviation where n=3)

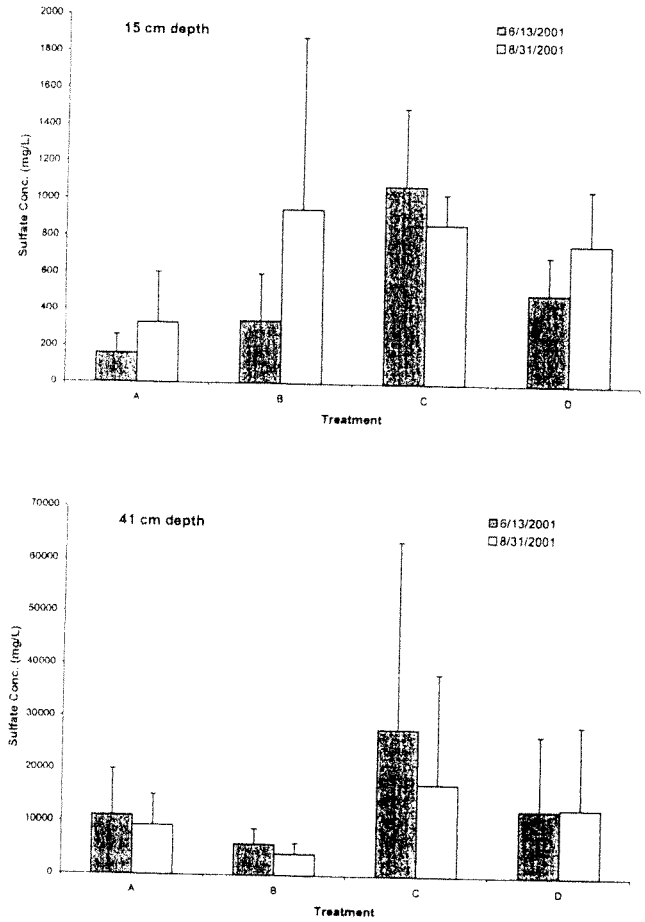


Figure 5. Sulfate concentration (mg L^{-1}) of soil solution/leachates from two sampling depths (15 and 41 cm) (mean and standard deviation where n=3)

4.4. Effect on Metal Concentration

As expected, Fe was the most dominant metal in the leachate. From these data, it appears that the biosolid + surfactant (Treatment B) was the most effective at reducing the concentrations of metals in the lower depth. This occurred even though the pH values of the treatments containing biosolid were similar.

Iron and aluminum concentrations for the 15 cm depth samples peaked around November 2001 coinciding with the fall of pH. For the 41 cm depth samples, the biosolid only (Treatment A) was consistently higher in both Fe and Al concentrations than the biosolid + surfactant (Treatment B); this may be due surfactant addition in Treatment B.

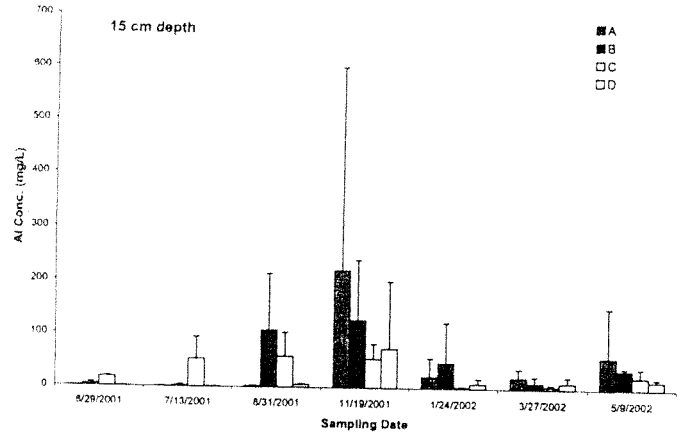
Based on initial chemical characteristics of the substrate material (Table 1), Treatments C and D were expected to have the highest Al concentration. Leachate data indicated that Treatment C had a much lower initial pH than the other treatments (pH ~ 3 or below); Al concentrations were correspondingly high (Fig. 6). While Fe could have been derived primarily from the dissolution of the pyrite in the CR, the Al could have been dissolved by such low pH from the clay minerals, the alumino silicates in the FA and Al oxyhydroxides.

Manganese concentrations for the 15 cm depth samples corresponded with the pH and Fe/Al data peaking around November 2001. Manganese concentrations for the 41 cm depth samples followed the same general trend peaking at around the same date. For the 41 cm sampling depth, samples from Treatment A had consistently higher Mn concentrations than those from Treatment B; once again this may be due to surfactant addition in Treatment B. The topsoil had a significantly higher concentration of Mn than the CR material (Table 1), and there were instances at the initial sampling dates in which treatments containing the topsoil (Treatments C and D) had higher concentration of Mn than treatments that did not contain it (Treatments A and B). At a pH above 4, Mn is not as readily available to plants, which may explain why it is not problematic. For the 15 cm sampling depth, the pH of the leachates has been above 4 for all of the treatments except Treatment C for most of the experiment.

5. CONCLUSIONS

The results indicate that revegetation of a FA + CR landfill is feasible for controlling AD with the addition of proper amendments. Differences in height of the pine seedlings appear to be due to biosolid application, with those growing in the treatments containing biosolid being significantly taller than the treatment without it; however, there were no significant differences concerning diameter, biomass, and plant tissue concentrations of Al, Fe, and Mn for the pines. Biosolid addition appears to be effective for mitigating proton generation, supplying plant nutrients, and enhancing physical soil properties. Surfactant and topsoil addition were not as important to plant survival and growth as biosolid addition; nonetheless, SLS and topsoil addition did not appear to be detrimental to growth in the treatment with biosolid addition (Treatment D). Based on leachate data, the topsoil + surfactant treatment had a much lower initial pH (pH ~ 3 or below) than the other treatments and Al concentrations were correspondingly high.

As such, differences in plant growth were observed. Based on these 1-year data, the most critical factor limiting plant establishment in pyritic coal waste (i.e., that has some resemblance to pyritic mine waste), i.e., extreme acidity, can be mitigated by adding amendments (especially biosolid and top soil) in order to limit the diffusive flux of O_2 from the atmosphere, to enhance the buffering capacity of the substrate, and to provide a more favorable rooting environment including initially supplying plant nutrients.



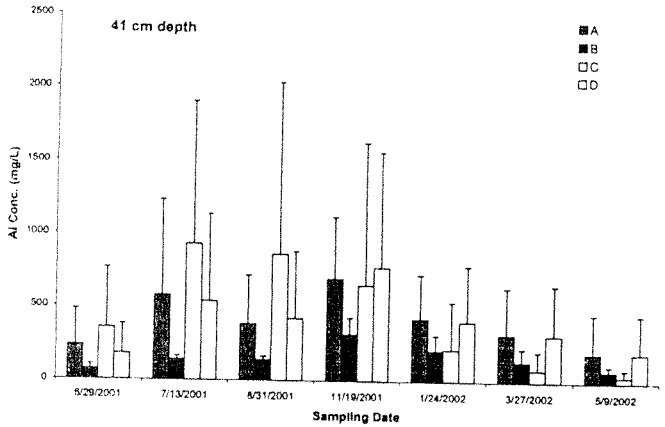
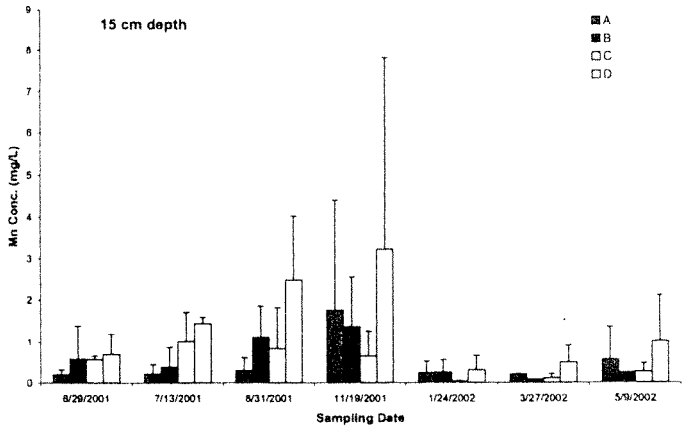


Figure 6. Fe and Al concentration (mg L^{-1}) of soil solution/leachates from two sampling depths (15 and 41 cm) (mean and standard deviation where n=3)



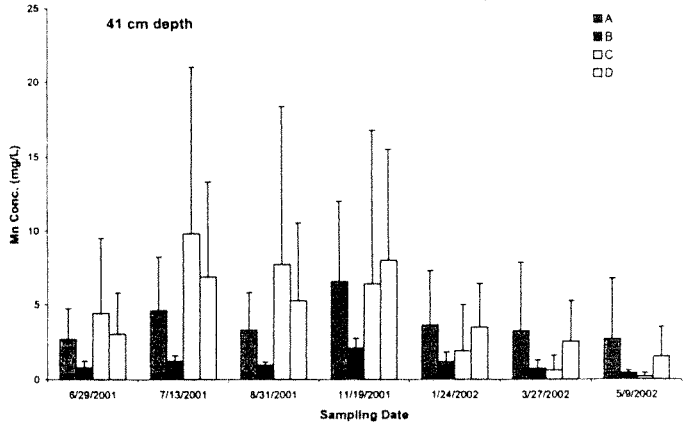


Figure 7. Mn concentration (mg L^{-1}) of soil solution /leachates from two sampling depths (15 and 41 cm) (mean and standard deviation where n=3)

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REFERENCES

1. Punshon, T., Seaman J. C., and Sajwan, K. S., Introduction: The production and use of coal combustion products, in *Chemistry of Trace Elements in Fly Ash,* Sajwan, K.S., Alva, A.K. and Keefer, R.F., Eds., Kluwer Academic Publishers, 2002.

2. Adriano, D. C., *Trace Elements in Terrestrial Environments*, Second Edition, Springer, New York, 2001, Chap. 3.

3. Adriano, D. C. and Weber, J. T., Influence of fly ash on soil physical properties and turfgrass establishment, *J. Environ. Qual.*, 30, 596, 2001.

4. Adriano, D. C., Page, A. L., Elseewi, A. A., Chang, A. C., and Straughan, I., Utilization and disposal of fly ash and other coal residues in terrestrial ecosystems: a review, *J. Environ. Qual.*, 9, 333, 1980.

5 Carlson, C. L. and Adriano, D. C., Environmental impacts of coal combustion residues, *J. Environ. Qual.*, 22(2), 227, 1993.

6. Keefer, R.F., Coal ashes - Industrial Wastes or Beneficial Byproducts? in *Trace Elements in Coal and Coal Combustion Residues*, Keefer, R. F. and. Sajwan, K. S., Eds., Lewis Publishers, Ann Arbor, 1993, 3-9.

7. Rowe, C. L., Hopkins, W. A., and Coffman, V.R., Failed recruitment of southern toads (*Bufo terrestris*) in a trace element-contaminated breeding habitat: direct and indirect effects that may lead to a local population sink, *Arch. Environ. Cont. Toxicol.*, 40, 399, 2001.

8. Barton, C. D., Marx, D. C., Adriano, D. C., and Bartley, H., Use of a vegetative cover to control acidic drainage from coal combustion waste, in Proceeding of the American Society For Mining Reclamation; 19th Annual National meeting, Barnheisel, R. I., Ed., ASSMR, Lexington, KY, 2002.

9. Evangelou, V. P., and Zhang, Y. L., A review: pyrite oxidation mechanisms and acid mine drainage prevention, *Crit. Rev. Env. Sci. Tec.*, 25(2), 141, 1995.

10. Nordstrom, D. K., Aqueous pyrite oxidation and the consequent formation of secondary iron minerals, in Acid sulfate weathering, Soil Science Society of America Special Publication 10, Kittrick, J.A., et al., Ed.,. Madison, WI, 1982.

11. Kleinman, R., L., P., and Rastogi, V., Reducing acid mine drainage liabilities using bactericides & other control technologies, in 13th Annual National Meeting American Society for Surface Mining and Reclamation Workshop #8, 1996.

12. Kleinman, R., L., P., and Erickson, P. M., Control of acid drainage from coal refuse using anionic surfactants, Bureau of Mines Report of Investigations 8847, 1983.

13. Barton, C., Romanek, R., Seaman, J., and Paddock, L., Geochemistry of an abandoned landfill containing coal combustion waste: implications for remediation, in *Chemistry of Trace Elements in Fly Ash,* Sajwan, K.S., Alva, A.K. and Keefer, R.F., Eds., Kluwer Academic Publishers, 2002.

14. Blowes, D. W., Reardon, E. J., Jambor, J. L., and Cherry, J. A., The formulation and potential importance of cemented layers in inactive sulfide mine tailings, *Geochem. Cosmochim. Acta*, 55, 965, 1991.

15. Nordstrom, D. K., Alpers, C. N., Ptacek, C. J., and Blowes, D W., Negative pH and extremely acidic mine waters from Iron Mountain, California, *Environ. Sci. Technol.*, 34, 254, 2000.

16. Thomas, G. W., Problems encountered in soil testing methods, in *Soil Testing and Plant Analysis, Part 1*, SSSA Spec. Publ. 2, SSSA, Madison, WI. 1967, 37-54.

17. Thomas, G. W., and Hargrove, W. H., The chemistry of soil acidity, in *Soil acidity and liming*, 2nd Ed. Agronomy Monographs 12, ASA, CSSA, and SSSA, Adams, F., Ed., Madison, WI, 1984, 3-56.

18. Sparks, D. L., *Environmental Soil Chemistry*, CA Academic Press, San Diego, 1995, Chap. 10.