Phytostabilization of a landfill containing coal combustion waste

Christopher Barton, Donald Marx, Domy Adriano, Bon Jun Koo, Lee Newman, Stephen Czapka, and John Blake

ABSTRACT

The establishment of a vegetative cover to enhance evapotranspiration and control runoff and drainage was examined as a method for stabilizing a landfill containing coal combustion waste. Suitable plant species and pretreatment techniques in the form of amendments, tilling, and chemical stabilization were evaluated. A randomized plot design consisting of three subsurface treatments (blocks) and five surface amendments (treatments) was implemented. The three blocks included (1) ripping and compost amended, (2) ripping only, and (3) control. Surface treatments included (1) topsoil, (2) fly ash, (3) compost, (4) apatite, and (5) control. Inoculated loblolly (*Pinus taeda*) and Virginia (*Pinus virginiana*) pine trees were planted on each plot. After three growing seasons, certain treatments were shown to be favorable for the establishment of vegetation on the basin. Seedlings located on block A developed a rooting system that penetrated into the basin media without significant adverse effects to the plant. However, seedlings on blocks B and C displayed poor rooting conditions and high mortality, regardless of surface treatment. Pore-water samples from lysimeters in block C were characterized by high acidity, Fe, Mn, Al, sulfate, and trace-element concentrations. Water-quality characteristics of the topsoil plots in block A, however, conformed to regulatory protocols. A decrease in soil-moisture content was observed in the rooting zone of plots that were successfully revegetated, which suggests that the trees, in combination with the surface treatments, influenced the water balance by facilitating water loss through transpiration and thereby reducing the likelihood of unwanted surface runoff and/or drainage effluent.

INTRODUCTION

Electric power generation from the burning of coal produces vast amounts of coal combustion waste (CCW) worldwide. In the United States alone, more than 850 million t of coal was burned in

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2000, producing nearly 100 million t of CCW (Punshon et al., 2003). Beneficial reuse of CCW has generated little interest, and current practices for handling this material generally include disposal and/or storage in landfills or settling ponds (Adriano and Weber, 2001). Potentially toxic trace elements, heavy metals, and excessive concentrations of soluble salts have been shown to leach from areas where CCWs were disposed (Adriano et al., 1980). Conventional techniques for eliminating offsite impacts commonly involve isolating the waste material from groundwater through the installation of impermeable liners and covers (plastic or clay). Although the short-term benefits of an impermeable cover are obvious, high costs associated with installation and the potential for failure in the long term is of concern.

Phytoremediation is a low-cost alternative to traditional environmental remediation techniques, where vegetation and associated microfauna are used to remove, contain, or render harmless environmental contaminants (Cunningham and Ow, 1996). A vegetative cover is one such technique that may be used for the physical and/or chemical sequestration of contaminants (i.e., phytostabilization). The vegetation provides a network of roots to stabilize surface soils, as well as above-ground biomass to absorb energy from wind and water forces that would otherwise lead to erosion and bulk contaminant transport (Brown et al., 2003). Layers of compost or other organic material (peat, hay, straw, sawdust) above the waste may be incorporated into the cover material to stimulate vegetative growth and to deplete oxygen through bacterial consumption, which may influence electrochemical conditions and metal solubility in the waste material (Pierce et al., 1994; Evangelou, 1995). Chemical additives such as lime ($CaCO_3$) or apatite ($CaPO_4$) may also be added to composted material to control acidity from the oxidation of pyrite, which is commonly found at CCW sites (Evangelou, 1995). Changes in the particle-size distribution of the cover over that of the waste may be engineered to enhance water storativity and limit water percolation through the underlying contaminated material. Under such a scenario, the use of vegetation may aid in the removal of excess water from the waste site through evapotranspiration (ET) (Dobson and Moffat, 1995; Abbott et al., 2001).

The 488-D ash basin is an unlined, earthen basin that contains approximately 1 million t of dry ash and coal reject material at the U.S. Department of Energy's Savannah River Site (SRS). The pyritic nature of the coal reject has resulted in the formation of acidic drainage (AD), which, in association with CCW leachate, has contributed to surface and groundwater-quality deterioration and threatens biota in downgradient wetlands. Establishment of a vegetative cover, as described above, was proposed as a remedial alternative for stabilizing the site. A mature closed-canopy pine forest with a dense rooting mass could intercept and use rainwater, thereby reducing infiltration and recharge through the contaminated media. In addition, development of a vegetative cover and subsequent litter layer could reduce erosion and runoff and potentially alter the electrochemical conditions in the waste material such that pyrite oxidation is lessened (Barton et al., 2005). Prior to initiating the study, however, the basin supported little vegetation, contained a highly compacted surface that promoted water runoff, and exhibited a hydrology that was controlled primarily by precipitation input and loss through evaporation and seepage. In addition, the low nutrient content, high acidity, and elevated salinity of the CCWs was inhibitive to most plants. As such, studies to identify pretreatment techniques in the form of amendments, tilling, and/or chemical stabilization were needed. Given these conditions, field experiments were conducted to identify parameters that may lead to the successful deployment of a vegetative cover on the 488-D reject coal basin.

MATERIALS AND METHODS

Field Study

A randomized plot design consisting of three subsurface treatments (blocks) and five duplicated surface amendments (treatments) was developed for the 488-D basin (Figure 1). The randomization was implemented so that potential bias associated with nonuniformity of the basin's geochemistry would be equally distributed between treatments. Subsurface blocks were established to evaluate the influence of compaction and nutrient loading on plant survival and root penetration in the basin material. The three blocks included

1. disturbed (ripped and disked) and compost amended (135 wet t ha^{-1} Carolina compost)
2. disturbed (ripped and disked) with no compost amendment
3. undisturbed (no ripping or disking)

The five surface treatments outlined below were applied randomly to 2 of the 10 plots in each of the above three blocks:

1. control (no additional amendments or mechanical treatment applied)
2. apatite and triple superphosphate
3. topsoil cover (10–15 cm; 4–6 in.)
4. compost (10–15 cm; 4–6 in.) (poultry litter, hardwood bark, wood chips, and limed flyash)
5. ash cover (10–15 cm; 4–6 in.) (from SRS A-area powerhouse)

Each block was approximately 0.5 ha (1.2 ac) in size, with each treatment covering a surface area of

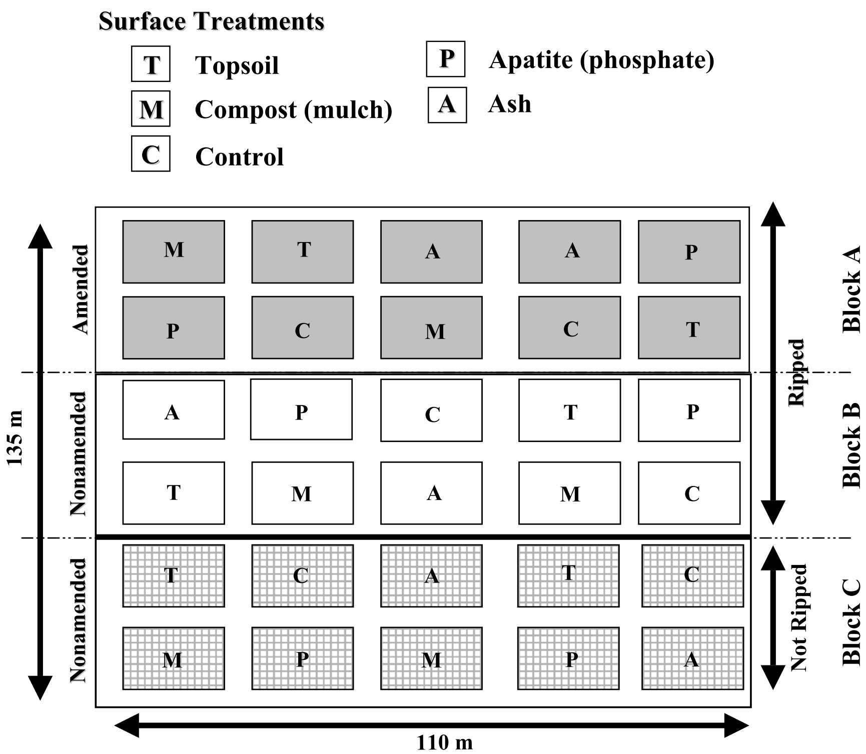

Figure 1. Randomized plot layout on the 488-D basin at the Savannah River Site, South Carolina.

232 m^2 (2497 ft^2). Each treatment cell was separated by 5-m (16-ft) buffer strips. None of the covers were incorporated with the basin material.

Site preparation began in December 1999 with the application of 135 wet t ha^{-1} Carolina compost to block A. Subsequently, blocks A and B were ripped to a depth of nearly 1 m (3.3 ft), then plowed with a cutting harrow. All tillage implements were pulled with dozers to minimize additional compaction. Soil samples were collected from the surface (0–15 cm; 0–6 in.) in triplicate from each treatment plot in April and September 2000 and analyzed for pH (1:1). Results indicated that the ripping and the addition of the compost had an acidifying effect on the surface material. Similar results were observed by Barth (1983) and Boon (1986) when amendments were added to pyritic mine waste. To partially neutralize the high surface acidity, 22 t ha^{-1} of agricultural lime ($CaCO_3$) was broadcast over the entire study area in October 2000. Surface amendments were applied from November 2000 to January 2001. Approximately 40 t of topsoil, compost, and ash were dumped on their respective plots, then leveled using a front-end loader. Apatite and triple superphosphate were applied to their respective plots at a rate of 3.4 kg of P ha^{-1}.

Prior to the application of cover material, samples were collected from each of the materials and the basin. The samples were analyzed for pH, electrical conductivity (EC), total recoverable metals (U.S. Environmental Protection Aagency [USEPA], 1994a, method 200.2), total exchangeable bases and nitrate (NRCS, 1996), and total N and C following standard methods (Sparks, et al., 1996). After amendment application, additional soil samples were collected in triplicate from each plot at depths of 0–10 and 40–50 cm (0–4 and 15–20 in.). These samples were analyzed for pH, EC, total recoverable metals, and total N and C using methods mentioned above. Samples for metal analysis were digested using the HCl/HNO_3–based microwave digestion method (USEPA, 1996) followed by inductively coupled plasma–mass spectrometry or optical emission spectrometry (ICP-MS, ICP-OES). Quality assurance-quality control protocols were followed for all analytical procedures (USEPA, 1994b). Additional soil samples were collected from each plot at depths of 0–10 and 40–50 cm (0–4 and 15–20 in.) after 1 yr and analyzed for pH and EC.

Containerized loblolly (*Pinus taeda*) and Virginia (*Pinus virginiana*) pine seedlings inoculated with *Pisolithus tinctorius* and *Scleroderma cepa* were transplanted on the basin in February 2001. Pines were used because of their long growing season (i.e., high ET rate) and demonstrated performance on acidic mine sites (D. Marx,1999, personal communication). Each plot received 100 trees on a 1.5-m (5-ft) spacing. A total of about 3000 seedlings were planted in the study area. Three additional plots of 100 seedlings, one on each edge of the basin and another on native soil (uncontaminated tilled forest site), were established to evaluate seedling survival and growth characteristics outside of the primary study area.

Growth and survival characteristics were monitored throughout the study period. Seedling height and stem diameter were measured in April 2001, October 2001, and October 2002. Plant root growth (depth and spread), plant biomass, and inoculation index were evaluated after one growing season (Grand and Harvey, 1982). Plant tissue samples were collected and analyzed for total elemental concentration using the same methods prescribed for soil analysis. Tissue samples were also analyzed for nutrient content using the wet ash $HNO_3 + H_2O_2$ procedure (Ellis et al., 1992).

Hydrology and Soil-Moisture Monitoring

Basin hydrology was monitored each month using a combination of wells and water-level gages. Shallow zero-tension wells (200 cm [78 in.] depth) were constructed using 5.0-cm (1.96-in.)-diameter schedule 40 PVC pipe that was slotted along its entire length. Borings for the wells were drilled by hand using an 8.5-cm (3.34-in.) bucket auger. Washed sand was packed from the base of the borings to approximately 25 cm (10 in.) above the screened area, and the remaining annulus was filled to just below the surface with slurry created from the bore cuttings. A plug of bentonite was placed at the surface to prevent short-circuiting. Water depths in the wells were measured using a portable water-level indicator. A semicontinuous recording data logger (WL-80®, Remote Data Systems) was installed to detect perched water conditions in the upper 2 m (6.6 ft) of the basin.

Open precipitation and event logging was measured using a HOBO® data-logging rain gauge. Other meteorological variables (net solar radiation, air temperature, humidity, and wind speed) were obtained from an onsite weather station. Mean daily reference ET rates were calculated using a modified version of the Penman-Monteith equation (Monteith, 1965; Allen et al., 1999). Mean solar radiation (MJ m^{-2} d^{-1}), air temperature (°C), wind speed (m s^{-1}), and humidity

(%) were obtained from the weather station located on the 488-D basin.

Soil moisture at 25-cm (10-in.) intervals, to a depth of 2 m (6.6 ft), was determined in block A on the ash and topsoil treatments; outside the study area in a non-vegetated location (control); and in an area that contained naturally established vegetation (reference site, Short Rotation Woody Crop experimental site), using time-domain reflectometry (TDR) (TRIME-FM®, IMKO GmbH). Soil compaction was evaluated using a cone penetrometer (Farnell A2451).

Water Quality

Subsurface water samples from the basin were collected on a quarterly basis using lysimeters (Soil Moisture Equipment, Santa Barbara, California). Suction (tension) lysimeters at 15- and 30-cm (6- and 12-in.) depths were installed in several treatment groups. An additional sampler at 200 cm (78 in.) was installed in each block near the well. Once installed, a vacuum of 0.06 MPa was applied to the lysimeter using a hand vacuum pump. A stopper assembly equipped with a neoprene tube and pinch clamp was used to contain the applied vacuum. Water was extracted from the lysimeters and analyzed for pH and EC in the field using a HYDROLAB®. Additional samples were transferred to polyethylene bottles, packed in ice, and transported to the laboratory where they were filtered (0.45 μm) and preserved as deemed necessary according to standard procedures (APHA, 1989), then refrigerated at 4°C until analyzed.

Statistical Analysis

Analysis of variance (ANOVA), general linear models (PROC GLMs), and PROC Univariate were performed to determine significant differences in elemental composition of the harvested seedlings. Survival data of the seedlings (loblolly only) were analyzed with repeated-measures logistic regression models (PROC GENMOD). The models included all main-effects and two-way interactions, with survival as the dependent variable, and subsurface (block) and surface treatments (cover) as the independent variables. Probabilities of seedling survival were calculated by backtransformation of the least-squares mean (LSM) from the logistic models $(e^{LSM})/(1 + e^{LSM})$. Seedling growth was estimated by subtracting the initial height (April 2001) from the height at the end of the second growing season (October 2002). Growth measures were analyzed with linear regression models (PROC MIXED). The models included all main-effects and two-way interactions, with seedling growth as the dependent variable and subsurface and surface treatments as the independent variables. Because of the high mortality in control and apatite plots and the loss of replication, statistical evaluation of the surface treatments was performed for the topsoil, ash, and mulch treatments only. Statistical significance was established where $P < 0.05$ in all cases. All statistical models were performed using SAS (SAS, 1999).

RESULTS AND DISCUSSION

Soils and Sediment Characterization

Chemical characteristics of the cover materials and the untreated basin material are presented in Table 1. The pH of the soil, compost, and ash materials were neutral to slightly acidic, whereas the 488-D basin material was highly acidic and potentially phytotoxic. The 488-D CCWs and the A-area ash were generally nutrient deficient. Both had no measurable NO_3^- or P concentrations and exhibited very low K content (<10 mg kg^{-1}). Both materials were also characterized by elevated Fe and Al concentrations, which were over the background levels for coastal-plain soils in South Carolina (Canova, 1999) but not in the critical range for plant growth and survival. Arsenic concentrations for the 488-D CCWs and the A-area ash, however, were within the critical range for phytotoxicity (20–50 mg kg^{-1}) (Alloway, 1990). The ash and CCWs also exhibited a relatively high C content, which may be attributed to unburned coal particles in the waste material. The topsoil and biosolid substrates were more enriched with basic plant nutrients (N, P, and K) and did not contain other elemental contents that may pose phytotoxicity concerns.

Soil pH levels from samples collected after treatment application was established exhibited wide variation (pH range 1.19–7.65) in the 0–10-cm (0–4-in.) depths (Table 2). Because of the incorporation of alkaline Carolina compost, the block A control treatment showed a slightly higher pH than that of blocks B and C (2.63 vs. <1.5). The compost cover treatment exhibited pH values that were nearly 2 pH units higher (average 6.82) than the topsoil or ash treatment. At the 40–50-cm (15–20-in.) depth, below the treated layer, pH values converged (pH range 1.58–3.84), and little influence from the amendments was observed.

Table 1. Average Chemical Characteristics of Substrate Materials Prior to Application*

Parameter	Soil	Compost	Ash	CCW 488-D
pH (1:1)	5.07 (0.62)	6.83 (1.03)	5.25 (0.35)	1.72 (0.75)
EC (1:5)	0.07 (0.08)	2.66 (0.53)	1.2 (0.28)	5.92 (1.86)
NO_3-N	10.3 (3.0)	31.0 (14.7)	BDL**	BDL**
P†	6.8 (2.9)	BDL**	BDL**	BDL**
K†	17.2 (10.0)	79.6 (19.2)	8.5 (0.7)	2.3 (1.5)
Mg†	48.7 (34.3)	146.0 (107.6)	7.5 (4.9)	174.3 (82.2)
Ca†	208.2 (118.3)	766.3 (64.5)	272 (67.8)	526.0 (47.0)
Al††	4193.8 (146.3)	430	3960	1767.9 (495)
Fe††	3510.5 (195.5)	351	8220	20,476.4 (13,827.1)
Mn††	222.3 (8.89)	2.33	42.5	7.18 (12.3)
Zn††	14.3 (11.1)	4.95	11.5	1.96 (6.00)
Cd††	BDL**	0.13	BDL**	0.1 (0.58)
Pb††	8.15 (1.1)		18.9	28.4 (12.4)
As††	9.88 (0.72)	BDL**	33.4	64.7 (43.0)
Se††	BDL**	BDL**	7.77	8.88 (5.80)
OM (%)		31.9		
C (%)	1.29 (1.22)	13.3 (1.0)	26.4 (1.2)	11.6 (2.25)
N (%)	0.08 (0.05)	0.41 (0.6)	0.48 (0.8)	0.21 (0.04)

*In mg/kg except where noted otherwise; standard error in parenthesis.
**BDL = below detection.
†Mehlich-1 method (HNO_3-H_2SO_4).
††USEPA method 200.2 (HNO_3-HCl).

After two growing seasons, soil pH exhibited a general increase over that observed during the initial sampling (Table 2). Changes in soil chemistry as influenced by litter layer development and plant establishment may have contributed to this increase. However, pH increases were noted in plots that exhibited complete mortality. This indicates that the pH variations between years could have been largely influenced by geochemical processes instead of biological processes. It is likely that the time of sampling and moisture conditions on the basin influenced the results. The first sampling was done during a prolonged hot and dry

Table 2. Average pH (1:1) of 488-D Sediments at 0–10 and 40–50-cm (0–4- and 15–19-in.) Depths (n = 3)*

Cover	Control	Compost	Topsoil	Ash	Apatite	Control	Compost	Topsoil	Ash	Apatite
Depth	0–10 cm (0–4 in.)					40–50 cm (15–19 in.)				
June 2001										
Block A	2.63	7.32	4.95	4.10	3.77**	2.29	3.84	2.29**	1.47	3.13
Block B	1.19**	5.51	5.05**	5.60	2.13	1.58	2.12	3.39	2.71	2.02
Block C	1.34**	7.65	4.65	4.58	1.70	1.79**	3.18	3.15	2.71**	2.30
Average	1.72	6.82	4.88	4.76	2.53	1.88	3.04	2.94	2.29	2.48
October 2002										
Block A	4.51	6.42	4.55	5.79	4.13	3.26	3.16	3.26	3.73	3.53
Block B	2.53	5.20	5.12**	4.54	3.73	2.3**	2.45	3.65**	3.08	3.19
Block C	3.68	6.54	5.31	4.44	2.34	2.74	3.19**	3.16	2.25	2.39
Average	3.57	6.05	4.99	4.92	3.40	2.76	2.93	3.35	3.02	3.03

*Standard deviation of the mean <20% for all samples except those identified with a **.

period, which was conducive for the formation and accumulation of evaporative salts on the basin surface. Efflorescent salts that were later identified as coquimbite ($Fe_2(SO_4)_3{\cdot}9H_2O$), were observed during this period. These salts are highly soluble and can be highly acidic (pH $\approx$ 1.0) and are commonly thought to be the primary source of acidity on waste sites containing appreciable amounts of pyrite (Barton et al., 2005).

Electrical conductivity can be used as an indirect measure of ionic strength and salinity in soils (Evangelou, 1995). Sediment EC concentrations from the control plots exhibited a general inverse correlation to that of pH (Table 3). This relationship supports the hypothesis that salts were present on the surface in 2001 but absent in 2002. Sediments from the topsoil and ash-amended plots at both depths, however, exhibited large increases in EC from 2001 to 2002 but did not show corresponding change in pH.

Average total elemental composition for samples collected on July 2001 at the 0–10- and 40–50-cm (0–4- and 15–20-in.) depths are presented in Table 4. Results represent an average of three samples from each surface treatment on all blocks. In general, the surface sediments contained lower elemental concentrations than the lower depths. The 0–10-cm (0–4-in.) compost treatment was characterized by a much higher calcium concentration than the other treatments, reflecting the addition of lime to the material during composting. As indicated earlier, iron concentrations were much higher than background levels for South Carolina soils, particularly at the lower depth. In addition, arsenic concentrations were within or above the critical toxic range for all samples. Total C (15–21%) and N (0.32–0.49%) content was similar for all treatments and blocks regardless of depth.

Vegetation Characterization

For a discussion of vegetation survival, data obtained during comprehensive surveys on October 2001 (first complete growing season) and 2002 (second growing season) were used. Examination of the blocking effect on seedling survival after 1 yr revealed that block A exhibited the highest survival (70%), followed by blocks B (52%) and C (37%) (Figure 2). After two growing seasons, block A still exhibited the highest survival (62%), followed again by blocks B (33%) and C (21%). For 2002, survival in block A was significantly greater than that in both blocks B and C. This response is likely the result of more favorable physicochemical characteristics of the plots caused by ripping and compost addition. Not only did block A exhibit a higher surface pH (especially in the control and apatite covers), but it also exhibited lower compaction that allowed for better root penetration, gas exchange, and water infiltration (Bledsoe et al., 1992) (Table 5). Growth curves of the loblolly seedlings in each block revealed a similar relationship, where plants from block A exhibited increased heights over that of the other blocks (Figure 3). The height of the loblolly seedlings in block A was also elevated over those in a noncontaminated site with native soil, particularly in the plots that

Table 3. Average EC (1:3) of 488-D Sediments at 0–10- and 40–50-cm (0–4- and 15–19-in.) Depths (n = 3)*

Cover	Control	Compost	Topsoil	Ash	Apatite	Control	Compost	Topsoil	Ash	Apatite
Depth	0–10 cm (0–4 in.)					40–50 cm (15–19 in.)				
June 2001										
Block A	1.97	2.70	0.04	0.56	1.08	2.20	2.02	0.30	0.05	2.35
Block B	5.70	3.06	0.08	0.57	4.53	3.69	2.72	0.19	0.39	2.54
Block C	4.86	3.29	0.24	0.87	5.23	2.78	2.39	0.22	0.81	4.99
Average**	4.17†	3.01	0.12†	0.66	3.61†	2.89	2.37	0.23	0.41†	3.29†
October 2002										
Block A	1.46	1.64	1.46	2.57	0.87	1.52	1.56	1.52	1.52	0.60
Block B	4.24	3.18	1.73	2.77	2.41	5.85	6.34	2.34	3.07	1.67
Block C	3.26	3.06	2.24	3.07	3.91	5.03	4.02	1.65	7.05	5.68
Average**	2.98†	2.62	1.81	2.80	2.39†	4.13†	3.97†	1.83	3.88†	2.65†

*Units of measurement = mS cm^{-1}.

**Standard deviation of the mean between blocks >50% for those indicated with a †.

Table 4. Average Total Elemental Composition of 488-D Sediments at 0–10- and 40–50-cm (0–4- and 15–19-in.) Depths ($n = 3$)*

Cover	Control	Compost	Topsoil	Ash	Apatite	Control	Compost	Topsoil	Ash	Apatite
Depth	0–10 cm (0–4 in.) (mg/kg)					40–50 cm (15–19 in.) (mg/kg)				
Al	1005.7	8365.1	3718.0	5951.5	3250.5	3988.5	6743.2	4559.8	5355.2	6600.6
As	50.4	85.0	45.2	53.23	110.2	108.2	119.9	29.6	120.6	69.6
Ca	7092.0	76,913.4	250.9	5973.2	3820.0	5513.9	6880.8	1884.2	4565.3	4736.8
Cd	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.1	BDL
Cr	3.8	27.9	7.3	9.94	13.4	10.5	21.2	14.4	17.4	13.2
Cu	14.6	52.5	7.6	35.3	29.2	24.5	43.2	28.7	34.3	27.3
Fe	22,936.5	7169.1	4329.5	11,954.5	58,816.6	30,850.0	53,979.3	27,044.3	38,627.2	46,628.5
K	700.0	1079.4	BDL	304.1	1177.1	749.7	978.2	460.3	1005.9	1316.7
Mg	292.2	2028.8	98.0	1550.6	400.4	423.6	575.9	371.7	844.7	245.2
Mn	23.9	198.4	62.9	48.7	87.6	64.1	206.1	124.4	134.6	100.4
Na	226.0	1045.2	103.1	186.7	527.5	319.0	348.9	248.1	432.6	349.4
Ni	8.8	19.2	7.3	29.7	23.1	9.6	14.9	9.2	22.2	10.4
Pb	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	4.0	6.1
Se	BDL	20.4	20.2	BDL	32.8	35.9	57.9	24.3	38.3	2.4
Zn	62.6	104.6	60.6	65.7	43.8	64.4	74.9	86.0	81.3	67.4
C**	18.7	19.1	15.1	21.5	20.7	19.6	18.2	18.1	15.9	17.1
N**	0.42	0.49	0.33	0.43	0.46	0.41	0.35	0.38	0.32	0.35

*USEPA method 200.2 (HNO_3-HCl digestion).
**Values in %.

received a surface amendment. Whole tree harvesting from the site, after one growing season, also indicated an elevated biomass and root volume in block A over blocks B and C and the native soil (Table 6). The inroculation index of plants growing on all plots was high. In addition, ectomycorrhizal Pt fruiting bodies were observed outside of the plot boundaries during the 2002 growing season, which indicated that the root was capable of growing out of the cover material and into the 488-D sediment.

Seedling surveys by surface treatment groups indicate that the ash and topsoil amendments greatly improved survival rate on the basin (Figure 4). Mortality of less than 25% was exhibited on block A treatments. The apatite treatment was unusual in one plot on block A, exhibiting 97% survival; however, survival in blocks B and C did not differ significantly from that observed in the control. The block A topsoil treatment exhibited a significantly higher survival than those with the same treatment in blocks B and C. The ash treatment in blocks A and B was significantly higher than that observed in block C. The compost treatment exhibited the most consistent survival characteristics across the blocking units, varying by less than 20% between blocks. The only significant difference in survival with respect to the interaction across surface treatments

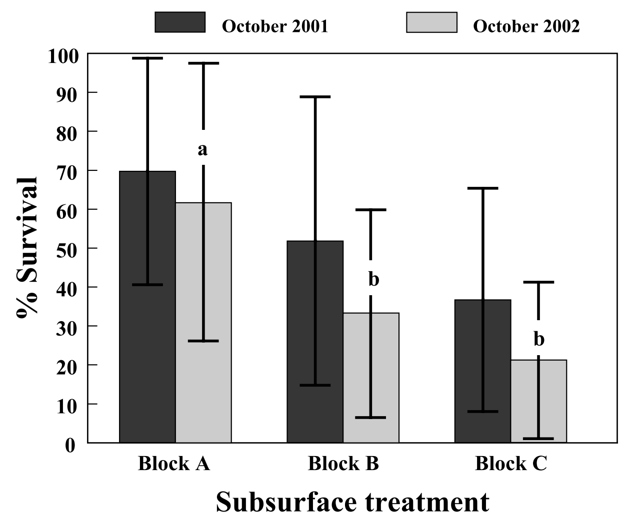

Figure 2. Seedling survival by subsurface treatment on the 488-D basin. Significant differences ($p < 0.05$) between treatments are denoted by differing lowercase letters on the October 2002 bar graphs. (Block A: ripped and compost amended; block B: ripped only; block C: control.) Survival of trees planted in native soil was 97, 93, and 90% for sample dates April 2001, October 2001, and October 2002, respectively.

Table 5. Penetrometer Resistance (psi) at the 488-D Basin

Depth (cm)	Block A	Block B	Block C
December 2001			
0–10	39	106	176
10–20	116	141	243
20–30	116	193	>300
30–40	174	255	>300
November 2002			
0–10	92	195	273
10–20	150	210	>300
20–30	190	280	>300
30–40	217	>300	>300

Table 6. Mean Growth Characteristics from Seedlings Harvested after 1 Yr (n = 4)

Site	Biomass (g)	Root Volume (L)	Inoculation Index (%)*		
			Pt	Sc	Tt
Block A	85.9	76.18	63	7	7
Block B	38.0	14.16	63	12	3
Block C	33.1	18.97	41	4	0
Native soil**	18.7	35.96	3	8	0

*Pt = *P. tinctorius*; Sc = *S. cepa*; Tt = *T. terrestris*.
**Planted in an uncontaminated area (n = 2).

was observed between block A topsoil and block A compost. Although statistical analyses were not possible for the apatite and control treatments because of complete mortality in some plots, the importance of the amendments on plant survival and growth was clearly evident (Figure 4).

Comparison of the treatment groups relevant to surface pH revealed that the ash and topsoil plots induced pH levels consistent with those of the native soils on the SRS (1:1 pH ≈ 5.0). In contrast, the apatite and control plots exhibited pH values in the 2–3 range, which are deleterious to plant growth and survival rate. However, the apatite plots responded positively in block A only, exhibiting a surface pH near 4.0 for both years sampled. The compost treatment, however, maintained pH values above 6.0 for most plots. Although this pH level appears ideal for tree culture given the preexisting conditions of the basin, some pines manifested developmental problems even under alkaline soil conditions. By examining the different pine species and stock under the varying treatments, the influence of the higher pH on survival of Virginia pine was revealed. Loblolly pine in the compost treatment showed moderate survival rates (≈50%), whereas the Virginia pine exhibited high mortality (95%). The Virginia pines actually outperformed the loblolly in the topsoil, apatite, and control plots; thus, mortality of the Virginia pine is likely attributed to certain chemical constituents of the compost that was not present in the other amendments.

Plant tissue analyses revealed that the nutrient sufficiency levels prescribed for loblolly pine (Campbell, 2000) (i.e., N = 1.1%, P = 0.1%, K = 0.35%, Ca = 0.12%, and Mg = 0.07%) were exceeded in all plots. Prior to planting, P levels were below detection levels in the 488-D basin material and all of the cover amendments

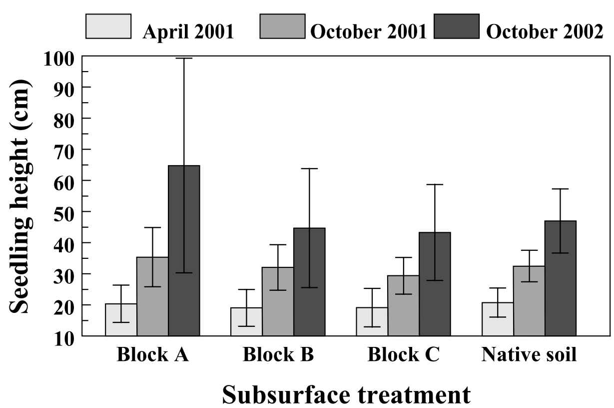

Figure 3. Seedling growth by subsurface treatment for two growing seasons on the 488-D basin. (Block A: ripped and compost amended; block B: ripped only; block C: control).

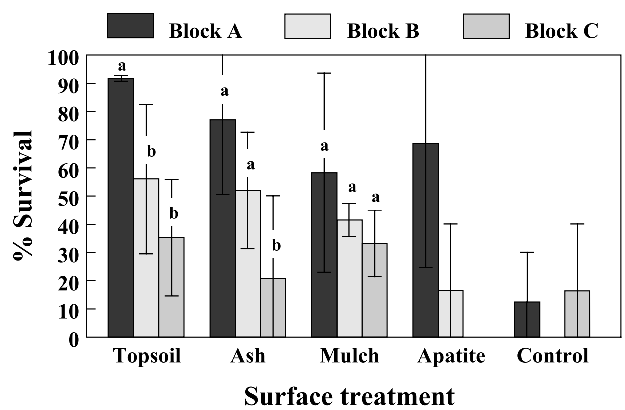

Figure 4. Seedling survival by surface treatment amendments and blocks on the 488-D basin. Significant differences (p < 0.05) in surface treatment by block are denoted by differing lowercase letters. (Block A: ripped and compost amended; block B: ripped only; block C: control).

with the exception of the topsoil (Table 1). The presence of adequate P levels in plant tissue is possibly attributed to the potting soil and residual fertilizers from the containers where the seedlings were germinated. Total elemental composition of the loblolly seedlings did reveal significantly higher tissue concentrations of Se and B in the ash and compost plots over that of the other surface treatments (Table 7). Phytotoxicity of B in *Pinus* is species specific but has been documented at levels ranging from 75 to 500 mg kg^{-1} (Adriano, 2001). Yellowing of needles, which is a sign of B toxicity, was noted on ash plots throughout the study. Although tissue analysis was not performed on the VA pine, the potential for B toxicity in these plots was likely, and an increased mortality caused by heightened sensitivity over that of the loblolly was possible. Arsenic concentrations were not significantly different between treatments, but levels on the basin seedlings were much greater than those observed at the native soil site. Because the native soil As levels were below detection, computation of a statistical difference between the plots on the basin was not possible.

Hydrology and Soil Moisture

A tipping bucket on the 488-D ash basin recorded rainfall quantity for the site. Throughout the study period, the Central Savannah River Region underwent prolonged drought. As such, monthly rainfall amounts that exceeded the 50-yr average for SRS were observed only twice in March and June 2001 (Figure 5a). The drought may have directly contributed to seedling mortality (aestivation) or indirectly through the formation of evaporative salts as described earlier. Calculated potential ET rates indicated an evaporative demand of 2797 mm (110.1 in.) for the 20-month period, which would suggest a substantial deficit of water to the basin (Figure 5b). In fact, the calculated ET is almost double that of the input water. Piezometers and monitoring wells in the upper 2 m (6.6 ft) of the basin material reflected this condition as they remained dry throughout the 2-yr study period. Unfortunately, the influence of ripping on hydraulic conductivity could not be ascertained because the medium was in an unsaturated state throughout the study period, and ponding (or perched water) from rain events was not detectable using these instruments.

An examination of data from the soil-moisture sensors revealed some interesting trends with respect to water percolation in the basin. A TRIME TDR sensor located at a reference site (recently harvested bare soil) provided an initial background moisture curve for a native soil on the SRS (Figure 6a). For the period of March–September 2001, the surface soil at the reference site exhibited soil-moisture contents of approximately 15%. This level was fairly consistent at the 25- and 55-cm (10- and 21-in.) depths throughout the studied period. Soil moisture increased on this site by approximately 10% in the deeper profiles (135 and 175 cm; 53 and 69 in.).

Soil-moisture patterns from the ash basin differed greatly with respect to the reference soil. Surface moisture contents obtained from the TRIME were greater than that observed in the native soil. High salinity and EC have been shown to result in erroneously high readings with TDR instruments (Dasberg and Dalton, 1985; Nadler et al., 1999). It is possible that soil-moisture levels could respond to evaporative salt formation as described earlier. Samples collected periodically over the 8-month period and determined gravimetrically, however, agreed considerably well ($r^2 = 0.73$) with the TRIME units. In addition to the higher moisture conditions, the instrument showed incongruent saturation curves with depth on the basin, which suggested the presence of perched water table. The compacted nature of the basin material was conducive for the formation of such saturation. The control TRIME sensor located in an undisturbed and unvegetated area on the basin exhibited surface moisture contents at nearly 30% (Figure 6b), decreasing with depth (50 and 100 cm; 20 and 39 in.) by approximately 10%. At 200 cm (78 in.), however, soil-moisture content was near saturation. Based on this information, we concluded that a restrictive layer had formed just below the surface.

The TRIME moisture sensors located in the planted area (ash and topsoil plots in block A) displayed lower moisture readings than those of the control at the surface level (Figure 6c, d). The topsoil cover exhibited the lowest moisture contents, which is likely attributable to greater water use by weeds and planted species, particularly in 2002. Unexpectedly, moisture content was higher in the 50-cm (20-in.) zone than that observed in the 100-cm (39-in.) zone in both plots. It is possible that a restrictive layer similar to a plow-pan was developed during the ripping process at the 1-m (3.3-ft) level. Ripping was performed to break compaction and promote infiltration, but the extent of the tillage was restricted to the upper part of the profile. Thus, water may have moved freely through the plowed zone, diminishing at the plowed-unplowed interface. Similar instances have been reported elsewhere by Barton and Karathanasis (2002).

Table 7. Average Total Elemental Composition (mg kg^{-1}) of Loblolly Pine Seedlings after 1-Yr Growth (n = 2)*

Cover		Control		Compost		Topsoil		Ash		Apatite**		Native†	
		Average	Standard Deviation	Average	Standard Deviation	Average	Standard Deviation	Average	Standard Deviation	Average	Standard Deviation	Average	Standard Deviation
Al	s††	1110	124	792	29	631	250	505	66	788		1224	56
	t	1298	337	1587	19	1942	2097	1147	122	2238		2692	319
As	s	7.28	1.10	4.42	2.15	0.95	0.82	7.48	0.92	8.73		BDL	BDL
	t	7.95	2.04	8.57	3.11	2.45	1.09	9.95	0.61	21.3		BDL	BDL
Cr	s	7.21	1.09	5.44	1.24	8.30	5.34	5.62	0.92	3.96		6.93	0.8
	t	17.5	6.98	10.2	1.31	15.0	6.03	14.2	5.63	12.8		13.6	1.54
Cu	s	9.86	2.91	13.0	1.01	8.51	2.67	12.5	1.51	13.8		6.2	0.36
	t	24.7	10.3	30.6	3.39	17.8	6.05	38.0	24.2	37.7		15.3	0.21
Fe	s	2704	668	603	117	416	185	501	51	517		350	62
	t	3961	1263	1785	9	1468	124	985	108	4585		1002	184
Mn	s	419	111	101	31	485	76	54.7	12.8	144		915	51
	t	602	133	147	44	621	138	84.0	15.7	178		1237	121
Mo	s	0.84	0.45	3.86	2.63	0.95	0.66	4.93	1.45	0.72		0.72	0.41
	t	1.41	0.27	26.8	13.4	1.81	0.98	49.0	34.0	4.16		1.26	0.48
Ni	s	9.39	0.73	4.98	0.32	6.48	1.81	13.4	6.59	11.6		7.74	3.78
	t	20.7	1.87	11.4	2.88	11.7	1.39	25.7	5.62	20.5		16.4	33.7
Pb	s	8.5	1.83	3.67	1.0	3.88	3.73	4.38	1.61	2.34		4.17	0.83
	t	13.8	3.19	6.24	0.94	8.19	7.52	8.24	3.14	5.92		17.4	12.2
Se	s	1.14	1.61	7.90	3.30	4.77	1.30	8.91	1.41	6.45		3.46	2.93
	t	1.14^{b}	1.61	17.1^{a}	5.34	5.43^{b}	1.97	21.4^{a}	2.55	10.8		4.86^{b}	5.33
Zn	s	32.5	11.0	42.4	15.7	74.8	2.69	61.5	12.0	56.3		71.0	19.3
	t	50.1	18.3	78.4	23.0	109	7.89	93.4	14.5	89.0		126	21.1
B	s	60.2	33.8	254	32	69.3	40.8	484	128	8.68		13.2	3.36
	t	67.1^{b}	32.5	309^{a}	35	81.8^{b}	43.8	561^{a}	147	44.1		21.8^{b}	2.92

*USEPA method 200.2 (HNO_3-HCl digestion).
**Only one loblolly pine harvested from this plot.
†Planted in an uncontaminated area (n = 2).
††s = shoot concentration; t = total concentration (shoot + root).
a,bSignificant differences for B (P = 0.0002, F = 19.04) and for Se (P = 0.0022, F = 9.82).

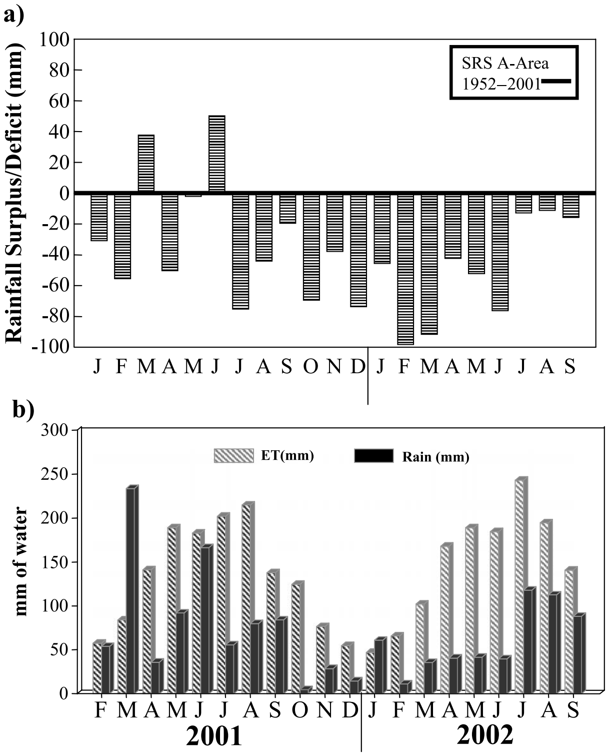

Figure 5. Monthly rainfall deviation from the 50-yr average (a) and monthly rainfall versus evapotranspiration (b) from January 2001 to September 2002 on the Savannah River Site, South Carolina.

Using TDR, gravimetric and well data, moisture distribution curves for the topsoil and control sites were developed for the period January to August 2002. The presence of a perched zone as described above is clearly shown in the curve (Figure 7). In addition, the impact of the vegetation is notable in the upper part of the profile. The whole tree harvesting indicated that the rooting zone was most prominent in the upper 50 cm (20 in.) of the basin (Table 6). As such, the impact of the vegetation on soil-moisture content, during this period, would likely occur in that zone. The difference in average soil moisture between the control and topsoil plots during the 8-month period of 2002 was 16.59%. Using a porosity of ~50% for the basin material (sampled average = 55 ± 16%), the total volume of the basin to 25 cm (10 in.) (9112.5 m^3; 321,804 ft^3), and the 16.59% difference in soil-moisture content, the potential loss/use of water by the vegetation cover (topsoil plot) was calculated to be more than 9.1 million L (2.4 million gal) over that of the control.

Water Quality

Water samples collected from three lysimeters at a depth of 200 cm (78 in.) contained high concentrations of Al, Fe, and sulfate, which are characteristic of AD

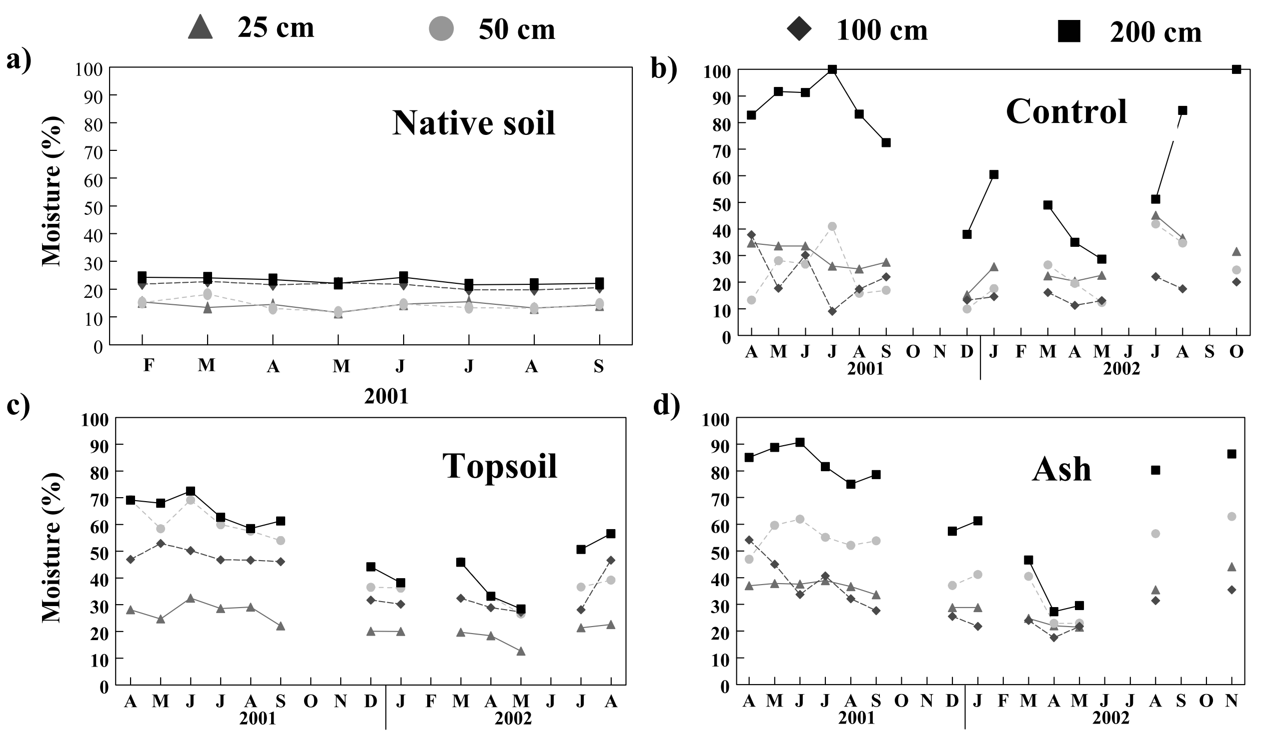

Figure 6. Soil moisture content (%) at various depths as detected by the TRIME TDR sensors at an uncontaminated reference site with native soil (a) and on the control (b), topsoil (c), and ash (d) plots of block A (ripped and compost amended) on the 488-D basin.

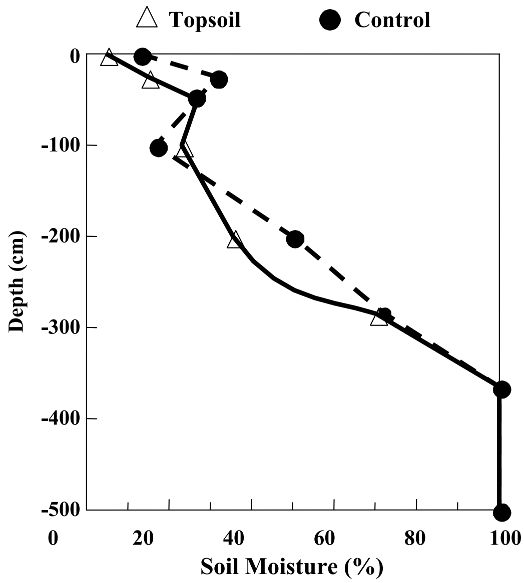

Figure 7. Soil moisture distribution at various depths in the block A: topsoil and control treatment plots on the 488-D basin.

from mining sites and CCW areas (Evangelou, 1995) (Table 8). Given the low permeability and high pyrite content of the substrate material, the high concentrations were not unexpected. The reactive material apparently stayed moist for an extended period of time, allowing for maximum oxidation of the sulfide materials and dissolution of evaporative salts (see Barton et al., 2005 for more details). As the pore water slowly moved through the sediments, oxygen consumption increased, pH rose, and metals precipitated as discrete as metal sulfide minerals in the substrate (Barton et al., 2005).

The influence of the cover treatments on water quality is not clearly evident at this time. Because of the prolonged drought, collection of shallow pore water was difficult to achieve. For example, only 7 lysimeter samplers out of 15 yielded water more than twice during the entire study. The average water-quality characteristics from those samplers are outlined in Table 8. Samples collected from block A topsoil at the 15- and 30-cm (6- and 12-in.) depths were relatively clean as compared to the 200-cm (78-in.) lysimeter samples. Both sample depths in the block A topsoil plots exhibited neutral pHs, low Fe and Al content, and negligible trace-element concentrations. Samples collected from block C topsoil at the 15- and 30-cm (6- and 12-in.) depths, however, exhibited a solution chemistry that was more similar to that of the 200-cm

Table 8. Average Water-Quality Characteristics from Lysimeters on the 488-D Ash Basin between April 2001 and October 2002*

Parameter	T-15-A**	T-30-A	T-15-C	T-30-C	200 cm-A	200 cm-B	200 cm-C
n	4	4	4	4	5	6	6
pH (su)	6.27 (0.20)	6.01 (0.26)	5.37 (2.71)	2.13 (0.13)	2.94 (0.70)	2.52 (0.16)	2.07 (0.70)
EC (mS)	3.11 (3.11)	3.50 (4.13)	5.04 (5.87)	7.39 (2.45)	35.7 (25.9)	21.8 (6.5)	52.2 (20.0)
Al (mg L^{-1})	0.50 (0.01)	0.59 (0.02)	86.1 (120.6)	111.5 (59.9)	298.1 (218.0)	1205.4 (932.2)	959.2 (715.1)
As (mg L^{-1})	0.02 (0.01)	0.03 (0.06)	0.13 (0.24)	0.08 (0.08)	BDL	4.55 (9.57)	3.79 (3.74)
Ca (mg L^{-1})	243.1 (83.8)	284.9 (321.9)	257.4 (278.2)	1493.6 (2050.5)	191.6 (40.2)	377.7 (83.8)	456.4 (85.3)
Cd (mg L^{-1})	BDL	BDL	0.01 (0.02)	0.10 (0.06)	0.53 (0.42)	0.78 (0.21)	1.34 (0.67)
Cr (mg L^{-1})	0.01 (0.01)	BDL	0.04 (0.06)	0.11 (0.15)	BDL	1.04 (1.19)	0.44 (0.50)
Cu (mg L^{-1})	0.02 (0.00)	BDL	0.80 (0.73)	8.42 (7.26)	1.73 (1.82)	16.3 (24.7)	4.98 (6.2)
Fe (mg L^{-1})	1.30 (0.80)	1.29 (1.44)	27.0 (28.6)	882.3 (653.2)	4697.2 (3833.6)	6039.7 (2862.2)	10,806.9 (2547.8)
K (mg L^{-1})	186.7 (81.6)	85.5 (67.3)	251.8 (207.7)	22.8 (36.2)	BDL	1.64 (4.12)	3.56 (10.0)
Mg (mg L^{-1})	91.3 (97.9)	157.0 (211.2)	76.2 (85.6)	182.1 (90.9)	323.2 (75.9)	325.0 (53.8)	603.1 (124.7)
Mn (mg L^{-1})	1.38 (1.28)	1.12 (1.31)	20.9 (29.5)	10.3 (7.5)	37.4 (10.7)	39.2 (13.9)	46.0 (22.4)
Na (mg L^{-1})	37.6 (27.8)	39.9 (44.1)	60.9 (64.7)	9.10 (6.29)	28.4 (11.0)	36.2 (23.1)	29.5 (17.3)
Ni (mg L^{-1})	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Pb (mg L^{-1})	BDL	BDL	0.04 (0.06)	0.06 (0.13)	0.07 (0.11)	0.35 (0.46)	0.29 (0.12)
Se (mg L^{-1})	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Zn (mg L^{-1})	0.23 (0.17)	0.18 (0.12)	4.25 (5.40)	12.8 (13.3)	6.94 (0.34)	19.2 (24.3)	14.3 (11.6)
SO_4 (g L^{-1})	†	†	†	5.37 (3.71)	61.0 (15.5)	62.0 (21.0)	28.0 (2.8)

*Standard deviation in parenthesis.
**T = topsoil cover; number = depth (cm); A, B, and C refer to the planting block on the basin.
†Insufficient sample volume for analysis.

(78-in.) lysimeters. Both samplers from block C yielded samples that would exceed discharge water-quality standards for Fe and Mn from active mine sites (Code of Federal Regulations, 1996). The 30-cm (12-in.) lysimeter from this block was also out of compliance for sulfate and pH. As described for the 200-cm (78-in.) lysimeters above, the lack of ripping and subsurface amendment in block C did not allow for the infiltration of water or penetration of roots. As such, contact of rainwater to the basin's surface was maximized, and water-quality deterioration primarily from the dissolution of contaminated salts ensued. Consequently, plant roots were subjected to the adverse conditions, and high seedling mortality resulted. The water chemistry in block A, in the near-surface rooting zone, was not degraded and resulted in low seedling mortality and high growth characteristics.

CONCLUSION

Physical, biological, and chemical treatments were applied to an extremely acidic ash-coal reject basin on the SRS in an attempt to demonstrate the potential use of a vegetative cover as a means for enhanced use of rainwater and subsequent nonpoint source water pollution control. Deep ripping, subsurface amendments, and surface covers were shown to be essential for the successful establishment of vegetation on the basin. Loblolly and Virginia pine seedlings inoculated with the ectomycorrhizal fungi *P. tinctorius* and *S. cepa* withstood the harsh environment of the 488-D basin and outperformed, in terms of growth, those on an uncontaminated site during the 2-yr evaluation period. Seedlings planted on block A (ripped and deep amended) in the topsoil plots developed a rooting system that penetrated into the basin media and exhibited apparent normal growth features. Trees growing in the ash and compost plots of block A achieved a survival rate greater than 50%, but tissue analysis indicated a potential problem caused by B toxicity. In contrast, seedlings on blocks B and C, regardless of the surface treatment, were apparently influenced by the lack of subsurface amendments and ripping, respectively, which resulted in poor rooting conditions, high acidity, and high mortality. A prolonged regional drought may have exacerbated the higher-than-expected mortality rate in all blocks because of aestivation and changes to the solution (water) chemistry of the basin by evaporative salt formation and subsequent acid generation. Water samples from lysimeter samplers in block C and in the deeper profile reflected this phenomenon with high acidity, Fe, Mn, Al, sulfate, and trace-element concentrations. Water-quality characteristics of the topsoil plots in block A were acceptable not only from a regulatory position, but also from a toxicity standpoint as demonstrated by good growth and survival rate of trees on these plots. The overall influence of the vegetation on water quality and quantity is difficult to ascertain because of the immaturity of the system. The full potential of the tree cover on subsurface hydrology and solution chemistry will likely not be achieved until canopy closure is achieved (another 4–5 yr). As such, continued research to evaluate the influence of the trees on the water budget at the 488-D is recommended. A general decrease in soil-moisture content, however, was observed in the rooting zone of plots that were successfully vegetated (block A topsoil), indicating substantial loss of water from the basin through transpiration that otherwise would leave the basin as an environmental contaminant through seepage and/or runoff.

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