Power Plant Combustion Byproducts For Improved Crop Productivity of Agricultural Soils

Project Number 02-CBRS-W09

Final Report

January 2005
June 2006

Prepared for:

U.S. Department of Energy National Energy Technology Laboratory
The Combustion Byproducts Recycling Consortium

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Report Issued June 30, 2006

DOE Award No.:

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Please note: Coal combustion products represent a component of a larger study involving both CCPs and composted biosolids. Statistical analysis was conducted on all industrial byproducts. For this report, only CCP data are presented in tables and figures but F tests and probabilities represent both CCPs and biosolids studied.

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ACKNOWLEDGEMENTS

The authors would like to thank the U.S. Department of Energy National Energy Technology Laboratory and the Combustion Byproducts Recycling Consortium for funding these studies.

Others individuals whose participation was vital were:

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- Renae Pablo
- Lynn Bekis
- Shirley Begay
- Marjorie Yazzie

NMSU SWAT Lab
- Barbara Foreman-Hunter

Marta Remmenga, NMSU

NMSU Soils Group Lab and Horticulture Greenhouse Facility, Las Cruces
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- Matt Baker
- Pauline Pao
- John Mexal

NMSU Agricultural Science Center at Farmington
- Rob Heyduck
- Kenny Kohler
- Merlin Begay
- Zach Williams
- Curtis Owen
- Dan Smeal
- Margaret West
- Rick Arnold

ABREVIATIONS

AW	Available Water
BA	Bottom ash
CCP	Coal combustion product
DTPA	Diethylene triamine pentaacetic acid
EC	Electrical conductivity
FA	Fly ash
f_a	Drainable porosity
f_e	Effective porosity
FGD	flue gas desulfurization products (synonymous with scrubber slurry)
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectroscopy
Ks	Saturated hydraulic conductivity
NAPI	Navajo Agricultural Products Industry
SAR	Sodium adsorption ratio
SMC	Soil moisture curve
SS	Scrubber slurry (synonymous with FGD – flue gas desulfurization products)
TCLP	Toxicity characteristic leaching procedure
UAN	Urea ammonium nitrate (32-0-0) nitrogen fertilizer

ABSTRACT

Two coal combustion power plants in the Four Corners region of north western New Mexico, San Juan County, consume approximately 14.5 million metric tons of coal on an annual basis for the generation of electricity. In addition, these power plants generate substantial coal combustion products (CCPs) in the form of 3.8 million metric tons of ash and 0.39 million metric tons of flue gas desulfurization (FGD) materials. Near the two power plants is the Navajo Agricultural Products Industry (NAPI), a large commercial farm currently operating over 600 automatic center pivot irrigation systems on 31,000 ha of farmland. The calcareous soils are generally sandy to sandy loam with limited water-holding capacity, low inherent nutrient status, and elevated pH. CCPs may increase water-holding capacity and contribute to the pool of micronutrients available for plant uptake. However, salinity may pose negative consequences if excessive loading of soluble salts on soil occurs.

This project was designed to 1) evaluate plant growth response cultivated in CCP amended soil, 2) characterize potentially beneficial or harmful constituents of CCPs in plant, soil, and water samples; and 3) examine potential benefits of soil physical properties by measuring water-holding capacity and saturated hydraulic conductivity of CCP-amended soils. This study was a collaborative project with New Mexico State University, NAPI, and the Arizona Public Service (APS) Four Corners Power Plant. The demonstration of environmentally sound management strategies for applying CCPs to agricultural lands addresses regional and national priorities established by the U.S. Department of Energy National Energy Technology Laboratory and the Combustion Byproducts Recycling Consortium for the increased utilization of these products.

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EXECUTIVE SUMMARY

Objectives were to test an indicator plant for growth responses and elemental uptake in two greenhouse studies, examine leachate and soil for elemental constituents, pH, and salinity in packed soil columns, and examine potential changes in water retention and transmission properties of CCP amended soils.

Analysis of the CCPs showed that the fly ash material had the highest pH (12.41) and EC (6.65 mS/cm). Sodium adsorption values were highest for the bottom ash, though well within normal levels. Phosphorous, Fe, Ca, and Ba were highest in the fly ash. Magnesium, Ca, Na, S, As, B, Cr, Sr, and Si were high in the scrubber slurry material. Zinc was highest in bottom ash.

2004 and 2005 Greenhouse Studies

The greenhouse studies were initiated in the fall and spring of 2004 and 2005, respectively. In the *2004 Greenhouse study*, the hybrid poplar clone OP-367 had higher leaf greenness values than NM-6. For OP-367, the highest scrubber slurry rate applied to soil produced the highest SPAD values followed by the bottom ash and fly ash treatments. This trend was not observed in the clone NM-6 possibly due to B toxicity. The scrubber slurry raised salinity but lowered SAR values of amended soil. The lowered SAR values were attributed to the high amounts of exchangeable Ca and Mg. Increased salinity with the scrubber slurry did not factor into decreased growth for either poplar clone. The pH increased in fly ash treated soil to 8.7, though this did not immediately impact biomass production, especially for the clone OP-367. Nutrition generally improved in hybrid poplar leaves: S, Mg, Ca, Na, Fe, and Mn were highest under scrubber slurry plus supplemental N amending; leaf P and Fe increased in fly ash plus N amended soils; Copper and Zn improved under bottom ash plus N amending.

In the *2005 Greenhouse Study*, only the hybrid poplar clone OP-367 and fly ash were investigated. Chlorosis evaluations showed that the fly ash at the highest rate plus supplemental N improved leaf greenness over the control. Biomass improved for most measured parameters under fly ash cultivation, although the highest fly ash rate was less productive than lower rates. Leaf P, Mg, Ca, and Na, as did micronutrient status, all increased in fly ash plus N amended soil. Boron also increased in leaves of poplars but were below toxicity limits

The following metals were analyzed in plant tissues and soils from acid digests: Cr, As, Ag, Se, Pb, Cd, and Ba. Of these, only Ba was detected in leaves and stems. Leaf Ba was highest under fly ash amending followed by bottom ash. Scrubber slurry did not increase Ba. Barium accumulation differed between the two poplar clones: Ba tended to accumulate more equally in stems and leaves for the clone NM-6 while preferentially accumulated in stems rather than leaves in OP-367. Lead, Cr, and Cd did not increase in soils in either study and were well below USEPA toxic level standards.

Leaching of CCPs in Soil Columns

The initial ECs were high for all treatments including the control, but fell to values below salt tolerance levels on the next irrigation. Consistent with the *Greenhouse Studies*, the scrubber slurry treatments had the highest ECs, eventually decreasing to the same levels as the control after 18 irrigations. pH levels dropped in all treatments at the onset before rising to static levels that ranged from 8.18 (BA 44.5) to 8.36 (FA 44.5) at the study's termination. The pH drop was attributed to soluble salt leaching. The fly ash leachate was generally the most alkaline.

Water soluble Al, Be, Bi, Cd, Cr, Pb, Mo, Se, Tl, V, and Zn were below minimum detection limits. For most measured elements, the highest values were found in the first leachate followed often by rapid declines. Nitrate levels were lower in CCPs than the control and fell below drinking water regulations on the second irrigation. Potassium, Mg, Ca, and Na levels were slightly higher in the scrubber slurry amendments. Leachate S was highest in the scrubber slurry which was consistent with the *Greenhouse Studies*. The detection of Fe and Mn in leachate likely coincided with reducing environments formed within the columns as the soil became saturated. Boron was highest in the scrubber slurry followed by the fly ash treatment leachate, but moved rapidly from columns after subsequent irrigations. Ni levels were below EPA water quality regulatory levels.

Arsenic generally increased in the leachate of CCP amended soil and was highest at the first collection, even for the control columns, before falling to < 0.05 mg/L 12 weeks into the study. These levels were above the newest EPA drinking water standards (even for the control) and require more investigation.

Leachate Ba also increased above EPA drinking water standards (depending on interpretation) in the initial leachate (even for the control). The Ba content rapidly lowered below regulatory limits after subsequent irrigations. Soil Ba was highest for the fly ash amendments but movement was largely confined to the upper portion of the soil profile where CCP loading had occurred.

Effect of CCP amending on Water Retention and Transmission Properties

No differences were observed between most soil retention and transmission properties but trends emerged. At 30 cm of suction, the FA 22.75 retained more water than the control, the SS 44.5 and FA 22.75 treatments retained the most water at 60 cm of suction, at 300 cm suction, SS 44.5 and BA 22.75 retained more water than the control, at 1,000 cm of suction, the BA 22.75 treatment retained the most water compared to the control, at 3,500 cm of suction, the FA 44.5 and SS 44.5 treatments both retained more water than the control and at 5,000 cm suction, the CCP treatments were the same as the control. The 15,000 cm suction was the only theta to show any significant difference; all, CCP treatments had the same moisture content but retained more moisture compared to the control.

Decreasing drainable (f_a) and effective porosity (f_e) values indicate a decrease in faster draining macropores. The fly ash 22.75 mT/ha and scrubber slurry treatments had the lowest *drainable porosity* values, while the two scrubber slurry treatments had two of the lowest *effective porosity* values. Saturated hydraulic conductivity values indicated that the finer particle size of the scrubber slurry and fly ash reduced water transmission rates through soil cores. A negative relationship between SAR values and AW was found. Sodium values were also negatively correlated with AW content while Ca was positively correlated with AW.

INTRODUCTION

Coal Combustion Products (CCPs)

Nearly 3.8 million metric tons of coal combustion products (ash + flue gas desulfurization products) are produced each year at two coal combustion power plants in New Mexico's San Juan County by the APS and Public Services of New Mexico (PNM) electrical generating plants (Salisbury, 2003). Although substantial, this represents only about 2% of the 95 million metric tons of CCPs produced in the United States in 1997 (Clark et al., 1999). The CCPs of primary interest in this report are bottom ash, fly ash and flue gas desulfurization (FGD or scrubber) materials.

Bottom Ash

Bottom ash are agglomerated ash particles formed in pulverized coal furnaces that are too large to be carried in the flue gases and impinge on the furnace walls or fall through open grates to an ash hopper at the bottom of the furnace (ACAA, 2003). This allows Bottom Ash to have several unique things happen to it during its production: 1) commixing with other mineral matter over long periods of time in a molten state, 2) interaction with a high velocity jet of compressed steam or air while in a molten state to remove buildup from the furnace wall, 3) extremely quick cooling in a water-filled container below the furnace, 4) crushing and grinding while still relatively unweathered to a size suitable for pumping to another holding pond for 5), rinsing with a large volume of water, decanting of the water and removal of the dry byproduct (Salisbury, 2006). Bottom ash typically is coarse in texture with particle sizes often greater than 2 mm due to the presence of boiler slag (Carlson and Adriano, 1993).

Fly Ash

Fly ash is ash that exits a combustion chamber in the flue gas and is captured by electrostatic precipitators, baghouses, and wet scrubbers (ACAA, 2003). Particle sizes range from 0.01 to 100 µm allowing a large amount of surface area to mass (Carlson and Adriano, 1993; Salisbury, 2006).

Flue Gas Desulfurization Byproduct or Scrubber Slurry

Flue gas desulfurization products (FGD; scrubber materials) are produced during the process of gaseous SO_2 capture from boiler exhaust gas (ACAA, 2003). During this process lime (CaO), dolomite ($CaMg(CO_3)_2$), and Na-based compounds are mixed with water, producing calcium and magnesium hydroxide which is reacted with SO_2 in the gaseous environment of the fluidized bed combustion chamber, chemically tying the Ca, Mg and Na to SO_2, resulting in calcium sulfite, magnesium sulfite, and sodium thiosulfate (Salisbury, 2006; World Bank, 1999). A few properties in this class of materials described by

Salisbury (2006) are: 1) reactions in an anaerobic environment, with little oxidation potential, 2) furnaced, calcined materials chemically combined with gaseous materials to make mineral matter, 3) highly evaporative environment, so there is a large accumulation of evaporates from the water used in the environment, such as carbonates and chlorides, and 4) complex mixture of salt species. The amount of S captured in the scrubber slurry is determined by the type of coal mined and exists in two predominant forms (pyritic and organic) of which western US coals are generally below 1% S (Meyers, 1977). Also of significant impact on the S forms found in scrubber slurry is the degree of forced oxidation used in the processes: sulfates, which are more mobile in soil, are produced under forced oxidation conditions while less mobile sulfites are produced under reduced conditions (Korcak, 1995).

CCP Agricultural Uses

Interest is growing to find alternative disposal approaches including reuse in construction, roadwork, manufacturing, and agriculture. The vast majority of the San Juan CCPs are returned to mine sites but both power plants are actively seeking local markets as alternatives to mine placement or expensive long distance hauling of marketable CCPs (Blankinship, 2001). The reuse option for local agricultural purposes presents an attractive alternative because of the large land area devoted to crop production within a relatively short distance from the power plant source.

The Navajo Agricultural Products Industry (NAPI), a large commercial farm near the two power plants, currently farms about 25,000 ha using nearly 600 center pivot systems for irrigating alfalfa, beans, corn, potatoes, pumpkins, and small grains. Contract partners produce a range of other commodities including short rotation *hybrid poplar* trees for fiber production. Common circle size of the center pivots used by NAPI is 40-60 ha. Soils are generally sandy to sandy loam with limited water-holding capacity, low inherent fertility, and relatively elevated pH (Keetch, 1980). NAPI is continually striving to increase water and fertilizer use efficiencies. Recent discussions have identified the use of CCPs for agriculture as potential alternative deposal strategies for the two nearby power plants while improving soil water-holding characteristics and fertility status of NAPI's fields.

A number of potential benefits of applying CCPs to agricultural soils have been reviewed (Cavaleri et al., 2004; Clark et al., 1999; Clark et al., 1995; Korcak, 1995; Schutter and Fuhrmann, 1999; Scotti et al., 1999; Stuczynski et al., 1998; Zaifnejad et al., 1998). They include chemical and physical improvements such as ameliorating nutrient status for plant growth, altering soil pH, and enhancing root penetration and water holding capacity. Fly ash is low in organic N (Aitken et al., 1984) but can provide plant available Fe and other micronutrients (Black and Zimmerman, 2002; Blankinship, 2001; Cavaleri et al., 2004; Korcak, 1995; Kumar and Kumar, 2002; Moral et al., 2002; Parkpian et al., 2002). This last point is important. Hybrid poplar, under commercial production at NAPI, experiences varied responses to Fe deficiency depending on clone

(Lombard et al., 2005). Iron may be prevalent in the soil, but bound in plant unavailable forms because of the inherently high pH of the soil. On some NAPI fields, annual crops such as corn, wheat and barley may also exhibit symptoms of Fe deficiency but is cost prohibitive to provide supplemental Fe nutrition to these crops (Onkin, 2005). On the other hand, hybrid poplar, with a rotation length of ten years, represents a considerable long-term investment for NAPI. Expensive chelated iron fertilizer is currently injected into the drip irrigation system to alleviate chlorosis symptoms but CCPs could potentially be a cheaper alternative source of Fe (Cavaleri et al., 2004).

The addition of bottom ash, fly ash and/or flue gas desulfurization (FGD or scrubber) materials to agricultural soils may also increase water-holding capacity which could decrease irrigation frequency, increasing water savings. Sandy soils found on NAPI could benefit from the addition of fine textured fly ash for moisture retention (Campbell et al., 1983; O'Neill, 2003; Pathan et al., 2004).

Environmental Cautions

Conversely, environmental cautions of CCP utilization may include excessive loading of boron, trace metals, soluble salts, and increased sodium concentrations to levels that impede water infiltration, sulfite accumulation, and leaching of toxic materials into groundwater (Aitken et al., 1984; Carlson and Adriano, 1993; Korcak, 1995; Lau and Wong, 2000).

Salinity Effects of CCP Application to Semi-Arid Agricultural Lands

High salt contents may limit CCP utilization (Aitken et al., 1984) in a region of low annual rainfall, low salt leaching potential, and exclusive reliance of river-fed irrigation systems. The potential to increase salinity and sodicity must be taken into consideration on these soils. Irrigation water utilized at NAPI originates from San Juan mountain snow melt diverted at Navajo dam and is consequently low in salts. Any addition of salts to the soil system will come from what is already present or added to the soil as an amendment. Leaching of salts during an irrigation event will flush salts beyond the root zone but could lead to salty agricultural drainages that re-enter the San Juan river, affecting downstream users.

pH effects of CCP to Semi-Arid Agricultural Lands

An abundance of literature on CCP application to soils as a liming agent on acid soils has been reviewed (Korcak, 1995) but little is known on what could be expected on Western U.S. soils which typically have elevated pH. Calcium carbonate may also be present in appreciable amounts which also affect micronutrient chemistry. As soil pH increase, availability of the micronutrients, especially Fe, Mn, and Zn, decrease (Brady, 1984). Any potential rise in soil pH through the action of CCP application would have negative consequences to crop production on NAPI.

Other Elements that Require Environmental Consideration

Heavy metal loading to agricultural soils is of primary concern to avoid excessive uptake in plants that may enter the food chain or contaminate groundwater through the action of leaching. For instance, previous studies have shown a total of 25 potentially toxic elements have been found in measurable amounts in fly ash; of these, Ba, B, Ca, Mo, Pb, S, Se, and Sr have been shown to accumulate in soils and Al, As, Ba, B, Mo, S, Se, and Sr have increased in plants (Keefer, 1993). While some of these are required by plants, B, for instance, can reach toxic levels in plants, and a number of these elements are toxic to animals. The high soil pH found in the Four Corners region may immobilize some trace metals and restrict their movement (Boyle, 1978). Like any soil amendment, it is important to chemically characterize CCPs being considered for agricultural use. Judicious application of characterized CCPs at rates that keep trace elements from exceeding loading limits set forth by environmental regulators will enable safe application (Heidrich, 2005).

OBJECTIVES

The effects of CCP application on local soil chemical, soil physical and plant elemental uptake must be considered in a land application scheme (Carlson and Adriano, 1993). With few exceptions, studies occur in humid environments not representative of the agro-climatic environment found in semi-arid New Mexico. Though indeed not a *novel* idea, this project was designed to address three central questions specific to a semi-arid climate and NAPI soil conditions: Can CCPs effect plant growth response and improve nutrient status of an indicator plant? What are the environmental consequences (potential heavy metal movement) of soil and drainage water after CCP application? And, what are the effects of CCP application to water retention and transmission properties?

The overall objectives of this project were to determine if applications of CCPs to agricultural soils have an effect on overall crop productivity. More specifically, the objectives of the project are to:

1. Identify micronutrients in CCPs generated at the APS Four Corners Power Plant that may be available for plant uptake.
2. Identify heavy metals in CCPs generated at the APS Four Corners Power Plant that may be contaminates to the environment.
3. Determine if the addition of CCPs generated at the APS Four Corners Power Plant affects the productivity of agricultural soils used by the Navajo Agricultural Products Industry.
4. Determine if the addition of CCPs generated at the APS Four Corners Power Plant affects the water retention and transmission properties of agricultural soils used by the Navajo Agricultural Products Industry.

The conclusion of the project will generate data needed to guide potential field studies and will contribute to the knowledge base of CCP use on irrigated agricultural systems in arid regions.

EXPERIMENTAL

Study 1: Effect of Evaluation of Hybrid Poplar Amended with Coal Combustion Products – A Greenhouse Study

Two studies were conducted and hence forth shall be referred to as the *2004 Greenhouse Study* and *2005 Greenhouse Study*.

Soil and Treatments

2004 Study Soil and Treatments

A Doak sandy loam (coarse loamy, mixed, calcareous, mesic, Typic Camborthid, (Anderson, 1970) was collected from the top 20-25 cm of the plow layer from an agricultural field located at the New Mexico State University Agricultural Science Center, Farmington, on leased land from NAPI. The Farmington soil was collected by shovel and sieved through ¼ in^2 (0.64 cm^2) mesh directly into a plastic-lined front-end loader bucket then transported to Las Cruces and placed into a pile. The soil pile was mixed by hand prior to pot filling to ensure homogeneity. A fiberglass mesh screen was used to line pots to prevent soil loss from drainage holes. Standard 2 gallon (7.5 L) nursery containers were filled to a dry weight of 9 kg.

The treatments consisted of three CCPs: bottom ash, fly ash, and FGD material (hence forth referred to as scrubber slurry) collected from the Arizona Public Service (APS) Four Corners Power Plant, Farmington, NM. Coal and ash samples previously analyzed for heavy metals showed little hazard for agricultural land application (Salisbury, 2003) (Tables 1-2). Still, for these studies soil and amendments were analyzed to collect baseline data on pH (1:2), NO_3-N, P, K, Ca, Mg, Na, Zn, Fe, Mn, and Cu at the NAPI Agricultural Testing and Research Lab in Farmington. Total digests, electrical conductivity (EC) and sodium adsorption ratio (SAR) of saturated paste extracts were conducted in the Agronomy and Horticulture Soils Research group and Soil, Water, and Air Testing (SWAT) labs (Las Cruces, NM). Baseline data for the soil and amendments are shown in Table 3. Saturated paste extract measurements of the CCPs alone and mixed with soil demonstrated that CCP salinity was high except for the bottom ash (Figure 1). From Table 3, the scrubber slurry has high levels of soluble Ca (though not as much as either NAPI soil alone or fly ash), Mg, Na, K, B, and most notably S.

The three CCP treatments were then applied to the surface of the soil filled containers at two rates (22.75 mT/ha and 45.5 mT/ha; common rates for other agricultural amendments such as animal manures). The rates were converted to grams based on the surface area of the container so that 82.1 g (for the 22.75 mT/ha rate) or 164 g (for the 44.5 mT/ha rate) were applied for each CCP treatment. Bottom ash, and fly ash treatments were applied dry. The scrubber slurry had separated into solid and liquid layers. When homogenized, it has a viscous, clay-like consistency which was applied wet as a slurry. CCP treatments were then incorporated by hand into the 10 cm of soil. Unamended soil served as controls.

2005 Study Soil and Treatments

Only fly ash obtained from the APS Farmington Plant was used in this study based on hybrid poplar performance in the 2004 study. Three rates were applied accordingly to the surface area of the 2 gal nursery container: 22.75 mT/ha, 44.5 mT/ ha. The third rate was based upon two criteria: 1) the extent of plant available Fe content found in Farmington soil using the DTPA extractable Fe test conducted at the SWAT Lab, and 2) the amount of supplemental plant available Fe found in fly ash needed to be applied as a fertilizer to correct deficiency based on criteria #1. The plant available Fe content of the Farmington soil was determined to be 1.24 mg/kg. For soils with a test report of 0.0 – 2.5 mg/kg Fe, a rate of 4.48 kg Fe /ha is recommended (Jones and Jacobsen, 2003). DTPA extractable iron content in the fly ash was determined to be 0.00609% Fe (60.90 mg Fe/kg of material). Using this percentage, the equivalent of 73.6 mT of fly /ha (or 269.54 g/pot) was applied to respective treatment containers.

The three fly ash rates (22.75 mT/ha, 44.5 mT/ha, and the rate based upon the DTPA extractable Fe) were applied in the following way: The top 10 cm of soil was removed from individual nursery containers and placed into a plastic bucket. Pre-weighed amendments were individually added to each bucket and mixed thoroughly with the soil by hand. The contents of the bucket were then poured back into the nursery container.

A Fe fertilizer check consisted of Sprint 138 (Becker Underwood, Ames Iowa) and was applied as a soil drench once during the onset of the experiment at an application rate of 4.48 kg Fe/ha (again based on the soil test report mentioned previously). Unamended Farmington soil again served as controls.

Table 1. Percent dry weight of oxide materials that make up sub-bituminous coal used and fly ash produced by the APS Four Corners Power Plant in northwest New Mexico (Salisbury, 2003).

Oxide	Coal Dry Weight (%)	Fly Ash Dry Weight (%)
SiO_2	58.8	58.7
Al_2O_3	25.6	25.0
Fe_2O_3	4.56	5.81
MnO	0.03	0.03
TiO_2	0.87	0.95
P_2O_5	0.27	0.35
CaO	2.84	3.48
MgO	1.10	1.54
Na_2O	4.04	1.79
K_2O	1.17	1.22
SO_3	3.71	1.07

Table 2. TCLP of bottom ash produced by the APS Four Corners Power Plant in northwest New Mexico (Salisbury, 2003).

Constituent Material	Concentration (mg/l)
Arsenic	<0.1
Barium	2.5
Cadmium	<0.01
Chromium	0.03
Lead	<0.1
Mercury	<0.01
Selenium	<0.1
Silver	<0.05

Table 3. Properties of various a Doak sandy loam collected from Farmington and coal combustion products analyzed May 26, 2004.

Characteristic	Soil [a]	Bottom Ash [b]	Fly Ash [b]	Scrubber Slurry [b]
pH (1:2) [y]	8.7	8.72	12.41	8.57
EC (mS/cm) [x]	1.39	1.18	6.65	5.00
SAR (mmol/L) [x]	0.68	2.99	2.04	2.06
NO_3-N (mg/kg) [z]	8.5	NT	NT	NT
P (mg/kg) [y]	2.4	2.88	17.00	5.47
K (mg/kg) [y]	164.8	8.83	11.70	19.55
Zn (mg/kg) [y]	0.5	1.040	0.613	0.684
Fe (mg/kg) [y]	4.2	19.2	78.4	30.4
Mn (mg/kg) [y]	2.3	1.95	8.10	5.59
Cu (mg/kg) [y]	1.3	0.421	1.15	1.32
Ca (mg/kg) [y]	3268.3	645	5650	3235
Mg (mg/kg) [y]	168.5	24.2	31.0	976.5
Na (mg/kg) [y]	12.0	51.7	53.6	185.0
S (mg/kg) [z]	200.9	383.6	306.7	2744.28
Al (mg/kg) [z]	1081.19	302.70	348.65	780.9
As (mg/kg) [z]	3.5	4.2	10.3	12.9
B (mg/kg) [z]	17.6	26.3	59.5	130.5
Ba (mg/kg) [z]	110.6	465.5	904.1	335.4
Be (mg/kg) [z]	ND	ND	ND	ND
Cd (mg/kg) [z]	0.3	1.0	1.3	0.5
Co (mg/kg) [z]	3.3	0.9	0.8	2.2
Cr (mg/kg) [z]	7.7	4.0	2.9	16.6
Mo (mg/kg) [z]	ND	ND	ND	4.2
Ni (mg/kg) [z]	5.5	2.1	1.9	5.4
Pb (mg/kg) [z]	6.5	ND	5.0	6.8
Se (mg/kg) [z]	ND	ND	ND	ND
Tl (mg/kg) [z]	ND	ND	ND	ND
V (mg/kg) [z]	20.0	3.1	8.4	22.0
Bi (mg/kg) [z]	ND	ND	ND	ND
Li (mg/kg) [z]	7.1	3.3	3.8	6.4
Sr (mg/kg) [z]	29.5	ND	37.9	76.8
Si (mg/kg) [z]	168.1	277.7	308.7	401.7
Ag (mg/kg) [z]	ND	ND	ND	ND

[a] Mean of 6 samples for pH, P, K, Zn, Fe, Mn, Cu, Ca, Mg, and Na; mean of 3 samples for S, Al, As, B, Ba, Be,Cd,Co,Cr,Mo,Ni, Pb, Se, Tl, V, Bi, Li, Sr, Si, and Ag.
[b] Mean of 3 samples.
[x] Analyzed at Soil Group Lab, NMSU, Las Cruces, NM.
[y] Analyzed at Agricultural Testing and Research Lab, NAPI, Farmington, NM.
[z] Analyzed at Soil, Water, and Air Testing Lab, Las Cruces, NM.

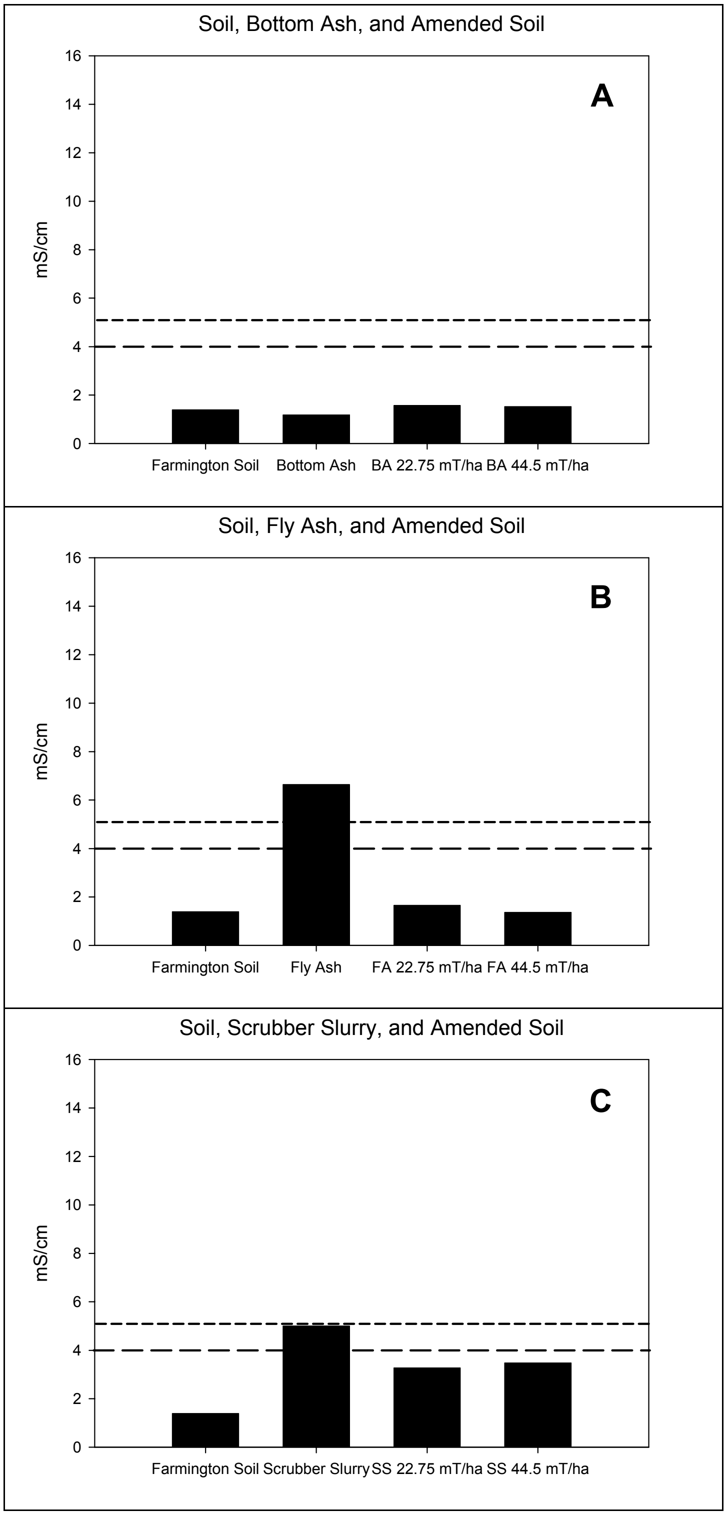


Figure 1 Baseline salinity content (EC) of a Doak sandy loam compared with bottom ash and amended soil at two rates (22/75 and 44.5 mT/ha) (A), fly ash and amended soil (B) and scrubber slurry and amended soil (C). Long dashed line indicates threshold tolerance level for most agricultural crops before yield reduction occurs (Allison et al., 1954; Maas and Hoffman, 1977). Short dashed line represents salinity tolerance for most hybrid poplar clones (Shannon et al., 1999).

Plant Material

Hybrid poplar was chosen as a test *crop* for three reasons: First, it is non-edible and least likely to receive political opposition in a land application/crop rotation system. Secondly, hybrid poplar has been proposed for inclusion in tradable carbon credit schemes sanctioned by the Kyoto agreement to sequester CO_2, another coal combustion byproduct implicated in global warming (McCarl and Schneider, 2000; Reedy, 2003). Lastly, hybrid poplar has been under investigation at the Agricultural Science Center at Farmington since 2002 (O'Neill et al., 2004). With commercial production underway at NAPI (currently at 40 ha and expected to rise to over 1000 ha within ten years), hybrid poplar was a logical *crop* to study under CCP amended soil.

Poplar clones used in the 2004 study were OP-367 (*Populus deltoides* x *P. nigra*) and NM-6 (*P. nigra* x *P. maximowiczii*), a clone known to exhibit a high degree of Fe chlorosis in Farmington research plots, were obtained from Segal Ranch (Grandview, WA). Uniform 20 cm long cuttings were soaked for 3 days in tap water before transplanting directly into nursery containers on September 23, 2004 (Figure 2). For the 2005 study, only the clone OP-367 was used, obtained from Broadacres nursery (Hubbard, Oregon).

Figure 2. General setup for 2004 and 2005 greenhouse studies. Standard 2 gal (7.5 L) black plastic containers were filled with Farmington soil. To these, the CCPs and an Fe fertilizer check were added as treatments and a control had no amendments or fertilizer.

Cultural Practices

Irrigation and Fertilization Schedule

Pots in both studies were kept at or below approximate field capacity. No leaching of pots occurred during the course of the studies to examine salt buildup effects and elemental uptake. The total amount of water applied in the 2004 study was 434.2 mm over 18 weeks. Total irrigation applied in the 2005 study over 17 weeks was 647 mm.

Nitrogen content is expected to be limiting in CCP because of volatilization during the combustion process (Carlson and Adriano, 1993). Therefore, urea-ammonium nitrate UAN (32-0-0) was applied in the irrigation water only to the CCP and Fe treatments at a rate of 28 kg N/ha (1.2 mL UAN in 18.9 L water). For the 2004 study, UAN was applied a total of 13 times during the course of the study. Fourteen applications were made in the 2005 study.

Greenhouse Temperatures and Lighting

Greenhouse temperature set points were kept at 15.5° C (60° F) night and 27° C (80° F) day. Low and high temperatures averaged 16.85° C and 31.4° C, respectively. On October 28, 2004 a temperature spike of 43.4° C caused by a malfunctioning fan was recorded in the greenhouse resulting in some leaf burn around the margins for some of the trees in the *2004 experiment*.

Metal halide lights provided supplemental lighting in 2004. The timer was adjusted once per week and set to follow sunset and sunrise times so that trees received 12 hours of light per day. A light interruption period was also added at 2 a.m. to prevent dormancy initiation because of the shortened winter photoperiod. Supplemental lighting was not needed in the *2005 study*.

Chlorosis Evaluations

Leaf chlorosis was monitored using a handheld SPAD (Soil Plant Analysis Development)-502 meter described for chlorophyll estimation (Yamamoto et al., 2002). This instrument measures transmittance of the leaf in the red and infrared wavelengths (650 and 940 nm respectively; Schepers et al., 1998) and has the advantage of portable, non-destructive leaf analysis which can be used to study the same sample area over time. The SPAD meter has been used to monitor Fe status in pear (López-Millán et al., 2001) and, likewise, we have found values to correlate highly with hybrid poplar leaf Fe status (Lombard et al., 2005). The SPAD meter produces a unit-less value essentially giving a “greenness” indicator. As SPAD values increase, leaf chlorosis decreases.

2004 Study. Leaf chlorophyll content was monitored on six occasions: October 11 (SPAD 1), October 26 (SPAD 2), November 9-11 (SPAD 3), November 28-December 1 (SPAD 4), December 17-19 (SPAD 5), and January 7-10 (SPAD 6). One reading per leaf was made on each of the top ten leaves for SPAD readings 1, 2, 4 and 5, while an average of three readings per leaf were made for SPAD readings 3. The first reading was taken from the first fully expanded leaf (usually 5-6 down from apical bud). Readings were taken toward the base of the leaf and between veins (Figure 3).

2005 Study. Leaf chlorophyll content was monitored on two occasions: April 12-14, and June 22-25, 2005. Three readings per leaf were made on each leaf on the first 10 fully expanded leaves.

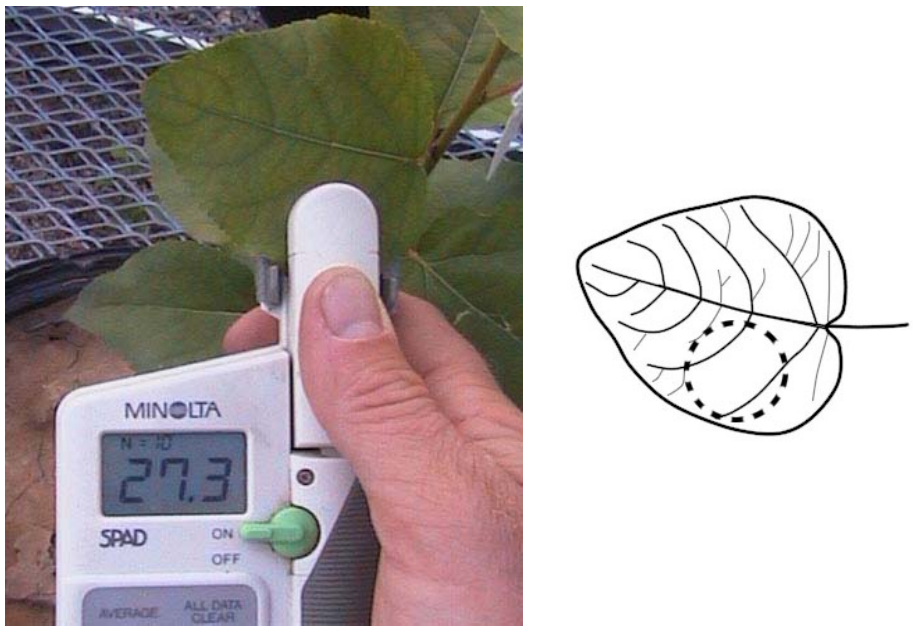


Figure 3. Region of leaf where SPAD readings occurred.

Soil and Tissue Chemical Analysis

Destructive Harvest

Leaf destructive harvest. Trees were destructively harvested by stripping the leaves in four segments: Top (first 5 unexpanded leaves closest to the apical bud), Side Branches (where present), Middle (next 10 leaves down), and Bottom (the remaining leaves on the plant (Figure 4).   Leaves were removed in stages and run through a leaf area meter to get area measurements for each section and combined for a total area.

After area measurements were made, leaves were then decontaminated of any potential Fe source from dust or soil according to Campbell and Plank (1998) in the following way: Leaves were first dipped in a 0.01% phosphate free detergent bath (1 mL detergent/10 mL tap H_20), then rinsed with tap water under low pressure, and finally dipped into two baths of distilled water before placing in paper bags according to plant section. Leaves that had senesced were collected from the container surfaces and also washed.   Leaves were dried for 24 hours at 70° C and then weighed. Dead leaves were unable to be read by the leaf area meter but were cleaned and dried for inclusion in the total leaf dry weight comparisons.

Stem destructive harvest. Stems were severed 2 cm from the top of the original cutting and measured for basal diameter and overall length (Figure 5). Stems were then cut into sections, placed into paper bags, and dried first in the greenhouse before being transferred to a drying oven set at 70° C for 72 hours before weighing.

Root destructive harvest. Most of the soil was removed from the roots by hand. Root masses were then individually dipped into six baths of tap water to remove any residual soil (Figure 5) and rinsed under low pressure in a household strainer. Soil from the nursery containers was sieved through 2 mm mesh to remove any roots that had broken off and these were then also washed in the six baths and bagged. Roots were then severed from the original cutting, and rinsed one more time with tap water under low pressure before being placed into paper bags to air dry. Bags were transferred to a drying oven set at 70° C for 72 hours before weighing.

Plant Tissue Macro and Micronutrient Analysis

The *middle section* leaves (described above) and stems of each plant were analyzed for macro, micro and heavy metal status. Symptoms of micronutrient deficiencies such as Fe are exhibited as interveinal chlorosis of juvenile leaves, hence the reasoning of analyzing the middle portion of the canopy. Roots were excluded because of the possible interference from soil in micronutrient determination. Dried leaves were ground to a fine powder using a coffee grinder (Braun). Stems material was cut into small pieces and fed into a Wiley Mill. Ground samples were stored in snap cap vials at room temperature until analysis.

Macro and micronutrients were analyzed at the NAPI Lab in the following manner: A 1 g subsample of ground tissue was placed into ceramic crucibles and dry ashed for 6 hours in a muffle furnace and allowed to cool overnight (Baker et al., 1964) . Alfalfa, bean and corn samples previously characterized served as standards and were treated similarly. To the ashed samples, 5 mL of 20% HCl was added to each crucible and allowed to sit for 20 minutes, after which the samples were filtered through Whatman 42 filter paper into 100 mL volumetric flasks. Crucibles were cleaned the following way: crucibles were rinsed with a squirt bottle into the filter paper with room temperature double distilled water followed by boiling distilled water poured into the crucible, the rinsate being poured into the filter paper. Lastly the crucibles were scoured and then rinsed with distilled water into the filter paper. Samples were allowed to filter for one hour before being brought to 100 mL volume with double distilled water. Samples were then transferred to ICP-OES (Perkin-Elmer Optima 4300 DV ICP-OES) for analysis of P, K, Mg, Ca, Na, Zn, Fe, Mn, and Cu. Tissue S and total nitrogen (TN) was determined directly by combustion (LECO TruSpec CNS).

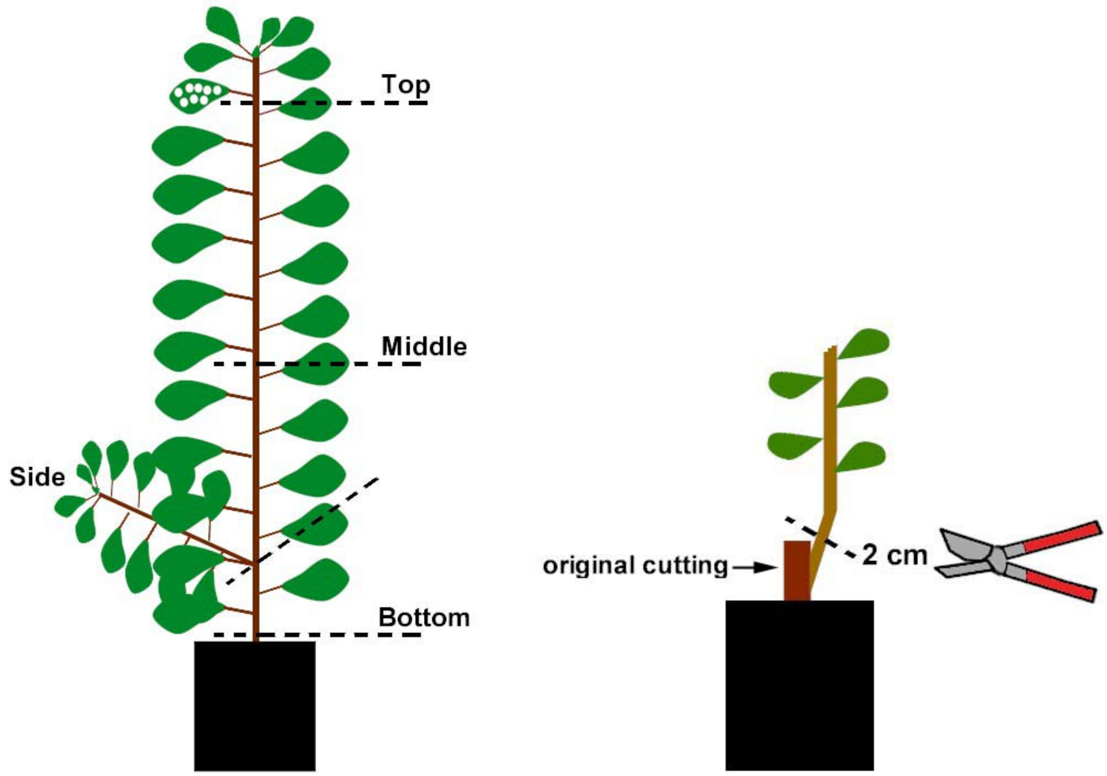


Figure 4. Destructive harvest methodology.

Figure 5. Stem diameter measurements (left) and root cleaning (right).

Soil Macro and Micronutrient Analysis

Soil NO_3-N, P, K, Zn, Fe, Mn, Cu, Ca, Mg, and Na were analyzed using the Soltanpour (Soltanpour and Schwab, 1977) and Ammonium Acetate (Knudsen et al., 1982) methods in the following manner: N, and S were determined directly through combustion (LECO TruSpec CNS); extractable P, K, Zn, Fe, Mn, and Cu by Ammonium Bicarbonate-DTPA (1.0 mol/L NH_4HCO_3 + 0.005 mol/L DTPA at pH 7.6); and Ca, Mg, K, and Na by Ammonium Acetate (1.0 mol/L NH_4OAc at pH 7.0). These samples were then analyzed by ICP-OES.

Trace and Heavy Metals

Microwave-assisted acid digestion of amended soil and plant tissue was conducted at the NMSU Soils Group laboratory in Las Cruces to determine the extent of plant uptake or soil retention of any potentially harmful metal. Total digestion of soil followed USEPA Method 3051A (USEPA, 1998) in the following manner: 5 g of soil or amendment were placed into Kevlar sleeved Teflon pressure digestion vessels. Sample blank and certified reference materials (NIST 2711 Montana II Soil) were used during digestion and analysis between every 14 samples for quality control and monitoring. To each vessel, 9 mL trace metal grade HNO_3 and 3 mL HCl were added. Vessels were sealed, arranged into a rotating carousel and placed into the microwave (CEM Corporation, Matthews, NC).

Total digestion of leaf samples was also undertaken by microwave assisted digestion described by Miller (1998) in the following manner: 2.5 g of dried, ground leaf tissue was placed into Kevlar sleeved plastic digestion vessels. To this was added 2 mL of 30% H_2O_2, 5 mL distilled water, and 5 mL trace metal grade HNO_3. NIST 1515, Apple Leaves, or 1547, Peach Leaves were used between every 14 samples for quality control.

Upon completion of the microwave step, digested soil and tissue samples were filtered through Whatman number 2 filter paper into 50 mL volumetric flasks, brought to volume with distilled water, and transferred to 50 mL centrifuge tubes for storage until ICP-OES analysis for Cr, Pb, Se, As, Ag, Ba, and Cd at either the NAPI lab or SWAT labs.

Experimental Design and Statistical Analysis

For the 2004 study, a completely randomized incomplete block design was used. Four greenhouse benches were blocked upon to take into account temperature gradients within the greenhouse. The blocks were incomplete because a third hybrid poplar entry originally designed into the study failed to root. Empty containers that had already been treated with the CCPs were replanted with OP-367 for blocks 1 and 3 and NM-6 cuttings for blocks 2 and 4. There were 6 containers for each treatment (control, BA 22.75, BA 44.5, FA 22.75, FA 44.5, SS 22.75, and SS 44.5 mT/ha rates) per clone (OP-367 and NM-6).

The 2005 study was a randomized complete block design – two benches again serving as blocks. There were eight containers per each treatment (control, Fe Check, FA 22.75 mT/ha, FA 44.5 mT/ha and FA DTPA rate).

Containers in each study were randomized on the benches at the beginning of the study and then randomized once per week within benches to ensure that shading by taller plants did not occur.

Analysis of variance for measured parameters was done in SAS using the PROC Mixed statement. Means separation for all measured responses were calculated by the method described by Littell et. al (2002) using Fishers protected LSD at an alpha 0.05 level.

Correlation analysis was performed on leaf macro and micronutrients with the last SPAD measurement to examine the relationship of SPAD values to measured elements from the tissue analysis.

Study 2: Leaching of Coal Combustion Products in Soil Columns

Soil and Treatments

Soil columns (30 cm length by 7.62 cm diameter) were constructed of clear PVC (United Plastics; Figure 6). Columns (minus Buchner funnel assembly) were weighed empty and then filled in 10 cm increments with air dried Doak sandy loam from Farmington (properties described previously in Table 3), using a rubber mallet to lightly tap around the outside to facilitate particle settling. The top 5 cm of each column was treated with soil amended with one of three coal combustion products from the APS Four Corners Power Plant (bottom ash, fly ash, and scrubber slurry) at one of two rates (22.75 mT/ha and 44.5 mT/ha). Control columns were filled entirely with the Doak sandy loam. Final bulk densities ranged from 1.4 to 1.6 g/cm. A wadded paper towel was placed in the top of each column to prevent preferential flow and splashing during irrigation events.

Irrigation and Leaching

Irrigation of columns was determined from literature values for 3 year poplars under drip irrigation in Oregon (127 cm) (Shock et al., 2002). A volume of 1.95 cm (88.5 mL) distilled water was applied every other day for 19 weeks beginning March 29, and ending August 9, 2005 for a total of 128.1 cm applied during the study.

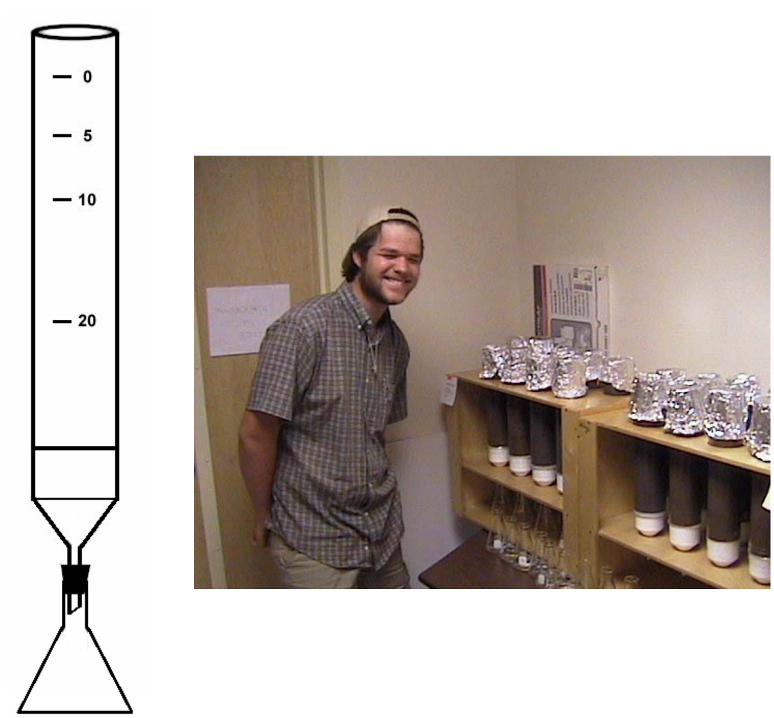


Figure 6. Schematic of packed soil column used in Study 2.

Leachate water was collected every other day just before applying irrigations. Leachate volumes were measured and salinity (EC) and pH determined. On 13 occasions spaced approximately two weeks apart, water samples were taken directly to ICP-OES (SWAT lab) for analysis of Al, As, B, Ba, Be, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Se, Tl, V, Zn, Ca, Li, Mg, P, Sr, K, Si, Na, S, Ag. Nitrate samples were also analyzed on the following dates: April 13, 17, 21, 25, and May 1, 2005.

Dissection of soil columns

At the conclusion of the study, columns were immediately dissected to determine metal movement within the soil profile in the following way: Soil was scooped out of the column in 2.5 cm sections for a total of 12 samples per column. Soil samples were then air dried, rolled to break up large aggregates, and then placed into plastic zip lock bags and stored at room temperature until analysis. Soil samples were digested according to USEPA Method 3051A described previously and analyzed for Cr, Pb, As, Ag, Se, Ba, and Cd at the NAPI Lab ICP-OES.

Experimental Design and Statistical Analysis

There were 3 columns for each treatment arranged in a completely randomized design. ICP measurements were made at the NAPI Lab on three different dates over a three month period which resulted in instrumentation variability between runs. A mixed model of fixed and random factors was designed using CCP treatments as a fixed factor and ICP-OES runs as a random blocking factor which resulted in an unbalanced design. PROC Mixed in SAS was used to generate proper error terms but resulted in slightly different LS means (or adjusted means) versus traditional means because of the unbalanced nature of the design. Means separation was calculated by the method described by Littell et al. (2002) using Fishers protected LSD at an alpha 0.05 level.

Study 3: Determination of Moisture Retention of Coal Combustion Byproduct Amended Soil

Gravimetric water holding capacity was increased with NAPI soil amended with 10 and 20 g of bottom ash/kg soil (O'Neill, 2003) spurring the development of this component.

Soil and Treatments

Sub-samples of soil and CCP amended soil collected from experimental containers used in the 2004 Greenhouse study were used to determine water retention and transmission properties. Only soil that had previously been under cultivation with the hybrid poplar clone OP-367 was used. In recap, the treatments included 2 rates for each CCP (22.75 mT/ha and 44.5 mT/ha) and an unamended control of soil only.

Preparation of Soil Cores

Prior to packing, the bottom of the aluminum cores (6 cm inner diameter x 8 cm length) were covered with a double layer of cheese cloth and placed unto screen wire mesh to prevent soil loss during the packing process (Figure 7). Air dried soil was sieved (2mm mesh) and packed into cores to a uniform bulk density by first determining the volume of the empty cylinder, weighing the empty aluminum cylinder, filling the aluminum cylinder with soil, and then reweighing. Bulk density was determined by taking the soil dry weight / cylinder volume of 226 cm^3. Columns were packed to a uniform bulk density and ranged from 1.3 to 1.5 g/cm^3 (coefficient of variation=0.02 or 2%; data not shown).

Soil moisture characteristic curve

Soil moisture characteristic curves (SMC) or $\psi(\theta)$ were determined on packed soil cores that had been saturated over night for 30 and 60 cm suctions using the tension table (Leamer and Shaw, 1941), and for 300 (field capacity), 1,000, 3,500, and 5,000 cm of suction using the pressure plate apparatus (Soil Moisture Corp., Santa Barbara, CA; (Klute, 1986). Samples were equilibrated for 24 hours at each suction level. The soil water content at 10,000 and 15,000 cm (permanent wilting point) was determined independently using the pressure plate apparatus in the following way: sieved soil (2mm mesh) was weighed and loosely packed into plastic discs arranged on a pre-moistened 15 bar plate (Figure 7). After 24 hours at each suction level, samples were removed, immediately weighed, dried for 48 hours at 105°C, and then re-weighed.

The difference between volumetric water content (θ) at saturation and 60 cm was computed to assess drainable porosity (f_a) which is defined as the drainable water from soil pores under gravitational pull. Effective porosity (f_e) was computed as the difference between θ at saturation and 300 cm representing the flow of water from pores at moisture contents between field capacity and complete saturation of the soil. Plant available water (AW) was defined as the difference between θ at 300 and 15,000 cm suction. The air entry value ($1/\alpha$) and the pore size distribution parameter (λ or n) of the Brooks and Corey (Brooks and Corey, 1964) equation (Equation 1) were estimated from measured SWC curves by inverse modeling technique using the RETC model (Genuchten et al., 1991).

Equation 1. Brooks and Corey (Brooks and Corey, 1964) equation for describing $\theta(h)$:

$$S_e = \frac{\theta - \theta_r}{\theta_s - \theta_r} = \begin{cases} (\alpha h)^{-\lambda} & (\alpha h > 1) \\ 1 & (\alpha h \leq 1) \end{cases}$$

Where:

S_e is the effective degree of saturation, also called the reduced water content ($0 \leq Se \leq 1$)

θ_r is the residual water content

θ_s is the saturated water content

α is an empirical parameter (L-1) whose inverse is often referred to as the air entry value or bubbling pressure

h denotes suction and is positive for unsaturated soil

λ is a pore-size distribution parameter affecting the slope of the retention function

Saturated Hydraulic Conductivity

Saturated hydraulic conductivity (*Ks*) was determined on the cores using the constant head method (Klute and Dirksen, 1986). Briefly, the packed cores were saturated overnight. An empty core of the same dimensions was duct taped above each saturated packed core and then placed on a rack below the Mariotte bottle with a clamped tube placed into the empty column illustrated in Figure 8, 4 cores at a time. When unclamped, a hydraulic head difference is imposed on the soil column. The resulting flux of water was measured in graduated cylinders at 10 minute intervals. An average of four volume measurements were made to represent the *Ks* of each packed core, calculated using Equation 2:

$$Ks = VL/[At(H_2 - H_1)]$$

where: *V* is the volume of water flowing through the sample of cross-sectional area *A* (28.26 cm^2) in time *t* (10 minutes), and $(H_2 - H_1)$ (which is 8 cm, H_2 minus the head of water measured from the top of the soil core, H_1) is the hydraulic head difference imposed across the sample of length *L* (8 cm).

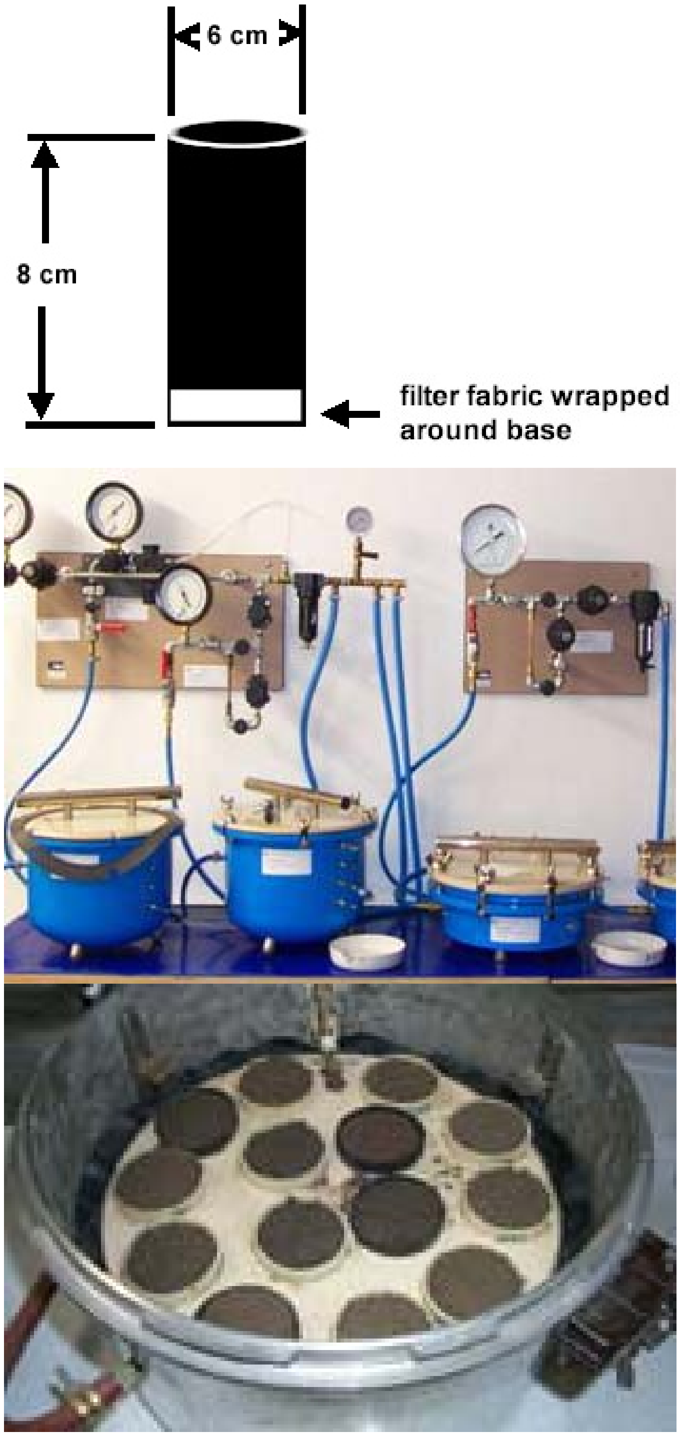


Figure 7. Schematic of packed soil column (top), and pressure plate apparatus (middle) and (bottom).

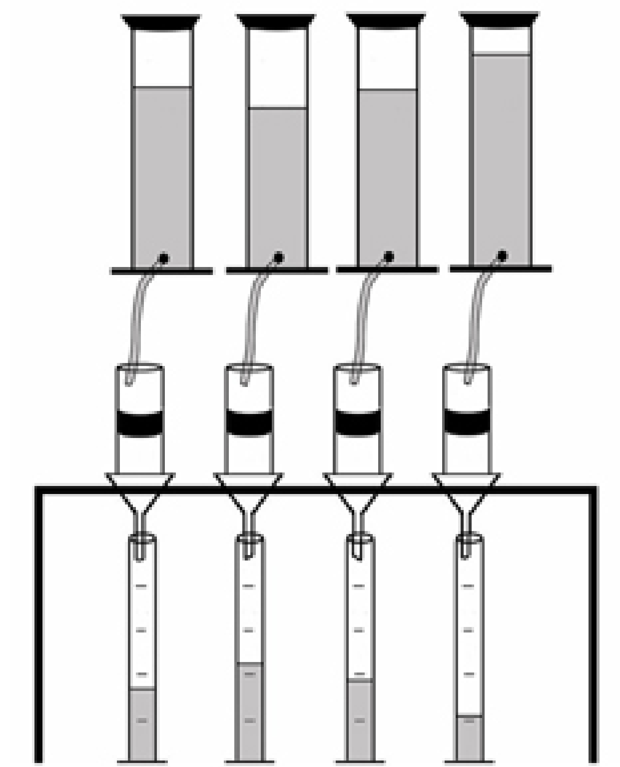


Figure 8. Schematic of system used to measure *Ks* at saturation.

Statistical Analysis

Analysis of variance for soil physical and water transmission properties were determined in SAS using Proc GLM as a completely randomized design structure on a total of 45 samples (n=5 per treatment). Mean separation was preformed using Fishers protected LSD at an alpha 0.05 level.

Soil pH (1:2), EC (saturated paste), SAR, Ca, Mg, and Na previously analyzed were used for correlation analysis with f_a, f_e, AW, α, n, and *Ks* to determine any relationships that may exist between chemical and physical parameters measured.

Treatment Codes

For ease of presentation for the 2004 Greenhouse Study, Column Leachate Study and Moisture Retention Study, the unamended control and individual CCP treatments at both rates shall be interchangeably referenced the following way: BA 22.75, BA 44.5 (for bottom ash at 22.75 mT/ha and 44.5 mT/ha application rates, respectively), FA 22.75, FA 44.5, SS 22.75 and SS 44.5. For the 2005 Greenhouse Study, the treatments shall be referenced as: control (no amendments), Fe (chelated Fe check), FA 22.75 (fly ash 22.75 mT/ha), FA 44.5 (fly ash applied at 44.5 mT/ha) and FA DTPA (fly ash applied at a rate based upon its DTPA extractable, plant available Fe).

RESULTS AND DISCUSSION

Study 1: Evaluation of Hybrid Poplar Amended with Coal Combustion Products – Greenhouse Studies

2004 Greenhouse Study

Chlorosis Evaluations

Except for the control, the hybrid poplar clone OP-367 had higher overall leaf greenness than NM-6 (Figure 9). For the clone OP-367, the highest SPAD values occurred at the SS 44.5 treatment (36.3) followed by the BA 44.5 and FA 44.5 mT/ha treatments (36,3 and 36.2, respectively) which were higher than the control (32.5; $P<0.0001$). The opposite trend occurred with the clone NM-6, as all CCP treated containers produced trees with slightly more chlorosis than the control, though these values were not significantly different from each another.

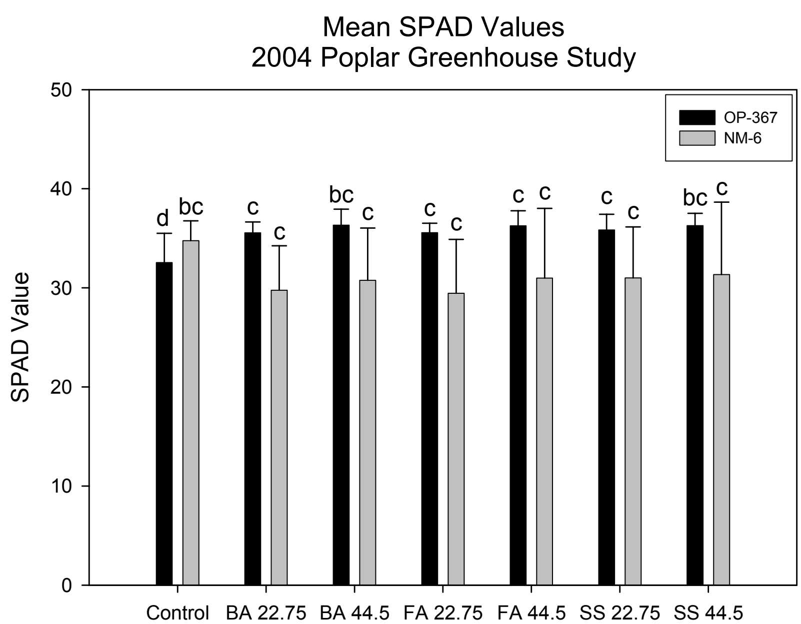


Figure 9. Pooled leaf chlorosis values for the hybrid poplar entries OP-367 and NM-6 from the 2004 Greenhouse Study. Data are means compared between the same colored bars. Means with the same letter are not significantly different (clone OP-367: LSD = 1.62, F value = 20.53, $P<0.0001$; clone NM-6: LSD=5.66, F value=4.92, $P=0.0002$).

Soil Conductivity, pH, and Sodium Adsorption Ratio

Salinity. An increasing trend in salinity occurred with the addition of scrubber slurry (Table 4). Both rates were highest in EC (3.21 and 3.85 mS/cm for the SS 22.75 and SS 44.5 rates, respectively; P<0.0001), a result of the high soluble salt content found in scrubber slurry. Still, these EC levels were below the USDA threshold level of 4 mS/cm. Fly ash and bottom ash EC levels were similar to the control. The fly ash has the highest Ca content of any of the amendments (Table 3) but is similar to the bottom ash for Na content. The bottom ash receives rinsing with water through the process of removal from the furnace described previously which could aid in the removal of soluble salts, hence the lower ECs. These results are consistent with the application of unweathered CCP materials (Carlson and Adriano, 1993).

Sodium Adsorption Ratio. Sodium adsorption ratios decreased with the addition of CCPs. Scrubber slurry treatments at both rates lowered SAR values (3.17 and 3.35 for the 44.5 and 22.75 mT/ha rates, respectively) below the control (4.09; P<0.0001; Table 4). Scrubber slurry contains appreciable amounts of cations K^+, Ca^{2+} and Mg^{2+} that exchange with Na on soil cation exchange sites, contributing to the lower SAR values (Tables 3 and 4).

pH. Soil pH increased above the control in fly ash treated soil (8.7 for both rates; P<0.0001) (Table 4). Recalling from Table 3, the APS fly ash had a pH of 12.41 and contained the highest Ca content than any of the CCP treatments. Low S-containing western coals typically produce alkaline ash (Carlson and Adriano, 1993). The soil pH decreased in scrubber slurry treated soil (8.5 and 8.4 for the SS 22.75 and SS 44.5 rates, respectively; P<0.0001; Table 4). The reason for this is likely two-fold: 1) that scrubber slurry is high in soluble salts. As salt concentration increases, soluble cations such as Ca^{2+} and Mg^{2+}, replace acidic exchangeable cations (H^+ and Al^{3+}) in the soil solution, lowering the pH (Al-Busaidi and Cookson, 2003; NRCS, 1993; Tisdale et al., 1985). Second, S, which was found in high concentrations in the scrubber slurry (discussed further below), has an acidulating effect on the soil depending on the form (Tisdale et al., 1985). The scrubber slurry environment promotes the presence of hydrogen sulfide and sulfuric acid (Salisbury, 2006). NAPI soils are well buffered but a small change in pH at the band of placement in the soil near the crop root zone could lower the pH enough to render micronutrients more available (discussed further below).

Biomass

The clone OP-367 exhibited superior growth characteristics over NM-6 for leaf and stem dry weights, leaf areas, stem length and diameters (Table 5). No entry by treatment interaction was present which permitted data pooling between both entries. Of the CCP treatments, soil amended at the FA 44.5 rate had the greatest leaf dry weights (15.2 g), leaf areas (1635.8 cm^2), stem dry weights (10.2 g), stem lengths (95.4 cm) and stem diameters (8.9 mm) (Table 5). CCP's equaled or improved all growth parameters compared to the control except for stem diameters which were lowest in the BA 22.75 treatment (8.0 mm).

An entry by treatment interaction was observed between both clones and treatments for root dry weight and as a result, responses are compared for each entry in Figure 10. The two scrubber slurry treatments produced the greatest root dry weights for clone OP-367 (10.5 and 10.3 g for the SS 22.75 and SS 44.5 rates, respectively), though these were not different from the control (P= 0.9277). For the clone NM-6, CCP treatments produced lower dry weights than the control. Soil amended with the FA 44.5 rate had the lowest root dry weights (6.9 g) followed by BA 22.75 (7.3 g) and FA 22.75 rate (7.5 g; P=0.0536).

Poplars are not particularly salt tolerant but will broadly tolerate EC levels between 1 – 5.53 dS/m (Bãnuelos et al., 1999; Howe and Wagner, 1996). At 9.33 dS/m, poplars will show a 50% decrease in yield (Bãnuelos et al., 1999). It isn't immediately clear if the increased ECs found in the scrubber slurry amendments had any affect on biomass parameters. On pooled and individual poplar clone data, no correlation between EC and biomass parameters were found (data not shown) and trees grown on the saltier scrubber slurry amended soil had equal or slightly better growth than the control for most measured parameters.

Nutrient Status of Leaves and Soil

No clone entry x treatment interaction was observed for leaf macro and micronutrient status which permitted data pooling of both clones for tissue elements (TN, S, P, K, Mg, Ca and Na; Tables 6 and 7) and soil elements (Ca, Mg, Na, Zn, Fe, and Mn; Tables 8 and 9) responses. Soil nitrate (NO_3-N), K and Cu could not be pooled because of a treatment x hybrid poplar clone interaction and as such these elements are presented separately for the clone OP-367 (Figure 11 A for NO_3-N), OP-367 and NM-6 for soil K (Figure 11 B), and soil Cu for the clone OP-367 (Figure 12).

Nitrogen. Urea ammonium nitrate (UAN) was applied to CCP treatments for supplemental nutrition which reflected higher total leaf nitrogen versus the control (Table 6). Soil NO_3-N levels in CCP treated soil remained unchanged from the control (Figure 11 A). Nitrogen is expected to be low in the CCPs because of volatilization during combustion and any increase above the control is likely due to the urea ammonium nitrate supplemental nutrition provided to CCP treatments during the study.

Sulfur. Leaf S increased in all CCP treated soil compared to the control and was highest for both the SS 22.75 and SS 44.5 amendment rates (0.27 and 0.31 %, respectively; Table 6). Scrubber slurry is inherently high in S captured during the scrubbing process (Table 3, Experimental). The form of S in the scrubber slurry was not investigated but reported to predominate as calcium, magnesium, sodium sulfite and modest amounts of hydrogen sulfide and sulfuric acid (Salisbury, 2006). Korcak (1995) reports that if a forced oxidation system step is incorporated into the scrubbing process, sulfate production would be promoted which would then be more soluble and immediately plant available. At any rate, the $CaSO_3$ in scrubber slurry converts in soil to $CaSO_4$ (gypsum) (Dick et al., 2000).

Phosphorous and Potassium. Leaf P in the FA 44.5 treated soil was highest followed by BA 22.75 (0.16 and 0.15 %, respectively) (Table 6). Increased levels of P within *Eucalypus obliqua* leaves have been linked to increases pH (Anderson and Ladiges, 1978). The increased pH of fly ash amended soil could have produced the same effect in poplars.

Similarly, leaf K was highest in the FA 44.5 (2.02 %) and BA 22.75 (2.02 %) treatments, followed by the FA 22.75 treatment (1.98 %; Table 6). For the clone OP-367, soil K content was highest for the control (207.1 mg/kg) and lowest for the FA 44.5 treatment (4.10 mg/kg; P<0.0001; Figure 11 B). Recall that biomass for most parameters and leaf K was greatest for the FA 44.5 rate (Tables 5 and 6) which could explain K depletion from the soil, especially for soil cultivated under the hybrid poplar clone OP-367. No differences with the control were observed in soil K for the clone NM-6 (Figure 11 B).

Calcium, Magnesium and Sodium. Leaf Mg contents were highest at the SS 44.5 rate (0.312 %) followed by the SS 22.75 rate (0.264 %; Table 6). Leaf Ca and Na were similarly high in the scrubber slurry amended soil. The SS 44.5 leaf Ca content was 1.79 % (P<0.0001) and the highest leaf Na was at the SS 22.75 rate (209 mg/kg) followed by the SS 44.5 rate (200.1 mg/kg; P<0.0001; Table 6). Except for Na, the clone NM-6 accumulated higher levels of the above macro elements than the clone OP-367. Calcium increases observed in hybrid poplar tissues were consistent with other reports after scrubber material application to soil (Punshon et al., 2001). Although we saw increases in tissue Na and Mg from scrubber slurry amending of an alkaline soil that were not generally seen by Punshon in herbaceous crops cultivated on an a scrubber material amended acid soil (baseline pH 5.4).

Soil Mg and Ca were also highest at the SS 44.5 rate followed by the SS 22.75 rate (P<0.0001; Table 8). Fly ash and bottom ash also slightly raised soil Ca levels, though these were not different from the control (Table 8). Soil Mg content decreased below the control at the FA 44.5 (P<0.0001; Table 8). The reasons for this are probably related to plant uptake as the FA 44.5 treatment produced high biomass responses for most measured parameters. Fly ash amendments raised soil Na content the greatest, though not significantly above the control (Table 8).

Zinc. The BA 22.75 rate raised leaf Zn content to 18.90 mg/kg followed by the BA 44.5 rate (16.72), though these levels were not significantly higher than the control (16.38 mg/kg) (Table 7). The BA 44.5 rate had the highest soil Zn content (0.427 mg/kg) though again this was not significantly higher than the control (0.415 mg/kg) (Table 9). The clone NM-6 accumulated higher levels of leaf Zn than the clone OP-367, though these were not significantly greater (P=0.2113; Table 7).

Iron and Manganese. The addition of scrubber slurry at 44.5 mT/ha raised leaf Fe content (12.64 mg/kg; P =0.0023) above the control (9.05 mg/kg; Table 7). The second highest leaf Fe content was found in the FA 44.5 treatment (12.4 mg/kg), though this was not different from the control. Soil Fe content was highest in the FA 44.5 treatment (4.13 mg/kg; Table 9), though again, not significantly higher than the control. Iron content was higher in OP-367 than NM-6 (P=0.0025), which could explain the higher SPAD values observed for that clone illustrated previously in Figure 9.

The SS 44.5 treatment also had the highest leaf Mn content (74 mg/kg; P<0.0001) compared to the control (55.0 mg/kg; Table 7) though there were no increases in soil Mn for any of the CCP amendments (Table 9). NM-6 accumulated higher levels of leaf Mn than OP-367 (P=0.0026; Table 7). The lowering pH by scrubber slurry treatments discussed previously could have factored into increased leaf concentrations of these micronutrients.

Copper. Pooled leaf Cu was raised in leaves under all CCP treatments, especially in bottom ash, followed next by fly ash and scrubber slurry amended soil; the control had the lowest leaf Cu content (P=0.0092; Table 7). Greater Cu uptake into the leaves by the CCP treatments translated to lower Cu levels in the soil compared to the control illustrated in Figure 12 for the clone OP-367.

Boron. Boron is an essential plant nutrient but can easily become toxic in sensitive plants. A treatment x hybrid poplar entry interaction was observed which did not permit data pooling. Each clone is presented individually. The highest leaf B contents occurred in the fly ash and scrubber slurry treatments (Figure 13). Both clones accumulated their highest B in leaves under SS 44.5 cultivation (94.4 mg/kg for OP-367 and 228.0 mg/kg for NM-6; P<0.0001). Recalling from Table 3 (under Experimental) B was highest in the scrubber slurry material. Boron content was also highly correlated to increasing salinity (r=0.62, P<000.1 for OP-367; r=0.51, P<0.0001 for NM-6, data not shown),

Observed increases in tissue B content from CCP soil amending is consistent with other studies (Punshon et al., 2001). Hybrid poplar are known to accumulate leaf B content when irrigated with industrial or saline agricultural drainages (Jessen, 1999; Renault et al., 1999; Shannon et al., 1999). Boron preferentially accumulates to toxic levels at the end of the transpiration stream, in lower leaves, especially as salinity increases from 1 to 15 dS/m and accumulates in stem tissue only at high salinity levels (Bãnuelos et al., 1999). The critical B leaf level before yield reductions could be observed for hybrid poplars of differing parental crosses ranged from 211 (most tolerant clone) to 62 mg B/kg (least tolerant) (Bãnuelos et al., 1999). Clone OP-367 has a critical B level of 141 mg B /kg which was not exceeded in this study, possibly explaining why OP-367 growth parameters in the scrubber slurry treatments never decreased below the control except for stem diameters and why B was not correlated to growth (data not shown). However the clone NM-6 reached 228 mg B/kg in leaves, higher than any tolerance level outlined by Bãnuelos, which correlated negatively with leaf areas (r=-0.37; P=0.0055), leaf dry weights (r=-0.53; P<0.0001), stem length (r=-0.32; P=0.017), stem diameter (r=-0.39; P=.0036), stem dry weight (r=-0.49; P=0.0002), and root dry weight (r=-0.28; P=0.0404; data not shown). Symptoms resembling B toxicity (burning of leaf margins especially toward the bottom of the canopies) were observed at the end of the study, for NM-6 under SS 44.5 cultivation.

Boron can be especially high in unweathered CCPs and may pose problems after initial agricultural applications until leaching beyond the root zone has occurred (Dick et al., 2000; Schwab, 1993). The CCPs in this study were relatively unweathered (Salisbury, 2006). Also, leaching of pots was not undertaken to examine the effects of potentially toxic elements or salt build-up. As B easily moves with irrigation waters, especially in sandy soils, accumulation in leaves may not have occurred if containers were leached and the CCP material more weathered.

Table 4. Soil conductivity (salinity), pH, and sodium adsorption ratio (SAR) of a Doak sandy loam amended with coal combustion products. Means are from the 2004 Hybrid Poplar Greenhouse Study and are pooled from both OP-367 and NM-6 containers.

2004 Greenhouse Study												
	EC				**SAR**				**pH**			
Treatment	**mS/cm**		**SD**		**mmol/L**		**SD**		**1:2**		**SD**	
Control	2.20	±	0.17	d	4.09	±	0.25	a	8.6	±	0.10	bc
Bottom Ash 22.75 mT/ha	2.35	±	0.36	d	4.06	±	0.23	ab	8.6	±	0.09	cd
Bottom Ash 44.50 mT/ha	2.31	±	0.30	d	3.98	±	0.18	abc	8.6	±	0.08	bc
Fly Ash 22.75 mT/ha	2.31	±	0.23	d	3.98	±	0.19	abc	8.7	±	0.09	a
Fly Ash 44.50 mT/ha	2.24	±	0.30	d	4.04	±	0.14	abc	8.7	±	0.08	ab
Scrubber Slurry 22.75 mT/ha	3.21	±	0.26	b	3.35	±	0.29	d	8.5	±	0.07	e
Scrubber Slurry 44.50 mT/ha	3.85	±	0.31	a	3.17	±	0.22	e	8.4	±	0.10	f
LSD	0.22				0.14				0.06			
F Value	52.94				41.8				16.83			
Pr > F	<.0001				<.0001				<.0001			
2005 Greenhouse Study												
Control	3.24	±	0.12	d	5.65	±	0.20	ab				
Fe (Sprint 138)	3.17	±	0.28	d	5.78	±	0.20	a				
Fly Ash 22.75 mT/ha	3.10	±	0.24	de	5.73	±	0.28	a				
Fly Ash 44.50 mT/ha	3.16	±	0.15	d	5.62	±	0.19	ab				
Fly Ash DTPA	3.03	±	0.12	e	5.67	±	0.27	a				
LSD	0.18				0.24							
F Value	31.71				9.32							
Pr > F	<0.0001				<0.0001							

Table 5. Biomass results. The 2004 study assessed two hybrid poplar clones cultivated under CCP amended soil; in 2005, only the clone OP-367 and fly ash were assessed. Means with the same letter are not significantly different.

2004 Study **Treatment**	Leaf Dry Wt (g)		Leaf Area (cm^2)		Stem Length (cm)		Stem Dia. (mm)		Stem Dry Wt (g)	
Control	14.0	c	1284.9	c	82.8	b	8.7	abc	9.5	c
Bottom Ash 22.75 mT/ha	14.3	c	1557.4	b	92.1	ab	8.0	d	9.1	c
Bottom Ash 44.50 mT/ha	14.6	bc	1545.1	b	94.6	a	8.8	abc	10.1	abc
Fly Ash 22.75 mT/ha	13.5	c	1455.3	bc	83.0	b	8.6	bcd	8.8	c
Fly Ash 44.50 mT/ha	15.2	abc	1635.8	ab	95.4	a	8.9	abc	10.2	abc
Scrubber Slurry 22.75 mT/ha	15.0	abc	1545.7	b	92.8	a	8.4	cd	9.9	bc
Scrubber Slurry 44.50 mT/ha	14.1	c	1557.4	b	92.3	ab	8.6	bcd	9.7	bc
LSD	2.4		232.9		9.7		0.67		1.64	
F Value	2.51		2.92		2.02		2.52		2.57	
Pr > F	0.0165		0.0061		0.0535		0.0164		0.0145	
Entry										
OP-367	17.7	a	1706.1	a	99.5	a	9.4	a	12.1	a
NM-6	12.3	b	1406.9	b	82.8	b	8.0	b	8.0	b
LSD	1.13		112.4		4.7		0.33		0.79	
F Value	90.73		27.96		49.78		68.05		104.73	
Pr > F	<.0001		<.0001		<.0001		<.0001		<.0001	
2005 Study										
Control	15.0	b	1419.27	d	124.6	abc	9.5	a	14.0	d
Fe (Sprint 138)	15.1	b	1551.95	bc	124.0	abc	9.4	a	14.5	bcd
Fly Ash 22.75 mT/ha	15.2	b	1527.36	bcd	122.5	bc	9.7	a	14.3	cd
Fly Ash 44.50 mT/ha	16.1	ab	1694.11	a	124.2	abc	9.8	a	14.8	bcd
Fly Ash DTPA	15.3	ab	1590.17	ab	119.5	c	9.7	a	14.3	cd
LSD	1.1		121.08		5.5		0.5		1.3	
F Value	2.3		3.79		2.5		0.85		2.84	
Pr > F	0.0397		0.002		0.0263		0.5509		0.0133	

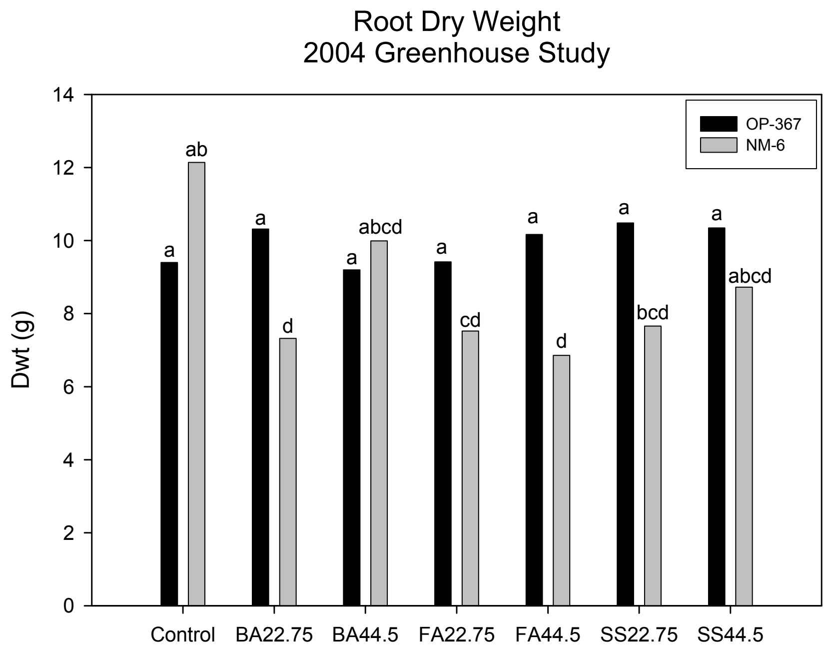


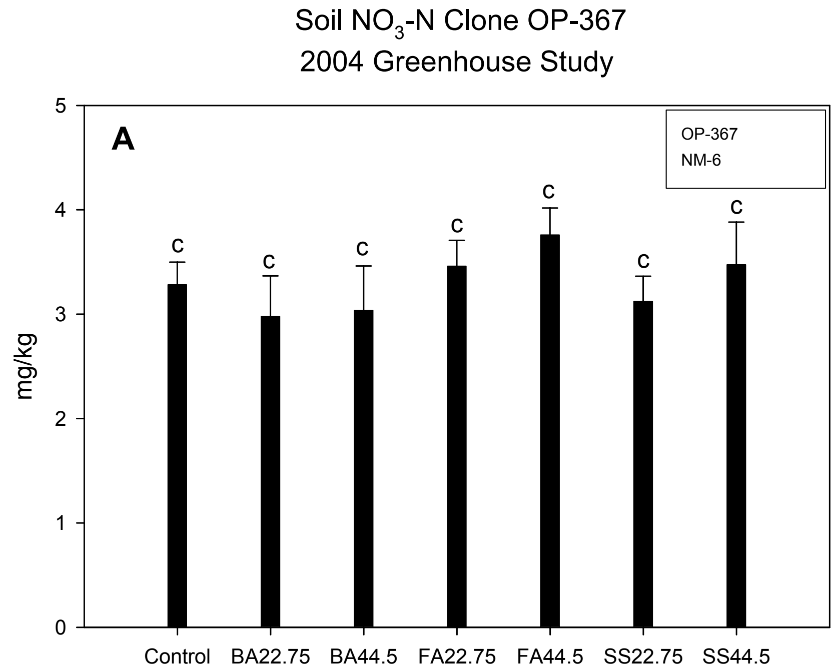
Figure 10. Root dry weight for the hybrid poplar entries OP-367 and NM-6 cultivated in CCP amended soil in 2004. Data are means compared between the same colored bars. Means with the same letter are not significantly different (clone OP-367: LSD = 2.4, F value = 0.38, Pr>F 0.9277; clone NM-6: LSD=4.5, F value=2.13, Pr>F 0.0536).

Table 6. Pooled leaf tissue TN, S, P, K, Mg, Ca, and Na levels from two hybrid poplar entries cultivated in a Doak sandy loam amended with coal combustion products. Means are from the 2004 Hybrid Poplar Greenhouse Study.

Treatment	**TN (%)**		**S (%)**		**P (%)**		**K (%)**		**Mg (%)**		**Ca (%)**		**Na (mg/kg)**	
Control	1.044	c	0.1622	d	0.10	b	1.40	b	0.197	cd	1.155	c	116.8	c
Bottom Ash 22.75 mT/ha	1.876	a	0.2383	bc	0.15	a	2.02	a	0.232	bc	1.266	bc	172.3	abc
Bottom Ash 44.50 mT/ha	1.749	ab	0.2467	abc	0.13	ab	1.91	ab	0.241	bc	1.368	bc	154.7	abc
Fly Ash 22.75 mT/ha	1.833	a	0.2663	ab	0.14	ab	1.98	a	0.261	b	1.552	ab	161.6	abc
Fly Ash 44.50 mT/ha	1.877	a	0.2359	bc	0.16	a	2.02	a	0.231	bc	1.297	bc	178.9	ab
Scrubber Slurry 22.75 mT/ha	1.741	ab	0.2714	ab	0.14	ab	1.84	b	0.264	b	1.489	ab	209.0	a
Scrubber Slurry 44.50 mT/ha	1.741	ab	0.3073	a	0.13	ab	1.90	b	0.312	a	1.729	a	200.1	a
LSD	0.434		0.066		0.05		0.52		0.044		0.330		61.9	
F Value	4.75		4.04		1.39		1.91		7.46		3.98		2.62	
Pr > F	<.0001		0.0004		0.2155		0.0696		<.0001		0.0005		0.0133	
Entry														
NM6	1.934	a	0.3081	a	0.153	a	2.02	a	0.278	a	1.604	a	61.7	b
OP367	1.273	b	0.1697	b	0.111	b	1.56	b	0.194	b	1.067	b	259.4	a
LSD	0.201		0.030		0.022		0.240		0.020		0.149		30.0	
F Value	43.06		79.78		13.6		14.02		67.88		52		170.85	
Pr > F	<.0001		<.0001		0.0004		0.0003		<.0001		<.0001		<.0001	

Table 7. Pooled leaf tissue micronutrients: Zn, Fe, Mn, and Cu levels from two hybrid poplar entries cultivated in a Doak sandy loam amended with coal combustion products. Means are from the 2004 Hybrid Poplar Greenhouse Study.

Treatment	**Zn mg/kg**		**Fe mg/kg**		**Mn mg/kg**		**Cu mg/kg**	
Control	16.38	b	9.05	c	55.0	b	3.60	b
Bottom Ash 22.75 mT/ha	18.90	b	9.30	bc	46.7	b	7.52	a
Bottom Ash 44.50 mT/ha	16.72	b	10.96	bc	56.4	ab	6.82	a
Fly Ash 22.75 mT/ha	13.13	b	10.09	bc	62.5	ab	7.12	a
Fly Ash 44.50 mT/ha	15.73	b	12.40	bc	59.4	ab	6.77	a
Scrubber Slurry 22.75 mT/ha	12.61	b	11.64	bc	61.7	ab	6.02	ab
Scrubber Slurry 44.50 mT/ha	12.60	b	12.64	ab	74.0	a	6.09	ab
LSD	9.57		3.46		18.90		3.02	
F Value	4.58		3.33		7.04		2.77	
Pr > F	0.0001		0.0023		<.0001		0.0092	
Entry								
NM6	19.16	a	10.30	b	58.4	a	7.69	a
OP367	16.37	a	12.75	a	45.1	b	3.59	b
LSD	4.41		1.55		8.55		1.42	
F Value	1.59		9.75		9.63		33.47	
Pr > F	0.2113		0.0025		0.0026		<.0001	



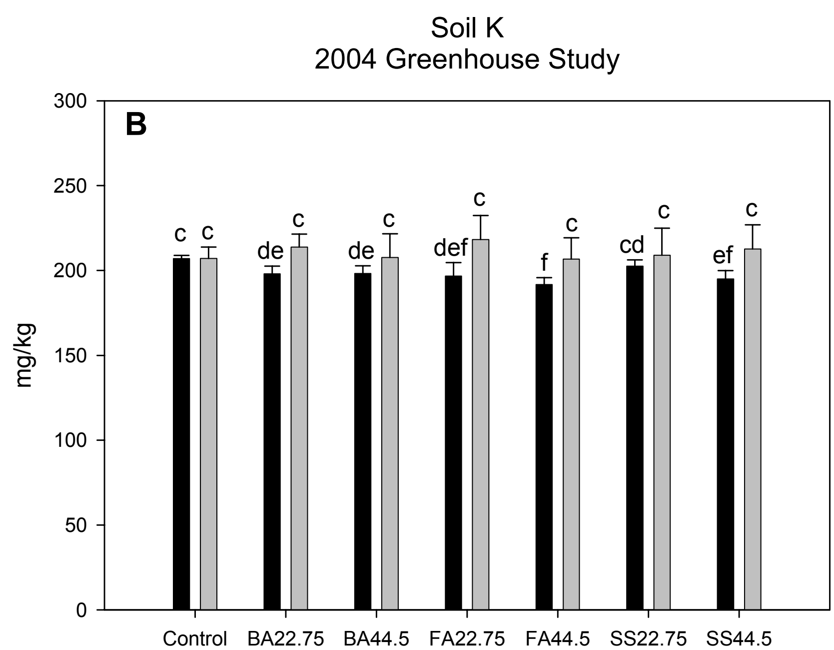


Figure 11. (A) Soil NO_3-N for CCP treated soil (LSD=1.33; F=400.66; P<0.0001); and (B) soil K (black bars cultivated with OP-367: LSD=6.06, F=205.43, P<0.0001), and NM-6 (grey bars; LSD=13.91, F=27.64, P<0.0001).

Table 8. Soil Ca, Mg, and Na of a Doak sandy loam amended with CCPs. Means are from the 2004 Hybrid Poplar Greenhouse Study.

	Ca				Mg				Na			
	mg/kg		**SD**		**mg/kg**		**SD**		**mg/kg**		**SD**	
Control	3578	±	243	c	196	±	6	d	126	±	6	c
Bottom Ash 22.75 mT/ha	3601	±	245	c	196	±	7	d	127	±	5	c
Bottom Ash 44.50 mT/ha	3588	±	221	c	195	±	5	d	125	±	4	c
Fly Ash 22.75 mT/ha	3627	±	248	c	194	±	8	d	128	±	5	c
Fly Ash 44.50 mT/ha	3623	±	249	c	188	±	7	e	128	±	5	c
Scrubber Slurry 22.75 mT/ha	3728	±	270	b	204	±	8	c	125	±	9	c
Scrubber Slurry 44.50 mT/ha	3809	±	249	a	211	±	8	a	126	±	5	c
LSD	54.4				2.97				4.28			
F Value	15.82				51.01				9.04			
Pr > F	<.0001				<.0001				<.0001			

Table 9. Soil micronutrients: Zn, Fe, and Mn of a Doak sandy loam amended with CCPs. Means are from the 2004 Hybrid Poplar Greenhouse Study.

	Zn				Fe				Mn			
Treatment	**mg/kg**		**SD**		**mg/kg**		**SD**		**mg/kg**		**SD**	
Control	0.415	±	0.071	c	3.25	±	0.24	c	5.96	±	0.86	c
Bottom Ash 22.75 mT/ha	0.406	±	0.054	c	3.23	±	0.57	c	5.59	±	1.25	c
Bottom Ash 44.50 mT/ha	0.427	±	0.033	c	3.20	±	0.48	c	5.66	±	1.15	c
Fly Ash 22.75 mT/ha	0.396	±	0.058	c	3.65	±	0.50	c	5.62	±	1.14	c
Fly Ash 44.50 mT/ha	0.386	±	0.050	c	4.13	±	0.79	c	5.76	±	1.30	c
Scrubber Slurry 22.75 mT/ha	0.401	±	0.087	c	3.36	±	0.46	c	5.76	±	0.77	c
Scrubber Slurry 44.50 mT/ha	0.401	±	0.070	c	3.69	±	0.48	c	5.88	±	0.87	c
LSD	0.06				1.81				0.85			
F Value	376.89				234.37				15.69			
Pr > F	<.0001				<.0001				<.0001			

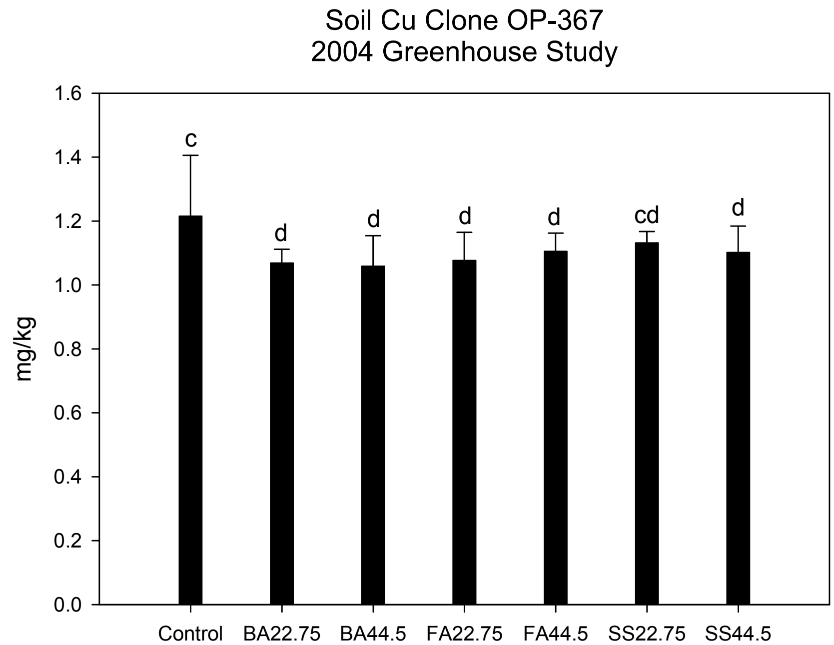


Figure 12. Soil Cu under cultivation with the hybrid poplar clone OP-367 (LSD 0.10, F=17.03, P<0.0001).

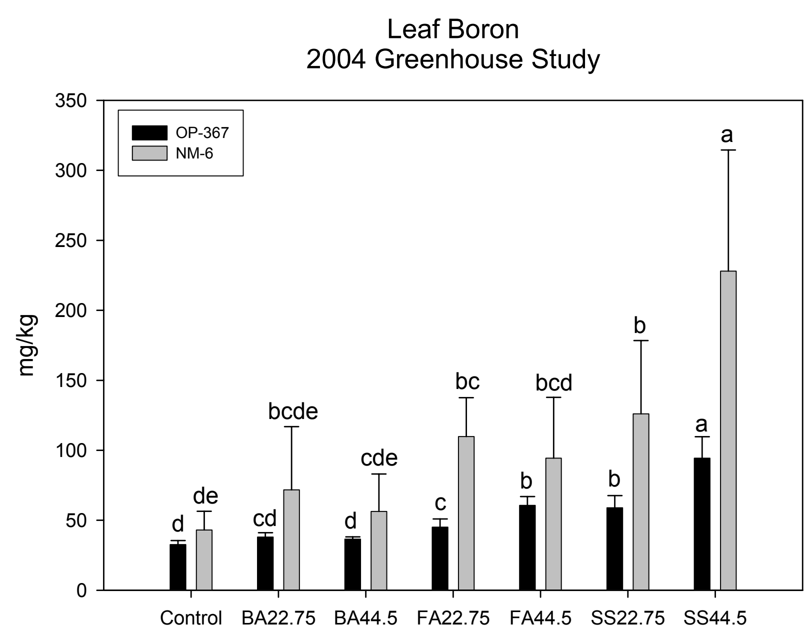


Figure 13. Boron accumulation in leaves of two hybrid poplar clones. (black bars cultivated with OP-367: LSD=7.50, F=58.82, P<0.0001), and NM-6 (grey bars; LSD=55.83, F=11.75, P<0.0001).

2005 Greenhouse Study

In the 2005 greenhouse study, only the clone OP-367 was cultivated under fly ash at three rates: FA 22.75, FA 44.5, and FA DTPA (which was the equivalent of 73.62 mT/ha) .

Chlorosis Evaluations

Addition of fly ash to soil gradually improved leaf greenness of the clone OP-367 as the study progressed. SPAD values for the fly ash treatments were not different from the control in April but had increased by June (P<0.0001; Figure 14). The June 22 SPAD values correlated highly with total nitrogen (r=0.78; *P*<0.0001), Fe (r=0.69; *P*<0.0001), S (r=0.63; *P*<0.0001), P (r=0.69; *P*<0.0001), K (r=-0.58; *P*<0.0001), Mg (r=0.57; *P*<0.0001), Ca (r=0.60; *P*<0.0001), Na (r=0.38; *P*=0.0017), Mn (r=0.42; *P*=0.0006), Cu (r=0.47; *P*<0.0001), and B (r=0.64; *P*<0.0001) (data not shown). Essentially, increasing SPAD values indicated an improvement in leaf nutrient status discussed further below.

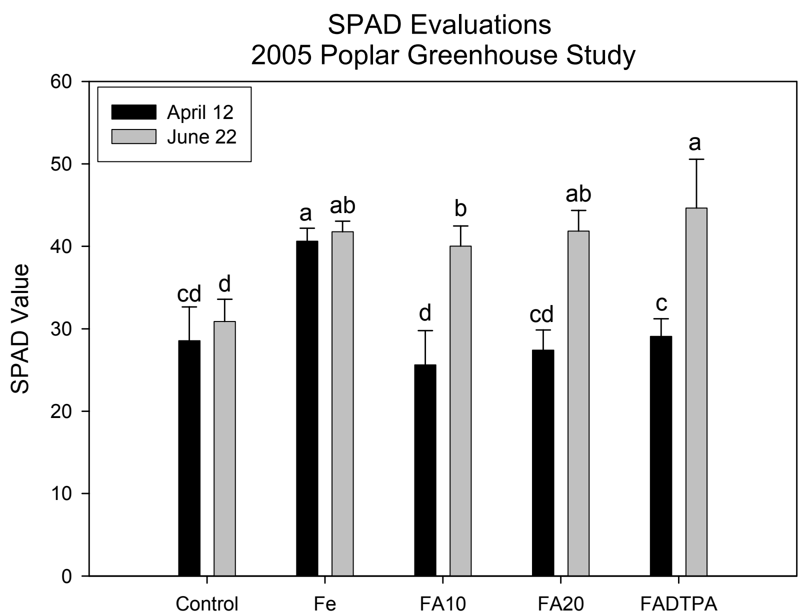


Figure 14. Leaf chlorosis values measured on two separate dates for the hybrid poplar clone OP-367 from the 2005 Greenhouse Study. Comparisons are made between like colored bars – bars with the same letter are not significantly different at α 0.05 level (April 12 SPAD reading: LSD = 3.01, F value = 22.74, *P*<0.0001; June 22 SPAD reading: LSD=3.01, F value=19.46, *P*<0.0001).

Soil Conductivity, pH, and Sodium Adsorption Ratio

As in the *2004 study*, salinity was found to be lower in the fly ash amended containers than the control. The FA DTPA rate was lowest (3.03 mS/cm) compared to the control (3.24 mS/cm; $P<0.0001$; Table 4). Both the 22.75 and 44.5 mT/ha fly ash rates were also lower than the control, though these were not significant. Sodium adsorption ratios remained unchanged compared to the control (Table 4). Data for pH was not available for inclusion but trends should be similar as those observed in the 2004 study: with increasing rates of fly ash likely came an increase in pH.

Biomass

Leaf dry weights and areas increased for the two highest rates of fly ash (FA 44.5 and the FA DTPA rate; $P=0.0397$; Table 5). Stem lengths did not improve with the addition of fly ash nor were stem diameters different from the control or Fe fertilizer check. Stem dry weights were slightly greater for the FA 44.5 rate, though these too were not different from the control. Root dry weights were greatest with the low fly ash rate (22.75 mT/ha; Figure 15). Increasing pH on alkaline soils through $CaCO_3$ applications has negative growth effects for pH sensitive plants (Tang et al., 1995). The highest fly ash application rate likely raised soil pH linearly as seen in the *2004 study* which could have been related to the lower growth rates for most biomass parameters of hybrid poplar grown at the highest fly ash amendment rate (FA DTPA) compared to the FA 22.75 and FA 44.5 rates.

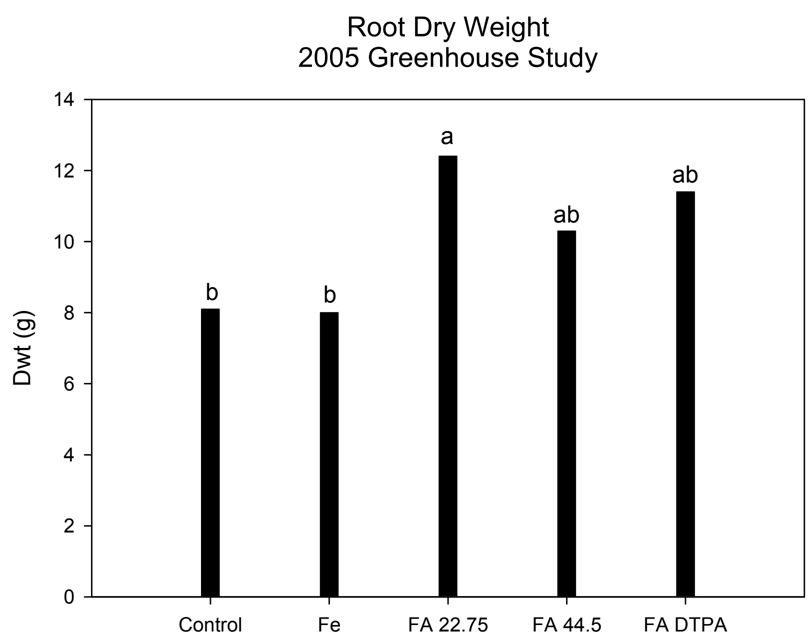


Figure 15. Root dry weight for the hybrid poplar entries OP-367 from the 2005 Greenhouse Study. Means with the same letter are not significantly different (LSD = 3.8, F value 1.64, P=0.1443)

Nutrient Status of Leaves and Soil

Nitrogen and Sulfur. Total nitrogen content improved in both leaves and stems with all treatments (*P*<0.0001), though again this was related to the supplemental N supplied by the UAN (32-0-0) (Figure 16 A). As with the *2004 study*, leaf S content also improved in both the CCP and Fe check treatments (*P*<0.0001) but remained unchanged from control values in stem material (Figure 16 B).

Phosphorus and Potassium. Leaf P increased above the control in all fly ash treated soil *P*<0.001; Figure 16 C) for reasons discussed earlier but could have been related to the potential increase soil pH with fly ash. The highest P accumulation occurred at the FA 22.75 rate (0.23%) but no differences in stem P were detected. Unlike the *2004 study* where a rise in pooled leaf K between two hybrid poplar clones was observed in fly ash amended soil, K leaf levels decreased below the control in all fly ash treatments for the clone OP-367 in 2005 (*P*=0.0011) but were not different in stems (Figure 16 D). Potassium solubility decreases with a rise in pH. As such, the liming properties of fly ash seen in the *2004 study* may have caused the observed response in leaves.

Calcium and Magnesium. Tissue Ca and Mg increased in fly ash amended soil (Figure 16 E, F, and G). Leaf Mg was highest at the FA 22.75 and FA DTPA rates (0.28 %) followed by the FA 44.5 rate (0.26%; *P*<0.0001). Stem Mg contents were similar for all fly ash treatments (0.15%), had Mg levels higher than the control (*P*<0.0001), but did not differ from the Fe check (Figure 16 E). Similarly, leaf Ca contents were highest at the FA 22.75 (1.32 %) and FA DTPA rates (1.31 %; *P*<0.0001; Figure 16 F). Stem Ca increased above the control (*P*<0.0001) and was highest in the FA 44.5 rate (1.27 %) followed by the FA DTPA (1.23 %) and FA 22.75 rates (1.18 %). Out of all the CCPs, the Ca content is highest (Table 3, Experimental). Ca and Mg become more available to hybrid poplar as soil pH increases (Timmer, 1985) which could explain the rise of both elements in tissues for FA amended soil.

Sodium. Sodium levels also increased in hybrid poplar tissues under fly ash amending. Leaf Na levels were highest at the FA DTPA rate (226.38 mg/kg) followed by the FA 22.75 rate (222.5 mg/kg), Fe fertilizer check (216.25 mg/kg), and FA 44.5 rate (208.88 mg/kg); all were higher than the control (161.25 mg/kg; *P*<0.0001; Figure 16 G). Sodium accumulation in stems also increased over the control (P<0.0001) and was highest in the Sprint 138 Fe fertilizer check (311.63 mg/kg) followed by the FA 22.75 (304.63 mg/kg), FA 44.5 (304.38 mg/kg) and FA DTPA rates (285.88 mg/kg) rates. Sprint 138 Fe fertilizer is derived from technical sodium ferric ethylenediamine di-(o-hydroxyphenyl-acetate) (Becker Underwood Inc., 2006). Other than the irrigation water, this was likely the reason of increased tissue Na for the Fe Check.

The degree of tolerance in hybrid poplar is under genetic control and has been described as the ability to exclude Na and Cl from tissues (Bãnuelos et al., 1999; Renault et al., 1999; Stanturf et al., 2001) The clone OP-367 accumulated more Na in stems than in leaves and has been characterized as moderately salt tolerant (Shannon et al., 1999).

Zinc, Iron, Manganese, and Copper. The addition of fly ash increased plant tissue micronutrients Zn, Fe, Mn, and Cu over the control (Figure 16 H, I, J, and K). Leaf Zn content was highest at the FA 22.75 rate (49.69 mg/kg; P=0.0001) followed by the FA 44.5 and FA DTPA rates (47.59 and 47.30 mg/kg, respectively; Figure 16 H). Stem Zn was highest for the FA 44.5 rate (31.79 mg/kg) and lowest for the control (26.91 mg/kg; P<0.0001). Not surprisingly, leaf Fe was highest in the Sprint 138 chelated Fe fertilizer check (26.59 mg/kg; P<0.0001), but the FA DTPA rate (24.65 mg/kg), followed by the FA 44.5 rate (24.33 mg/kg) compared favorably to the Fe fertilizer check (Figure 16 I). Iron also increased in stems above the control with the highest content in the Sprint 138 Fe check (11.72 mg/kg; P<0.0001) followed by the FA 44.5 (7.01 mg/kg), FA DTPA (6.76 mg/kg) and FA 22.75 rates (5.57 mg/kg), though the fly ash treatments did not differ from the control (5.37 mg/kg). Fly ash treatments raised Mn in both leaves and stems (P<0.0001), the highest contents coming from the FA DTPA rate (62.70 and 19.23 mg/kg for leaves and stems respectively; Figure 16 J). Copper was highest in the Sprint 138 Fe fertilizer check (4.49 and 7.22 mg/kg for leaves and stems, respectively; P<0.0001) followed by the FA 22.75 (4.39 mg/kg, leaves) and FA DTPA rates (6.05 mg/kg, stems; Figure 16 K). As with Na, Cu accumulated highest in stems over leaves.

Micronutrient uptake in plants is highly influenced by pH. As pH increases, many micronutrients become less soluble, causing deficiency symptoms. Growth decreased, and lowered Mn, Fe, and Zn were observed in foliage of hybrid poplar clone DTAC-32 grown in containers limed to a pH of 7.6 (Timmer, 1985). Timmer suggest an optimum pH for hybrid poplar in the range of 6.0-7.0 for some clones. That is not to say that this range is ideal for all clones of hybrid poplar. In the *2004 Study*, the highest soil pH was observed on FA 44.5 amended soil (pH 8.7; Table 4). But the FA 44.5 rate also produced the greatest biomass for all categories except root dry weights (Table 5 and Figure 10). Except for stem length, in the *2005 Study* the FA 44.5 rate also had the greatest amount of biomass (Table 5 and Figure 15). In the *2004 Study*, except for Zn, Fe, Mn, and Cu accumulated in both hybrid poplar clones at slightly higher levels than the control under fly ash cultivation, under the highest pH. Similarly, in the *2005 Study*, Zn, Fe, Mn, and Cu all increased above the control in leaves and stems under presumably increasing soil pH with increasing fly ash rate.

Boron. As seen in the *2004 Study*, increasing the application rates of fly ash raised B content in plant tissues. Boron was highest in leaves amended at the highest FA DTPA rate (93.55 mg/kg) followed by the FA 44.5 and FA 22.75 rates (67.96 and 57.70 mg/kg, respectively; P<0.0001; Figure 16 L). Boron preferentially accumulated in leaves over stems, though the highest stem B content was again found at the FA DTPA rate (24.71 mg/kg; P=0.1719).

It doesn't appear that B toxicity symptoms emerged as they did in the *2004 study* for the clone NM-6. Leaf B concentrations never exceed tolerance limits for OP-367 discussed earlier and, if considering biomass parameters as an indicator of toxicity, the highest two rates of fly ash applied (FA 44.5 and FA DTPA rates) produced greater biomass for most measured parameters except stem lengths.

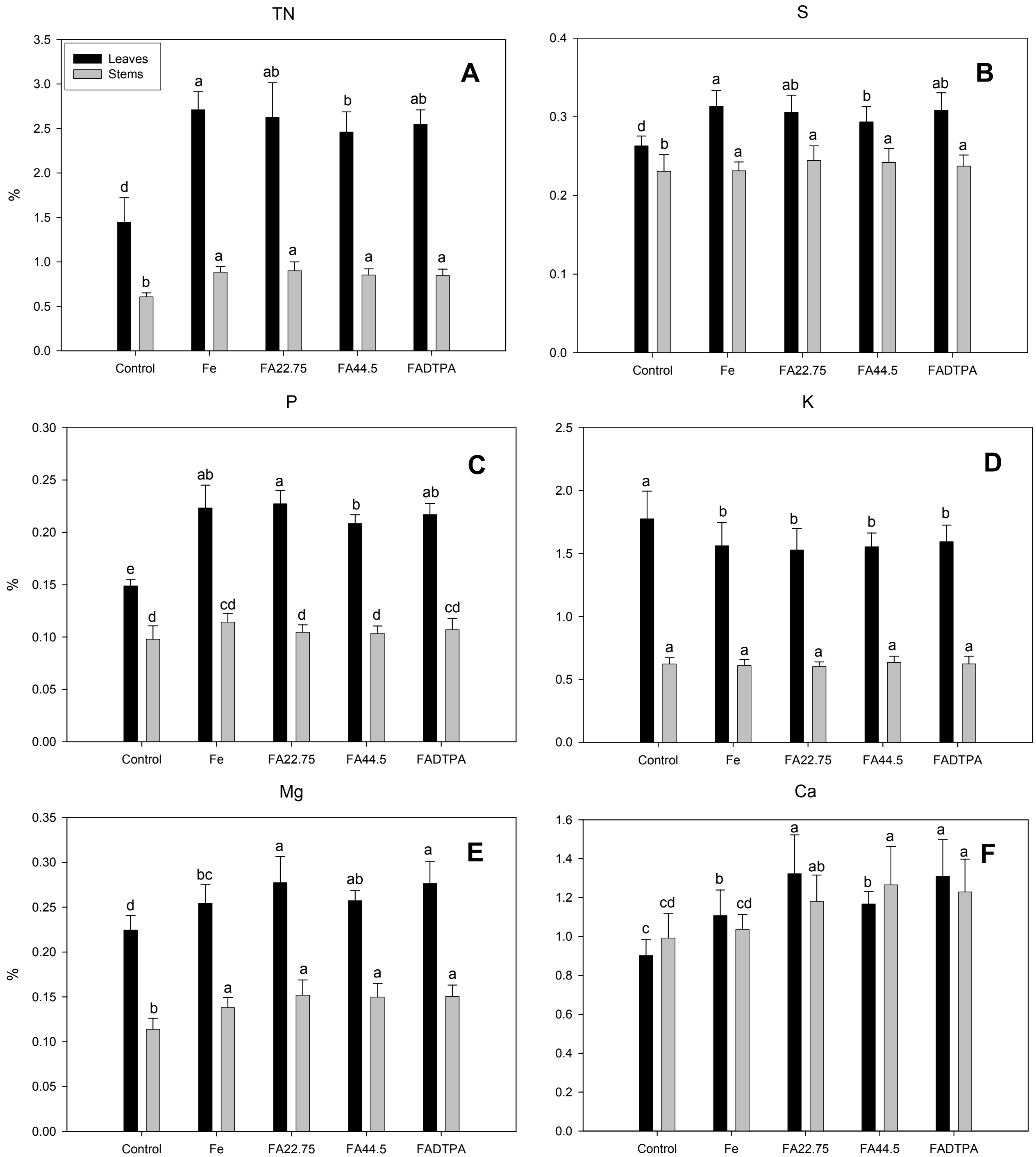


Figure 16. 2005 Leaf and stem elements of the hybrid poplar clone OP-367 cultivated in soil amended with fly ash. The unamended control and Sprint 138 chelated Fe fertilizer served as checks. Elements are: total nitrogen (A), sulfur (B), phosphorous (C), potassium (D), magnesium (E), and calcium (F). Leaf material is represented by black columns; stem by grey. Means comparisons are between like colored columns. Means with the same letter are not significantly different at the α=0.05 level.

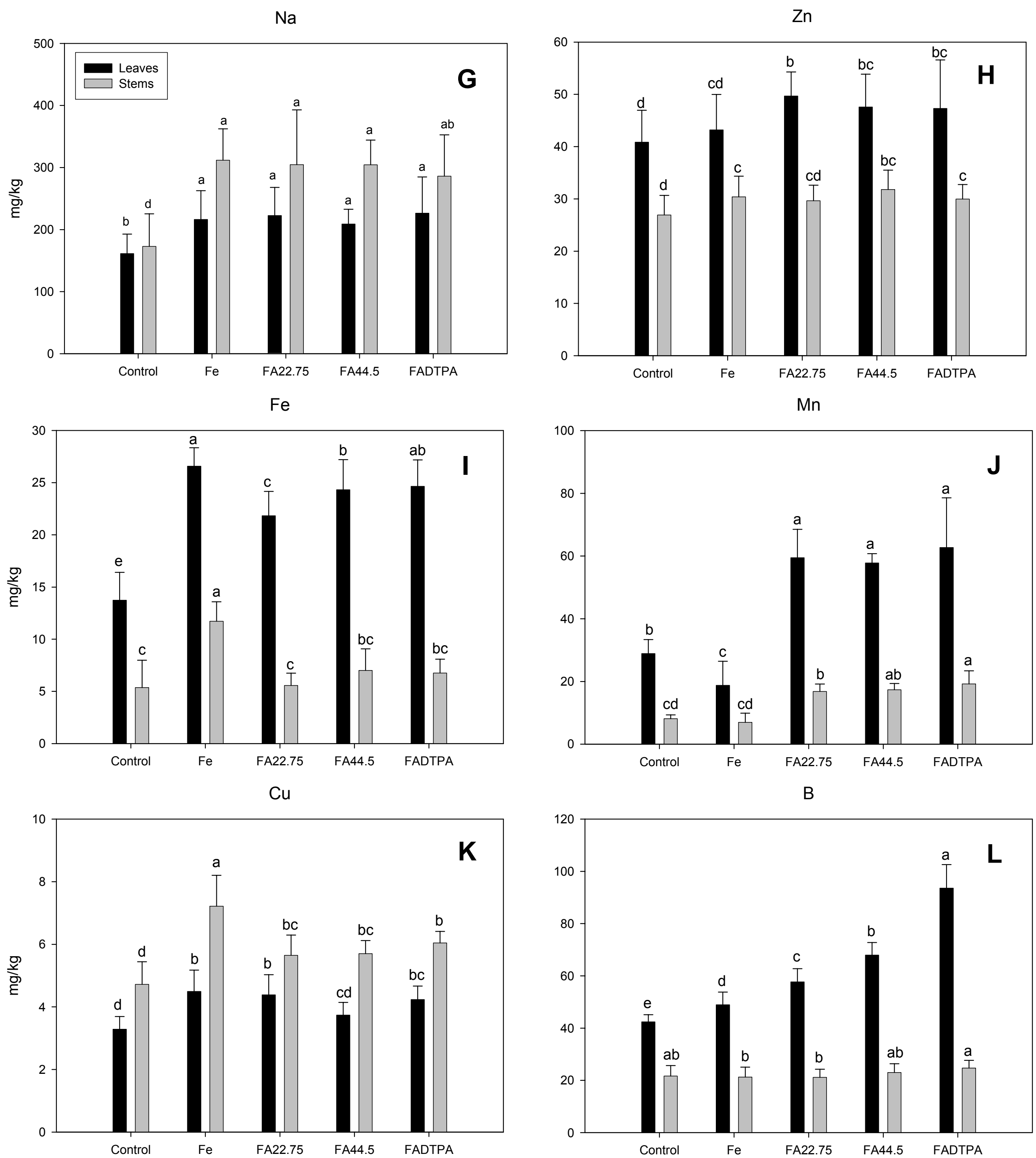


Figure 16 (continued). 2005 Leaf and stem elements of the hybrid poplar clone OP-367 cultivated in soil amended with fly ash. The unamended control and Sprint 138 chelated Fe fertilizer served as checks. Elements are: sodium (G), zinc (H), iron (I), manganese (J), copper (K), and boron (L). Leaf material is represented by black columns; stem by grey. Means comparisons are between like colored columns. Means with the same letter are not significantly different at the α=0.05 level.

Barium and Other Elements that may Pose an Environmental Risk

The following metals were analyzed in plant tissues and soils from acid digests: Cr, As, Ag, Se, Pb, Cd, and Ba. Of these, only Ba was detected in leaves and stems. Both *2004* and *2005* studies are presented together.

2004 Greenhouse Study

A treatment by entry interaction prevented data pooling between the two hybrid poplar clones, therefore, means are presented for leaves and stems separately for OP-367 and NM-6. For the clone OP-367, leaf barium was highest in fly ash amended soil (19.99 and 18.83 mg/kg respectively for the FA 22.75 and FA 44.5 rates) followed by bottom ash (18.54 and 17.31 mg/kg respectively for the BA 22.75 and BA 44.5 rates) (Figure 17 A). The two scrubber slurry treatments were lower than the control (6.63 and 4.52 mg/kg respectively for the SS 22.75 and SS 44.5 rates). Stem Ba was also highest in the two fly ash treatments (30.8 and 32.49 mg/kg respectively for the FA 22.75 and FA 44.5 mT/ha rates). Again, stem Ba contents were lowest in the scrubber slurry treatments.

Among the treatments, similar Ba accumulation trends were observed with the entry NM-6 for leaves and stems, the exception being the SS 22.75 treatment (Figure 17 B). Interestingly, with NM-6, Ba tended to accumulate more equally in stems and leaves than in the clone OP-367, where Ba preferentially accumulated in stems. Op-367 possibly has a leaf exclusion mechanism Ba similar to Na which warrants further study.

Soil Cr and Pb were not different than the control (P=0.7934 and P=0.8844, respectively; Table 10). All CCP treatments had lower Cd levels than the control (P=0.0966). Only the highest fly ash rate of 44.5 mT/ha (120.92 mg/kg) raised soil Ba levels significantly above the control (105.10 mg/kg; P=0.0004).

2005 Greenhouse Study

Similarly, tissue Ba content increased with increasing rates of fly ash. The highest concentrations in the leaves were found in the FA DTPA rate, the lowest in the control (28.66 and 11.71 mg/kg respectively; P<0.0001) (Figure 18). As with OP-367 grown in *2004*, Stem Ba was higher than in leaves and also increased with increasing fly ash rates: 23.44, 28.15, and 32.14 mg/kg Ba for the FA 22.75, FA 44.5, and FA DTPA application rates, respectively, compared to the control (17.19 mg/kg; P<0.0001).

The addition of fly ash did not increase soil Cr, Pb or Cd compared to the control (P=0.9302, P=0.4274, and P=0.4800, respectively; Table 10). However, soil Ba concentrations increased with increasing rates of fly ash in the order of the FA 22.75 rate (111.48 mg/kg) followed by the FA 44.5 rate (119.25 mg/kg) and lastly the FA DTPA rate (137.63 mg/kg) compared to the control (105.10 mg/kg; P<0.0001).

Of the elements analyzed in the two greenhouse studies Ba, B, and S are known to generally increase in plant tissues while Ba, B, Ca, Pb and S are reported to increase in fly ash amended soil (Keefer, 1993). Lead, Cr, and Cd did not increase in soils in either study and were well below USEPA toxic level standards if applying the Part 503 Rule used for heavy metal loading rates in biosolids on agricultural lands and European Union if applying the Directive 86/278/EEC or proposed addendums to their rule (Committee on Toxicants and Pathogens in Biosolids Applied to Land, 2002).

In both studies Ba increased in fly ash and bottom ash amended soil and plant tissues but did not in scrubber slurry treatments. Barium accumulation in plants under fly ash amendments are consistent with other studies (Schwab, 1993). The form of Ba was not determined for this study but The LD_{50} for rats (that is, lethal dose to kill 50% of a rat population) is 630 mg/kg for barium carbonate, 118 mg/kg for barium chloride, and 921 mg/kg for barium acetate (Apedaile et al., 2002). Plant tissue levels in both studies never rose above 40 mg/kg. Since hybrid poplar would not enter the food chain, this would not be a problem anyway.

More discussion is below in ‘Leachate Study’ section.

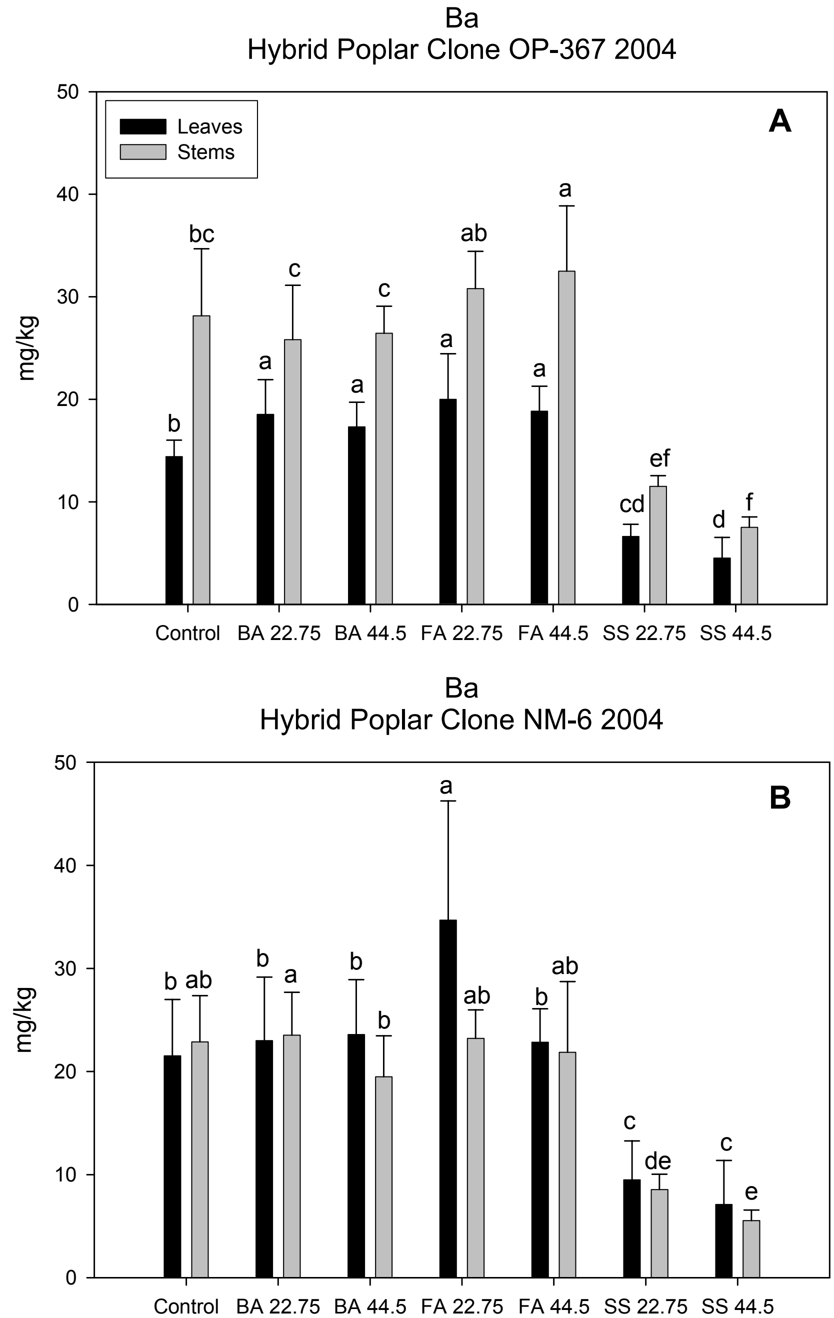


Figure 17. Leaf and stem Ba in the hybrid poplar clone OP-367 (A) and NM-6 (B) cultivated in 2004 under bottom ash, fly ash, and scrubber slurry amended soil at two rates: 22.75 and 44.5 mT/ha. Leaf material is represented by black columns; stem by grey. Means comparisons are between like colored columns. Means with the same letter are not significantly different at the α=0.05 level.

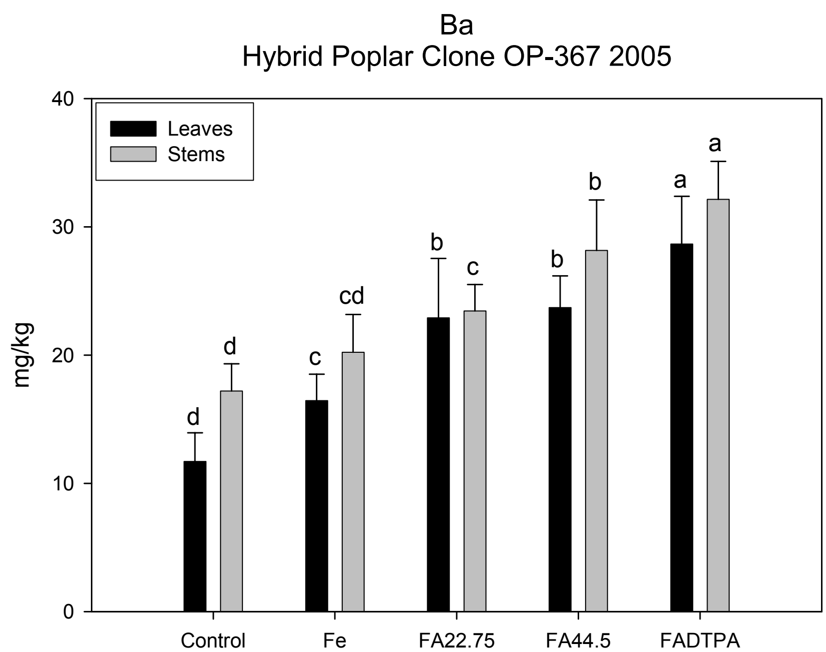


Figure 18. Leaf and stem Ba in the hybrid poplar clone OP-367 cultivated in 2005 under fly ash amended soil at three rates: 22.75 and 44.5 mT/ha and a DTPA plant available Fe rate. Leaf material is represented by black columns; stem by grey. Means comparisons are between like colored columns. Means with the same letter are not significantly different at the α=0.05 level.

Table 10. Soil Cr, Pb, Ba, and Cd levels in a Doak sandy loam amended with coal combustion products. LS Means generated in SAS are from the 2004 Hybrid Poplar Greenhouse Study, means are displayed for the 2005 Study.

	Cr				Pb				Ba				Cd			
	mg/kg				mg/kg				mg/kg				mg/kg			
U.S. EPA 40 CFR 503 Rule[a]	-				300				-				39			
European Union limit values[b]	-				750-1,200				-				20-40			
E.U. proposed	1000				750				-				10			
NAPI soil	7.7				6.5				110.6				0.30			
Bottom ash	4.0				ND				465.5				1.00			
Fly ash	2.9				5.0				904.1				1.30			
Scrubber slurry	16.6				6.8				335.4				0.50			
2004 Greenhouse Study																
Treatment	**mg/kg**		**SD**		**mg/kg**		**SD**		**mg/kg**		**SD**		**mg/kg**		**SD**	
Control	7.45	±	0.78	a	4.79	±	0.75	a	105.10	±	10.28	bc	0.29	±	0.14	a
Bottom Ash 22.75 mT/ha	7.41	±	1.04	a	4.82	±	0.26	a	103.07	±	9.97	bc	0.22	±	0.09	abc
Bottom Ash 44.50 mT/ha	7.48	±	0.72	a	4.93	±	0.44	a	107.05	±	12.87	bc	0.21	±	0.14	abc
Fly Ash 22.75 mT/ha	7.80	±	0.64	a	4.97	±	0.33	a	112.03	±	7.81	ab	0.20	±	0.09	bc
Fly Ash 44.50 mT/ha	7.31	±	1.09	a	4.92	±	0.98	a	120.92	±	18.35	a	0.27	±	0.14	ab
Scrubber Slurry 22.75 mT/ha	7.36	±	0.68	a	5.07	±	0.60	a	103.39	±	9.62	bc	0.25	±	0.11	abc
Scrubber Slurry 44.50 mT/ha	7.66	±	0.58	a	4.97	±	0.63	a	105.63	±	7.94	bc	0.23	±	0.10	abc
LSD	0.68				0.49				9.09				0.08			
F Value	0.58				0.45				4.03				1.75			
Pr > F	0.7934				0.8844				0.0004				0.0966			
2005 Greenhouse Study																
Treatment																
Control	7.28	±	0.90	a	5.19	±	0.54	a	97.23	±	3.59	e	0.16	±	0.03	a
Fe (Sprint 138)	7.60	±	1.19	a	5.19	±	0.40	a	98.18	±	4.97	de	0.17	±	0.02	a
Fly Ash 22.75 mT/ha	7.68	±	1.46	a	5.22	±	0.56	a	111.48	±	8.76	bc	0.17	±	0.01	a
Fly Ash 44.50 mT/ha	7.51	±	1.20	a	4.93	±	0.18	a	119.25	±	6.78	b	0.17	±	0.02	a
Fly Ash DTPA	7.53	±	1.49	a	4.86	±	0.26	a	137.63	±	10.38	a	0.17	±	0.02	a
LSD	1.55				0.36				8.46				0.02			
F Value	0.34				1.02				20.93				0.95			
Pr > F	0.9302				0.4274				<.0001				0.48			

[a] Pollutant concentration limit for land application in the United States. [b] European Union limit values for concentrations of heavy metals in biosolids for use on land (Committee on Toxicants and Pathogens in Biosolids Applied to Land, 2002)

Study 2: Leaching of Coal Combustion Products in Soil Columns

Leachate

EC

Salinity was high for all CCP treatments, *including* the unamended control, in the first leachate collected April 11, ranging from 7.26 mS/cm (BA 44.5 rate) to 9.23 mS/cm (SS 44.5; Figure 19). After the initial flush of salts from the column profile, EC levels fell below 4 mS/cm by April 13, ranging from 1.17 to 3.65 mS/cm for the 44.5 mT/ha bottom ash and scrubber slurry treatments respectively. Four mS/cm is the threshold level defined by the USDA Salinity Lab above which yield reductions may occur for most agricultural crops (Allison et al., 1954; Maas and Hoffman, 1977) and illustrated as a dashed line. Columns amended with scrubber slurry eventually fell to the same levels as the control columns after 18 irrigations.

The mean of 13 leachate measurements showed that both scrubber slurry treatments increased salinity, although this was not significantly different from the control (P=0.9998; data not shown). Scrubber slurry constituents depend on the sorbents used to remove SO_2 (Korcak, 1995). The APS Power plant scrubber slurry contains calcium sulfite, magnesium sulfite, and sodium thiosulfate (Salisbury, 2006).

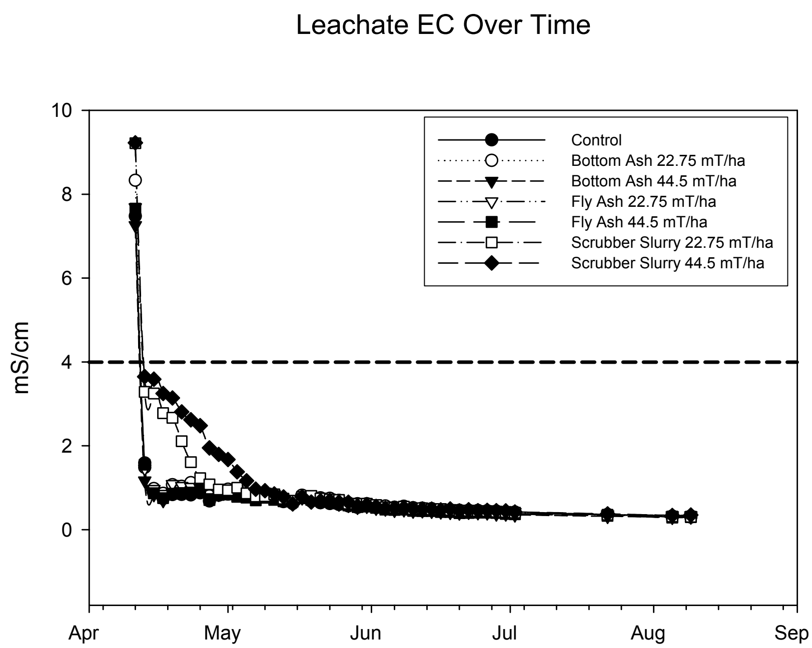


Figure 19. Salinity (EC) of leachate water measured over time collected from columns packed with a Doak sandy loam collected from Farmington and amended with CCPs (bottom ash, fly ash and scrubber slurry) at two rates (22.75 and 44.5 mT/ha).

pH

From April 11 to May 5, leachate pH was measured from a subsample in 50 mL centrifuge tubes and from May 7th to termination, measured directly from the 250 mL collection flasks. The first pH measurements on April 11 ranged from 7.79 (BA 22.75 and SS 22.75 rates) to 8.06 for the BA 44.5 rate (Figure 20). By April 29, pH levels for all treatments had dropped to their lowest recorded values (7.67 for the SS 44.5 rate to 7.77 for the SS 22.75 rate) before rising again in early May where values generally remained static. At the termination of the study in August, values ranged from 8.18 (BA 44.5) to 8.36 (FA 44.5). All treatments and the control exhibited the same trend in declining and increasing pH values.

The influence of salts flushing out of the columns could have lowered the initial leachate pH collected in April and early May (also refer to Greenhouse Study discussions on pH). Leachate pH was lowest for the SS 44.5 treatment between April 15 and May 3 (on 10 sample dates) which corresponded to peak salt flushing from the column profile at the start of the experiment. The scrubber slurry treatments were highest for S, K, Ca, Mg, B, and Li (discussed further below), all except B were negatively correlated with pH (data not shown). That is, as the concentration of these salts increased in the leachate water, the more pH declined.

The trend of increasing pH with fly ash amending to NAPI soil seen in the *Greenhouse Studies* was similarly observed: out of a total of 45 collection periods between April and August, the FA 44.5 treatment leachate had the highest pH on 31 sampling dates.

Nitrate and Macro Elements

Nitrate. As expected, leachate NO_3-N content was low in CCP treatments and below control levels. Concentrations in the April 13 leachate ranged from 41.97 mg/L (SS 44.5) to 114.87 mg/L (control; Figure 21). It would be expected that NO_3-N levels would be similar to the control in the initial leachate because, unlike in the *Greenhouse studies*, no supplemental N was incorporated with the CCP treatments. The trend observed was a sharp decrease from the control in the order of fly ash > bottom ash > scrubber slurry. The reasons for this remain unanswered. The act of irrigating crops can potentially leach harmful elements to groundwater. Table 11 presents the EPA National Primary Drinking Water Standards from two literature sources versus the maximum concentration of elements detected in leachate samples over the 19 week study. Nitrate levels were above EPA drinking water guidelines in the first leachate but rapidly fell below detectable limits after two irrigations.

Leachate P, K, S, Ca, Mg, and Na were measured on 13 dates beginning April 11 through August 9, 2005 and are presented in Figure 22A-F.

Phosphorous. Phosphorous collected April 11 ranged from 0.324 mg/L (control) to 0.534 mg/L (SS 22.75; Figure 22 A). Concentrations fell at the April 17 measurement but gradually rose on the May 1^{rst} and 9th collection periods before decreasing again. Phosphorous leaching has been observed to occur at similar times as Fe reduction (Jensen et al., 1998) and requires further investigation.

Leachate pH Over Time

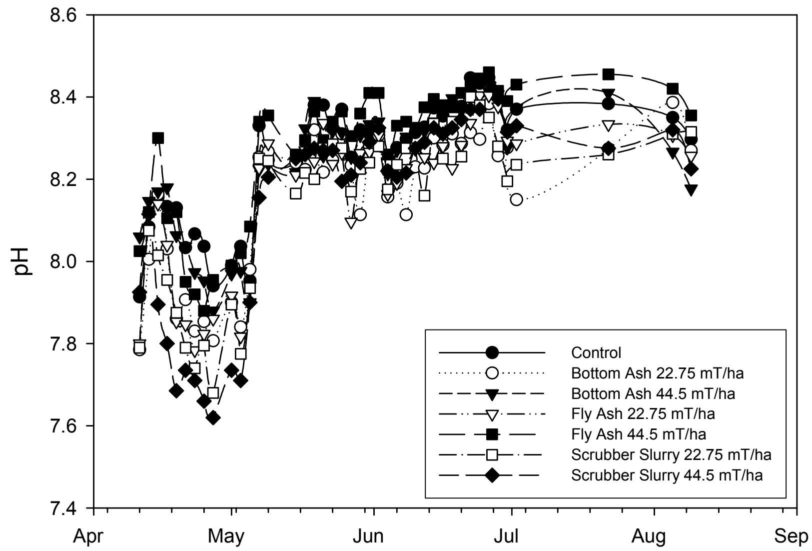


Figure 20. The pH of leachate water measured over time collected from columns packed with a Doak sandy loam collected from Farmington, NM and amended with CCPs (bottom ash, fly ash and scrubber slurry) at two rates (22.75 and 44.5 mT/ha).

Leachate Nitrate Over Time

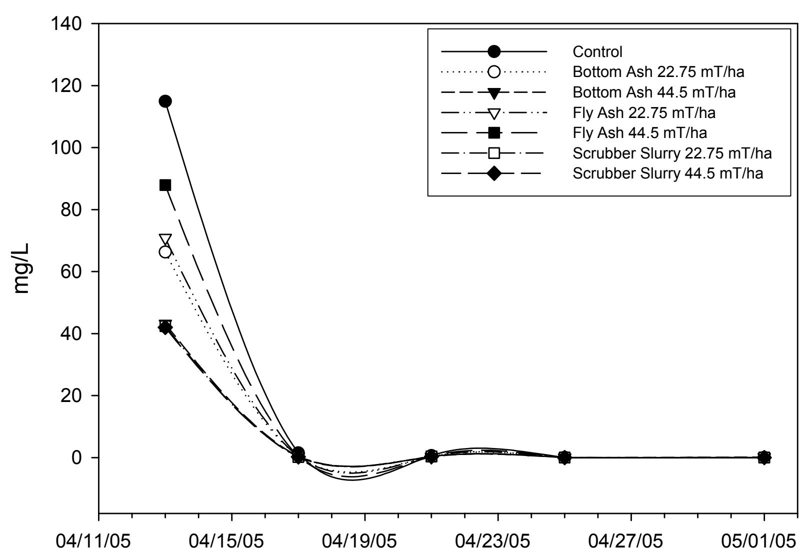


Figure 21. Nitrate measured over a three week period in leachate water collected from columns packed with a Doak sandy loam soil from Farmington and amended CCPs (bottom ash, fly ash and scrubber slurry) at two rates (22.75 and 44.5 mT/ha). Unamended soil served as controls.

Potassium. Potassium measured April 11 ranged from 56.5 mg/L (BA 44.5) to 67.1 mg/L (SS 22.75) (Figure 22 B). Concentrations of K fell by the next measurement period with the exception of the two scrubber slurry treatments which were slightly higher in K content compared to the other CCPs until mid-May.

Sulfur. Leachate S levels in the initial collection April 11 were highest in the scrubber slurry treatments (456 and 470 mg/L for the SS 22.75 and SS 44.5 rates, respectively) compared to the control (123.33 mg/L) (Figure 22 C). While the bottom ash, fly ash and control columns declined in S levels, both scrubber slurry rates peaked April 17 (550 and 571.5 mg/L for the SS 22.75 and SS 44.5 rates, respectively) before falling to 17.8 mg/L (SS 22.75 rate) and 182 mg/L (SS 44.5 rate) at the May 1 measurement. By May 29, 14 irrigations later, levels were the same as the other treatments. Refer to the *2004 Greenhouse Study* for previous discussion on S.

Calcium, Magnesium, and Sodium. Leachate Ca, Mg and Na followed the same general trends as K: the two scrubber slurry treatments were higher in these elements compared to the other CCPs for reasons described previously for salinity (Figure 22 D, E, and F). The April 11 collection period was highest for all three elements with the highest concentrations being 1,735 (Ca), 245.5 (Mg), and 126.5 mg/L (Na) at the SS 22.75 rate. During this same measurement date, the control contents were 1253.33 (Ca), 178.33 (Mg), and 103.7 mg/L for Na.

Trace Elements and Micronutrients

Water soluble Al, Be, Bi, Cd, Cr, Pb, Mo, Se, Tl, V, and Zn were below minimum detection limits of the ICP-OES instrument and will not be discussed further. Leachate Fe, Mn, B, Ni, and Co collected over 19 weeks from soil columns are shown in Figure 23 A-E.

Iron. Total Fe was below the minimum detection of the instrument until May 1, peaking on May 9th. Concentrations ranged from 4.19 mg/L in the SS 44.5 treatment to 7.83 mg/L in the BA 44.5 treatment on May 9th (Figure 23 A). Concentrations fell May 19th, continuing downward for the duration of the study.

Manganese. Manganese followed a similar trend as Fe with levels in the leachate generally peaking also on May 9th and having a range of 2.46 mg/L (SS 22.75) to 4.06 mg/L (FA 22.75) (Figure 23 B). The detection of water soluble Mn and Fe on this date may have resulted from reduced soil conditions as the profile became saturated which promoted reduction of Fe^{3+} to Fe^{2+} and Mn^{3+} to Mn^{2+} increasing mobility from the soil into the leachate.

Boron. Leachate boron levels were highest in both scrubber slurry rates followed by fly ash. The control was generally the lowest for B content (Figure 23 C). Maximum leaching occurred again on the May 9th collection, the highest content found in the scrubber slurry treatments (0.56 and 1.29 mg/L for the SS

22.75 and SS 44.5 rates, respectively). The CCP samples used in these studies were unweathered and contributed the higher amounts of B in the leachate than what may have been seen if weathered materials were used (see previous discussions above).

Nickel. Nickel levels were highest in the two scrubber slurry treatments collected April 11 (0.018 and 0.021 mg/L for the SS 22.75 and SS 44.5 rate, respectively; Figure 23 D). Although required for plant nutrition, Ni is a suspected carcinogen in high concentrations. There is currently no legal limit of Ni in drinking water but the maximum concentration limit has previously been set at 1.0 mg/kg (USEPA, 2006a).

Cobalt. Cobalt is required by ruminant animals, a constituent of vitamin B_{12} and is also required by nitrogen fixing *Rhizobium* bacteria (Smith, 1990). Water soluble Co peaked on May 9th, the highest content measured in the BA 44.5 treatment (0.013 mg/L), the lowest concentrations were found in the scrubber slurry applications (0.009 and 0.007 mg/L for the SS 22.75 and SS 44.5 rates, respectively; Figure 23 E). The oxide, hydroxide and carbonate of Co are insoluble at high pH (Smith, 1990) and expected not to move in Farmington soils but peaking may be indicative of the gradual formation of a more reduced environment. Redistribution of Co is known to occur rapidly in arid soils under saturating conditions (Han et al., 2002).

Miscellaneous Elements

Arsenic. Water soluble As levels were highest between April 11 and May 1 (Figure 24 A). The highest As content on April 11 was in the SS 22.75 treatment (0.146 mg/L), on April 17 in the SS 44.5 treatment (0.108 mg/L), and on May 1 in the BA 44.5 treatment leachate (0.109 mg/L) followed by the SS 44.5 treatment (0.106 mg/L). By the May 9th collection, As in the leachate from CCP treatments ranged from 0.05 (SS 22.75 mT/ha rate) to 0.06 mg/L (SS 44.5 rate), remaining below these levels for the duration of the study.

Inorganic forms of As have been linked with cancer and pose an environmental concern being elevated in some CCPs (Carlson and Adriano, 1993). Depending on interpretation of the National Primary Drinking Water Standards, As was below pollutant standards (Murarka et al., 1993) but above levels located at the USEPA website (USEPA, 2003), even for the NAPI soil Table 11. The Toxicity Characterization Leaching Procedure (TCLP) data in Table 2 also showed that As was <0.1 mg/L. The maximum concentrations observed were generally in the initial leachate and fell below levels considered toxic as reviewed by Murarka et al. (1993) in subsequent collections. With a high percentage of igneous geology and naturally occurring levels of arsenic, 41% of New Mexico's water systems will have source water in exceedance of the new EPA arsenic MCL (State of New Mexico, 2004). Erring on the side of caution, As should be investigated further including a comprehensive analysis of the species (the more mobile As III versus the less mobile As V), hydrological considerations, and regulatory limits and/or guidelines.

Barium. Barium levels were at their highest April 11 on the first leachate collected. Concentrations ranged from 2.05 to 2.91 mg/L (SS 44.5 and BA 22.75, respectively (Figure 24 B). Levels increased slightly May 1 to May 19, before falling below minimum detection limits on June 10. The main threat of Ba is contamination of drinking water with short term health effects being gastrointestinal disturbances and muscular weakness, while long term exposure above the MCL has the potential to cause high blood pressure (USEPA, 2006b). From Table 11, Ba concentrations in the initial leachate were above recent EPA Drinking Water Guidelines, even for the control. The TCLP data in Table 2 also showed that Ba was 2.5 mg/kg for the bottom ash was above EPA regulations. Though, in subsequent leachate collections, Ba levels dropped below detection limits and likely would not be problematic. Barium movement in soil is discussed further below.

Lithium and Strontium. Lithium and Sr followed similar patterns (Figure 24 C and D). Lithium levels were highest in both scrubber slurry treatments, peaking on the first leachate collection April 11 (0.155 mg/L for both rates, respectively). Both scrubber slurry rates were higher than the other CCPs on April 17 and May 1. Strontium is an alkaline earth element that substitutes for Ca and any CCP with high Ca enrichments are likely to have increased Sr contents (Hurst et al., 1993). Strontium levels collected April 11 were highest in the BA 22.75 treatment (10.04 mg/L). By the next collection, April 17, the scrubber slurry treatments were highest (4.06 and 4.82 mg/L for the SS 22.75 and SS 44.5 rates, respectively) before dropping to levels similar to the control and other CCPs. The pattern of Sr leaching in scrubber slurry was coincidental to Ca and Mg and reported to occur with an initial pH decline (Anderson et al., 1993) as observed in this study.

Soil Metals

After 19 weeks, the 30 cm columns were dissected in 2.5 cm sections for a total of 12 samples per column. The following metals were analyzed: Cr, Pb, Se, As, Ag, Ba, and Cd of which Se, As, and Ag were not detected. Table 12 presents pooled data of all depths per column to give an overall heavy metal status for each treatment irrespective of soil depth. The data are least squared means estimates (or adjusted means) given in SAS using the Mixed procedure. The addition of CCPs to soil did not change Cr content from the control (P=0.3431; Table 12). Chromium was highest for fly ash amended soil at the FA 22.75 rate (8.50 mg/kg), lowest in the SS 22.75 treatment (8.09 mg/kg). Lead and Cd were also not different from the control (P=0.6857 and P=0.6912 for Pb and Cd, respectively).

Barium was the only metal that differed from the control among the CCP treated soils and, as seen in the *Greenhouse Studies*, was highest in the fly ash amendments (110.01 and 106.19 mg/kg for the FA 22.75 and FA 44.5 rates, respectively; P<0.0001), and lowest in the two scrubber slurry treatments (Table 12). Barium generally did not migrate and was highest in the upper portions of the soil profile (*P*=0.0023; Table 13). This is graphically illustrated further in Figure 25 for the FA 44.5 treatment.

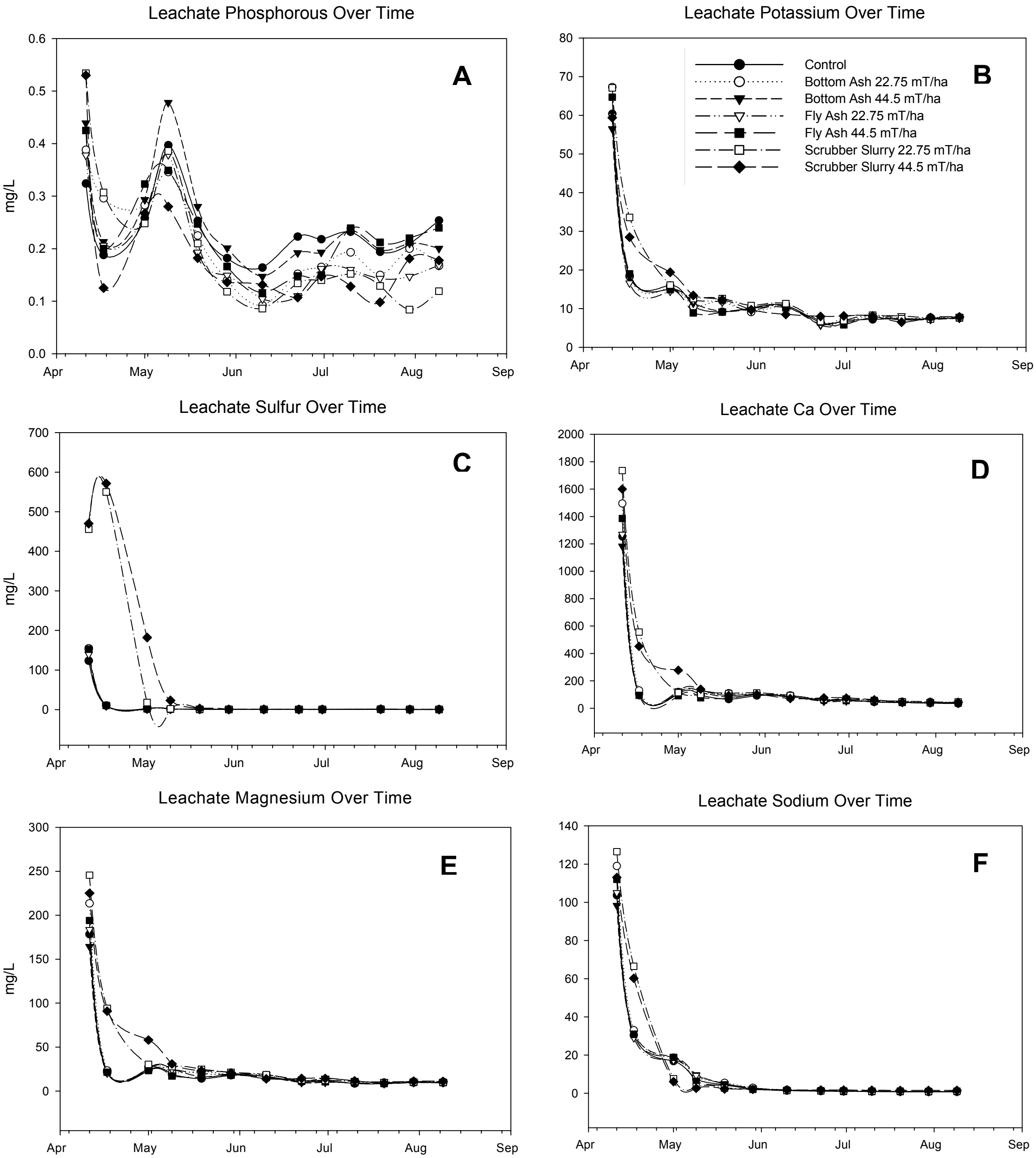


Figure 22. Phosphorous (A), potassium (B), sulfur (C), calcium (D), magnesium (E), and sodium (F) found in leachate water collected from columns packed with a Doak sandy loam amended with CCPs (bottom ash, fly ash and scrubber slurry) at two rates (22.75 and 44.5 mT/ha). Unamended soil served as controls. Leachate was collected 13 times over the 19 week study and analyzed directly by ICP-OES.

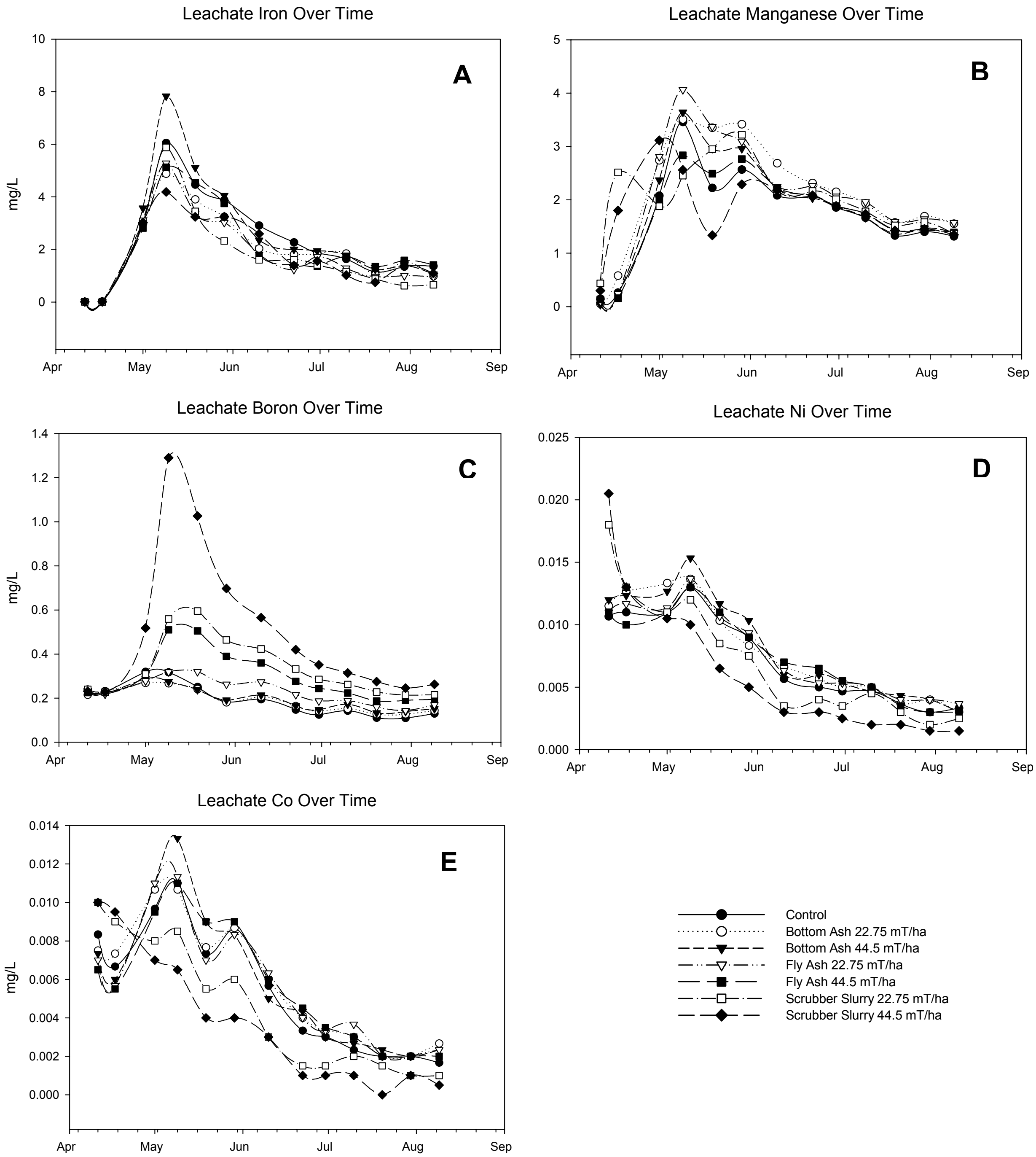


Figure 23. Iron (A), manganese (B), boron (C), nickel (D), and cobalt (E) found in leachate water collected from columns packed with a Doak sandy loam from Farmington amended with CCPs (bottom ash, fly ash and scrubber slurry) at two rates (22.75 and 44.5 mT/ha). Unamended soil served as controls. Leachate was collected 13 times over the 19 week study and analyzed directly by ICP-OES.

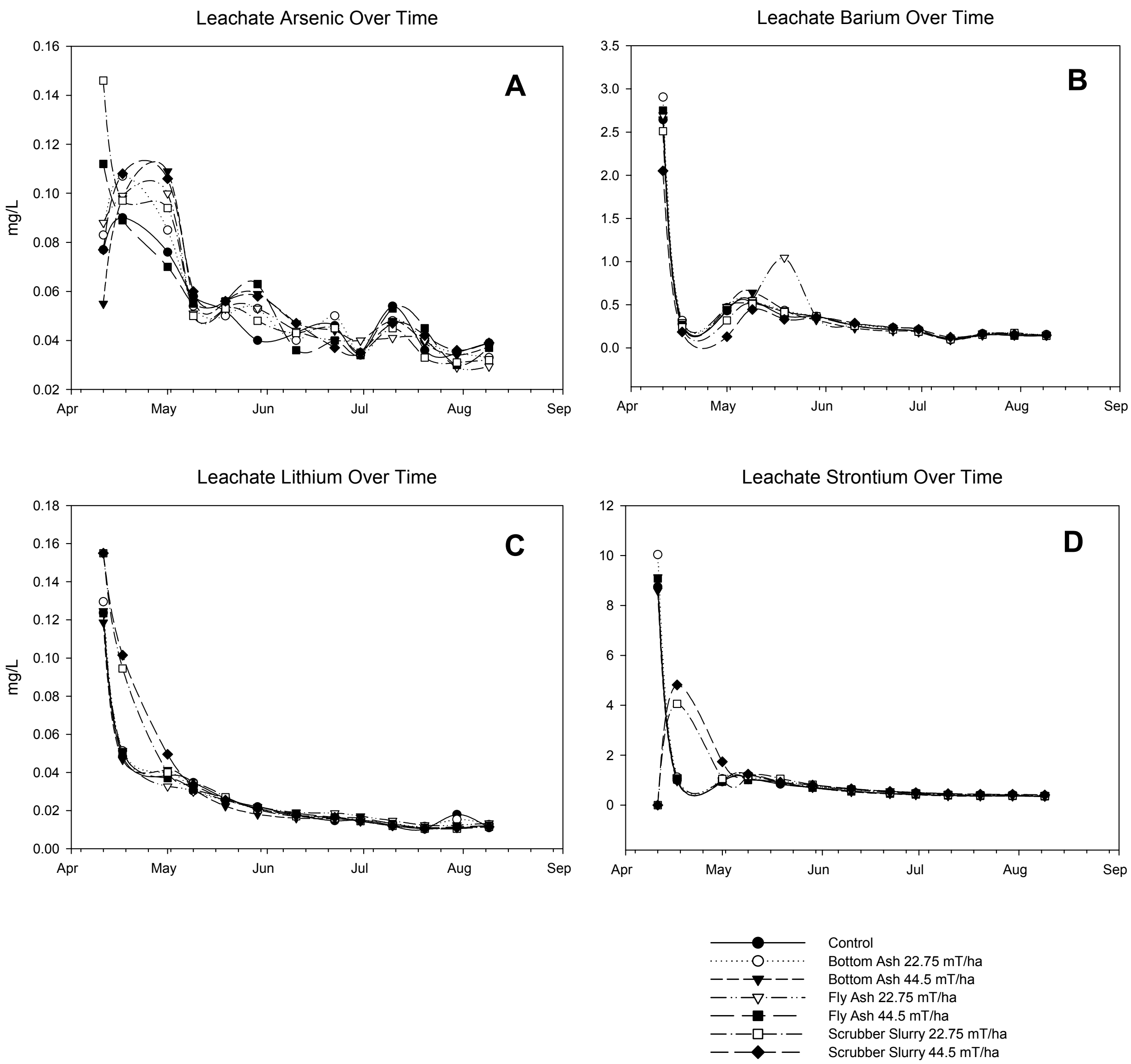


Figure 24. Arsenic (A), barium (B), lithium (C), and strontium (D) found in leachate water collected from columns packed with a Doak sandy loam from Farmington amended with CCPs (bottom ash, fly ash and scrubber slurry) at two rates (22.75 and 44.5 mT/ha). Unamended soil served as controls. Leachate was collected 13 times over the 19 week study and analyzed directly by ICP-OES.

Table 11. *Maximum* concentration detected in leachate (generally the first leachate) with references of 1980 and 2003 primary drinking water standards (elements considered by the EPA as being toxic in drinking water with the limit of acceptability; Murarka et al., 1993; USEPA, 2003). Note: after the second irrigation, all elements generally fell below detection limits of the instrument (see Figures 22-24). Also please note unamended soil in comparison to CCP amended soil.

	National Primary Drinking Water Standards		Maximum Concentration Detected in Leachate						
			Unamended	Bottom Ash		Fly Ash		Scrubber Slurry	
	1980[a]	2003[b]	Soil	22.75	44.5	22.75	44.5	22.75	44.5
Element	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
As	5.0	0.010 [c]	0.090	0.107	0.109	0.100	0.112	0.146	0.108
Ba	100.0	2.0	2.643	2.905	2.647	2.697	2.750	2.510	2.050
Cd	1.0	0.005	ND	ND	ND	ND	ND	ND	ND
Cr (total)	5.0	0.1	ND	ND	ND	ND	ND	ND	ND
Cu	-	1.3	0.040	0.044	0.042	0.044	0.050	0.083	0.052
Pb	5.0	0.015	ND	ND	ND	ND	ND	ND	ND
NO_3-N	-	10	114.9 [d]	66.3	43.2	70.8	87.9	42.4	42.0
Se	1.0	0.05	ND	ND	ND	ND	ND	ND	ND
Tl	-	0.002	ND	ND	ND	ND	ND	ND	ND

[a] EPA regulations x 100 referenced by (Murarka et al., 1993). [b] EPA regulations as of 2003 (USEPA, 2003) [c] Arsenic levels as of1/23/06. [d] NO_3-N fell below minimum detectable levels after one irrigation.

Table 12. Soil metals remaining in packed soil columns amended with CCPs after 19 weeks of leaching. Values are least square mean estimates of pooled 0-30 cm depth samples.

Treatment	Chromium mg/kg		Lead mg/kg		Barium mg/kg		Cadmium mg/kg	
Control	8.27	a	6.61	a	99.70	bc	0.164	a
Bottom Ash 22.75 mT/ha	8.23	a	6.56	a	99.69	bc	0.221	a
Bottom Ash 44.5 mT/ha	8.34	a	7.03	a	104.57	abc	0.194	a
Fly Ash 22.75 mT/ha	8.50	a	6.85	a	110.01	a	0.186	a
Fly Ash 44.5 mT/ha	8.27	a	6.87	a	106.19	ab	0.170	a
Scrubber Slurry 22.75 mT/ha	8.09	a	6.81	a	98.83	bc	0.176	a
Scrubber Slurry 44.5 mT/ha	8.11	a	6.46	a	98.30	c	0.199	a
LSD	0.47		0.78		7.74		0.079	
F Value	1.13		0.71		4.62		0.7	
Pr > F	0.3431		0.6857		<.0001		0.6912	

Table 13. Barium concentration (mg/kg) by depth of 30 cm columns amended with coal combustion products.

	Treatment						
Column Depth (cm)	Control (mg/kg)	Bottom Ash 22.75 mT/ha (mg/kg)	Bottom Ash 45.5 mT/ha (mg/kg)	Fly Ash 22.75 mT/ha (mg/kg)	Fly Ash 45.5 mT/ha (mg/kg)	Scrubber Slurry 22.75 mT/ha (mg/kg)	Scrubber Slurry 45.5 mT/ha (mg/kg)
0-2.5	91.98 a	112.67 a	109.16 a	129.52 a	130.00 a	102.29 a	116.10 a
2.5-5.0	92.08 a	115.00 a	117.43 a	131.19 a	126.21 a	102.06 a	115.50 a
5.0-7.5	90.64 a	108.87 a	97.66 b	114.36bc	94.51 b	97.25 a	111.50 a
7.5-10.0	90.36 a	103.90 a	96.73 b	110.49 cde	88.63 b	93.88 a	112.05 a
10.0-12.5	96.11 a	109.20 a	92.38 b	104.06 f	88.96 b	93.19 a	107.65 a
12.5-15.0	92.00 a	108.00 a	97.21 b	111.26 cde	86.48 b	96.80 a	110.00 a
15.0-17.5	94.59 a	109.00 a	95.33 b	110.76 cde	87.46 b	96.55 a	110.35 a
17.5-20.0	95.18 a	103.97 a	94.09 b	105.72 ef	84.82 b	103.40 a	116.00 a
20.0-22.5	92.49 a	105.47 a	92.83 b	111.99 cd	87.72 b	100.11 a	109.00 a
22.5-25.0	94.11 a	113.87 a	95.98 b	118.52 b	87.82 b	101.32 a	112.50 a
25.0-27.5	92.11 a	103.90 a	93.00 b	106.59 def	85.48 b	104.25 a	109.00 a
27.5-30.0	93.24 a	102.37 a	95.07 b	107.86 def	83.88 b	102.35 a	107.20 a
n	3	3	3	3	2	2	2
LSD	8.23	21.06	10.82	5.57	20.20	14.42	40.42
F Value	0.40	0.34	4.14	2.64	5.98	0.66	0.06
Pr>F	0.9395	0.9651	0.002	0.0239	0.0023	0.7469	1.0000

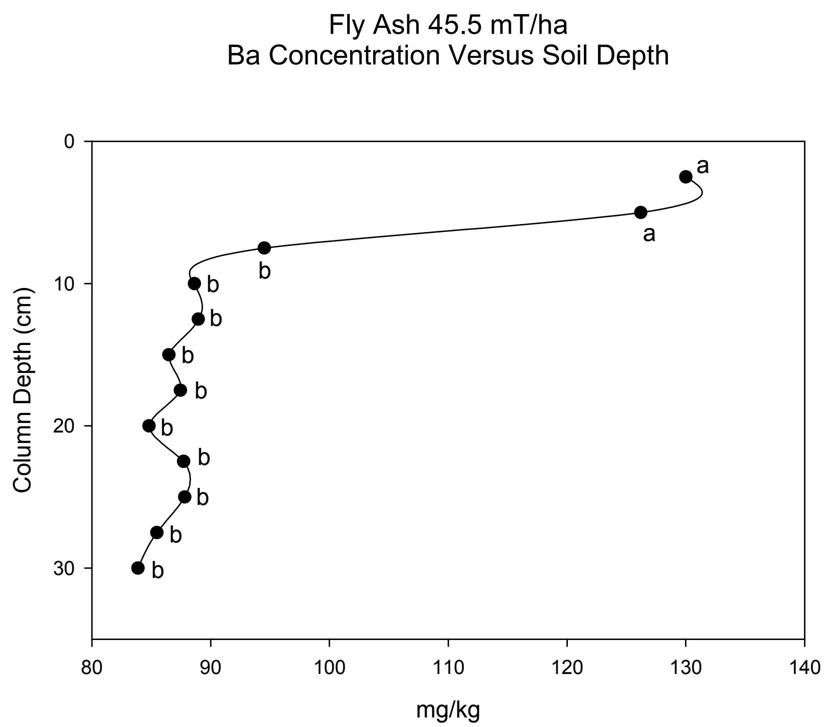


Figure 25. Ba in soil remaining by depth after leaching for 19 weeks. Means with the same letter are not significantly different (alpha=0.05; LSD = 20.20; F Value = 5.98; *P*=0.0023).

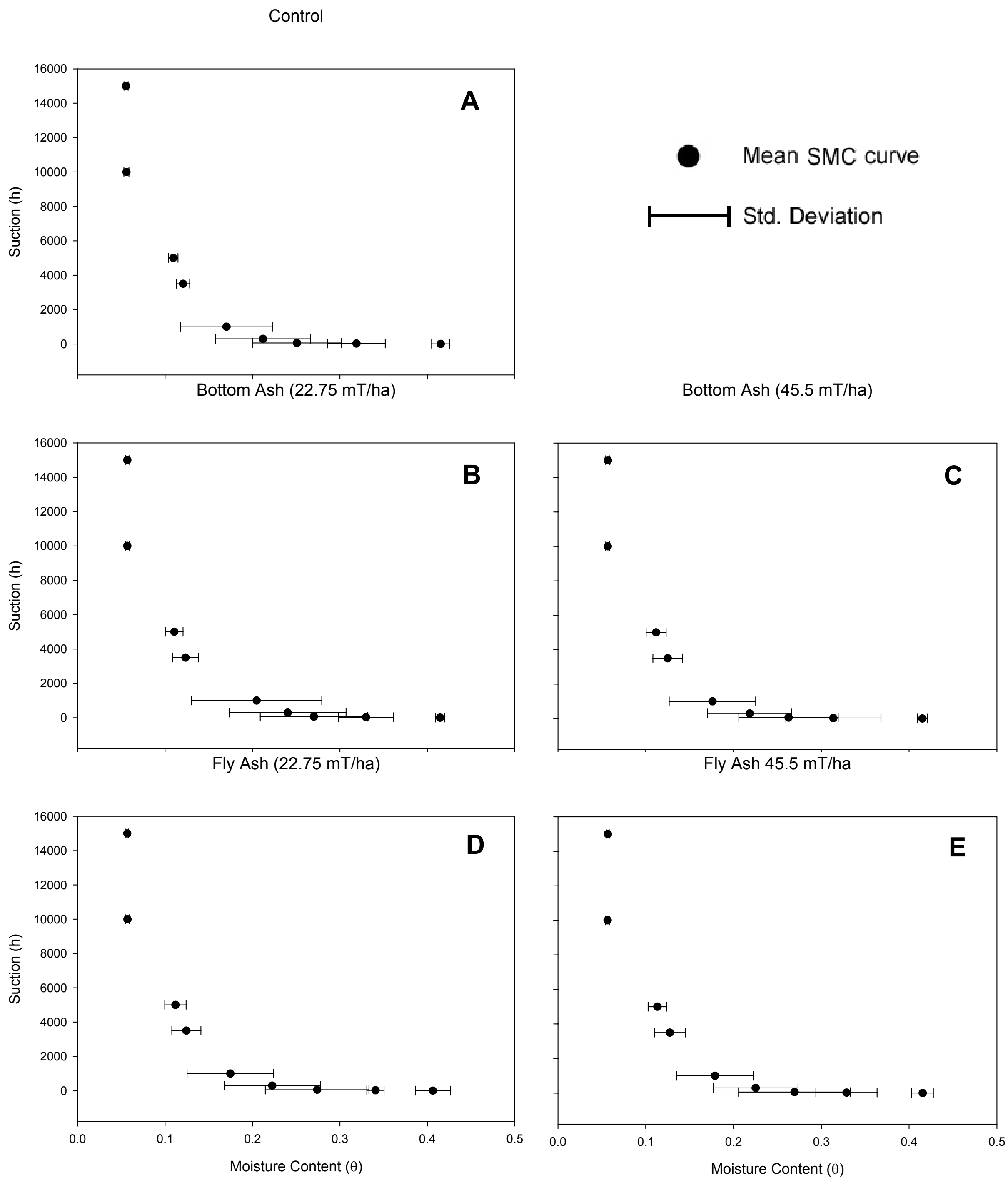
Study 3: Determination of Moisture Retention of Coal Combustion Byproduct Amended Soil

Moisture Release Curves

No differences were observed in the soil moisture retention curves except at the 15,000 cm suction (Figure 26 A to G). At 30 cm of suction, the FA 22.75 (0.34 cm^3/cm^3) retained more water than the control (0.32 cm^3/cm^3; *P*=0.9601). The SS 44.5 and FA 22.75 treatments retained the most water at 60 cm of suction (0.30 cm^3/cm^3) compared to the control (0.27 cm^3/cm^3; *P*=0.998). At 300 cm suction, SS 44.5 and BA 22.75 had 0.26 cm^3/cm^3 water retained compared to the control (0.23 cm^3/cm^3; *P*=0.9968). At 1,000 cm of suction, the BA 22.75 treatment retained the most water (0.22 cm^3/cm^3) compared to the control (0.18 cm^3/cm^3; *P*=9815). At 3,500 cm of suction, the FA 44.5 and SS 44.5 treatments both retained more water (0.13 cm^3/cm^3) than the control (0.12 cm^3/cm^3; *P*=0.8545) and at 5,000 cm suction, the CCP treatments were the same as the control at 0.11 cm^3/cm^3; *P*=0.6393). The 15,000 cm suction was the only theta to show any significant difference with the control; all, CCP treatments had the same moisture content (0.057 cm^3/cm^3) but retained more moisture compared to the control (0.055 cm^3/cm^3; *P*=0.0064).

Standard deviations of the mean were plotted to determine the extent of variability around the means of the data set (Figure 27). Standard deviations were widest between 30 and 1,000 cm of suction (peak deviations were at the 1,000 cm of suction) but narrowed and were virtually the same as desaturation of the cores increased. Bottom Ash at 22.75 mT/ha had the widest standard deviations from the mean, while the rest of the treatment standard deviations narrowed but followed the same pattern.

Although the hypothesis was that CCPs would improve water retention properties, lack of differences between the thetas except at 15,000 cm of suction and the similarities of SD and the trends illustrated in Figure 27 indicate that the samples were nearly identical, the result of uniform packing of cores with the treatment soil and amendments at the onset of the study. Though not an option during this study, intact soil cores taken from the field under CCP amending would likely delineate if there are differences in moisture retention properties among treatments and should be the subject of a future investigation.


Control
A
Mean SMC curve
Std. Deviation
Bottom Ash (22.75 mT/ha)
Bottom Ash (45.5 mT/ha)
B
C
Fly Ash (22.75 mT/ha)
Fly Ash 45.5 mT/ha
D
E
Suction (h)
Moisture Content (θ)
16000
14000
12000
10000
8000
6000
4000
2000
0
0.0
0.1
0.2
0.3
0.4
0.5

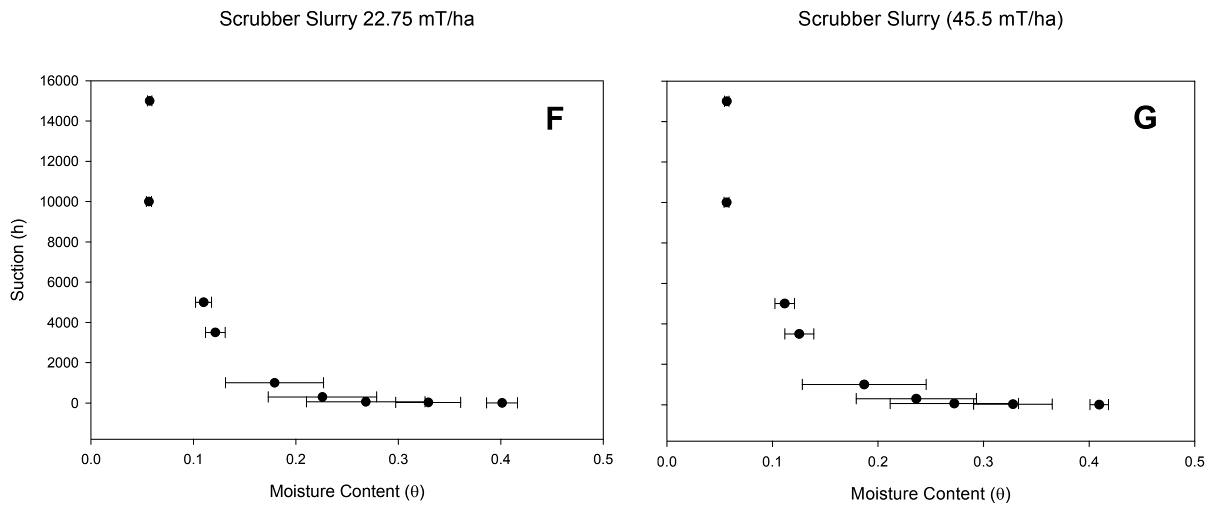


Figure 26. Soil moisture release curves of cores packed with a Doak sandy loam amended with CCPs at 2 rates (22.75 and 44.5 mT/ha). Control (A), BA 22.75 (B) and BA 44.5 (C), FA 22.75 (D) FA 44.5 (E), SS 22.75 (F) and SS 44.5 (G).

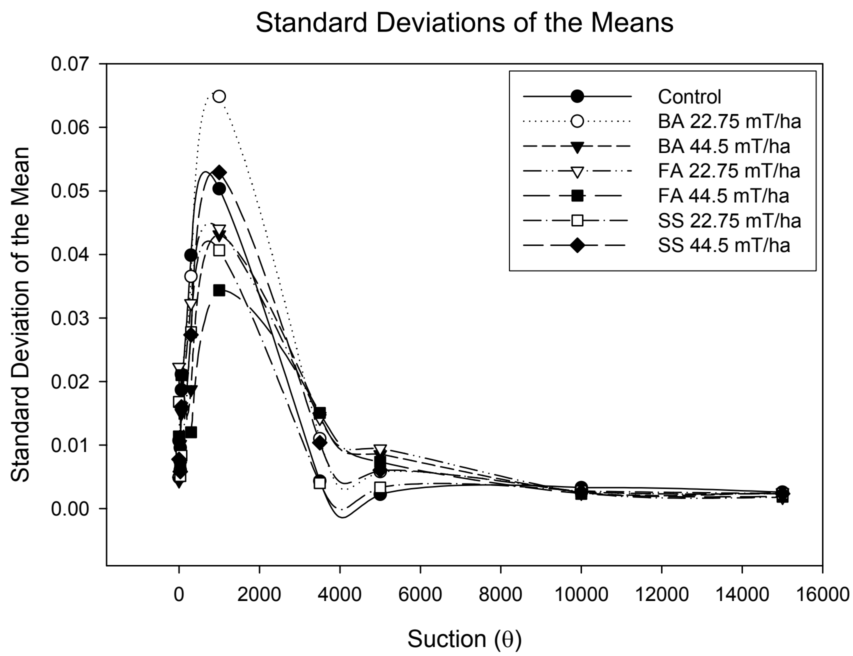


Figure 27. Standard deviation of the means for soil and amended soil θ's. Columns were packed to uniform bulk densities indicated by the similar distribution.

Drainable Porosity (f_a), Effective Porosity (f_e) and Available Water Content (AW)

No differences were observed between the CCP treatments and the control for weakly held water between saturation and field capacity (f_a) (P=0.1512; Table 14). Likewise, no differences were observed for f_e (P=0.5551) or AW (P=0.7905) content. Decreasing f_a and f_e, values indicate a decrease in faster draining macropores. The FA 22.75 and scrubber slurry treatments had the lowest *drainable porosity* values, while the two scrubber slurry treatments had two of the lowest *effective porosity* values. The trend with AW was less well defined.

Saturated Hydraulic Conductivity (Ks)

Although no differences were detected between treatments, mean saturated hydraulic conductivity values were lowest for fly ash and scrubber slurry amended soils at both the high and low rates (Figure 28). This agrees with results found by Chang, et. al (1977) who found that as % fly ash increased in California soils, *Ks* decreased. Conversely, the two bottom ash treatments had higher *Ks* than the control.

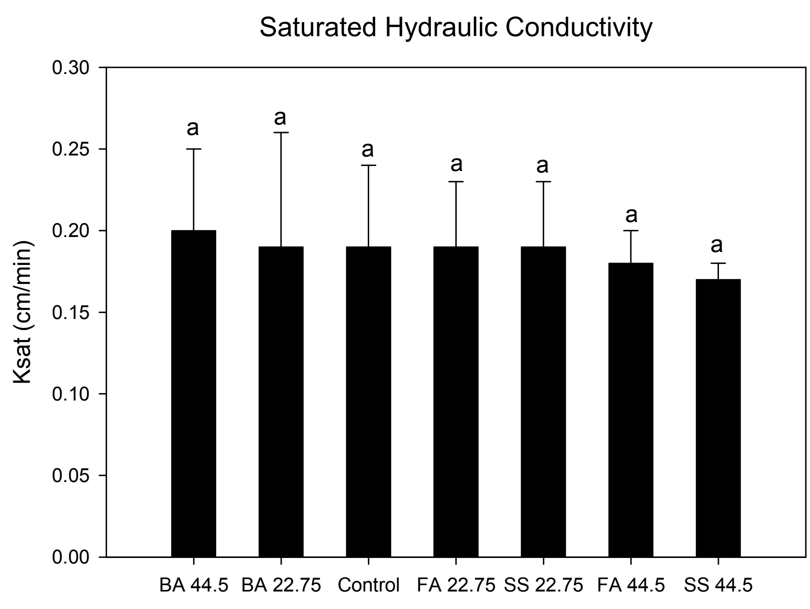


Figure 28. Saturated hydraulic conductivities of a Doak sandy loam amended with various CCPs at two rates (22.75 mT/ha and 44.5 mT/ha). Means with the same letter are not significant at the alpha = 0.05 level (LSD=0.07; F Value=0.27 P=0.97).

Table 14. Soil physical properties f_a, f_e and AW of a Doak sandy loam amended with CCPs at two rates (22.75 mT/ha and 44.5 mT/ha).

	Drainable Porosity (f_a) (θ sat-θ 60 cm)				Effective Porosity (f_e) (θ sat-θ 300 cm)				Available Water Content (θ 300 cm-θ 15000cm)			
Treatment	**Mean**		**SD**		**Mean**		**SD**		**Mean**		**SD**	
Control	0.144	±	0.011	a	0.184	±	0.03	a	0.172	±	0.041	a
Bottom Ash 22.75 mT/ha	0.120	±	0.019	a	0.150	±	0.04	a	0.206	±	0.038	a
Bottom Ash 44.5 mT/ha	0.132	±	0.016	a	0.180	±	0.02	a	0.182	±	0.019	a
Fly Ash 22.75 mT/ha	0.106	±	0.025	a	0.162	±	0.03	a	0.186	±	0.034	a
Fly Ash 44.5 mT/ha	0.124	±	0.018	a	0.172	±	0.01	a	0.188	±	0.011	a
Scrubber Slurry 22.75 mT/ha	0.110	±	0.014	a	0.156	±	0.02	a	0.188	±	0.029	a
Scrubber Slurry 44.5 mT/ha	0.116	±	0.018	a	0.154	±	0.03	a	0.200	±	0.025	a
LSD	0.029				0.037				0.0375			
F Value	1.63				0.86				0.58			
Pr > F	0.1512				0.5551				0.7905			

The reason for the lower *Ks* values in the scrubber slurry treatments appears to be influenced more by texture. Particle size was not determined in this study so the mechanisms cannot be fully explained, but the fly ash and scrubber slurry (when dry) are visibly finer than the bottom ash. *Ks* values generally increase as texture becomes coarser because of an increase in the size and number of water conducting macropores (Reynolds et al., 2002) which may explain the observed trends. Both fly ash and scrubber slurry have a fine textured particle size which are 0.01 to 100 μm for fly ash, and 5 to 50 μm for scrubber slurry, respectively (Carlson and Adriano, 1993) which could be decreasing macropore size, influencing water drainage. Fly ash may also exhibit pozzolonic activity resulting in cementing of soil particles (Korcak, 1995) which may also have influenced the results. Bottom ash is courser in texture with some particles larger than 2 mm (Carlson and Adriano, 1993) which would increase macropore formation.

The BA 22.75 rate also had a low f_e value but seems to be an anomaly since bottom ash is coarser in texture with particle sizes barely passing through 2 mm mesh screen and therefore more likely to increase macropore size more than fly ash or scrubber slurry.

Alpha and n (λ) values

The alpha value is an empirical parameter whose inverse equals the air entry value is the minimum pressure at which water starts to flow out of the soil and the n (λ) is the pore size distribution parameter which effects the slope of the retention curve (Brooks and Corey, 1964). Both values were not significantly different in this study (Table 15). The reason for this was that cores were packed in the lab and the soils are near identical (see above discussion).

Table 15. Alpha and λ values from the Brooks and Correy Equation (1964) of a Doak sandy loam amended with various CCPs amended at two rates (22.75 mT/ha and 44.5 mT/ha).

	Alpha				n			
Treatment	**Mean**		**SD**		**Mean**		**SD**	
Control	0.0372	±	0.0380	a	0.4092	±	0.0943	a
Bottom Ash 22.75 mT/ha	0.0206	±	0.0273	a	0.4194	±	0.0648	a
Bottom Ash 44.5 mT/ha	0.0352	±	0.0327	a	0.3791	±	0.0790	a
Fly Ash 22.75 mT/ha	0.0204	±	0.0204	a	0.4086	±	0.0608	a
Fly Ash 44.5 mT/ha	0.0122	±	0.0024	a	0.4349	±	0.0289	a
Scrubber Slurry 22.75 mT/ha	0.0163	±	0.0154	a	0.4320	±	0.0690	a
Scrubber Slurry 44.5 mT/ha	0.0203	±	0.0266	a	0.4311	±	0.0790	a
LSD	0.038				0.0877			
F Value	0.58				0.37			
Pr > F	0.784				0.9313			

Electrical Conductivity, pH, SAR, Ca, Mg, and Na

EC, pH, SAR, Ca, Mg, and Na were discussed in previous studies above but are reanalyzed here for comparison purposes with the same soil that was used to determine physical water retention and transmission properties.

The scrubber slurry treatments had the highest EC (3.35 mS/cm for the SS 22.75 treatment and 4.04 mS/cm for the SS 44.5 treatment) and lowest SAR values (3.42 mmol/L for the SS 22.75 rate and 3.23 mmol/L for SS 44.5 rate) (Table 16). Mean soil Ca was highest in both scrubber slurry rates (3632 mg/kg for the SS 22.75 rate and 3748 mg/kg for the SS 44.5 rate) as were Mg concentrations (201 and 208 mg/kg for SS 22.75 and SS 44.5 rates, respectively). Though fly ash amending slightly increased the soil Na content CCPs were not significantly different from the control (Table 16). Soil pH was higher in the fly ash treatments and lower in the scrubber slurry treatments.

Correlation of Chemical and Physical Properties

The soil physical parameters of α, n, f_a, f_e, AW, and *Ks* were examined for relationships with the chemical parameters pH, EC, SAR, Ca, Mg and Na. Of these, correlations occurred between AW with SAR, Ca, and Na values presented in Figure 29 A-C.

A negative relationship between SAR values and AW was found indicating that as SAR increases the plant available water decreases (Figure 29 A). Sodium values were also negatively correlated with AW content (Figure 29 B) while Ca was positively correlated with AW (Figure 29 C). Sodium adsorption values reflect a ratio of exchangeable Na^+ to Ca^{2+} and Mg^{2+}. The higher the SAR values, the more sodic the soil is. That is, Na^+ is dominating the cation exchange sites on clay particles. A consequence of sodic soils is the dispersion of clay particles which clog macropores. SAR values of the data set were within normal ranges but illustrate that the scrubber slurry treatments contributed appreciable amounts of Ca and Mg to the soil which likely resulted in the lower SAR values which could have resulted in a increase, albeit non-significant above the control, in AW content for scrubber slurry treated soil, presented earlier in Table 14. The additional Ca and Mg provided by the scrubber slurry may aid in water redistribution in the soil profile, increase infiltration and increase available water (So and Aylmore, 1993) requiring further study.

Table 16. EC, pH, SAR, Ca, Mg, and Na from a Doak sandy loam soil amended with CCPs at two rates (22.75 and 44.5 mT/ha).

Treatment	EC mS/cm Mean[z]		SD		pH 1:2 Mean		SD		SAR mmol/L Mean		SD	
Control	2.25	±	0.13	d	8.58	±	0.04	abc	4.03	±	0.21	a
Bottom Ash 22.75 mT/ha	2.31	±	0.21	d	8.56	±	0.12	abc	3.99	±	0.16	a
Bottom Ash 44.5 mT/ha	2.31	±	0.14	d	8.54	±	0.04	bc	3.91	±	0.18	a
Fly Ash 22.75 mT/ha	2.30	±	0.17	d	8.65	±	0.10	a	4.01	±	0.26	a
Fly Ash 44.5 mT/ha	2.21	±	0.25	d	8.64	±	0.06	ab	4.04	±	0.14	a
Scrubber Slurry 22.75 mT/ha	3.35	±	0.16	b	8.48	±	0.05	dc	3.42	±	0.38	b
Scrubber Slurry 44.5 mT/ha	4.04	±	0.32	a	8.38	±	0.11	d	3.23	±	0.29	b
LSD	0.2852				0.1039				0.3228			
F Value	43.81				6.84				6.8			
Pr > F	<.0001				<.0001				<.0001			

Treatment	Ca mg/kg Mean		SD		Mg mg/kg Mean		SD		Na mg/kg Mean		SD	
Control	3458	±	196	b	193	±	5	bc	126	±	5	c
Bottom Ash 22.75 mT/ha	3512	±	249	ab	191	±	6	cd	126	±	4	c
Bottom Ash 44.5 mT/ha	3524	±	224	ab	192	±	5	cd	126	±	3	c
Fly Ash 22.75 mT/ha	3554	±	207	ab	190	±	6	cd	129	±	6	bc
Fly Ash 44.5 mT/ha	3550	±	236	ab	185	±	5	d	127	±	6	c
Scrubber Slurry 22.75 mT/ha	3632	±	220	ab	201	±	7	a	126	±	3	c
Scrubber Slurry 44.5 mT/ha	3748	±	231	a	208	±	6	a	126	±	5	c
LSD	282				8				6			
F Value	0.76				7.6				5.89			
Pr > F	0.6367				<.0001				<.0001			

[z]Means with the same letter are not significant at the alpha = 0.05 level.

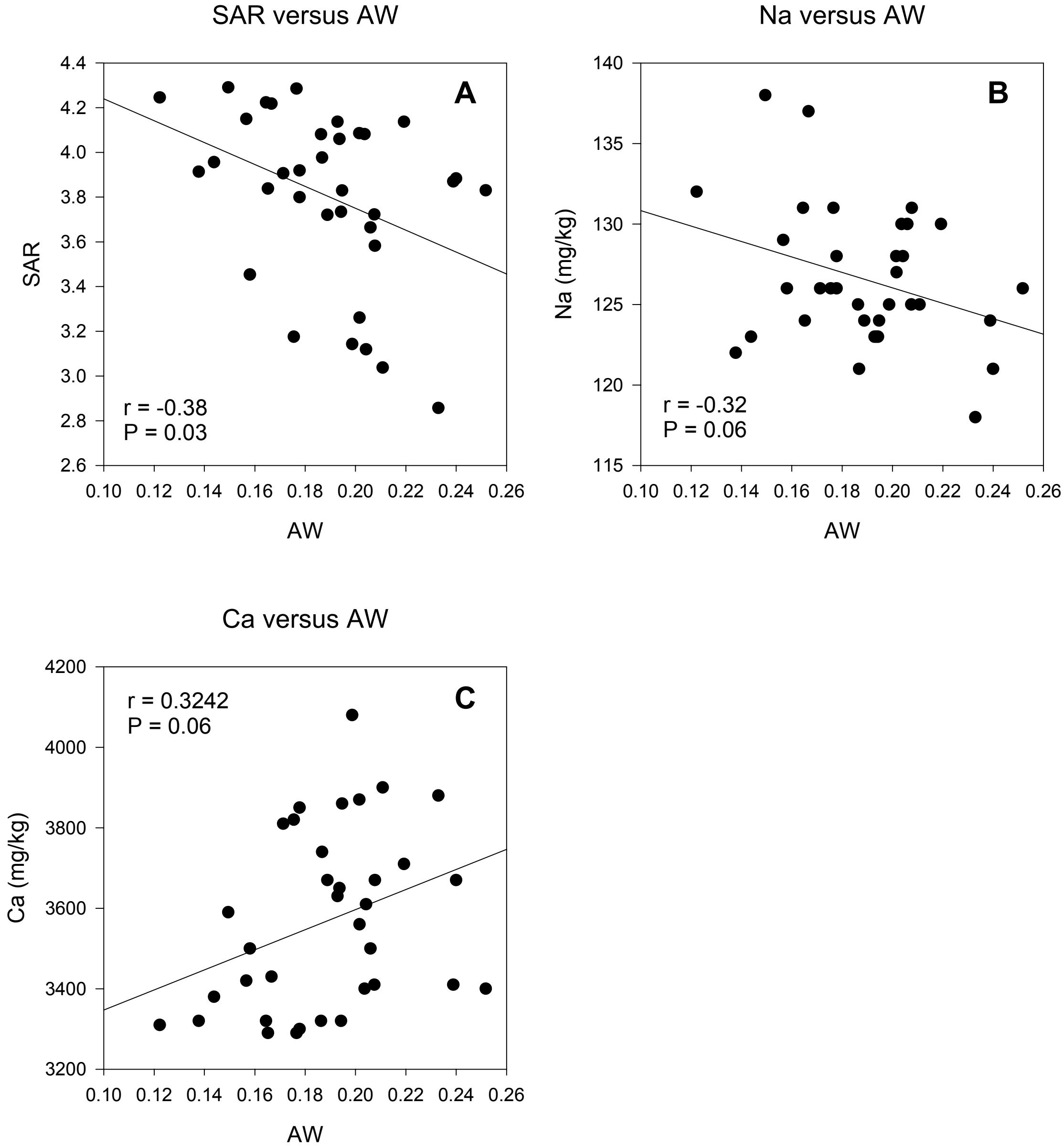


Figure 29. Relationship between chemical and physical soil properties. Sodium adsorption ratio versus available water (A), Na content versus AW (B), and Ca versus AW (C).

OVERALL CONCLUSIONS

Possible Benefits of Amending Soils with CCPs

Bottom ash, fly ash, and scrubber slurry were amended to a Doak sandy loam from NAPI. The hybrid poplar clone NM-6 and OP-367 were cultivated under the amended soil. Periodic N supplementation was given to poplars as CCPs are low in N. Also, a leachate column study was performed and water retention and transmission properties studied. Specific benefits observed are outlined below.

Benefits of Bottom Ash Amended Soil

The bottom ash had the least influence on EC and pH of the CCPs. In the *2004 Greenhouse Study*, bottom ash amended soil raise hybrid poplar Zn tissue and soil contents higher than the control. Leaf Cu content also improved under bottom ash cultivation. The two bottom ash treatments had higher saturated hydraulic conductivities than the control because of their coarser textural properties.

Benefits of fly ash amended soil.

In the *2004 Greenhouse Study*, soil pH increased above the control in fly ash treated soil (8.7 for both the low and high application rates). This was not translated to biomass as the highest fly ash rate had the greatest pooled biomass response between two hybrid poplar clones for most measured parameters. Leaf P was highest at the fly ash 22.75 mT/ha rate. The second highest leaf Fe content and highest soil Fe content were achieved at the fly ash 44.5 mT/ha rate.

In the *2005 Greenhouse Study*, addition of fly ash to soil improved leaf greenness of the clone OP-367. Salinity did not increase above the control in fly ash amended containers. Leaf and stem dry weights and leaf areas increased above the control for the two highest rates. Stem lengths and stem diameters were not higher than the control. Root dry weights were greatest with the low fly ash rate. Leaf P increased above the control; K levels decreased; Mg, Ca and Na all increased in fly ash amended soil. The addition of fly ash increased the plant tissue micronutrients Zn, Fe, Mn, and Cu over the control. Increasing the application rates of fly ash raised B content in plant tissues, though not above toxicity levels for the clone OP-367.

Fly ash lowered saturated hydraulic conductivities likely because of the finer particle size. Drainable porosity, or slowing of faster draining macropores, decreased with the application of fly ash.

Benefits of Scrubber Slurry Amended Soil

Soil pH decreased in scrubber slurry amended soil. Leachate pH was lowest for the SS 44.5 treatment between April 15 and May 3 (on 10 sample dates) which corresponded to peak salt flushing from the column profile. The scrubber slurry treatments were highest for S, K, Ca, Mg, B, and Li; all except B were negatively correlated with pH.

In the *2004 Greenhouse Study*, the scrubber slurry treatments produced the greatest amount of root biomass for the hybrid poplar clone OP-367 but had lower root growth in the clone NM-6. Leaf S increased in all CCP treated soil compared to the control and was highest for both the SS 22.75 and SS 44.5 amendment rates. Leaf Mg contents were highest in the scrubber slurry 44.5 mT/ha followed by the scrubber slurry 22.75 mT/ha treatment. Leaf Ca and Na were similarly high in the scrubber slurry amended soil. Soil Mg and Ca were also highest in the scrubber slurry 44.5 mT/ha rate followed by the 22.75 mT/ha rate. The addition of scrubber slurry at 44.5 mT/ha raised leaf Fe and Mn content above the control. The lowering pH by scrubber slurry treatments could have factored into increased leaf concentrations of these micronutrients. Boron was highest on scrubber slurry materials.

Similar to fly ash, saturated hydraulic conductivities were lower in the scrubber material also likely due to the fine particle size of the material. Effective porosity was lowered with both amendment rates of the scrubber slurry. Pozzolonic activity may have also factored into reduced water transmission for both the fly ash and scrubber material. A negative relationship between sodium adsorption (SAR) values and AW was found indicating that as SAR increases the plant available water decreases. SAR values were lowest in the scrubber slurry. The additional Ca and Mg provided by the scrubber slurry may aid in water redistribution in the soil profile, increase infiltration and increase available water-requiring further study.

Environmental Concerns

Salinity

Saturated paste extract measurements of the CCPs alone and mixed with soil demonstrated that baseline salinity was high except for the bottom ash. Both scrubber slurry application rates increased mean salinity over the control in the *2004 Greenhouse Study* (3.21 and 3.85 mS/cm for the 22.75 and 44.5 mT/ha rates, respectively), though these levels were below tolerance levels for most crops including hybrid poplar. EC remained unchanged from the control for soil amended with bottom ash and fly. Similarly, leachate collected from the columns was initially high in salts for all CCP treatments (including the control) but fell below 4 mS/cm after two irrigations.

Nonetheless, salt levels should be judiciously characterized to base loading rates before the application of scrubber slurry. Leaching fractions should be calculated to provide for ample movement of soluble salts beyond the rootzone. The use of weathered materials would likely be lower in soluble salts.

pH

Fly ash slightly raised soil pH. Biomass parameters generally were not effected and micronutrient status improved in fly ash amended soil presumably from loading in sufficient quantities and plant available forms for uptake. The scrubber slurry slightly lowered the pH and also improved micronutrient status of the soil. The same trends of salinity and pH were observed in the *Leachate Study*.

Boron

The highest leaf B contents occurred in the fly ash and scrubber slurry treatments. Both hybrid poplar clones accumulated their highest B in leaves under SS 44.5 cultivation. The clone NM-6 was more susceptible to B toxicity than OP-367 which necessitates clonal selection for higher tolerance if hybrid poplar are to be cultivated on CCP amended soil. B toxicity increased with increasing salinity. Two characteristics contributed to the experimental rise in B observed in these studies: 1) the CCPs were relatively unweathered, and 2) no leaching accompanied irrigations to examine salt and ion uptake effects. Boron toxicity would likely have not occurred if weathered material was used and leaching of B beyond the rootzone was achieved.

Metal Contamination

The following metals were analyzed in plant tissues and soils from acid digests: Cr, As, Ag, Se, Pb, Cd, and Ba. Of these, only Ba was detected in leaves and stems in both *2004* and *2005 studies*. In soil, Cr, Cd, Ba, and Pb were detected but only Ba increased in soil above the control. Ba was also detected in leachate water but fell below regulatory limits as the study progressed. Movement of Ba for fly ash amended soil was limited to the top 0-7.5 cm portion of the soil profile.

Water soluble As levels were highest between April 11 and May 1. The highest As content on April 11 was in the SS 22.75 treatment (0.146 mg/L), on April 17 in the SS 44.5 treatment (0.108 mg/L), and on May 1 in the BA 44.5 treatment leachate (0.109 mg/L) followed by the SS 44.5 treatment (0.106 mg/L). By the May 9th collection, As in the leachate ranged from 0.05 (SS 22.75 mT/ha rate) to 0.06 mg/L (SS 44.5 rate), remaining below these levels for the duration of the study. On January 23, new EPA drinking water guidelines went into effect for As, lowering the toxicity level from 0.05 to 0.01 mg/L. As such As levels, even for the control leachate, were above regulatory limits. New Mexico has a high level of naturally occurring As. In light of new regulations and erring on the side of caution, As should be investigated further including a comprehensive analysis of the species (the more mobile As III versus the less mobile As V), hydrological considerations in a field setting, and other chemical and physical parameters in relation to regulatory laws.

Water soluble Al, Be, Bi, Cd, Cr, Pb, Mo, Se, Tl, V, and Zn were below minimum detection limits of the ICP-OES.

RECCOMENDATIONS FOR FURTHER STUDY

Lab and greenhouse studies were used to gain knowledge on chemical and physical reactions that may pose environmental and political challenges to agricultural land application of CCPs on NAPI soils in the semi arid southwestern U.S. The use of hybrid poplar as a test *crop* was based on reducing political barriers to agricultural application by local farmers as a non-edible crop currently under large scale production at NAPI. However, greenhouse studies approximate, but do not substitute for field studies. Current data generated from this study suggests that 1) biomass of hybrid poplar were increased by CCP amended soil, 2) salinity and pH changes were observed but did not have any short-term adverse plant responses except in the case of B with the clone NM-6, and 3) heavy metal content was not an issue.

The next step would be to conduct field plot studies. Specific recommendations include:

1. Field plots under hybrid poplar cultivation using similar rates in the greenhouse studies to verify results.
2. Co-mixing of CCPs with composted biosolids to examine benefits of both industrial byproducts together.
3. Utilizing in-situ plant analysis combined with intact field soil sampling to examine elemental movement under field conditions.
4. Weathered material versus unweathered. Weathered material will be lower in salts and B.
5. Measurement of water retention and transmission properties on field plots after soil pore formation has stabilized – at least after one year. Use double ring infiltrometer or intact soil cores to generate moisture release curves.
6. pH determination with KCl or $CaCl_2$ to determine the scope of influence soluble salts from the scrubber slurry have on soil pH. Investigate the forms of S in the scrubber slurry and influence on pH.
7. Comprehensive chemical analysis of arsenic species.
8. Installation of lysymeters and catchment devises to monitor leaching through the soil profile and surface runoff movement of elements, especially As.
9. The ease of application will influence adaptability of CCP application to agricultural lands. The scrubber slurry demonstrated some interesting properties but was difficult to apply because of its tendency to separate into a liquid and solid phase within a storage container and its clay-like consistency once homogenized, making application difficult using conventional spreaders. One option could be the decanting or evaporation of the liquid phase and drying which would facilitate even application. However, when dry, as with the fly ash, scrubber slurry is very fine in texture and apt to be wind blown. It was for this reason that

the scrubber slurry was not investigated in the 2005 Greenhouse Study and perhaps pre-judged in quarterly reports. With the full story in place, the scrubber slurry warrants further investigation.

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