PLANT GROWTH EFFECTS OF COAL COMBUSTION PRODUCT AMENDMENT TO MINE SPOILS AND ASSOCIATED LEACHING POTENTIALS[1]

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Abstract: Research on the beneficial utilization of coal combustion products (CCPs) as surface amendments in mining environments has focused upon bulk acid-base balances and heavy metal (Cu, Zn, Fe, Al, Mn, etc.) mobility to local groundwater. Currently, the public and regulatory communities are placing greater focus on the potential of As, B and Se mobility from CCP utilization. Five CCPs were selected from a regional set of 28 materials following complete chemical characterization for greenhouse bioassay trials. Acidic sandstone mine spoil was amended at 0, 10, and 20% (v:v) with the CCPs. The bioassay trial was designed to test the presumed effectiveness of CCPs as surface-applied amendments to mine soils for improving pH and water holding capacity. The procedures were modified to include a "pour-through" protocol where we leached greenhouse pots with excess water starting one month after establishment of the trial, and then collected leachates for analyses of pH, EC, As, B, Se and other parameters. The trial was conducted using soybean (*Glycine max*) as an indicator plant sensitive to substrate chemical conditions (EC, pH, elemental toxicity) and tall fescue (*Festuca arundinaceae*) as a species exhibiting relative tolerance to low pH, metals, and salts. Tall fescue dry matter yield tended to increase with increasing CCP rate as long as the bulk soil pH remained at pH 8.0 or less. Depending on the liming capacity (as measured by calcium carbonate equivalence - CCE) of the CCP applied, the 20% application had the greatest positive effect on plant yield (e.g. at CCE = 7.7). However, in case of a CCP with a high liming potential (CCE = 47.7), a 5% application was most beneficial to dry matter yield. The EC and pH from various mixes related well to CCE of the respective CCP and the loading rate. Leaching of oxyanion forming elements (As, Mo, Se) under these soil conditions and loading rates does not appear to be a concern, although some Se was observed in the first leachates. As expected, B along with S (as SO_4^{2-}) were the two elements at highest concentration in the leachates. However, correlation and stepwise regression analysis of yield data with the elemental concentrations from the pour-through solutions indicated these two elements did not negatively affect fescue yield. However, stepwise regression analysis did show that fescue yield was affected by pH ($p > 0.0034$). Our combined results indicate that a few relatively simple lab measurements (pH, EC, CCE) coupled with a simple soybean bioassay such as reported here can readily predict both the relative effectiveness and potential toxicity of a given CCP when used as either a bulk mine soil amendment or an alkaline additive for mine soil acidity control.

Additional Key Words: Fly ash, flue gas desulfurization sludge, beneficial use, phytotoxicity.

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Introduction

Utilization of coal fly ash and flue gas desulfurization (FGD) materials as soil amendments is limited by their variability in chemical properties and interaction with soils. Development of utilization guidance for one-time or multiple applications of coal combustion products (CCPs) to different soils/substrates (agricultural soil, mine spoil, or coal refuse) would be beneficial for the utilization of vast quantities of fly ash created by coal-fired power plants. Previous work by our group on CCPs (Daniels et al., 1996 & 2002; Stewart et al., 1997) focused primarily on potential water quality benefits and risks of fly ash utilization in various mine environments, with a principal focus upon bulk acid-base balances and heavy metal (Cu, Zn, Fe, Al, Mn, etc.) mobility to local groundwater. However, the possibility of As, Mo, and Se mobility in ash/mine spoil leachates were not evaluated mainly because of a lack of "regulatory concern" at the time. Currently, the public and the environmental regulatory community are placing much greater focus on the potential for As, B, Mo and Se mobility from CCP utilization on/in active coal mines, along with a strong emphasis on defining Hg levels and mobility in coal combustion products in general. As an example, the USEPA recently reaffirmed its 1993 position exempting CCPs from regulation as Resource Conservation and Recovery Act (RCRA) subtitle C (toxic) wastes, but specifically reserved judgment on the use of CCPs in coal mining environments. In April of 2006, in response to citizen and regulatory concerns over water quality issues, the National Academy of Sciences released its detailed report (NRC, 2006) on potential mine site impacts of CCP utilization. While the report did offer overall support for beneficial utilization of CCPs in mining environments, it specifically cautioned potential permittees to: (1) Carefully characterize the geochemical properties of the CCP to be utilized; (2) understand and predict long-term reactions and contaminant release patterns; and (3) fully characterize potential site hydrologic impacts. Thus, the prediction of the relative mobility of As, B, Mo, Se, and other potentially water soluble trace ions is the current focus of our continuing cooperative research program.

As part of our earlier cooperative efforts with the Virginia Division of Mined Land Reclamation (VDMLR), and the Virginia Department of Environmental Quality (DEQ) in the 1990's (see Daniels et al., 2002), we developed a routine and inexpensive greenhouse bioassay approach to screening plant growth effects of various land applied residuals. The protocol uses soybeans and tall fescue grown in a mine spoil or native soil substrate which is amended with various rates of the CCP proposed for beneficial use. Therefore, the overall objectives of this study were:

1. To predict the relative bioavailability/leaching risk of As, Se, and B in common southwestern Virginia coal mining/CCP utilization environments.
2. To test a combined laboratory and greenhouse screening technique to predict the beneficial use potential of CCPs when used as topical mine soil amendments and bulk-blended treatments for acidic mine spoil.

Materials and Methods

We worked with industry cooperators and collected 28 representative composite samples of their current CCP streams from regional utilities burning Virginia coals. The 28 primary composite samples were subjected to a suite of chemical analyses and characterization. Based on these results, five CCPs were selected for the greenhouse bioassay study on the plant growth effects of land-application of the various CCPs to mined lands. Full results on chemical analyses of all 28 CCPs are available in Daniels et al. (2006). Acidic sandstone mine spoil was collected at an active Powell River/Red River surface coal mine in Wise County, Virginia (laboratory pH = 4.75, with a liming requirement of 4.5 Mg/ha). The mine spoil was air dried and sieved to pass a 2 mm sieve.

Coal Combustion Products and Mine Spoil Analyses

- All analyses were conducted in triplicate except for the Toxicity Characteristic Leachate Procedure (TCLP) which is conducted on a large (50 g) bulk sample as indicated by USEPA.
- pH and Electrical Conductance (EC, an indirect measurement of salt content; Rhoades, 1982) were determined on saturated paste extracts of CCPs. The CCP was mixed with distilled DI water until it formed a glistening paste. The paste was filtered after 1 hr equilibration and the filtrate analyzed for pH and EC.
- Hot $CaCl_2$ extractable B (Bingham, 1982) was determined by boiling 20ml 0.01M $CaCl_2$ with 10g ash for 10 minutes. The filtrate was analyzed by ICPES for total B.
- Total elemental analysis was determined by microwave digestion of 0.5 g CCP with 3 ml concentrated HCl and 9 ml concentrated HNO_3. The extract was brought up to 50 ml volume with distilled DI water and analyzed by ICPES (U.S. EPA, 1996).

- We used the TCLP test for priority elements (U.S. EPA, 1992).
- Mehlich-1 extraction (0.05*M* HCl + 0.025*M* H_2SO_4) was utilized for extractable P, Ca, B, and Fe (Mehlich, 1953) followed by ICPES (Type FTMOA85D, Spectro Analytical Instruments, Inc).

We completed analyses of the primary composite samples of 28 CCPs as outlined above. The overall results are discussed below along with our rationale for selection of five CCPs (4 fly ashes and 1 FGD) that we felt best represented the overall analyzed sample set. These five materials were then used in the greenhouse plant growth bioassay trial and pot leaching procedure.

Methods for Greenhouse Bioassay Trial

General design, methods, and techniques used for our greenhouse bioassay (mine soil amendment scenario) are fully documented and cited by Daniels et al. (2002 and 2006). The procedures were modified to include a "pour-through" protocol (Wright, 1986) where we eluted greenhouse pots with excess leaching waters approximately one month after establishment of the trial, and then collected the leachates for analyses including pH, EC, As, B, Cr, Mo, and Se. The trial was conducted using soybeans (*Glycine max*) as an indicator plant sensitive to substrate chemical conditions (EC, pH, elemental toxicity) and tall fescue (*Festuca arundinaceae*) as a test crop exhibiting relative tolerance to low pH, metals, and salts.

Experimental Design & Treatments:

- Trials were conducted separately for fescue and soybeans. The statistical design was a completely randomized block (CRB) with 4 replications per treatment combination.
- CCP rates: 5%, 10%, 20% (v:v basis, but measured on a weight basis to reduce variability) as well as 100% mine spoil control pots for each crop
- Volume of substrate / pot = 700 ml / pot (900 g pot^{-1})
- 3 ash rates X 5 CCP's X 2 crops X 4 replications
- Control pots: Control (-) no-lime mine spoil only (4 per crop)
  Limed control (+) pots (4.5 Mg ha^{-1} equivalent)
  Highly limed control (++) pots (9 Mg ha^{-1} equivalent)

- Approximately every month, pots were allowed to equilibrate at field capacity for 24 hours and then eluted with excess water to obtain 50 ml (± 5 ml) of leachate. This is a modification of the pour-through technique of Wright (1986).
- Soybean pots were seeded (4 seeds per pot) and subsequently thinned to the healthiest plant of each pot 1 month after seeding. Fescue was cut, dried, and weighed approximately every 3 weeks. Overall fertility was maintained with periodic fertigation using a 20-20-20 Peter's liquid fertilizer at 75 µg N ml^{-1}.

Results and Discussion

CCP Chemical Properties

We obtained a set of 28 CCPs with wide range of important chemical properties as detailed by Daniels et al. (2006). While the range in pH was 3.57 to 12.35, only 3 CCPs had a pH below 7. Soluble salt content of CCPs also varied greatly with a range of EC of 0.66 to 26.85 dS m^{-1}; however, the distribution was more uniform across the range than for pH. The liming capacity of the CCPs ranged from 0 to 52% CCE, and tended to be either low (<10%) or high (>30%), with only 6 CCPs in the 10 to 30% range. Of the 28 CCPs tested, 14 had CCE of <5%.

Using the data sets discussed above, we categorized the 28 materials into a somewhat modified 2 X 2 matrix of As levels (low and high) by CCE (levels low and high). Electrical conductance (EC) was a strong covariate. Low CCE ashes exist with high and low EC, and high CCE materials exist with high and low EC. Five CCPs were selected from the larger sample set for a greenhouse bioassay study. The selection criteria for the 5 CCPs chosen for the greenhouse bioassay trial are given in Table 1.

Results of the TCLP analysis (data not shown) on the five CCPs indicated that all elements of concerns were below EPA critical limits by a factor of 10 or greater. Mercury was below detection limits in the TCLP test extracts. However, a major limitation to most lab tests (like TCLP) designed to simulate element release (leaching) is that these tests do not provide information on actual release under a wide range of expected disposal or land application geochemical environments (NRC, 2006). In the case of highly alkaline fly ash or non-acidic coal refuse, for example, the TCLP procedure tests these materials in a moderately acidic (glacial acetic acid) environment. This extraction environment may be drastically different from the conditions governing leachability under actual co-disposal conditions, and we have previously reported (Stewart et al., 2001) significant metal leaching from fly ash materials that easily "passed" the TCLP test.

Table 1. CCPs selected for greenhouse bioassay trial.

Ash #	Type of Ash	Ash properties
11	Fly ash	High As, low CCE, low EC, high extr. B.
28	Fly ash	High As, low CCE, mod. high EC, low extr. B.
16	Fly ash	Low As, high CCE, low EC, low extr. B.
27	Fly ash	Low As, high CCE, high EC, low extr. B.
7	FGD	Rel. low As, high CCE, mod. EC, med. extr. B.

General chemical properties and total elemental concentrations of As, Se, Cr, and Mo obtained by total digestion of the five selected CCPs are presented in Table 2. The data show major differences in liming capacity (CCE) and salt contents of the CCPs and reveal some implications of these properties upon mixing with a slightly acidic mine spoil. While CCP #11 has substantially higher total As content than the other CCPs, the mixing of these ashes at the relatively low amendment rates will result in only very low levels of As additions, and even lower levels of bioavailable As. In a separate study (Daniels et al., 2006) on the chemical properties of the 28 CCPs we found that in general, < 30% of total As is in exchangeable and carbonate forms which are considered bioavailable (Tessier et al., 1979). The results of the soil test analysis by Mehlich-1 extraction of the various blends of mine spoil amended with the respective CCPs are presented in Table 3. Ashes # 16 and 27 had a very strong liming effect on the mine spoil. Even the 5% amendment rate raised the soil pH to >10. Depending on the plant species, this could have a very negative effect on plant growth. However, from a plant nutrition standpoint, the CCP amendments did not appear to affect substrates to the point where any element was clearly phytotoxic.

Table 2. Chemical properties of five CCPs selected for use in greenhouse bioassay experiments.

		Saturated Paste				---------- Total Elemental Analysis -----------				
CCP #	Bd g cm^{-3}	pH	EC dS m^{-1}	CCE %	Extr. B mg L^{-1}	Total B mg kg^{-1}	As mg kg^{-1}	Se mg kg^{-1}	Cr mg kg^{-1}	Mo mg kg^{-1}
7	0.80	9.1	5.3	49	23	225	19	3	36	8
11	1.50	8.9	3.3	0	185	574	179	15	130	50
16	1.15	12.6	14.9	53	16	789	14	11	73	37
27	1.20	11.9	4.5	57	17.4	841	23	4	86	9
28	1.12	11.5	3.1	16.3	3.6	82	57	11	70	11

Bd = Dry bulk density

Table 3. Selected Mehlich-1 extractable chemical properties of CCPs, mine spoil, and CCP amended mine spoil at the onset of the bioassay greenhouse trial.

Mine spoil +	2 : 1	-------------------------------- mg kg^{-1} ------------------------------------						
% of CCP	pH	Zn	Mn	B	Cu	Fe	P	Mg
Mine spoil	4.75	0.6	7.6	0.9	0.1	12.0	2	32
#7 – 100%	9.09	0.1	1.0	39	0.1	4	4	1101
#11 – 100%	9.15	5.5	12.6	183	5.1	373	109	277
#16 – 100%	11.71	0.1	0.6	21	0.1	11	2	227
#27 – 100%	11.68	0.1	0.1	27	0.1	0	2	372
#28 – 100%	8.47	4.1	7.4	33	2.9	7	2	203
#7 – 5%	6.72	0.9	126	9	0.1	94	9	307
#7 – 10%	7.07	0.9	97.4	12	0.1	69	4	422
#7 – 20%	7.73	0.8	46.1	19	0.1	21	2	619
#11 – 5%	5.34	0.8	64.6	12	0.1	76	19	85
#11 – 10%	4.90	0.7	23.4	16	0.1	82	24	50
#11 – 20%	4.94	1.7	14.6	40	0.4	177	54	82
#16 – 5%	9.93	1.4	8.4	18	1.9	11	2	424
#16 – 10%	10.72	1.5	6.8	22	1.4	5	2	472
#16 – 20%	11.39	0.1	2.4	26	0.1	1	2	378
#27 – 5%	10.08	2.4	6.6	22	1.8	5	2	429
#27 – 10%	10.42	2.8	6	24	1.9	4	2	455
#27 – 20%	10.84	2	5.8	33	0.1	1	2	431
#28 – 5%	5.08	0.8	9.1	2	0.2	36	7	41
#28 – 10%	5.59	1.4	12.6	4	0.2	96	19	68
#28 – 20%	6.24	2.2	17	10	1.6	176	32	136

Greenhouse Bioassay Experiment

Dry matter yields from the first cutting (30 days) of tall fescue, along with corresponding leachate EC and pH from the pots at that time, are presented in Fig. 1 and Table 4a, b. Dry matter yield tended to increase with increasing CCP rate as long as the bulk soil pH remained at pH 8.0 or less. Depending on the liming capacity (as indicated by CCE) of the CCP applied, the 20% application had the greatest positive effect on plant yield (e.g. see CCP # 28 with a CCE of 7.7).

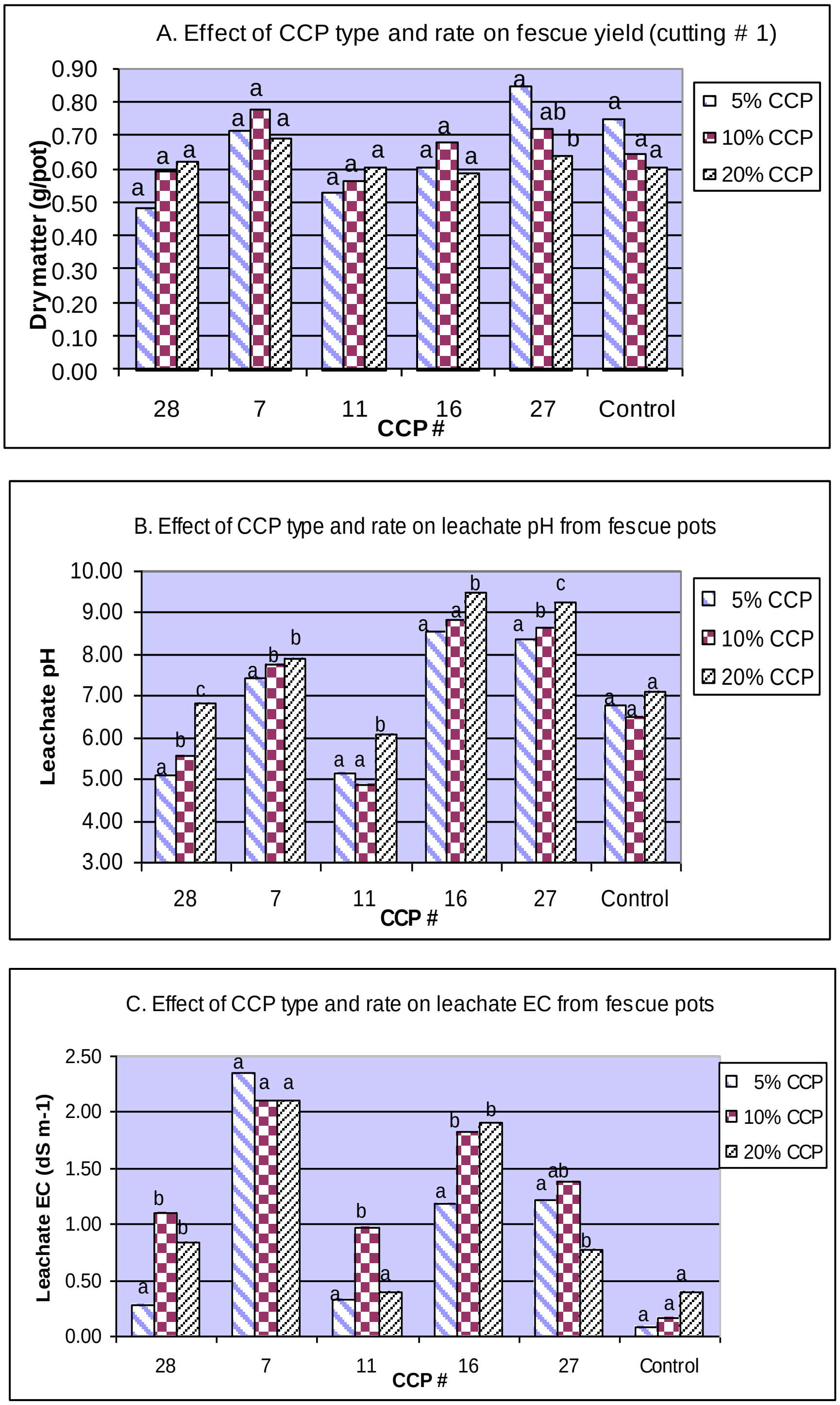

Figure 1. Tall fescue dry matter yield and corresponding pH and EC from pot leachates. Note: for Controls, the 5% corresponds to no-lime, 10% to low lime (4.5 Mg/ha), and 20% to high lime (9 Mg/ha). For each CCP #, bars with differing letters for each CCP are different at $p < 0.05$.

However, in case of CCPs with high liming potential (e.g. #27, CCE = 47.7), a 5% application was most beneficial to dry matter yield. Higher amendment rates (10 & 20%) of CCPs with high liming capacities elevated the substrate pH above 8.0 which limited or decreased plant yield. The limited CCE of CCP #11 and #28 was reflected in the limited liming effect and lower pH of the pour-through leachate solutions.

Results from the soybean trial are given in Fig. 2 and indicate a similar overall response to the varied CCP amendments after 32 days of growth. Yields increased with increasing amendment rates for CCPs # 11 and 28, but there were either no effect, or actual yield decreases for all other CCPs and for the highest liming rate in the control pots. Results of the analysis of variance (ANOVA) of the fescue and soybean yield data revealed highly significant effects of both CCP source and application rate (Table 5). The same highly significant effects were observed for EC and pH, except that for these two variables, the CCP source by application rate interaction (CCP x rate) was also highly significant (ANOVA results not shown). Pour-through data for the soybean pots (not shown) indicated that EC values significantly exceeded the critical limit (for salt sensitive species) of 2 dS m^{-1} in pots treated with CCP # 7, and, slightly exceeded the limit for CCP #'s 11, 16 and 28. While the CCPs differed widely in their total elemental composition (Table 2), the dominant chemical property with a wide ranging effect was CCE. This property (CCE) through its effect on pH controls the solubility and/or release of the elements of interest, either from the added CCP or from the amended mine spoil. This is most evident for the Cr and Mo from the pour-through data of the tall fescue pots (Table 4b). Once the substrate pH exceeds 8, greater concentrations of these elements are observed in the leachate solutions. Yield reductions and plant stress symptoms are likely due to factors such as exceedingly high pH and EC (reduced yield with highest liming rate in control pots), high concentrations of B, Se, and Mo, and/or combinations of these factors.

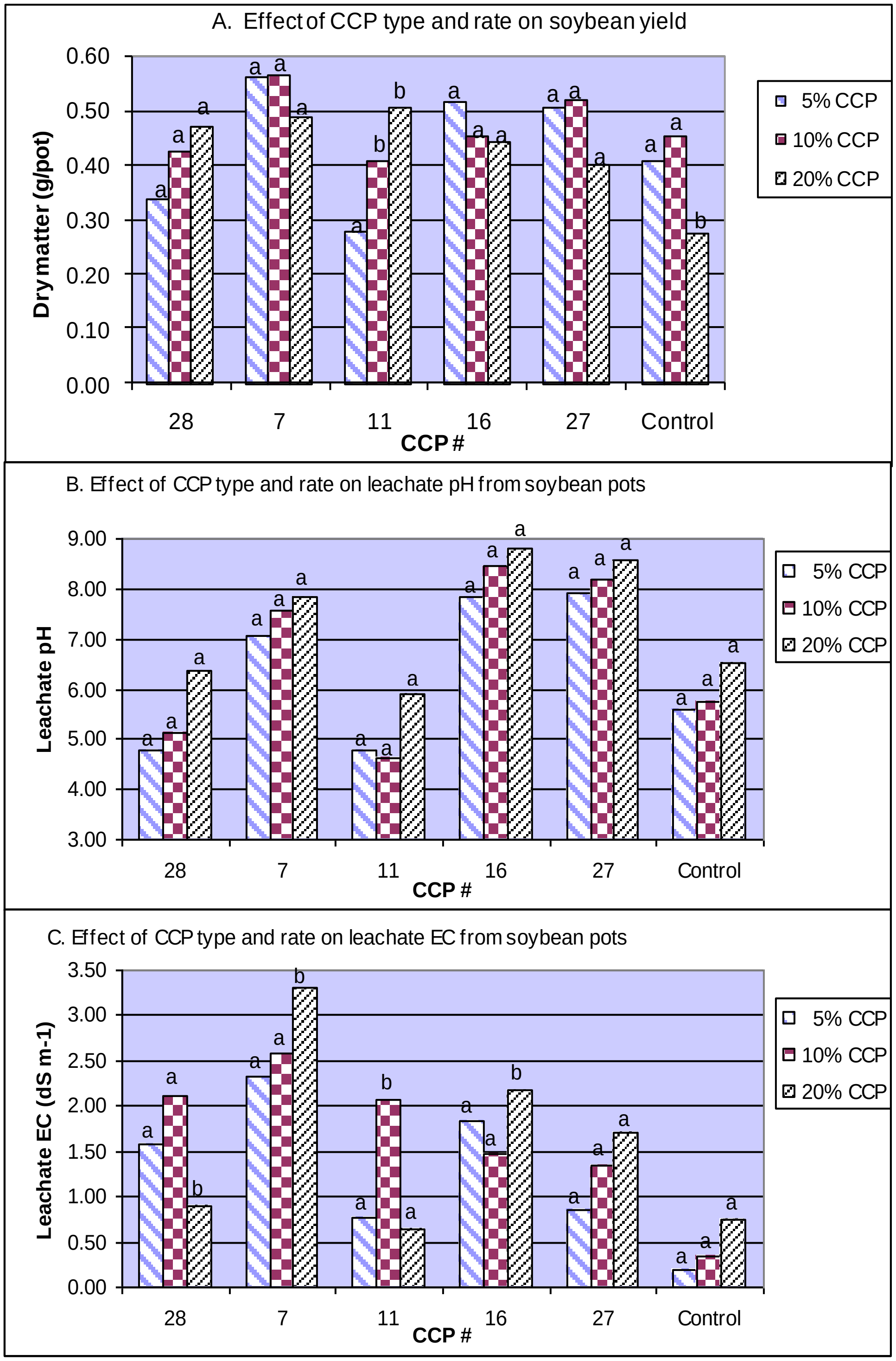

Figure 2. Soybean dry matter yield and corresponding pH and EC from pot leachates. Note: for Controls, the 5% corresponds to no-lime, 10% to low lime (4.5 Mg/ha), and 20% to high lime (9 Mg/ha). For each CCP #, bars with different letters are different at $p < 0.05$.

Table 4a. Fescue grass clipping yields (g pot^{-1}) and pour-through leachate pH, EC (dS m^{-1}), and As (mg L^{-1}) from acidic mine spoil amended with various CCPs at 0, 5, 10, or 20% (v:v) and seeded to tall fescue. Observations from 3 pour-through events and associated harvest of grass clippings.

		Yield			**pH**			**EC**			**As**		
CCP#	CCP rate	1†	2	3	1	2	3	1	2	3	1	2	3
28	5%	0.49	0.76	1.24	5.12	5.16	5.84	0.27	0.34	0.33	<0.024	<0.024	<0.024
28	10%	0.60	1.04	1.46	5.56	6.04	6.58	1.11	0.71	0.38	0.026	<0.024	<0.024
28	20%	0.63	0.93	1.44	6.81	7.11	7.77	0.84	0.78	0.55	<0.024	<0.024	<0.024
7	5%	0.72	1.23	1.53	7.42	7.42	7.61	2.36	2.44	2.44	<0.024	<0.024	0.031
7	10%	0.78	1.23	1.50	7.76	7.96	8.05	2.10	2.54	2.61	<0.024	<0.024	0.060
7	20%	0.70	1.06	1.26	7.90	7.96	8.14	2.11	2.49	2.71	<0.024	<0.024	<0.024
11	5%	0.53	0.87	1.03	5.14	6.43	6.23	0.33	0.19	0.25	0.026	<0.024	<0.024
11	10%	0.57	0.94	1.06	4.89	5.80	6.35	0.97	0.56	0.30	0.037	<0.024	<0.024
11	20%	0.61	0.78	1.07	6.08	6.53	7.05	0.39	0.72	0.40	<0.024	<0.024	<0.024
16	5%	0.61	1.29	1.52	8.54	8.33	8.79	1.18	1.85	1.09	<0.024	<0.024	<0.024
16	10%	0.69	1.41	1.45	8.85	8.35	8.58	1.83	2.34	2.26	<0.024	<0.024	0.047
16	20%	0.59	0.87	1.06	9.49	8.73	8.59	1.92	1.18	0.85	<0.024	<0.024	<0.024
27	5%	0.85	1.39	1.42	8.37	8.30	8.58	1.22	0.94	0.69	<0.024	<0.024	<0.024
27	10%	0.72	1.44	1.56	8.64	8.24	8.43	1.38	1.93	0.98	<0.024	<0.024	<0.024
27	20%	0.64	1.20	1.28	9.27	8.40	8.42	0.78	1.48	1.15	<0.024	<0.024	<0.024
Control -	0	0.75	0.99	0.97	6.78	6.45	5.61	0.08	0.09	0.12	<0.024	<0.024	<0.024
Control +	0	0.65	1.25	1.54	6.49	6.39	6.13	0.16	0.16	0.11	<0.024	<0.024	<0.024
Control++	0	0.61	1.01	1.16	7.10	7.57	7.84	0.40	0.31	0.23	<0.024	<0.024	<0.024

† Denotes pour-through events 1 – 3.
Note: Values listed as < denote detection limit for parameter/instrument employed.

Table 4b. Pour-through leachate concentrations (mg L^{-1}) of selected elements from acidic mine spoil amended with various CCPs at 0, 5, 10, or 20% (v:v) and seeded to tall fescue. Observations from 3 pour-through events and associated harvest of grass clippings.

		------------- **Cr** -------------			------------- **Mo** ------------			-------------- **B** --------------			-------------- **Se** --------------		
CCP#	CCP rate	1	2	3	1	2	3	1	2	3	1	2	3
28	5%	<0.004	<0.004	0.003	<0.008	<0.010	<0.018	0.551	0.523	0.260	0.026	<0.024	<0.024
28	10%	<0.004	<0.004	0.007	0.009	0.015	0.044	4.011	1.382	0.588	0.060	<0.024	<0.024
28	20%	0.006	<0.004	0.003	0.235	0.431	0.337	1.744	1.860	0.475	0.035	<0.024	<0.024
7	5%	<0.004	<0.004	<0.002	0.009	0.013	<0.018	5.318	4.051	1.327	0.048	<0.024	<0.024
7	10%	<0.004	<0.004	<0.002	0.022	0.049	0.048	3.743	6.251	2.355	0.042	<0.024	<0.024
7	20%	<0.004	<0.004	<0.002	0.049	0.071	0.071	5.356	8.056	4.220	0.035	<0.024	<0.024
11	5%	<0.004	<0.004	<0.002	<0.008	<0.010	<0.018	3.752	1.039	0.850	0.026	<0.024	<0.024
11	10%	0.005	<0.004	<0.002	<0.008	<0.010	<0.018	20.091	3.078	1.584	0.026	0.030	<0.024
11	20%	<0.004	<0.004	<0.002	<0.008	<0.024	0.056	3.274	5.169	2.674	0.032	<0.024	<0.024
16	5%	0.115	0.079	0.025	0.132	0.172	0.147	3.977	13.655	11.344	0.035	<0.024	<0.024
16	10%	0.346	0.127	0.086	0.411	0.220	0.154	4.523	10.679	12.364	0.138	0.077	0.046
16	20%	0.287	0.166	0.067	0.391	0.158	0.090	5.598	5.942	4.782	0.096	<0.024	<0.024
27	5%	0.145	0.030	0.010	0.176	0.244	0.091	9.719	10.752	4.637	0.026	<0.024	<0.024
27	10%	0.416	0.178	0.036	0.371	0.342	0.165	6.073	13.590	11.051	0.072	<0.024	<0.024
27	20%	0.259	0.365	0.124	0.302	0.427	0.202	3.644	9.016	7.888	0.050	<0.024	<0.024
Control -	0	<0.004	<0.004	<0.002	<0.008	<0.010	<0.018	0.030	0.037	0.057	<0.024	<0.024	<0.024
Control +	0	<0.004	<0.004	0.011	<0.008	<0.010	<0.018	<0.024	0.031	<0.03	0.026	<0.024	<0.024
Control++	0	<0.004	<0.004	0.012	<0.008	<0.010	<0.018	<0.03	0.040	0.058	0.026	<0.024	<0.024

Note: Values listed as < denote detection limit for parameter/instrument employed.

Table 5. Analysis of variance (ANOVA) of dry matter yield for tall fescue (cuttings # 1 -3) and soybeans from bioassay trials

Source	df	Fescue 1	Fescue 2	Fescue 3	Soybean 1
		Pr > F value			
Rep	3	ns	ns	ns	ns
CCP	7*	.001	<.0001	<.0001	.004
Rate	3	ns	.004	.03	ns
CCP x rate	8	ns	ns	ns	.02

* df (n-1) = 5 for CCPs and 3 control treatments

Visual symptoms of stress and phytotoxicity (Figs. 3 and 4) on plants due to different CCPs and amendment rates confirmed the susceptibility of soybeans versus tall fescue. Soybeans showed moderate to severe chlorosis and necrosis in all treatments other than the 5% rate of CCPs # 11 (low in CCE) and #16 (low extractable B). Overall, affected soybean plants looked very unhealthy and stunted in growth in the 10% and 20% treatments. Tall fescue, on the other hand, displayed symptoms of chlorosis and necrosis on the tips (Fig. 5) for only the 10 and 20% rates of high CCE ashes (# 16 and 27). Furthermore, those symptoms disappeared over time and were not noticeable after the third harvest.

Figure 3. Soybean plant growing in acidic mine soil amended with 5% of CCP # 28. Note marginal necrosis and chlorosis of lower leaves; typical of combined soluble salt + B damage.

Figure 4. Soybean plant growing in acidic mine soil amended with 10% of CCP # 16. Note heavy stunting and complete loss/drop of lower leaves; typical of heavy soluble salt + B damage. Also note dropped leaves in pot that were totaled in yield estimates for Fig. 4.

Figure 5. Tall fescue growing in acidic mine soil amended with 20% of CCP # 27 after 30 days. Note slight tip burn due to combined salts+B effect. Soluble salt effects were not noticed at later sampling dates.

Combined plant yield and leachate data from control samples confirmed that the sandstone-derived mine soil utilized was a relatively inert substrate with respect the release or leaching of the elements of interest. The slight rise in pH of no-lime control samples (likely due to the irrigation water and fertilizer solution) indicates its very low buffering capacity. The quartzitic composition of this acidic sandstone mine spoil indicates there will be little release of any element of concern even with drastic pH changes due to heavy amendment with CCPs. Any release of elements of concern would presumably come from the amending CCP.

Overall, fescue and soybean growth data revealed highly significant effects of both CCP type and application rate, and the two species (soybeans vs. fescue) exhibited clear differences in tolerance to growth substrate chemical properties. Using leachate pour-through data from soybean pots along with the data from pre- and post-harvest analysis of the growth substrates, we could not single out any individual element as directly limiting overall soybean yield. Substrate pH, as a function of CCE was the dominant chemical property affecting relative plant growth. CCE directly controls the substrate pH and consequently the solubility and/or release of the elements of interest, be it from the CCP or the amended mine spoil. Plant appearance and visual toxicity symptoms, particularly on soybeans, were a very good and consistent indicator of apparent stress to the plants, while overall biomass yield was not as good of an indicator.

Conclusions

The various components of this study represent a multi faceted attempt to predict relative leachability/bioavailability of As, Cr, Mo, Se, and B from CCPs as mine soil amendments and their effect on plant growth. The approach includes laboratory analyses and a greenhouse bioassay method for screening of CCPs as potential amendments. Results indicate that net CCE is the most important characteristic of CCPs that affects bioavailability or leachability for most elements of concern. The CCE is the critical property that determines the bulk pH of the CCPs, but also affects the pH of the amended mine soil and thereby has a predominant impact on plant growth and the bioavailabilty/leachability of various oxyanions and heavy metals. The importance of predicting and adding adequate total alkalinity (CCE) to completely offset bulk acidification of CCP/mine spoil blends was demonstrated here with decreased plant growth when the substrate pH exceeded 8.0. The critical issue is whether or not sufficient and/or appropriate total alkalinity is loaded into the system for long-term and permanent acid control. Our combined results indicate that a few relatively simple lab measurements (pH, EC, CCE) coupled with a simple soybean bioassay such as reported here can readily predict both the relative effectiveness and potential toxicity of a given CCP when used as either a bulk mine soil amendment or an alkaline additive for acid control.

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Literature Cited

Bingham, F.T. 1982. Boron. *In* Methods of soil analysis, Part 2. Chemical and Microbiological Properties. ASA-SSSA.

Daniels, W.L., B.R. Stewart, and D. Dove. 1996. Powell River Project Reclamation Guidelines for surface-mined land in Southwest Virginia. Reclamation of coal refuse disposal areas. Virginia Coop. Ext. Pub. 460-131. Available on-line at http://www.ext.vt.edu/pubs/mines/ 460-131.html.

Daniels, W.L., B.R. Stewart, K.C. Haering and C.E. Zipper. 2002. The Potential for Beneficial Reuse of Coal Fly Ash in Southwest Virginia Mining Environments. Publication Number 460-134, Va. Coop. Extension Service, Blacksburg. http://www.ext.vt.edu/pubs/mines/460-134/460-134.html.

Daniels W.L., M. Beck, and M. Eick. 2006. Development of Rapid Assessment Protocols for Beneficial Use of Post-2000 Coal Combustion Products in Virginia Coal Mines. 57 p. Description: Final report to USDI OSM for 2005-2006 Applied Science Program. USDI OSM, Parkway Center, Pittsburgh.

Mehlich, A. 1953. Determination of P, Ca, Mg, K, Na, and NH_4. North Carolina Soil Test Division (Mimeo 1953).

NRC, 2006. Managing Coal Combustion Residues in Mines, National Research Council, National Academy Press, Washington, D.C. (http://www.nap.edu/catalog/ 11592.html).

Rhoades, J.D. 1982. Soluble salts. *In* Methods of soil analysis, Part 2: Chemical and microbiological properties - Agronomy Mono. No. 9. ASA-SSSA, Madison, WI, USA.

Stewart, B.R., W.L. Daniels and M.L. Jackson. 1997. Evaluation of leachate quality from the co-disposal of coal fly ash and coal refuse. J. Env. Quality 26; 1417-1424. http://dx.doi.org/10.2134/jeq1997.00472425002600050031x.

Stewart, B.R., W.L. Daniels, L.W. Zelazny and M.L. Jackson. 2001. Evaluation of leachates from coal refuse blended with fly ash at different rates. J. Env. Qual. 30:1382-1391. http://dx.doi.org/10.2134/jeq2001.3041382x.

Tessier, A., P.G.C. Campbell, and M. Bisson. 1979. Sequential extraction procedure for the speciation of particulate trace metals. Anal. Chem. 51:7, 844-851. http://dx.doi.org/10.1021/ac50043a017.

U.S. EPA. 1992. Toxicity characteristic leaching procedure. Method 1311, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods (SW-846), 35pp.

U.S.EPA, 1996. SW-846 Acid Digestion of Sediments, Sludges, and Soils, Method 3050B.

Wright, R.D. 1986. The pour-through nutrient extraction procedure. HortScience 21:227-22.