Final Summary Report
2004 - 2007 Powell River Project

Properties and Potential Water Quality Effects of Post-2000 Coal Combustion Products

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Introduction, Overall Objectives and Approach

This report summarizes the results of a three-year research effort (2004-2007) funded by the Powell River Project on the properties and potential water quality effects of post-2000 coal combustion products. In the mid-1990's, we conducted a detailed study of the properties and environmental behavior of coal fly ash in SW Virginia mining environments (Daniels et al., 2002). That cooperative Powell River Project research program focused specifically on coal fly ash materials that were generated in the mid-Atlantic region from coals mined in SW Virginia. However, the basic properties and nature of coal combustion products (CCPs) have changed considerably in the past 10 years, and further significant changes to properties important for their utilization in mining environments are likely over the next decade. For example, the National Research Council (2006) recently issued a report on issues related to management of CCPs in mining environments, which detailed a range of public and agency concerns focused on local impacts to ground water quality. Similarly, the potential for Se release from valley fills and coal waste piles is currently under detailed scrutiny in our region due to very low ($\leq$ 5 ppb) water quality criteria and significantly higher observed discharge levels in West Virginia. Greater detail on CCP utilization issues and our past research findings are provided in past years' Powell River Project Annual Progress Reports.

This study was initially funded in January of 2004 with the following multi-year objectives:

1. To determine the basic chemical and physical properties of a large set of modern CCPs generated by combustion of SW Virginia coals, including flue gas desulfurization (FGD) materials and fly ash produced by emerging air emission control technologies.

2. To estimate the likely effect of changes in coal combustion technologies such as low NO_x boilers and various mercury removal strategies on ash chemical and physical properties.

3. To predict the relative leaching risk of oxyanions such as As, B, Mo and Se in common SW Virginia coal mining/ash utilization environments.

4. To evaluate the full range of CCP products that will likely be available for back-haul utilization and co-disposal for their suitability as (a) topical mine soil amendments, (b) geochemically stable backfill materials, and (c) bulk-blended treatments for acidic coal waste materials.

General Research Methods and Procedures

As reported in past annual reports, work over the 2004/2005 project year focused on obtaining broad sample set of CCPs currently generated by coal-fired utilities burning primarily SW Virginia coals and used various laboratory methods to estimate the potential mobility of various elements of concern (including As, Mo, Se and B) from the CCPs. Our two main collaborating utility companies were American Electric Power (AEP) and Dominion - Virginia Power. With their cooperation, we obtained a much larger sample set (28 ashes) than originally anticipated. These samples cover a wide range of basic CCP properties and include fly ash, FGD, and bottom ash. For the year 2005/2006, we evaluated the plant growth response to various CCPs in a greenhouse setting and initiated the long-term column leaching study. In the final year of the project, we completed all lab and greenhouse analyses and determined which CCP components should be used to limit maximum land application rates for the wide variety of CCPs likely to be generated in the coming decade. Finally, we integrated our complete findings into this summary report on the nature of CCPs in relation to mined land utilization on/in coal mines.

All 28 primary CCP samples were subjected to the following analyses:

1. pH and Electrical Conductance (EC).
2. Hot $CaCl_2$ extractable boron.
3. Total elemental analysis.
4. Sequential fractionation analysis (e.g. water soluble, exchangeable, acid-extractable, oxide-bound, total, etc.) to determine the speciation/partitioning of all major and minor elements of environmental concern, including As, Se, B, and Hg.
5. Calcium carbonate equivalence (CCE).
6. Toxicity Characteristic Leachate Procedure (TCLP) for priority metals.

Five CCPs were selected from this larger sample set for a greenhouse bioassay study on the plant growth effects of land-application of CCPs to mine soils at typical soil amendment rates. Similarly, the same CCPs (with one substitution) were selected for a laboratory long-term leaching study to assess the effect of differing CCP properties and loading rates on leachate quality from acidic coal refuse.

This report summarizes our findings in three major sections. Each section is being prepared as a separate manuscript for publication in refereed journals for maximum distribution of our findings.

Section I. Chemical Properties of Coal Combustion Products

Introduction

As discussed above, the basic geochemical properties and nature of coal combustion products (CCPs) have changed considerably in the past 10 to 15 years, and further significant changes to properties important for their utilization in mining environments are likely over the next decade. Detailed characterization of CCPs' chemical properties is essential to establish base-line reference information and to assess potential water quality impacts as CCPs' properties change with the introduction emission control technology.

Material and Methods

- All analyses were conducted in triplicate with the exception of the TCLP which is conducted on a large (50g) bulk sample as indicated by USEPA.
- pH and Electrical Conductance (EC) (Rhoades, 1982): were determined in saturated paste extracts from the CCPs. The CCP was mixed with distilled DI water until it formed a glistening paste. The paste was filtered after equilibration and analyzed for pH and EC.
- Hot $CaCl_2$ extractable boron (Bingham, 1982) was determined by boiling 20ml 0.01M $CaCl_2$ with 10g ash for 10 minutes. The filtrate was analyzed by ICP for B.
- Total elemental analysis (U.S. EPA, 1992a) was determined by microwave digestion of 0.5g ash with 3ml conc. HCl and 9ml conc. HNO_3. The extract was brought up to 50ml volume with distilled DI water and analyzed by ICP.
- The sequential fractionation procedure (SEP) by Tessier, et al., (1979) sequentially extracts readily available forms of elements down to more recalcitrant forms of the elements. We modified the method for use on fly ash, high S material by substituting $MgSO_4$ with $MgCl_2$ in the first extraction step. We also omitted the extraction step for elements associated with organic matter. This speciation/partitioning of major and minor elements of environmental concern, including As, Se, Cr, Mo, B, and Hg, uses a series of extractants to dissolve metals associated with particular ligand phases in a complex sample. The sample size used for extraction was 5.00g at a solution:solid ratio of 5:1. The procedure involves sequential extraction with 1M $MgCl_2$ for soluble/exchangeable metals, followed by extraction with 1M Acetic Acid/NaOac for carbonates, followed by extraction with 0.2M ammonium oxalate (pH 3) shaken in the dark for 2 hours for amorphous Fe/Mn compounds, followed by 0.04 M hydroxylamine hydrochloride/acetic acid for Fe/Mn crystalline bound forms, and finally, concentrated HCl and HNO_3 for residual bound metals.
- We also used the Toxicity Characteristic Leachate Procedure (TCLP) for priority elements (U.S. EPA, 1992b).
- Mehlich-1 extraction ($0.05M$ HCl + $0.025M$ H_2SO_4) was utilized for extractable P, Ca, B, and Fe (Mehlich, 1953) followed by inductively coupled plasma emission spectrometry (ICPES, type FTMOA85D, Spectro Analytical Instruments, Inc).

Results

The data reported in Table 1 demonstrate that we successfully obtained a set of CCPs with wide range of important chemical properties. While the range in pH was 3.57 to 12.35, only

3 CCPs had a pH below 7. The salt content of the CCPs also varied greatly with a range of 0.66 to 26.85 dS m^{-1}. However, the distribution was more uniform for EC 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 4 CCPs in the 10 to 30% range. Of the 28 CCPs tested, 14 had CCE of <5%. This may be a critical limitation where CCPs are to be used in co-disposal/amendment scenarios with acidic coal refuse or mine spoil. The CCP identified as #10 is an FGD product and stands out from the others because of its very low concentrations of metals of concern.

The results of the TCLP analysis are also presented in Table 1. Mercury was below detection limits in the TCLP test and was also below detection in all but the residual fraction of the SEP (data not shown), and is therefore omitted from further discussion. 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 disposal conditions, and we have previously reported (Stewart et al., 2001) significant metal leaching from fly ash materials that passed the TCLP.

The results of the sequential extraction procedure (Tessier et al., 1979) are graphically presented in Appendix A, Figures a-g. While there are general trends for the fractional distribution of various elements, the data also indicate a broad distribution among the CCPs for any given element. This indicates the need for the testing of individual CCPs prior to large-scale use or applications for a particular CCP. Generally, little As was found in the exchangeable phase and the majority of As is found in the carbonate and moderately recalcitrant amorphous oxide fractions. Only approximately 32% of total As was contained in the fractions of low solubility (fractions 4 & 5). A subgroup of 5 CCPs had 96% of total As in fractions 4&5, and the total As content of those CCPs were also low. The majority of total Cr (83%) was found in the very recalcitrant residual fraction. In contrast, significant quantities of total Mo (75%) and Se (70%) were generally found in the exchangeable, carbonate, and amorphous Fe & Mn phases. Although trace elements bound or co-precipitated in the carbonate fraction would have low bioavailability at high pH values, their solubility would increase with a decrease in bulk pH over extended periods of time. The high level of As in the amorphous bound phase (Step 3 of SEP) could potentially be of concern, depending on the long term geochemical stability of these amorphous phases in the final disposal environment.

Table 2 presents the total elemental concentrations of As, Se, Cr, and Mo obtained by total digestion of CCP subsamples, and also as the sum of the fractions from the sequential extraction procedure (SEP). Our efforts were focused particularly on As, Se, Cr, and Mo as these

Table 1. Selected chemical properties and TCLP extractable As, Cr, Mo, and Se for 28 different coal combustion by-products.

Footnote to Table 1: * The total B for these samples appear incorrect as Mehlich-1 extractable and hot $CaCl_2$ extractable B are substantially higher than the values obtained for total B content of the CCP. na = not applicable.

Lab #	Type of CCB	pH Sat. Paste	EC dS m^{-1}	CCE %	Extr. B mg kg^{-1}	Total B mg kg^{-1}	Extr. B as % of total B	TCLP As mg L^{-1}	TCLP Cr mg L^{-1}	TCLP Mo mg L^{-1}	TCLP Se mg L^{-1}
1	Fly ash	5.27	3.19	3.0	9.3	27	34	0.07	0.08	0.18	0.21
2	Fly ash	8.89	2.91	21.5	192.7	781	25	<0.015	0.01	0.30	0.36
3	Fly ash	9.42	4.01	7.1	29.2	116	25	<0.015	0.39	0.19	0.11
4	Fly ash	9.30	3.39	3.2	22.5	54	42	0.02	0.31	0.35	0.17
5	Ash	10.69	4.11	13.2	118.6	1022	12	0.04	0.17	0.19	0.10
6	Fly ash	5.83	4.41	3.2	28.6	61	47	0.04	0.42	0.40	0.23
7	FGD	9.14	5.25	41.0	29.2	282	10	0.21	0.30	0.09	0.11
8	Fly ash	12.35	12.12	2.0	46.0	204	23	0.03	0.09	0.09	<0.012
9	Fly ash	12.26	8.08	51.3	31.0	779	4	<0.015	0.05	0.07	0.13
10	FGD	8.17	19.72	0	3.4	53	6	<0.015	<0.006	0.11	0.02
11	Fly ash	8.85	3.25	0.3	123.4	383	32	0.12	0.03	0.11	0.04
12	FGD	9.26	3.84	52.0	33.7	271	12	0.20	0.15	0.11	0.07
13	Fly ash	9.90	4.56	39.8	39.0	616	6	<0.015	0.28	0.04	0.10
14	Bottom ash	8.80	1.61	2.5	11.3	47	24	<0.015	0.05	0.04	0.09
15	Screened ash	8.19	0.66	0.2	2.0	14	15	<0.015	0.01	0.01	0.02
16	Fly ash	12.58	14.87	46.3	14.1	686	2	0.05	0.01	0.08	0.24
17	Fly ash	12.11	5.12	28.3	24.2	677	4	<0.015	0.32	0.03	0.11
18	Fly ash	3.57	11.79	0	91.6	220	42	0.38	0.68	0.12	0.32
19	Fly ash	7.18	11.86	1.0	43.7	55	79	0.22	0.02	0.09	0.36
20	Fly ash	8.45	1.26	1.5	3.7	3*	na	0.35	0.01	0.02	0.25
21	Fly ash	9.32	26.85	22.5	16.6	183	9	0.02	<0.006	0.16	0.14
22	Fly ash	9.36	3.67	1.3	23.3	70	33	0.05	0.01	0.12	0.19
23	Fly ash	8.90	8.01	2.5	14.2	50	28	0.11	0.01	0.12	0.37
24	Fly ash	7.50	2.92	1.8	13.3	8*	na	0.04	0.02	0.07	0.02
25	Fly ash	12.15	11.24	29.8	0.3	22	1	<0.015	0.05	0.12	0.10
26	Fly ash	10.89	15.63	16.3	2.0	104	2	0.08	0.03	0.12	0.47
27	Fly ash	11.93	4.54	47.7	17.4	701	2	<0.015	0.26	0.06	0.11
28	Fly ash	11.54	3.15	7.7	3.6	82	4	0.51	0.16	0.23	0.13
		EPA CFR 261 Reg. TCLP Limits:						5.0	5.0	None	1.0

Table 2. Total elemental concentrations of As, Se, Cr, and Mo by single extraction or as the sum of the fractions of the SEP.

CCP		Total Elemental by Microwave Digestion -------------------- (mg/kg) ---------------------				Total Elemental by Sum of Fractions ---------------- (mg/kg) ------------------			
Lab #	Type of CCP	As	Se	Cr	Mo	As	Se	Cr	Mo
1	Fly ash	57.4	15.7	72.9	46.0	59.4	12.0	53.6	10.7
2	Fly ash	24.4	30.2	48.1	7.3	21.7	17.1	37.5	6.3
3	Fly ash	25.0	13.8	85.1	43.4	25.3	15.5	68.9	11.2
4	Fly ash	28.55	10.2	79.2	69.6	32.0	9.7	64.4	11.5
5	Ash	17.0	11.0	63.2	56.1	19.9	10.3	50.5	9.2
6	Fly ash	42.1	16.0	101.8	72.0	42.5	14.1	83.0	15.4
7	FGD	24.2	4.1	44.8	10.4	24.1	6.8	32.6	2.4
8	Fly ash	34.9	4.7	81.2	22.0	46.8	10.7	48.1	5.0
9	Fly ash	22.7	18.5	57.1	7.5	15.6	16.6	44.8	3.0
10	FGD	0.8	1.2	0.8	11.4	1.1	1.2	0.7	< 1.0
11	Fly ash	119.1	10.1	86.6	33.3	118.7	15.4	59.1	16.0
12	FGD	27.0	4.4	24.7	3.7	22.6	5.6	18.1	3.1
13	Fly ash	8.7	7.9	52.5	23.8	8.1	9.6	41.7	2.1
14	Bottom ash	45.7	10.0	70.7	3.3	43.2	10.1	55.0	2.4
15	Screened ash	5.0	1.2	20.6	52.8	6.9	5.3	15.4	1.0
16	Fly ash	12.4	9.1	63.8	32.0	12.1	12.1	46.6	3.3
17	Fly ash	8.7	11.0	61.3	15.2	11.4	11.3	51.4	3.7
18	Fly ash	184.3	82.7	153.3	32.2	120.4	48.2	95.9	18.8
19	Fly ash	69.8	9.0	37.6	6.4	64.1	12.4	47.2	7.5
20	Fly ash	59.3	3.6	41.5	0.8	35.3	7.3	6.5	2.9
21	Fly ash	20.7	23.7	28.8	4.1	11.8	17.0	30.8	3.6
22	Fly ash	160.7	3.6	57.1	15.3	153.1	16.3	45.2	18.8
23	Fly ash	94.4	13.8	63.9	9.5	90.5	16.6	63.2	13.1
24	Fly ash	60.0	3.6	50.9	13.7	55.2	1.7	55.4	13.1
25	Fly ash	32.2	3.6	67.2	2.3	14.2	2.6	47.0	3.8
26	Fly ash	24.0	9.7	21.6	2.7	16.4	10.7	22.8	3.4
27	Fly ash	19.0	3.6	71.4	7.2	12.0	17.5	61.0	4.7
28	Fly ash	63.2	12.6	80.5	17.1	57.2	11.1	70.0	11.5
Mean of all CCPs		46.1	12.5	60.3	22.2	40.8	12.2	47.0	7.1

elements were found to have interesting leaching patterns and potential water quality impacts. We conducted a correlation analysis on the fractional distribution of As, Cr, Mo, and Se with other bulk CCP chemical properties. The data reveal marked differences among the fractions with strong ash-specific variability. We expected that release/solubility of the elements tested is generally pH dependent. We found that pH was reasonably well correlated with CCE ($r^2 = 0.56$), but the fractional distributions of As, Cr, Mo, and Se appear to be more strongly linked to CCE than to pH.

The correlation analysis indicated that CCE was the one chemical property, of all the examined properties, that was most strongly related to As level and distribution among the various SEP fractions. CCE was negatively correlated to As levels in the first four SEP fractions ($r^2 = -0.38$ to -0.53), but positively correlated to the residual fraction ($r^2 = 0.78$). For CCPs with low total As (< 20 mg kg^{-1}), As resided up to 90% in the residual fraction. For CCPs with high total As (> 100 mg kg^{-1}), however, the As was up to 90% allocated among the labile and moderately labile fractions. The fractional distribution for Chromium (Cr) (Figs. a-g, Appendix A) was most consistent across all CCPs with 60 to 80% of the Cr being in the recalcitrant residual fraction. The distribution for As, Mo, and Se was much more variable the CCPs tested. Yet for all four elements, CCE was the one property most often and most strongly correlated with the respective elements, and in all fractions. The bulk soluble salt content (EC) of the CCPs appears to be only related to Se in fractions 3 and 5.

Table 3 presents results for the Mehlich-1 acid extractable elements for all CCPs. The data again show a broad distribution of properties across all CCPs, yet do not document any obviously high extractable metal levels that in themselves would cause a problem for plant growth. Using the data sets discussed above, we categorized the 27 materials (excluding CCP #10) into a somewhat modified 2 X 2 matrix of As levels (low and high) by CCE (levels low and high). Electrical conductivity (EC, an indirect measurement of the salt content) was a strong covariate. Low CCE ashes exist with high and low EC, and high CCE materials exist with high and low EC. From this matrix we selected CCPs that then were used for greenhouse plant growth bioassay trials and the laboratory column leaching procedure.

Conclusions

- The sequential fractionation procedure (SEP) demonstrated that the fractional distribution of oxyanions and Cr are CCP specific and vary widely.

- Calcium carbonate equivalence (CCE) is highly correlated with the fractional distribution of oxyanions and Cr. It is property that is analytically easy to determine. It gives a direct indication of the liming capacity of the CCP and may be used as a predictor of the pH effect in possible disposal environment scenarios.

Table 3. Mehlich-1 extractable elemental data of 28 coal combustion products (CCPs).

CCP		2 : 1 ---------	---------------------------- mg kg^{-1} ----------------------						
Lab #	Type of CCB	pH	Zn	Mn	B	Cu	Fe	P	Mg
1	Fly ash	6.98	1.9	2.9	9	1.1	78	46	91
2	Fly ash	8.65	0.6	8.1	186	0.1	14	2	232
3	Fly ash	9.10	2.7	10.3	59	3.1	16	8	383
4	Fly ash	9.53	2.1	6.5	32	2.0	100	55	117
5	Ash	9.57	2.5	11.7	309	1.8	13	2	658
6	Fly ash	8.22	1.4	4.2	39	0.3	75	53	139
7	FGD	9.09	0.1	1.0	39	0.1	4	4	1101
8	Fly ash	10.11	1.4	14.2	120	0.7	5	33	142
9	Fly ash	12.02	0.1	0.5	29	0.1	1	2	242
10	FGD	8.94	0.3	2.5	5	0.2	13	2	348
11	Fly ash	9.15	5.5	12.6	183	5.1	373	109	277
12	FGD	8.99	0.3	1.8	55	0.4	43	14	727
13	Fly ash	9.27	0.1	0.2	39	0.1	1	2	204
14	Bottom ash	8.68	1.3	7.7	21	0.1	23	2	214
15	Screened ash	8.64	1.5	12.3	4	1.4	203	37	156
16	Fly ash	11.71	0.1	0.6	21	0.1	11	2	227
17	Fly ash	11.68	0.1	1.5	46	0.1	1	2	341
18	Fly ash	4.10	5.4	6.8	44	0.5	194	97	181
19	Fly ash	7.24	2.3	18	35	2.7	158	60	473
20	Fly ash	7.95	1.6	8.8	8	4.3	152	171	103
21	Fly ash	8.18	0.2	1.0	59	0.3	8	11	147
22	Fly ash	7.01	2.9	4.5	30	7.6	222	73	130
23	Fly ash	8.00	2.4	5.7	20	4.2	150	64	178
24	Fly ash	7.29	3.5	1.7	9	22.2	68	90	73
25	Fly ash	12.09	0.1	0.1	3	0.6	3	4	124
26	Fly ash	8.44	0.1	0.6	22	0.1	0	2	67
27	Fly ash	11.68	0.1	0.1	27	0.1	0	2	372
28	Fly ash	8.47	4.1	7.4	33	2.9	7	2	203
Means across all ashes		9.0	1.6	5.5	52.9	2.2	69.1	34.0	273

Section II. Plant Growth Effect of CCP Amendment to Mine Spoil & Associated Leaching Potential

Criteria for Selection of 5 CCPs for the Greenhouse Bioassay Trial

The main determinants for the selection of the five CCPs for the greenhouse bioassay trial were bulk soluble salts (EC), and total As concentration and distribution among the 5 sequential extraction (SEP) fractions. We also chose materials that presented a wide range of soluble B concentrations. Statistical analyses indicated that CCE was the one chemical property most strongly related to As levels and distribution among the various SEP fractions. Therefore, the five CCP products chosen for detailed study were selected to provide the full combination of high/low As vs. high/low EC conditions. Thus, the selected of CCPs for the greenhouse bioassay trial were as follows:

Ash #	Type of Ash	Ash properties
22	fly ash	high As; low CCE; low EC
28	fly ash	high As; low CCE; mod. high EC
16	fly ash	low As; high CCE; low EC
27	fly ash	low As; high CCE; high EC
7	FGD	relatively low As; high CCE; mod. EC

Methods for Greenhouse Bioassay Trial

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 general design, methods, and techniques used for our greenhouse bioassay (mine soil amendment scenario) are fully documented and cited by Daniels et al. (2002). The procedures were modified to include a "pour-through" procedure where we leached the greenhouse pots with excess leaching waters approximately one month after establishment of the trial, and then collected the leachates for analyses such as pH, EC, As, Se, B and other parameters we deemed important.

- Acidic sandstone mine spoil was collected at an active Powell River/Red River operation, Wise County, Virginia. Laboratory pH = 4.75, with a liming requirement equivalent to 4.5 Mg/ha. The mine spoil was air-dried and sieved to pass a 2 mm sieve.

- 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.

- Selected properties of the five CCPs utilized are given in Table 4 below.

Table 4. Properties of five CCPs selected for use in greenhouse bioassay experiments.

			Saturated Paste				Total Elemental Analysis via Micro Digestion				
CCP #	Type	Bulk Density g cm^{-3}	pH	EC dS m^{-1}	CCE %	Ext. 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}
28	Fly ash	1.12	11.5	3.1	16.3	3.6	82	57	11	70	11
11	Fly ash	1.50	8.9	3.3	0	185	574	179	15	130	50
16	Fly ash	1.15	12.6	14.9	53	16	789	14	11	73	37
27	Fly ash	1.20	11.9	4.5	57	nd	841	23	4	86	9
7	FGD	0.80	9.1	5.3	49	23	225	19	3	36	8

Experimental Design & Treatments:

- The trials were conducted separately for fescue and soybean. The statistical design was a completely randomized block (RCB) with 4 replications per treatment combination.
- 3 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 = 700ml / pot (900g)

3 ash rates X 5 CCPs X 2 crops X 4 replications = 120 pots

Control pots: Control (-) no-lime mine spoil only (4 per crop)
Limed control (-) pots (4.5 Mg/ha equivalent)
Highly limed control (++) pots (9 Mg/ha equivalent)

- Soil substrate moisture was maintained near container capacity.
- Approximately every month, pots were allowed to equilibrate at field capacity for 24 hours and then eluted with excess water to obtain 50ml (± 5ml) of leachate.
- Soybean pots were seeded for 4 plants with thinning 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 a 20-20-20 Peter’s liquid fertilizer.

Results and Discussion

Chemical properties relevant to plant growth of the various mine spoil and CCP mixtures are presented in Table 5. The pH of the mixes tended to increase with higher loading rates of the CCP. The large differences in pH among the mixtures of the various CCPs attest to the very effective liming capacities of some of the CCPs. The very high pH values obtained with amendment # 16 and 27 indicates that CCP amendment rates need to be limited to avoid adverse effects on plant growth due to incorrect soil pH.

Dry matter yields from the first cutting of the tall fescue, along with corresponding EC and pH of the leachates from the pots at the time of cutting, are presented in Figures 1 a-c. 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 (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). However, in case of a CCP with a high liming potential (e.g. #27, CCE = 47.7), a 5% application was most beneficial to dry matter yield. Higher amendment (10 & 20%) rates of CCP with high liming capacities elevated the pH above 8.0 which limited or decreased plant yield.

Table 5. Selected Mehlich-1 extractable chemical properties of mine spoil and CCP amended mine spoil at the onset of the bioassay greenhouse trial.

Substrate % of CCP	2 : 1	mg kg^{-1}						
	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 – 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	6.0	24	1.9	4	2	455
#27 – 20%	10.84	2.0	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

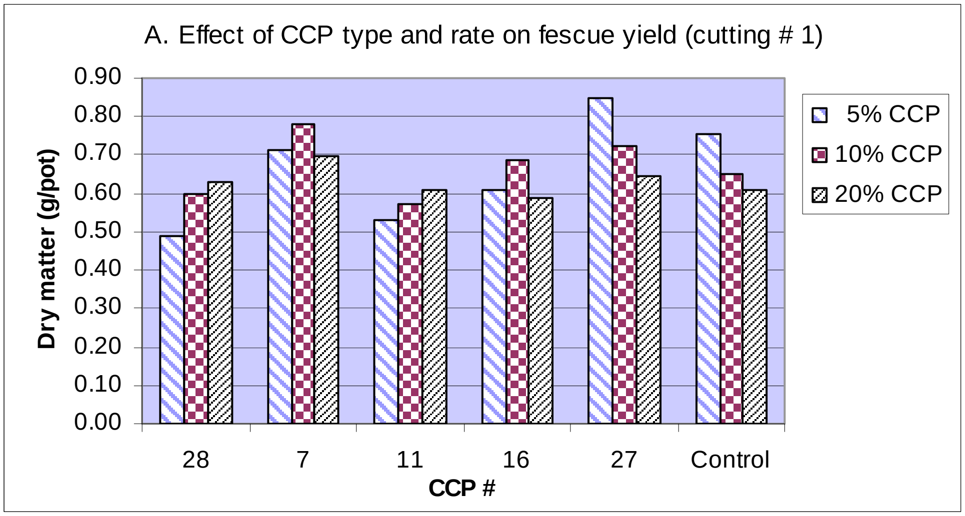
Results of the analysis of variance (ANOVA) (Table 6) on the fescue yield data revealed highly significant (0.001) effects of both CCP source and application rate. The same strongly significant effects were seen for EC and pH (results not shown), except that for these two variables, the CCP source X application rate interaction was also highly significant. Only the type of CCP had an effect on soybean yield. While the CCPs differ in their total elemental composition (Table 1) and among the fractional distribution, the dominant chemical property with a wide-ranging effect was CCE. This property directly controls the solubility and/or release of the elements of interest, be it from the CCP or the amended mine spoil. The limited CCE of CCP# 11 and 28 is reflected in the limited liming effect and lower pH of the pour-through leachate solution.

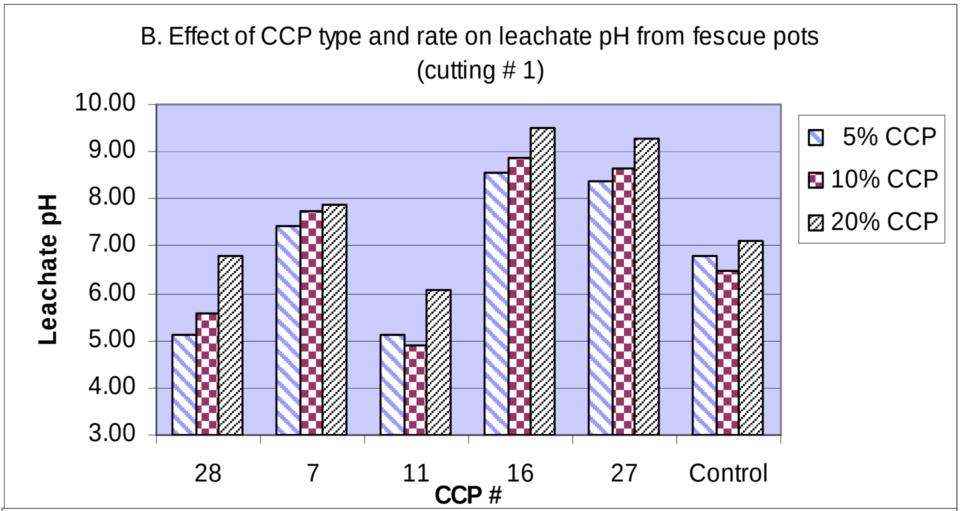
Table 6. Analysis of variance (ANOVA) of dry matter yield for tall fescue (cuttings # 1 -3) and soybeans from bioassay trials

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

Figure 1 a,b,c. Tall fescue dry matter yield and corresponding pH and EC from pot leachates in response to differing CCPs and application rate. Note: in the control treatments, no CCP was added, but the 5% corresponds to no-lime, 10% to low lime (4.5 Mg/ha), the 20% to high lime (9 Mg/ha).


A. Effect of CCP type and rate on fescue yield (cutting # 1)


B. Effect of CCP type and rate on leachate pH from fescue pots (cutting # 1)

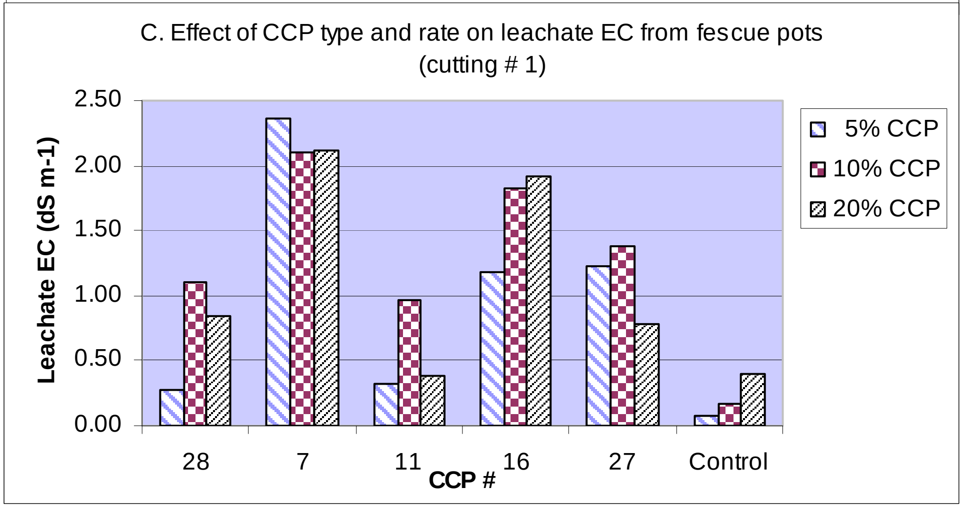

C. Effect of CCP type and rate on leachate EC from fescue pots (cutting # 1)

Table 7 reports the chemical properties of the pour-through solutions for the three fescue grass harvests. The EC and pH from the various mixes relates well to the CCE of the respective CCP and the loading rate. Leaching of oxyanions at these pH appears not to be a concern as concentrations for As, and Cr, were very low or below detection, and even the detectable Mo levels were below levels of concern. Selenium was detectable only in the first leaching event. As expected, boron (B) along with sulfur (as SO_4;data not shown) were the two elements at highest concentration in the leachates. However, correlation and stepwise regression analysis of the yield data with the elemental concentrations from the pour-through solutions shows that these two elements did not negatively affect fescue yield. The stepwise regression analysis did show that fescue yield was affected by pH ($p > 0.0034$). However, the overall r^2 of the statistical model was relatively weak at 0.38.

The leachate data from the control samples document that the mine spoil was an inert substrate with respect the release/leaching of the elements of interest. The rise in pH of the no-lime control samples (likely due to the irrigation water and fertilizer solution) indicates its low buffering capacity. The general mineralogical 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 the amendment with CCPs. Any release of elements of concern would come from the amending CCPs.

Conclusions

- The amending mine spoil with CCPs did not result in result in leaching of oxyanions at concentration levels that would signal reasons for concern.

- Unless some other external factors would significantly alter the pH environment of the amended mine spoil, the oxyanions contained in the CCPs are expected to be stable and not prone to leach at concentrations higher than those observed.

- The pH of the amended mine spoil was the one factor that directly affected plant growth as measured by biomass yield.

- The CCPs’ application must be limited according to its CCE as not to result in excessively high substrate pH that would limit plant growth.

- The mine spoil itself appears to not be a source of any potentially toxic constituent.

Table 7. Pour-through leachate pH, EC (dS m^{-1}), B and Se (µg ml^{-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 at time of harvest of grass clippings.

		----------- pH ----------			**------------- EC -------------**			**------------- B -------------**			**------------- Se --------------**		
CCP#	CCP rate	1	2	3	1	2	3	1	2	3	1	2	3
28	5%	5.12	5.16	5.84	0.27	0.34	0.33	0.5	0.5	0.2	0.026	<0.024	<0.024
28	10%	5.56	6.04	6.58	1.11	0.71	0.38	4.0	1.3	0.6	0.060	<0.024	<0.024
28	20%	6.81	7.11	7.77	0.84	0.78	0.55	1.7	1.8	0.5	0.035	<0.024	<0.024
7	5%	7.42	7.42	7.61	2.36	2.44	2.44	5.3	4.0	1.3	0.048	<0.024	<0.024
7	10%	7.76	7.96	8.05	2.10	2.54	2.61	3.7	6.2	2.3	0.042	<0.024	<0.024
7	20%	7.90	7.96	8.14	2.11	2.49	2.71	5.3	8.0	4.2	0.035	<0.024	<0.024
11	5%	5.14	6.43	6.23	0.33	0.19	0.25	3.7	1.0	0.8	0.026	<0.024	<0.024
11	10%	4.89	5.80	6.35	0.97	0.56	0.30	20.1	3.0	1.5	0.026	0.030	<0.024
11	20%	6.08	6.53	7.05	0.39	0.72	0.40	3.2	5.2	2.6	0.032	<0.024	<0.024
16	5%	8.54	8.33	8.79	1.18	1.85	1.09	3.9	13.5	11.3	0.035	<0.024	<0.024
16	10%	8.85	8.35	8.58	1.83	2.34	2.26	4.5	10.9	12.3	0.138	0.077	0.046
16	20%	9.49	8.73	8.59	1.92	1.18	0.85	5.5	5.9	4.7	0.096	<0.024	<0.024
27	5%	8.37	8.30	8.58	1.22	0.94	0.69	9.7	10.7	4.6	0.026	<0.024	<0.024
27	10%	8.64	8.24	8.43	1.38	1.93	0.98	6.0	13.5	11.0	0.072	<0.024	<0.024
27	20%	9.27	8.40	8.42	0.78	1.48	1.15	3.6	9.0	7.8	0.050	<0.024	<0.024
control-	0	6.78	6.45	5.61	0.08	0.09	0.12	0.03	0.03	0.06	<0.024	<0.024	<0.024
control+	0	6.49	6.39	6.13	0.16	0.16	0.11	0.02	0.03	0.03	0.026	<0.024	<0.024
control++	0	7.10	7.57	7.84	0.40	0.31	0.23	0.03	0.04	0.06	0.026	<0.024	<0.024

Note: Whenever a concentration for a specific element occurs with a < symbol, this represents the detection limit of the analytical instrument.

Section III. Leaching Potentials from Acidic Coal Refuse Amended with CCPs of Differing Chemical Properties

Methods for Leaching Column Study

The selection criteria of five CCPs to be used as an amendment to the acidic coal refuse were the same as those for the bioassay trial with one exception/substitution. For this experiment, CCP # 28 was substituted with CCP # 18. This CCP has high total As, Se and Cr concentrations, 0 CCE, and a very low pH of 3.57. Including this CCP gave us a maximum range in potential chemical composition and leaching risk once the acid forming coal refuse was amended with the various CCPs.

- Known acid- forming coal refuse was collected fresh from the Red River Coal Co. prep-plant in Wise County, Virginia.
- The refuse was air dried and sieved to maximum 1.25 cm particle size.
- A modified hydrogen peroxide oxidation procedure (Barnhisel and Harrison, 1976) was used to determine the potential acidity (PPA) of the coal refuse. PPA = 34.5 Mg CCE per 1000 Mg material; or agricultural lime demand = 34.5 tons of lime per acre per six inch depth.
- The refuse was repeatedly moistened and allowed to dry out in order to accelerate the oxidation of sulfides. Once the pH of the refuse dropped to 4.5, the material was deemed ready for amendment with CCPs.
- Selected properties of the CCPs are given in Table 8 below.

Table 8. Properties of five CCPs selected for use in column leaching experiment.

			Saturated Paste				------ Total Elemental via Micro Digestion ----				
CCP #	Type	Bd	pH	EC	CCE	Extr. B	Total B	As	Se	Cr	Mo
		g cm^{-3}		dS m^{-1}	%	mg L^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}
18	Fly ash	0.68	3.57	11.79	0.0	3.6	82	57	11	70	11
11	Fly ash	1.50	8.9	3.3	0.3	185	574	179	15	130	50
16	Fly ash	1.15	12.6	14.9	53	16	789	14	11	73	37
27	Fly ash	1.20	11.9	4.5	57	nd	841	23	4	86	9
7	FGD	0.80	9.1	5.3	49	23	225	19	3	36	8
Coal Refuse		1.92	<3.0	0.6	0						

Leaching Column Design:

The columns we built were of similar design as those previously used by our group in CCP leaching studies (Stewart et al., 1997, 2001) but scaled down to approximately 1300 cm^3 sample size. The columns were made from 7.5 cm PVC pipe, 38 cm long, with a rounded endcap at one end. Fine nylon mesh was in the endcap was topped with 2 cm of 1 mm acid-washed glass beads. Test columns were constructed to determine the proper weight ratios of the respective CCP and coal refuse to reflect by-volume CCP amendment of 10 and 20%. Columns were then filled on a by-weight basis to reduce replicate variability. Columns were packed in increments of 100 cm^3. A thin layer of glass beads was added between increments to fill any large voids in order to minimize/eliminate preferential flow. The treatment mixes were topped with 2.5 cm of glass beads in aid infiltration. Leaching water was applied by setting a 6 cm diameter plastic cup with perforated bottom onto the glass beads. This ensured uniform distribution of the leaching water on the head of the column.

Statistical Design & Treatments:

- The statistical design was a completely randomized block (RCB) with 3 replications per treatment combination.
- 2 CCP rates: 10%, 20% (v:v basis, but mixed on a weight basis to reduce variability) as well as 100% coal refuse control (-) columns with no lime added; plus 100% coal refuse control (+) columns with lime added, equivalent to 34.5 Mg/1000 (tons/acre) per the PPA procedure.
- Columns were leached with 100 ml deionized water (equivalent to approximately 2.5 cm or 1” rainfall event) twice per week.
- Leachates were allowed to drain freely for 24 hours into acid-washed polyethylene collection bottles.
- EC and pH were determined on all leachates on the day of collection.
- Elemental concentrations were determined by ICPES analysis on composite samples made up of 6 ml leachate from each replicate of a treatment combination.
- Leachate samples were analyzed for the following elements: As, B, Cr, Cu, Fe, Mo, Ni, S, Se, and Zn.
- Columns were run in the laboratory with room temperature of 22 ^{o}C (±2).
- Columns were moistened to container capacity and allowed to equilibrate for 24 hours prior to the first leaching event.

Results

The 2005-2006 annual report presented leaching column results covering the first 46 days. As part of past year’s work, we continued the column leaching experiment for an additional 190 days. Figures 2 a-h present the complete long-term leaching data. Important changes in the leaching patterns were observed with the continuation of this experiment.

Figure 2a. Leachate pH during 236 days of leaching of acidic coal refuse amended with 0, 10, or 20% of respective CCP.

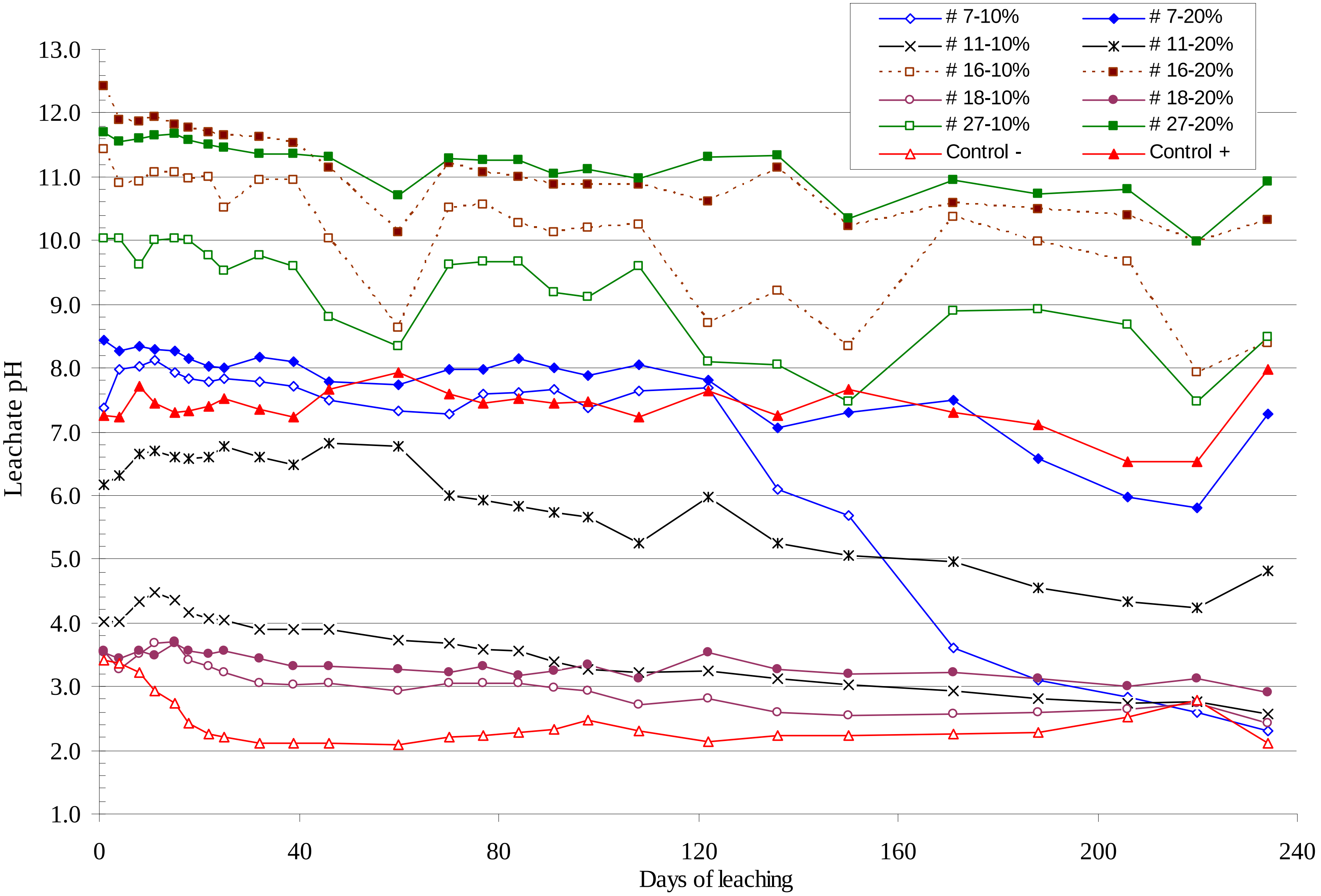


Figure 2b. Leachate EC during 236 days of leaching of acidic coal refuse amended with 0, 10, or 20% of respective CCP.

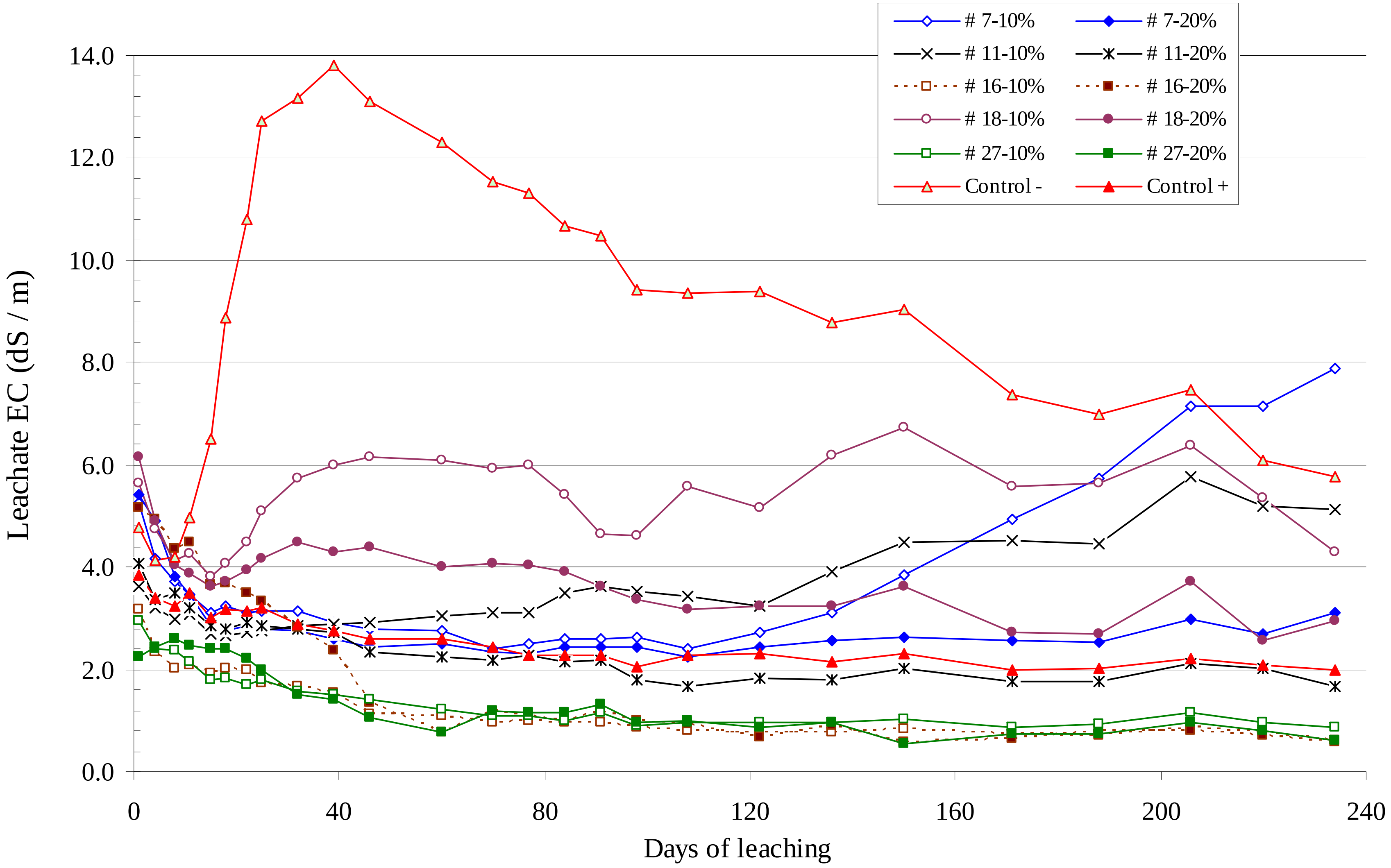


Figure 2c. Leachate As concentrations (mg L^{-1}) during 172 days of leaching of acidic coal refuse amended with 0, 10, or 20% of respective CCP.

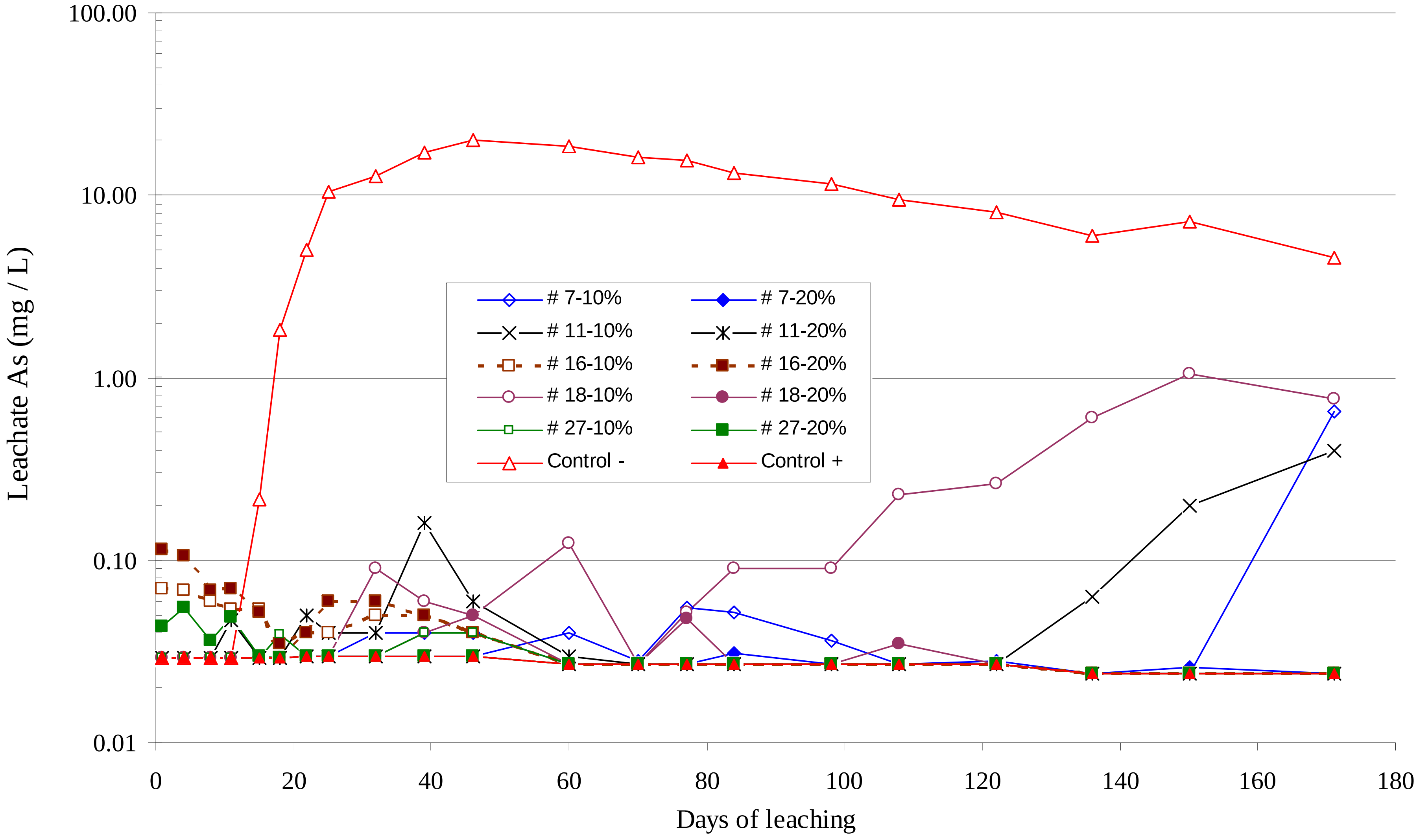


Figure 2d. Leachate Cr concentrations (mg L^{-1}) during 172 days of leaching of acidic coal refuse amended with 0, 10, or 20% of respective CCP.

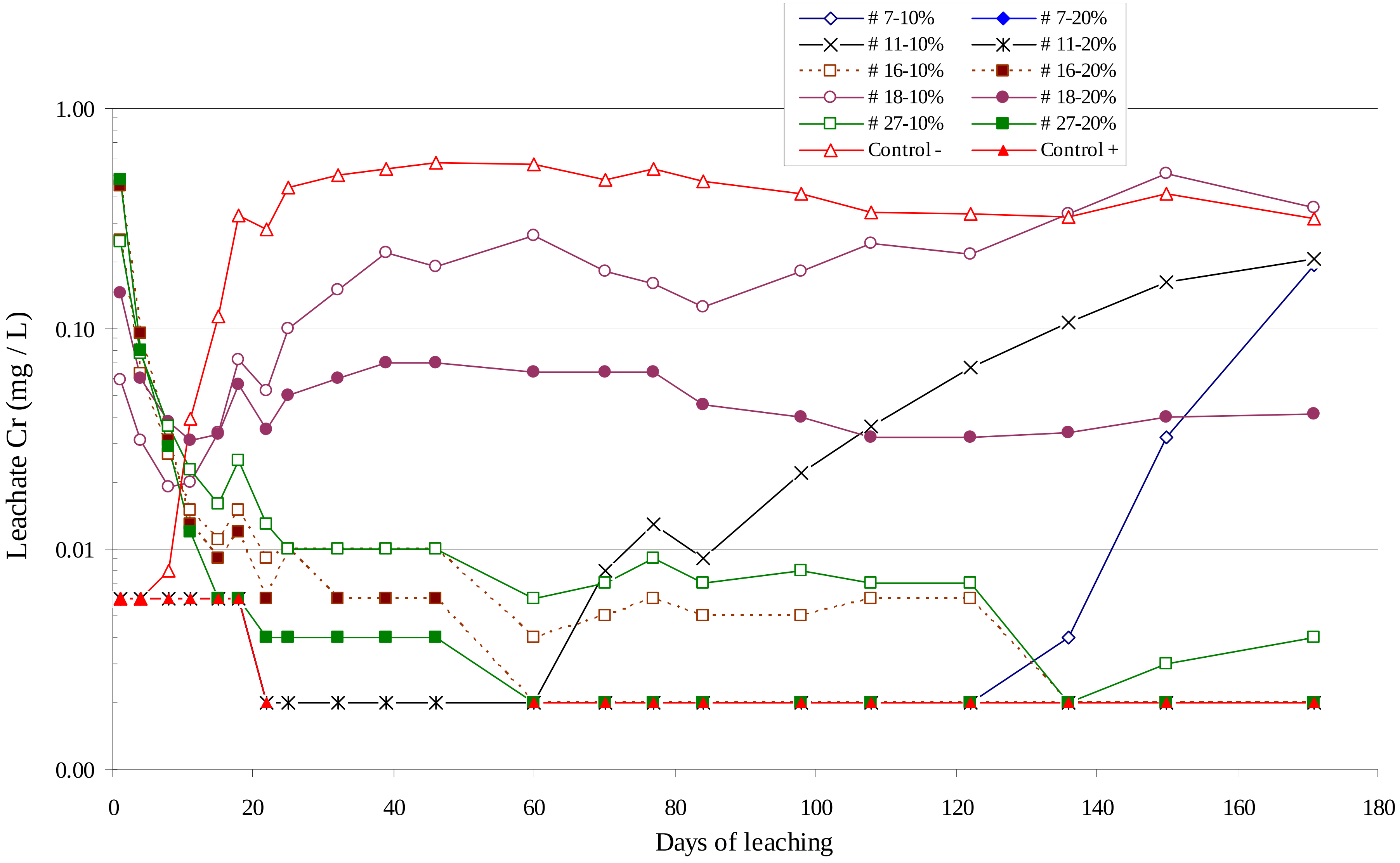


Figure 2e. Leachate Mo concentrations (mg L^{-1}) during 172 days of leaching of acidic coal refuse amended with 0, 10, or 20% of respective CCP.

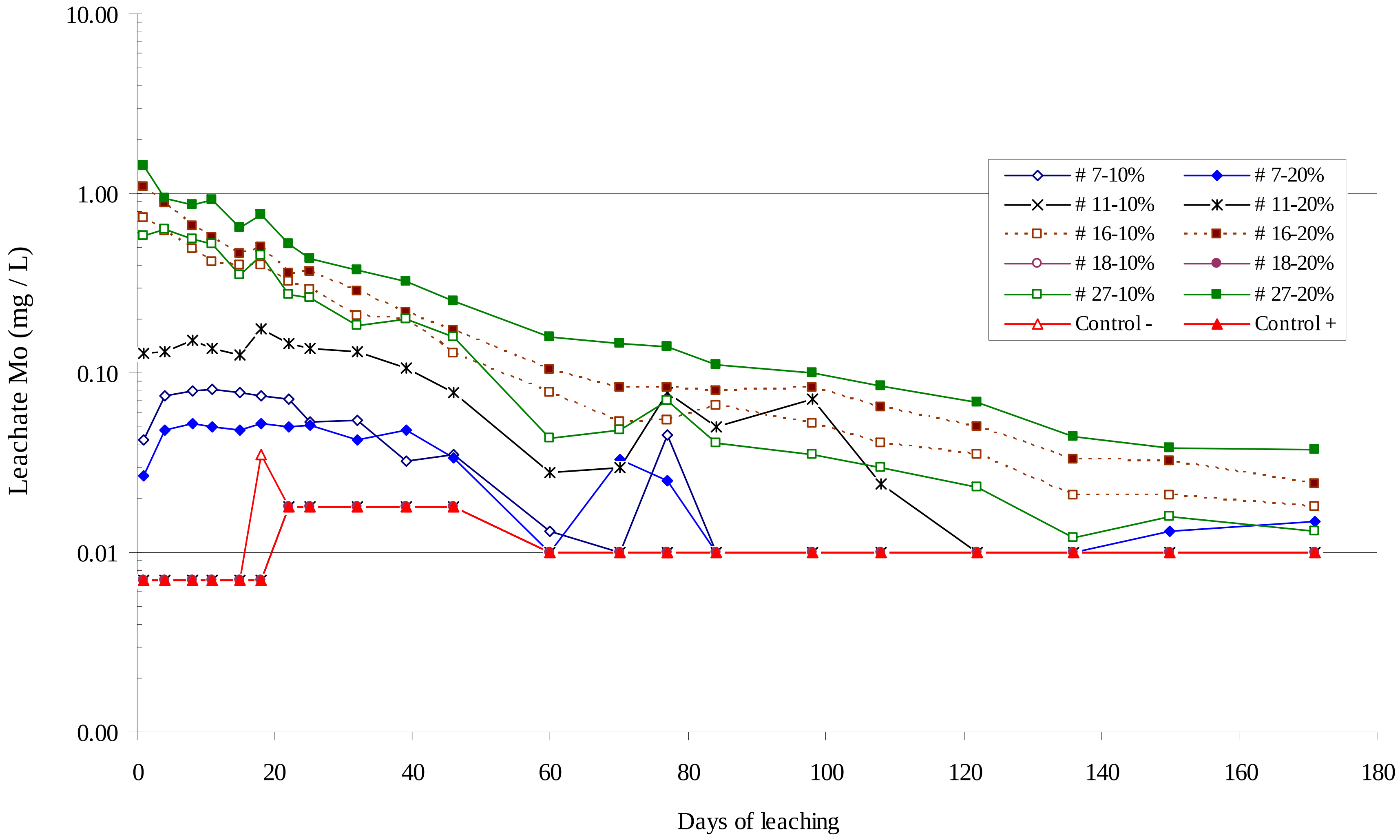


Figure 2f. Leachate Se concentrations (mg L^{-1}) during 172 days of leaching of acidic coal refuse amended with 0, 10, or 20% of respective CCP.

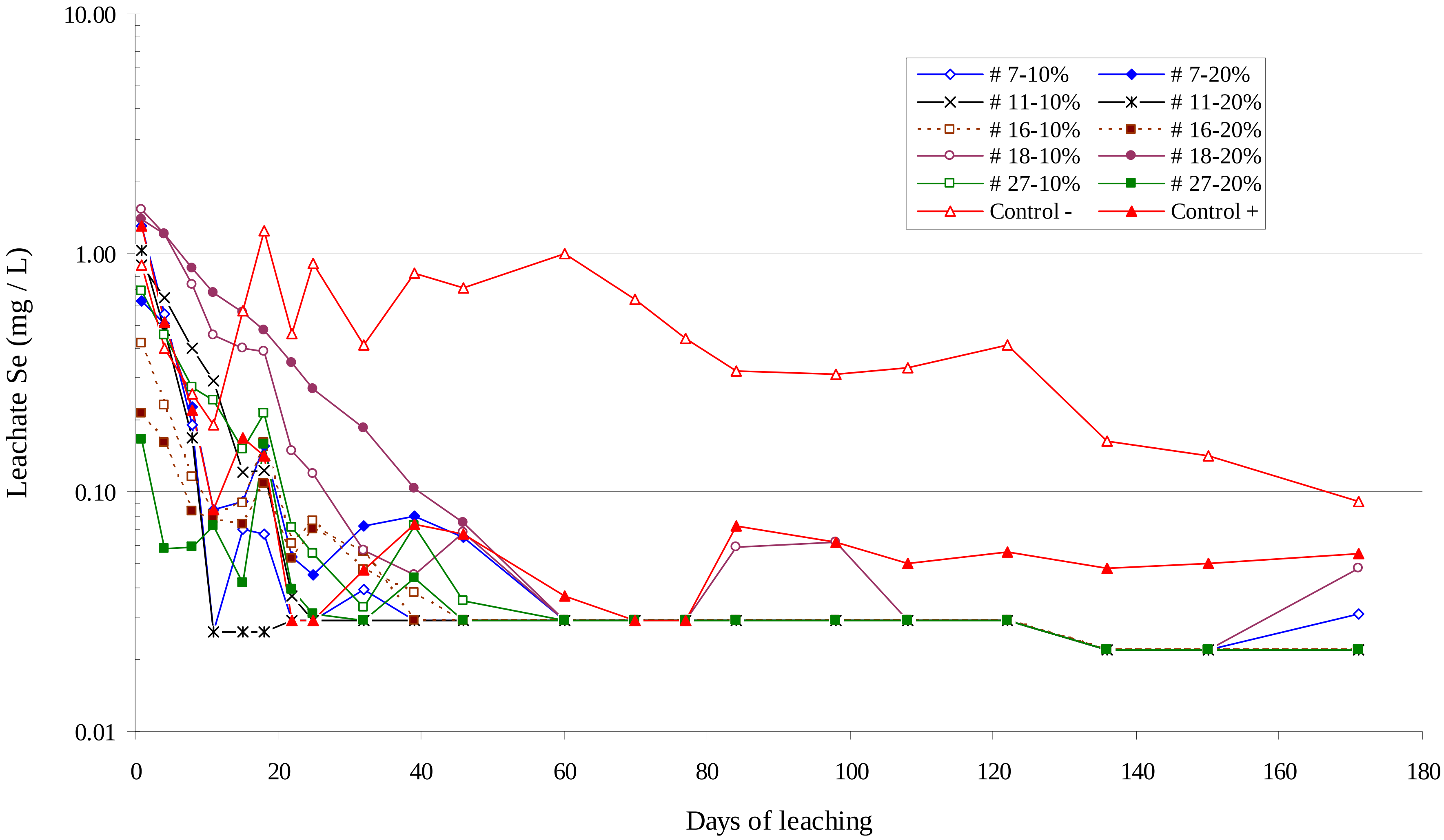


Figure 2g. Leachate S concentrations (mg L^{-1}) during 172 days of leaching of acidic coal refuse amended with 0, 10, or 20% of respective CCP.

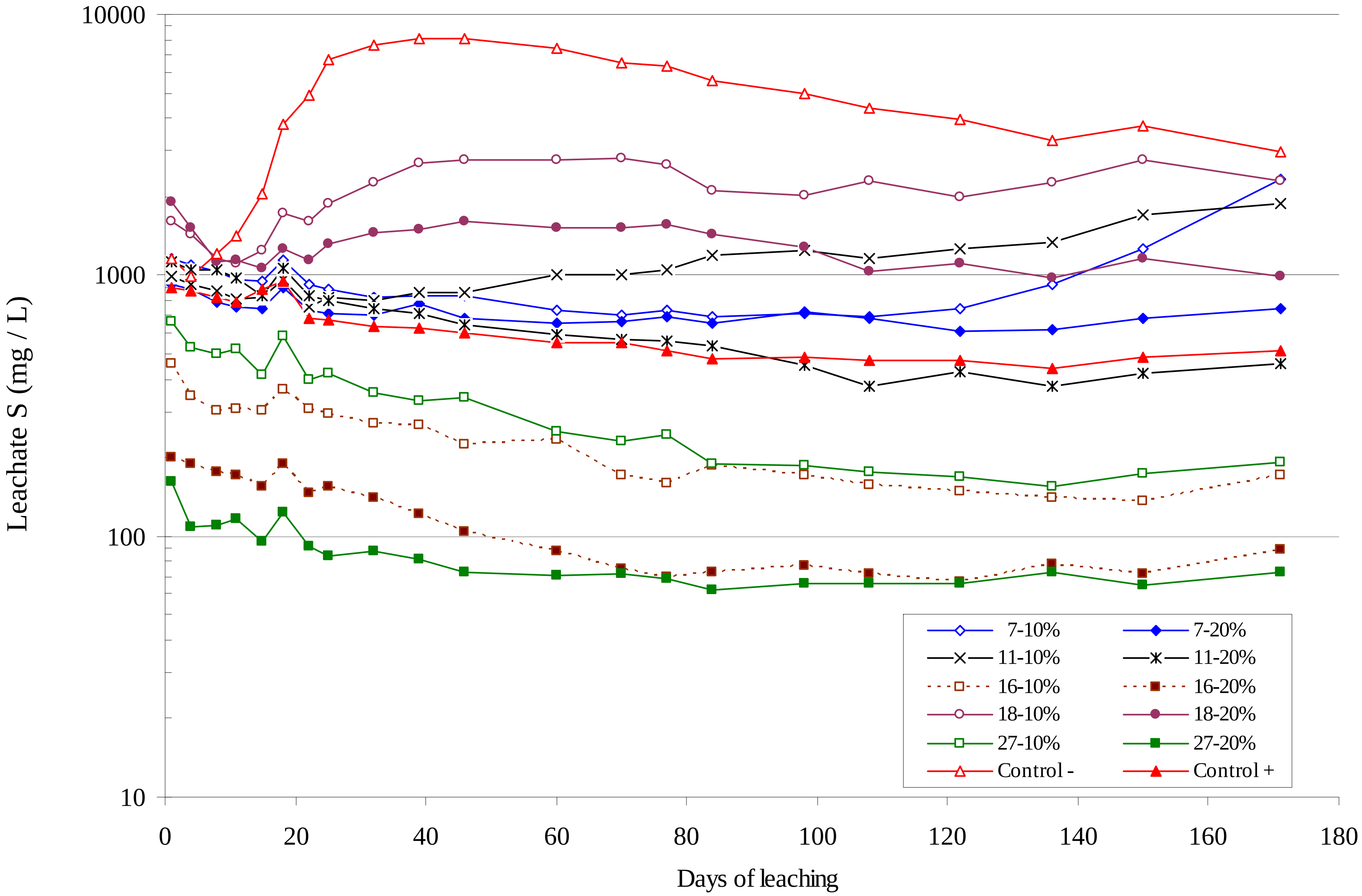
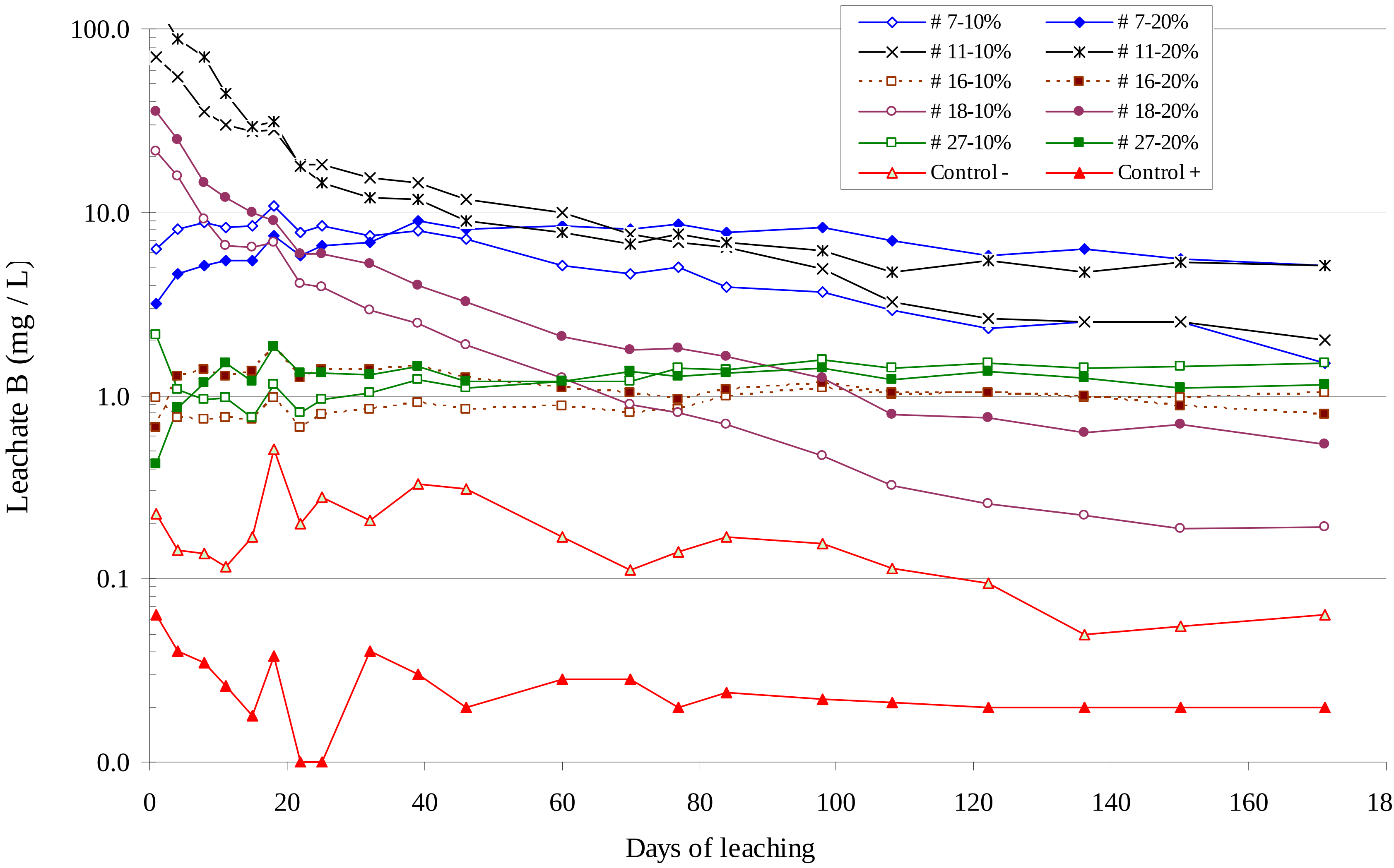


Figure 2h. Leachate B concentrations (mg L^{-1}) during 172 days of leaching of acidic coal refuse amended with 0, 10, or 20% of respective CCP.



Most of the significant trends that were noted for the first 46 days did not continue over the course of 236 days of leaching. Most consequential were the trends in leachate pH for the various mixtures. For mixtures with low or intermediate leachate pH, the pH levels appeared relatively stable over time (Fig. 2 a). Higher pH mixtures appeared to generate leachates that subsequently declined in pH over time. While this trend continued for the high pH mixtures, mixtures in the intermediate pH range (6 to 8) appeared to run out of liming capacity to counteract the acidic refuse. Once this point was reached, the pH dropped rapidly. The resulting dissolution effect of lower pH on mineral constituents is clearly documented by the corresponding increase in dissolved/leachable salts in the leachate solution, as measured by the EC (Fig. 2 b). For example, the pH of the #7-10% mixture dropped rapidly after 120 days and the Cr concentration (Fig. 2 d) increased correspondingly.

The mineralogical differences between the CCPs as indicated by the fractional distribution using SEP and the respective total elemental content exerted further control on the release patterns. Samples #18-10% and #11-10% had very low (<4.0) pH values from the onset of the leaching process, but released only low concentrations of As (Fig. 2 c) until pH dropped to <2.8 and 3.2, respectively. Significant release from mix #7-10 was at pH 3.7. There was no significant As release from mix #18-20% despite a pH in the range of 3.2 – 3.7 over a 170 day leaching period. The release patterns of other elements, like Mo (Fig. 2 e) and B (Fig. 2 h) were not linked to the mixtures' pH, but appeared to be controlled by overall loading rate and the inherent initial content by the CCPs.

Selenium release (Fig. 2 f) from non-limed coal refuse material declined over time, but was still at 0.1 mg L-1 after 170 days of leaching. Coal refuse that was amended with CCPs with low or no CCE (mixtures #18-10%, #18-20%, #11-10%, #11-20%) had very little effect on the leachate pH. However, addition of these CCps did suppress continued long-term release of Se.

Based on the SEP results (Appendix), we expected that As and Cr would have a lower solubility or "leachability" when compared to Mo and Se because they are found in less soluble/bioavailable forms. The TCLP data (Table 3) corroborated the results from the SEP. Although both As and Cr were found at higher total concentrations in the ash compared to Mo and Se, they were found in lower concentrations in the TCLP leachate. The SEP data also corresponded well to the column leachate data.

The oxidation of sulfidic material and associated formation of acid drainage resultrf in more rapid dissolution reactions and significant increases in solution EC (Fig. 2 b). The importance of controlling acid/base balance conditions in reactive refuse is reinforced by the effects of acidification on retention/release of specific elements. Acid formation and associated mineral phase dissolution generated very high leachate levels of S (Fig. 2 g) and Fe (data not shown), but perhaps of greater concern were the significant releases of As, Cr, Cu, and Zn. However, liming with agricultural lime (e.g. as in limed-control columns) or adding CCPs with adequate CCE largely prevented the release of these elements of concern due to acidification.

For differential treatment analysis, we compared the release patterns of elements from the control columns (both limed and no-lime) to those of the CCP amended columns. This allowed us to attribute the elements in the leachate to source, either the coal refuse or a specific CCP. Via this analysis, we conclude that weathering coal refuse was the primary source for As, Cu, Fe, Ni, S, and Se released to leachates. The CCPs were the primary source for B, Cr, and Mo.

Conclusions

- The pH of the leaching environment is most critical to the retention/release of the elements of interest.

- The liming potential of CCPs differed greatly, with a range in CCE of 0 to 52%. The potential peroxide acidity (PPA) test indicated a required liming rate for this coal refuse of 34.5 Mg/1000 Mg (tons/acre). Applying lime to the coal refuse at this rate has maintained the pH of the limed coal refuse control columns in the range of 7.2 to 7.9, further supporting the accuracy and utility of this lime estimation technique.

- Using CCPs as liming agents contributed to additional leaching of Mo and B. The Cr introduced into the system by the CCP is leached only if the pH level drops to < 3.0. Amending coal refuse with CCPs with adequate CCE was very effective in preventing high solute concentrations and leaching losses of As, Cu, Se, Ni, Zn and Cr.

Overall Summary and Conclusions

The results of our combined studies to date reveal several important overall considerations for safely managing CCPs in mining environments. Overall, it’s clear that many present-day CCPs have substantial liming ability; much more than seen in our studies in the early and mid-1990’s. The greenhouse trials reported here reveal that CCPs can be quite effective as topical mine soil amendments, but loading rates must be constrained to avoid over-liming or application of excess bulk salts, both of which limit plant growth of even tolerant species like tall fescue. The SEP approach to fractional characterization of the CCPs’ mineral phase for critical elements is very useful and cost effective. It gives important indications of the potential implications for utilization on mined lands and storage of CCPs in general. The very diverse chemical properties of the CCPs will necessitate detailed chemical characterization of each CCP prior to its use in open environments. We are encouraged by the obvious bulk liming capacity of a number of the CCPs utilized, and by the relative lack of leaching of elements of environmental concern when the CCPs were utilized at relatively high loading rates.

The column leaching data reemphasized the importance of the work reported by Daniels, et al., (2002) and Stewart et al, (1997, 2001) on acid-base balance of CCPs’ use to control AMD. The column leachate data indicated that acidic coal refuse can be a potential source of As and Se, but that certain fly ash materials may also be local sources of a range of potential mobile oxyanions like B and Mo.

Benefits for Southwestern Virginia

The appropriate utilization of CCPs on and in southwest Virginia coal mines could directly improve water quality via the offset of acid mine drainage production and increased mine soil productivity. The southwest Virginia coal and transportation industries could also realize substantial efficiencies and improved marketing arrangements through the back-haul of CCPs from coal-fired utilities. However, any such large-scale utilization of CCPs on or in mined landscapes must appropriately balance potential benefits against any long term potentials for water quality degradation via losses of potentially mobile constituents such as B and Mo. Acidic coal refuse can be a source of leachable As and Se. Significant benefit of reduced AMD can be obtained from amending acidic coal refuse with CCPs with high liming capacity. This also reduces significantly the risk of As and Se leaching losses. The column leaching study also showed that CCPs with little or no liming capacity are effective in controlling As and Se release from acidic coal refuse

Acknowledgements

We greatly appreciate the support of the Powell River Project, Alpha Natural Resources (Matt Cartier), American Electric Power (Greg Keenan and Claudia Banner) and Dominion - Virginia Power (Ron Birckhead). The financial support of Virginia DMLR and OSM over the 2005/2006 project year was also critical to the completion of work reported here. The assistance of Julie Burger and W.T. Price in the laboratory is also appreciated.

Literature Cited

Barnhisel, R. I. and J. Harrison. 1976. Estimating lime requirement by a modified hydrogen peroxide potential acidity method. (Unpublished method for KY Agr. Ex. Sta., Soil Testing Laboratory) Lexington, KY.

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

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.

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., USA.

Rhoades, J.D. 1982. Soluble salts. *in* Methods of soil analysis, Part 2. Chemical and Microbiological Properties. ASA-SSSA.

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.

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.

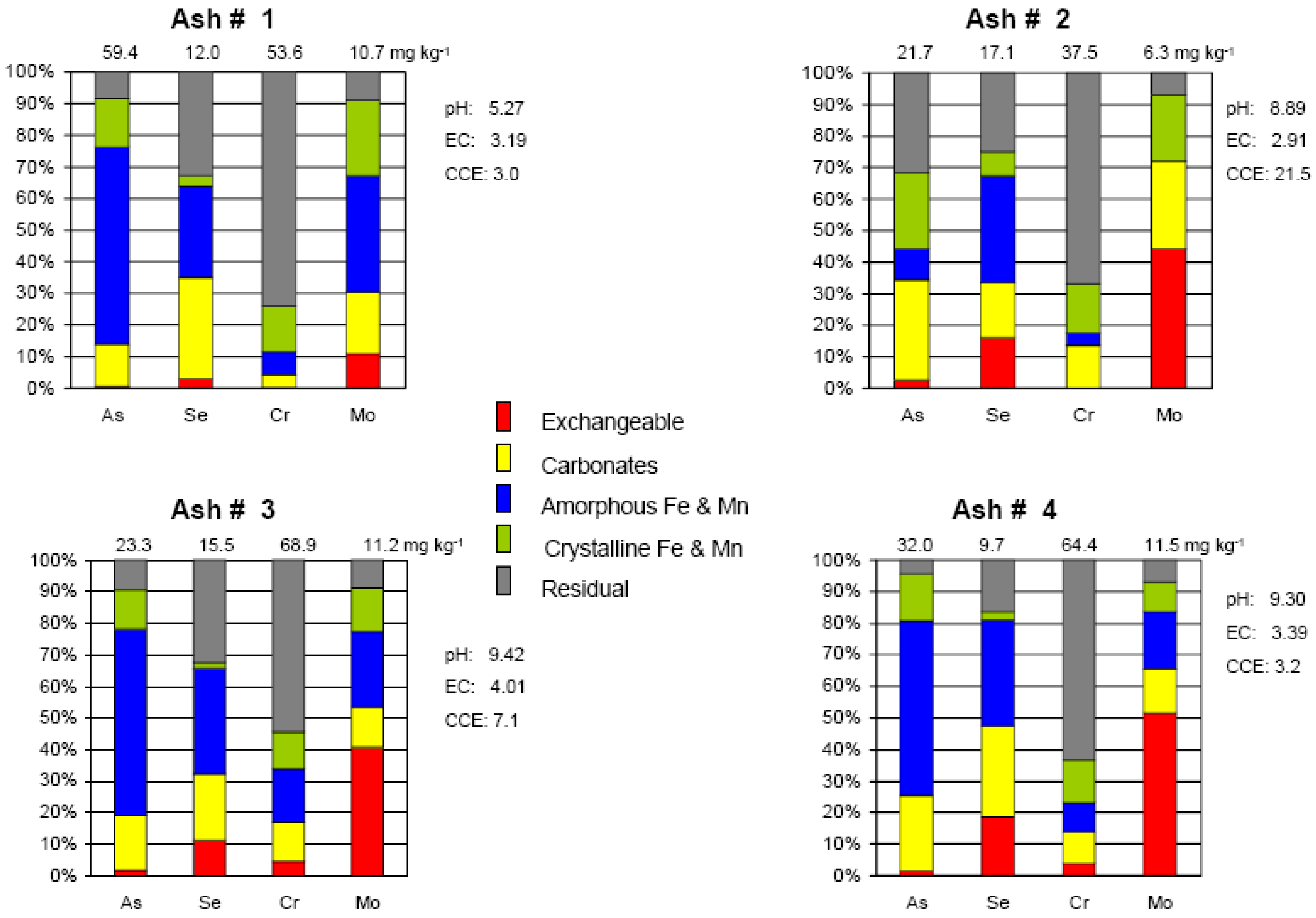
Tessier, A., P.G.C. Campbell, and M.Bisson. 1979. Sequential extraction procedure for the speciation of particulate trace metals. Analytical Chemistry, vol. 51, no.7, pp. 844 – 850.

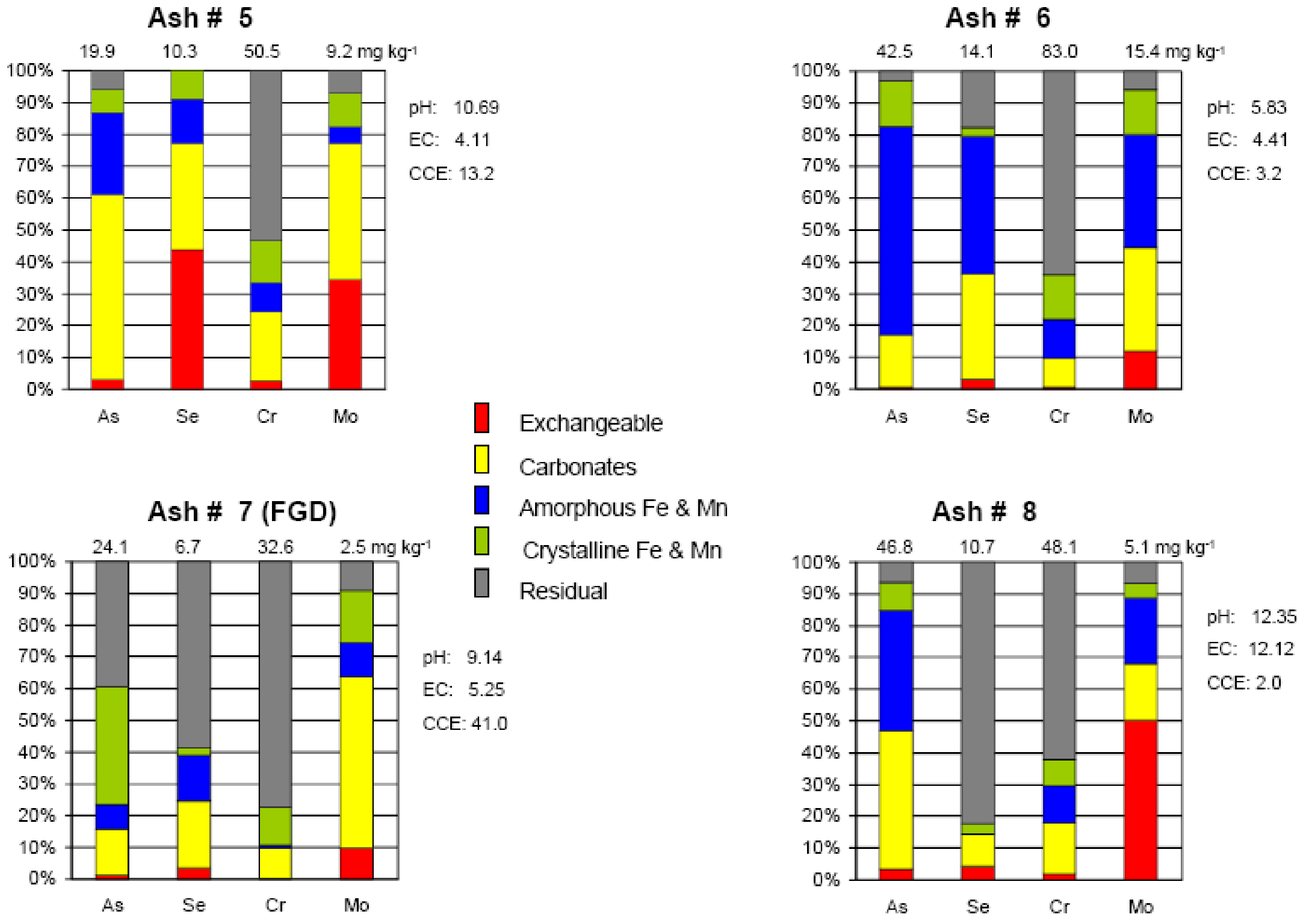
U.S.EPA, 2003. Introduction to hazardous waste identification (40 CRF Parts 261). http://www.epa.gov/epaoswer/hotline/training/hwid.pdf

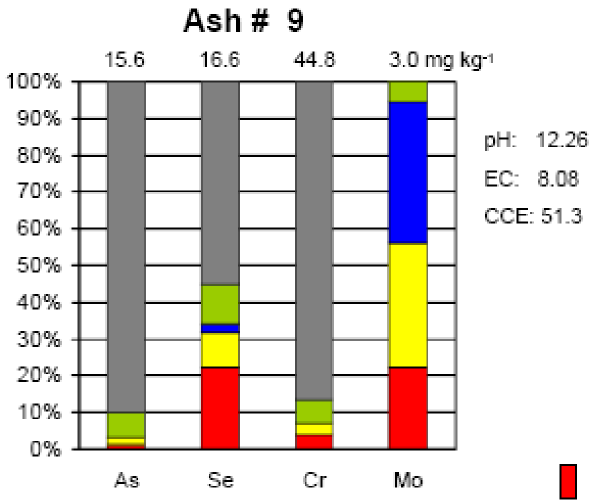
U.S. Environmental Protection Agency. 1992. Toxicity characteristic leaching procedure. Method 1311, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods (SW-846), 35pp.

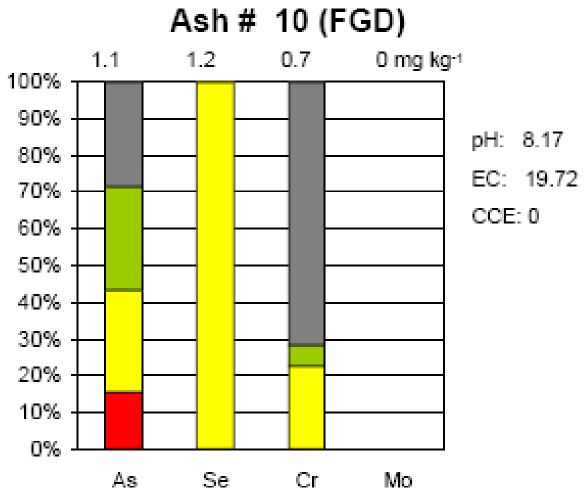
APPENDIX A – Following Pages

Data of the sequential extraction procedure for 28 CCPs are the mean in three replications.


Ash # 1
59.4
12.0
53.6
10.7 mg kg⁻¹
pH: 5.27
EC: 3.19
CCE: 3.0
Ash # 2
21.7
17.1
37.5
6.3 mg kg⁻¹
pH: 8.89
EC: 2.91
CCE: 21.5
Ash # 3
23.3
15.5
68.9
11.2 mg kg⁻¹
pH: 9.42
EC: 4.01
CCE: 7.1
Ash # 4
32.0
9.7
64.4
11.5 mg kg⁻¹
pH: 9.30
EC: 3.39
CCE: 3.2
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
As
Se
Cr
Mo
Exchangeable
Carbonates
Amorphous Fe & Mn
Crystalline Fe & Mn
Residual


Ash # 5
19.9
10.3
50.5
9.2 mg kg-1
pH: 10.69
EC: 4.11
CCE: 13.2
Ash # 6
42.5
14.1
83.0
15.4 mg kg-1
pH: 5.83
EC: 4.41
CCE: 3.2
Ash # 7 (FGD)
24.1
6.7
32.6
2.5 mg kg-1
pH: 9.14
EC: 5.25
CCE: 41.0
Ash # 8
46.8
10.7
48.1
5.1 mg kg-1
pH: 12.35
EC: 12.12
CCE: 2.0
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
As
Se
Cr
Mo
🟥 Exchangeable
🟨 Carbonates
🟦 Amorphous Fe & Mn
🟩 Crystalline Fe & Mn
⬜ Residual





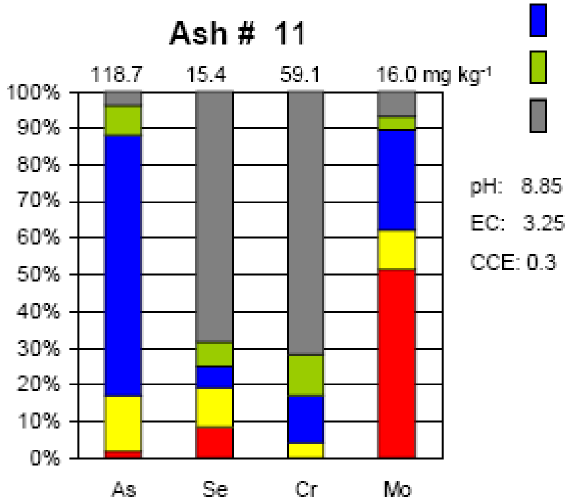
🟥 Exchangeable

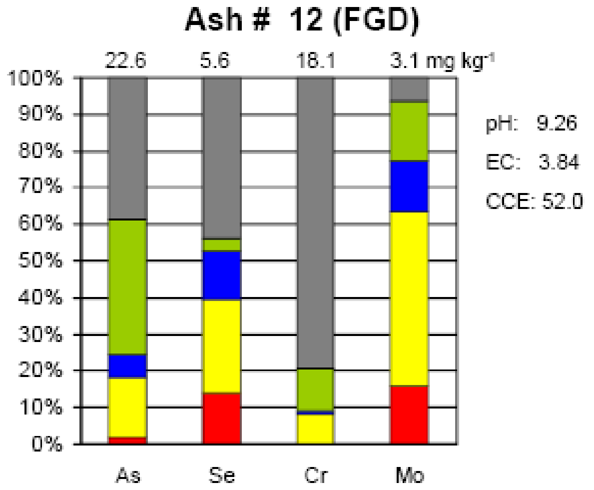
🟨 Carbonates

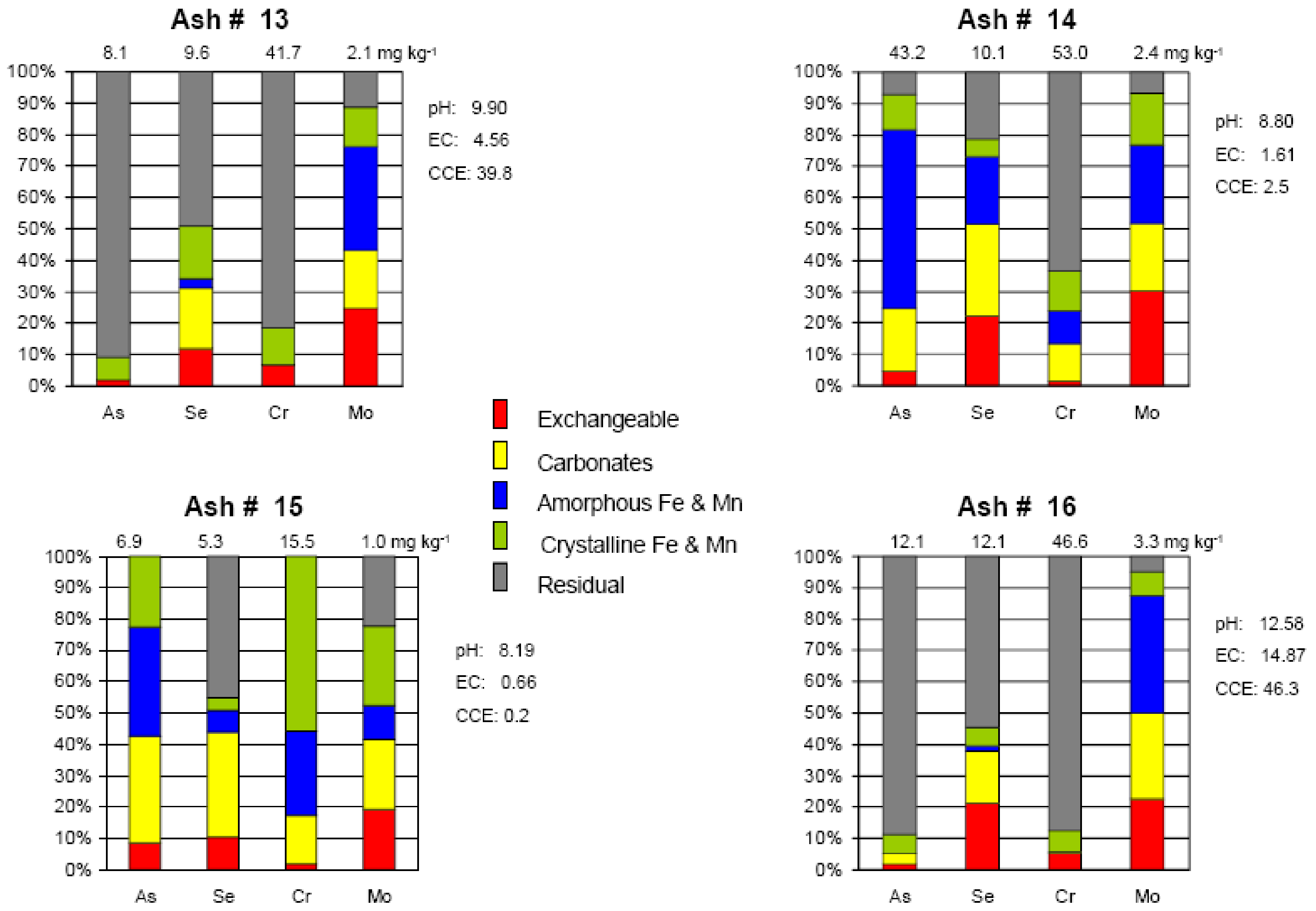
🟦 Amorphous Fe & Mn

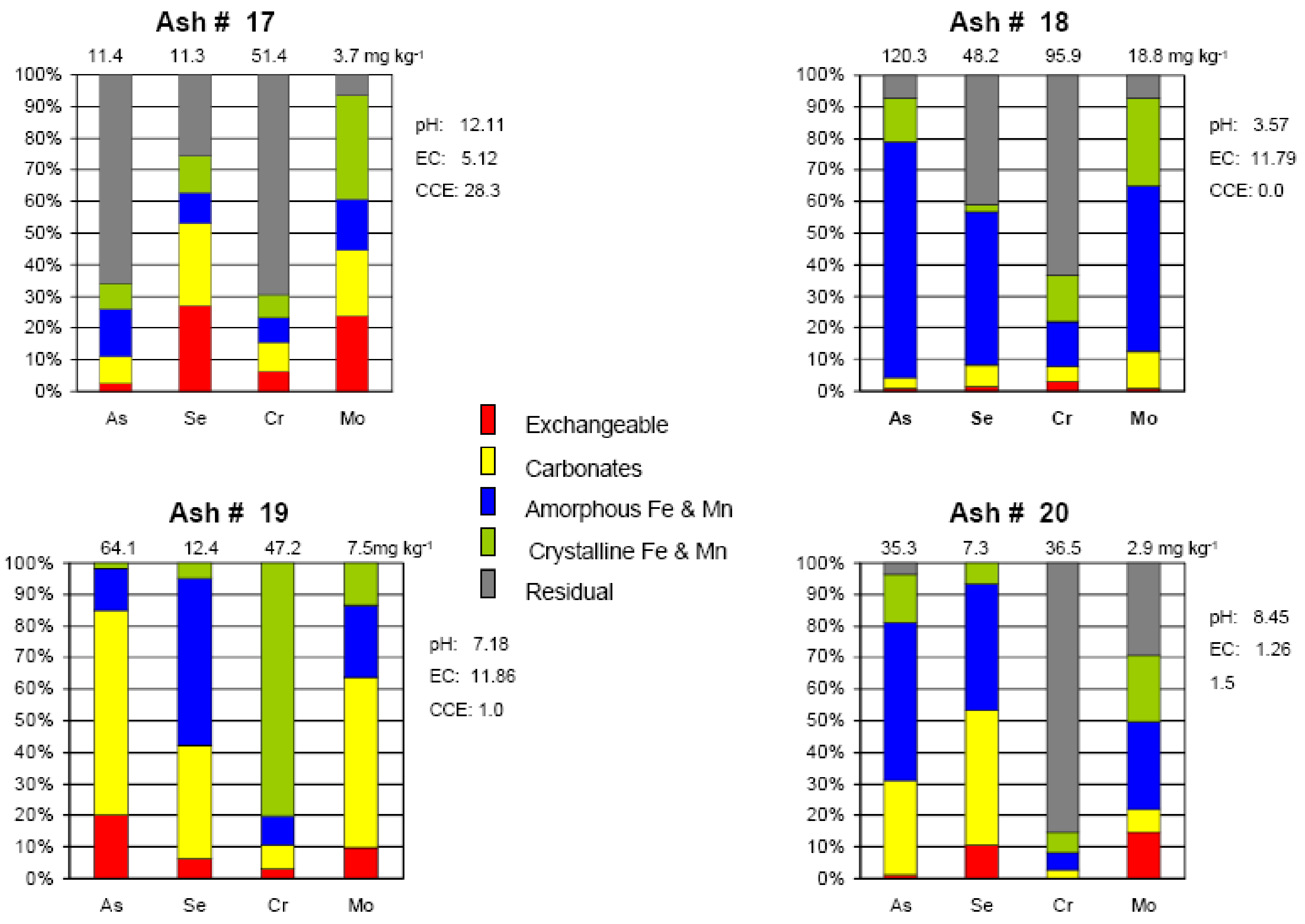
🟩 Crystalline Fe & Mn

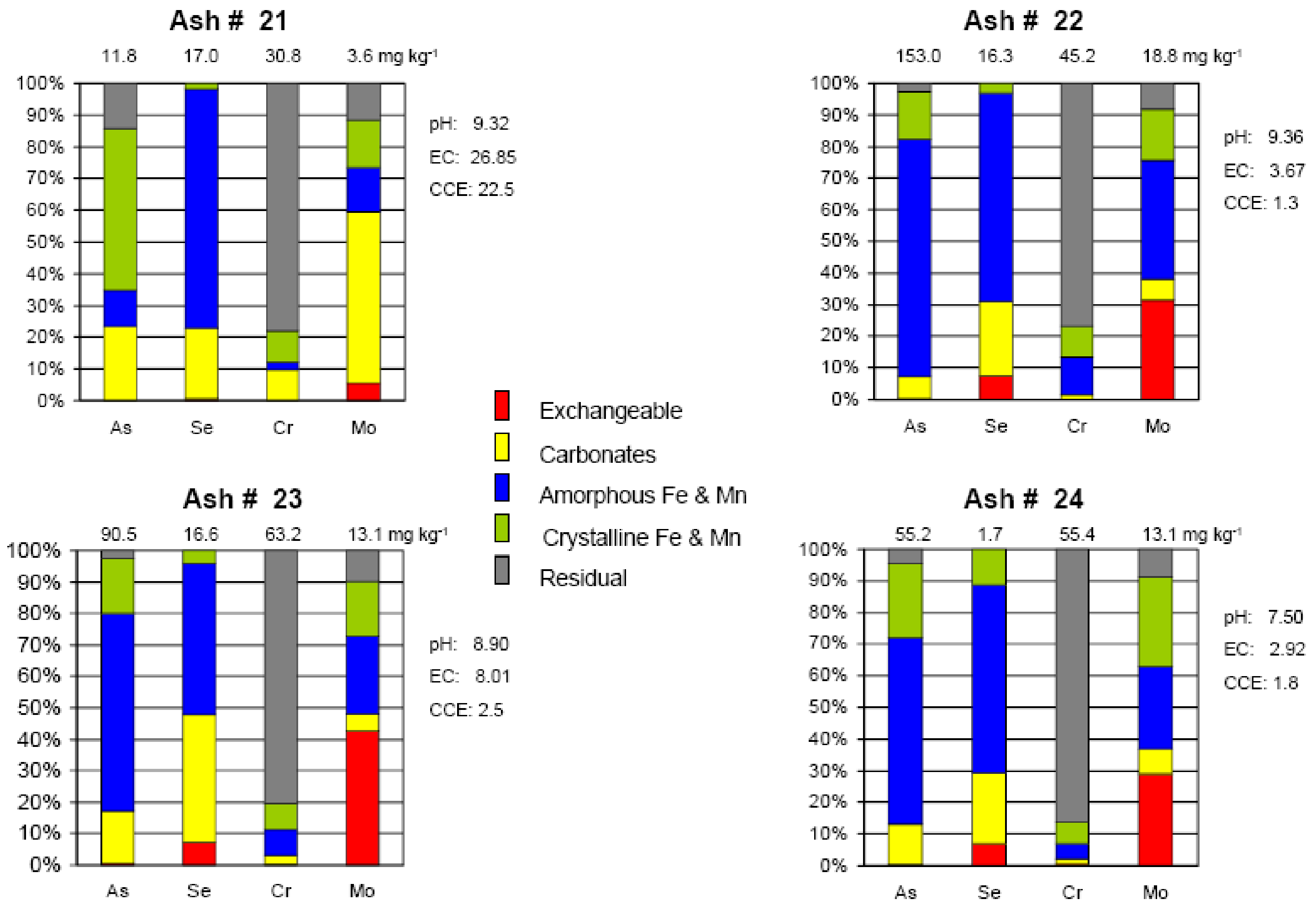
⬛ Residual



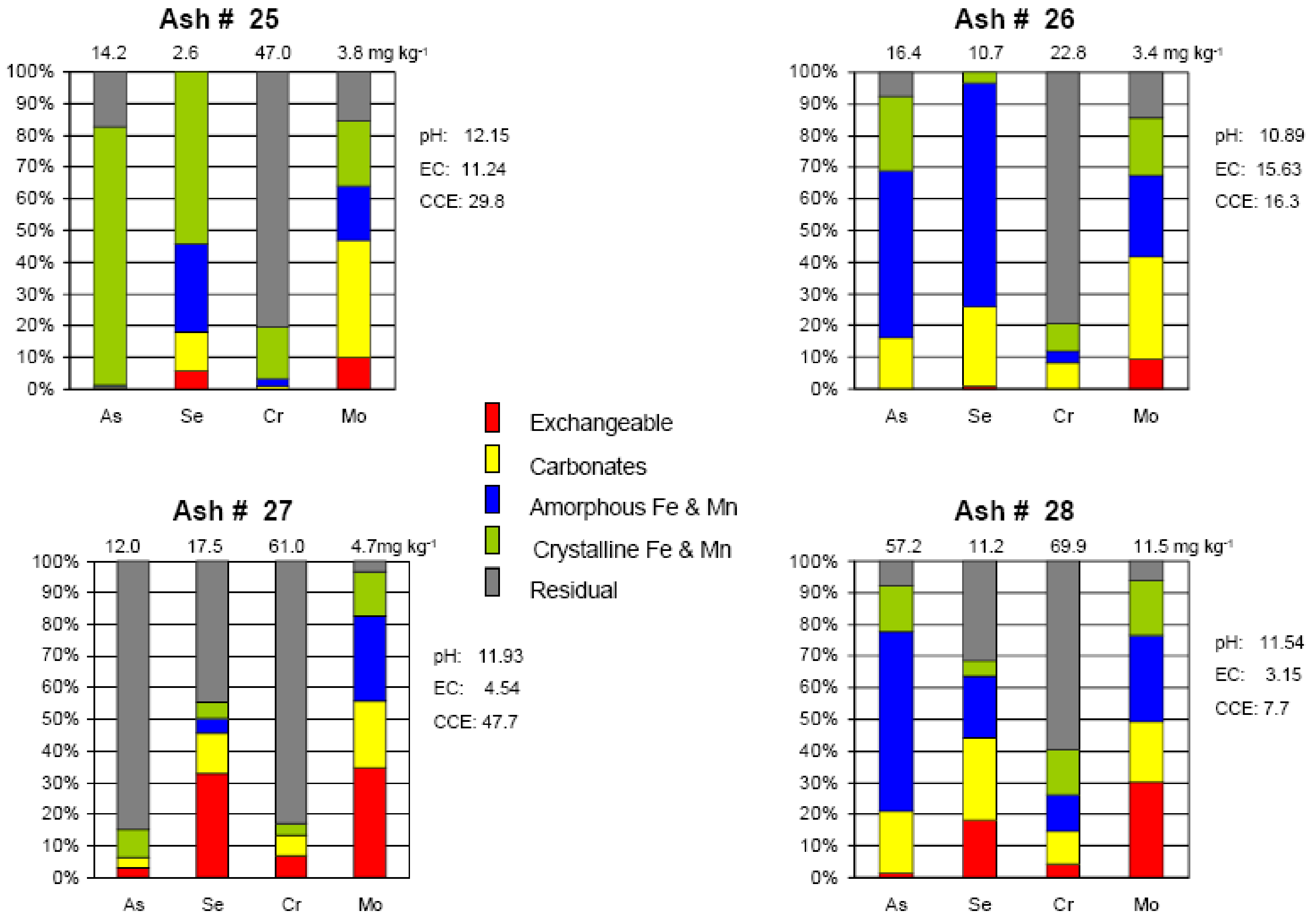



Ash # 13
8.1
9.6
41.7
2.1 mg kg⁻¹
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
As
Se
Cr
Mo
pH: 9.90
EC: 4.56
CCE: 39.8
Ash # 14
43.2
10.1
53.0
2.4 mg kg⁻¹
pH: 8.80
EC: 1.61
CCE: 2.5
🟥 Exchangeable
🟨 Carbonates
🟦 Amorphous Fe & Mn
🟩 Crystalline Fe & Mn
⬛ Residual
Ash # 15
6.9
5.3
15.5
1.0 mg kg⁻¹
pH: 8.19
EC: 0.66
CCE: 0.2
Ash # 16
12.1
12.1
46.6
3.3 mg kg⁻¹
pH: 12.58
EC: 14.87
CCE: 46.3


Ash # 17
11.4
11.3
51.4
3.7 mg kg-1
pH: 12.11
EC: 5.12
CCE: 28.3
Ash # 18
120.3
48.2
95.9
18.8 mg kg-1
pH: 3.57
EC: 11.79
CCE: 0.0
Ash # 19
64.1
12.4
47.2
7.5mg kg-1
pH: 7.18
EC: 11.86
CCE: 1.0
Ash # 20
35.3
7.3
36.5
2.9 mg kg-1
pH: 8.45
EC: 1.26
1.5
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
As
Se
Cr
Mo
Exchangeable
Carbonates
Amorphous Fe & Mn
Crystalline Fe & Mn
Residual



Ash # 21
11.8 17.0 30.8 3.6 mg kg⁻¹
100% 90% 80% 70% 60% 50% 40% 30% 20% 10% 0%
As Se Cr Mo
pH: 9.32
EC: 26.85
CCE: 22.5
Ash # 22
153.0 16.3 45.2 18.8 mg kg⁻¹
100% 90% 80% 70% 60% 50% 40% 30% 20% 10% 0%
As Se Cr Mo
pH: 9.36
EC: 3.67
CCE: 1.3
🟥 Exchangeable
🟨 Carbonates
🟦 Amorphous Fe & Mn
🟩 Crystalline Fe & Mn
⬛ Residual
Ash # 23
90.5 16.6 63.2 13.1 mg kg⁻¹
100% 90% 80% 70% 60% 50% 40% 30% 20% 10% 0%
As Se Cr Mo
pH: 8.90
EC: 8.01
CCE: 2.5
Ash # 24
55.2 1.7 55.4 13.1 mg kg⁻¹
100% 90% 80% 70% 60% 50% 40% 30% 20% 10% 0%
As Se Cr Mo
pH: 7.50
EC: 2.92
CCE: 1.8


Ash # 25
14.2
2.6
47.0
3.8 mg kg-1
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
As
Se
Cr
Mo
pH: 12.15
EC: 11.24
CCE: 29.8
Ash # 26
16.4
10.7
22.8
3.4 mg kg-1
pH: 10.89
EC: 15.63
CCE: 16.3
Exchangeable
Carbonates
Amorphous Fe & Mn
Crystalline Fe & Mn
Residual
Ash # 27
12.0
17.5
61.0
4.7mg kg-1
pH: 11.93
EC: 4.54
CCE: 47.7
Ash # 28
57.2
11.2
69.9
11.5 mg kg-1
pH: 11.54
EC: 3.15
CCE: 7.7