

Final Report - OSM Applied Science Research Program

**Predicting Contaminant Leaching Potentials for Central
Appalachian Overburden and Coal Refuse Materials.**

Principal Investigators:

W. Lee Daniels, Mike Beck, Matt Eick and Zenah Orndorff

**Dept. of Crop and Soil Environmental Sciences
Virginia Tech
Blacksburg, VA 24061
wdaniels@vt.edu; 540-231-7175**

December 7, 2009

TABLE OF CONTENTS

EXECUTIVE SUMMARY	VI
INTRODUCTION AND OVERALL OBJECTIVES.....	1
GENERAL RESEARCH APPROACH AND SPECIFIC TASKS	2
MATERIALS AND METHODS	2
Mineralogy and Geologic Association	2
Mine Spoil, Coal Refuse, and Leachate Analytical Methods.....	5
RESULTS OF INITIAL CHARACTERIZATION.....	6
Chemical Properties of 25 Samples	6
Total Elemental Analysis and Fractional Distribution by SEP of 25 Samples.....	9
Selection of Samples for the Column Leaching Trial	15
Experimental Procedures for Column Leaching Trial.....	16
RESULTS OF LEACHING COLUMN TRIAL	17
pH	18
EC	20
TDS	20
Bicarbonate	23
Sulfate	23
B.....	26
Na.....	26
Ca.....	26
Se	26
Fe	26
Mn.....	26
COMPOSITION OF TOTAL DISSOLVED SOLIDS (TDS)	33
SUMMARY AND CONCLUSIONS	38
IMPORTANT FINDINGS FROM THIS STUDY.....	40
REFERENCES.....	41
APPENDIX A	44
APPENDIX B	49

LIST OF TABLES

		Page #
Table 1.	Geologic description and associated information for 15 mine spoil and 10 coal refuse samples collected for this study.	3
Table 2.	Selected chemical properties of the 25 study samples.	7
Table 3.	Results of Mehlich-1 dilute acid extractions, pH (2:1 water:soil), and bioavailable extractable B for the 25 study samples.	8
Table 4.	Results of sample total elemental analysis for selected elements.	10

LIST OF FIGURES

	Page #
Figure 1a-e. Results of sequential extraction procedure (SEP) presented as fractional distribution of total elemental content.	11
Figure 2. Leachate pH from selected mine spoils, coarse coal refuse, and fine coal refuse under saturated and unsaturated conditions.	19
Figure 3. Leachate EC from selected mine spoils, coarse coal refuse, and fine coal refuse under saturated and unsaturated conditions.	21
Figure 4. Leachate TDS from selected mine spoils, coarse coal refuse, and fine coal refuse under saturated and unsaturated conditions.	22
Figure 5. Bicarbonate leached from selected mine spoils, coarse coal refuse and fine coal refuse under saturated and unsaturated conditions.	24
Figure 6. Sulfate leached from selected mine spoils, coarse coal refuse and fine coal refuse under saturated and unsaturated conditions.	25
Figure 7. Leachate B leached from selected mine spoils, coarse coal refuse and fine coal refuse under saturated and unsaturated conditions.	27
Figure 8. Leachate Na leached from selected mine spoils, coarse coal refuse and fine coal refuse under saturated and unsaturated conditions.	28
Figure 9. Leachate Ca leached from selected mine spoils, coarse coal refuse and fine coal refuse under saturated and unsaturated conditions.	29
Figure 10. Leachate Se leached from selected mine spoils, coarse coal refuse and fine coal refuse under saturated and unsaturated conditions.	30
Figure 11. Leachate Fe leached from selected mine spoils, coarse coal refuse and fine coal refuse under saturated and unsaturated conditions.	31
Figure 12. Leachate Mn leached from selected mine spoils, coarse coal refuse and fine coal refuse under saturated and unsaturated conditions.	32
Figure 13a-c. Quantitative distribution of major elements in leachate solutions and the respective TDS values from mine spoil.	35

Figure 14.	Leachate Al from selected mine spoils, coarse coal refuse and fine coal refuse under saturated and unsaturated conditions.	44
Figure 15.	Leachate K from selected mine spoils, coarse coal refuse and fine coal refuse under saturated and unsaturated conditions.	45
Figure 16.	Leachate Mg from selected mine spoils, coarse coal refuse and fine coal refuse under saturated and unsaturated conditions.	46
Figure 17.	Leachate Mo from selected mine spoils, coarse coal refuse and fine coal refuse under saturated and unsaturated conditions.	47
Figure 18.	Leachate Si from selected mine spoils, coarse coal refuse and fine coal refuse under saturated and unsaturated conditions.	48
Figure 19.	Leachate pH of each replicate from selected mine spoil, coarse refuse, and fine coal refuse samples under saturated and unsaturated conditions.	49

Executive Summary

The primary goal of this research program was to determine the leaching potential of a number of contaminants of concern (As, Cr, Mo, Se, total dissolved solids - TDS, and others) from overburden spoils and coarse/fine coal refuse. Over the winter/spring of 2008, we collected 25 bulk field samples of mine spoils and coal refuse (coarse/fine) from SW Virginia and E Kentucky and analyzed them via total and sequential extraction analyses to evaluate the distribution, solubility and bioavailability of elements of concern. From this sample set, we selected 3 spoils and 3 pairs of coarse/fine refuse samples for column leaching. These 9 materials were then column leached (saturated and unsaturated) for 45 leaching events (four months) and leachates analyzed for pH, electrical conductance (EC), TDS, metals and oxyanions of concern.

The pH of the spoil and refuse samples was generally in the neutral to alkaline range which is typical of fresh, relatively unweathered materials from this region. The soluble salt content (by EC) was low with the exception of several mine spoils and refuse samples. The total S content of these materials was also relatively low. Surprisingly, paired coarse/fine refuse samples showed no consistent differences in %S, calcium carbonate equivalence (CCE) or potential acidity, however, Mehlich-1 extractable Ca was substantially higher in fine refuse. Pairing of weathered mine spoil vs. unweathered mine spoils indicated weathered mine spoils had lower pH as expected. The bulk spoil and refuse samples represented a broad range in elemental content, yet did not include extreme values for any elements analyzed with the exception of relatively high As ($> 30 \text{ mg kg}^{-1}$) in several samples. The fractional distribution of As, Cr, Mo, and Se indicated that across all materials, these elements occur primarily in recalcitrant mineral fractions (e.g. crystalline oxides and residual). Therefore, under normal coal mining fill leaching conditions we would predict low solubility/bioavailability and leaching potentials.

In the column leaching experiment, both unweathered mine spoils and fine refuse generated high initial TDS levels (500 to $> 5000 \text{ mg L}^{-1}$) which dropped quickly to relatively constant levels ($< 1000 \text{ mg L}^{-1}$) in all but two samples. As expected, leachate pH, bicarbonate, Ca, Fe, Mn and sulfate elution were all directly related to fundamental internal acid-base reactions and water saturation. Levels of Se released into initial leachates were significant relative to the current drinking water standard (0.050 mg L^{-1}), even though total Se was relatively low in these samples and predicted to be recalcitrant. Leachate concentrations of other elements of interest such as As, Be, Cr, Cu, Mo, Ni and Zn were at or below detection limits ($\leq 0.010 \text{ mg L}^{-1}$). With respect to TDS composition, bicarbonate, Ca, K, Mg, Na, and sulfate were predominant. Under saturated conditions, spoil leachate TDS was dominated by sulfate and bicarbonate. Under unsaturated conditions spoil TDS components were more variable due to acid-base reactions driven by sulfide oxidation and carbonate neutralization interactions. Refuse samples released higher levels of Na than spoils. Surprisingly, this study revealed no major significant or consistent difference between coarse and fine refuse materials for most parameters of long term leaching concern.

Our results indicate that relatively straightforward batch extraction procedures such as the sequential fractionation procedure utilized here can be quite useful in predicting the relative “leachability” of many elements of interest. Sequential extraction correctly predicted that very little As, Cr and Mo would leach from these materials under the conditions present in the columns. However, that same procedure predicted that very little of the total Se in these samples would leach, which was incorrect.

Introduction and Overall Objectives

This document is submitted as a final report to the Office of Surface Mining (OSM) to document our efforts on the cooperative research program entitled *Predicting Contaminant Leaching Potentials for Central Appalachian Overburden and Coal Refuse Materials*. Until recently, regulation and monitoring of coal mine discharges to surface and ground-waters in the central Appalachian coalfields (WV-VA-TN) focused primarily on pH, Fe and Mn. Associated research at Virginia Tech over the past decade (Daniels et al., 1996 & 2002; Stewart et al., 2001) documented the 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 ground-water. However, recent reports of elevated Se discharges from valley fills in West Virginia have heightened agency and public concerns (e.g. Hansen and Christ, 2005) that a number of additional contaminants of concern (As, Cr, Mo, Se, etc.) could potentially be mobilized from coal spoil and processing waste fill environments. Work funded in the past three years by the coal industry and OSM (Daniels et al., 2006) also indicated that (A) significant leaching of oxyanions (As, Se, Mo) occurs when refuse/CCP mixtures remain at high pH (> 9.0), but that significant release of many of these same elements occurs directly from unamended coal refuse as it acidifies over time. In contrast, a recent internal study by the Virginia Division of Mined Land Reclamation (DMLR, 2005) found relatively low levels of these elements in Virginia coalfield streams.

To date, our work (and that of our regional colleagues) has focused almost entirely on leaching potentials from coarse coal refuse with very little effort being focused on fine refuse (slurry) which may be disposed of in a number of differing environments. The leaching of both mine spoils and refuse materials is also a primary source of total dissolved solids (TDS) discharges and their subsequent effect on surface water quality in mined areas. Chapman et al. (2000) and other recent studies have implicated bulk TDS as a major stressor upon receiving streams in the coalfields. Thus, the primary focus of this work was to determine the net leaching potential of a number of contaminants of concern (As, Cr, Mo, Se, TDS and others) from overburden spoils and coarse/fine coal refuse materials that have not been studied in detail to date. A secondary objective was to use our combined results to evaluate short-term batch extraction procedures vs. longer term leaching predictive tools.

Objectives

- I. To obtain a representative regional sample set of mine spoils and coal refuse (fine + coarse) and to determine total elemental composition and relative solubility of As, Cr, Mo, Se and other elements of interest.
- II. To characterize the potential leaching behavior of selected mine spoil, coarse coal refuse, and fine coal refuse slurries via column leaching analyses for the elements of interest as well as TDS, electrical conductance (EC), and pH.
- III. To determine the relationships among the relative solubility of these elements of interest in the materials studied, their column leaching behavior, and relevant literature and field observations.

General Research Approach and Specific Tasks

To achieve these objectives, we first worked with our coal industry cooperators (via the Powell River Project) to collect a representative set of spoil and coarse/fine refuse samples for our region. Over the winter and spring of 2008, we were able to collect a total of 25 field samples of bulk mine spoil and coal refuse (coarse and fine) from 12 different locations (Table 1). The samples were processed and characterized for physical properties and geologic association. We then subjected those samples to an array of batch and sequential extraction analyses to evaluate total and fractional pools of various elements of concern. From this larger sample set, we selected 3 spoils and 3 pairs of coarse/fine refuse samples to subject to column leaching studies (where the coarse and the fine refuse were “paired” from the same prep-plant processing a particular mix of coal seams). These 9 materials were placed into columns and subjected to saturated and unsaturated leaching conditions for a period of four months. The leachates were analyzed for pH, EC, TDS, metals and oxyanions of concern. Those results were then related to the initial chemical characteristics of the various materials and their fractional distributions. We then looked for relationships between the various extraction techniques and the quantities of various elements eluted from the leaching columns over time. The data sets and results were also related to existing and emerging data on field occurrence of these parameters, particularly Se, TDS and TDS components.

Materials and Methods

Mineralogy and Geologic Associations

Fifteen mine spoil and ten coal refuse samples were collected from six mine sites in southwest Virginia and eastern Kentucky. Geologic descriptions and associated information for all 25 samples are presented in Table 1. Six of the refuse samples were eventually used in the column leaching study. Of the fifteen spoil samples, three (OSM 2, OSM 3, and OSM 11) were evaluated in the leaching columns. Sample OSM 2 was dominantly (~93%) dark gray carbonaceous silty mudstone (seat rock), with about 6% fine-grained, unweathered, gray sandstone and siltstone, and 1% coal fragments. This spoil was produced from the Four Corners Formation of the Breathitt Group, and is associated with the Hazard #7 and Hazard #8 coal seams. Sample OSM 3 consisted of approximately 50% highly weathered feldspathic sandstone, with lesser amounts of unweathered silty mudstone (30%), unweathered sandstone (10%), weathered silty mudstone (8%), and coal fragments (2%). This spoil was produced from the middle of the Wise Formation and is associated with the Imboden coal seam. Sample OSM 11 was dominantly weathered sandstone, with trace amounts of silty mudstone. This spoil was produced from upper-middle Wise Formation and is associated with the Taggart and Taggart Marker coal seams. All of these mine spoil samples were associated with major surface mining activity and valley fills in SW Virginia and E Kentucky. As mentioned above, six (3 pairs) of the 10 collected coal refuse samples were also used in the leaching columns.

Table 1. Geologic description and associated information for 15 mine spoil and 10 coal refuse samples collected for this study. Samples used in the column leaching study and are **noted in bold font**. Coal refuse samples are shown in red font.

Lab-ID	Material	Geologic Description	Geologic formation	Coal Seam	Particle size %	
					< 1 cm	> 1 cm
OSM 1	Mine spoil Unweathered	98% unweathered, gray and orange, medium to coarse grained, feldspathic sandstone; 2% unweathered gray silty mudstone. (No coal apparent.)	Norton	Raven1	23	77
OSM 2	Mine spoil Unweathered	93% dark gray carbonaceous silty mudstone; 6% unweathered, gray, fine-grained sandstone and siltstone; 1% coal.	Four Corners Formation; Breathitt Group	Hazard #7 and Hazard #8	60	40
OSM 3	Mine spoil Part. weathered	50% highly weathered, gray and orange, fine grained and medium to coarse grained, feldspathic sandstone; 30% unweathered gray silty mudstone ; 10% unweathered feldspathic sandstone; 8% unweathered gray silty mudstone; 2% coal.	Middle Wise	Kelly/Imboden	87	13
OSM 4	Mine spoil Weathered	98% weathered, reddish-brown silty mudstone; 1% weathered sandstone; 1% coal.	Lower Wise	Clintwood/Blair	85	15
OSM 5	Mine spoil Part. weathered	60% weathered feldspathic ss; 35% unweathered feldspathic sandstone; 4% unweathered silty mudstone; 1% coal.	Lower Wise	Clintwood/Blair	79	21
OSM 6	Mine spoil Unweathered	90% minimally weathered gray clayey siltstone; 10% brown silty mudstone; trace coal.	Lower Wise	Clintwood/Blair	79	21
OSM 7	Mine spoil Weathered	85% weathered brown-gray silty mudstone; 13% unweathered gray silty mudstone; 2% weathered sandstone. (No coal apparent.)	Middle Wise	Kelly/Imboden	62	38
OSM 8	Mine spoil Unweathered	99% unweathered gray silty mudstone; 1 % coal.	Middle Wise	Kelly/Imboden	69	31
OSM 9	Mine spoil Part. weathered	65% weathered and unweathered, gray and orange, medium grained feldspathic sandstone; 34% weathered and unweathered gray silty mudstone; 1% coal.	Middle Wise	Kelly/Imboden	49	51
OSM 10	Mine spoil Unweathered	97% unweathered gray silty mudstone; 2% coal; <1% unweathered sandstone; <1% brown shale.	Upper-middle Wise	Phillips	72	28

Note: Samples in **bold** print were used in the column leaching study

Table 1, Continued. Geologic description and associated information for 15 mine spoil and 10 coal refuse samples. Samples used in the column leaching study and are noted in a **bold font**. **Coal refuse samples are in red font**.

Lab-ID	Material	Geologic Description	Geologic formation	Coal Seam	Particle size %	
					< 1 cm	> 1 cm
OSM 11	Mine spoil Weathered	99% weathered sandstone; 1% silty mudstone; trace coal.	Upper-middle Wise	Taggart	68	32
OSM 12	Mine spoil Unweathered	98% unweathered, gray, medium grained sandstone; 1% weathered sandstone; 1% silty mudstone.	Upper-middle Wise	Taggart	45	55
OSM 13	Mine spoil Part. weathered	60% weathered and unweathered, medium to coarse grained, feldspathic sandstone; 40% very fine grained gray sandstone. (No coal apparent.)	Middle Wise	Bolling (Imboden) (as reported by mine operator)	64	36
OSM 14	Mine spoil Weathered	80% weathered, gray and orange, feldspathic sandstone; 20% gray silty mudstone. (No coal apparent.)	Lower Wise	Clintwood/Blair	65	35
OSM 15	Mine spoil Unweathered	100% light and dark gray unweathered siltstone. (No coal apparent.)	Lower Wise	Clintwood/Blair	47	53
OSM 16*	Coarse refuse	Carbonaceous shales, mudstones and coal.	Norton	Lower Banner, Jawbone, and Splashdam	45	55
OSM 22	Fine refuse	Carbonaceous shales, mudstones and coal	Norton		100	0
OSM 17	Coarse refuse	Shales, mudstones and coal mixture	Norton		46	54
OSM 23	Fine refuse	Shales, mudstones and coal mixture	Norton		100	0
OSM 18	Coarse refuse	Shales, mudstones and coal mixture	Upper-middle Wise	Taggart, Taggart	46	54
OSM 19	Fine refuse	Shales, mudstones and coal mixture	Upper-middle Wise	Marker, Phillips and Standiford	100	0
OSM 20	Coarse refuse	Shales, mudstones and coal mixture	Pikeville	Amburgey	na	na
OSM 24	Fine refuse	Shales, mudstones and coal mixture	Pikeville		100	0
OSM 21	Coarse refuse	Shales, mudstones and coal mixture	Norton	Norton, Lower	57	43
OSM 25	Fine refuse	Shales, mudstones and coal mixture	Norton	Banner	100	0

*The sample numbers as shown here are out of order to more readily indicate the “pairing” of the fine and coarse refuse samples according to common sources (preparation plant).

Mine Spoil, Coal Refuse, and Leachate Analytical Methods

- All analyses were conducted in triplicate unless specifically noted otherwise.
- pH and Electrical Conductance (EC) (Rhoades, 1982) were determined on saturated paste extracts from the materials. Each spoil or refuse sample was mixed with deionized (DI) water until it formed a glistening paste. The paste was filtered after equilibration for ≥ 2 hours and 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 inductively coupled plasma emission spectrometry (ICPES, type FTMOA85D, Spectro Analytical Instruments, Inc).
- Total elemental analysis was determined by USEPA 3050B digestion followed by analysis by ICPES. This work was performed by SGS-Canada due to an equipment failure in our labs.
- 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 using a series of increasingly aggressive extractants. We modified the method for use on potentially high sulfate materials by substituting MgSO_4 with MgCl_2 in the first extraction step. We also omitted the extraction step for elements associated with soil organic matter. The sample size used for extraction was 5.0 g at a solution:solid ratio of 5:1. The procedure involved 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.
- Mehlich-1 extraction (0.05M HCl + 0.025M H_2SO_4) was utilized to estimate weak acid (or plant available) B, Ca, Fe and P (Mehlich, 1953) followed by ICPES.
- Peroxide potential acidity (PPA) was determined by a modified hydrogen peroxide oxidation technique as described by Orndorff et al. (2008). The method oxidizes all sulfides with 30% H_2O_2 and assumes net internal reaction of acids formed with carbonates and other neutralizers. Total net acidity is determined by whole sample titration following full reaction.
- Total S was run via combustion on an Elementar CNS analyzer.
- The calcium carbonate equivalence (CCE) was determined via AOAC method FM-871.
- Dissolved inorganic carbon (IC) and total carbon (TC) in column leachates (see later column methods section) were run on the Sievers 900 Laboratory TOC.

- Simulated acid precipitation (pH 4.8) was prepared according to Halvorson & Gentry (1990) and used in the leaching columns.
- Total dissolved solids in column leachate solutions were determined according to USEPA method 160.1 (USEPA, 2008).

Results of Initial Characterization

Chemical Properties of 25 Samples

Presented in Table 2 are selected chemical properties of the full sample set. The pH of the samples was generally in the neutral to alkaline range which is typical of fresh, relatively unweathered materials from this region due to hydrolysis reactions involving broken primary mineral grains and carbonate dissolution. Only a few of the mine spoils were slightly acidic with no sample pH below 6.2. The soluble salt content (by EC) was low with the exception of several mine spoils and refuse samples. Samples with elevated EC values appeared well related to either the potential acidity (as estimated by PPA) and/or CCE. It is interesting that some samples (e.g. OSM 21) that were high in potential acidity (by PPA) would have been predicted to be non-acid forming using a conventional acid-base accounting approach where all the total S (e.g. 1.27 % or 40 T/1000 T maximum acidity for OSM 21) would be assumed to be sulfidic and balanced against the CCE (5.6% or 56 T/1000 T net neutralizers). Only three out of the 25 samples had a total sulfur content of > 0.70%, which again is not unusual for the region sampled. Somewhat surprisingly, paired coarse and fine refuse samples showed no consistent differences in %S, CCE or PPA. We had assumed that finely divided reactive pyrites would have been selectively concentrated into the fine refuse, but this appears not to be the case for these facilities and their associated coal cleaning technologies.

Dilute acid extractable (bioavailable) B concentrations were very low for all samples (Table 3). The results of the Mehlich-1 extraction (Table 3) also showed no unusually high concentrations of Zn, Cu (data not shown) or Fe and Mn. As expected, based on the moderate to high initial pH values, the extractable Ca levels were high for most samples. The comparison of the pH values determined by saturated paste (Table 2) versus pH determined in a 2:1 water:sample mix, generated lower pH values by the 2:1 method for the samples at pH < 7.0. This may well be due to the difference in equilibration time (much longer for the saturated paste method) that may have allowed some of the alkaline mineral surfaces to react with acidic components.

Direct comparisons of properties from weathered mine spoils versus unweathered mine spoils showed that weathered mine spoils had lower pH (Table 3) as expected. Only one weathered sample (OSM #7) had a neutral pH, 7.03, the other weathered samples all had pH values between 5.22 and 5.74. The pH among the partially weathered/unweathered mine spoils followed the trend that those with higher percentages of weathered material generated lower pH. The same trend held for Mehlich-1 extractable Ca, Fe, and Mn values as reported in Tables 3. The paired samples of coarse versus fine coal refuse revealed only one particular trend: Mehlich-1 extractable Ca was substantially higher in fine refuse than in coarse refuse. This, however, may be strictly a particle size (greater surface area) response rather than potentially different chemical composition of the refuse.

Table 2. Selected chemical properties of the 25 study samples. **Coal refuse samples in red font.**

Lab-ID	Material	Saturated paste		PPA*	CCE**	Total S
		pH	EC dS m ⁻¹	- Tons CCE / 1000 Tons	%	%
OSM 1	MS unweathered	6.88	1.27	0	2.7	0.06
OSM 2	MS unweathered	7.04	3.48	0	4.6	0.23
OSM 3	MS partly weath.	6.93	0.94	3.58	1.3	0.07
OSM 4	MS weathered	6.46	0.29	0.22	1.6	0.03
OSM 5	MS partly weath.	6.23	0.90	0.15	0.7	0.04
OSM 6	MS unweathered	7.26	1.40	0	2.1	0.14
OSM 7	MS weathered	7.66	0.20	0.12	4.7	0.03
OSM 8	MS unweathered	7.58	0.47	0.24	5.9	0.18
OSM 9	MS partly weath.	7.72	0.40	0	5.9	0.08
OSM 10	MS unweathered	7.85	0.66	0	6.0	0.11
OSM 11	MS weathered	6.28	0.56	0.28	3.7	0.03
OSM 12	MS unweathered	7.84	0.40	0	5.3	0.12
OSM 13	MS partly weath.	7.59	0.28	0	4.7	0.04
OSM 14	MS weathered	7.49	0.36	0.12	3.4	0.03
OSM 15	MS unweathered	8.18	0.67	0	8.3	0.09
OSM 16	Coarse refuse	9.13	0.99	0.06	6.2	0.26
OSM 22	Fine refuse	8.43	0.83	0	6.0	0.74
OSM 17	Coarse refuse	8.34	2.07	0	4.9	0.21
OSM 23	Fine refuse	8.12	1.52	0	6.9	0.49
OSM 18	Coarse refuse	9.03	0.96	2.20	5.0	0.41
OSM 19	Fine refuse	7.58	2.79	10.45	6.0	0.62
OSM 20	Coarse refuse	9.03	0.70	2.23	6.5	0.32
OSM 24	Fine refuse	8.44	1.07	3.69	5.1	0.37
OSM 21	Coarse refuse	8.75	0.90	31.16	5.6	1.27
OSM 25	Fine refuse	8.10	1.16	0.61	6.6	0.76

* Potential Peroxide Acidity (PPA). Values shown represent net acidity/lime demand.

** Calcium Carbonate Equivalent (CCE)

Samples in **bold** are those selected for the column leaching study

MS = Mine spoil

Coal Refuse Pairs: Coarse & fine refuse from same source material at prep-plant

= OSM # 16 & 22, OSM # 17 & 23, OSM # 18 & 19, OSM # 20 & 24, OSM # 21 & 25

Table 3. Results of Mehlich-1 dilute acid extractions, pH (2:1), and bioavailable extractable B for the 25 study samples. **Coal refuse samples in red font.**

Lab-ID	Material	pH 2:1	B*	P	Ca ----- mg Kg ⁻¹ -----	Fe -----	Mn -----
OSM 1	MS unweathered	7.98	0.17	46	1148	202	65
OSM 2	MS unweathered	7.14	0.52	79	1594	277	71
OSM 3	MS partly weath.	5.24	0.46	7	1902	65	46
OSM 4	MS weathered	5.22	0.43	11	560	44	36
OSM 5	MS partly weath.	5.34	0.50	21	563	91	91
OSM 6	MS unweathered	7.02	0.37	39	1930	143	102
OSM 7	MS weathered	7.03	0.53	65	1064	63	49
OSM 8	MS unweathered	7.55	0.22	86	936	224	17
OSM 9	MS partly weath.	8.10	0.29	54	1546	305	65
OSM 10	MS unweathered	8.14	0.55	85	1544	230	75
OSM 11	MS weathered	5.24	0.23	18	473	78	53
OSM 12	MS unweathered	8.64	0.18	47	1907	309	29
OSM 13	MS partly weath.	7.96	0.21	63	1087	88	113
OSM 14	MS weathered	5.74	0.34	10	618	46	56
OSM 15	MS unweathered	8.63	0.26	23	3255	457	57
OSM 16	Coarse refuse	9.40	0.35	50	1834	295	26
OSM 22	Fine refuse	8.98	0.35	28	3878	231	26
OSM 17	Coarse refuse	8.40	0.28	14	3313	243	22
OSM 23	Fine refuse	8.30	0.49	2	4619	132	19
OSM 18	Coarse refuse	9.35	0.29	51	985	330	19
OSM 19	Fine refuse	6.60	0.33	29	3462	118	53
OSM 20	Coarse refuse	9.32	0.62	76	535	214	10
OSM 24	Fine refuse	9.32	0.65	63	1656	202	10
OSM 21	Coarse refuse	9.12	0.43	88	741	336	13
OSM 25	Fine refuse	9.02	0.38	62	2780	207	16

*Hot 0.01M CaCl₂ extractable B

Samples in **bold** are those selected for the column leaching study.

MS = Mine spoil

Coal Refuse Pairs: Coarse & fine refuse from same source material at prep-plant

= OSM # 16 & 22, OSM # 17 & 23, OSM # 18 & 19, OSM # 20 & 24, OSM # 21 & 25

Total Elemental Analysis and Fractional Distribution by SEP of 25 Samples

The sample elemental analysis data for a range of elements of interest are given in Table 4. The samples appear to represent a broad range in elemental content, yet they do not include extreme values for any of the elements relative to levels reported by Adriano et al. (1980). While a few of the refuse samples had relatively high As levels ($> 30 \text{ mg kg}^{-1}$), no other elements of concern had unusually high concentrations. Noticeable differences in elemental content between mine spoil and coal refuse samples appeared only for As, Ba, Ca, and Se, which were all higher in refuse. Direct comparison of total elemental content of weathered vs. unweathered mine spoils showed that as expected, weathered spoils were considerably leached of Ca compared to unweathered mine spoil. Interestingly, this was not the case for other basic cations like K and Mg.

The results of the sequential extraction procedure (SEP) for As, Cr, Mo, and Se are presented graphically in Figures 1 a-e. It is important to note that the total elemental values shown at the top of each bar are the sum of SEP fractions and vary somewhat from the total values reported in Table 4 due to differences in lab methods. These data do allow the assessment of the relative bioavailability of the high As content in certain samples (e.g. 47 mg kg^{-1} for coal refuse OSM #21). The first fraction (black bar fill in Figure 1) is the highly bioavailable water soluble + exchangeable fraction while the second carbonate bound fraction (red bar fill) would be expected to become bioavailable for root uptake or leaching over longer periods of time under acidic leaching conditions. Presumably, the non-crystalline Fe+Mn oxide bound forms of these elements (green bar fill in Fig. 1) will convert over to more highly crystalline and recalcitrant forms as these materials oxidize and weather. Regardless, the overall fractional distributions of As, Cr, Mo, and Se indicate that across all materials, these elements occurred primarily in the recalcitrant, weathering resistant mineral fractions (e.g. primarily in crystalline oxides and residual forms). This means that under normal coal mining fill environmental conditions, with the pH between 3.5 and 9.0, we would predict low solubility and subsequent leaching (Daniels et al., 2006). The consequences of extreme pH conditions beyond this range would be the dissolution and potential leaching of elements in the recalcitrant mineral fractions (fraction 4 & 5 of SEP). In a recent OSM funded study (Daniels et al., 2006) with coal refuse similar to sample OSM #21, leachate As concentrations of $> 5 \text{ mg L}^{-1}$ were eluted over more than 40 leaching events from columns where the pH dropped to < 3.5 . Approximately 64% of the total As content of the coal refuse leached during that period. We did not detect any particular patterns of differences in SEP fractions for the various elements between the mine spoils (weathered vs. unweathered), and the coal refuse (coarse vs. fine) samples.

As discussed earlier, the amount of total Se and its fractional distribution and leaching potential were of particular interest in this study. Total Se in mine spoil samples was less than 1 mg kg^{-1} , but those levels did increase uniformly in the coal refuse materials. The levels reported here and their relative distribution based on lithology were very similar to those recently reported by Vesper et al. (2008) for a suite of rocks and coal seams in the Kanawha Formation in nearby southern West Virginia. While our data do indicate that the vast majority of the Se in these materials was held in relatively recalcitrant forms, the ratio of Se held in crystalline Fe+Mn oxide bound vs. residual forms did vary considerably. Two samples (#21 and #25) did contain minor amounts of Se in more bioavailable/leachable forms. Vesper et al. (2008) also concluded that the form of Se varied considerably across the range of lithologies they studied.

Table 4. Results of sample total elemental analysis for selected elements. Analysis by SGS Canada. **Coal refuse samples in red font.**

ANALYTE	As	B	Ba	Cr	Cu	Mn	Mo	Ni	Se	Zn	Al	Ca	Fe	K	Mg	Na
Detection limit	3	10	1	1	0.5	2	0.05	1	1	0.5	0.01	0.01	0.01	0.01	0.01	0.01
Sample ID	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	%	%	%	%	%	%
OSM 1	4	<10	124	118	13.9	364	1.45	18	<1	48.1	0.70	0.21	1.97	0.21	0.26	0.04
OSM 2	7	<10	209	43	26.3	556	0.94	26	1	74.0	1.14	0.33	2.73	0.25	0.48	0.03
OSM 3	5	<10	85	68	26.4	320	0.83	23	<1	63.3	1.28	0.36	2.38	0.22	0.31	0.02
OSM 4	7	<10	172	38	33	652	0.8	29	<1	94.3	1.81	0.07	4.05	0.28	0.45	0.03
OSM 5	5	<10	105	73	12.8	406	1.99	16	<1	50.9	0.75	0.08	2.25	0.17	0.17	0.02
OSM 6	8	<10	159	29	30.7	559	4.68	30	1	88.3	1.51	0.34	3.58	0.26	0.53	0.03
OSM 7	10	<10	170	42	29.3	797	0.74	30	<1	94.0	1.63	0.17	4.26	0.28	0.53	0.03
OSM 8	5	<10	143	26	28.9	565	0.62	34	<1	98.0	1.30	0.21	3.54	0.23	0.52	0.03
OSM 9	5	<10	103	67	20.5	473	1.06	19	<1	58.3	0.93	0.33	2.55	0.18	0.46	0.03
OSM 10	5	<10	146	29	38.6	759	0.66	36	<1	108.0	1.57	0.36	3.97	0.28	0.74	0.03
OSM 11	5	<10	117	64	16.6	419	0.83	22	<1	61.4	1.23	0.07	2.81	0.19	0.25	0.03
OSM 12	5	<10	126	86	20.3	615	1.34	23	<1	62.5	0.91	0.38	2.87	0.21	0.45	0.03
OSM 13	3	<10	109	60	26.9	767	0.92	26	<1	75.1	1.02	0.22	3.77	0.23	0.47	0.03
OSM 14	8	<10	94	84	25.4	661	1.16	23	<1	64.1	1.19	0.09	3.71	0.2	0.25	0.03
OSM 15	7	<10	127	36	36.2	810	0.71	42	<1	101.0	1.60	0.89	4.50	0.31	0.97	0.04
OSM 16	15	<10	165	24	42.5	463	5.24	33	5	86.4	1.21	0.41	2.84	0.27	0.59	0.09
OSM 22	16	<10	246	18	39.1	344	0.91	27	3	89.9	0.90	0.84	2.47	0.22	0.46	0.05
OSM 17	8	<10	220	25	37.8	400	0.55	31	1	83.2	1.17	0.43	2.61	0.27	0.52	0.07
OSM 23	7	<10	379	28	39.9	282	1.26	22	2	60.3	1.00	1.26	2.61	0.29	0.44	0.06
OSM 18	11	<10	186	24	42.2	524	0.67	31	1	99.5	1.32	0.28	3.63	0.26	0.65	0.08
OSM 19	35	<10	181	24	43.5	548	1.1	37	2	114.0	1.30	0.84	4.00	0.26	0.73	0.03
OSM 20	14	<10	194	25	47.8	456	0.6	35	2	88.8	1.59	0.17	3.12	0.36	0.52	0.13
OSM 24	11	<10	194	19	39.9	226	0.51	23	2	71.9	0.78	0.29	1.77	0.27	0.31	0.08
OSM 21	57	<10	161	23	47.1	612	3.09	41	2	97.4	1.21	0.22	4.38	0.25	0.62	0.07
OSM 25	16	<10	327	33	37.4	377	1.34	28	2	73.5	0.90	0.68	2.36	0.23	0.44	0.07

Note: Hg was near below detection limit of 0.01 mg kg⁻¹ and not reported here.

Samples in **bold** are those selected for the column leaching study

Coal Refuse Pairs: OSM # 16 & 22, OSM # 17 & 23, OSM # 18 & 19, OSM # 20 & 24, OSM # 21 & 25

Figure 1a. Results of sequential extraction procedure (SEP) presented as fractional distribution of total elemental content. Total content (mg kg⁻¹) of respective element is given at the top of the bar graph. Presented are results for OSM samples # 1-6.

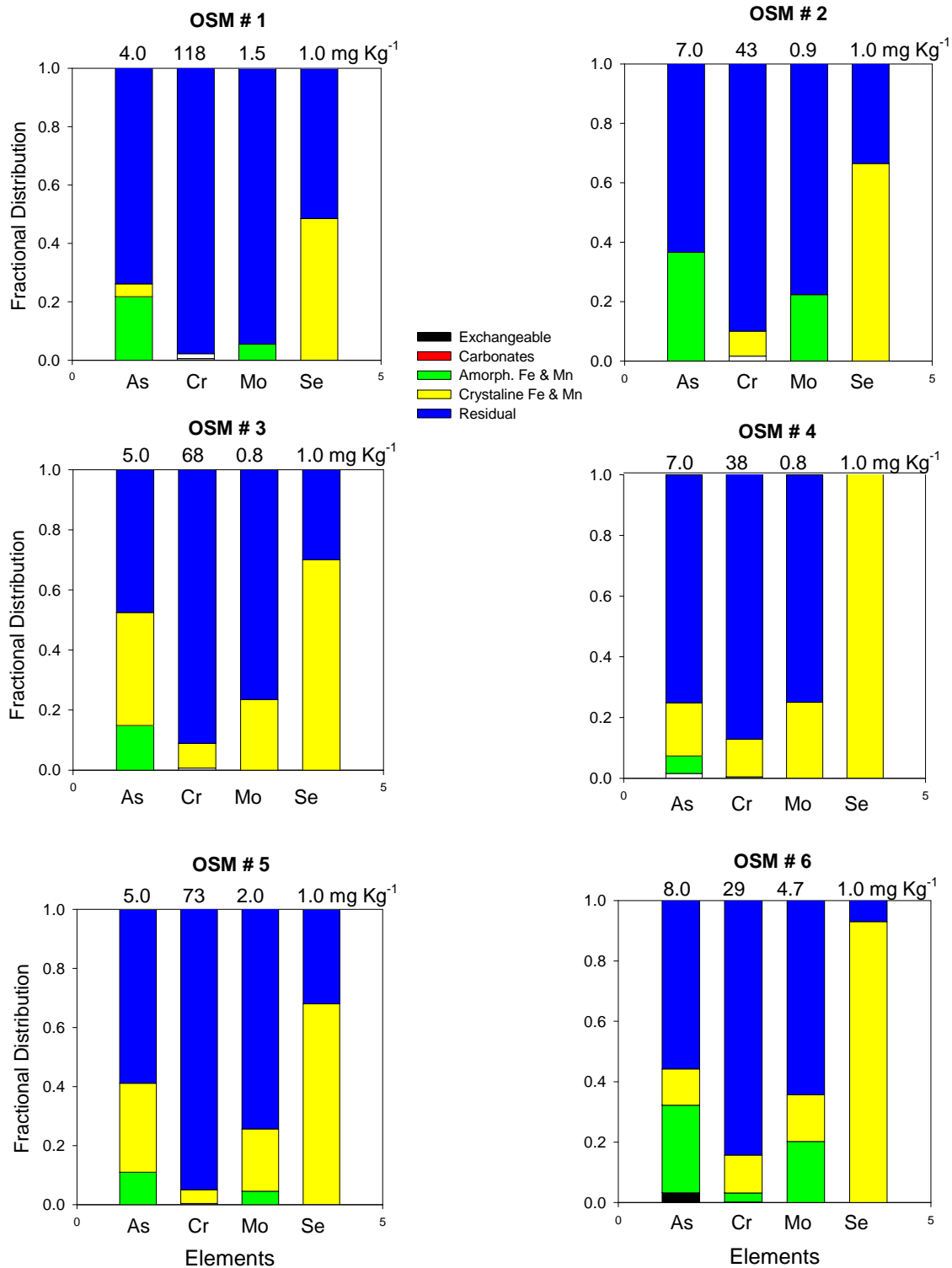


Figure 1b. Results of sequential extraction procedure (SEP) presented as fractional distribution of total elemental content. Total content (mg kg⁻¹) of respective element is given at the top of the bar graph. Presented are results for OSM samples # 7-12.

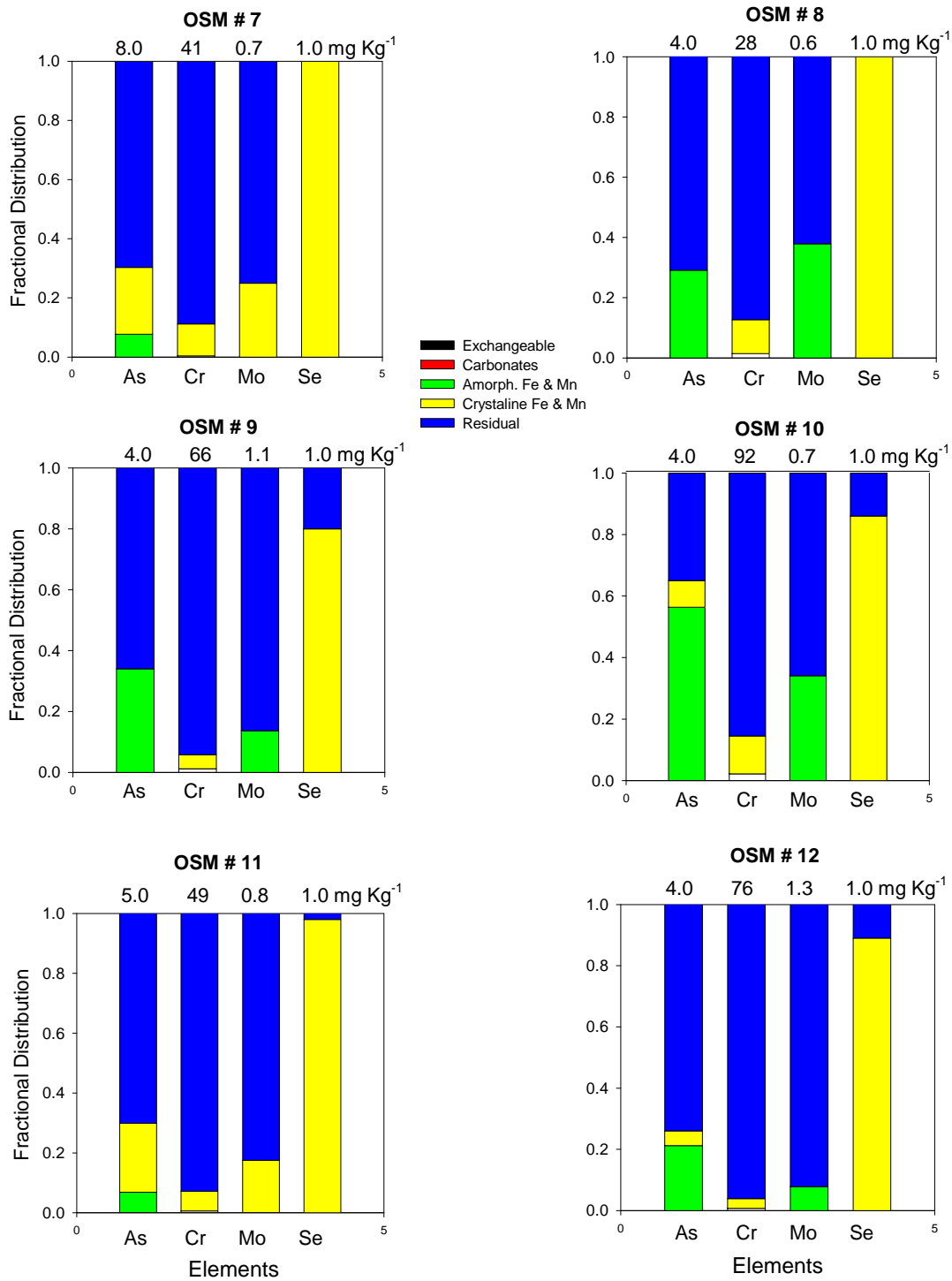


Figure 1c. Results of sequential extraction procedure (SEP) presented as fractional distribution of total elemental content. Total content (mg kg⁻¹) of respective element is given at the top of the bar graph. Presented are results for OSM samples # 13-18.

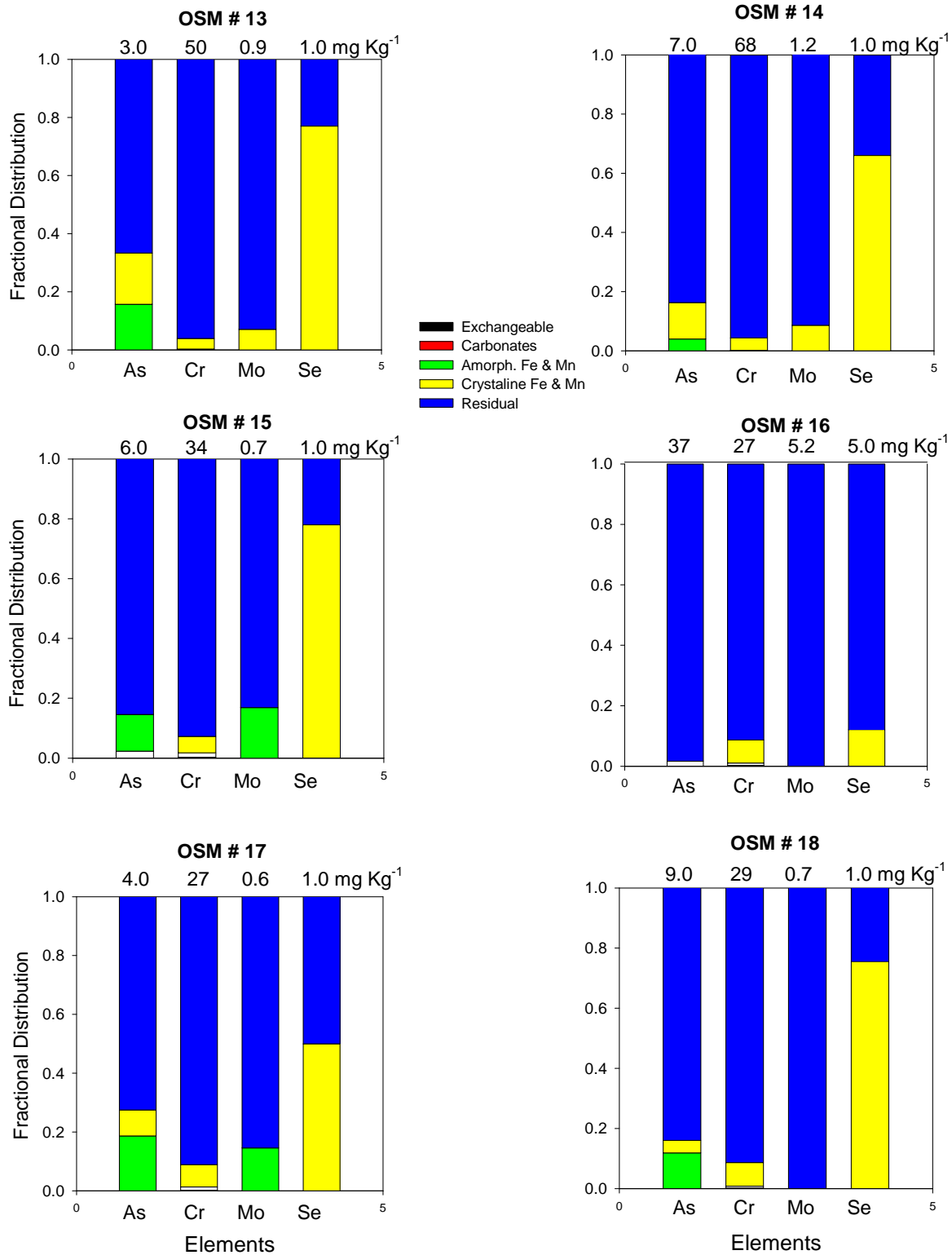


Figure 1d. Results of sequential extraction procedure (SEP) presented as fractional distribution of total elemental content. Total content (mg kg⁻¹) of respective element is given at the top of the bar graph. Presented are results for OSM samples # 19-24.

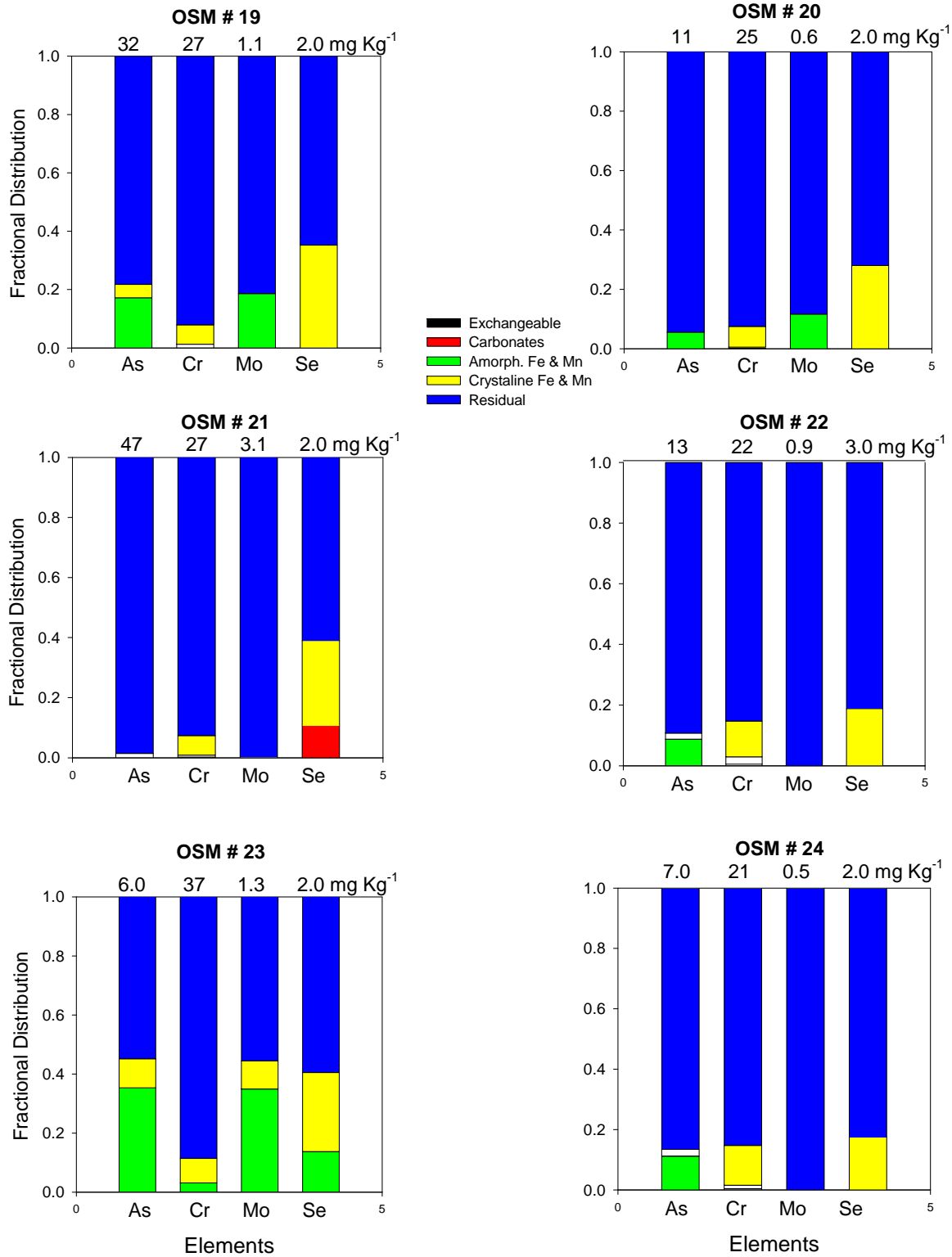


Figure 13a. Quantitative distribution of major elements in leachate solutions and the respective TDS values from mine spoil. Samples represent leaching events # 3, 12, 27, and 45. Values within charts represent total leachate analyses while the determined TDS value for filtered (< 2 μ) samples is given at top of each bar for each element.

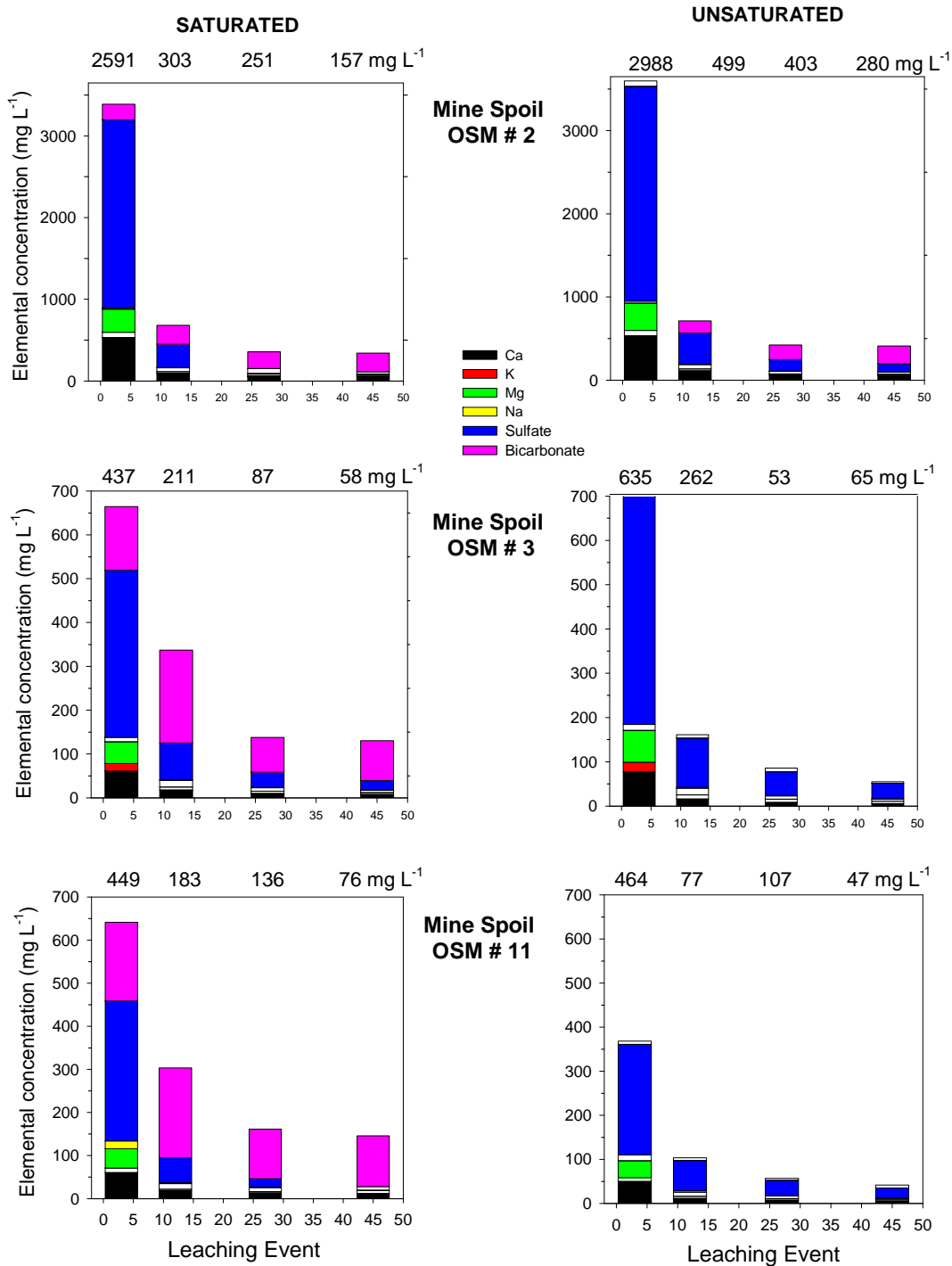


Figure 13b. Quantitative distribution of major elements in leachate solutions and the respective TDS values from coarse coal refuse. Samples represent leaching events # 3, 12, 27, and 45. Values within charts represent total leachate analyses. Values within charts represent total leachate analyses while the determined TDS value for filtered samples ($< 2 \mu$) is given at top of each bar for each element.

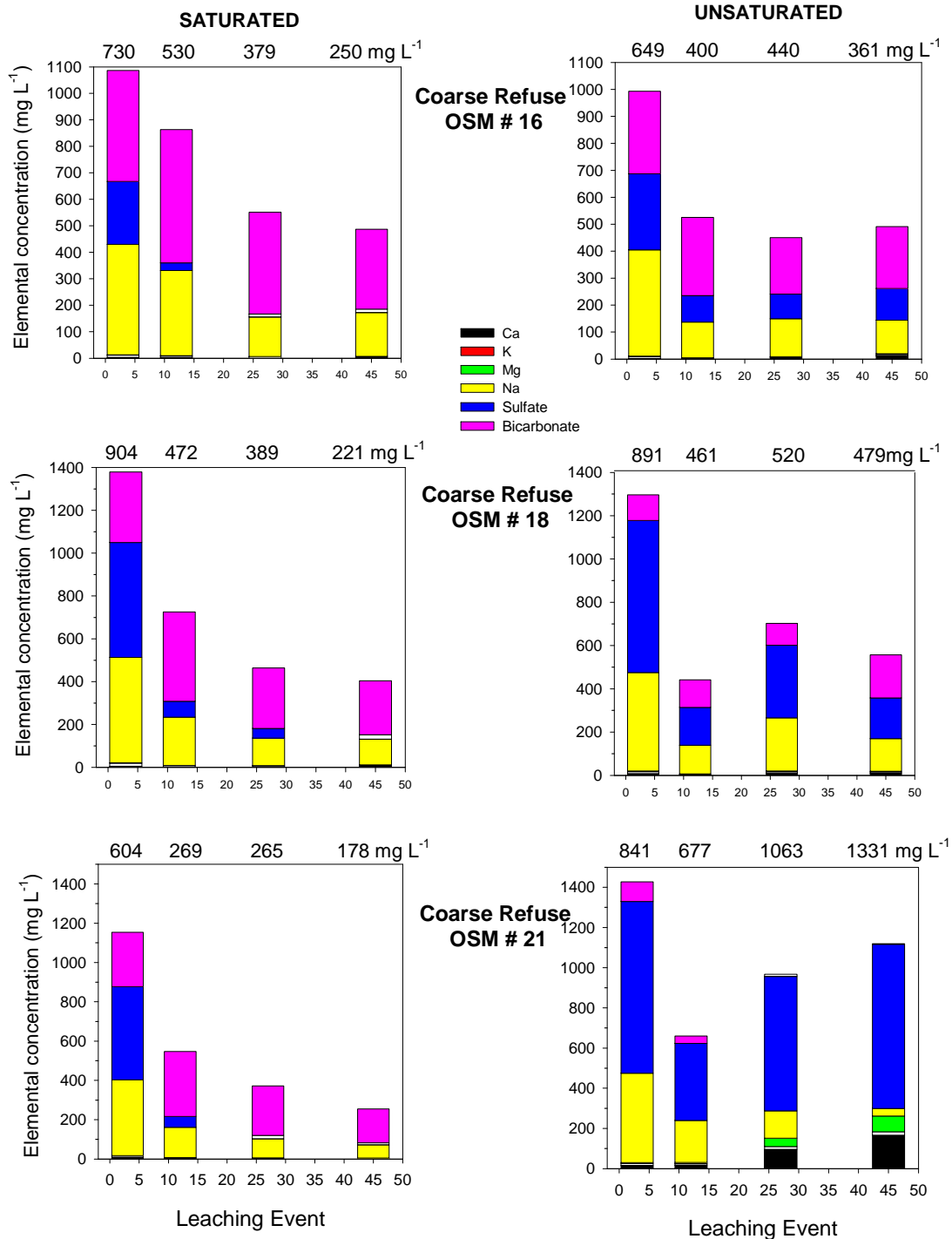
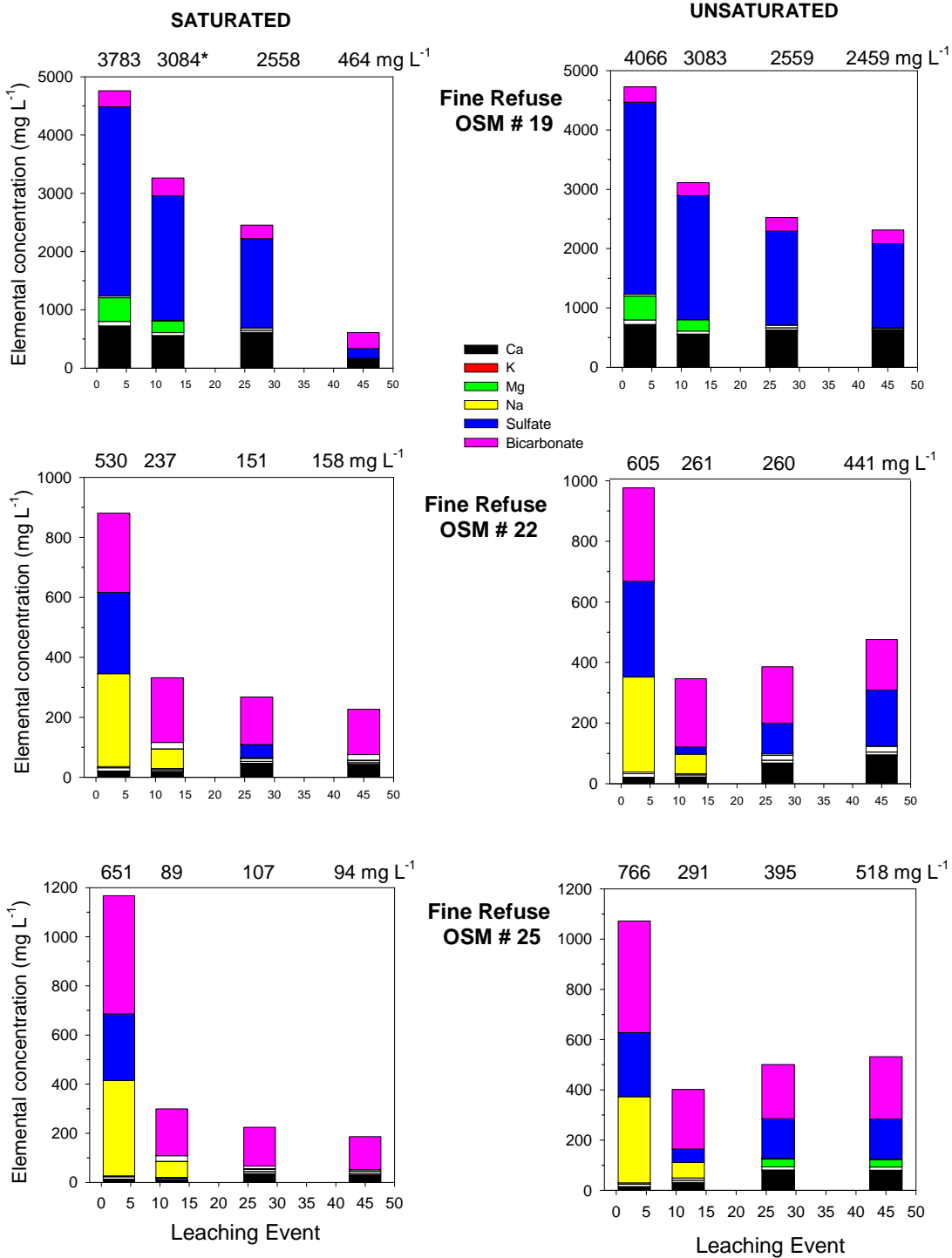


Figure 13c. Quantitative distribution of major elements in leachate solutions and the respective TDS values from fine coal refuse. Samples represent leaching events # 3, 12, 27, and 45. Values within charts represent total leachate analyses. Values within charts represent total leachate analyses while the determined TDS value for filtered samples ($< 2 \mu$) is given at top of each bar for each element.



As discussed earlier, fine refuse sample #19 was distinctly different from the other two fine refuse samples. Its leachate was strongly dominated by the sulfate ion with only a minor bicarbonate component. The overall leachate concentrations dropped with time due to declines of sulfate and other ions, with the exception of bicarbonate whose release remained constant over time. Under *saturated* conditions, the bicarbonate became the dominant ion in solution as the concentrations of the other companion ions dropped significantly. However, under *unsaturated* conditions the sulfate concentrations tended to stabilize and it remained the dominant ion, again indicating significant sulfide oxidation.

Summary and Conclusions

The 15 mine spoils sampled in this study were typical of surface mined overburden in the central and southern Appalachians in that they were largely non-acid forming and moderate (> 6.0) in initial pH and prolonged leachate pH effects. The 10 coal refuse samples (5 pairs of coarse & fine) were much more variable with potential acidities ranging from 0 to -31 tons of CCE lime demand per 1000 tons material and 0.21 to 1.27 % total S. The CCE of all materials tested was supposedly high enough to completely offset acid generation by sulfides, but one sample still generated net acid drainage over the study period, and several produced substantial sulfates. This reinforces that fact that standard acid-base accounting approaches to predict acid drainage are subject to a number of potential errors including their underlying assumption of similar rates of sulfide oxidation vs. carbonate dissolution. In this study, even though none of these samples was strongly acid forming, the version of the hydrogen peroxide oxidation test used (PPA) was a better predictor of which materials would produce large amounts of sulfate salts and TDS over time at the moderate pH levels observed in our columns.

Mine spoils that were significantly pre-weathered were lower in pH and Ca as expected. The samples appear to represent a broad range in elemental content, yet they did not include extreme values for any of the elements analyzed. The fractional distribution of As, Cr, Mo, and Se indicated that across all materials, these elements occurred primarily in recalcitrant mineral fractions (e.g. crystalline oxides and residual) that are presumably resistant to weathering and leaching. This means that under normal environmental conditions, with the pH between 3.5 and 9.0, there should be low solubility and subsequent leaching. Other metals (e.g. Cu, Ni and Zn) were also very low in leachate concentrations. Total Se in mine spoil samples was less than 1 mg kg⁻¹, but those levels did increase uniformly in the coal refuse materials as reported elsewhere (Vesper et al., 2008)

Due to their relatively high carbonate content (CCE), the majority of samples tested maintained a moderate pH (6.0 to 8.0) in leachates over the full study period (22 weeks). However, all samples eluted considerable levels (> 500 mg L⁻¹) of TDS (with high EC) over their initial leaching cycles and samples that contained significant reactive sulfides continued to elute high TDS levels for the duration of the study, regardless of their leachate pH values. Of the materials studied here, the fine refuse samples eluted the highest initial TDS (> 4000 mg L⁻¹), but two of the three fine refuse materials tested rapidly dropped to low levels of TDS/EC. However, prolonged and significant TDS release was observed from a shale spoil from Kentucky (saturated and unsaturated), one mine spoil (unsaturated) and one pair of coarse/fine refuse materials (saturated

and unsaturated). These differences in TDS release were all clearly related to basic sulfide oxidation reactions with subsequent generation of sulfate and other reaction and dissolution products.

The relative concentrations of Ca, bicarbonate, Fe, Mn, and SO_4^{-2} in column leachates over time were controlled primarily by acid-base reactions, pH solubility controls, and relative saturation. Leachate levels of As, Cr, Mo, and Ni were either below detection or very low due to the moderate pH conditions maintained by carbonate dissolution as discussed above. However, levels of Se released into initial leachates were significant relative to current drinking water MCL's of 0.050 mg L^{-1} . This was particularly true of total release from sample #3 (shale from Kentucky) and #19 (fine refuse from Virginia). It is also interesting to note that even though total Se was relatively low in these samples, and was predicted to be recalcitrant by sequential extraction, significant "first flush" leaching occurred.

The elemental composition of leachate solutions from our column leaching study was strongly affected by the saturated versus unsaturated conditions, but there were also differences within the sample groups, mine spoil, and coarse vs. fine refuse. Overall, TDS mass was dominated by six elements/compounds: (HCO_3^- , Ca, K, Mg, Na, and SO_4^{-2}). TDS release from the mine spoil samples was dominated by sulfate under unsaturated conditions and by sulfate and bicarbonate under saturated conditions. However, TDS release from coarse and fine coal refuse was very different and contained significant amounts of Na in all but one case (#19). The differences observed here in bicarbonate vs. sulfate TDS loading could be significant since Mount et al. (1997) report that bicarbonate is a considerably more toxic component of TDS than is sulfate. They also report that K and Mg are considerably more toxic than Ca or Na, and all of these cations occurred at widely varying levels in the leachates tested here. Finally, we also see strong evidence in our data for the presence of significant amounts of colloidal materials occurring in leachates in the > 2.0 micron size fraction that are not measured by the conventional TDS technique, but that did contain significant mass of the major TDS elements analyzed.

Overall, we noted no or very limited risk for leaching of As, Cr, Cu, Mo, Ni and Zn from these materials under these moderate pH conditions. Selenium was present at relatively low levels in these materials, but was leached at levels of concern (relative to stream MCL's) in initial leachates. These column leachate values represent worst case conditions, however, and certainly do not predict what actual mine discharge levels would be. That being said, all materials tested eluted significant levels (500 to $> 4000 \text{ mg L}^{-1}$) of TDS in their initial leaching events. This behavior would support continued TDS loadings to discharge waters on active operations that continued to disturb and place fresh spoils or refuse materials over extended periods of time. Surprisingly, this study revealed no major significant or consistent difference between coarse and fine refuse materials for any parameter of long term leaching concern.

We believe that our results indicate that relatively straightforward batch extraction procedures such as the sequential fractionation procedure utilized here can be quite useful in predicting the relative "leachability" of many elements of interest. Our extraction results correctly predicted that very little As, Cr and Mo would leach from these materials under the conditions present in the columns. However, that same procedure predicted that very little of the total Se in these sampled would leach, which was incorrect. Finally, the hydrogen peroxide oxidation potential

acidity procedure (PPA) generated a more reliable prediction of which materials would generate significant sulfate and associated TDS/EC levels than more conventional acid-base type accounting methods.

Important Findings from This Study

- The fractional distribution of As, Cr, Mo, and Se indicated that across all materials, these elements occurred primarily in recalcitrant mineral fractions (e.g. crystalline oxides and residual) that are presumably resistant to weathering and leaching. This means that under normal environmental conditions, with the pH between 3.5 and 9.0, we would predict low solubility and subsequent leaching of these elements.
- Direct comparison of total elemental content of weathered vs. unweathered mine spoils showed that as expected, weathered spoils were considerably leached of Ca compared to unweathered mine spoil. Interestingly, this was not the case for other basic cations like K and Mg.
- The elemental composition of leachate solutions from our column leaching study was strongly affected by internal acid-base reactions and saturated versus unsaturated conditions, but there were also differences within the sample groups, mine spoil, and coarse vs. fine refuse.
- All samples eluted considerable levels ($> 500 \text{ mg L}^{-1}$) of TDS (with high EC) over their initial leaching cycles and samples that contained significant reactive sulfides continued to elute high TDS levels for the duration of the study, regardless of their leachate pH values. Of the materials studied here, the fine refuse samples eluted the highest initial TDS ($> 4000 \text{ mg L}^{-1}$), but one shale overburden also eluted considerable TDS.
- We noted no or very limited risk for leaching of As, Cr, Cu, Mo, Ni and Zn from these materials under these moderate pH conditions. However, while Se was present at relatively low levels in these materials, it was leached at levels of concern (relative to drinking water MCL's) in initial leachates despite relatively low levels in soluble/bioavailable SEP fractions.
- Overall, TDS mass was dominated by six elements/compounds: (HCO_3^- , Ca, K, Mg, Na, and SO_4^{2-}). TDS release from the mine spoil samples was dominated by sulfate under unsaturated conditions and by sulfate and bicarbonate under saturated conditions.
- TDS release from coarse and fine coal refuse was very different from mine spoils and contained significant amounts of Na.
- Surprisingly, this study revealed no major significant or consistent difference between coarse and fine refuse materials for any parameter of long term leaching concern.

- Our results indicate that relatively straightforward batch extraction procedures such as the sequential fractionation procedure (SEP) utilized here can be quite useful in predicting the relative “leachability” of most elements of interest. Selenium appears to be an exception to this finding, however.
- Finally, the hydrogen peroxide oxidation potential acidity procedure (PPA) generated a more reliable prediction of which materials would generate significant sulfate and associated TDS/EC levels than more conventional acid-base type accounting methods.

References

Adriano, D.C, A.L. Page, A.A. Elsewi, A.C. Chang, and I. Straughan. 1980. Utilization and disposal of fly ash and other residues in terrestrial ecosystems: A review. *J. Environ. Qual.*, 9, 333-344.

Barnhisel, R.I. and H.G. Massey. 1969. Chemical, mineralogical and physical properties of eastern Kentucky acid-forming coal spoil materials. *Soil Science*, 108:367-372.

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

Chapman, P.M., H.B. Bailey, and E. Canaria. 2000. Toxicity of Total Dissolved Solids Associated With Two Mine Effluents to Chironomid Larvae and Early Life Stages of Rainbow Trout. *Environmental Toxicology and Chemistry*, Vol. 19(1), pp. 210-214.

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 Cooperative Extension Publication 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. Final report to VDMLR and OSM, October 2006.

Evangelou, V.P. 1995. Pyrite Oxidation and its Control. CRC Press. Boca Raton.

Halvorson, H.G. and C.E. Gentry. 1990. Long-term leaching of mine spoil with simulated precipitation. In Skousen, J., J. Sencindiver, and D. Samuel ed. Proceedings of the 1990 mining and reclamation conference and exhibition, volume 1 pp.27-32.

- Hansen, E. and M. Christ. 2005. Water Quality Impacts of Coal Combustion Waste Disposal in Two West Virginia Coal Mines. Available at www.downstreamstrategies.com. 2921 Halleck Road, Morgantown, WV, 26508. 55 p.
- Howard, J.L. 1979. Physical, chemical, and mineralogical properties of mine spoil derived from the Wise Formation, Buchanan county, Virginia. M.S. thesis. Virginia Polytech. Inst. and State Univ., Blacksburg, VA.
- Howard JL, Amos DF, Daniels WL (1988) Phosphorus and potassium relationships in southwestern Virginia mine spoils. *J. Environ. Qual.* 17(4) :695-671
- Kennedy, A.J., D.S. Cherry, and C.E. Zipper, 2005. Evaluation of Ionic Contribution to the Toxicity of a Coal-Mine Effluent Using *Ceriodaphnia dubia*. *Archives of environmental contamination and toxicology*. pp. 155-162.
- Malmstrom, M.E., M. Gleisner, and R.B. Herbert. 2006. Element discharge from pyritic mine tailings at limited oxygen availability in column experiments. *Applied Geochemistry*. 21(1): 184-202.
- Mehlich, A. 1953. Determination of P, Ca, Mg, K, Na, and NH₄. North Carolina Soil Test Division (Mimeo 1953).
- Mount, D.R., D.D. Gulley, J.R. Hockett, T.D. Garrison, and J.M. Evans. 1997. Statistical models to predict the toxicity of major ions to *Ceriodaphnia Dubia*, *Daphnia Magna* and *Pimephales Promelas* (Fathead Minnows). *Environ. Tox. Chem.* 16(10)pp.2009-2019.
- Orndorff, Z.W. and W. Lee Daniels. 2004. Evaluation of acid-producing sulfidic materials in Virginia highway corridors. *Environmental Geology*. Vol. 46:209-216.
- Orndorff, Z.W., W.L. Daniels and D.S. Fanning. 2008. Reclamation of Acid Sulfate Soils Using Lime-Stabilized Biosolids. *J. Env. Qual.* 37:1447-1455 (2008).
- Roberts, J.A., W.L. Daniels, J.C. Bell, and J.A. Burger. 1988. Early stages of mine soil genesis in a Southwest Virginia spoil lithosequence. *Soil Sci. Soc. Am. J.* 52:716-723.
- 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.
- 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.

Sobek, A.A., J.G. Skousen, and S.E. Fisher, Jr. 2000. Chemical and physical properties of overburdens and minesoils. p. 77-104. *In* R.I. Barnhisel et al. (ed.) Reclamation of drastically disturbed lands. Agron. Monogr. 41. ASA, CSSA, and SSSA, Madison, WI.

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.

Vesper, D.J., M. Roy and C.L. Rhoads. 2008. Selenium distribution and mode of occurrence in the Kanawha Formation, southern West Virginia, USA. *International Journal of Coal Geology* **73**: 237-249.

Virginia DMLR. 2005. A preliminary review of Selenium, Aluminum, Copper, and Nickel concentrations in Virginia's Southwestern Coalfield Surface Waters. Technical Report Number 2462. Commonwealth of Virginia, Department of Mines, Minerals, and Energy.

Weber-Scannell, P.K., and L.K.Duffy. 2007. Effects of total dissolved solids on aquatic organisms: a review of literature and recommendation for Salmonid Species. *American Journal of Environmental Sciences.* 3(1): 1-6.

Xu, T., S.P. White, and K. Pruess. 2008. Pyrite oxidation in saturated and unsaturated porous media flow: A comparison of alternative mathematical modeling approaches. Lawrence Berkeley National Laboratory (University of California), Paper LBNL-42049. <http://repositories.cdlib.org/lbnl/LBNL-42049>

Appendix A – Column Leaching Data not Discussed in Detail in Text

Figure 14. Leachate Al from selected mine spoils, coarse coal refuse, and fine coal refuse under saturated and unsaturated conditions. The 45 leachate events occurred over 153 days.

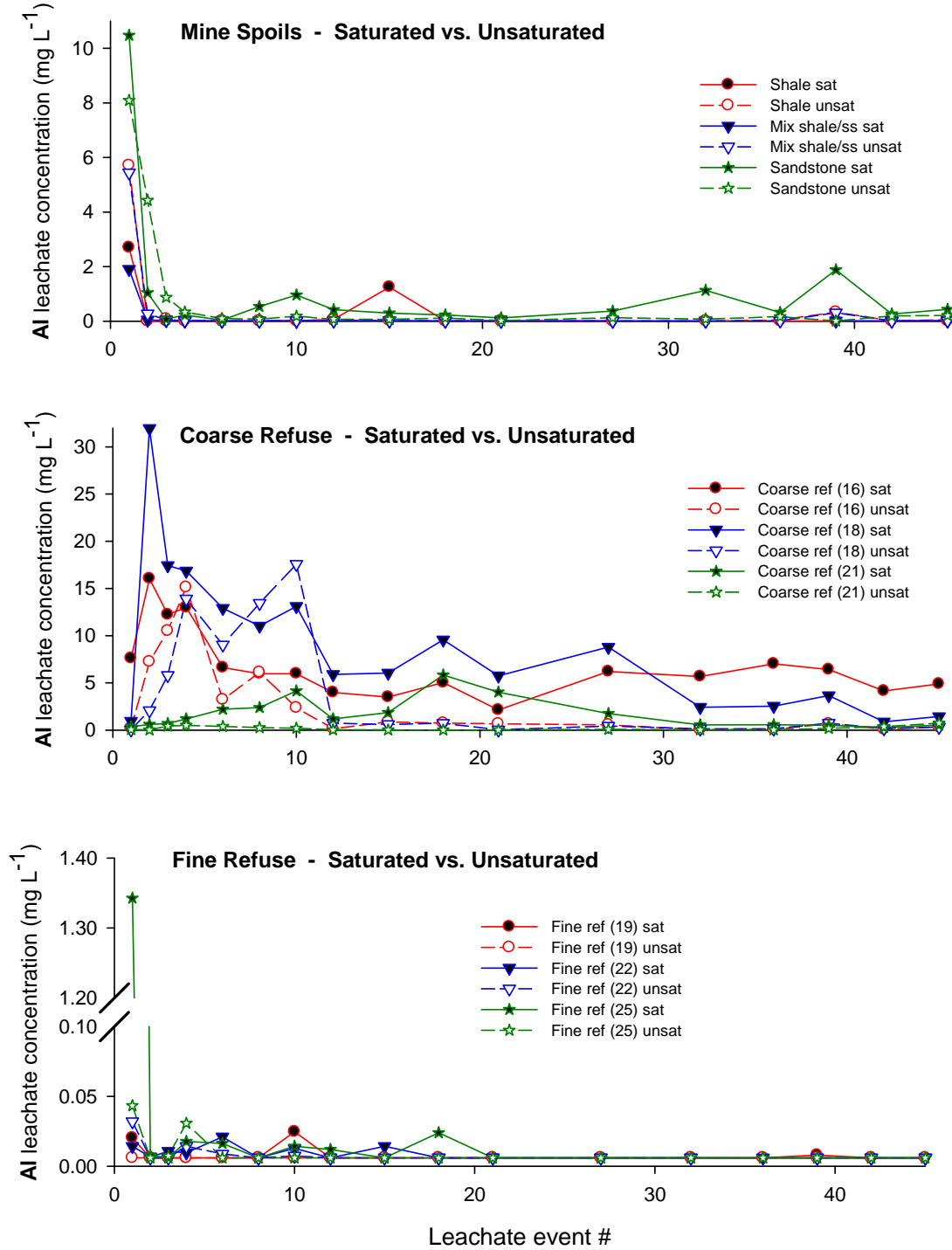


Figure 15. Leachate K from selected mine spoils, coarse coal refuse, and fine coal refuse under saturated and unsaturated conditions. The 45 leachate events occurred over 153 days.

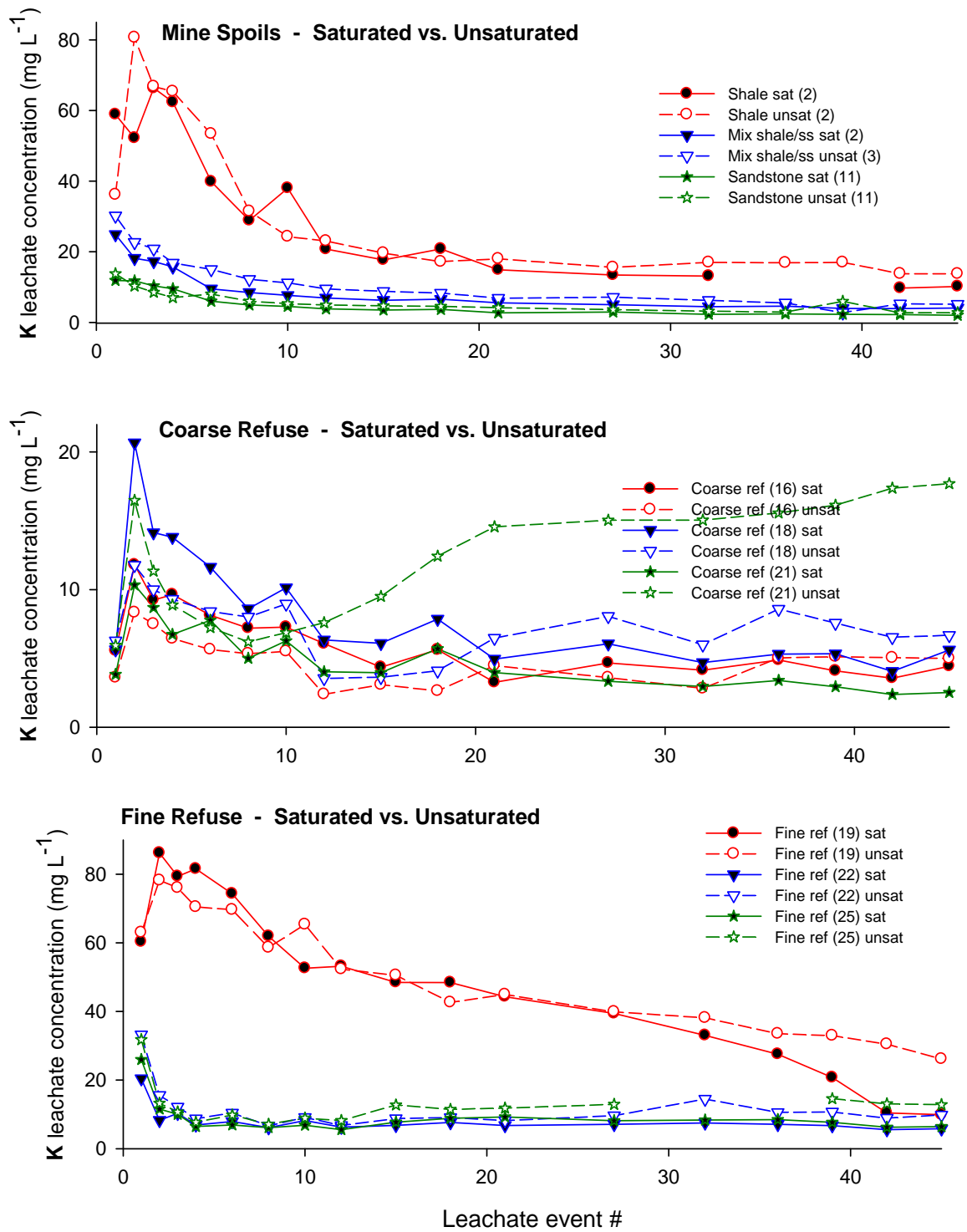


Figure 16. Leachate Mg from selected mine spoils, coarse coal refuse, and fine coal refuse under saturated and unsaturated conditions. The 45 leachate events occurred over 153 days.

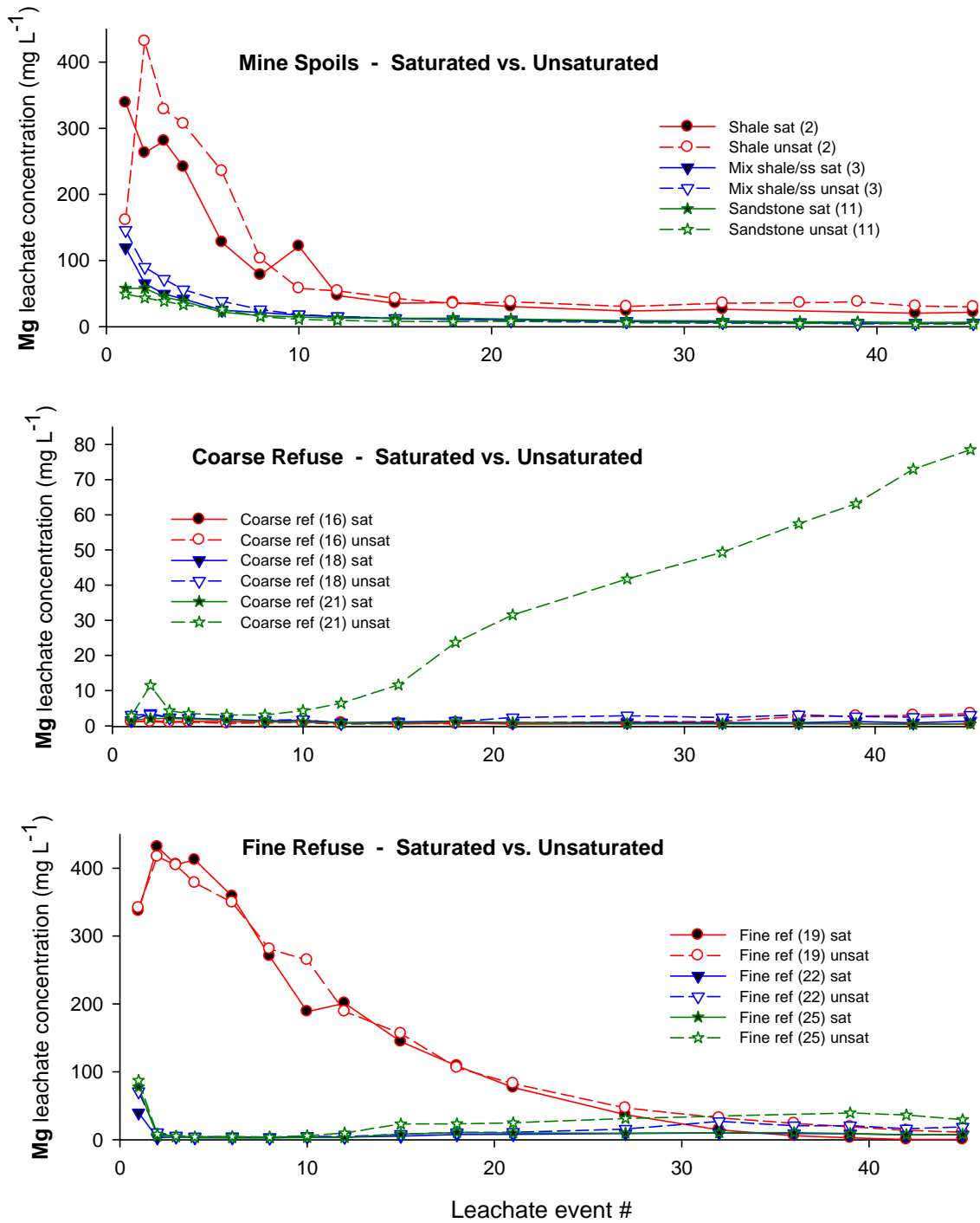


Figure 17. Leachate Mo from selected mine spoils, coarse coal refuse, and fine coal refuse under saturated and unsaturated conditions. The 45 leachate events occurred over 153 days.

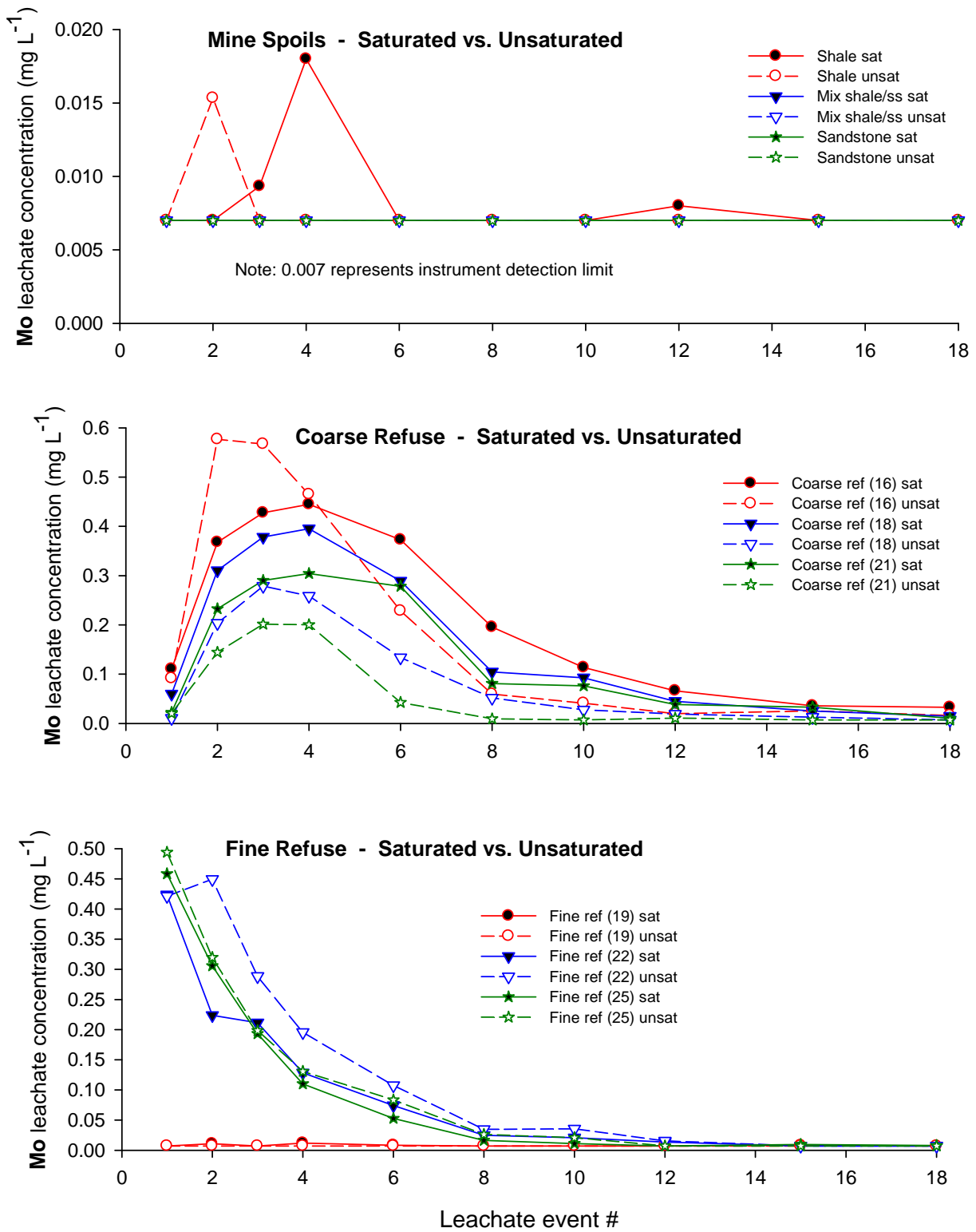
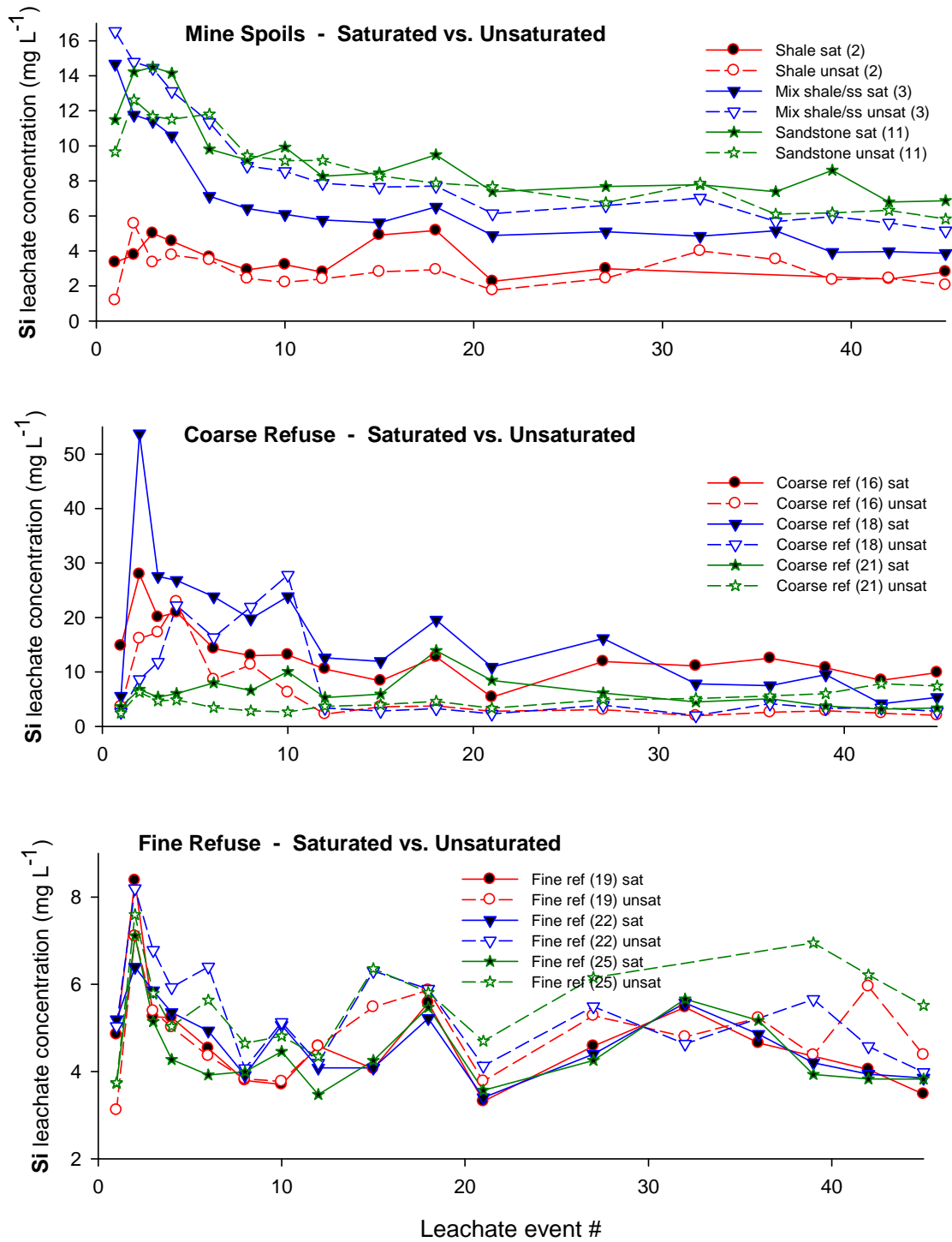


Figure 18. Leachate Si from selected mine spoils, coarse coal refuse, and fine coal refuse under saturated and unsaturated conditions. The 45 leachate events occurred over 153 days.



APPENDIX B – Example of Replicate (3) Data Sets for Leachate pH

Figure 19. Leachate pH of **each replicate** from selected mine spoil, coarse coal refuse, and fine coal refuse samples under saturated and unsaturated conditions. The 45 leachate events occurred over 153 days. NOTE: The figures here show all data points observed regardless of whether it was determined that a given observation was deemed to be an ‘outlier’.

