Final Report - OSM Applied Science Research Program

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

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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 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 mg L^{-1}) which dropped quickly to relatively constant levels ($<$ 1000 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 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 Marker, Phillips and Standiford	46	54
OSM 19	Fine refuse	Shales, mudstones and coal mixture	Upper-middle Wise		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 Banner	57	43
OSM 25	Fine refuse	Shales, mudstones and coal mixture	Norton		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	Fe	Mn
				---------------- mg Kg^{-1} ----------------			
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 CaCl$_2$ 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 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 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.

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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

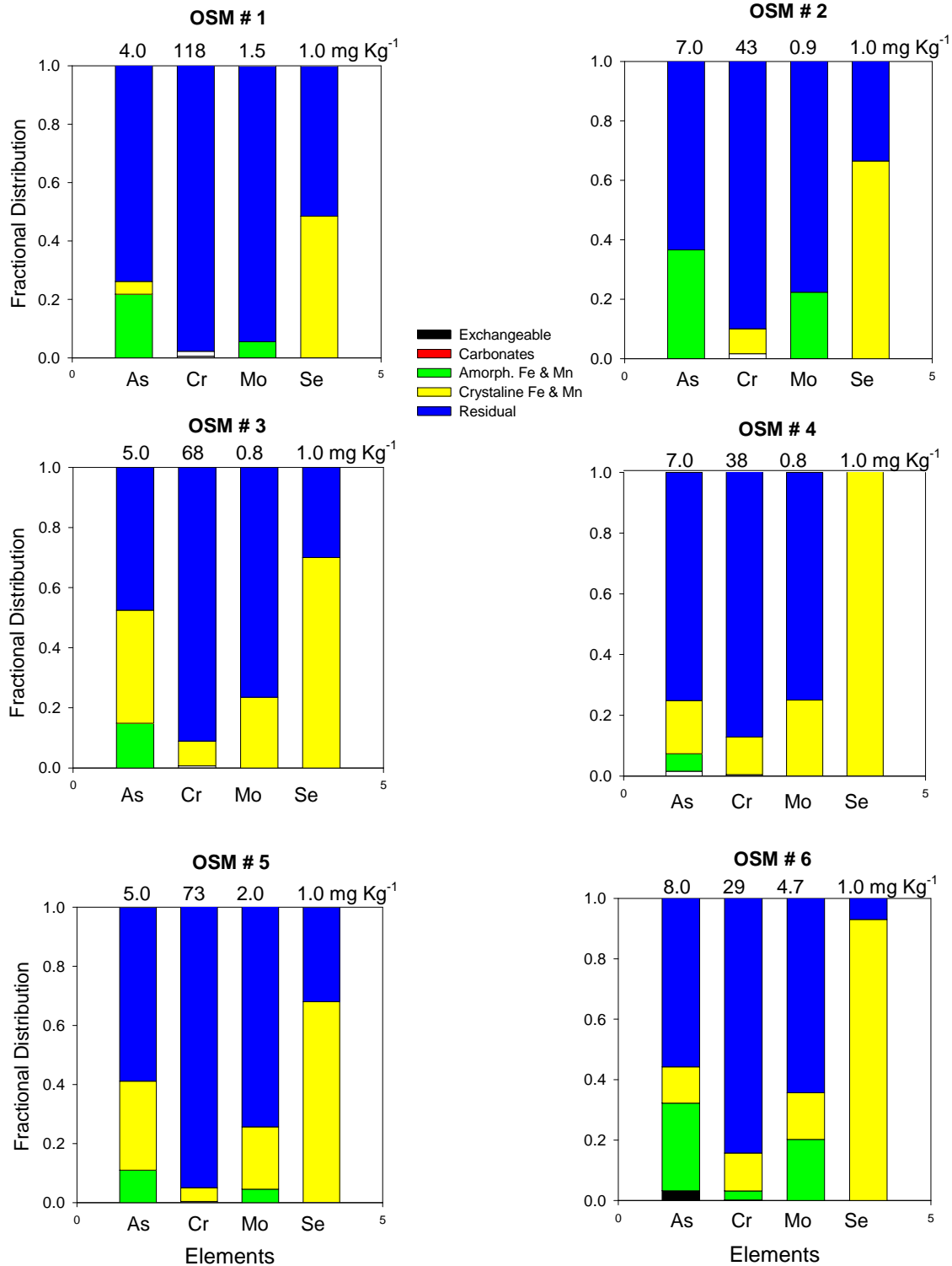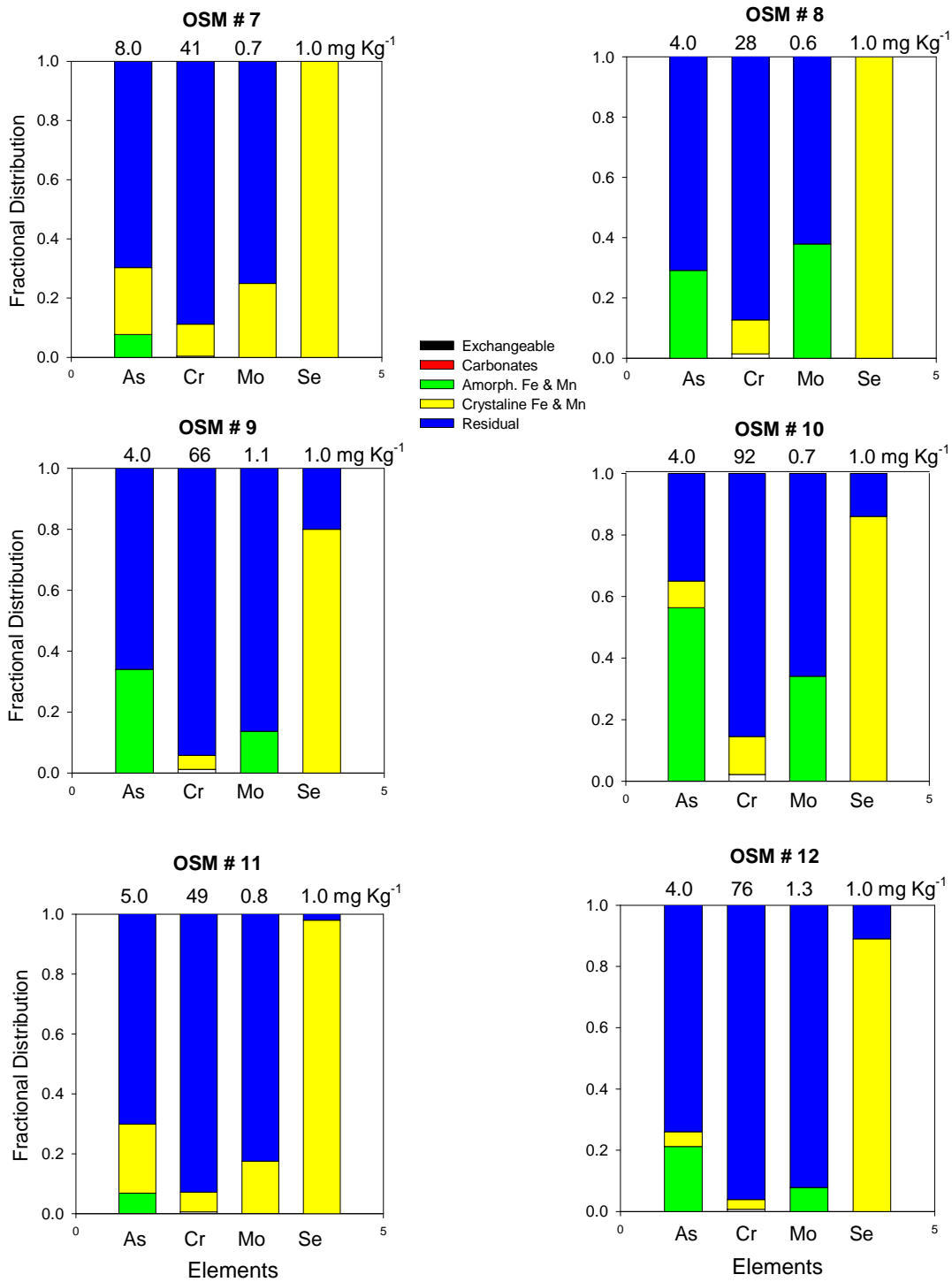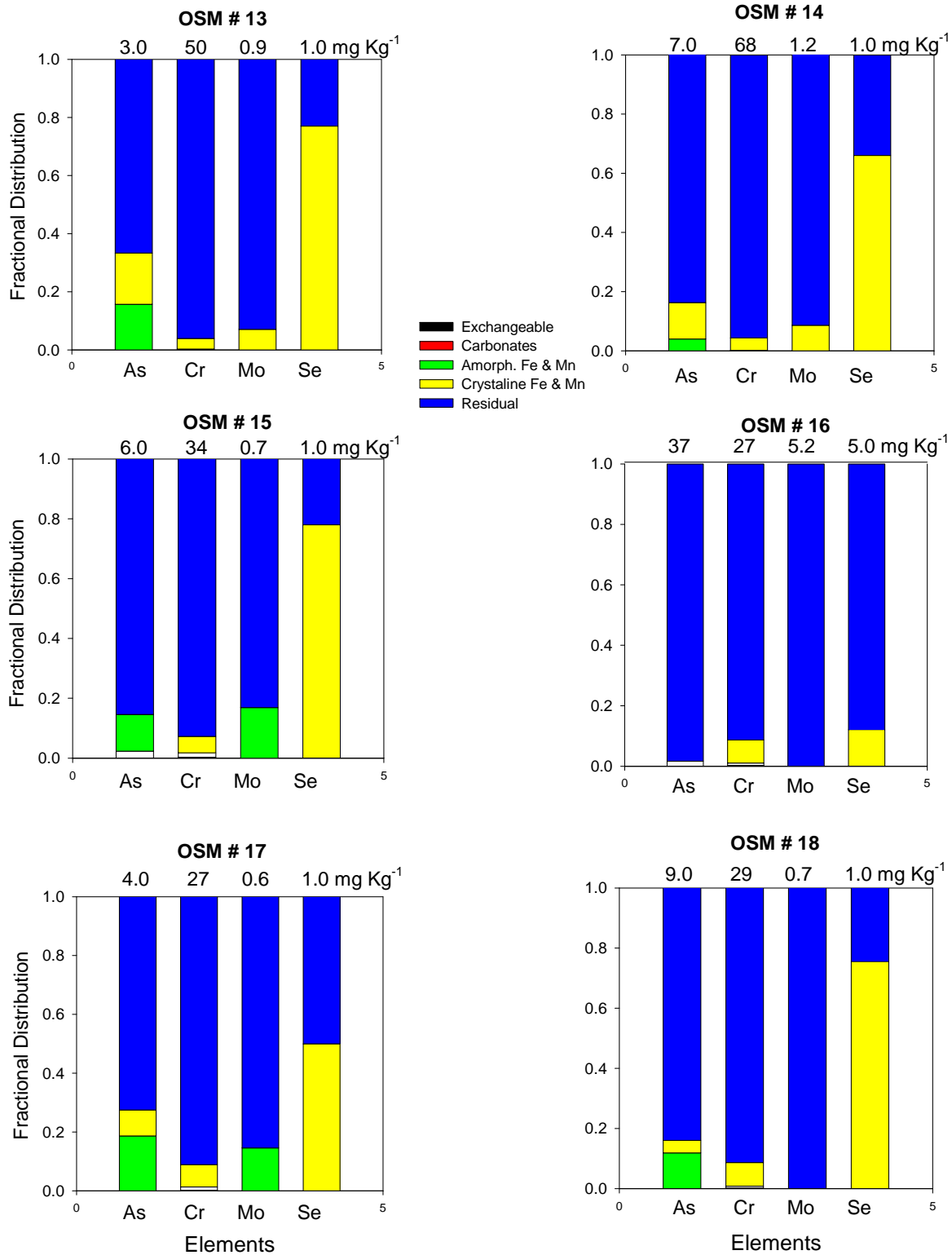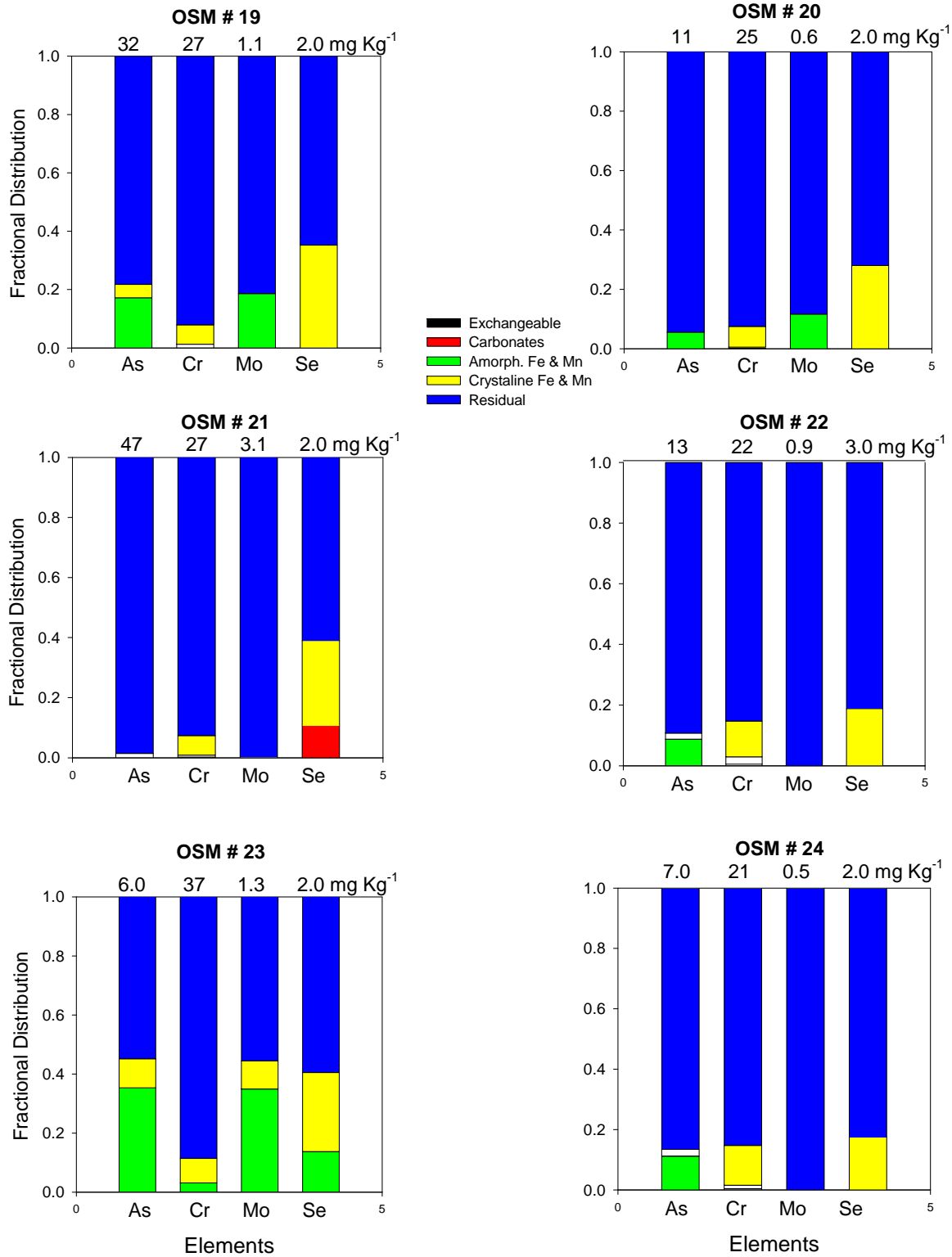**Coal Refuse Pairs:** OSM # 16 & 22, OSM # 17 & 23, OSM # 18 & 19, OSM # 20 & 24, OSM # 21 & 25

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 1e. 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 graph. Presented are results for OSM sample #25.
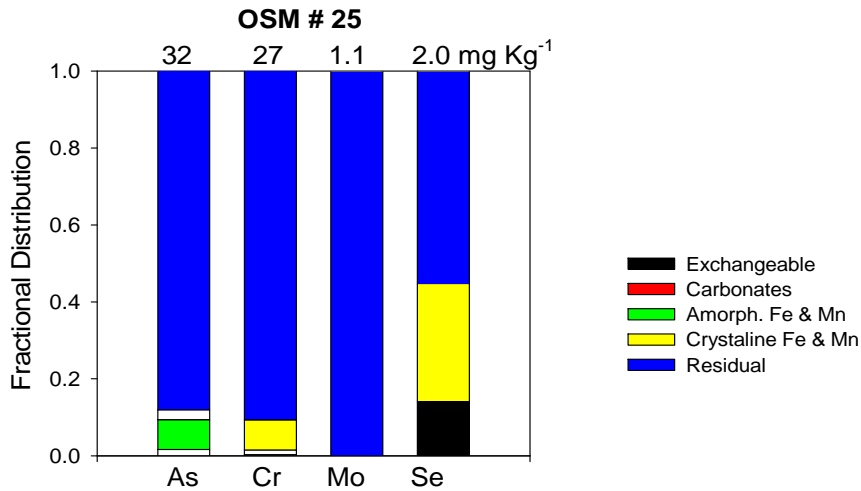
Selection of Samples for the Column Leaching Trial

The sample mass elemental data along with SEP and general chemical data were used to select three mine spoils and three pair of coarse and fine refuse samples for the column leaching trial. Presented below are details of the selection criteria.

The selection of the nine samples utilized for the column leaching trial was primarily based on the following chemical properties and differences:

Mine spoils: **OSM samples # 2, 3, and 11**. The primary reasons for selection were:
- Similar fractional distribution of the selected elements along with similar pH and EC, *but* different potential acidity (PPA) between sample # 3 vs. #11.
- Sample # 2 differed in fractional distribution of the selected elements from samples # 3 and 11, which had the highest EC value of the mine spoils tested.

Coal refuse: **OSM samples (paired) # 16 & 22, # 18 & 19, and # 21 & 25**. The reasons for selection of these were:
- Within pairs, the fractional distribution of the selected elements tended to be similar overall, but a particular element was absent in one sample but not in the other (for example Mo in samples # 18 vs. # 19).
- The pH and potential acidity tended to be different within pairs (#18 vs. #19 and # 21 vs. #25) but not for #16 vs. #22.
- For the coarse refuse samples, we selected a range of predicted potential acidities from -0.06 (#16) to -2.20 (#18) to -31.1 T/1000 T CCE for sample #21.

Experimental Procedures for Column Leaching Trial

Sample Preparation: All samples were air-dried prior to processing. To eliminate preferential flow within the column, coarse and large fragments of coal refuse and mine spoil were crushed to pass a 1 cm sieve and then carefully back-blended. Particulates in the slurry of fine coal refuse were allowed to settle for one month after which time the clear waste water was decanted. The "paste-like" fine refuse was spread out to air dry and subsequently sieved to pass a 2 mm sieve.

Column Details: The leaching columns were built from 7.6 cm PVC pipe with inside diameter of 7.4 cm, length of 40 cm, with a concave PVC endcap to hold the material. Prior to use, the columns were acid washed with 1 M HCl. A 0.1 mm nylon mesh circle of 6 cm diameter was glued into the endcap to assure no blockage of the drainage hole by particulates. Prior to filling the columns, we inserted a 7.6 cm diameter Whatman #1 filter paper to prevent leaching losses of particulate matter. The column was drained through a 1 cm PVC pipe nipple fitted and glued with two-component adhesive into the center of the endcap. An attached Tygon tube served to drain the leachate and provided the flexibility to create anaerobic conditions in the saturated columns by preventing drainage and gas exchange via a saturated loop at the bottom of the column. A 2.5 cm layer of acid washed coarse sand on top of the Whatman #1 filter paper assured optimal sample material/filter paper interface for uniform drainage. The layer of sand also served as a leachate reservoir to ensure that the bottom section of the sample material remained unsaturated in those treatment columns. The sample material was also capped with a 2.5 cm layer of sand to facilitate uniform distribution of the applied leaching solution.

Experimental Design: 9 refuse/mine spoil samples x 3 replications x 2 moisture regimes (saturated vs. unsaturated) = 54 columns. The sample volume in each column was 1200 cm^3.

Leaching - Sampling Procedures: Simulated rainfall (pH 4.8, prepared according to Halvorson and Gentry, 1990) was applied twice per week for the equivalent amount of 2.5 cm of rainfall per event (This is equivalent to 110 ml per leaching event). The water was dispensed into a perforated cup placed on top of the sand to uniformly apply the solution to the sample material.

Unsaturated long-term leaching:
During the first week of the experiment we accelerated the dosing cycle to satisfy the hydration demand to a point where leachates were generated in essentially a "piston flow" response to the surface dosing regime. Following a 'precipitation event', the columns were allowed to drain freely into collection bottles. The leachates were analyzed and/or preserved after an 18 hour leaching/collection period. This precipitation/sampling procedure was repeated every three/four days (twice a week, Mondays and Thursdays with sample collection and analysis on Tuesdays and Fridays).

Saturated long-term leaching:
A set of saturated columns was simultaneously leached. The columns were constructed identically to the unsaturated columns. During the first week of the experiment, we accelerated the dosing cycle (one precipitation event per day) until the columns were completely saturated. Subsequently, the sampling procedure was as follows: 100ml of simulated precipitation were applied (which resulted in temporary ponding, < 5 min) followed by the elution of the leachate

from the bottom of the column by opening the Tygon tubing until 100 ml were eluted into a calibrated sample bottles. This precipitation/sampling regime assured essentially a "piston flow" response to the surface dosing regime. At times and as needed, small amounts of simulated rainfall water were added to the columns to compensate for evaporative losses and to assure that the top of the columns also remain saturated.

Column Leachate Data Collection and Analysis

Sequence for Leachate Analysis:
1) Determination of EC and pH in sample bottle
2) Subsampling for IC/TC & total elemental analysis (50 ml).
3) Subsampling for TDS analysis (20-40 ml)
4) Transfer of remaining sample into plastic vials for storage.

Column leachates for all treatments were collected into individual acid-washed bottles. Once the leachate was collected it was immediately analyzed for pH, EC. Based on the EC, variable quantities of leachate solution were used for TDS determination. A subsample of the leachate solution was analyzed for all major cations (Ca, Mg, K, Na), metals (Al, Fe, Cu, Zn), Si, and other elements of specific interest like As, B, Cl, Cr, Mo and Se. The majority of elements were analyzed by ICPES; Cl was determined by ion chromatography.

Organic Carbon / Total Carbon Analysis

Inorganic vs. organic carbon in leachates was determined on a Sievers 900 Laboratory TOC analyzer. This analysis was conducted after the determination of EC/pH, and following subsampling for TDS determination. Upon completion of carbon analyses, the solutions were analyzed for multiple elements by ICP-AES. Bicarbonate was assumed to be (based on the leachate solution pH) the prevalent ionic form of the inorganic carbon. We calculated the bicarbonate leachate concentration (mg L^{-1}) by multiplying the IC concentration by 5.083.

TDS – Total Dissolved Solids

Total dissolved solids were analyzed according to EPA Method 160.1. Total dissolved solids are defined as the portion of solids that passes through a filter of 2.0 microns nominal pore size. The solution samples were filtered through a standard fiber filter. The filtrate was poured into a pre-weighed beaker and the solution evaporated at 180°C. The beaker were cooled in a desiccator, weighed and results used to compute the TDS of the sample solution.

Results of Leaching Column Trial

The data presented in Figures 2-12 report results from 45 leaching events over a 22 week period. The data are presented in groupings of the source materials, mine spoil, coarse refuse, and fine refuse, and to contrast the results from saturated versus unsaturated conditions. We highlight pH, EC, TDS, sulfate, bicarbonate and several other elements of interest. The figures presenting the data for elements not shown in this main part of this report are found in Appendix A. The data presented are the mean observations from three replicate columns. Given in Appendix B are the

pH curves for each replicate column for one mine spoil, one coarse refuse, and one fine refuse material, contrasting the results from the saturated versus unsaturated treatment. We selected these three materials because of their curves differ from the others within their material category (mine spoil, coarse refuse, and fine refuse material). The close response of the replicates for each sample and their clear separation between saturated vs. unsaturated treatments is clearly evident in these plots. For this reason, all the leachate response figures that follow in this report plot the average values for the three replicate columns for each treatment.

pH: Leachate pH (Fig. 2) values from the first leaching events were substantially lower than from the initial data determined by batch techniques. For most materials, leachate pH increased within a few leaching events to those determined by the batch technique. For two of the mine spoil samples, the sandstone (weathered/oxidized) and the sandstone/shale (partially weathered), it took nearly 20 leaching events for them to reach initial batch pH levels. Overall, there were no major pH changes over the 153 days (45 leaching events) for any materials with the exception of OSM #21 under unsaturated conditions.

Unweathered overburden in southwestern Virginia can contain significant amounts of carbonates (Howard, 1979) and to a more limited extent, reactive pyrite (Sobek et al., 2000). Depending on the distribution and quantity of these minerals, the pH of unoxidized overburden is between 6.5 and 8.0 (Roberts et al., 1988) while that of weathered/partially weathered overburden is generally between 4.5 and 6.0. The pH of coal refuse materials as they leach and weather depends primarily upon pyrite content vs. neutralizers and their relative rates of reaction. When exposed to an oxidizing environment, the pH of highly sulfidic, reactive leached refuse can quickly drop to < 2.5 (Daniels et al., 2006).

In our leaching trial, the unsaturated columns were generally higher in pH than for the same material under saturated conditions. This could potentially be due to effects of CO_2 partial pressures on carbonate dissolution in the unsaturated columns or perhaps siderite ($FeCO_3$) formation in the saturated columns. The mine spoils and coarse refuse samples' pH remained steady except for OSM #21, which had also the highest PPA of any sample. The pH of the fine refuse also tended to decrease slowly over time. We anticipated, based on the PPA values of some of the refuse samples that we would observe drastic drops in pH values as the sulfidic materials oxidized. However, only the unsaturated treatment of the coarse refuse with the highest PPA value (OSM #21) exhibited a significant drop (from pH 8.0 to 5.1). We continued to leach the columns beyond the full data sets reported here, and by leachate volume # 65, the pH for this treatment dropped to 4.0. These observations contrast with previous trials (Daniels et al. 2006) where very rapid drops in pH down to 2.0 occurred. A major difference between the two sets of results, however, is that all but one sample (OSM #3) used in this column trial had substantial liming capacities (range of 4.0 to 6.2% CCE) while the refuse used in the 2006 study was lower in CCE. Thus, any acidity produced by the oxidation of sulfidic materials was neutralized by the dissolution of the carbonates, with the exception being the later leachates produced by OSM 21. The effects of these complex S oxidation and carbonate dissolution reactions are also indicated by changes in leachate EC, TDS, Ca and SO_4^{-2} as discussed below. However, we have no reasonable explanation for the erratic pH pattern in unsaturated fine refuse sample #19 other than redox cycling appeared to be active in the unsaturated columns of this particular treatment for some reason, perhaps plugging by fines and limited gas exchange with the column surface.

Figure 2. Leachate pH from selected mine spoils, coarse coal refuse, and fine coal refuse under saturated and unsaturated conditions. The 45 leachate events occurred over 153 days.
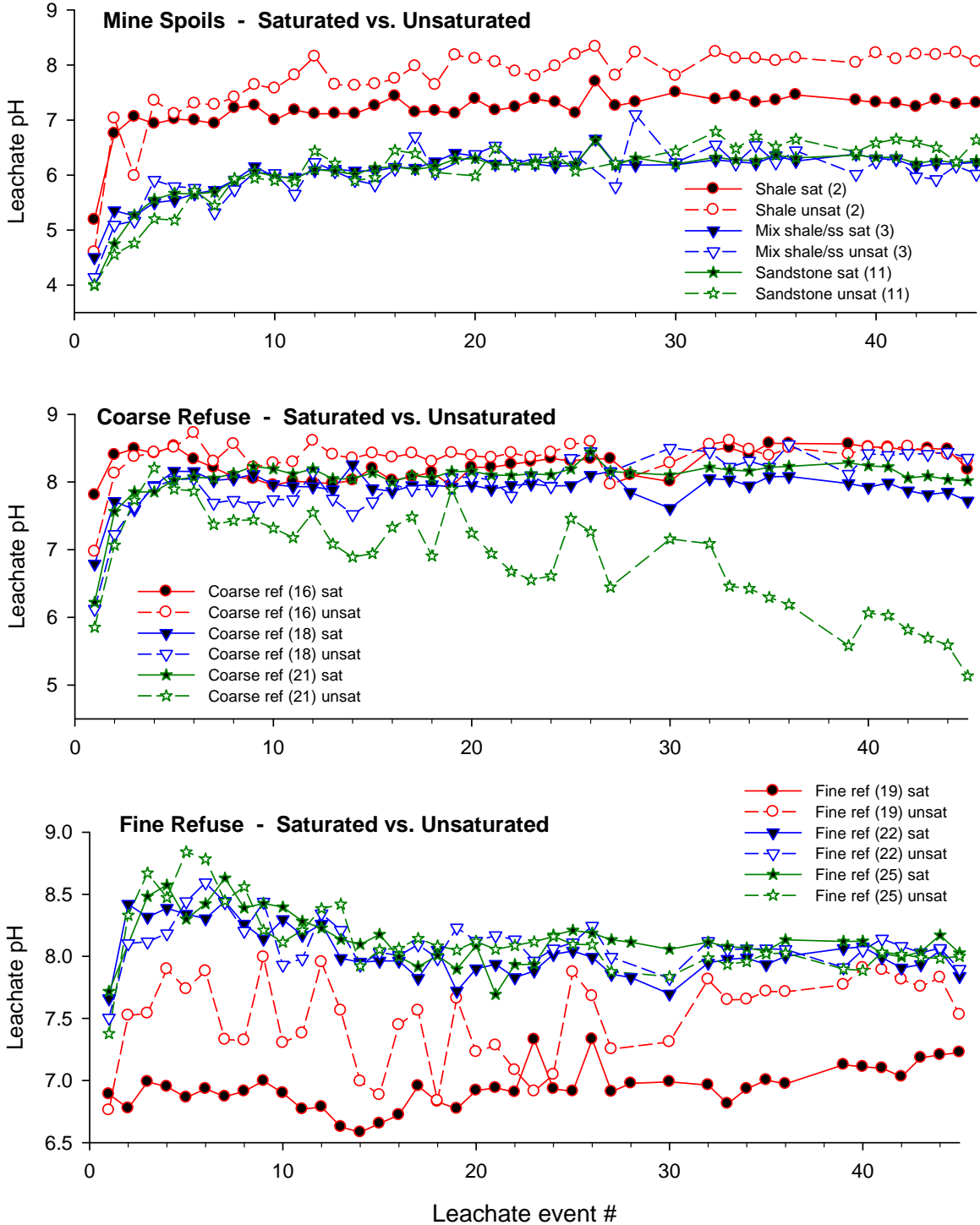
EC: As would be expected, leachate EC (Fig. 3) from unweathered mine spoil (OSM #2) was consistently higher than from its paired partially oxidized and weathered sample. Initial EC values dropped quickly to a steady state at relatively low levels for the remainder of the leaching trial. Fine refuse samples generated very high EC values in initial leachates, particularly for samples OSM 22 & 25. However, these two samples dropped to EC < 1.0 dS m^{-1} by the third leaching. In contrast, leachate from fine refuse sample OSM #19 produced an initial EC of 3.8 dS m^{-1}, but this value dropped little over time and was still around 3.0 dS m^{-1} after 40 leaching events (5 months). There was no treatment effect of saturated versus unsaturated conditions for either mine spoils or the fine refuse materials. However, differences due to saturation were pronounced for the coarse refuse samples where leachate EC was substantially higher for the unsaturated materials. The EC for the saturated treatments showed a steady decline from 1.5 dS m^{-1} to around 0.5 dS m^{-1} after 5 months while the EC of the unsaturated materials remained fairly steady at elevated levels between 1.0 and 1.5 dS m^{-1}, depending on the material. As discussed below, this was obviously related to oxidation of sulfidic materials.

TDS: The plotted data for TDS (Fig. 4) and EC were nearly identical other than the scale of the y-axis. The major difference between the two parameters is that the EC was determined on the bulk unfiltered leachate sample and the TDS is determined on a filtered sample with corresponding possible reduction/changes in the solution composition. Thus, the high correlation coefficient of r=.98 between the two variables is not surprising, and underpins the regulatory assumption that EC can be used as an effective proxy for TDS.

Overall, three major release patterns stand out. First of all, the large TDS release from the shale sample (OSM #2) is surprising given the moderate S content and high pH of this material. Secondly, the steady increase for the unsaturated coarse refuse (OSM #21) after leaching event #10 is clearly related to S oxidation and sulfate elution, while thirdly, the drop for the saturated fine refuse (OSM #19) at the end of the trial is also notable. Collectively, these patterns point out the complex interacting geochemical processes that occur with materials that contain both acid producing and acid neutralizing compounds. For example, coarse refuse OSM #21 had the highest PPA of all samples, but also contained an apparent surplus of CCE neutralizing capacity. Based on these data, it appears the rate carbonate dissolution was sufficient for approximately 8 to 10 leaching cycles to neutralize the acid sulfide reaction products, but the rate of pyrite oxidation eventually exceeded the carbonate dissolution rate, leading to the subsequent progressive drop in pH and increase in EC and TDS (Figs. 2-4).

In the case of fine refuse sample #19, the same source/mechanism for salt generation was present under both saturated and unsaturated conditions, but it finally became suppressed under saturated conditions after 35 leachings with a steady decline of TDS from 2800 mg L^{-1} to 400 mg L^{-1}. Finally, the large elution of bulk EC and TDS from the shale sample from eastern Kentucky probably represents the presence of a highly reactive sulfide (framboidal?), that even though present in relatively low amounts (0.23% S), reacted quickly with substrate carbonates to produce sulfates and prolonged sulfate release over the extent of this experiment. Collectively, this acid-base reaction control on leachate chemistry was also reflected in leachate bicarbonate, sulfate, and Ca concentrations as discussed below. Finally, the combined data indicate that first flush TDS leaching from spoils and coal refuse can vary between 500 and > 4000 mg L^{-1} based on material type and source. Patterns of prolonged release were highly variable, however.

Figure 3. Leachate EC from selected mine spoils, coarse coal refuse, and fine coal refuse under saturated and unsaturated conditions. The 45 leachate events occurred over 153 days.
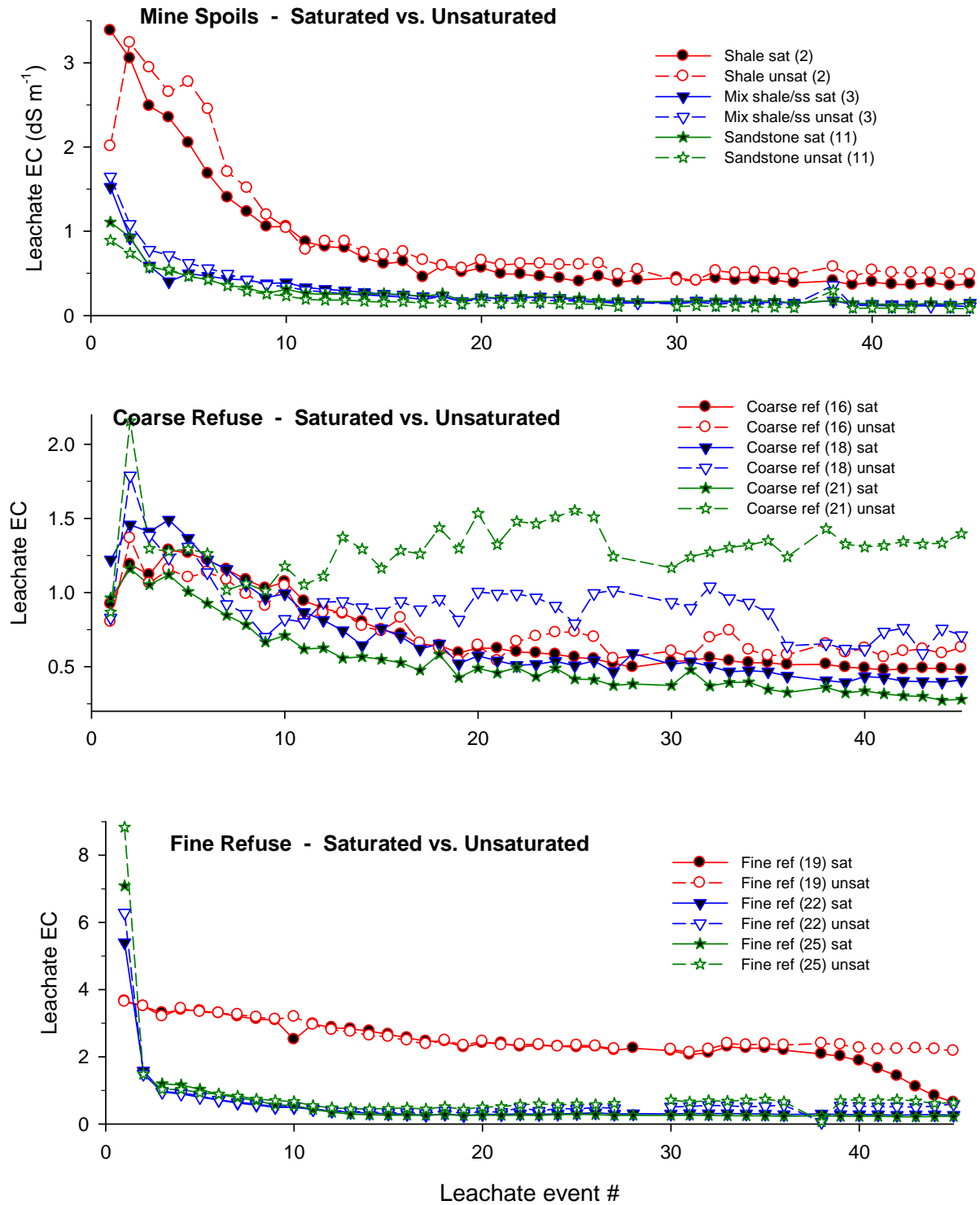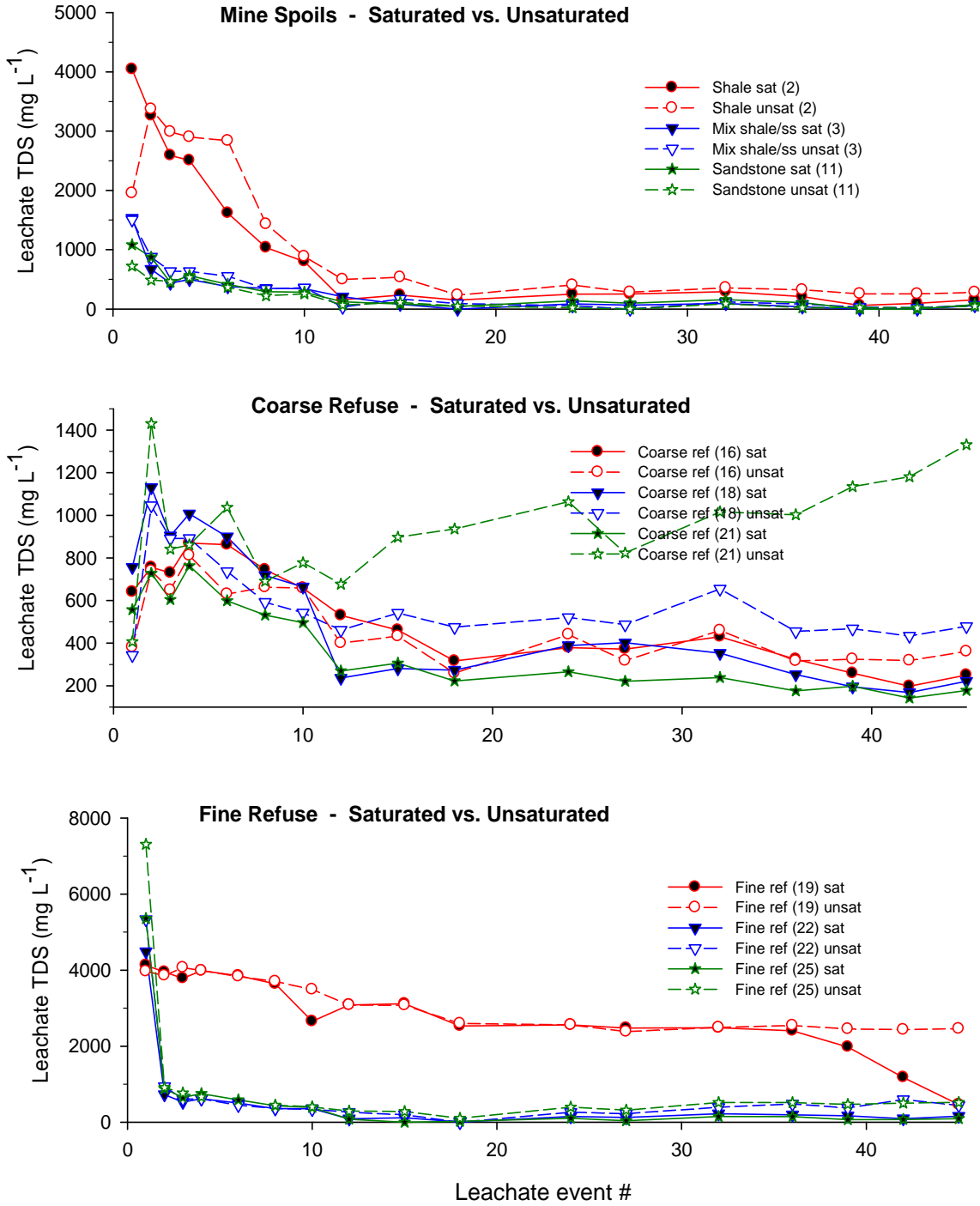
Figure 4. Leachate TDS from selected mine spoils, coarse coal refuse, and fine coal refuse under saturated and unsaturated conditions. The 45 leachate events occurred over 153 days.

Bicarbonate: The release of bicarbonate (Fig. 5) reflected the effects of saturated versus unsaturated conditions more than any other measured parameter in this study. Vastly more bicarbonate was leached under saturated conditions for both mine spoil and coarse refuse materials. The lower levels from the unsaturated columns presumably reflect acid neutralization reactions, even when relatively low amounts of S were present. The differences due to saturation were not as pronounced for the fine refuse materials and bicarbonate release was much more uniform among the different fine refuse materials compared to the mine spoils and coarse refuse. This may have been due to the finer texture of the fine refuse materials limiting oxidation in the unsaturated columns relative to the coarser spoils and coarse refuse.

Sulfate: Sulfate release patterns (Fig. 6) reflect the acid-base reaction discussed above which are due to fundamental differences in the geology/ mineralogy of the samples and are reflective of the total-S content of the materials (Table 2). In SW Virginia, where most of these samples originated, the vast majority of strata within the Pennsylvanian system are fluvial-deltaic facies which are generally low in pyritic-S. Many of the massive sandstones that dominate the Lee, Norton and Wise formations contain secondary carbonate cementing agents (Howard et al., 1988) which offset the relatively minor amounts of sulfidic minerals found in most geologic sections (like OSM #11). Significant accumulations of sulfides do occur in coal seams and underclays throughout the region; however, these seams are relatively thin (< 3 m). Several relatively minor sections of overburden in Virginia (e.g. the Standiford seam interburden of the middle Wise formation) do generate rock spoils with significant (> 20 Mg/1000 Mg) levels of potential acidity (Orndorff & Daniels, 2004). However, sample #2 is from the Breathitt Formation in eastern Kentucky, which has long been noted and studied for its acid forming potential (Barnhisel et al., 1976).

The pairing of the coarse and fine refuse samples (by the source of the materials) resulted in two pairs (OSM #16 & 22 and OSM #18 & 19) with low total-S & PPA in the coarse fraction and high total-S & PPA in the fine fraction, and the reverse being the case for the third pair, OSM #21 & 25 (Table 2). These differences were clearly reflected in higher sulfate concentrations in leachates.

The total-S content among the fine refuse samples was similar (Table 2) as were sulfate concentration in initial leachates. However, fine refuse #19 produced significantly higher and sustained sulfate release than the other two samples. While this sample was not significantly higher in total S vs. CCE, it did test higher in PPA, indicating a potentially more reactive sulfide type or size.

The effect of saturated conditions on sulfate leaching was clearly apparent in the coarse refuse materials (Fig. 6) due to the fact that pyrite oxidation rates are controlled by oxygen gas diffusion (Xu et al., 2000) when the pH is > 4.5. Thus, the better aerated coarse refuse readily promoted pyrite oxidation in the unsaturated columns, although a certain amount occurred initially in the saturated columns as well. Subsequently, the solubility and release of other ions such as Ca, Fe, and Zn would be affected by the interaction of O_2 diffusion rates, sulfide oxidation, carbonate dissolution and bulk solution pH (Malmstrom et al., 2006).

Figure 5. Bicarbonate leached from selected mine spoils, coarse coal refuse, and fine coal refuse under saturated and unsaturated conditions. The 45 leachate events occurred over 153 days.
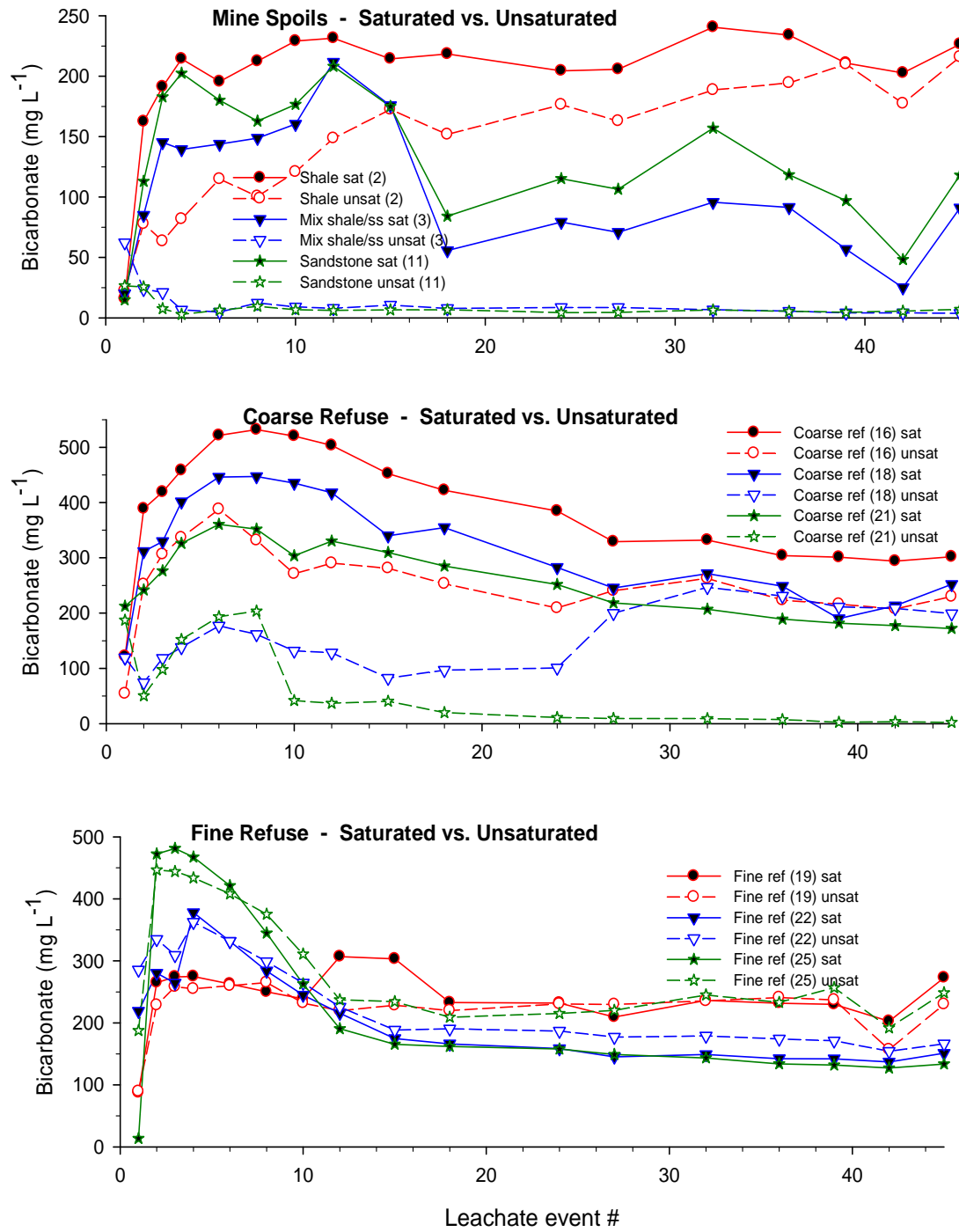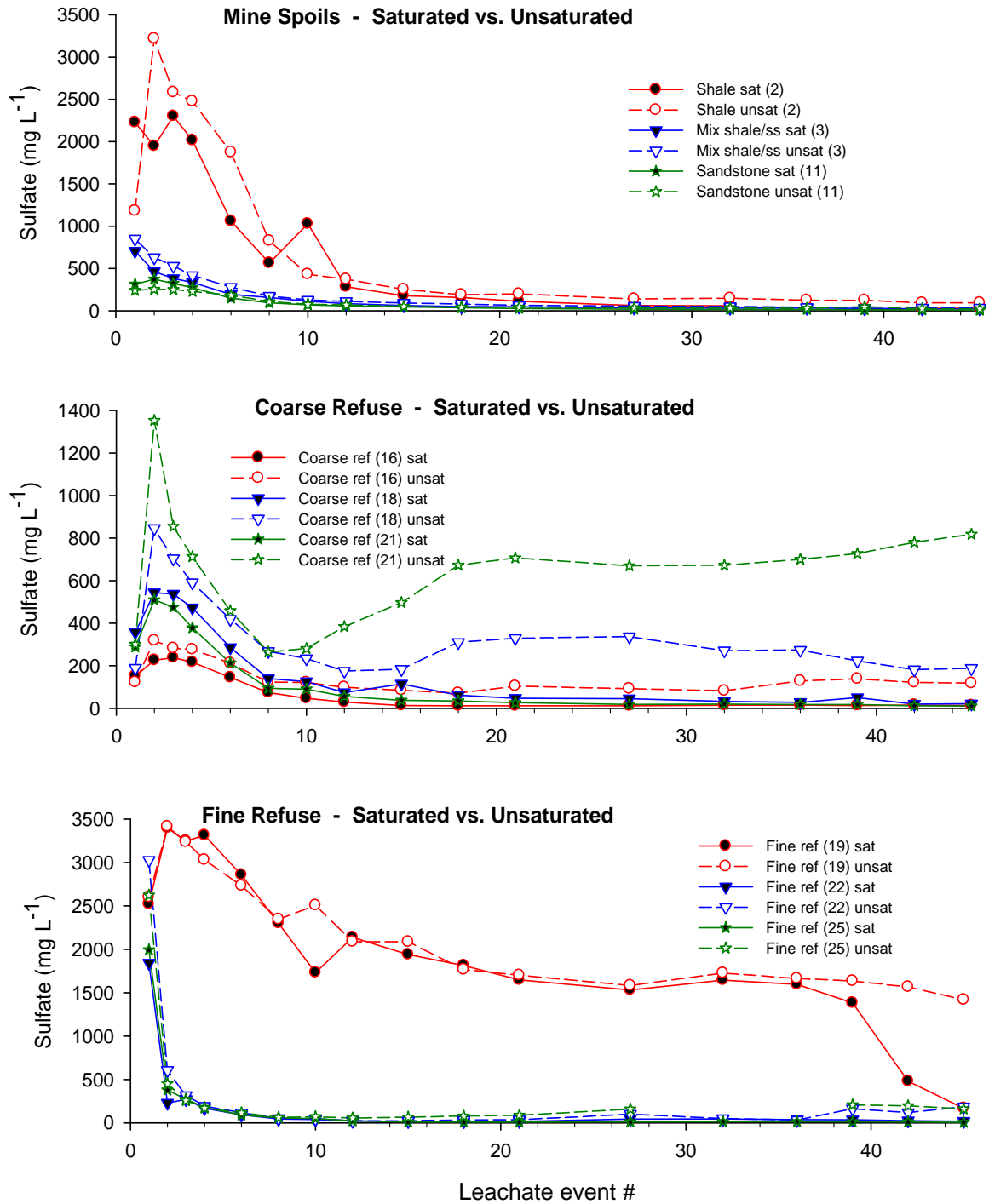
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Figure 6. Sulfate leached from selected mine spoils, coarse coal refuse, and fine coal refuse under saturated and unsaturated conditions. The 45 leachate events occurred over 153 days.

B: Boron, being relatively soluble and mobile, was quickly leached and its release was steady and at low levels after approximately 10 leaching events (Fig. 7). The lack of marked differences among samples and saturation treatments indicates its absence as part of any weatherable mineral structures. We assume B was found predominantly as the borate anion in all leachates.

Na: Sodium release (Fig. 8) followed a somewhat similar trend to B with high initial concentrations that rapidly decreased with time as would be expected. However, the release of Na from the refuse samples was notably higher. Initial Na concentrations were very high for fine refuse, but then dropped to near zero after 20 leaching events. Initial coarse refuse leachate Na concentrations were not as high as for the fine refuse, but after 45 leaching events (153 days) the concentration remained between 100 and 200 mg L^{-1}. Sodium is often mentioned as a significant component of TDS (Mount et al., 1997) that may have a mitigating effect on otherwise toxic concentrations of other components. This is discussed further below.

Ca: The Ca leaching pattern (Fig. 9) for the mine spoils followed the pattern of sulfate very closely with distinctly higher release by spoil sample #2. While this sample had a substantially higher total S content (Table 2) than the other mine spoil samples tested, the total Ca and Mehlich-1 extractable Ca was equal or less than that of mine spoil #3. The release patterns of the coarse and fine refuse samples are characterized by changes associated with oxidation of sulfidic material and the corresponding changes in pH and TDS/EC as discussed earlier.

Se: Selenium release (Fig. 10) dropped below our detection limit of 0.022 mg L^{-1} after the 18th leaching event for all samples. At first, large differences in release were observed between the saturated and unsaturated coarse refuse samples due to oxidation reactions, but this effect disappeared by the 10th leaching event. 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 predicted to be recalcitrant as reported earlier, significant "first flush" leaching occurred.

Fe: The Fe release patterns (Fig. 11) did not mirror those of other pyrite oxidation reaction products like sulfate. Due to the relatively high pH of the leachates, the vast majority of Fe was precipitated and retained within the columns in various oxy-hydroxide forms. However, the leachates from certain columns (e.g. #21) did exhibit a red Fe-oxide coloration that became more pronounced as the pH dropped over time. The relatively high release of Fe from saturated spoil #11 is notable and may be the result of reduction of original Fe-oxides to soluble Fe^{+2} over time.

Mn: Overall, leachate Mn concentrations were much higher than Fe due to the higher solubility of Mn than Fe in this pH range. Furthermore, Evangelou (1995) pointed out that amorphous Mn^{+4} oxides may also serve as an alternative electron acceptor (oxidizing agent) in moderate pH sulfide oxidation environments which can lead to large amounts of water soluble Mn^{+2} being mobilized. Manganese release patterns (Fig. 12) from refuse were more closely related to Ca and sulfate, with very high release by fine refuse #19. However, Mn release from the spoils was the opposite, with much less release from the Kentucky shale (#3) than from either of the spoils from Virginia. This is presumably due to differences in the inherent Mn oxide forms in the differing spoils.

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Figure 7. Leachate B from selected mine spoils, coarse coal refuse, and fine coal refuse under saturated and unsaturated conditions. The 45 leachate events occurred over 153 days.
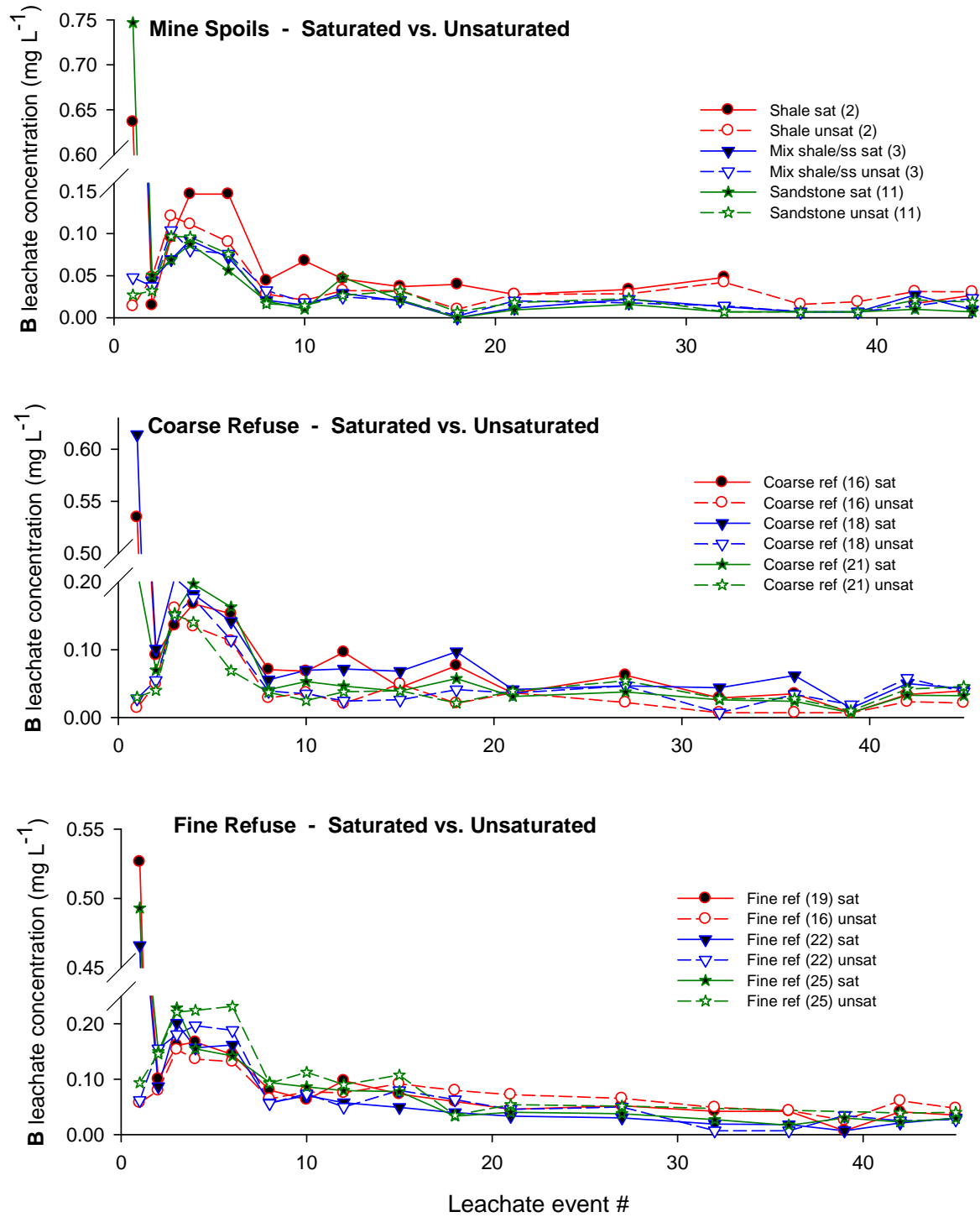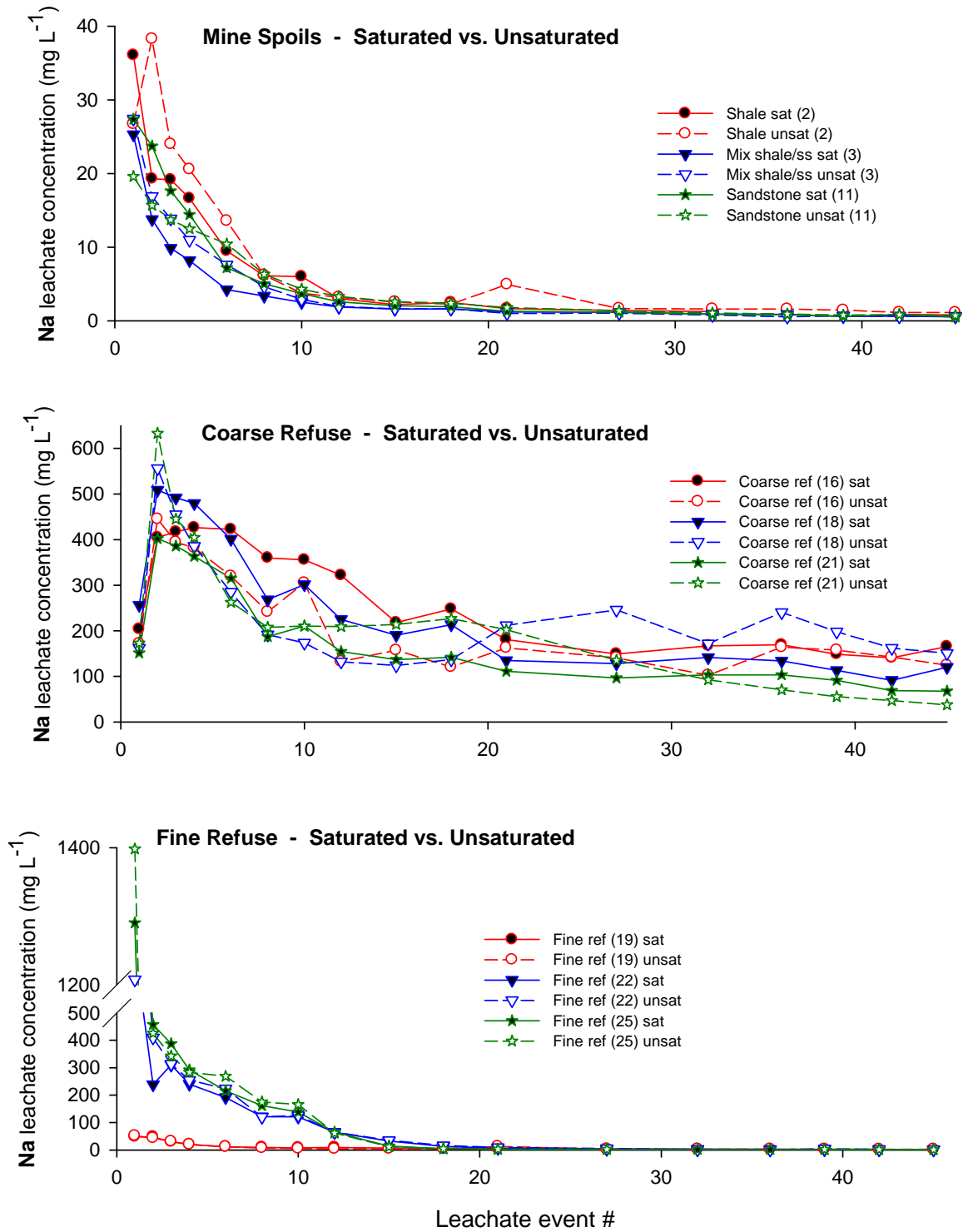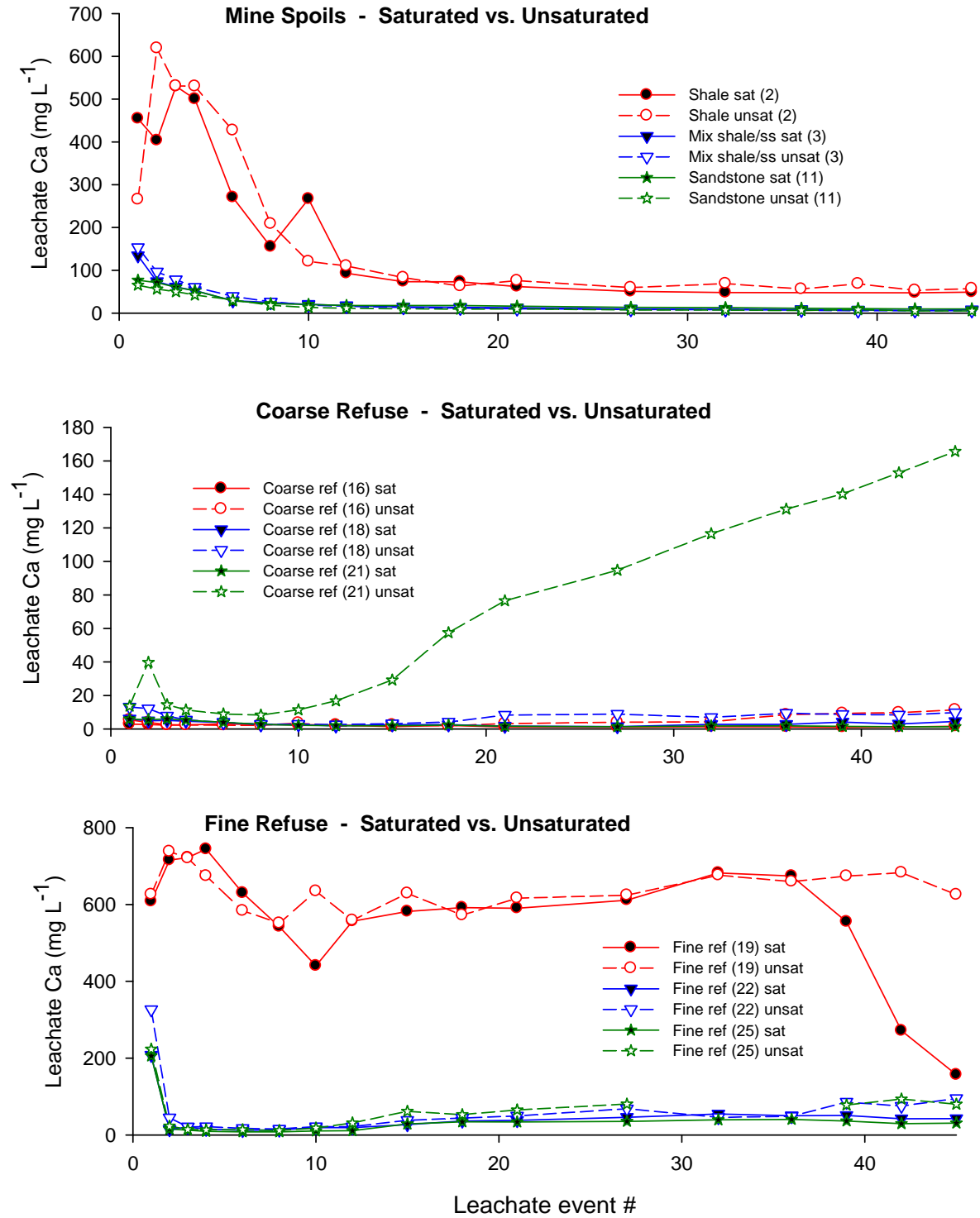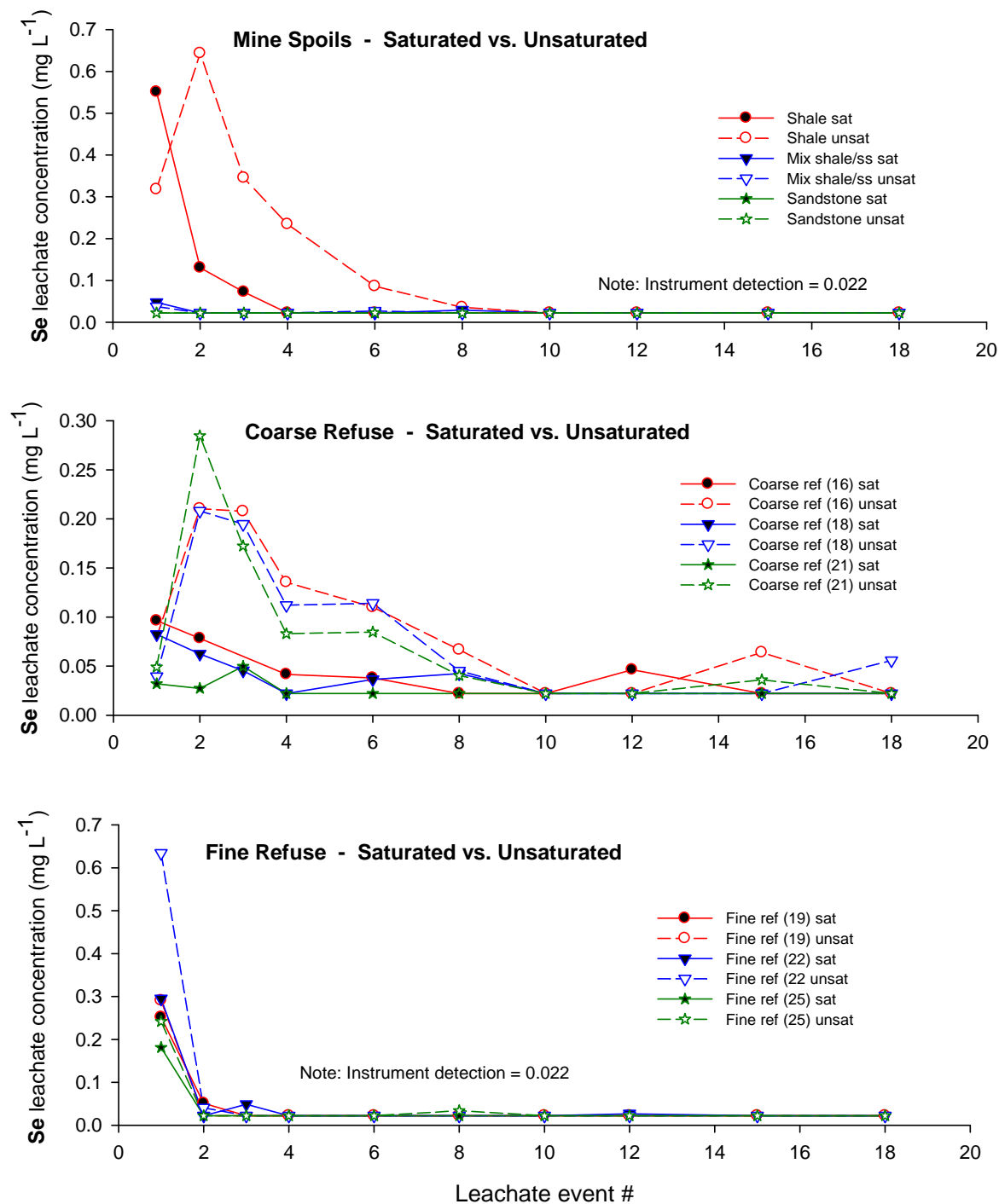
Figure 8. Leachate Na from selected mine spoils, coarse coal refuse, and fine coal refuse under saturated and unsaturated conditions. The 45 leachate events occurred over 153 days.
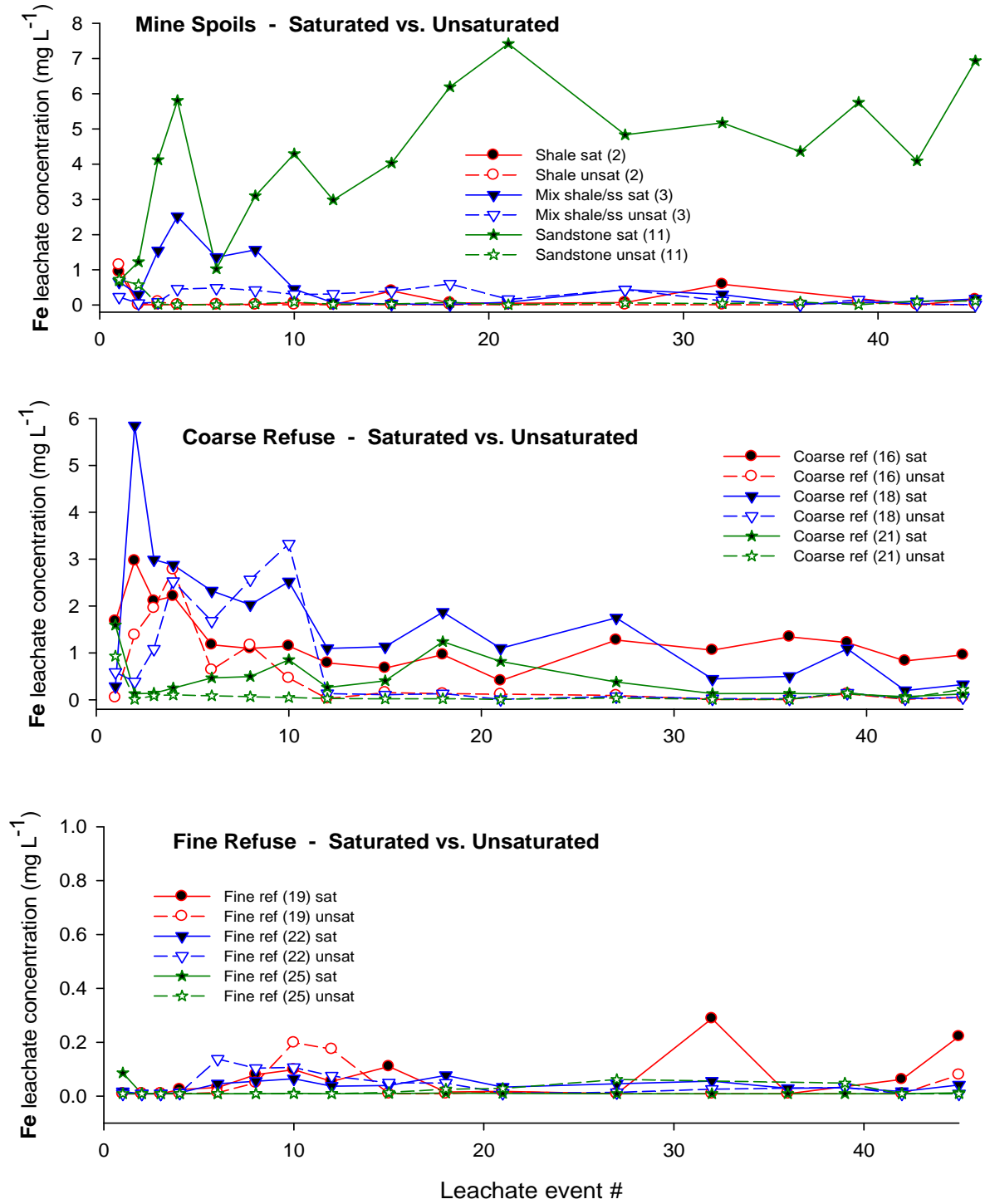
Figure 9. Leachate Ca from selected mine spoils, coarse coal refuse, and fine coal refuse under saturated and unsaturated conditions. The 45 leachate events occurred over 153 days.

Figure 10. Leachate Se 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 11. Leachate Fe 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 12. Leachate Mn from selected mine spoils, coarse coal refuse, and fine coal refuse under saturated and unsaturated conditions. The 45 leachate events occurred over 153 days.
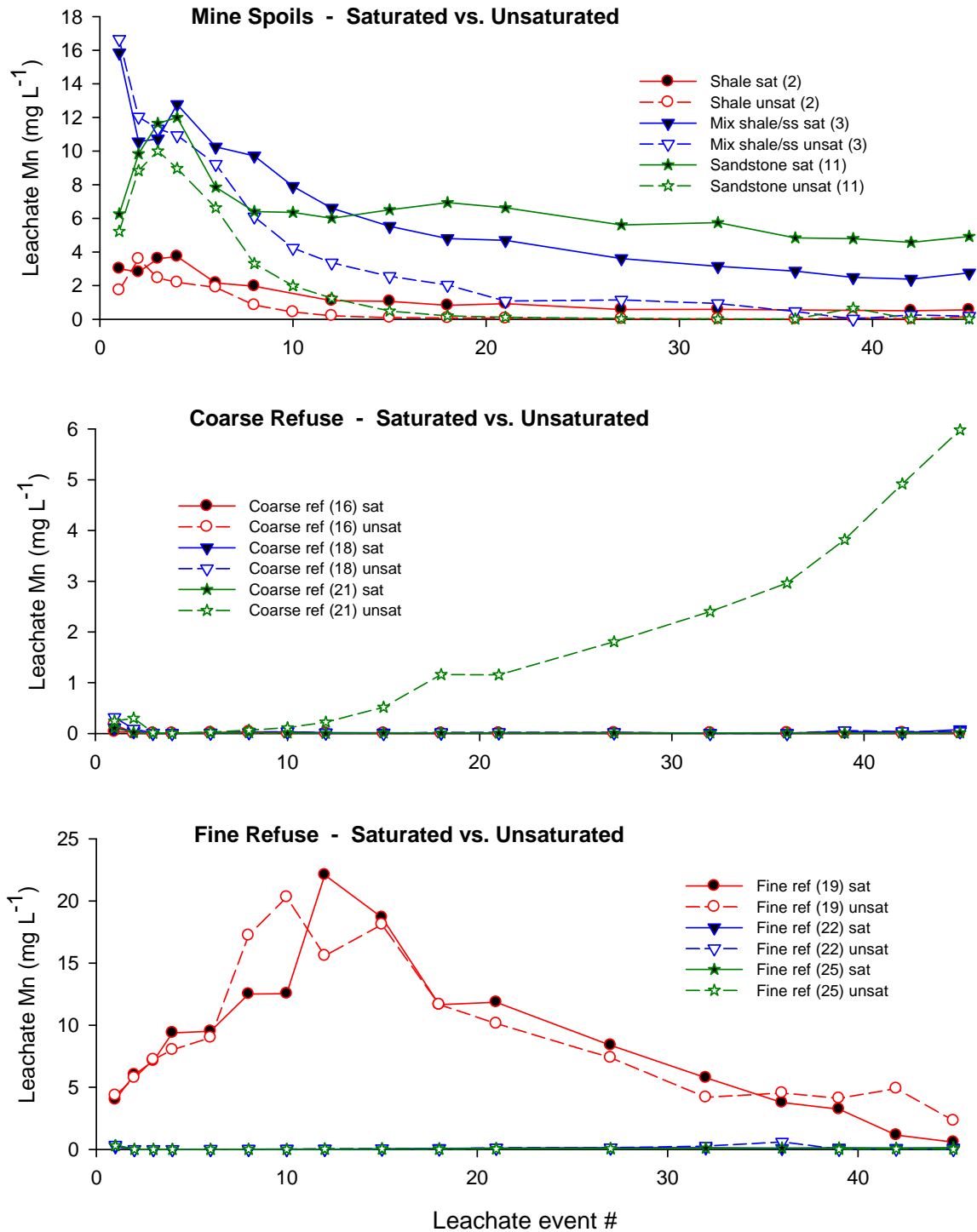
The leachate concentrations of other elements of interest, such as As, Be, Cr, Cu, Ni and Zn, were at or below detection limits (generally ≤ 0.010 mg L^{-1}). In a report to OSM on a different study that included a coal refuse material and fly ash, we (Daniels et al., 2006) reported that leachate concentrations for these elements remained at or below detection limits if the pH remained >3.5. Once the pH dropped below that, leachate concentrations drastically increased above levels of concern. The leaching data for Al, K, Mg, Mo, and Si are also presented in Appendix A. The Mo concentrations were relatively low and dropped below detection limit for all the materials and treatments. The data for Al, K, Mg and Si provide additional information, but are not essential to the discussion here since they were relatively minor contributors to TDS.

Composition of Total Dissolved Solids (TDS)

We investigated the relationship of leachate TDS to its mass elemental composition (mg L^{-1}) for leaching events (# 3, 12, 27, and 45). These data are graphically presented in Figure 13 a-c. Six elements, Ca, K, Mg, Na, S, and C (as bicarbonate) were found to be either quantitatively and/or functionally the major components of the leachate solutions. In all but one instance, the sum of the elements in the leachate solution (measured analytically, in mg L^{-1}, with S as sulfate and C as bicarbonate) exceeded the TDS values. This is due primarily to methodological differences. The TDS was determined on the filtered leachate (<2.0 microns) while the leachate mass elemental composition was determined on a total basis on the bulk solution eluted from the columns. This leachate had passed a Whatman #1 filter (2.5 microns) at the bottom of the leaching column, but was not filtered again before analysis. Thus, we believe that the mass leachate concentrations probably contained colloidal suspended phases and the sum of elements generally exceeded TDS in the range of 20 to 40%, but approached 90% for certain samples.

The elemental composition of leachate solutions from our column leaching study was strongly affected by the moisture conditions, saturated versus unsaturated, but there were also differences within the sample groups, mine spoil, and coarse vs. fine refuse.

Mine spoil: The elemental composition from the three samples under *saturated* conditions was dominated by sulfate and bicarbonate (Figure 13 a). The sulfate component decreased over the course of the leaching trial while the bicarbonate component remained approximately the same in mass, and thus became the dominant anion. The release of bicarbonate for sample #2 under *unsaturated* conditions was approximately equal to that under saturated conditions. For the other two mine spoils, however, the elemental composition was dominated by the elution of sulfate and bicarbonate was nearly absent for reasons (acid neutralization) discussed earlier. The release of all other elements which contributed only minor amounts to TDS, were very similar under saturated and unsaturated conditions.

Coarse refuse: The initial TDS for all three refuse samples under *saturated* conditions was dominated by Na, sulfate, and bicarbonate (Figure 13 b). A large sulfate component was only observed for the initial leachate event (#3). As the total TDS decreased over time, the proportion of bicarbonate to Na remained relatively constant. The elemental composition and relative distribution of TDS under *unsaturated* conditions was affected to varying degrees by oxidation of sulfidic material as discussed earlier. In sample OSM #16, the proportions of Na:sulfate: bicarbonate remained approximately constant throughout the trial period. Sulfate release

continued after the initial flush as recorded in leaching event #3, yet S oxidation did not produce enough acid to limit the bicarbonate fraction. In sample OSM #18, S oxidation resulted in a proportional increase in sulfate with a corresponding decrease in the bicarbonate fraction. The oxidation and corresponding neutralization of acid by bicarbonate was not adequate to produce a drop in pH (Fig. 2). This however, was not the case for sample #21. The production of acid and associated neutralization consumed virtually all solution bicarbonate. This is evidenced by the increasing quantity, and proportion to other elements, of sulfate in the leachate solution and absence of bicarbonate. The lack of adequate bicarbonate to balance the acid produced resulted in a continued drop in pH over time (Fig. 2). Associated with that drop in pH was the dissolution/dissociation of other compounds and the corresponding increase in other elements like Ca, K, and Mg.

Fine refuse: The TDS analysis indicates that samples #22 and #25 were very similar in concentration and ionic species composition, as well as in the temporal release pattern (Figure 13 c). The initial leachate was comprised of approximately similar mass fractions of sulfate, bicarbonate, and Na. Under *saturated* conditions, overall concentrations drop drastically and the bicarbonate became the dominant ion. In the discussion above on Figures 6-12, it was suggested that the conditions in *unsaturated* treatments for the fine refuse were perhaps limited in O_2 diffusion to some extent and resembled the saturated columns for certain treatment combinations. Sulfate concentrations, based on the oxidation of sulfidic material, increased over time and its proportion relative to the other ions increased. Also, as is typical under these conditions, the total leachate concentrations increased over time (leachate events 12 to 45) instead of the continued decline observed under saturated conditions.

Discussion: There is increasing evidence that toxicity related to TDS is due to the specific combination and concentration of ions and is not directly or solely predictable from TDS concentrations (Chapman et al., 2000). Mount et al. (1997) developed regression models to predict the toxicity attributable to major ions such as K, HCO_3, Mg, Cl, and SO_4. This study found that the presence of multiple ions tended to be less toxic than comparable solutions with only one ion. Also, as hardness increases, TDS toxicity may decrease. Modifications of the ionic composition of water can exclude some aquatic species while encouraging an increase of others (Weber-Scannell and Duffy, 2007). A recent study by Kennedy et al. (2005) demonstrated the wide range in TDS and the interaction elemental components. In "*laboratory testing of several effluent-mimicking media, sodium- and sulfate-dominated TDS were acutely toxic at approximately 7000 μS/cm (5143 mg TDS/L), and chronic toxicity occurred at approximately 3200 μS/cm (2331 mg TDS/L). At a lower hardness (88 mg/L as $CaCO_3$), acute and chronic toxicity end-points were decreased to approximately 5000 μS/cm (3663 mg TDS/L) and approximately 2000 μS/cm (1443 mg TDS/L), respectively*". Chapman et al. (2000) observed no toxicity with embryos or fry at > 2000mg L^{-1} of TDS, but Chironomids exhibited signs of toxicity at TDS of > 1100mg L^{-1} for two coal mine effluents. These varying data contribute to the widely ranging approaches by state agencies in regulating TDS. Oregon uses a TDS standard of 100 mg L^{-1} for all fresh water streams, Mississippi a TDS monthly average of 750 mg L^{-1}, and Alaska uses a criterion of 1000 mg L^{-1}. Illinois is looking into changing from a strictly TDS limit to limits on specific ions, such as sulfate. Finally, Virginia has proposed a voluntary TDS standard of 334 mg L^{-1} for new TMDL watershed determinations which has been widely questioned by the coal industry.

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.
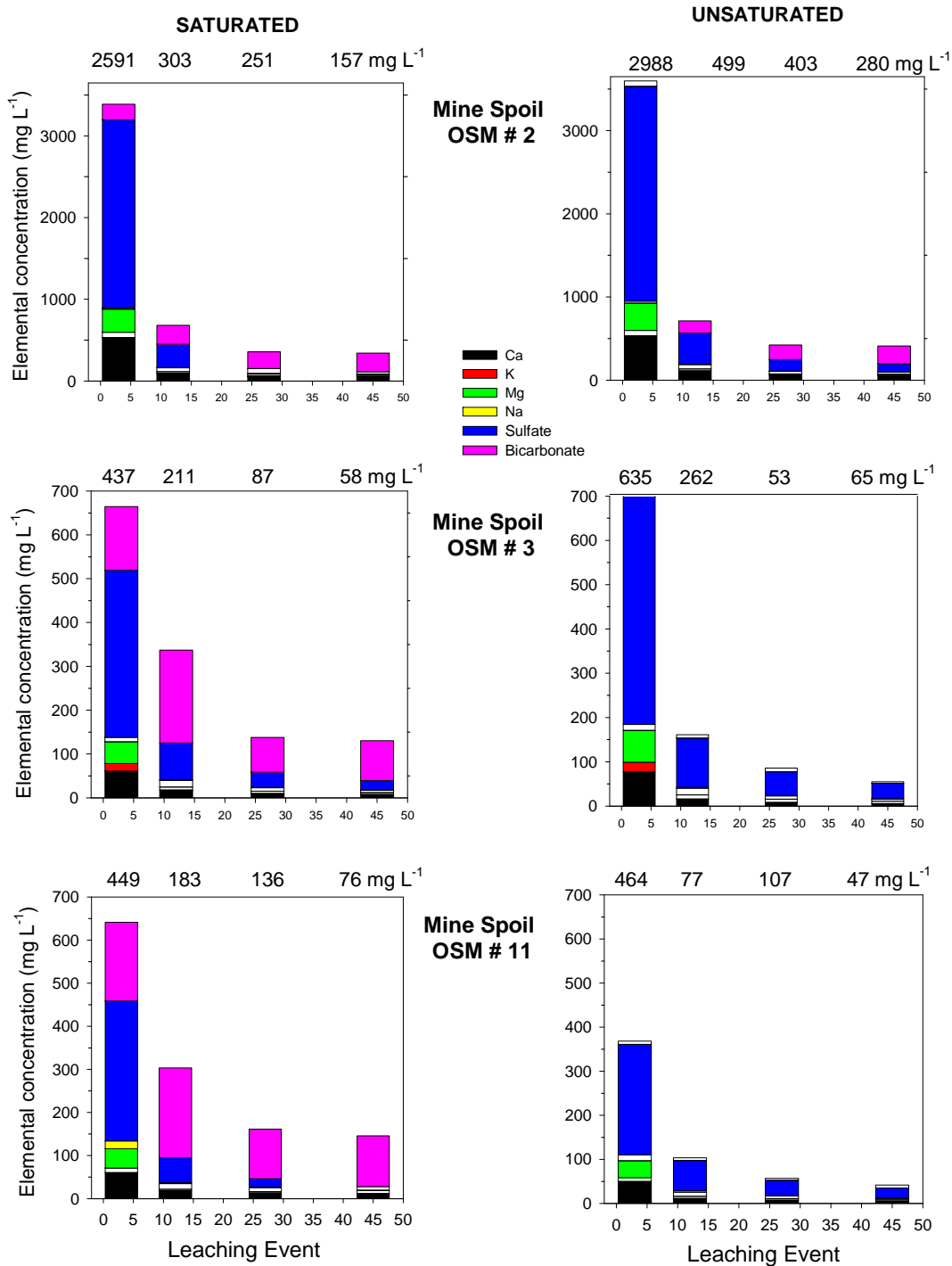
Figure 13b. Quantitative distribution of major elements in leachate solutions and the respective TDS values from coarse coal refuse. Samples represent leaching events # 3, 12, 27, and 45. Values within charts represent total leachate analyses Values within charts represent total leachate analyses while the determined TDS value for filtered samples ($< 2\ \mu$) is given at top of each bar for each element.
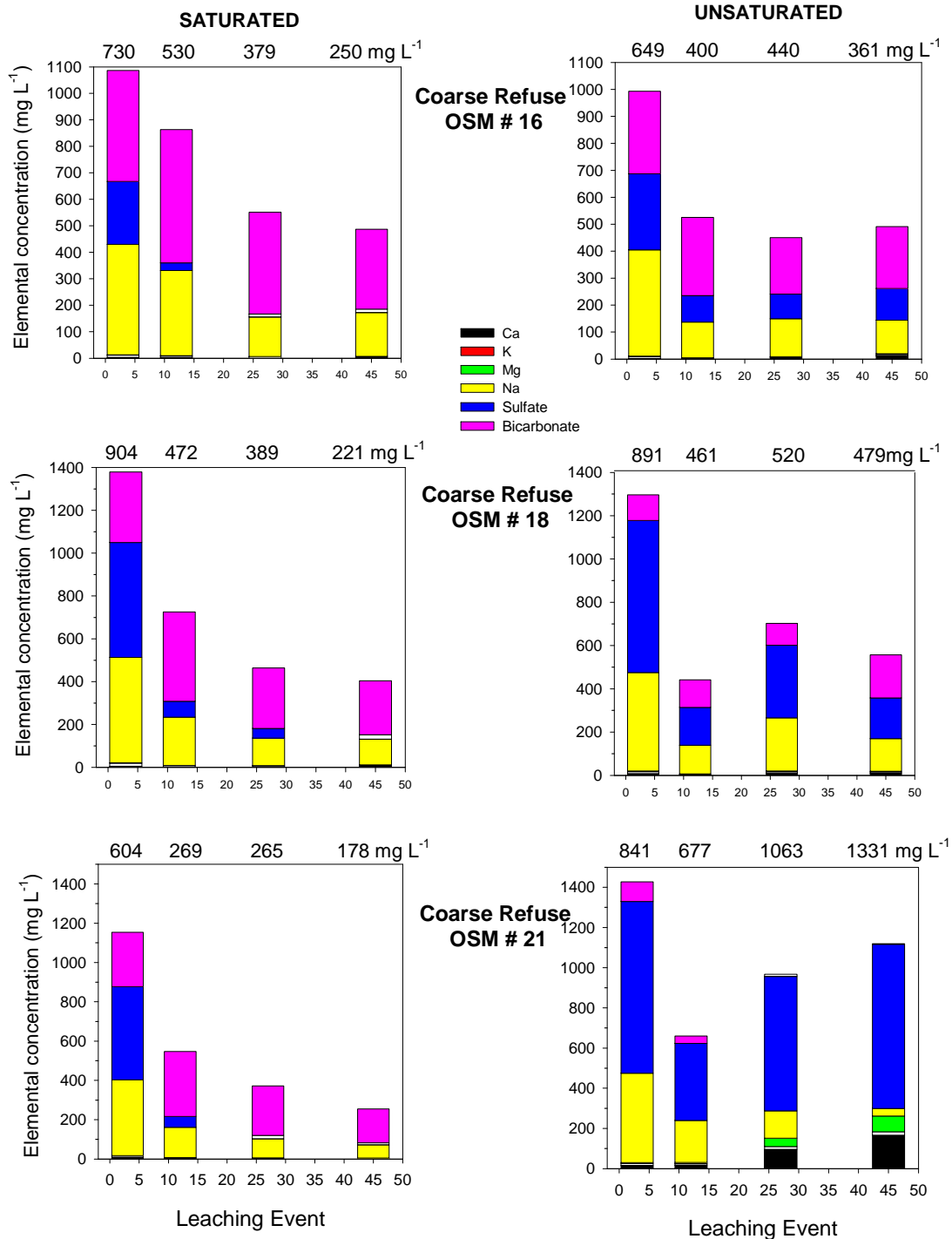
Figure 13c. Quantitative distribution of major elements in leachate solutions and the respective TDS values from fine coal refuse. Samples represent leaching events # 3, 12, 27, and 45. Values within charts represent total leachate analyses Values within charts represent total leachate analyses while the determined TDS value for filtered samples ($< 2\ \mu$) is given at top of each bar for each element.
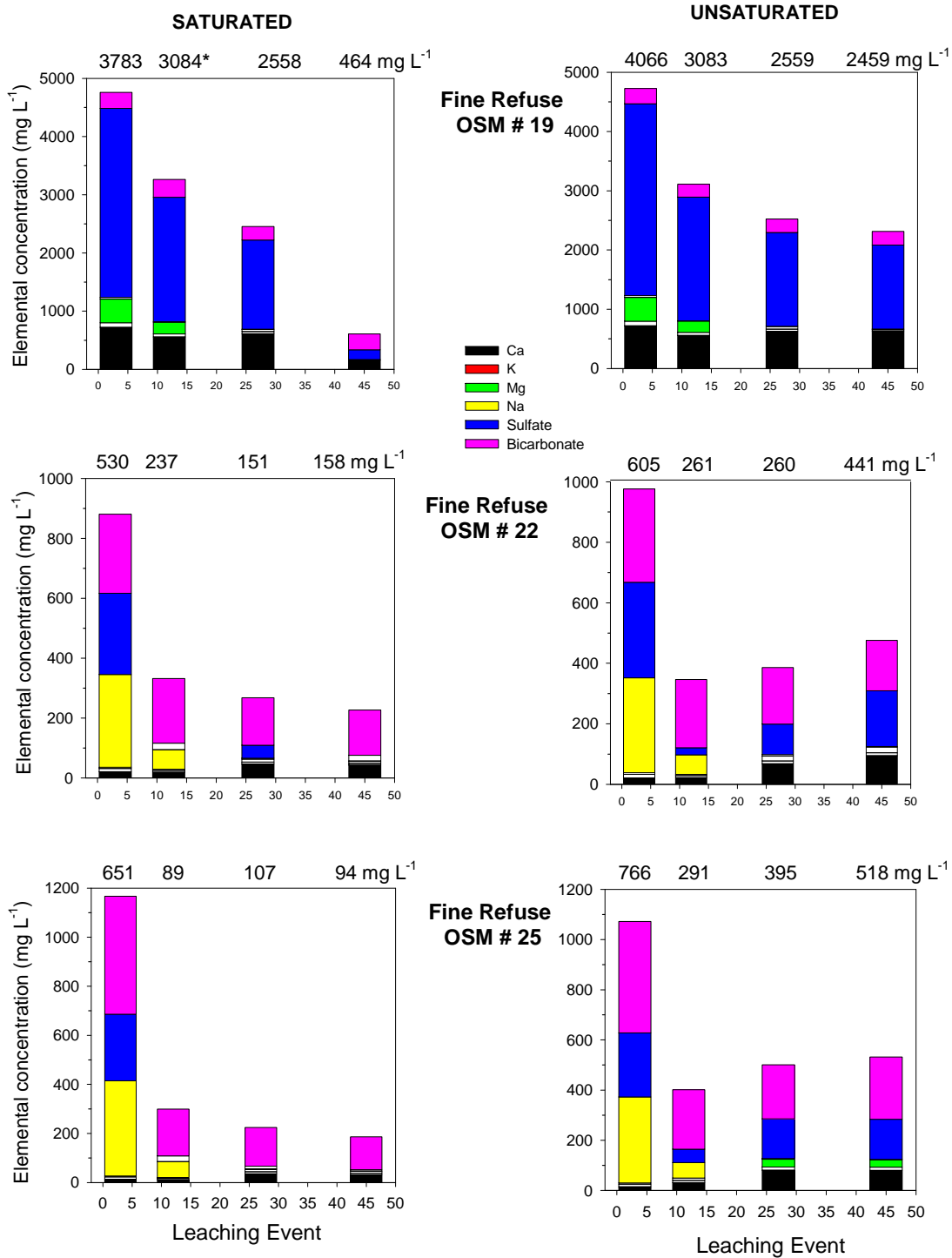
As discussed earlier, fine refuse sample #19 was distinctly different from the other two fine refuse samples. Its leachate was strongly dominated by the sulfate ion with only a minor bicarbonate component. The overall leachate concentrations dropped with time due to declines of sulfate and other ions, 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 worse 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 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 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 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. Elseewi, 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 NH_4. 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.
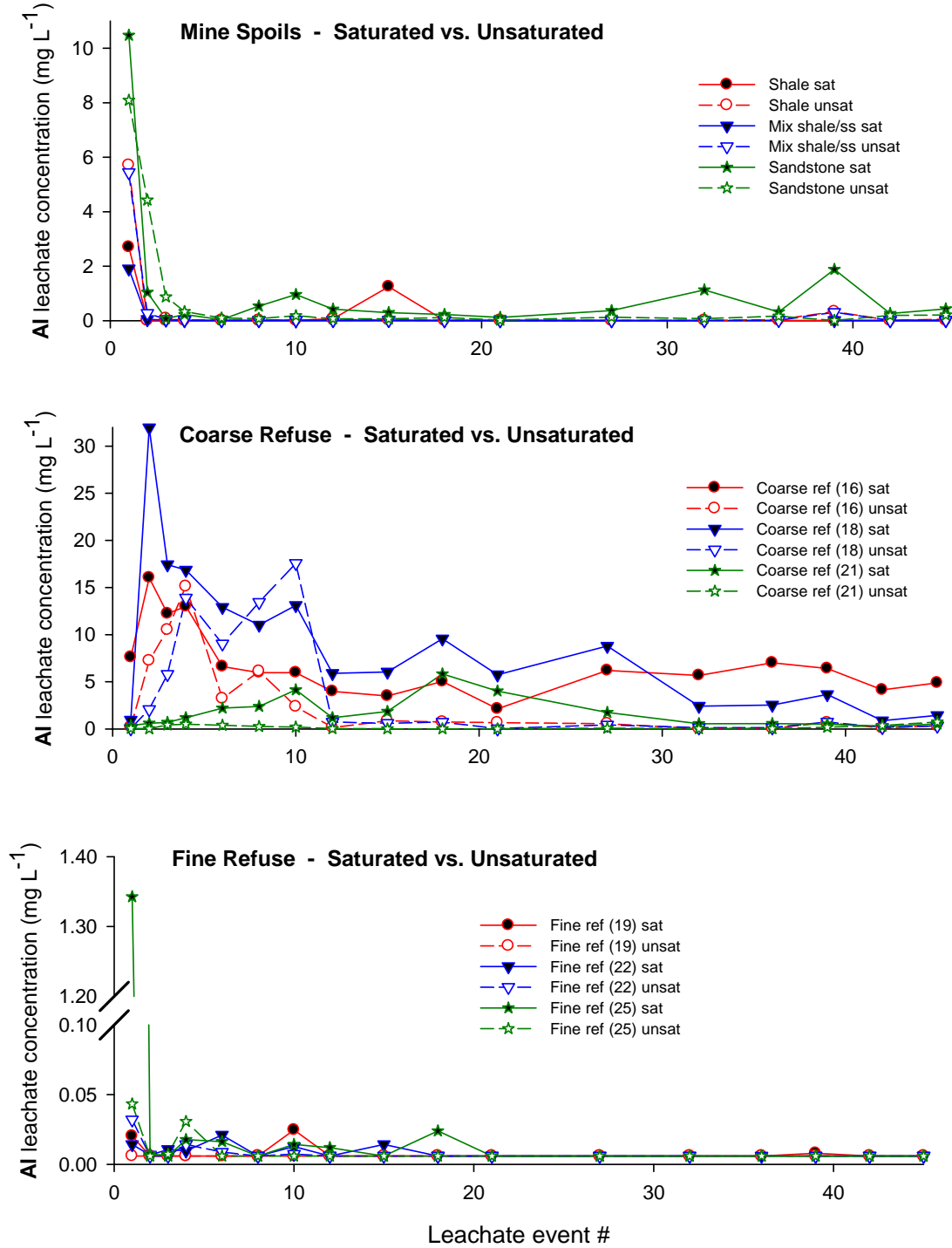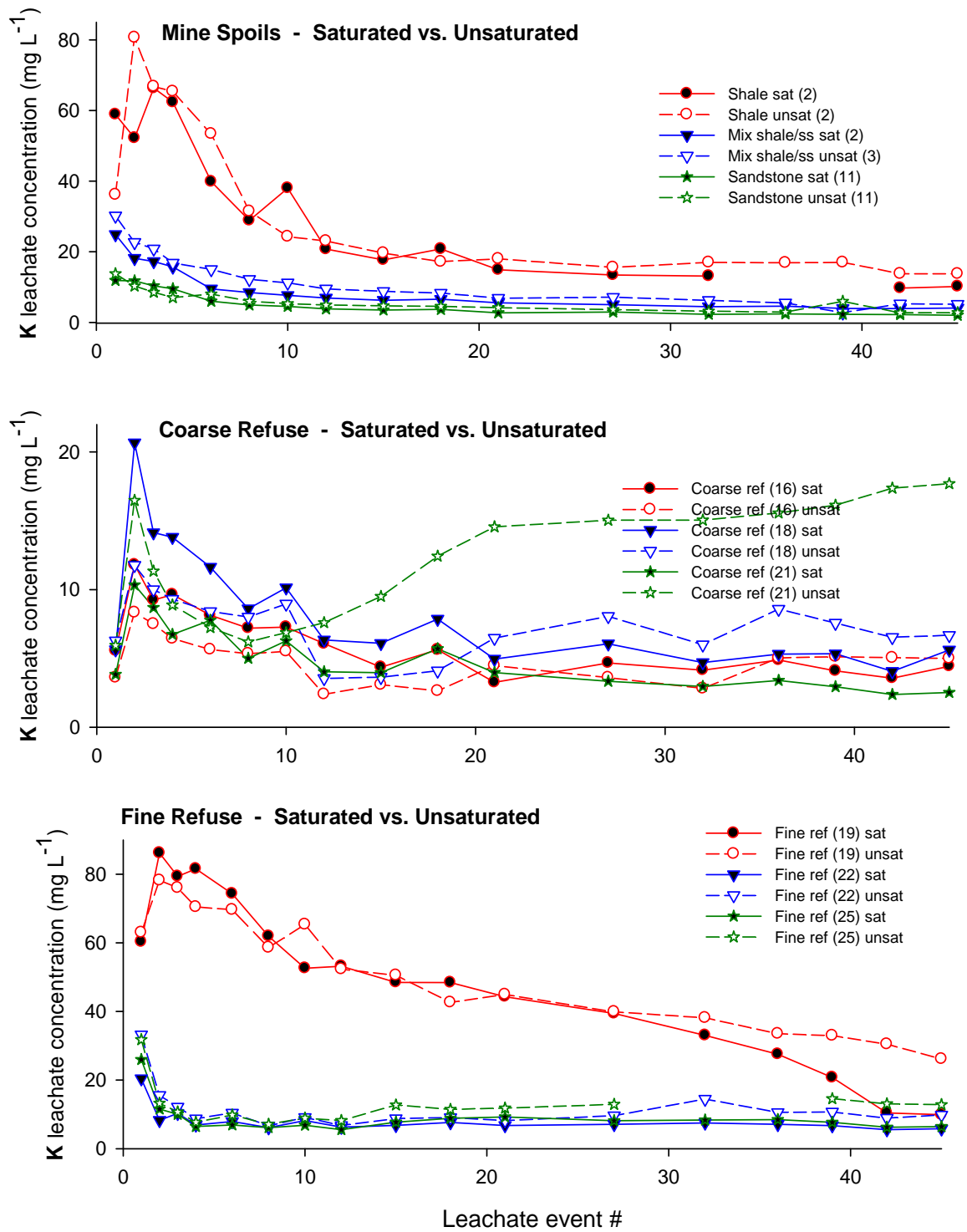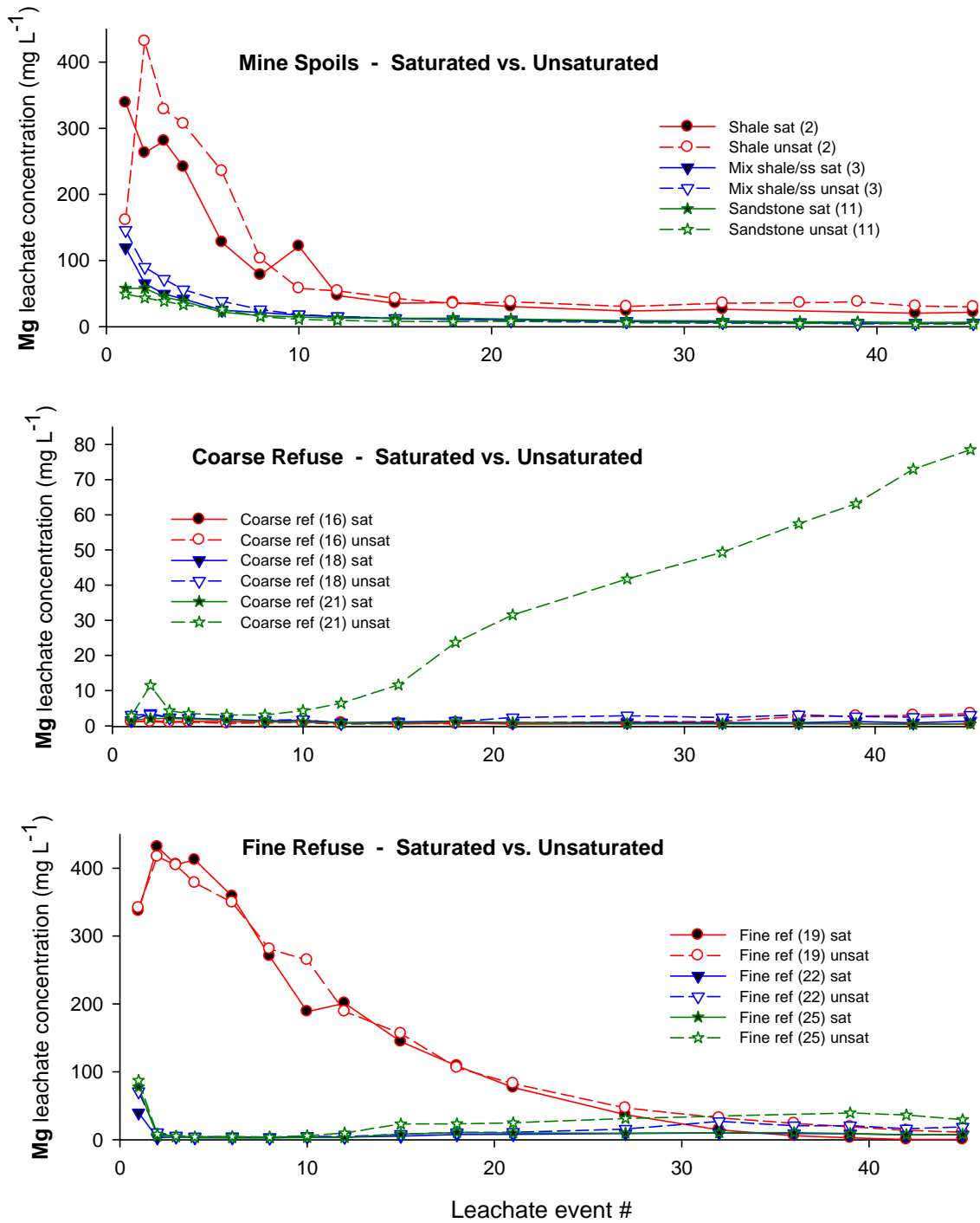
Figure 15. Leachate K from selected mine spoils, coarse coal refuse, and fine coal refuse under saturated and unsaturated conditions. The 45 leachate events occurred over 153 days.
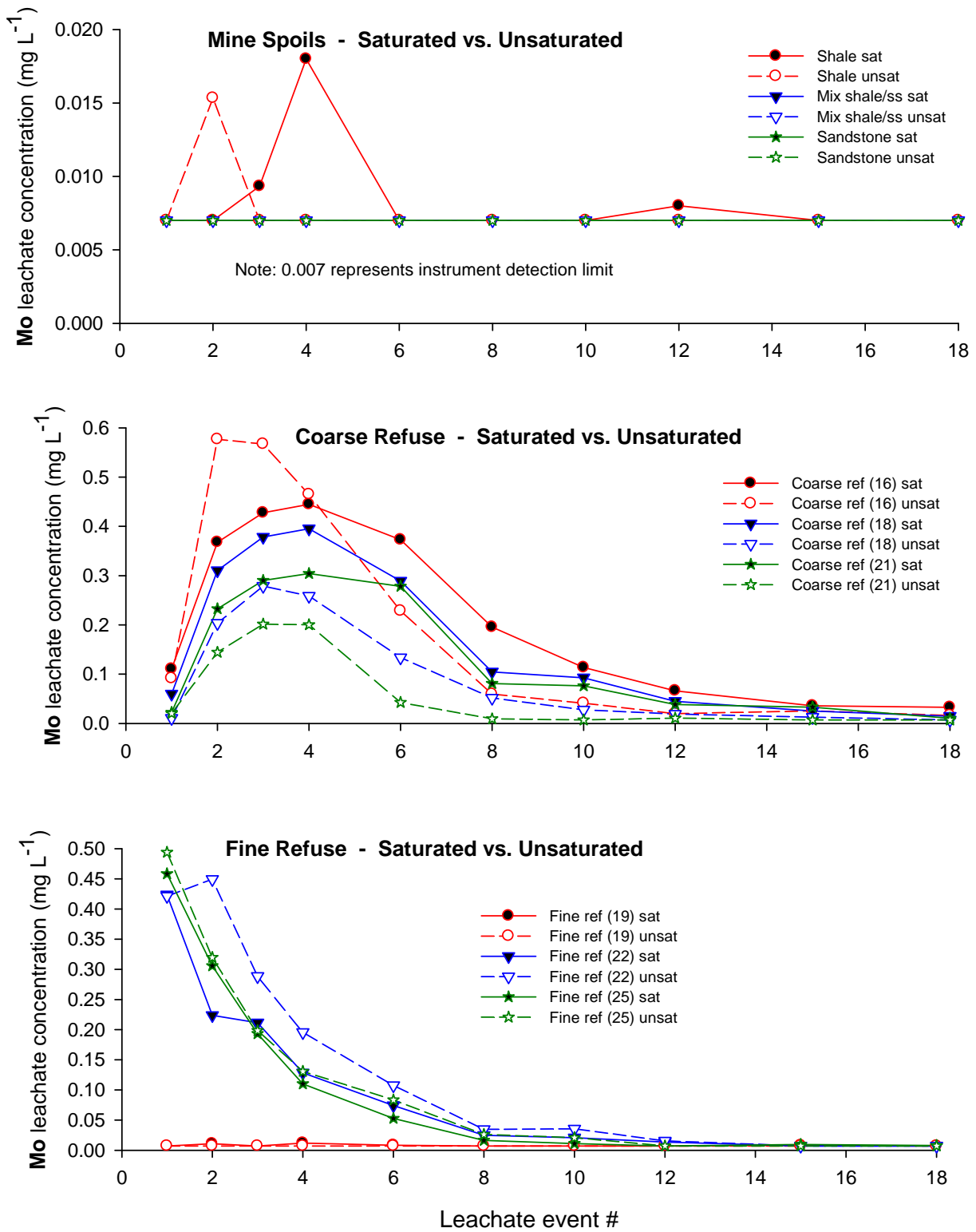
Figure 16. Leachate Mg from selected mine spoils, coarse coal refuse, and fine coal refuse under saturated and unsaturated conditions. The 45 leachate events occurred over 153 days.

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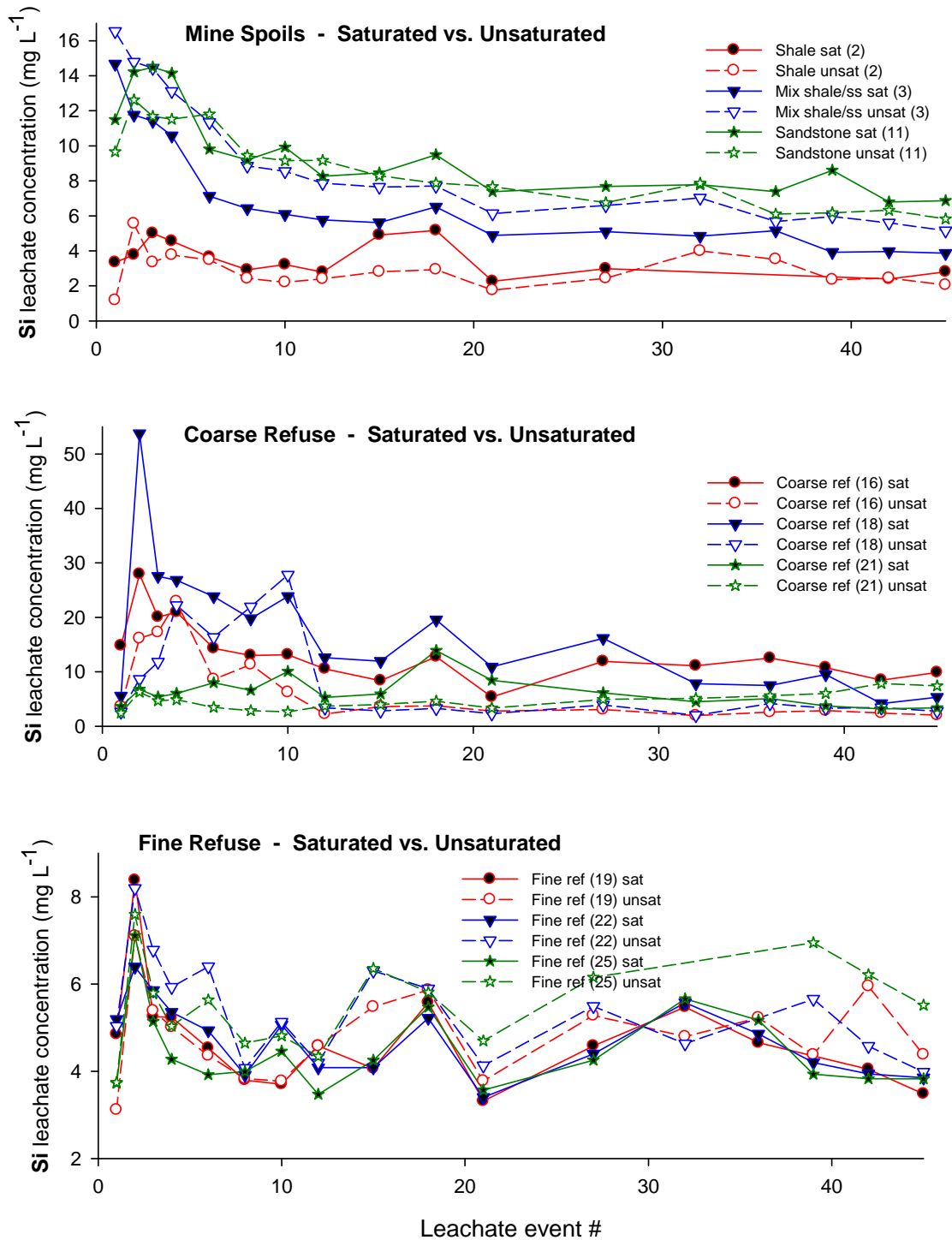
Figure 18. Leachate Si from selected mine spoils, coarse coal refuse, and fine coal refuse under saturated and unsaturated conditions. The 45 leachate events occurred over 153 days.

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'.