Final Report

Correlation of TDS Release Potentials with Field Leaching Behaviors for Appalachian Coal Mine Spoils and Coarse Refuse

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1. Executive Summary

Over the past decade concerns about the biological effects of elevated long-term emission of total dissolved solids (TDS) from coal mine backfills and valley fills have emerged. This research program focused on determination of leaching potentials of coal mine spoils from Tennessee along with a selection of coarse coal refuse materials from the region. Major goals were to characterize the elemental composition of the leachates, to determine the temporal pattern of elemental release, and to compare the results obtained from column leaching trials with larger scale leaching methods. In parallel, we investigated the ability of static laboratory tests to predict TDS elution potentials. Finally, we conducted a regional assessment of TDS elution trends over time from > 100 existing valley fills in Virginia by utilizing the existing NPDES/VDMLR water quality data base and by tracking changes in specific conductance (SC) at numerous locations before, during and after coal mining activity.

The mine spoils (5) and coal refuse (4) studied in our leaching columns released significant amounts of TDS in their initial leaching events with spoils generally producing electrical conductance (EC) > 1500 µs/cm and refuse samples considerably higher. Leachate EC dropped quickly in all spoils after one to two pore volumes and stabilized at levels < 500 µs/cm. The EC response in the refuse materials studied was more variable, however, with several materials maintaining high (> 1000 µs/cm) EC while others dropped below 500 µs/cm over the course of the study (40 x 2.5 cm leaching). Trace element (e.g. As, Ca, Se) release varied widely among the materials and was generally higher from the more reactive refuse materials. Initial Se release was significant (> 100 µg/L) for all materials, but subsequently declined to range from ~1 to > 10 µg/L for longer term quasi-equilibrium release. For the spoil materials tested here, both total-S and CCE were relatively strong predictors of EC levels, but at different phases of leaching.

One spoil and two refuse samples were also subjected to larger scale (200 L barrels for both and mesocosm tanks for the spoil) leaching to compare results against the columns. For the spoils, levels of bulk EC and leachate elements produced by the lab columns were very similar to those produced by two larger scale leaching systems. However, two important differences were noted: (a) Initial EC levels were higher in the larger mesocosm tanks and (b) the EC in the barrels and mesocosms began to rise again slowly at the end of the study. In contrast to the spoil, the two coal refuse materials studied at two scales (lab columns vs. 200 L barrels) produced very different results for bulk pH, EC and elemental release response over the leaching period studied.

Results from our field valley fill discharge indicated that observed field specific conductance levels were quite similar to peak and average EC levels observed for a wide range of spoils in our column studies. The field discharge data also indicate that over the long term, valley fill TDS discharges in the region studied are declining, and we predict a lag time of approximately 20 years for the average fill to decline to < 500 µs/cm. Finally, we need to note that our data sets continue to reinforce the fact that overall TDS production and trace element release from coarse coal refuse is a much larger concern than from hard rock coal mine spoils.

2. Introduction, Background and Research Objectives

The Surface Mine Control and Reclamation Act (SMCRA) of 1977 contained a number of contentious provisions including the allowance for use of pre-selected overburden materials as topsoil substitutes when (1) the native A+E horizon materials are less than 15 cm (6") thick, and (2) the physical and chemical properties of the proposed substitute spoil materials are deemed suitable for such use. Since native topsoil layers throughout the Appalachian coalfields are usually less than 15 cm thick, and removing them from steep slopes is difficult and expensive, the vast majority of coal mined lands in the region have employed topsoil substitutes. Thus, the final graded and revegetated surfaces usually consist of overburden derived topsoil substitutes which are commonly much higher in pH and weatherable minerals, including carbonates, than native soil profiles and rock saprolites. Similarly, SMCRA requires the isolation of acid-forming materials ($\geq$ 5 tons CCE / 1000 tons net acid-forming) away from contact with surface runoff and isolation away from internal drainage in mining fills. However, where (1) acid-forming strata are thin relative to adjacent net alkaline strata or (2) where they can be blended with sufficient volumes of other net alkaline materials in the blasting-hauling-placement sequence, the industry has relied upon appropriate application of acid-base-accounting procedures (ABA; Skousen et al., 2002) to ensure that the drainage from highwall backfills and valley fills is non-acidic and complies with discharge limits for Fe, Mn and pH. As described below, both of these practices (topsoil substitution and acid/alkaline spoil blending) have more than likely led to enhanced levels of total dissolved solids (TDS) in Appalachian coal mine discharge waters vs. undisturbed pre-mine conditions.

The dominant constituent ions of TDS released by weathering of central Appalachian mine spoil materials are typically Ca, K, Mg, Na, SO_4^{-2} and HCO_3^- in circumneutral waters and higher amounts of Al, Fe and Mn in strongly acidified systems (Skousen et al., 2000). All of these components are released by various chemical weathering reactions, particularly when deeper unweathered and unoxidized strata are unearthed and exposed to rapid oxidation, hydrolysis, hydration and dissolution reactions in the surfaces and fills of active coal mines. The upper 5 to 15 m of overburden is typically oxidized to some extent by long-term geochemical weathering (Haering et al., 2004) and leaching of these materials is therefore much less likely to generate significant TDS after blasting and placement. However, deeper strata commonly contain significant amounts of reactive sulfides, carbonates, feldspars and other mineral phases that rapidly produce varying loads of soluble ions to percolating water and runoff, particularly as they interact with their initial pore volumes of bathing waters. Unweathered overburden in the central Appalachians can contain significant amounts (0.5 to > 3.0%) of complex carbonates (Howard et al., 1988) which occur primarily as secondary cementing agents along with highly variable amounts of reactive sulfides (Sobek et al., 2000). Depending on the distribution and quantity of these minerals, the pH of freshly exposed unoxidized overburden is between 6.5 and 8.2 (Roberts et al., 1988) while that of weathered/partially weathered overburden is generally between 4.5 and 6.0.

Essentially, surface coal mining in the Appalachian region creates a set of "weathering conditions" for disturbed overburden whereby generation of TDS loading to leaching waters and runoff can be significant and certain levels of release are unavoidable. That being said, the fact that current regulations and mining practice mandates that all potentially acid forming materials (potential acidity > 5 tons/1000 tons CCE net acid) must be isolated away from the surface and from significant ground water interaction certainly eliminates the largest potential source of net TDS release. However, many non-isolated strata contain significant amounts of reactive sulfides that are essentially balanced by carbonates in terms of their ABA, such that these materials can still contribute substantially to TDS loadings (particularly Ca, Mg, HCO_3^- and SO_4^{-2}) as they weather while maintaining moderate to circumneutral pH conditions in that drainage (Daniels et al., 2009). In addition to these acid-base reactions, fresh spoils can also contribute to TDS due to simple dissolution reactions of carbonate cements, hydrolysis weathering of feldspars and other primary mineral grains and traces of entrained Cl salts.

Over the past decade, the concept of topsoil substitution has been criticized from a number of perspectives including potential effects on water quality due to inclusion of higher pH and more chemically reactive overburden in contact with surface water runoff. Similar concerns about elevated long-term emission of TDS from backfills and valley fills have also emerged. In a series of actions between 2009 and 2011, the USEPA attempted to use its Clean Water Act Section 404 authority that to establish 500 µS cm^{-1} electrical conductivity (equivalent to about 350 mg L^{-1} TDS) as a potential or *de facto* standard, at least within heavily mined watersheds. For example, citing Pond et al. (2008), an EPA official testified to the US Congress that "*These dissolved ions are not readily sequestered by the surrounding geology and may ultimately emanate from the fills for decades. ... This impairs the use of the streams and ultimately leads to listing of these streams as 'impaired water bodies' in EPA's water quality reports …*" (Pomponio, 2009). Several recent studies (Chapman et al., 2000; Goodfellow et al., 2000; Pond et al., 2008; Timpano et al., 2010) have addressed the issue of TDS as a major stressor upon receiving streams in mined watersheds. More recent EPA guidance (issued in 2011; now withdrawn) was based on the belief that mine discharges with EC levels <300 µS cm^{-1} generally will not cause significant degradation of the aquatic ecosystem while in-stream conductivity levels >500 µS cm^{-1} are likely to be associated with significant adverse impacts on the aquatic ecosystem. The proposed guidelines suggested that projects expected to increase conductivity to levels >300 µS cm^{-1} should require adaptive remedial action to prevent conductivity from rising to levels that may contribute to water quality degradation and sites with discharges >500 µS cm^{-1} should not be allowed to continue to operate. While the ability of USEPA to directly implement this guidance was rejected in U.S. Federal Court, the decision (Walton, 2012) left it open for OSM and the states to develop and establish TDS regulatory limits based upon the "best available science". Thus, coal mining discharges could still potentially be directly regulated for TDS (via measurement of EC) at some point in time.

2.1. TDS Production and Prediction

As discussed above, rapid oxidation of trace sulfides and parallel neutralization reactions (primarily by complex carbonates) are presumed to be the primary sources of TDS components from actively weathering and leaching mine spoils. The primary mechanism of pyrite oxidation is shown below (Singer and Stumm, 1970).

$$FeS_2 + 7/2O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$$
$$Fe^{2+} + 7/H_2O + 1/4O_2 \rightarrow Fe(OH)_3(s) + 2H^+$$
$$Fe^{2+} + 1/2O_2 + H^+ \rightarrow Fe^{3+} + 1/2H_2O$$
$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+$$
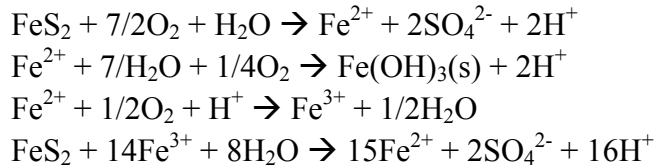
Even relatively small amounts (<0.1%) of pyritic-S can generate substantial release of acidity and sulfate to percolating mine waters. Carbonates, when present, can dissolve and subsequently neutralize the acidity as shown below (Berner and Morse, 1974).

$$CaCO_3 \rightarrow Ca^{2+} + CO_3^{2-}$$
$$H^+ + CaCO_3 \rightarrow Ca^{2+} + HCO_3^-$$
$$2H^+ + CaCO_3 \rightarrow Ca^{2+} + H_2CO_3$$
$$H_2CO_3 + CaCO_3 \rightarrow Ca^{2+} + 2HCO_3^-$$
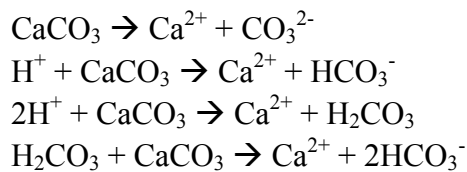
The reactions depicted above reflect idealized conditions and do not account for a wide range of complicating factors including differences in reaction kinetics, formation of intermediary compounds, and the potential for carbonates to become coated or "armored" with iron, thus limiting their reactivity. The presence of siderite ($FeCO_3$) also greatly complicates conventional ABA. These issues and many others are reviewed in detail by Evangelou (1995).

In addition to the direct acid-base reactions detailed above, hydrolysis weathering reactions involving feldspars and micas can also release substantial amounts of other base cations such as K and Na to percolating waters. Thus, TDS in discharge from coal mines is dominated by HCO_3^-, SO_4^{2-}, Ca^{2+}, K^+, Mg^{2+}, and Na^+ (Agouridis et al., 2012; Hartman et al., 2005; Orndorff et al., 2010) with SO_4^{2-} and Ca^{2+} dominating the mass of ions released in circumneutral waters. Total dissolved solids is only rarely measured directly due to it being very labor intensive and is generally estimated via electrical conductance (EC) or specific conductance (SC; which is EC corrected to 25° C). Most studies show correlation coefficients greater than 0.95 between TDS and EC, thus making EC a very effective indicator for TDS (Daniels et al., 2009; Hood and Oertel, 1984). However, it is important to point out that the slope of the EC x SC relationship differs depending on the mix of ions present (Evangelou, 1995).

Historically, pre-mining overburden analysis to minimize water quality impacts has focused upon conventional ABA (Sobek et al., 2000) since discharge pH, SO_4^{-2}, Fe and Mn levels have

been the principal compliance parameters. The seminal study by Skousen et al. (2002) demonstrated that conventional ABA was effective at predicting and limiting strongly acidic discharge from central Appalachian coal mines. However, little if any work has been reported to date on the utility of either ABA or other techniques to predict bulk TDS, primarily due the fact that regulatory pressure on TDS discharge is relatively recent. Several significant recent studies are documented below including the large scale field spoil leaching study by Agouridis et al. (2012) in Kentucky and column leaching studies (Daniels et al., 2013; Orndorff et al., 2010) on Virginia spoils.

Over the past thirty years, many researchers have attempted to gain a better prediction of the complex interactions occurring in weathering mine spoils via a variety of techniques and some of the more notable examples are discussed below. Caruccio et al. (1993) performed an overburden analysis and leachate prediction study comparing acid-base accounting, humidity weathering cells, column tests (large and small), and Soxhlet reactors for the purpose of predicting field leaching conditions. They concluded that the leaching columns provided the best approximations of field weathering conditions. Historically, column leaching studies have been favored for the more accurate prediction of pH/acidity generation via pyrite oxidation, TDS release from mine spoil, and the kinetics of trace metal leaching (Caruccio et al., 1993; Daniels et al., 2009; Halverson and Gentry 1990; Hood and Oertel 1984; Orndorff et al., 2010). However, column leaching studies are labor intensive and take many months to complete while static tests such as the components of ABA (pyritic-S, neutralization potentials, etc.) are completed quickly at much lower relative cost. It is also important to point out that while certain authors (e.g. Vengosh et al., 2013) refer to short-term solution:solid extracts of crushed spoils as "leaching tests", such procedures are short-term lab extractions and do not provide the kinetic/temporal data of column or field leaching trials.

In a recent column study, Orndorff et al. (2010) found that regardless of leachate pH, samples with significant levels of sulfides release much larger quantities of TDS over extended periods of time. Thus, even circumneutral mine discharges can contain high levels of sulfates as long as sufficient reactive carbonates are present in the source spoils. On a mass basis, initial TDS mass release is dominated by sulfates under unsaturated flow conditions and by a mix of sulfates and bicarbonate under saturated flow conditions. Furthermore, the anion complement shifts dramatically from sulfate to bicarbonate as leaching progresses for non-acid forming mine spoils. As reactive sulfides are largely oxidized, carbonate dissolution becomes dominant, and TDS emission slows (Daniels et al., 2013). In non-sulfidic materials, leachate EC/TDS values peak within the first few leaching cycles and then drop quickly and eventually level off after 10 to 20 leaching events (Halverson and Gentry, 1990; Hood and Oertel, 1984; Orndorff et al. 2010; see Fig. 2.1). In the previously mentioned large scale field study by Agouridis et al. (2012), EC levels from unweathered gray sandstone initially exceeded 1500 μS cm^{-1}, but approached 500 μS cm^{-1} within two years. Additionally, leachate EC is typically higher in leachates from

unweathered mine spoil than from weathered materials from the same local strata, and this observed difference is most profound in finer textured mudstones and shales (Agouridis et al., 2012; Daniels et al., 2013).
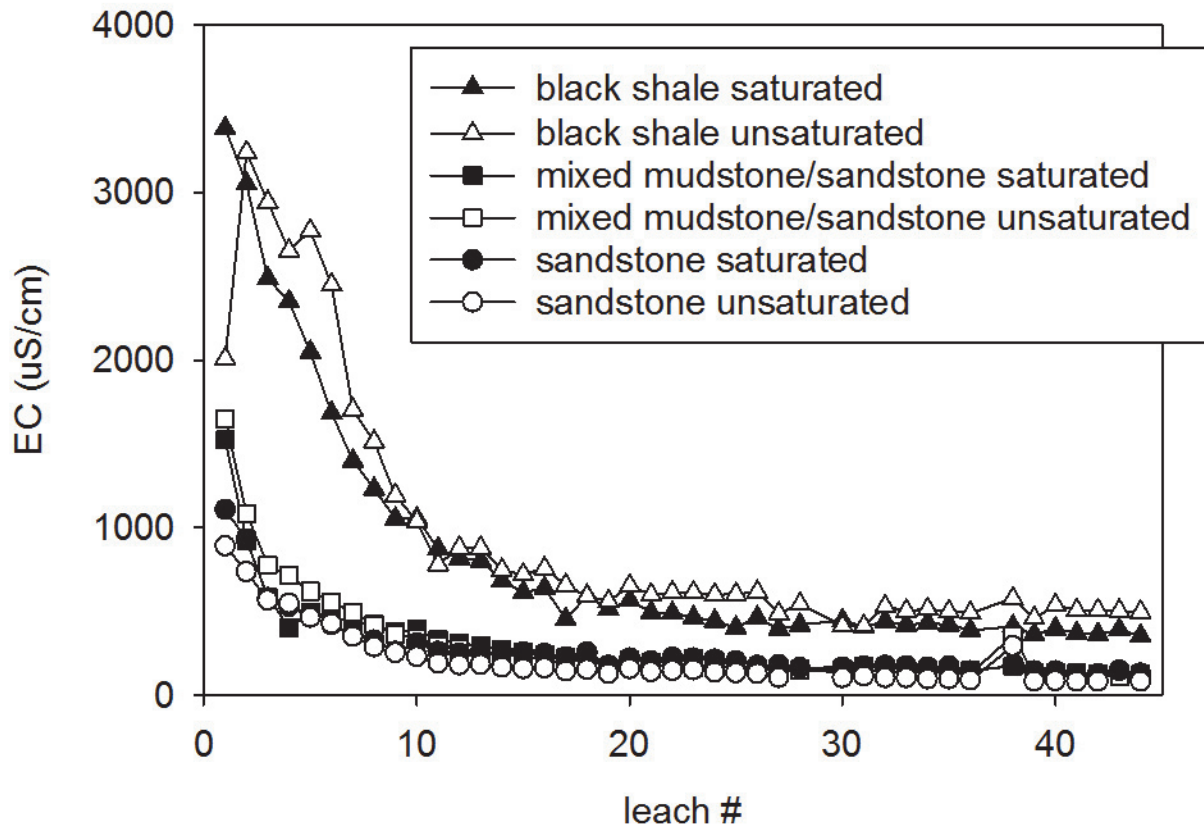
Figure 2.1. Mine spoil leachate electrical conductivity (EC) from selected non-weathered SW Virginia spoil materials. Finer textured rock spoils generally produce higher overall EC. All three spoils evaluated here were non-acid forming materials and the saturation regime had little influence on bulk leachate EC. Initial leachate EC is typically > 1000 µS cm^{-1}, but drops rapidly after one to two pore volumes (5 to 8 leaching cycles). The 45 leachate events (2.54 cm each) occurred over 22 weeks. Data points are means of three replicate columns. Figure based on column leaching data reported by Orndorff et al. (2010) and Daniels et al. (2013).

Earlier related research at Virginia Tech (e.g. Daniels et al., 1996 & 2002; Stewart et al., 2001) documented the potential water quality benefits and risks of coal combustion product (CCP) utilization in various co-disposal/utilization environments with coarse coal refuse materials. Since the vast majority of coal refuse materials produced in the Appalachian region are net acid-forming, this work was principally focused upon bulk acid-base balances and potential heavy metal (Cu, Zn, Fe, Al, Mn, etc.) mobility to local discharge points. The basic column leaching approach utilized in this current research program was developed and refined by these earlier studies. Subsequent work funded in the past decade by the coal industry and OSM (Daniels et al., 2006) also indicated that (A) significant leaching of oxyanions (As, Se, Mo) could occur when refuse/CCP mixtures remain at high pH (> 9.0), but that significant (and often much higher) release of these same elements occurs directly from non-amended coal refuse as it acidifies over time. These studies also revealed that coal refuse in general produces much higher and complex TDS loadings than locally associated hard rock mine spoils, but for a variety of reasons, potential for discharge from coal refuse disposal facilities has not received the same level of scrutiny as surface mines and valley fills.

2.2. Summary of Prediction Studies and Research Needs

Very few studies to date have focused on TDS production by non-acidic spoils, but some general conclusions can be drawn at this time. As expected, mine spoils that are significantly pre-weathered are lower in pH and EC production than unweathered materials of similar geology. Most unweathered spoil samples will produce moderate initial leachate EC levels ($\geq$ 1000 µS cm^{-1}) over their initial leaching cycles. Differences in TDS release appear to be clearly related to sulfide oxidation reactions with subsequent generation of sulfate and other acid-base reaction and carbonate dissolution products. It is interesting to note that the field-scale study of Agouridis et al. (2012) and the column leaching results reported by Daniels et al. (2013) reached very similar conclusions with respect to the overall levels and temporal response of leachate EC to rock type and pre-weathering even though they were conducted completely independently.

While column leaching tests are favored for prediction of mine spoil discharge quality, they are expensive, time-consuming and not a practical alternative for routine mine planning and permitting. Overall, results from several recent studies cited here indicate that identification of high TDS producing strata could potentially be utilized as a part of pre-mine planning and permitting procedures to minimize TDS release to receiving streams. We suggest that active mine operations should be modified to place high TDS producing materials in ways that reduce contact with percolating drainage waters. It is also clear from multiple studies that near-surface pre-oxidized and weathered strata will be much lower in their TDS producing potentials and their use as topsoil substitutes should be emphasized and encouraged. We believe that these practices would minimize TDS of surface runoff waters.

In parallel work to this study, we are working with the Appalachian Research Initiative for Environmental Science (ARIES; http://www.energy.vt.edu/aries/) to compare the column leachate response from over 45 different Appalachian mine spoils to more conventional static test parameters such as pyritic-S, neutralization potentials, saturated paste specific conductance (with and without H_2O_2 additions) and other extractants and analyses. The overall goal of this program is to determine which combination of static tests are the best predictor(s) for both peak and long-term TDS production for a given spoil. At the point in time that this study was approved for funding by OSM it was important for us to clearly differentiate the suite of materials tested to avoid duplication of effort and funding among the two research programs (ARIES vs. OSM). Thus, the work proposed here focused on testing leachates produced by mine spoils from Tennessee (TN) and selected coarse coal refuse materials from the central Appalachian region to clearly differentiate our results from the ARIES funded program.

Thus, based upon our review of past work by our group and others, and upon our interactions with OSM staff, this research project was established in September 2011 with the following original objectives:

I.   To obtain a representative regional sample set of mine spoils from Tennessee and coarse coal refuse from the central Appalachian region with varying potentials for TDS release.

II.   To fully characterize these materials via a wide range of laboratory analytical procedures for their potential to release important TDS components upon leaching and weathering.

III.   To characterize the TDS elution behavior of selected mine spoil and refuse materials via column leaching analyses for TDS and component ions of interest.

IV.   To determine whether predictive relationships exist between the various lab procedures employed to estimate TDS release potential and the actual TDS flux behavior observed from the leaching columns.

V.   To investigate the effect of leaching column scale on the quantity and temporal nature of TDS release from selected mine spoil and refuse materials.

VI.   To relate laboratory TDS predictors to actual field data sets for coal mining operations dominated by the spoils and refuse tested in this study.

3. Methods and Materials Used

3.1. Spoil Material Selection

The Tennessee mine spoils used for column leaching were selected with the assistance of Ms. Whitney Nash (OSM Knoxville office) as being representative of larger mining operations and stratigraphic sequences in northeast Tennessee. Freshly exposed overburden was collected from as close to the active mining operation as possible. In some instances mining had ceased a few weeks prior to collection and the sample was gathered at the last actively mined area with careful consideration taken to avoid reclaimed areas. Sample TN-1 consisted of 4 5-gallon buckets of spoil; all other samples consisted of 2 5-gallon buckets of spoil. Detailed descriptions of the geologic groups associated with these sites can be found in Wilson et al. (1956). A brief description of the geology and sampling protocol for each site, based on information provided by W. Nash of OSM, follows.

Sample TN-1 was collected in Campbell County TN, north of Lafollette. This site is associated with the Rich Mountain coal seam (also known as Blue Gem) which occurs within the upper Slatestone Group (Fig. 3.1).

Sample TN-2 was collected on the north end of Buffalo Mountain in Anderson County, Tennessee. This site is associated with the Windrock, Lower Dean, and Dean (also known as Upper Dean or Big Mary) coal seams occurring within the Graves Gap Group and Redoak Mountain Group (Fig. 3.1).

Sample TN-3 was collected in the Tackett Creek area of Claiborne County, Tennessee. This site is associated with the Coal Creek (also known as Jellico or Kent) and the Rich Mountain (also known as Blue Gem) coal seams occurring within the Slatestone Formation (Fig. 3.1). Mining in this area was completed one week prior to sampling. The sample was taken from the last mined area and no reseeding had occurred.

Sample TN-4 was taken in the Zeb Mountain area of bordering Scott and Campbell Counties, Tennessee. This site is associated with the Splint, Windrock, Big Mary, Red Ash, Walnut Mountain, and Peewee coal seams, occurring within the Graves Gap Group, Red Oak Mountain Group, and Vowell Mountain Group (Fig. 3.2). Mining ceased in late February of 2012 and the sample was collected in late April from the last actively mined point.

Sample TN-5 was collected in the Davis Creek community of Campbell County, Tennessee. This site is associated with the Rich Mountain (also known as Blue Gem) and Log Mountain (also known as Jellico or Mingo) coal seams, occurring within the Breathitt Formation (Fig. 3.2).

An additional spoil sample was selected for use in the scaled (mesocosms) leaching study. The Harlan sandstone spoil, collected from Wise County, VA, was chosen to closely resemble material that was used in a parallel detailed column leaching method validation study (Parker, 2013), as well as to be "typical" of the larger regional sample set currently under study for TDS prediction by ARIES as described earlier.
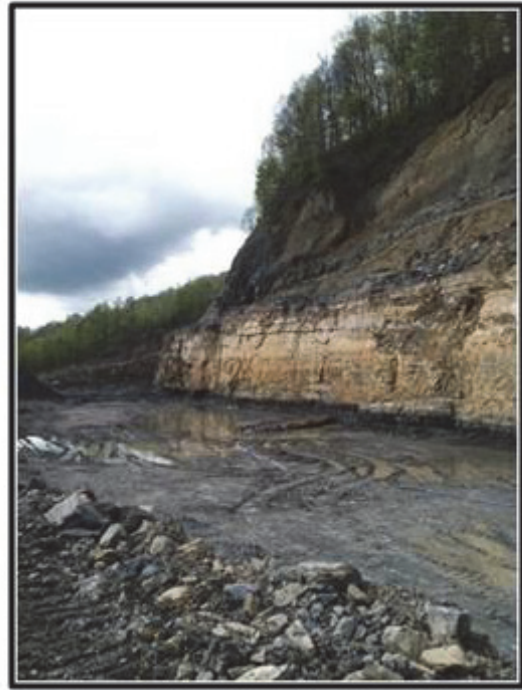
Figure 3.1. Exposed geology at TN-1 (upper left) and TN-2 (upper right), and graded spoils for TN-3 (bottom) sampled April, 2012. Photos by W. Nash.
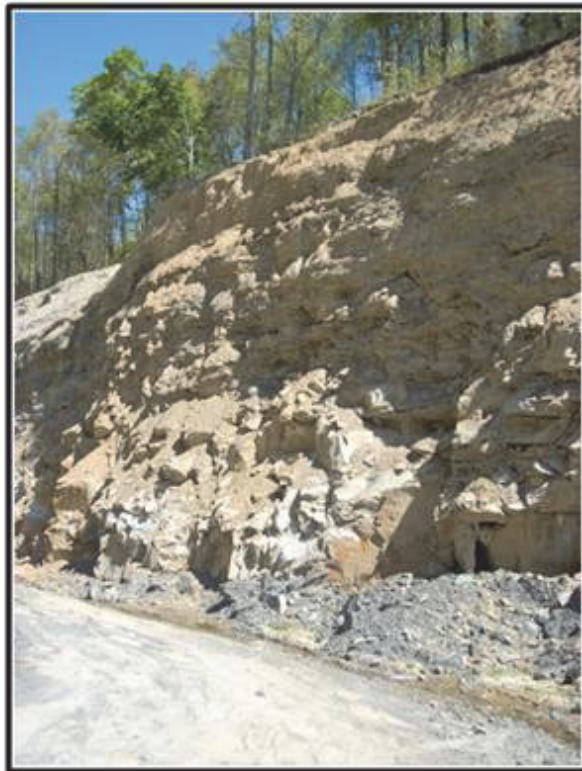
Figure 3.2. Exposed geology at TN-4 (top) and TN-5 (bottom) sampled April, 2012. Photos by W. Nash

3.2. Refuse Material Selection

Coarse coal refuse samples from 3 Tennessee, 5 Virginia, and 1 West Virginia locations\ were collected and compared for major parameters of water quality concern such as pH and EC (see section 3.3 for methods). Basic characterization of the full refuse sample set is presented in Table 3.1. Based on this preliminary information, and with concurrence from OSM, we selected 4 samples (TNR-1, TNR-2, TNR-3, and VA-21) for column leaching. These samples were selected with the intention of prioritizing TN samples while including a representative range of properties for typical materials. Samples TNR-1 and TNR-3 were selected for further evaluation in the scaled leaching study based on their differing total-S and CCE values. Additional bulk samples of TNR-1 and TNR-3 were collected by OSM personnel and delivered to VT.

Table 3.1. Basic characterization and acid-base accounting for coarse refuse samples from TN, VA, and WV.

ID	pH[1]	EC[1] (uS/cm)	PPA[2]	Total-S (%)	MPA[3] T/1000	CCE (NP)[4] T/1000	NNP[5] T/1000	NP/MPA[6]
VA-16	9.13	990	-0.06	0.27	8.4	62.0	53.6	7.3
VA-17	8.34	2070	0.00	0.23	7.2	49.0	41.8	6.8
VA-18	9.03	960	-2.20	0.42	13.1	50.0	36.9	3.8
VA-20a	9.19	1280	-2.30	0.45	14.1	65.0	50.9	4.6
VA-20b	9.03	700	-2.23	0.32	10.0	56.0	46.0	5.6
VA-21	8.75	900	-31.16	1.25	39.2	60.0	20.8	1.5
WVR-1	8.13	6820	-120.6	6.98	218.1	ND	ND	ND
TNR-1	7.41	2510	-15.97	0.76	23.8	39.5	15.8	1.7
TNR-2	8.03	2820	0.00	1.09	34.1	75.8	41.7	2.2
TNR-3	8.36	2520	-22.28	1.13	35.3	67.8	32.5	1.9

[1] Based on saturated paste extract.
[2] Potential Peroxide Acidity, expressed as tons $CaCO_3$/1000 tons material needed to neutralize potential acidity.
[3] Maximum Potential Acidity = total-S% * 31.25, expressed as tons $CaCO_3$/1000 tons material needed to neutralize acidity assuming all S is in sulfide form.
[4] Calcium Carbonate Equivalent, a method of determining neutralization potential (NP) expressed as the equivalence to tons $CaCO_3$/1000 tons material.
[5] Net Neutralization Potential = NP - MPA. Values < -5 indicate high potential for acid drainage and > 20 indicates high potential for alkaline drainage.
[6] NP/MPA, another approach to interpreting acid-base accounting. Values < 1.1 indicate high potential for acid drainage production in a field setting and >2.1 indicate low potential for acid drainage (Skousen et al., 2002)

3.3. Material Characterization

For each sample, the entire bulk of material was air-dried then thoroughly mixed to ensure uniformity. All spoil and refuse materials selected for column leaching were air-dried and ground as appropriate for the following procedures. For saturated paste pH and electrical conductance (EC; Rhoades, 1982) each material was mixed with deionized (DI) water until it formed a glistening paste, equilibrated for ≥ 2 hours, then filtered and analyzed. Peroxide potential acidity

(PPA) was determined by a modified hydrogen peroxide oxidation technique as described by Orndorff et al. (2008). By this method, sulfides are oxidized with 30% H_2O_2 and following full reaction (assuming net internal reaction of generated acids with carbonates and other neutralizers), total net acidity is determined by whole sample titration. Acid-base accounting was completed in a manner similar to the standard approach used in the Appalachian coal mining industry. The maximum potential acidity (MPA) was calculated based on the amount of acidity theoretically produced by the complete oxidation of sulfide-S. As is common practice, total-S was used for this calculation with the assumption that all S is in sulfide form. Total-S was determined by dry combustion/infrared analysis using a LECO S632 Sulfur analyzer. Neutralization potential (NP) was determined using AOAC method 955.01 (AOAC International, 2002) for carbonate equivalent (CCE). This method is similar to Sobek NP which is more commonly used in the mining industry, but utilizes a stronger acid concentration and solid:solution ratio. Net neutralization potential (NNP) was determined by calculating the difference between NP and MPA (NNP = NP – MPA). Elemental composition was determined by acid digestion of a 0.5 g spoil sample according to EPA Method 3051A, Revision 1 (USEPA, 2007) and analyzing the extracts for elements of interest using a Thermo Electron Corporation ICP-MS, X-Series USEPA method SW 846 6020A, revision 1 (USEPA 2007).

3.4. Column Leaching

The column leaching procedures employed here were similar to those described by Orndorff et al. (2010) and Daniels et al. (2013). All samples were air-dried prior to processing. To minimize preferential flow through the column, coarse fragments were crushed to pass a 1.25 cm sieve and then carefully back-blended with the finer material. Particle size analysis was completed on the crushed material to evaluate the distribution of coarse and fine particles. The leaching columns were built from PVC pipe with an inside diameter of 7.4 cm, and length of 40 cm. A concave PVC endcap was securely attached to one end, and a 0.6 cm hole was drilled into the center of the endcap and fitted with a PVC pipe nipple. An attached Tygon tube drained the leachate to a nalgene sample bottle. A 7.4 cm disc of perforated plastic was placed at the bottom of the column (within the end cap) to stabilize materials above the drain hole. To prevent leaching losses of particulates and blockage of the drainage hole, a 0.1 mm nylon mesh circle was placed above the plastic disc and covered with a Whatman #1 filter paper. The filter paper was covered with a 5 cm layer of acid washed coarse quartz sand to promote uniform drainage and to serve as a leachate reservoir, ensuring that the bottom section of the sample material remained unsaturated (when specified). The column was then packed with a sample volume of 1200 cm^3 (mass recorded), and capped with a 5 cm sand layer to facilitate uniform distribution of the applied leaching solution. Each sample was run in triplicate (i.e. 3 columns per sample).

Simulated rainfall (pH 4.6; Halverson and Gentry, 1990) initially was applied slowly in 100 ml increments to allow the columns to moisten to their maximum water holding capacity. For each column, as leachate began to drain out the bottom, smaller initial additions were applied as necessary until 125 ml of leachate had drained. In this manner, the hydration demand was satisfied to a point where leachates were generated in a "piston flow" response to the surface dosing regime. For saturated columns, a similar procedure was utilized, but the drainage was blocked until the columns were saturated/ponded.

Subsequent additions of leaching solution were applied twice per week (Mondays and Thursdays) to provide approximately 2.5 cm (125 ml) of rainfall per event. The leaching solution

was dispensed into a perforated cup placed on top of the sand for uniform application. The leachate samples were analyzed and/or preserved after a 24 hour leaching/collection period. The leachate samples were weighed and analyzed for pH and EC after every leaching event. For selected leach events, total Al, As, Ca, Cd, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Se, and Zn were determined by USEPA method SW 846 6020A, revision 1 (USEPA, 2007) using a Thermo Electron Corporation ICP-MS, X-Series, total S was determined by USEPA method SW 846 6010B, revision 2 (USEPA, 2001) using a Spectro ARCOS ICPES Model FHS16 with CETAC ASX-520 Autosampler, and inorganic carbon (IC) was determined on a Shimadzu TOC analyzer.

3.5. Scaled Leaching (Mesocosm) Studies

3.5.1. Spoil

The coal mine spoil used for the scaled leaching experiment was collected from the Harlan Formation in Wise County, VA (Red River Coal Co.) on August 12, 2012. At the time of collection, the spoil was passed through a 15 cm screen so that ample finer materials were collected and large rock fragments did not dominate the collection volume. However, to more accurately match field conditions, many larger rock fragments (up to ~50 cm) were collected by hand to be used in the experiment.

At VT, the spoil was placed into three different sized leaching vessels: mesocosm tanks, barrels, and columns. The tanks and barrels were installed and monitored at the Turfgrass Research Center in Blacksburg where they were exposed to natural environmental conditions and rainfall. This allowed evaluation of how TDS elution rates and composition developed under more natural field leaching conditions when compared to results from controlled leaching of laboratory columns. The leaching columns for each material were installed and monitored as described above.

The mesocosms were the largest vessels with a capacity of 1.5 cubic meter each (Figure 3.3). Three replicates were constructed from plastic tanks and placed side by side within a wooden frame. Once the vessels were in place, they were plumbed to a thick-walled PVC pipe which drained down the natural slope to three 200 L (55 gallon) drums where the leachate was collected. The opening of the PVC pipe was covered by a coarse mesh (filter fabric) material to minimize sediments in the leachate. The leachate collection drums were placed mostly underground so the leachate would drain to the top of the barrels allowing for sufficient collection volume. Approximately 20 cm of washed quartz gravel was placed in the bottom of each barrel to keep it weighted down (e.g. so the barrel would not be buoyant if the surrounding soil became saturated). A narrow PVC pipe was anchored in the gravel to the bottom of the drum so that the water collection tubing reached the bottom of the barrel for leachate collection.

The mesocosms were filled with the spoil on November 5, 2012. Prior to placement, the mine spoil was dried and mixed on a large tarp (Figure 3.4). Approximately 20 cm of quartz gravel were placed at the bottom of the mesocosms, to protect the drain pipes, and covered with a piece of landscape fabric (Figure 3.5). Each mesocosm was filled with spoil to approximately 15 cm from the top, for a total volume of approximately 0.85 m^3. Rocks, ranging from 15 to 50 cm, were placed randomly into the mesocosms to better reflect the coarse rocky nature of mine spoils in the field. The material was evenly distributed among the mesocosms, and within each mesocosm, the material was placed as similar to field spoil conditions as possible (Figure 3.6).

Lastly, the vessels were covered with bird netting and surrounded by a fence to discourage tampering by humans or wildlife (Figure 3.7).

The Harlan sandstone spoil also was placed into three 55-gallon (~200 L) drums which served as the medium sized vessels in the experiment. These barrels were set up adjacent to the mesocosms and thus were exposed to the same natural environmental conditions and rainfall. Holes were excavated to allow about 1/4 of each leaching barrel to be placed below grade, and excess soil was mounded around their base. This provided both stability and insulation to prevent freezing of the leachates. Like the mesocosms, a layer of washed quartz gravel was placed in the bottom of the barrel. A piece of landscape fabric was placed on top of the gravel to prevent spoil material from collecting in the bottom of the barrel and clogging the collection pipes. Two PVC pipes were anchored within each barrel to allow for air flow return as leachates were evacuated under suction from the bottom of the barrels. The Harlan sandstone spoil was placed in each barrel (November 5, 2012) to approximately 25 cm of the top of the barrel, for a total volume of approximately 0.15 m^3. The material placed in the barrels was identical to the mesocosms, but without the addition of the larger rocks. Bird netting was placed over the barrels to decrease the chance of contamination. A "blank" barrel that was constructed using the same methods detailed above; however, no spoil was placed in the barrel.

The mesocosm tanks and leaching barrels were monitored and sampled over time, particularly following storm events. When water was present and weather conditions allowed, the leachate collection vessels were pumped dry as soon as possible (usually within 48 hours). The leachate was pumped into a 20 L carboy, which was rinsed with deionized water after each sample was collected. Total volume was noted for each pumping, and a 500 mL subsample was collected for further laboratory analyses.

Upon return to the laboratory, untreated samples were measured immediately for pH and EC. A 15 mL subsample was decanted into a sterile test tube and preserved with 8N nitric acid for metals analysis, including Al, As, Ca, Cd, Cl, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Se, and Zn by USEPA method SW 846 6020A, revision 1 (USEPA 2007) using a Thermo Electron Corporation ICP-MS, X-Series. A 60 mL amber vial was completely filled (no head space) and analyzed within 3 days of collection for inorganic carbon (IC) using a Shimadzu Carbon Analyzer. A 20 ml subsample was decanted into nalgene bottles for sulfur analysis by USEPA method SW 846 6010B, revision 2 (USEPA, 2001) using a Spectro ARCOS ICP Model FHS16 with CETAC ASX-520 autosampler. A 125 mL archive subsample (no acid) and a 60 mL acid-preserved archive subsample were decanted into nalgene bottles.

Figure 3.3. Mesocosms prior to being filled with Harlan sandstone spoil.

Figure 3.4. Homogenizing Harlan sandstone spoil prior to placement in mesocosms and barrels.

Figure 3.5. Initial placement of Harlan sandstone spoil over landscape fabric in the mesocosms.

Figure 3.6. Three replicate mesocosms with Harlan sandstone spoil.

Figure 3.7. Layout of mesocosms (uphill, to left) and leachate collection barrels (downhill, to right).

3.5.2. Refuse

Samples TNR-1 and TNR-3 were evaluated at two scales: leaching barrels and laboratory columns. A set of leaching barrels is illustrated in Figure 3.8. For each material, a subsample of the bulk material was analyzed for coarse and fine particle size distribution. All methods of barrel and column installation and analysis were identical to those described above for spoil materials.

Figure 3.8. Leaching barrels filled with refuse (mesocosms tanks in the background).

4. Results and Discussion

4.1. Characterization of Chemical Properties

A summary of sample identification, associated coal seams, and geology is presented in Table 4.1. Selected chemical properties of the spoil and refuse sample set are presented in Table 4.2. Saturated paste pH for all samples was generally in the neutral to alkaline range which is typical of fresh, relatively unweathered materials from this region due to hydrolysis reactions with primary mineral grains and carbonate dissolution. Two of the mine spoils yielded acidic saturated paste pH values of 5.48 and 4.68. The soluble salt content, as indicated by saturated paste EC, was moderate for all TN samples, ranging from 1930 – 2820 uS/cm (1.9 – 2.8 dS/m). The VA samples, both spoil and refuse, had relatively low saturated paste EC, with values ≤900 uS/cm (0.9 dS/cm). None of the spoil samples were predicted to be acid-forming by conventional acid-base accounting (ABA) given their low total-S content, ranging from 0.04 – 0.15%, accompanied by moderate neutralizing potential as measured by the calcium carbonate equivalent (CCE; 2.44 – 4.84%) procedure. Low acid-producing potential also was indicated by very low peroxide potential acidity (PPA) values ($\geq$ -0.58 tons $CaCO_3$/1000 tons material).

The refuse samples contained potentially problematic amounts of total-S (0.52 – 1.25%), with relatively high levels of CCE (6.00 – 7.98%). By conventional acid-base accounting (Table 4.2) rationale (Skousen et al., 2002) all four refuse samples were predicted to produce alkaline drainage. In comparison, by PPA testing, samples TNR-1, TNR-3, and VA-21 were predicted to be acid-forming. The difference in prediction between the conventional ABA approach and PPA here is notable and will be discussed again later.

The spoil and refuse materials used in this study contained metal concentrations typical of sedimentary rocks and surficial materials (Table 4.3; Adriano, 2001; Shacklette and Boergen, 1984). The refuse materials were also higher in S and trace metals as expected. Total Fe concentrations ranged from 2.0 – 5.1%, and on average, were slightly higher in the spoils than the refuse. Manganese was notably higher in the spoils, ranging from 363 to 930 mg/kg as compared to 137 – 601 mg/kg for the refuse samples. Conversely, the refuse samples yielded higher concentrations for several elements, most notably As, Na, and Se. Arsenic ranged from 14.0 – 44.8 mg/kg in refuse samples, and from 4.19 – 8.10 mg/kg in spoil samples. Sodium ranged from 513 – 1166 mg/kg in refuse samples, and from 217 – 850 mg/kg in spoil samples. Selenium ranged from 1.36 – 3.09 mg/kg in refuse samples and from <0.25 – 0.55 mg/kg in spoil samples.

Table 4.1. Final column selection spoil and refuse sample identification, location, and associated coal seams and geology.

	Sample ID	County, State	Geologic Formation	Associated Coal Seam (alternative names)	Basic Geology
S P O I L	TN1	Campbell, TN	Slatestone Group	Rich Mountain (Blue Gem)	~50% brown shale ~50% soft black shale
	TN2	Anderson, TN	Graves Gap Group Redoak Formation	Windrock, Lower Dean, and Dean (Upper Dean, Big Mary)	~60% gray mudstone ~40% orange sandstone <2% coal
	TN3	Claiborne, TN	Slatestone Group	Rich Mountain (Blue Gem), Coal Creek (Jellico)	~60% gray mudstone; ~40% orange and gray sandstone
	TN4	Campbell/Scott, TN	Graves Gap Formation Redoak Formation	Splint, Windrock, Big Mary, Red Ash, Walnut Mountain, Peewee	~65% orange sandstone ~35% gray mudstone
	TN5	Campbell, TN	Breathitt Formation	Rich Mountain (Blue Gem), Log Mountain (Jellico, Mingo)	~50% orange sandstone ~50% gray mudstone
	VA16M	Wise, VA	Harlan	High Splint	100% gray sandstone
R E F U S E	TNR1	Campbell, TN	Not provided	Not provided	NA
	TNR2	Scott, TN	Not provided	Not provided	NA
	TNR3	Claiborne, TN	Not provided	Not provided	NA
	VA21	Wise, VA	Norton	Norton, Lower Banner	NA

Table 4.2. Chemical characteristics and acid-base accounting of spoil and refuse samples used for column, barrel, and tank leaching.

| | | Saturated paste | | PPA[1] | Total-S % | MPA[2] | CCE[3] | NP[4] | NNP[5] | NP/MPA[6] |
		pH	EC (uS/cm)							
SPOIL	TN-1	7.26	2250	0	0.06	1.82	3.14	31.4	29.6	17.2
	TN-2	7.80	2610	0	0.12	3.68	5.23	52.3	48.6	14.2
	TN-3	7.52	2680	0	0.09	2.88	2.44	24.4	21.5	8.5
	TN-4	4.68	1930	-0.3	0.08	2.62	2.9	29	26.4	11.1
	TN-5	5.84	2570	-0.6	0.15	4.61	3.64	36.4	31.8	7.9
	VA-16M	7.68	882	0	0.04	1.25	4.84	48.4	47.2	38.7
REFUSE	VA-21	8.75	900	-31.2	1.25	-39.21	6.00	60.0	20.8	1.5
	TNR-1[7]	7.95	1261	-8.3	0.52	-16.25	6.97	69.7	53.5	4.3
	TNR-2[7]	8.03	2820	0.00	1.09	-34.1	7.58	75.8	41.7	2.2
	TNR-3[7]	8.08	1945	-20.5	1.22	-38.02	6.13	61.3	23.3	1.6

[1] Peroxide Potential Acidity: results expressed as tons $CaCO_3$/1000 tons material needed to neutralize acidity (e.g. negative values = lime need).

[2] Maximum Potential Acidity = total-S% * 31.25, expressed as tons $CaCO_3$/1000 tons material needed to neutralize acidity assuming all S is in sulfide form.

[3] Calcium Carbonate Equivalent

[4] Neutralization Potential = CCE*10

[5] Net Neutralization Potential = NP - MPA. Values < -5 indicate high potential for acid drainage and > 20 indicates high potential for alkaline drainage.

[6] NP/MPA; an alternative approach to interpreting acid base accounting. Values < 1.1 indicate high potential for acid drainage and >2.1 indicates low potential for acid drainage. Intermediate values produce variable drainage response (Skousen et al., 2002)

[7] For TNR-1 and TNR-3, the materials characterized here and used for the leaching columns and barrels were from large bulk samples collected separately from the preliminary samples characterized in Table 3.1. For TNR-2, the preliminary sample was used for characterization and column leaching.

Table 4.3. Total elemental analysis for spoil and refuse samples.

Element	Detection limit	SPOIL						REFUSE[2]			
		TN-1	TN-2	TN-3	TN-4	TN-5	VA16-M	TNR-1	TNR-2	TNR-3	VA-21
		------- % -------									
Al	0.000025	4.39	3.86	4.23	2.93	2.53	2.58	4.89	5.05	4.35	5.14
Ca	0.00025	0.20	0.58	0.23	0.08	0.11	2.01	0.22	2.11	0.21	0.24
Fe	0.00025	5.05	2.62	3.88	3.43	2.79	2.02	2.15	2.02	2.54	3.99
K	0.00025	0.86	0.74	0.90	0.67	0.59	0.67	1.14	1.15	1.06	1.46
Mg	0.00025	0.60	0.45	0.57	0.31	0.31	0.37	0.48	0.45	0.50	0.73
		------- mg/kg -------									
As	0.25	8.1	6.6	5.6	6.7	5.4	4.2	14.0	25.0	34.1	44.8
B	0.25	16.7	19.0	18.4	16.1	10.0	nd[1]	50.8	38.3	43.1	24.0
Ba	0.25	199	155	197	114	111	nd	166	188	184	265
Cd	0.13	0.18	0.16	0.17	0.15	0.13	<0.13	0.26	0.16	0.17	0.14
Co	0.25	15.4	13.7	16.3	13.4	11.4	nd	10.6	8.2	10.6	14.5
Cr	0.25	45.3	33.1	47.2	31.6	27.9	nd	47.2	47.1	39.0	49.3
Cu	0.25	25.3	20.5	25.0	18.1	17.1	12.9	28.7	30.5	34.5	52.5
Hg	0.13	0.13	0.14	0.13	<0.13	0.13	nd	0.21	0.28	0.17	0.17
Mn	0.25	930	450	736	570	363	496	149	137	199	601
Mo	1.25	<1.25	<1.25	<1.25	<1.25	<1.25	nd	<1.25	<1.25	<1.25	1.35
Na	2.50	427	321	408	254	217	850	550	513	945	1166
Ni	0.25	37.2	29.9	40.2	27.0	23.6	16.9	32.8	29.6	28.6	41.7
Pb	0.25	17.1	16.9	15.2	12.6	11.1	8.54	17.3	19.5	15.6	17.9
Se	0.25	0.50	0.42	0.55	<0.25	<0.25	<0.25	3.09	2.28	3.05	1.36
Zn	0.25	108.6	79.7	92.1	78.7	62.8	46.0	85.4	57.5	71.0	89.8

[1] Value not determined.
[2] For TNR-1 and TNR-3, elemental analysis was conducted on preliminary sample (vs bulk sample used in leaching columns and barrels).

4.2. Leaching Column Trial

The data in Figures 4.1 – 4.12 report results from 40 leaching events over a 20-week period for the spoil and refuse samples. We highlight pH, EC, calcium, sulfate, bicarbonate and selenium as being particularly relevant to acid-base reactions and/or water quality. The data points in these figures represent (for each sample) the standard error above and below the mean of three replicates. In general, column replicability was excellent. Data summaries for other relevant ions from leach events are presented in Tables 4.4 (spoil) and 4.5 (refuse).

<u>pH</u>

Leachate pH for the spoil samples (Fig. 4.1) initially reflected the acidic nature of the leaching solution until surface reactions characteristic of the spoil compositions established chemical control for each sample. Four of the spoils produced alkaline leachate, which would be expected from typical sedimentary materials containing weatherable silicates and/or carbonates with low sulfide content. A combination of hydrolysis reactions for primary mineral grains (e.g. feldspars) coupled with dissolution of complex carbonate cements lead to the high pH levels observed. These systems are buffered by the carbonate-bicarbonate reaction and thus these samples equilibrated to pH values approaching or in the low 8.0s. Weathered materials are less effective at increasing leachate pH due to natural depletion of reactive acid-consuming materials. This was apparent in sample TN-4 which equilibrated at a slightly acidic pH. Consistent with previous studies, higher pH levels were observed from unsaturated conditions, likely due to higher CO_2 partial pressures increasing carbonate dissolution in the unsaturated columns.

Leachate pH of the refuse materials (Fig. 4.2) reflected the presence of pyritic-S, as well as 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 < 3.0 (Daniels et al., 2006). This was observed in sample VA-21 (unsaturated), where pH values were < 3.0 for most of the study period. Sample TNR-1 (unsaturated) also produced acidic leachate, equilibrating at pH ~5.1. This sample showed the greatest variability among columns, with two replications equilibrating to pH~4.5 and the third equilibrating at pH~6.1. Both VA-21 and TNR-1, were predicted to be acid-forming by PPA analysis, but not by conventional ABA results. For samples TNR-2 and TNR-3 (unsaturated), the effects of sulfide oxidation were mitigated by an abundance of readily available neutralizers and the materials equilibrated with slightly alkaline leachate (pH ~7.6). While TNR-2 was not predicted to be acid-forming by either PPA or ABA, TNR-3 was predicted to be acid-forming by PPA. Although TNR-3 maintained alkaline drainage throughout the study period, and ABA predicted alkaline drainage, conflicting PPA results suggest that over time this material potentially could generate acidic drainage. Unlike the spoil samples, all four refuse samples generated higher leachate pH from saturated columns than from the unsaturated columns. We presume that this was due to saturation suppressing sulfide oxidation and resulting acid generation.

Figure 4.1. Top: Column leachate pH from five TN spoils under unsaturated conditions. Bottom: Leachate pH for two of the spoils comparing saturated and unsaturated conditions. The 40 leach events occurred over 20 weeks; one pore volume is approximately 3 - 5 leaching doses. Bars around each point indicate one standard error above and below the mean of 3 replications.

Figure 4.2. Column leachate pH for refuse samples comparing saturated and unsaturated conditions. The 40 leach events occurred over 20 weeks; one pore volume is approximately 3 - 5 leaching doses. Bars around each point indicate one standard error above and below the mean of 3 replications.
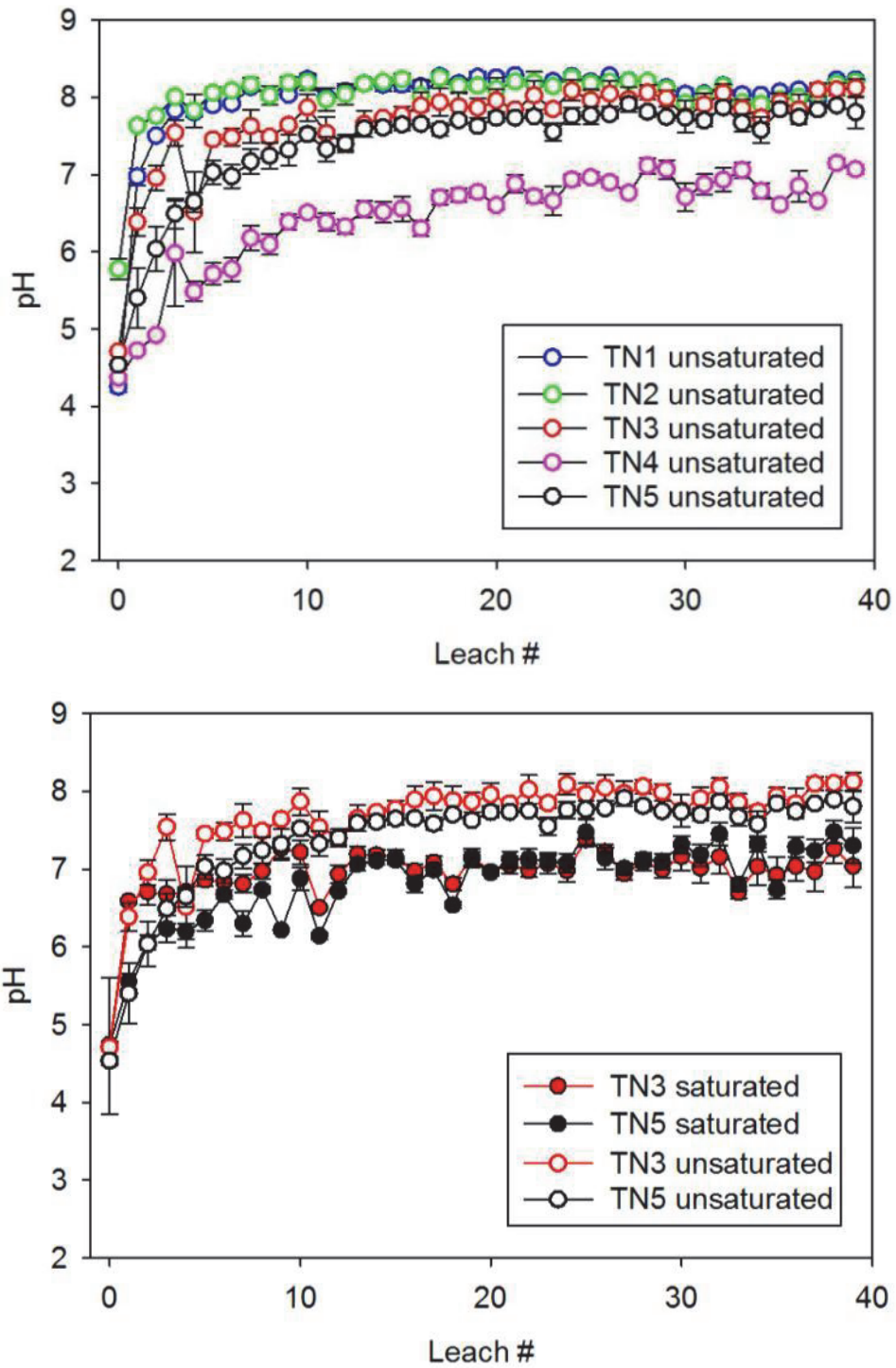
Figure 4.3. Top: Column leachate EC from five TN spoils under unsaturated conditions. Bottom: Leachate EC for two of the spoils comparing saturated and unsaturated conditions. The 40 leach events occurred over 20 weeks; one pore volume is approximately 3 - 5 leaching doses. Bars around each point indicate one standard error above and below the mean of 3 replications.

Figure 4.4. Column leachate EC for refuse samples under saturated and unsaturated conditions. The 40 leach events occurred over 20 weeks; one pore volume is approximately 3 - 5 leaching doses. Bars around each point indicate one standard error above and below the mean of 3 replications. Note log scale on Y axis.

Figure 4.5. Top: Column leachate Sulfate concentrations from five TN spoils under unsaturated conditions. Bottom: Leachate sulfate concentrations for two of the spoils under saturated and unsaturated conditions. The 40 leach events occurred over 20 weeks; one pore volume is approximately 3 - 5 leaching doses. Bars around each point indicate one standard error above and below the mean of 3 replications.
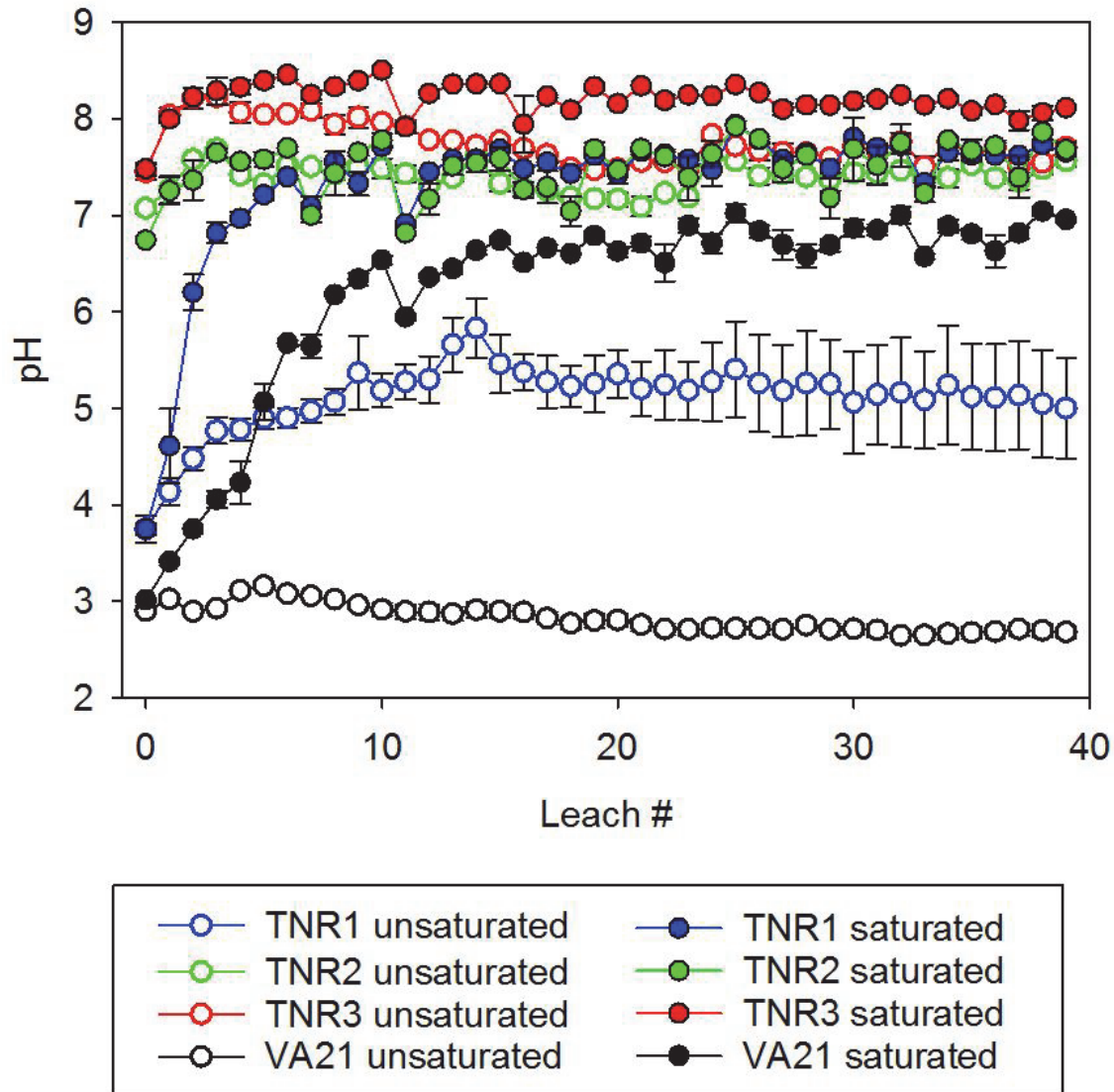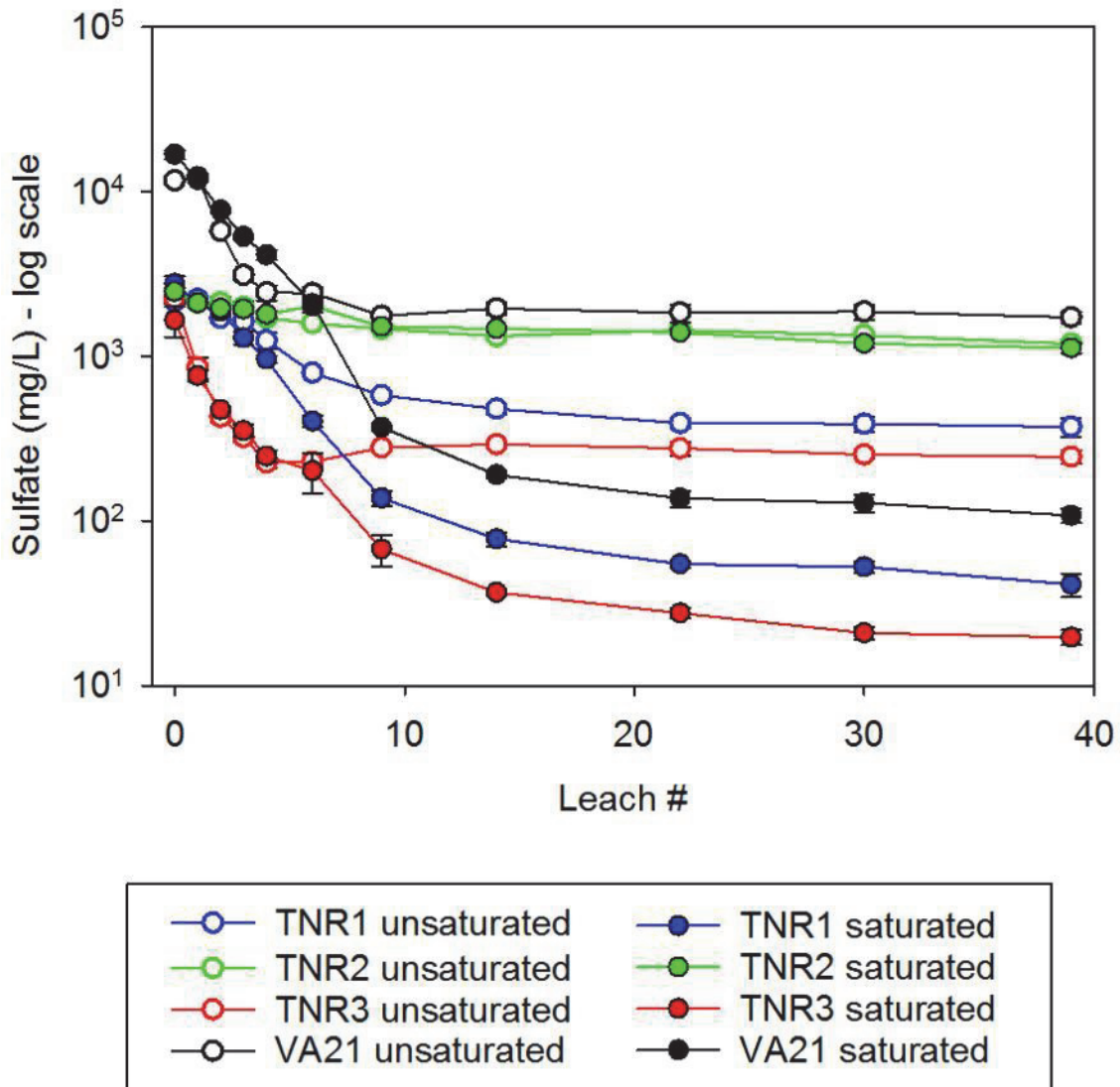
Figure 4.6. Column leachate Sulfate concentrations for refuse samples under saturated and unsaturated conditions. The 40 leach events occurred over 20 weeks; one pore volume is approximately 3 - 5 leaching doses. Bars around each point indicate one standard error above and below the mean of 3 replications. Note log scale on Y-axis.
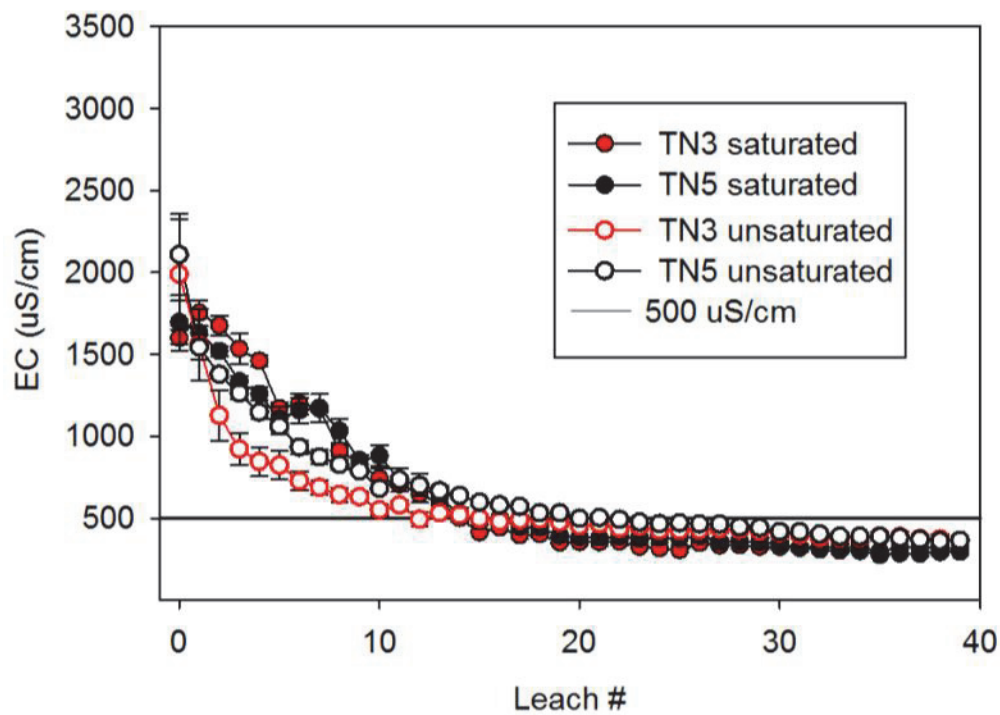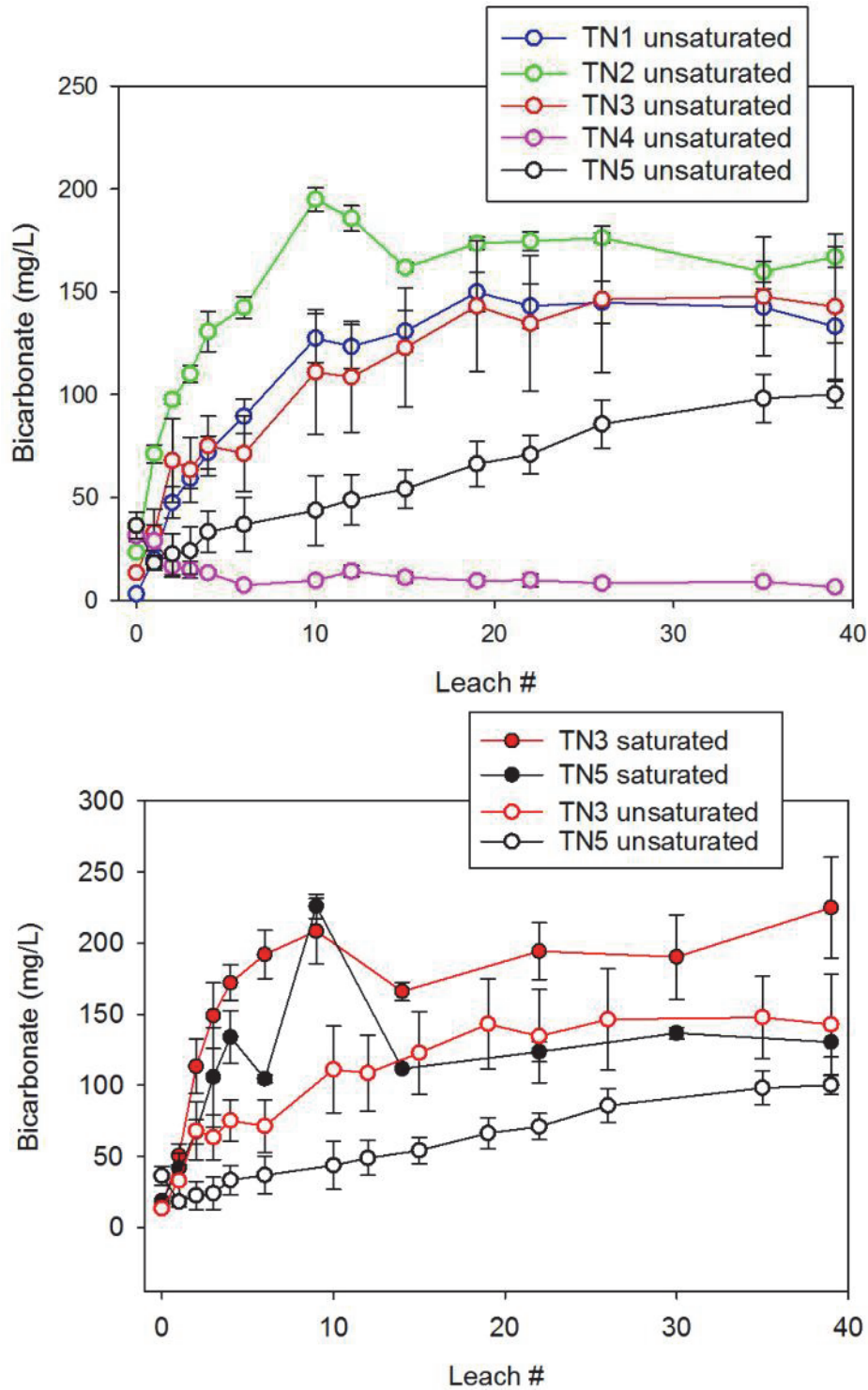
Figure 4.7. Top: Column leachate bicarbonate concentrations from five TN spoils under unsaturated conditions. Bottom: Leachate bicarbonate concentrations for two of the spoils under saturated and unsaturated conditions. The 40 leach events occurred over 20 weeks; one pore volume is approximately 3 - 5 leaching doses. Bars around each point indicate one standard error above and below the mean of 3 replications.
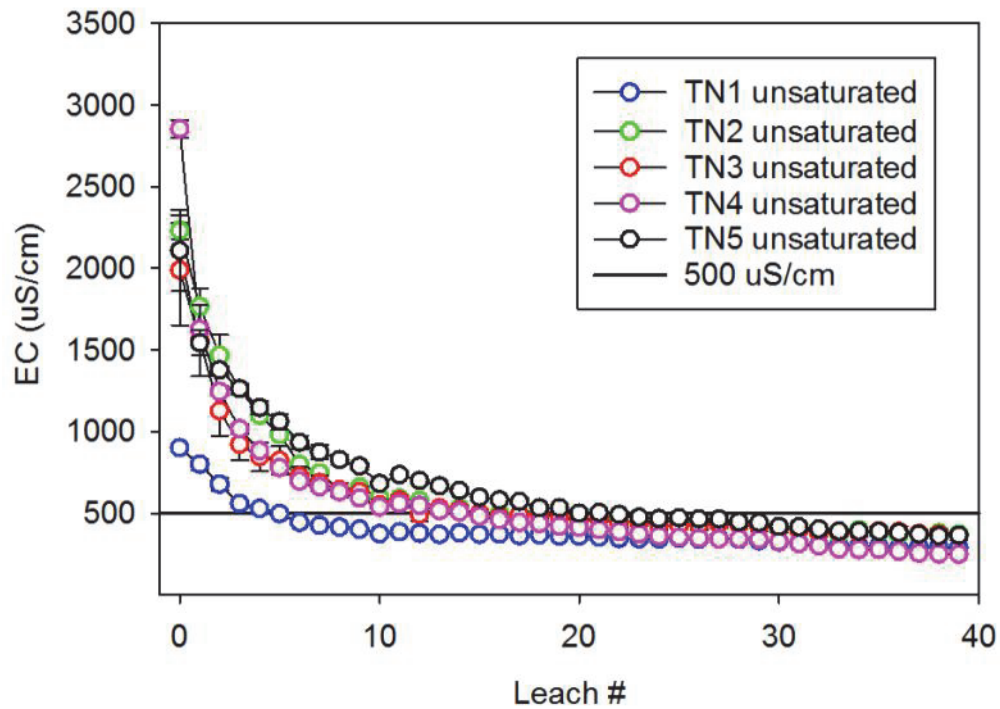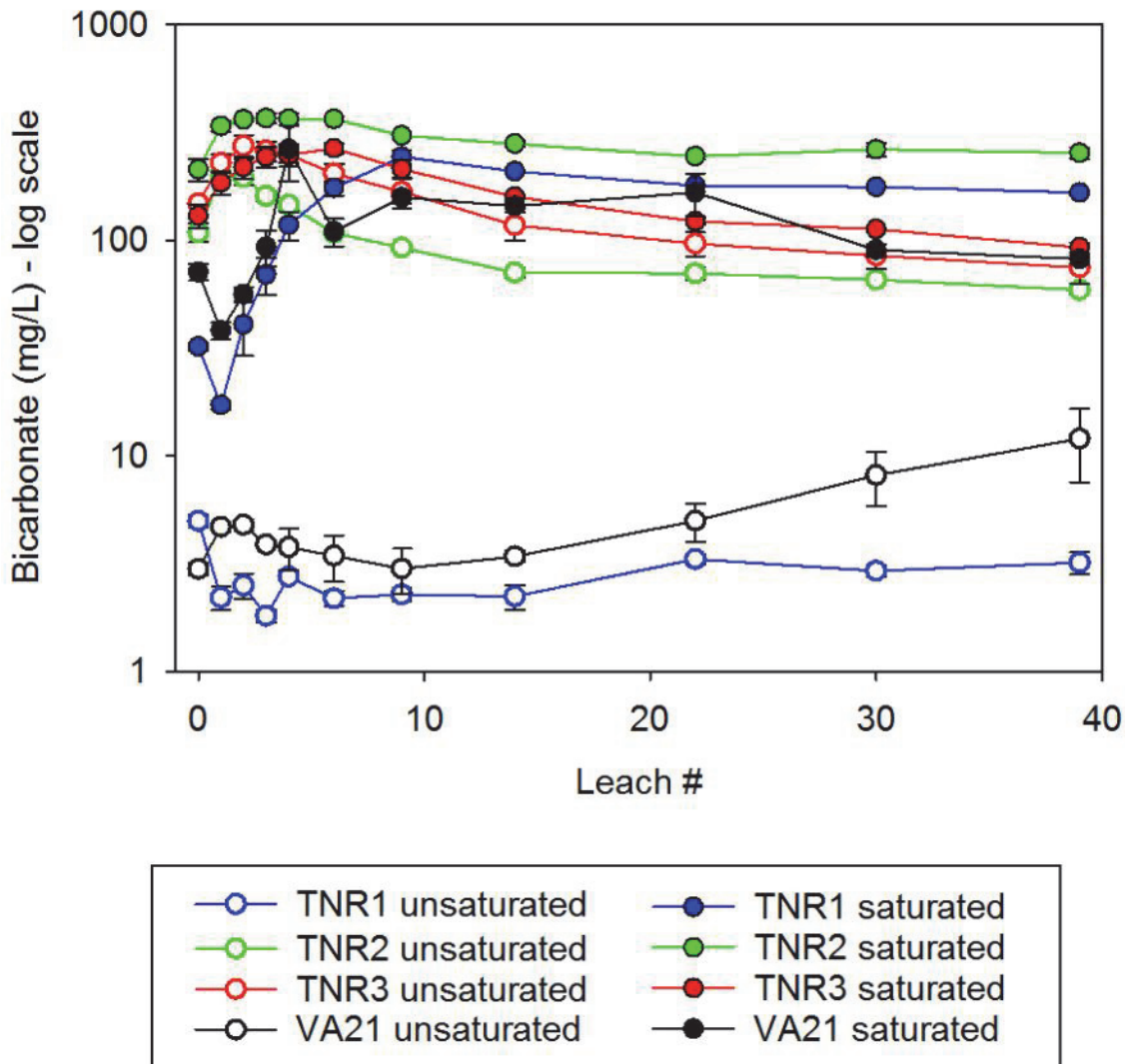
Figure 4.8. Column leachate bicarbonate concentrations for refuse samples under saturated and unsaturated conditions. The 40 leach events occurred over 20 weeks; one pore volume is approximately 3 - 5 leaching doses. Bars around each point indicate one standard error above and below the mean of 3 replications. Note log scale on Y axis.
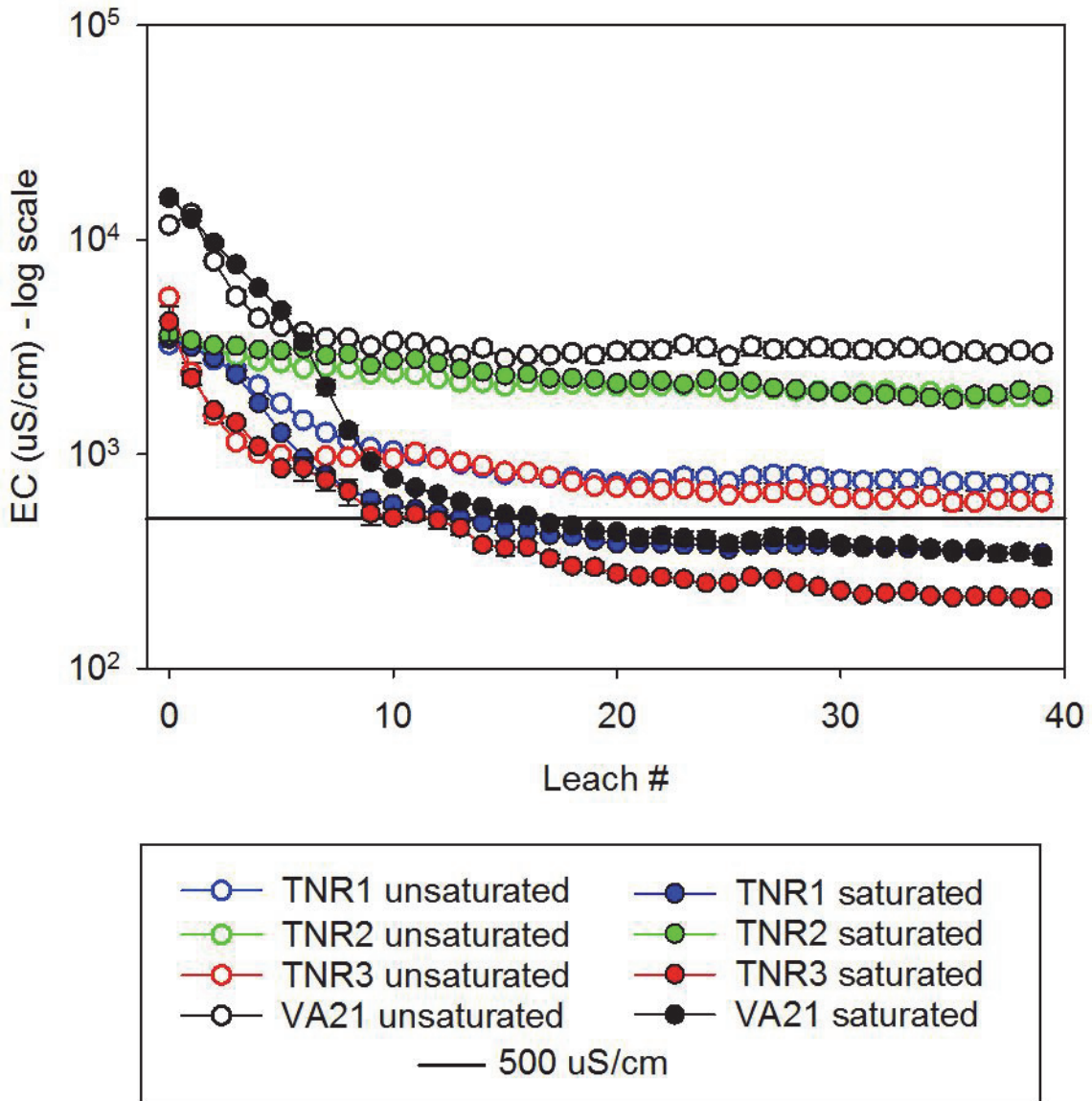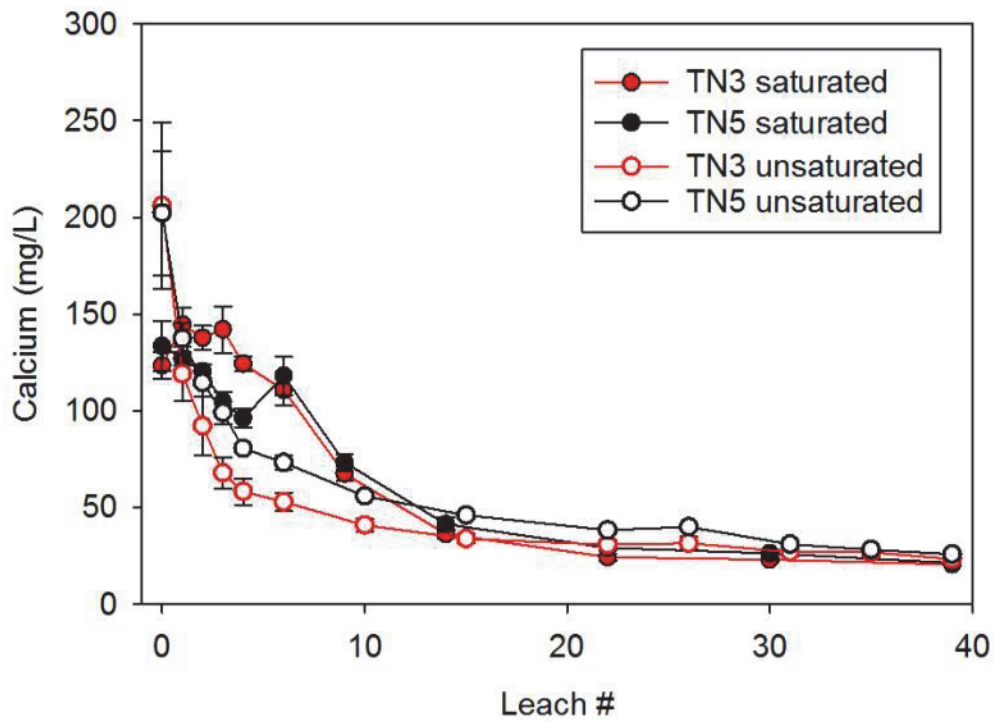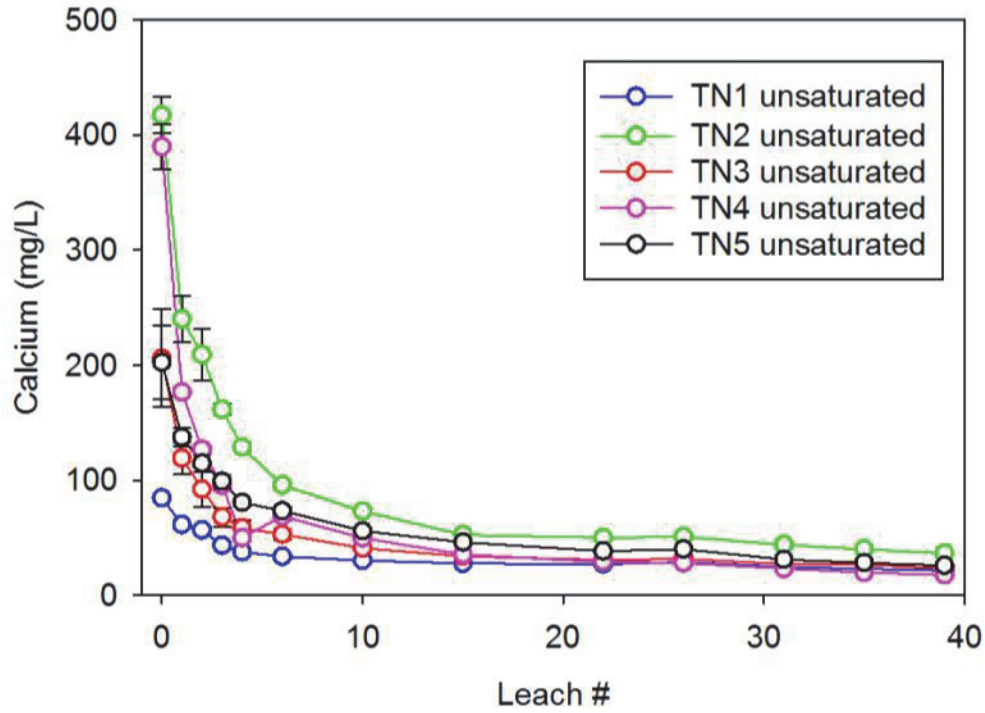
Figure 4.9. Top: Column leachate Ca concentrations from five TN spoils under unsaturated conditions. Bottom: Leachate Ca concentrations for two of the spoils under saturated and unsaturated conditions. The 40 leach events occurred over 20 weeks; one pore volume is approximately 3 - 5 leaching doses. Bars around each point indicate one standard error above and below the mean of 3 replications.
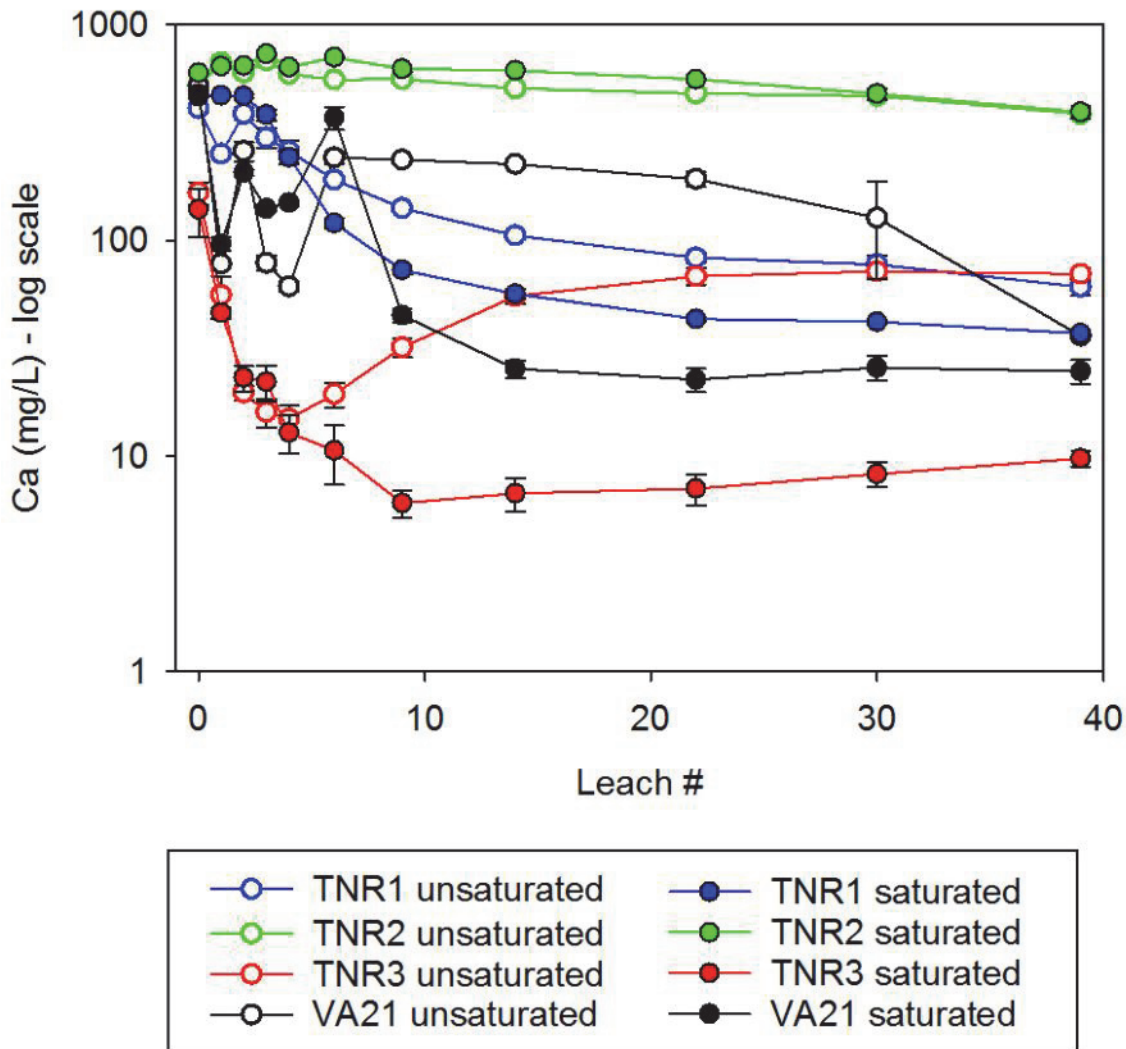
Figure 4.10. Column leachate Ca concentrations for refuse samples under saturated and unsaturated conditions. The 40 leach events occurred over 20 weeks; one pore volume is approximately 3 - 5 leaching doses. Bars around each point indicate one standard error above and below the mean of 3 replications. Note log scale on Y axis.
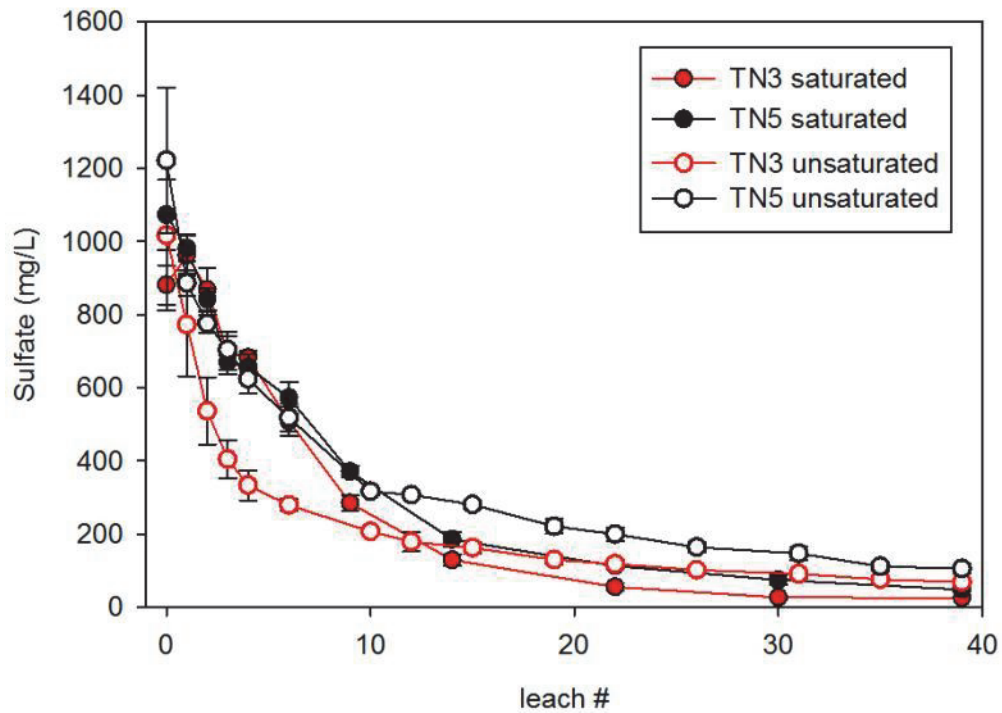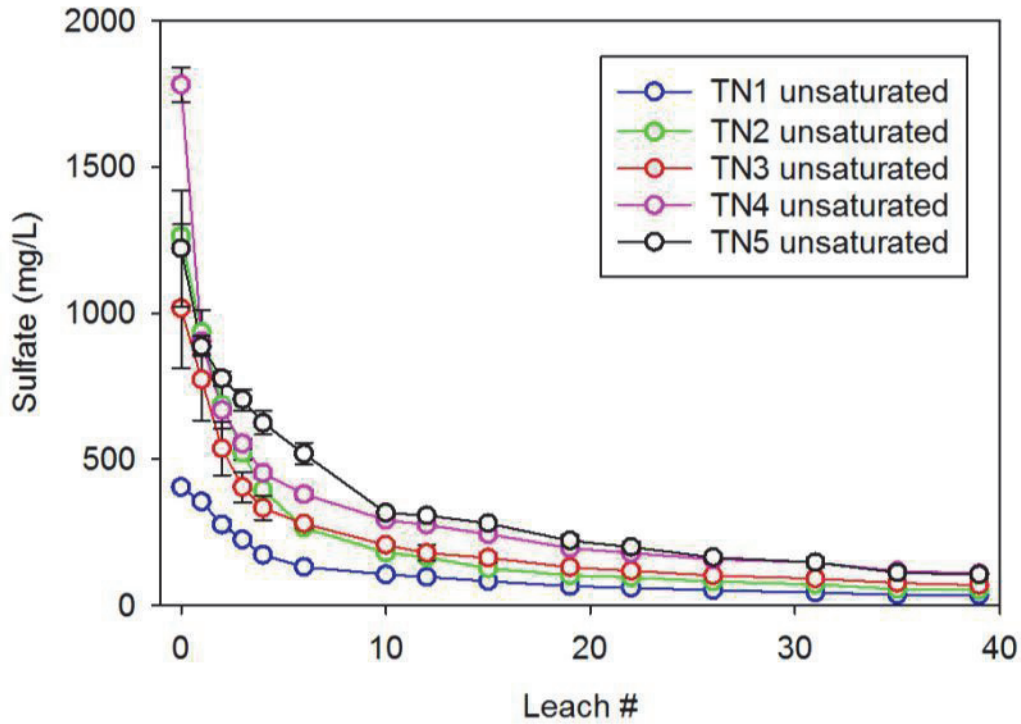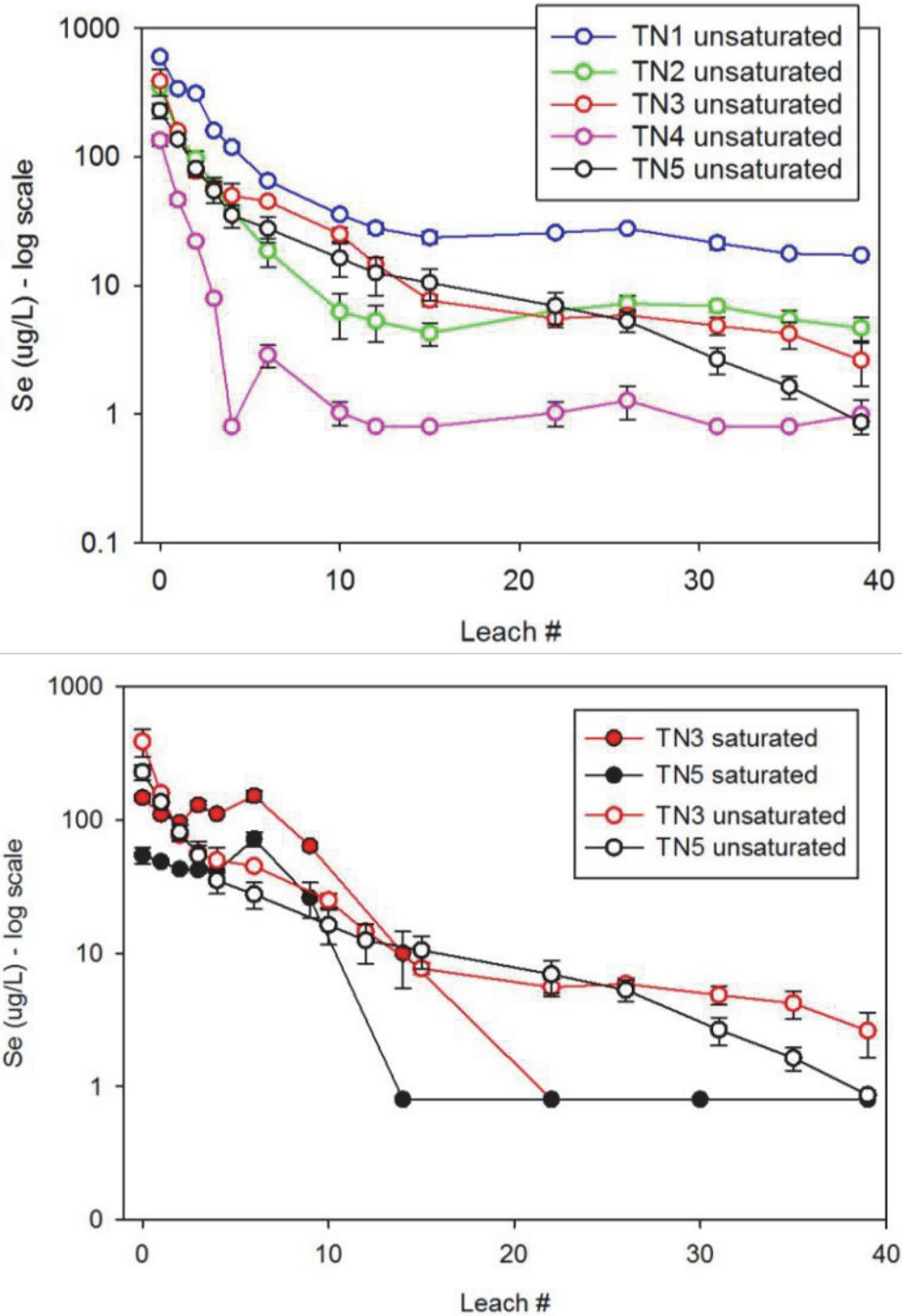
Figure 4.11. Top: Column leachate Se concentrations from five TN spoils under unsaturated conditions. Bottom: Leachate Se concentrations for two of the spoils under saturated and unsaturated conditions. The 40 leach events occurred over 20 weeks; one pore volume is approximately 3 - 5 leaching doses. Bars around each point indicate one standard error above and below the mean of 3 replications. Values shown as 0.8 µg/L illustrate concentrations below the method detection limit of 0.8 µg/L.

Figure 4.12. Column leachate Se concentrations for refuse samples under saturated and unsaturated conditions. The 40 leach events occurred over 20 weeks; one pore volume is approximately 3 - 5 leaching doses. Bars around each point indicate one standard error above and below the mean of 3 replications. Note log scale on Y axis.
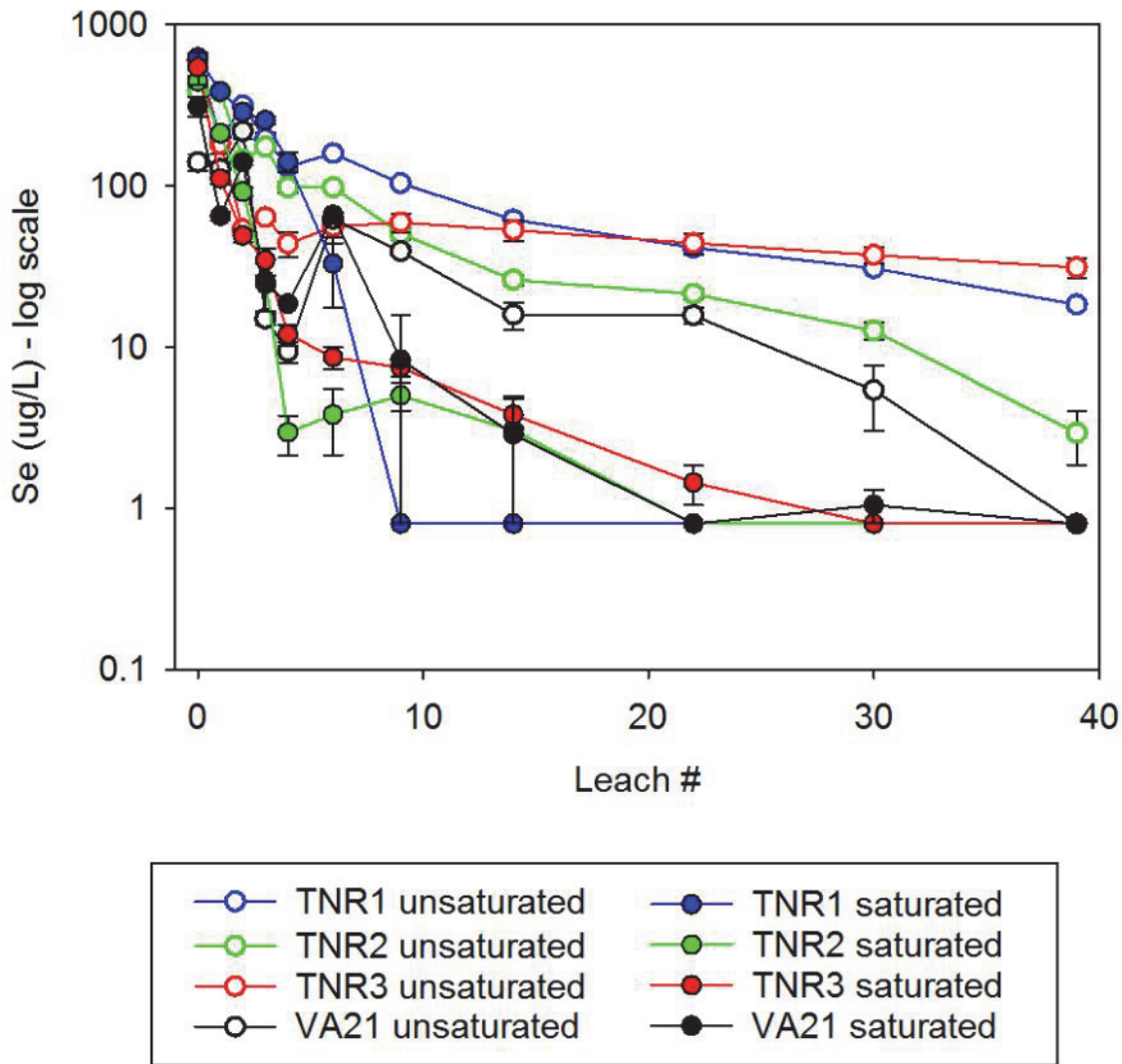
Table 4.4. Metal concentrations in spoil column leachate, under saturated and unsaturated conditions, from selected leach cycles.

	Unsaturated					Saturated	
	TN1	TN2	TN3	TN4	TN5	TN3	TN5
Leach #	--- As (µg/L) ---						
0	1.1	1.8	0.9	3.3	2.3	7.0	<0.3
2	0.6	0.8	0.9	1.7	1.0	<0.3	<0.3
10	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3
22	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3
39	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3
	--- Cd (µg/L) ---						
0	0.8	0.8	3.0	28.2	7.1	0.9	3.5
2	0.1	<0.1	0.4	7.4	2.3	0.8	2.5
10	<0.1	<0.1	<0.1	2.0	0.3	0.3	0.8
22	<0.1	<0.1	<0.1	1.0	<0.1	<0.1	0.1
39	<0.1	<0.1	<0.1	0.6	<0.1	<0.1	<0.1
	--- Cu (µg/L) ---						
0	17.2	13.0	11.8	104.07	30.3	4.7	10.7
2	0.8	1.8	0.8	17.0	2.9	1.3	1.8
10	0.9	2.0	1.8	3.0	0.9	0.6	4.1
22	0.8	1.2	1.1	2.4	1.1	0.6	0.6
39	0.8	1.0	1.3	0.8	0.7	0.6	0.6
	--- Fe (µg/L) ---						
0	355	386	900	246	1162	3407	1979
2	81	16	9	5	6	442	99
10	163	76	103	50	5	72	53
22	129	95	109	33	5	2474	1255
39	196	111	128	5	20	1772	1002
	--- Mn (µg/L) ---						
0	1117	1506	9182	60,377	33766	3711	21152
2	500	600	4009	19,820	15950	4934	19287
10	145	5	68	8819	5425	2685	8235
22	6	3	8	4729	408	2120	3471
39	6	3	5	2239	14	1498	2340
	--- Ni (µg/L) ---						
0	54.1	57.8	311.6	2147.6	1308.4	0.3	589.3
2	6.2	7.5	51.6	527.4	443.1	133.7	520.0
10	1.6	3.2	5.5	160.8	29.1	47.8	109.5
22	1.2	2.0	1.8	63.7	1.9	15.0	19.5
39	1.1	1.8	3.9	33.6	1.7	6.5	5.8
	--- Pb (µg/L) ---						
0	4.2	3.1	6.0	7.3	11.8	0.7	1.7
2	<0.5	<0.5	<0.5	2.7	1.2	<0.5	<0.5
10	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
22	0.6	1.1	1.4	<0.5	<0.5	<0.5	<0.5
39	<0.5	1.0	0.6	0.79	<0.5	<0.5	<0.5
	--- Zn (µg/L) ---						
0	130.8	81.2	212.0	4323.4	1343.7	102.3	523.4
2	5.6	3.7	19.7	1080.8	291.7	45.4	245.6
10	1.5	2.4	5.7	232.2	20.1	18.8	46.8
22	2.4	3.3	5.8	71.2	8.6	3.5	5.6
39	40.4	44.0	26.5	91.2	38.3	2.8	1.3

Table 4.4. Metal concentrations (µg/L) in refuse column leachate, under saturated and unsaturated conditions, from selected leach cycles.

	Unsaturated				Saturated			
	TNR1	TNR2	TNR3	VA21	TNR1	TNR2	TNR3	VA21
Leach#	-- As (µg/L) --							
0	<0.3	<0.3	<0.3	6368	<0.3	<0.3	<0.3	4984
2	<0.3	<0.3	<0.3	135	<0.3	<0.3	<0.3	71
9	<0.3	<0.3	<0.3	5	<0.3	<0.3	<0.3	50
22	<0.3	<0.3	<0.3	36	<0.3	<0.3	<0.3	86
39	<0.3	<0.3	<0.3	38	<0.3	0.6	<0.3	29
	-- Cd (µg/L) --							
0	24.7	0.9	0.1	14.1	29.1	1.6	0.2	22.6
2	12.9	0.2	<0.1	14.3	12.0	0.6	<0.1	4.7
9	3.1	<0.1	<0.1	4.87	0.4	0.3	<0.1	<0.1
22	2.7	<0.1	<0.1	8.46	0.1	<0.1	<0.1	<0.1
39	3.5	<0.1	<0.1	11.0	<0.1	0.11	<0.1	<0.1
	-- Cu (µg/L) --							
0	266.0	2.8	3.1	2793.2	317.3	7.2	4.1	4180.7
2	56.6	2.8	0.6	948.5	21.4	4.1	1.3	274.5
9	8.9	2.1	0.8	641.7	1.0	5.0	0.7	0.7
22	11.34	1.6	0.5	814.0	<0.6	1.2	<0.6	<0.6
39	10.7	<0.6	<0.6	88.56	<0.6	<0.6	<0.6	<0.6
	-- Fe (µg/L) --							
0	31728	192	<5	3,404,833	26062	911	571	5,563,667
2	48	28	41	381,100	365	40	57	663,500
9	6	<5	48	26,613	60	<5	126	22,423
22	7	<5	7	66,610	79	1359	34	6880
39	<5	7	8	9930	468	517	23	4020
	-- Mn (µg/L) --							
0	5216	1874	139	34,730	5585	2594	141	53,735
2	3814	523	7	26,160	4033	960	14	15,640
9	908	13	25	35,290	387	337	5	1570
22	392	6	7	39,060	227	822	7	929
39	309	3	3	5793	209	222	22	1199
	-- Ni (µg/L) --							
0	1569	<0.3	17.9	4021	3040	52	44.2	6376
2	1034	27.3	2.9	3565	1216	68	5.2	2049
9	192	11.7	1.3	2159	<0.3	<0.3	1.4	137
22	72	8.0	1.4	1945	6	<0.3	0.6	32
39	159	4.9	1.3	200	4	9	0.4	20
	-- Pb (µg/L) --							
0	17.7	<0.5	<0.5	41.8	32.7	<0.5	<0.5	6.7
2	4.8	<0.5	<0.5	<0.5	1.6	0.3	<0.5	<0.5
9	0.6	<0.5	<0.5	<0.5	0.9	<0.5	<0.5	<0.5
22	1.0	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
39	2.1	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
	-- Zn (µg/L) --							
0	4163	62	31	5372	5312	95	12	9565
2	1479	17	4	4796	1422	23	4	2544
9	348	5	3	4332	19	17	1	126
22	338	3	3	5062	6.3	4.4	1	22
39	365	1	2	499	1.9	2.4	1	7

EC

For all spoil samples, EC (Fig. 4.3) dropped rapidly over the first few leaching events then continued declining slowly over the course of the study. The initial response reflected a flush of more readily soluble products from rock surfaces which may be affected by mineralogy, stage of weathering, and recent field conditions at the time of sampling. This effect was most evident from TN-4, but also was quite notable from TN-2, TN-3, and TN-5, and was likely related to soluble sulfate precipitates (see sulfate discussion below) accumulated from partial weathering and oxidation of the samples before we began leaching them. Sample TN-1, which had the lowest total-S, generated the lowest EC for most of the study equilibrating to <500 uS/cm by the 6th leach event. For the other four samples, EC values equilibrated below the suggested field effects criteria of 500 uS/cm between the 16th to the 21st leach event (~8 to 10 weeks). Little difference was observed in leachate EC under saturated vs. unsaturated conditions. For TN-3, leachate EC was slightly higher under saturated conditions over the first several leach events, but was comparable to unsaturated EC after the 12th leach event. Overall, these results reconfirm our earlier findings (Orndorff et al., 2010) that maximum EC/TDS elution from fresh mine spoil materials occurs dominantly in the early pore volumes followed by a rapid drop to a longer term baseline level.

Leachate EC from the refuse samples was quite high (> 1500 uS/cm), particularly over the first several leach events. Elevated EC levels observed in the unsaturated columns were related to the oxidation of highly reactive sulfides which reacted quickly with neutralizing agents to produce higher and more prolonged TDS release over the extent of the study. This was particularly evident in TNR-2 and VA-21. Collectively, acid-base reaction control on leachate chemistry also was reflected in leachate bicarbonate, sulfate, and Ca concentrations (discussed below).

Leachate EC from the refuse samples initially was comparable (per sample pairs) under saturated and unsaturated conditions; however, after 5 – 7 leach events, saturation effects were clearly evident for samples TNR-1, TNR-3, and VA-21 with unsaturated columns maintaining much higher EC. The effect of saturation was particularly profound for VA-21. This likely was related to the suppression of sulfide oxidation in the saturated columns, which would limit acid-base reactions and hence the generation of reaction products. Only TNR-2 maintained equivalent EC values for both moisture regimes throughout the study period. It is interesting to note that unlike the other 3 refuse sample, TNR-2 did not exhibit a dramatic decline in EC over the first few leach events. We can only speculate that the sulfidic materials in this particular sample are physically distributed in such a way that they continued to react over the full study period rather than rapidly oxidizing in the initial pore volumes.

A preliminary effort was made to evaluate possible predictive relationships between leachate EC over time and common static test methods including saturated paste pH and EC, total-S, CCE, and PPA. The following correlation and regression analysis was completed on a sample set

including the five TN spoils and the three TN refuse samples; however, refuse sample VA-21 was excluded as it proved to be an outlier. Total-S was most strongly correlated to leachate EC for the first leach event (r=0.85, p<0.01), but decreased over subsequent leach events maintaining, on average, correlation values of approximately r=0.74 (p<0.04) from the 6th leach event through the remainder of the study period. For CCE, the relationship was reversed; correlation values were lowest in the first few leach events (r=0.69, p<0.06), but strengthened after the 4th leach event maintaining correlation values, on average, of approximately r=0.75 (p<0.03) from the 10th leach event through the rest of the study period. Saturated paste EC proved to be a poor predictor of leachate EC for this sample set; correlation values increased over the first few leach events achieving values of approximately r=0.55 (p>0.15) for the 5th leach event through the end of the study period. Stepwise regression of leachate EC on sample properties indicated that total-S alone was the best predictor of leachate EC through the first eleven leach cycles, then CCE was the better predictor from leach 12 through the end of the study. While these results are promising, analysis would need to be completed on a much larger set of materials before stating definitive conclusions. In the near future, we will combine the data from this study with the same data sets for over 45 different spoils from the regional (KY, VA and WV) ARIES study. We have preliminary evidence from that combined work that peak spoil EC/TDS is most related to a combination of S content and saturated paste EC values while long term EC/TDS appears to be controlled by a combination of CCE and S content.

Sulfate

Sulfate release patterns (Figs. 4.5 and 4.6) were controlled by initial rapid dissolution of soluble sulfate precipitates as well as prolonged acid-base reactions, discussed above, which in turn are controlled by fundamental differences in the geology/mineralogy among materials (i.e. total-S and carbonate content; Table 4.1) as well as the oxidation potential of the environment. For all samples, as expected, sulfate release was closely related to EC. The spoil samples contained relatively low total-S (≤0.15%), releasing 404 – 1782 mg/L in their initial pore volume and then equilibrating to concentrations ≤120 mg/L by the end of 20 week study. Saturation had minimal effect on sulfate release from the spoil materials. The most evident difference occurred for TN-3 where saturated columns yielded slightly more sulfate in the first several leachings, but showed little difference after the 12th leach event.

In comparison, the refuse materials contained higher total-S (0.76 – 1.25%), releasing 1661 – 16,820 mg/L in their initial pore volumes and equilibrating to concentrations ranging from 17 – 1725 mg/L by the end of the study. The effect of saturated conditions on sulfate leaching was readily apparent, with TNR-1, TNR-3, and VA-21 releasing significantly less sulfate under saturated conditions. As discussed above, saturation inhibited the sulfide oxidation reactions which generate sulfate. For TNR-2, saturation did not have a significant effect on sulfate release, which was relatively high from this sample, suggesting that sulfide oxidation continued in this sample despite saturated conditions.

Bicarbonate

Bicarbonate release (Fig. 4.7 and 4.8) clearly reflected saturation effects, with significantly more bicarbonate leached under saturated conditions for both spoil and refuse materials. The lower levels released from unsaturated materials presumably reflected bicarbonate consumption by acid neutralization reactions, even when relatively low amounts of S were present. Consistent with limited previous work (Daniels et al. 2006), a direct relationship between bicarbonate concentrations and pH was not observed for the spoil materials, but was evident for the refuse samples. Prolonged bicarbonate release clearly varied by material and per above, we believe is a major controller of long-term EC/TDS levels.

Major Cations

Major cations exhibited release patterns that were similar to EC and sulfate (See Tables 4.4 and 4.5). Calcium release (Fig. 4.9 and 4.10) is shown here as an example.

Iron and Manganese Release

As expected, patterns of Fe and Mn release varied between spoils (Table 4.4) and refuse (Table 4.5) and were affected by saturation regimes, but somewhat counterintuitively. Mass Fe release from spoils was quite low due to higher pH for most samples, coupled with much lower S as discussed earlier. In spoils, more Fe eluted from the saturated spoils (for TN-3 and TN-5) and from all refuse materials than from the unsaturated materials. The Fe elution was also highest in initial pore volumes and declined quickly, similar to sulfate and cations. We presume that the Fe was eluting primarily in the ferrous form since we did not observe reddish precipitates or coloration in initial leachates. We also assume that most of the Fe is generated by the rapid oxidation of sulfides that is simultaneously driving sulfate and overall TDS release.

On the other hand, Mn release was much more prolonged from both the spoil and refuse columns and the effects of saturation were not consistent or as dramatic as for Fe. The overall release of Mn was substantial, however, particularly from the refuse materials. Also, the total Mn release from the spoils was much higher than Fe, but mass Mn release from the refuse materials was much lower than Fe. Manganese can remain soluble at higher pH values than Fe in these systems and can also form a complex redox pair with sulfides whereby Mn is reduced as pyrite is oxidized.

Trace Element Release

As expected, trace element release was clearly related to pH and S-oxidation with VA-21 and TNR-1 typically leaching the highest concentrations of ions such as As, Cu, Ni, Pb, and Zn (Tables 4.4 and 4.5). Arsenic release was highest in initial leachates, but was less than 10 µg/L in all materials except VA-21 (refuse) which produced unusually high levels (5 to 6 mg/L) in initial leachates with prolonged releases over 20 µg/L. Release of other metals of concern (Cd, Cu, Pb, Ni, and Zn) was highly variable among materials, but consistently higher from refuse

materials than spoils. Certain materials generated initial leachate concentrations of concern such as TN-4 (spoil) and VA-21 (refuse).

Overall, metal release decreased over time; however, in a few instances metal concentrations fluctuated or initially decreased then slowly increased towards the end of the study period. Saturation had a mixed or no effect on trace element release and was much less important than spoil/refuse type. As noted above, TN-4 and VA-21 produced highly problematic leachates despite the fact that their total elemental analysis (Table 4.3) was similar for these trace elements when compared with other materials that generated much lower mass release.

Selenium release from the spoils (Fig. 4.11) was initially quite high (> 100 µg/L), dropped in subsequent leachates, and appeared to equilibrate at differing material specific levels between ~1 and 50 µg/L. Interestingly, Se release from TN-4 was lowest, even though this material generated much higher levels of other trace metals as noted above. Effects of saturation were inconsistent and negligible (Fig. 4.11) relative to total mass release x material interactions.

Interestingly, Se mass release levels from refuse (Fig. 4.12) were somewhat higher but similar to spoils, even though the total Se in the refuse samples was much higher (Table 4.3). Each refuse material generated very different long term release levels that ranged from less than 1.0 to approximately 50 µg/L. The effect of saturation on Se release was much more pronounced for the refuse samples, with saturated samples eluting much lower levels over time. It is likely that Se exists in a primary reduced elemental form in these organic rich refuse materials (Jason Unrine, UK, personal communication) which would explain why the saturation effects here are more profound. It is also interesting to note that sample VA-21 did not generate substantially higher levels of Se release even though it clearly released much higher levels of other trace elements among the refuse sample set.

4.3. Scaled Leaching Studies: Mesocosm Tanks and Barrels

Scaled leaching studies included mesocosm tanks, barrels, and columns for one spoil material (Harlan/VA-16M), as well as barrels and columns for two refuse materials (TNR-1 and TNR-3). Our overall objective here was to determine how our observed results from our leaching columns would (a) be affected by the size consist of the material leached, (b) the volume of material actually leached, and (c), normal field rainfall and temperature conditions. In short, we wanted to determine how effectively our column results might predict "real world field conditions" with respect to internal leachate properties within spoil and refuse disposal fills (not discharge conditions).

In the following discussion, the terms "applied" and "rainfall" refer to both the naturally occurring rainfall which drove the mesocosm tanks and barrels in the field setting as well as to the synthetic acid rain which was manually applied to the columns in the lab. Figure 4.13

illustrates the cumulative amount of rainfall applied to the leaching vessels versus the amount of leachate collected over the course of the study.

These data are presented in two formats. The first section below presents the data on a cumulative (cm) of rainfall applied basis to allow comparisons on a net water leached basis. The second section below compares the field barrel and mesocosm results as an actual time series to allow discussion of seasonal effects, etc.

4.3.1. Effects of Leaching Scale by Rainfall Volume

<u>**pH**</u>
Leachate from all three scales for the Harlan spoil exhibited comparable pH values (Fig. 4.14). As typically seen in column studies for net alkaline materials, pH increased over the first few leach events until neutralization reactions were established. At all three scales, pH equilibrated at 7.5 – 8.0 after approximately 10 cm of rainfall.

In contrast, scaling effects (e.g. columns vs. barrels) on leachate pH were quite notable for the refuse materials (Fig. 4.15). For TNR-1, leachate from the column study was typically 1.5 to 2.0 pH units lower than the barrel leachate. The reason for this difference in results is not clear to us at this time. The materials placed into the columns were ground and much finer, and this may have exposed internal reactive sulfides to oxidation that were protected in the larger run of mine size consist that was packed into the barrels. This explanation is speculative at best, however.

On the other hand, for TNR-3, the column leachate (Fig. 4.15) maintained a slightly higher pH (~8.1) than the barrel leachate (pH~7.4) for the first 30cm of rainfall, after which barrel leachate's pH rapidly decreased to pH 3.5. In this instance, pyrite oxidation appears to have been inhibited in the column environment, perhaps by maintenance of a saturated relative humidity and higher pCO_2 effects on carbonate dissolution, while the coarser materials in the barrel rapidly acidified after approximately 35 cm of leaching.

<u>**Electrical Conductance**</u>
The overall pattern of leachate EC (Fig. 4.16) was similar for the spoil columns, barrels and mesocosms, but the initial EC produced by the mesocosms was higher by almost 800 us/cm from the larger mesocosm tanks. We assume this is due to accumulation of sulfate weathering salts etc. in the tanks over the approximate two months of time that elapsed between when the tanks were filled and the first leachates emerged following a heavy December snow/rain event. However, the rate of EC decline was quite similar among all three scales. Interestingly, the EC
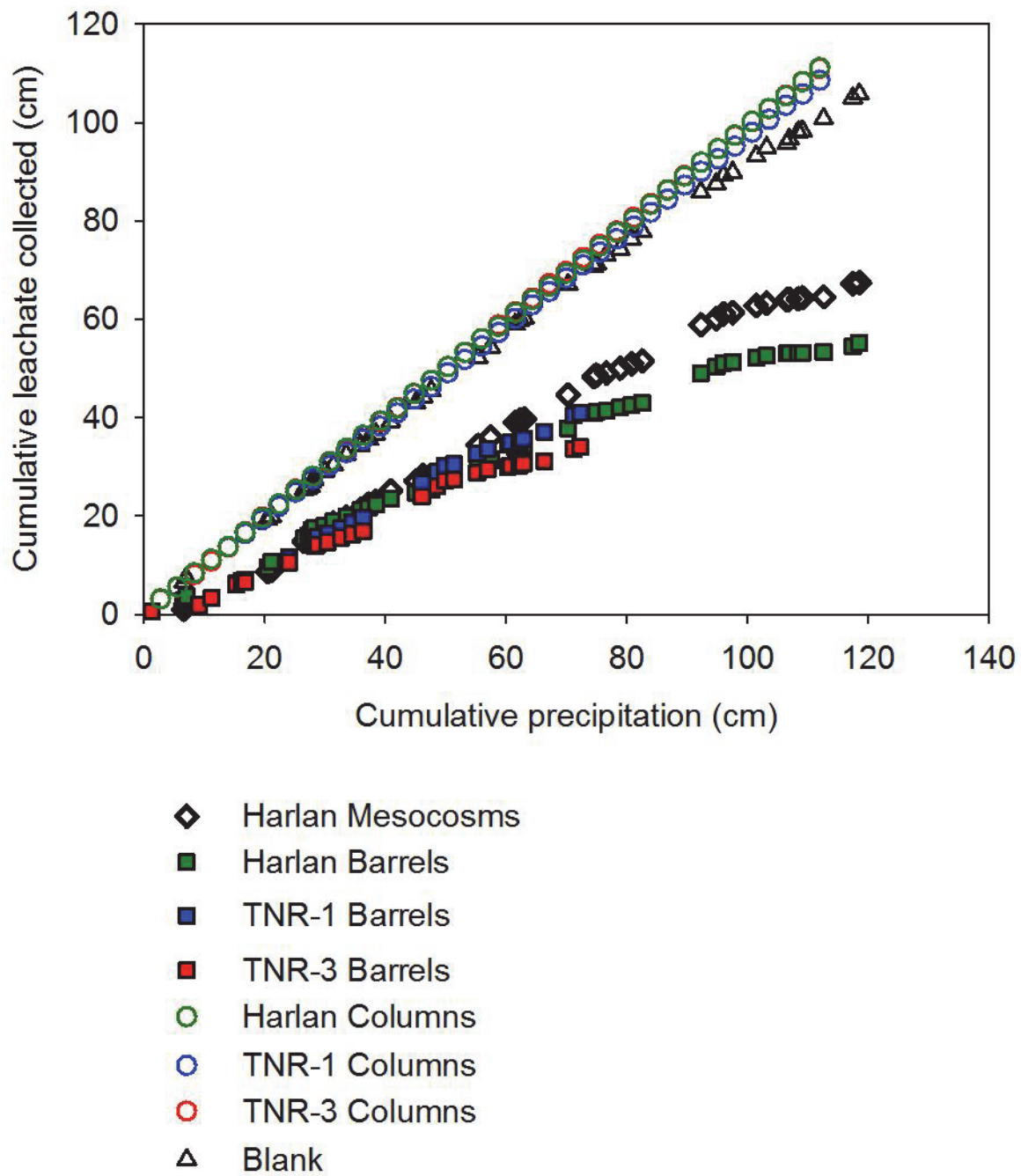
Figure 4.13. Cumulative precipitation versus cumulative eluted leachate at three scales (columns, barrels, and mesocosms). All samples were initially wetted to field capacity.
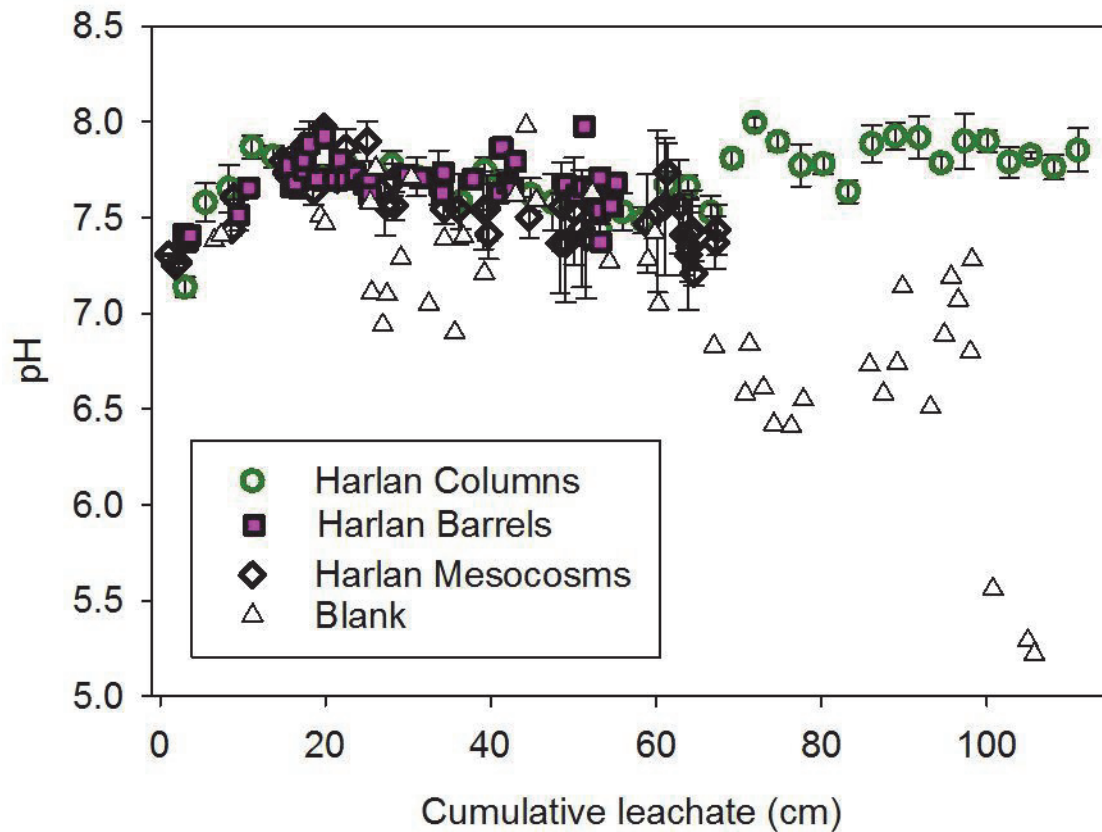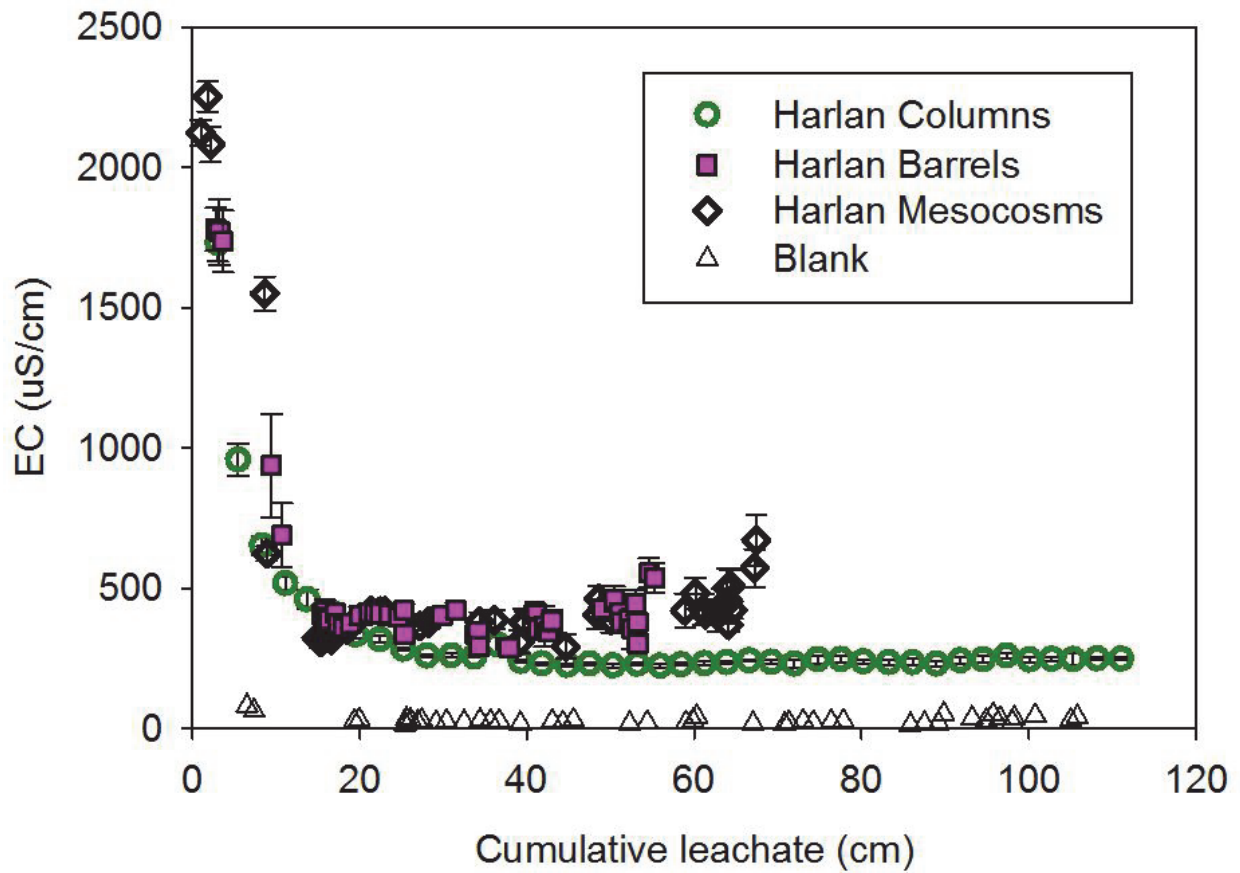
Figure 4.14. Harlan sandstone spoil leachate pH for three different size leaching vessels: mesocosms, barrels, and columns. Blank values reflect rainwater passing through gravel in control (no spoil) barrels. Bars around each point indicate one standard error above and below the mean of 3 replications. The X-axis reflects cumulative amount of leaching through each type of vessel.
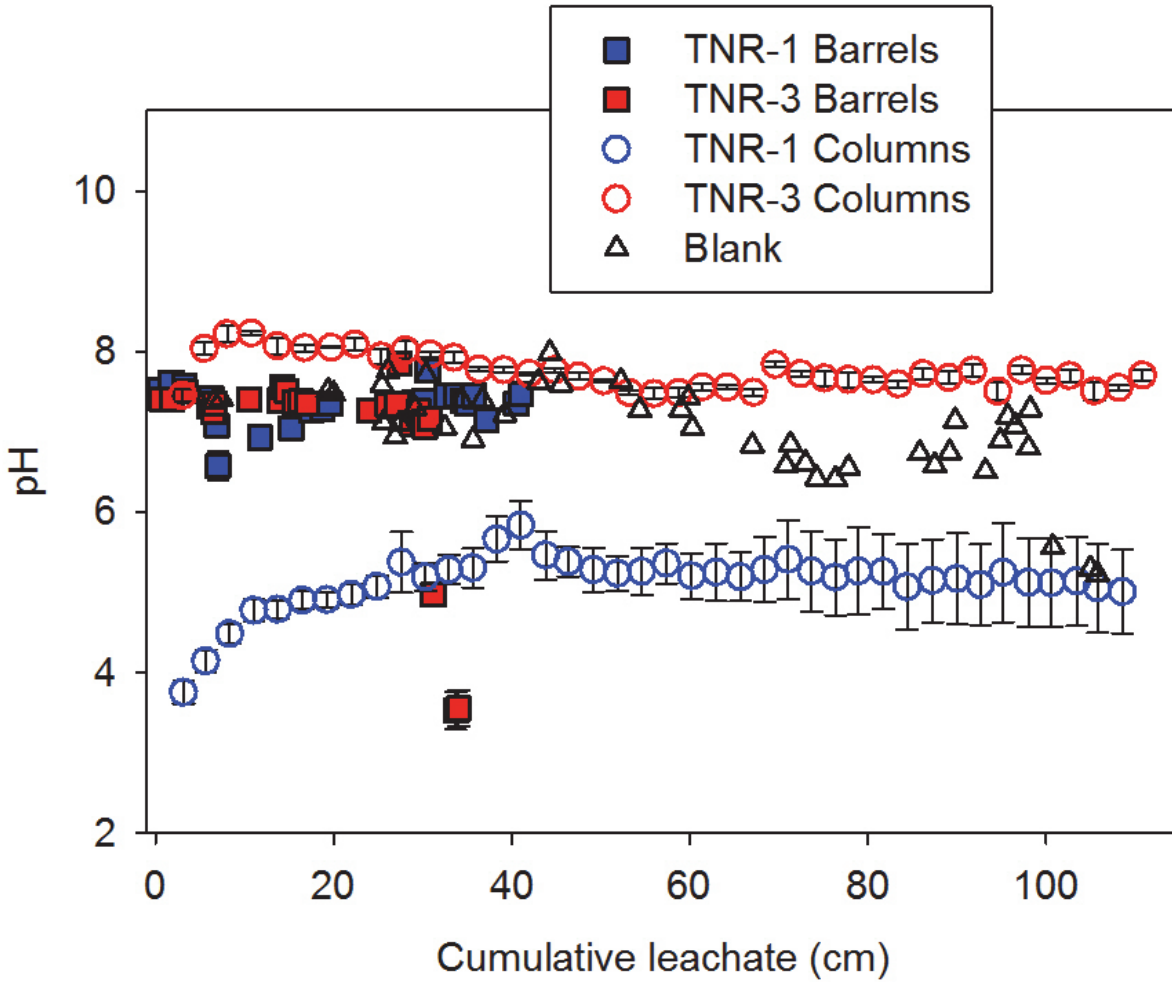
Figure 4.15. Refuse leachate pH for unsaturated leaching columns and barrels. Blank values reflect rainwater passing through gravel in barrels. Bars around each point indicate one standard error above and below the mean of 3 replications. The X-axis reflects cumulative amount of leaching through each type of vessel.

Figure 4.16. Harlan sandstone spoil leachate EC for three different size leaching vessels: mesocosms, barrels, and columns. Blank values reflect rainwater passing through gravel in barrels. Bars around each point indicate one standard error above and below the mean of 3 replications. The X-axis reflects cumulative amount of leaching through each type of vessel.

levels produced by the barrels and mesocosm tanks appeared to increase again towards the end of the one-year study period while the columns remained constant. This may reflect more rapid long-term carbonate dissolution in the field setting, although this conclusion is also speculative.

For the two scales of comparison (columns vs. barrels) for the two refuse materials, the results were less consistent over time/leaching volume (Fig. 4.17). Peak initial EC values were similar for the TNR-3 material at both scales, but the barrel leachates were much more variable and higher in EC over prolonged leaching cycles/volumes. In contrast, the TNR-1 materials were quite different with the columns producing initially high EC levels while the barrels started at very low levels and quickly increased to match the columns after 15 to 20 cm of leaching volume and then dropped in similar fashion. In this instance, it again appears that the column environment was somehow suppressing sulfide reactivity for the TNR-3 material, but the grinding and smaller size consist of the TNR-1 material enhanced its reactivity in the columns.

Sulfate

Leachate sulfate levels (Fig. 4.18) for the Harlan spoils mirrored the EC response and levels at the three different scales as expected. However, the increase in sulfate toward the end of the study in the barrels and mesocosms may indicate that some sort of time-lagged sulfide weathering may be driving the associated increase in EC rather than simple long-term carbonate dissolution as proposed above. The sulfate release levels for the refuse samples (Fig. 4.19) also mirrored the EC variations discussed above and show the same higher level of variance for the barrels vs. the columns. We assume the higher variance observed over time in the barrels is due to their larger size consist generating more preferential flow and reaction zones vs. the much more uniform size consist and packing in the columns.

Bicarbonate

Bicarbonate release (Fig. 4.20) was similar across scales for the spoils, but very different for the refuse barrels vs. columns (Fig. 4.21). In particular, the TNR-1 columns generated very low bicarbonate release and were associated with much lower pH as discussed above while the TNR-3 columns generated much higher bicarbonate release than the field barrels. Again, it's clear that the reactivity of these two refuse materials was clearly affected by these two scales.

Major Cations

For the spoils, Ca release was very similar among the three scales of leaching with more initial Ca release occurring in the mesocosms (Fig. 4.22). As noted for other parameters, the Ca release from refuse was quite different between the columns and field barrels (Fig. 4.23) due to the very different reactivity of the materials discussed above. Interestingly, mass Ca release was higher for the more acidic TNR-1 columns than the pH. 8.0 TNR-3 columns.
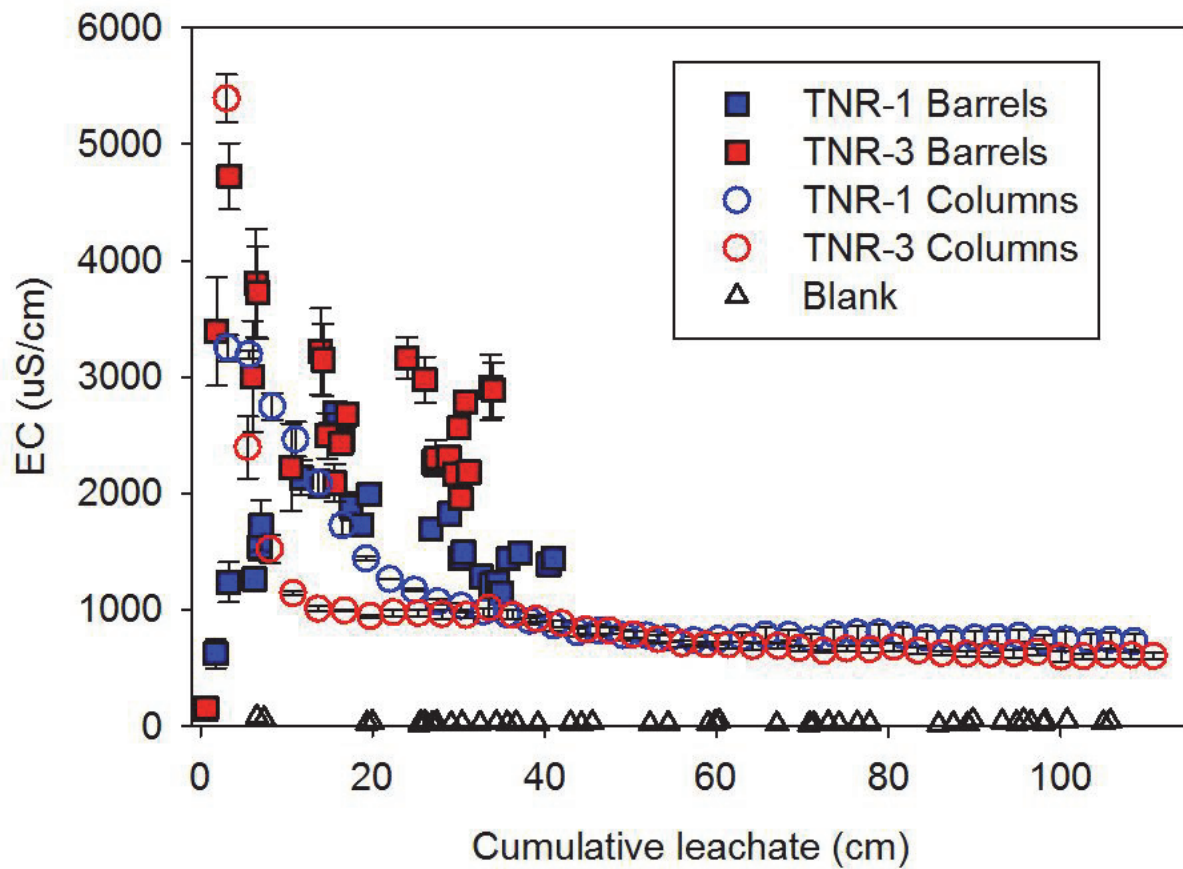
Figure 4.17. Refuse leachate EC for leaching columns and barrels. Blank values reflect rainwater passing through gravel in barrels. Bars around each point indicate one standard error above and below the mean of 3 replications. The X-axis reflects cumulative amount of leaching through each type of vessel.
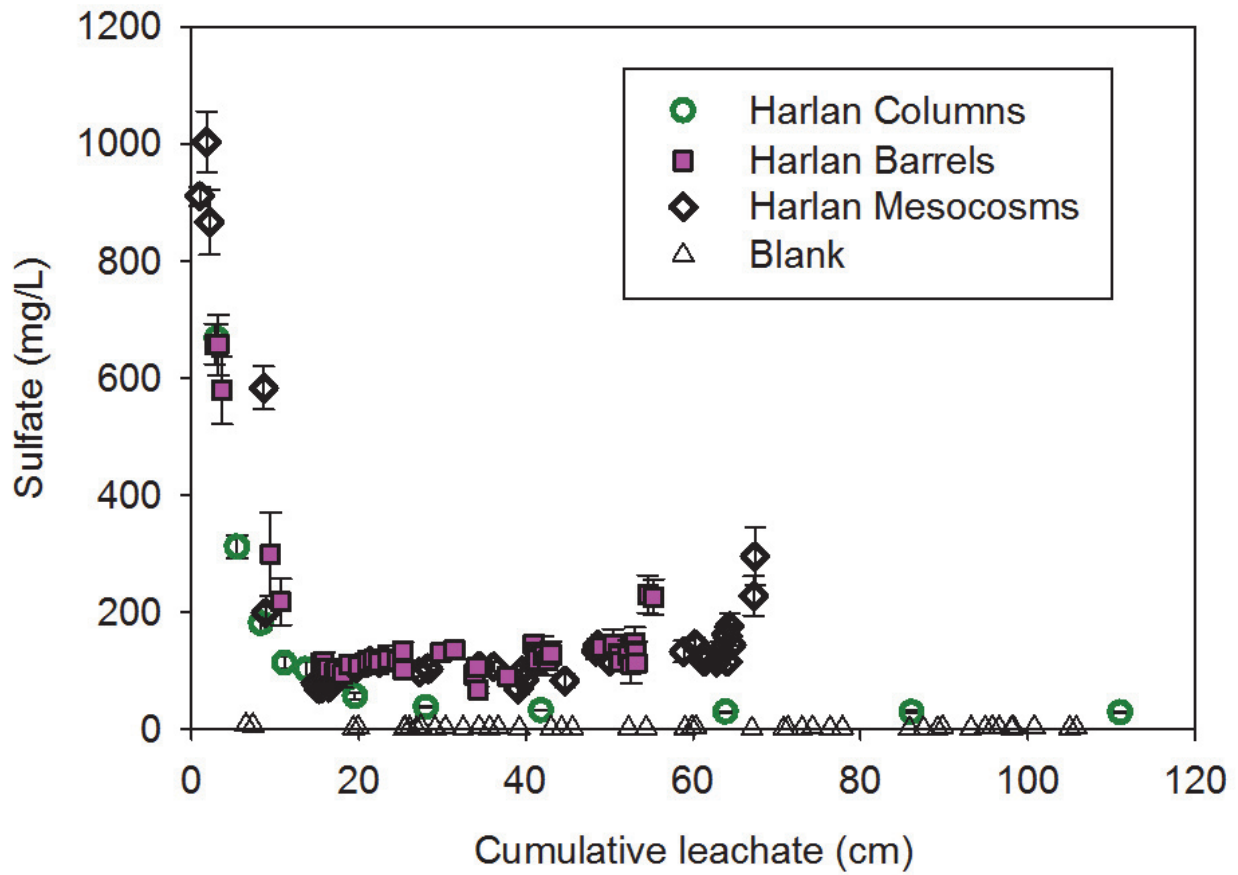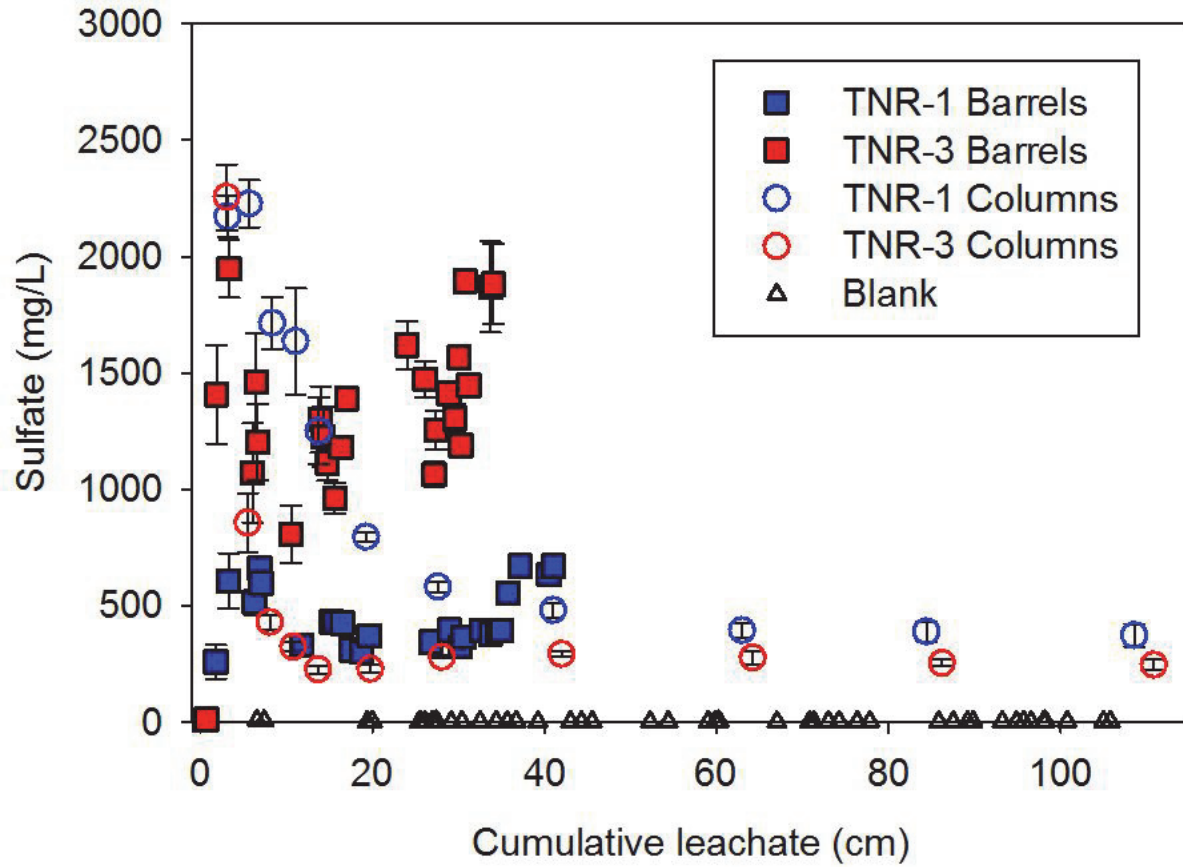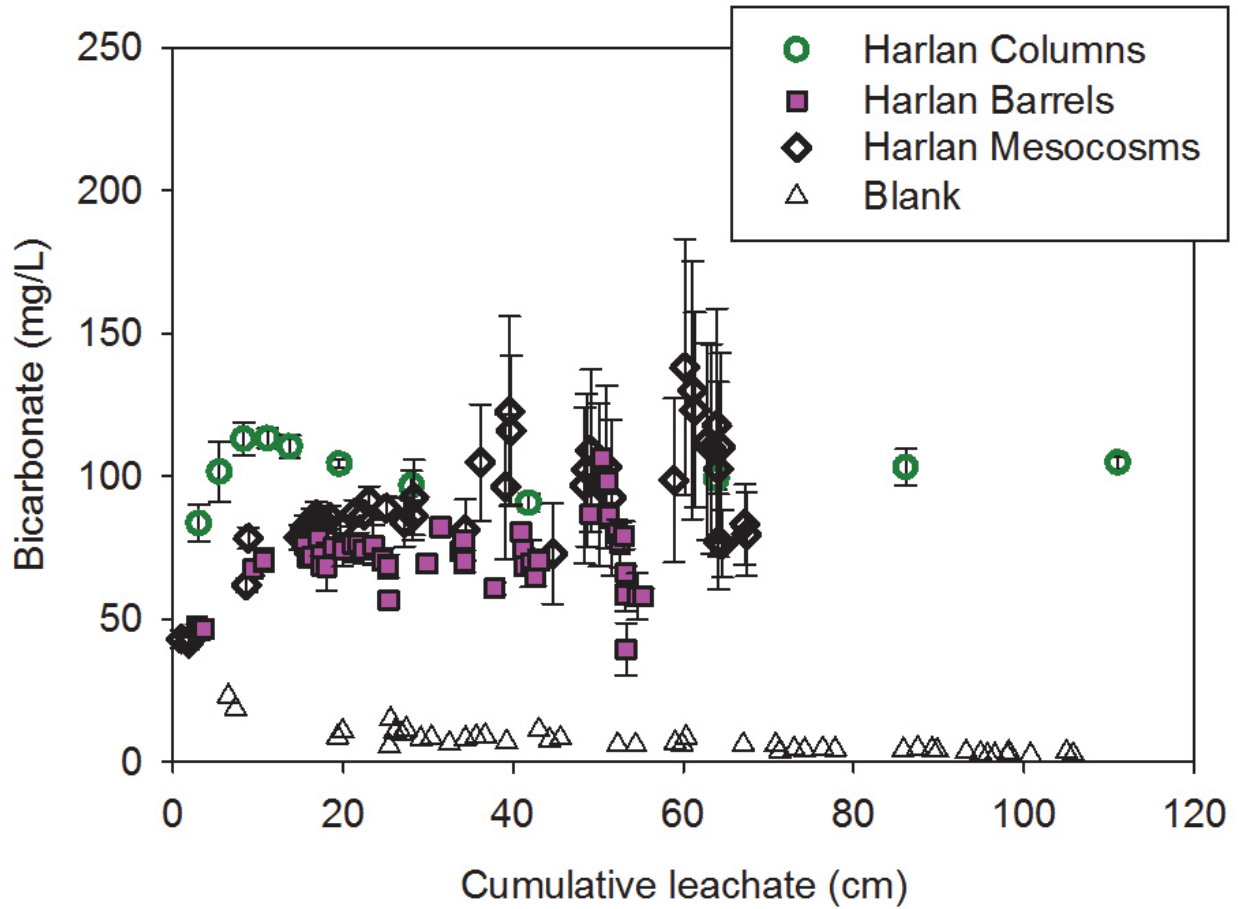
Figure 4.18. Harlan sandstone spoil leachate sulfate for three different size leaching vessels: mesocosms, barrels, and columns. Blank values reflect rainwater passing through gravel in barrels. Bars around each point indicate one standard error above and below the mean of 3 replications. The X-axis reflects cumulative amount of leaching through each type of vessel.

Figure 4.19. Refuse leachate sulfate for leaching columns and barrels. Blank values reflect rainwater passing through gravel in barrels. Bars around each point indicate one standard error above and below the mean of 3 replications. The X-axis reflects cumulative amount of leaching through each type of vessel.
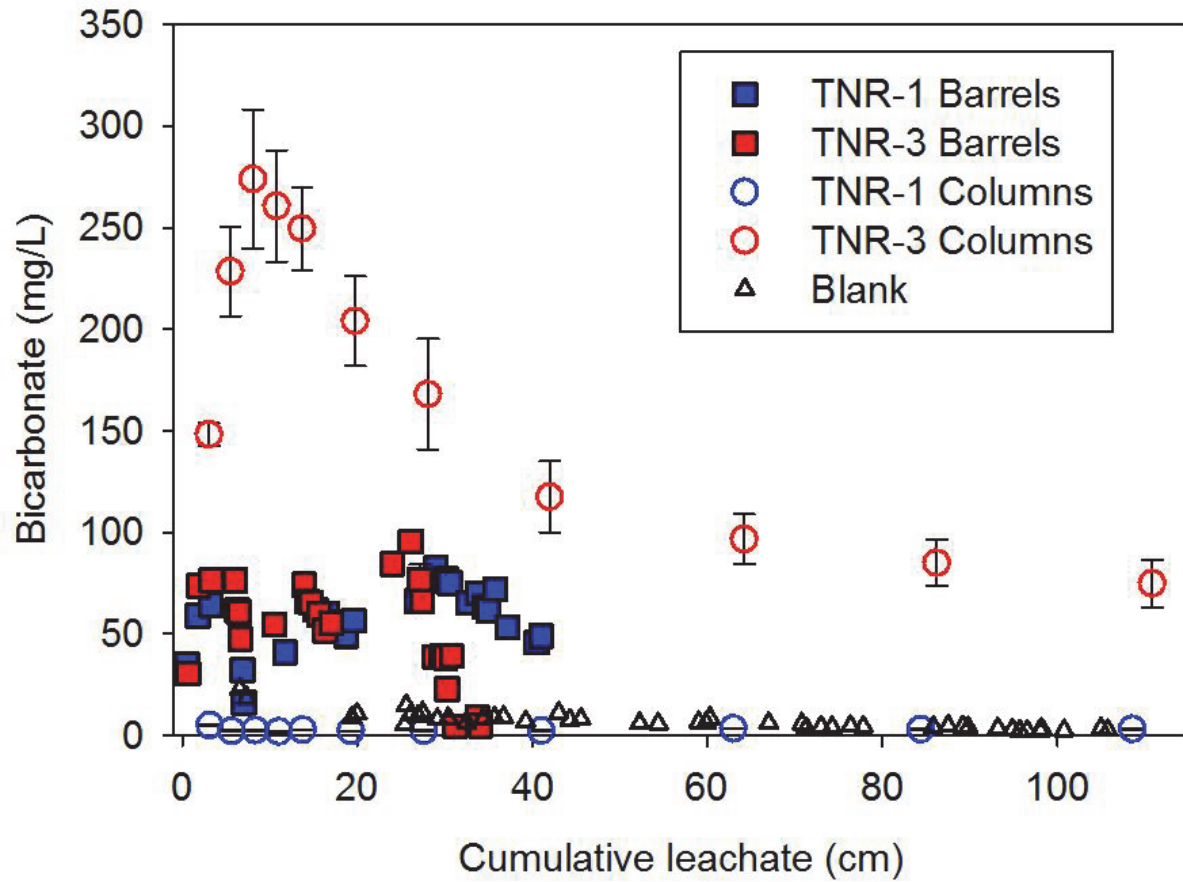
Figure 4.20. Harlan sandstone spoil leachate bicarbonate for three different size leaching vessels: mesocosms, barrels, and columns. Blank values reflect rainwater passing through gravel in barrels. Bars around each point indicate one standard error above and below the mean of 3 replications. The X-axis reflects cumulative amount of leaching through each type of vessel.
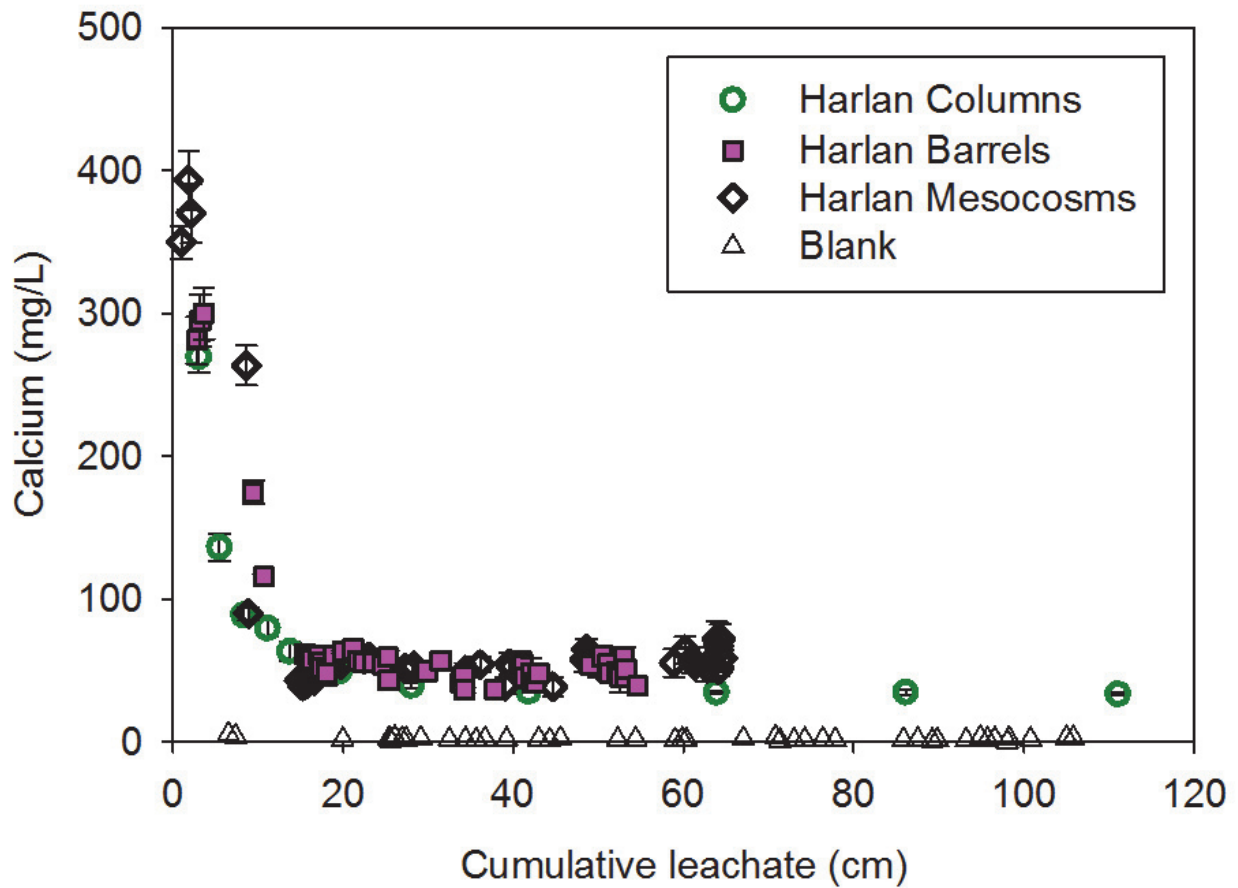
Figure 4.21. Refuse leachate bicarbonate for leaching columns and barrels. Blank values reflect rainwater passing through gravel in barrels. Bars around each point indicate one standard error above and below the mean of 3 replications. The X-axis reflects cumulative amount of leaching through each type of vessel.

Figure 4.22. Harlan sandstone spoil leachate calcium for three different size leaching vessels: mesocosms, barrels, and columns. Blank values reflect rainwater passing through gravel in barrels. Bars around each point indicate one standard error above and below the mean of 3 replications. The X-axis reflects cumulative amount of leaching through each type of vessel.
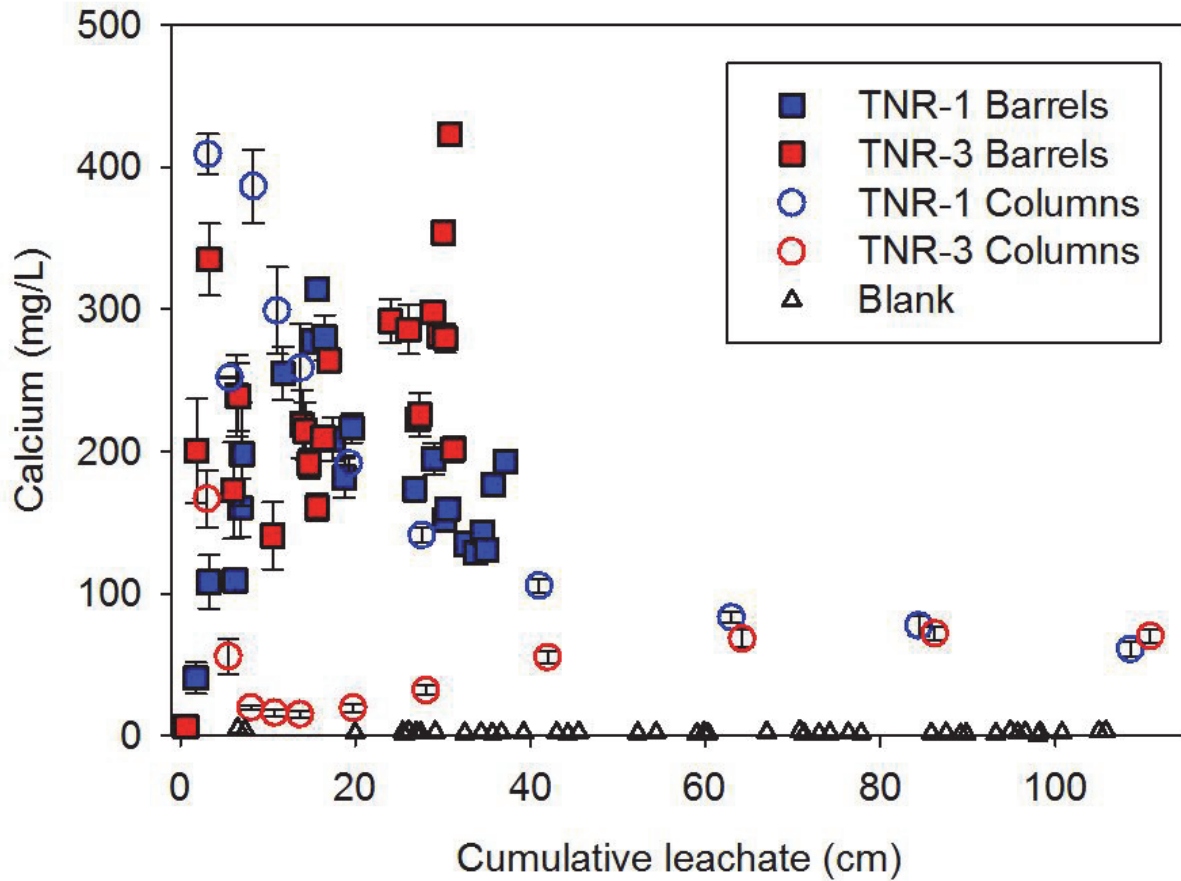
Figure 4.23. Refuse leachate calcium for leaching columns and barrels. Blank values reflect rainwater passing through gravel in barrels. Bars around each point indicate one standard error above and below the mean of 3 replications. The X-axis reflects cumulative amount of leaching through each type of vessel.

Trace Elements

Complete data sets for major trace element release generally followed the same temporal pattern and overall solubility control due to pH effects discussed earlier. The effects of leaching scale on Se release are presented in Figure 4.24 for the Harlan spoil materials. While the overall pattern of release was quite similar across all three scales, the mesocosms again produced higher initial Se concentrations in leachates, presumably due to their protracted (two month) field weathering phase in the late fall of 2012 before significant precipitation occurred to produce leachates.

For the two refuse leaching scales (columns and barrels), the overall Se levels were much higher (Fig. 4.25) than for the Harlan spoil, and the levels produced by the barrels were consistently higher over more extended periods of time than the lab columns. In the field barrels, initial leaching Se values were very low and then quickly increased with subsequent leaching. It is also important to note that sample TNR-1 was still producing very high levels of Se at the end of the study period (~ 40 cm of leaching) while the matching columns were very low. Among all the data generated by this scaling study, this appears to be the strongest difference and does not appear to be related to pH or other conventional controlling variables.

4.3.2. Effects of Leaching Scale over Time for Spoils in Barrels and Mesocosm Tanks

The differences between the two scales of field leaching (barrels vs. tanks) for the Harlan spoil are presented in Figures 4.26 – 4.31. While the field leaching systems were actually installed in late October, the first leachates were not eluted until December 27. There were no differences in pH (Fig. 4.26) between the two over time, although the larger tank mesocosms were more variable in pH and slightly lower over the summer of 2013. It also appears that sample variability was higher during the drier summer months. As noted earlier, the tank mesocosms produced a considerably higher initial EC (Fig. 4.27) than the barrels, but they both dropped very quickly and remained at or below 500 us/cm for the balance of the study. We had expected to see higher "EC flushes" during the summer of 2013 due to accumulated reaction products, but that did not occur. It is also interesting to note the slight increase in EC at the end of the study period as discussed earlier.

Leachate Ca (Fig. 4.28) and sulfate (Fig. 4.29) levels were similar between both scales with initial concentrations higher in the mesocosm tanks. The increase in sulfate towards the end of the study period is notable as discussed earlier. Leachate bicarbonate levels (Fig. 4.30) were consistently higher in the large mesocosm tanks than the barrels and were much more variable, particularly over the summer. The reasons for the overall higher levels in the larger tanks are not obvious at this time since pH values etc., were not that different. Initial Se levels (Fig. 4.31) were higher in the leachates from the mesocosm tanks as noted earlier, but both fell rapidly to very low levels and showed no dry/wet weather related variance effects.
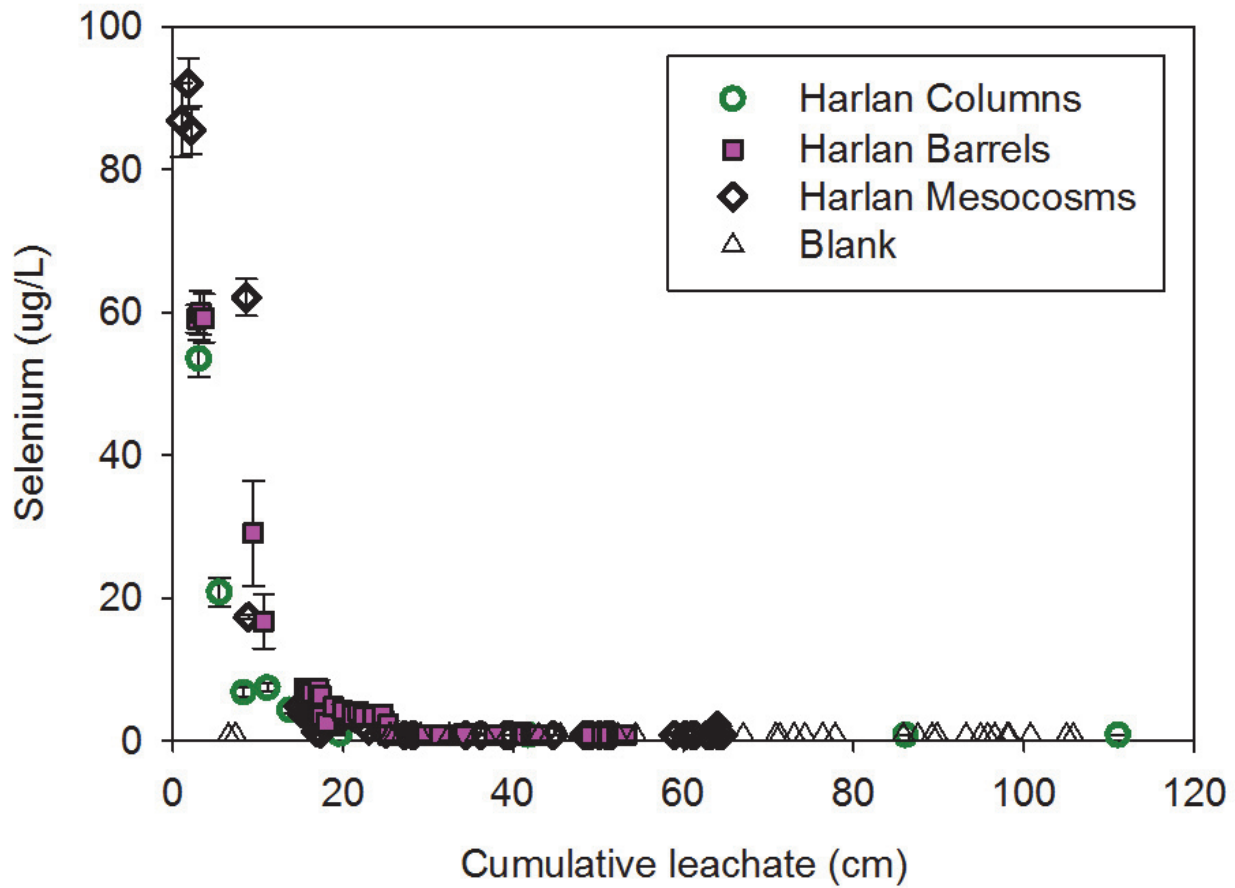
Figure 4.24. Harlan sandstone spoil leachate selenium for three different size leaching vessels: mesocosms, barrels, and columns. Blank values reflect rainwater passing through gravel in barrels. Bars around each point indicate one standard error above and below the mean of 3 replications. The X-axis reflects cumulative amount of leaching through each type of vessel.
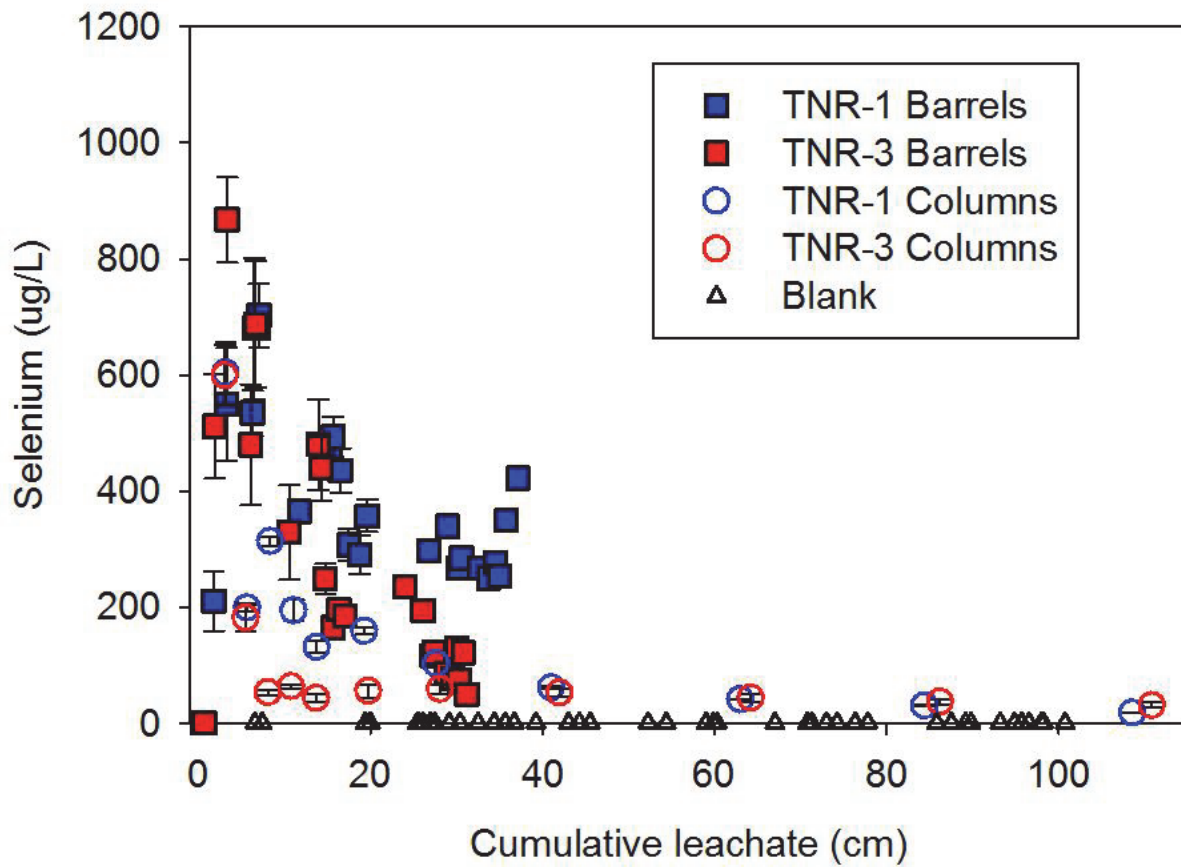
Figure 4.25. Refuse leachate selenium for leaching columns and barrels. Blank values reflect rainwater passing through gravel in barrels. Bars around each point indicate one standard error above and below the mean of 3 replications. The X-axis reflects cumulative amount of leaching through each type of vessel.
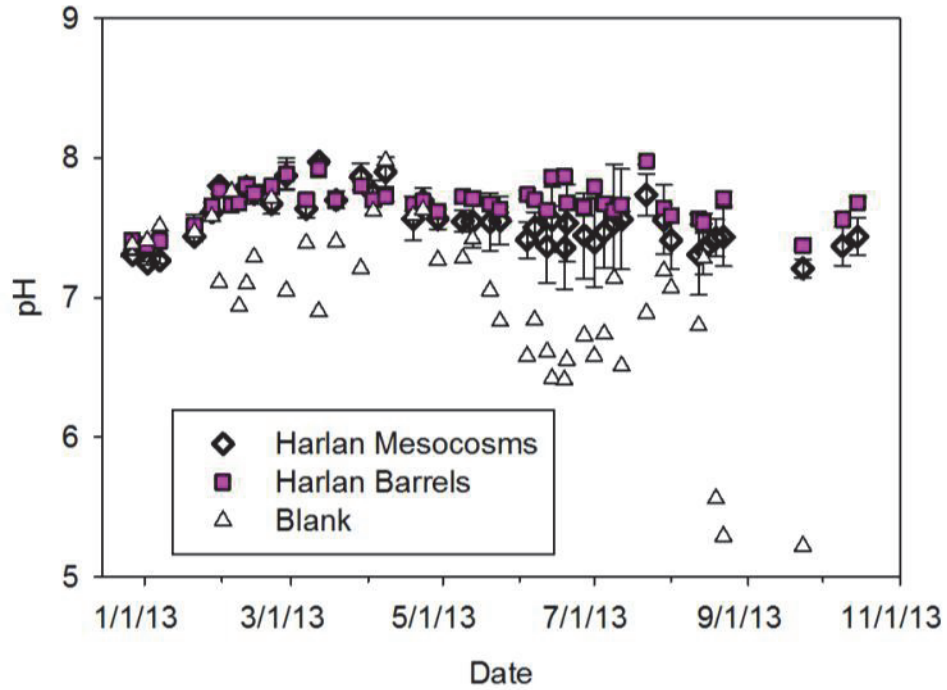
Figure 4.26. Leachate pH from Harlan spoil mesocosms and barrels over time. Blank values reflect rainwater passing through gravel in barrels. Bars around each point indicate one standard error above and below the mean of 3 replications.
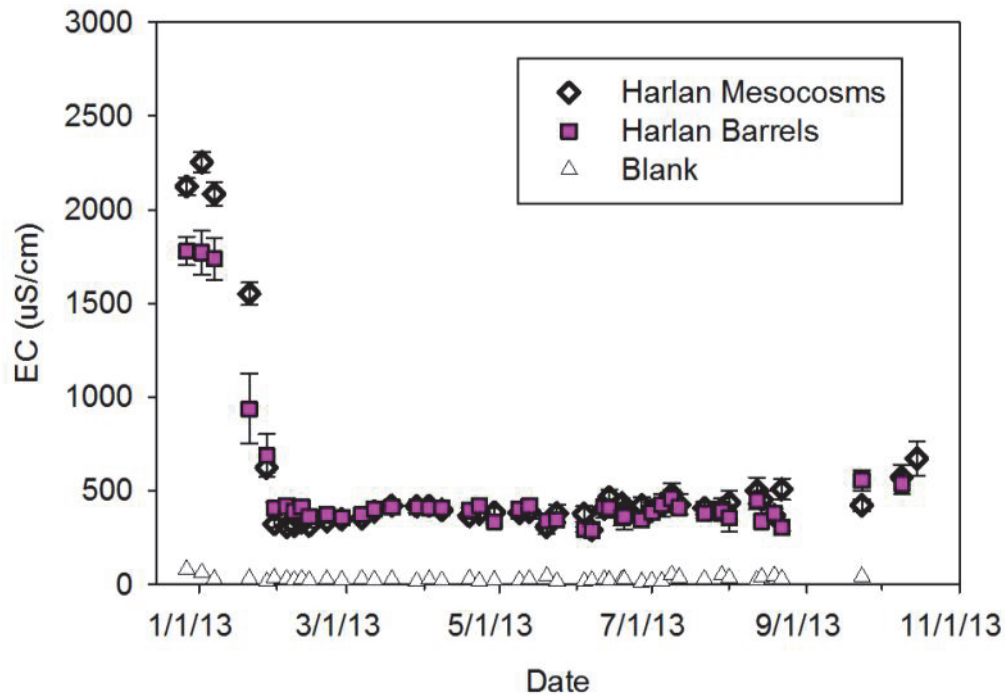

Figure 4.27. Leachate EC from Harlan spoil mesocosms and barrels over time. Blank values reflect rainwater passing through gravel in barrels. Bars around each point indicate one standard error above and below the mean of 3 replications.
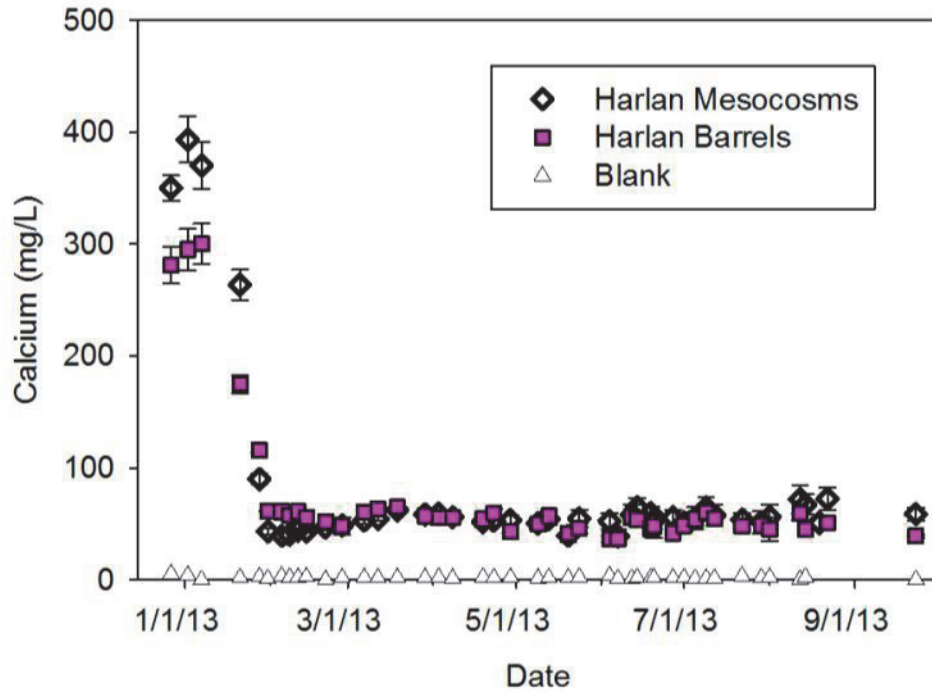
Figure 4.28. Leachate calcium from spoil mesocosms and barrels over time. Blank values reflect rainwater passing through gravel in barrels. Bars around each point indicate one standard error above and below the mean of 3 replications.
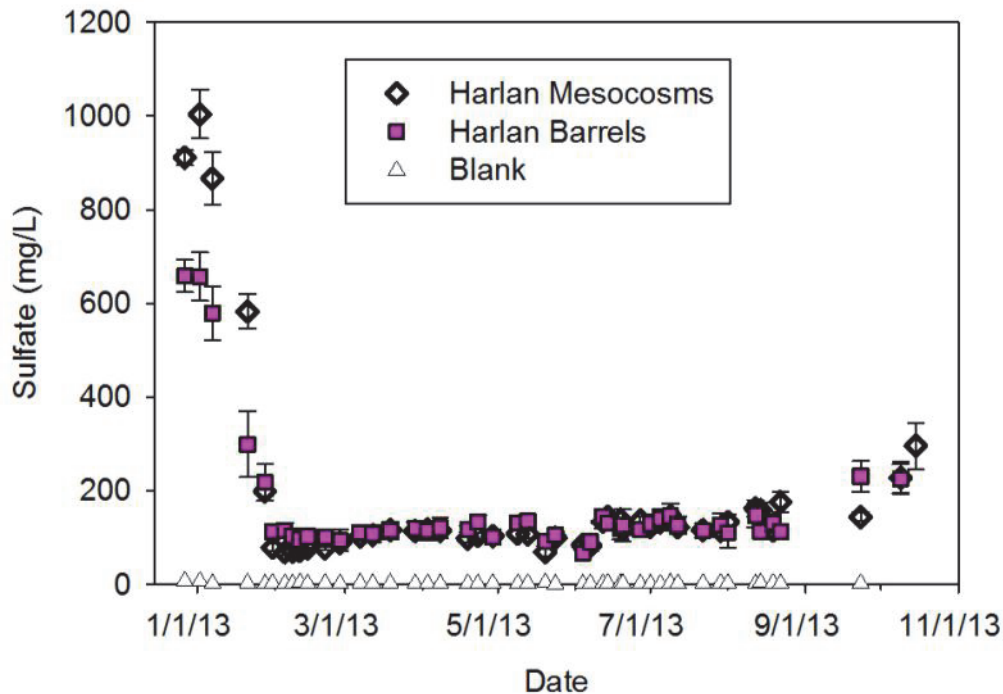

Figure 4.29. Leachate sulfate from Harlan spoil mesocosms and barrels over time. Blank values reflect rainwater passing through gravel in barrels. Bars around each point indicate one standard error above and below the mean of 3 replications.
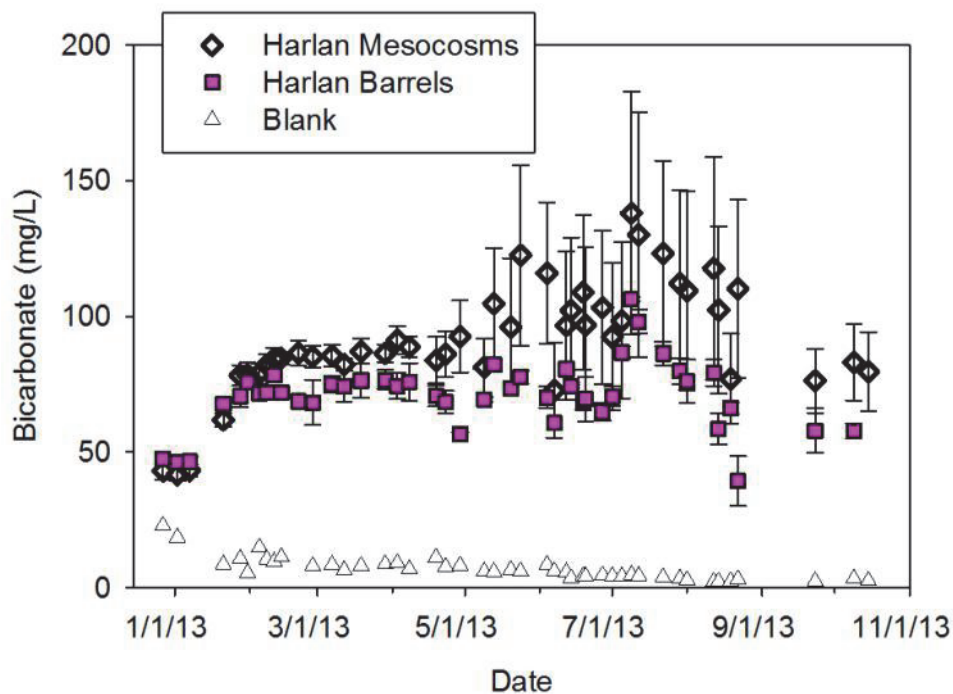
Figure 4.30. Leachate bicarbonate from Harlan spoil mesocosms and barrels over time. Blank values reflect rainwater passing through gravel in barrels. Bars around each point indicate one standard error above and below the mean of 3 replications.
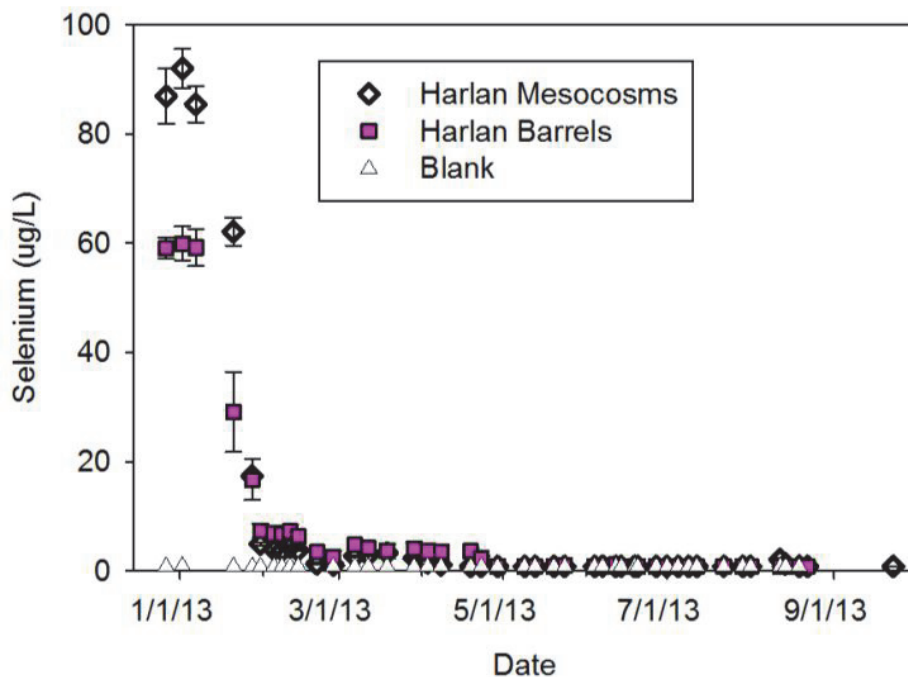

Figure 4.31. Leachate selenium from Harlan spoil mesocosms and barrels over time. Blank values reflect rainwater passing through gravel in barrels. Bars around each point indicate one standard error above and below the mean of 3 replications.

4.3.3 Effects of Time on Refuse Leaching in Field Barrels

The leachate data for important parameters vs. time for the refuse barrels in the field are presented in Figs. 4.32 to 4.37. The relative treatment effects were discussed above and are not repeated here. Differences in pH (Fig. 4.32), EC (Fig. 4.33), Ca (Fig. 4.34), sulfate (Fig. 4.35) and bicarbonate (Fig. 4.37) among the two materials were clearly due to the differences in reactivity discussed earlier and did not show a summer seasonal effect in 2013 as we expected. Again, we had hypothesized that over the warmer and drier summer months reaction salts would accumulate in the barrels and that we would then see spikes or much higher sample-to-sample variability. While we did see more variability in these parameters from date to date over the summer months, we did not see large increases in levels or concentrations (e.g. sulfate) as expected. Interestingly, Se release was different (Fig. 4.37) in that it was more variable both within and between dates in the first half of the leaching period and then stabilized. Overall, it is important to note that the spring and summer of 2013 were much wetter than normal in Blacksburg, but August and September were quite dry.

4.4. Field Studies of TDS Release over Time from NPDES Monitoring Points

One of our original study objectives was to review and analyze the actual long-term field discharge NPDES data for a wide array of mine spoil fills in SW Virginia to determine if (a) their actual levels and patterns could be related to our column leaching studies and (b) what the effect of time after closure was upon actual observed TDS levels. This work was supported jointly by OSM through this project, ARIES, and Powell River Project, and is addressed in a manuscript (Evans et al., 2014) recently published in the Journal of the American Water Resources Association. The abstract for that publication is presented in Appendix 1.

In summary, the results of this work indicate that observed levels of SC in valley fill discharge were quite similar to those that we have observed in our column studies with similar hard rock spoils from the region. It is also apparent that highest SC values at discharge points are seen during the active mining construction phase, but that SC also often rises for some period of years following mine closure. We presume this reflects the slow migration of the initial weathering salt release from these materials along with some effects of preferential flow path development in large fills vs. our columns. Finally, despite the assertions of many, it does appear that over the long-term (e.g. 20 years), that SC levels in valley fill discharges do drop with time in a similar fashion to our lab column predictions. However, the influence of scale here is obvious.

Figure 4.32. Leachate pH from refuse barrels over time. Blank values reflect rainwater passing through gravel in barrels. Bars around each point indicate one standard error above and below the mean of 3 replications.

Figure 4.33. Leachate EC from refuse barrels over time. Blank values reflect rainwater passing through gravel in barrels. Bars around each point indicate one standard error above and below the mean of 3 replications.
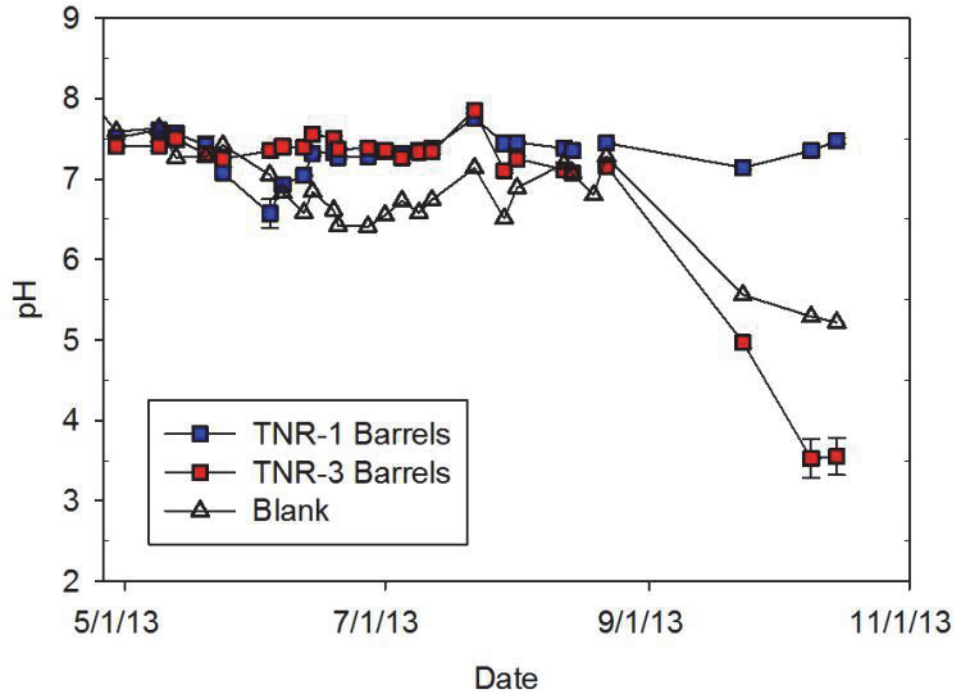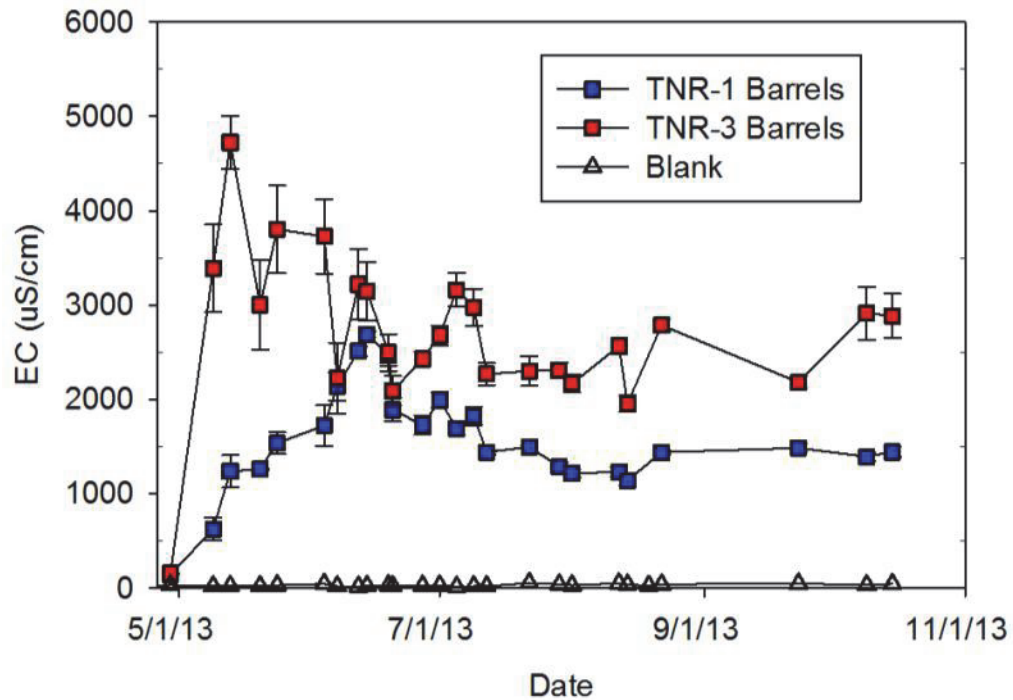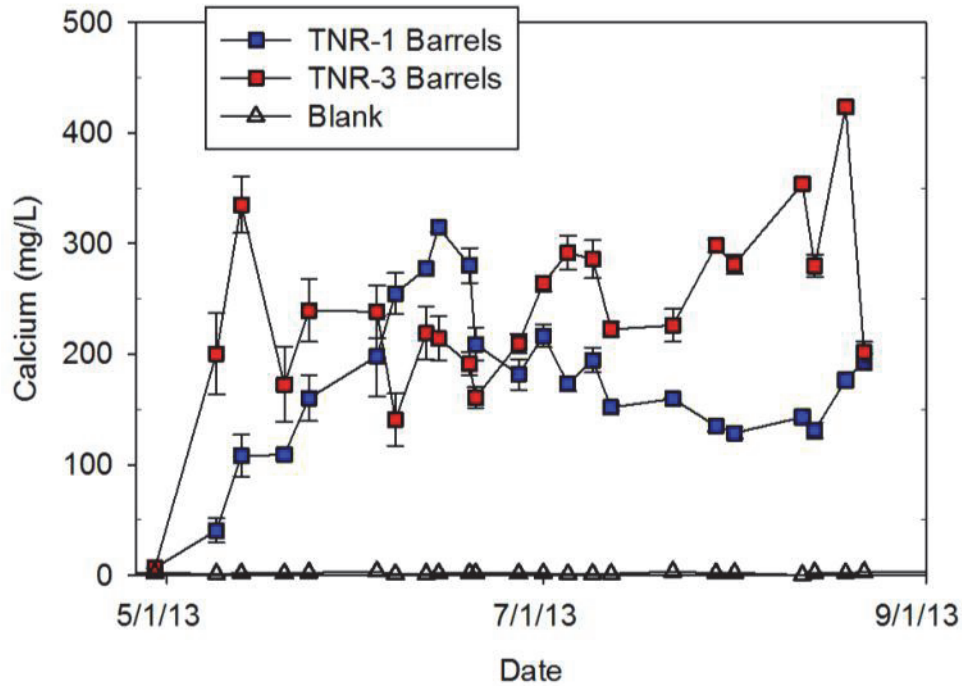
Figure 4.34. Leachate calcium from refuse barrels over time. Blank values reflect rainwater passing through gravel in barrels. Bars around each point indicate one standard error above and below the mean of 3 replications.
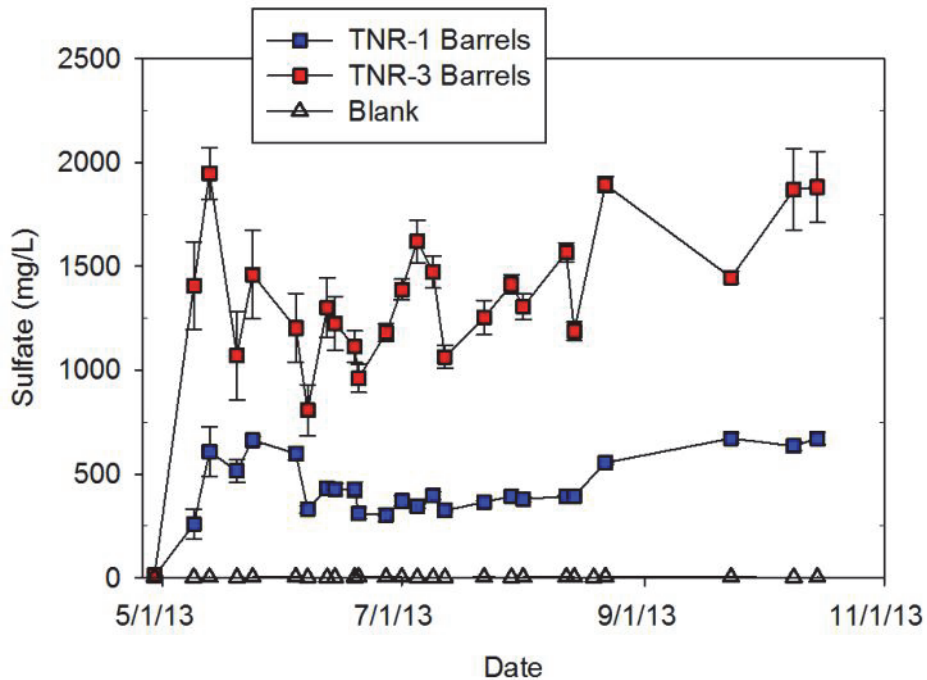
Figure 4.35. Leachate sulfate from refuse barrels over time. Blank values reflect rainwater passing through gravel in barrels. Bars around each point indicate one standard error above and below the mean of 3 replications.

Figure 4.36. Leachate bicarbonate from refuse barrels over time. Blank values reflect rainwater passing through gravel in barrels. Bars around each point indicate one standard error above and below the mean of 3 replications.

Figure 4.37. Leachate selenium from refuse barrels over time. Blank values reflect rainwater passing through gravel in barrels. Bars around each point indicate one standard error above and below the mean of 3 replications.
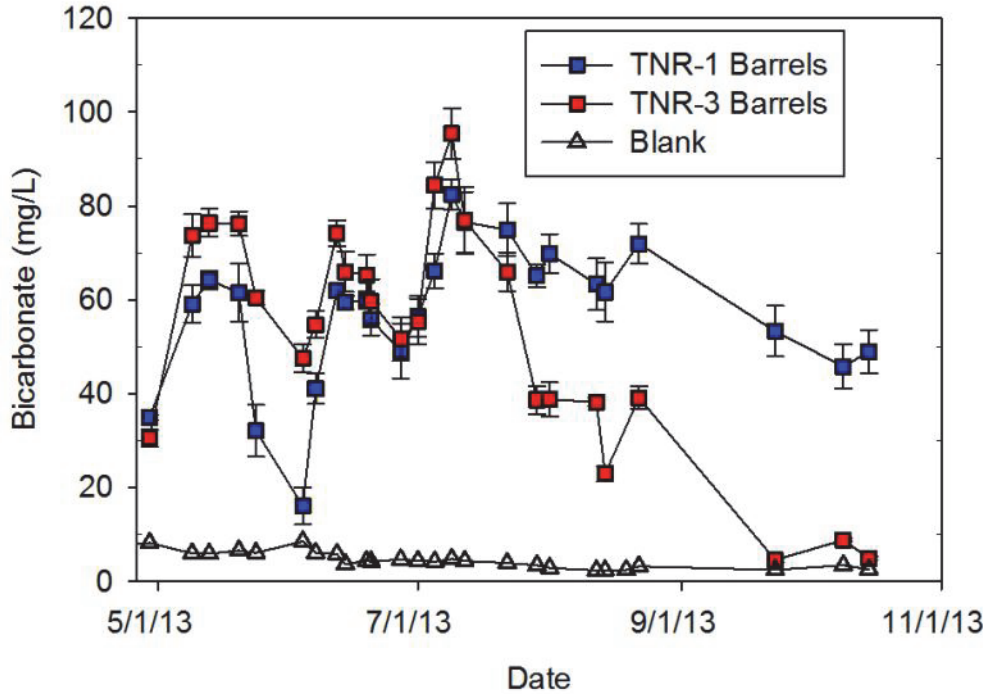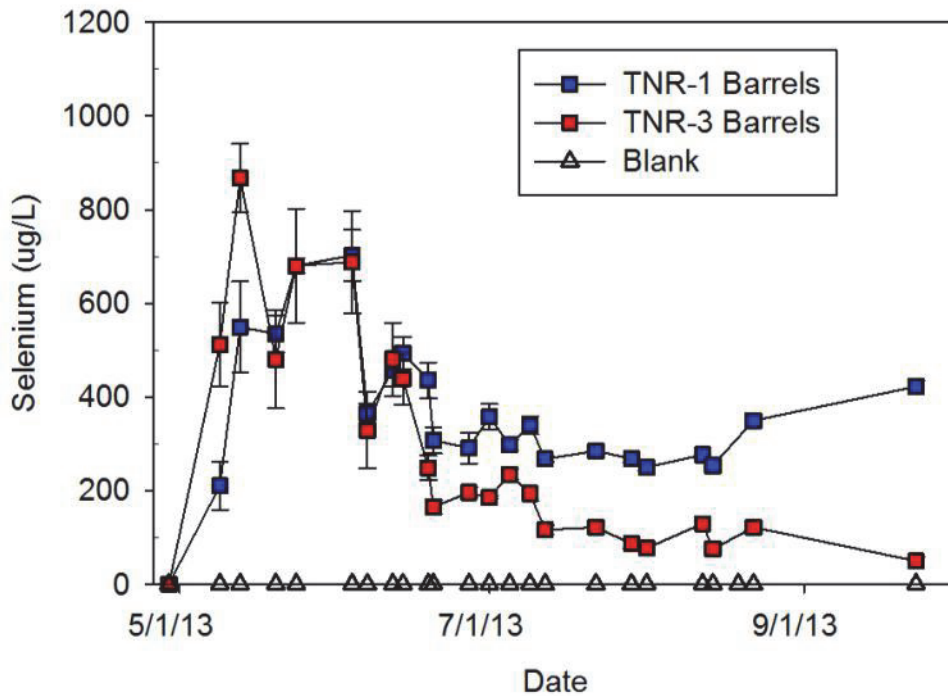
5. Summary and Conclusions

This research program focused on determination of leaching potentials of coal mine spoils from Tennessee (TN) along with a selection of coarse coal refuse materials from the central Appalachian region. The dominant issue was the propensity of these materials to release total dissolved solids (TDS) to surface waters where significant biological impacts have been reported. Our major goals were to characterize the elemental composition of the leachates, to determine the temporal pattern of elemental release, and to compare the results obtained from column leaching trials with larger scale leaching containers. We used electrical conductance (EC) as our proxy measure for TDS, but we also quantified the mass of major cations, anions and important trace elements in the leachates. As a parallel component of this work, we investigated the reliability of various static laboratory tests at predicting the peak TDS elution potential of these materials. Finally, we conducted a regional assessment of TDS elution trends over time from > 100 existing valley fills in Virginia by utilizing the existing NPDES/VDMLR water quality data base and tracking changes in specific conductance (SC) at numerous locations before, during, and after coal mining activity.

Both the mine spoils and coal refuses studied in our leaching columns released significant amounts of TDS in their initial first flush leaching event with spoils generally producing EC > 1500 us/cm and refuse samples considerably higher. This initial peak elution may be due to trace salts accumulated via weathering and hydration during sample preparation, but is primarily driven by rapid oxidation of trace sulfides in the materials coupled with carbonate neutralization and dissolution reactions. This hypothesis is confirmed by EC being dominated by sulfate, calcium, and bicarbonate in this early leaching phase. Hydrolysis of primary mineral grains like feldspars and micas probably also contributes. Leachate EC dropped quickly in all spoils after one to two pore volumes and stabilized at levels < 500 µs/cm.

The EC response over time in the refuse materials studied was more variable, however, with several materials maintaining high (> 1000 µs/cm) EC for the duration of the study (40 leaching cycles of 2.5 cm each) while others dropped below 500 µs/cm when they were maintained in a saturated regime. Thus, the refuse materials studied here showed a marked response to saturation (lower TDS production), while the spoils did not. The refuse materials were more reactive than spoils due to their higher levels of sulfides, carbonates/neutralizers, and finer texture, and therefore generated a much more variable set of leaching responses than the spoils.

Mass release of most elements closely followed bulk solution EC levels for both spoils and refuse in this study. Certain elements (e.g. Mn) did not follow this trend, however, and were seen in leachates at relatively high concentrations over extended leaching periods. Trace element release varied widely among the materials and was generally higher from the more reactive refuse materials as expected. Two of the materials tested, Spoil TN-4 and Refuse VA-21 leached much higher levels of multiple trace metals (e.g. As, Cd, Ni, Zn) than others in this sample set even though their total elemental composition of these elements was not significantly elevated.

We assume that these metals were contained in highly reactive sulfide forms that were quickly released in the initial rapid weathering event. Initial Se release was significant (> 100 µg/L) for all materials, declined in subsequent leaching cycles, but did not drop proportionally as quickly as bulk EC and other major ions like sulfate. Longer term quasi-equilibrium levels of Se release varied from ~1 to > 10 µg/L from these materials. Interestingly, the two materials (TN-4 and VA-21) that released much higher levels of other trace elements did not release higher levels of Se, indicating that Se probably does not reside in the same sulfide mineral host.

The effects of sample volume, sample preparation and size consist, leaching scale and laboratory vs. field leaching conditions were also evaluated. For the spoils, in general, levels of bulk EC and component elements produced by the lab column technique were very similar in levels and temporal response to those produced by two larger leaching systems (200 L barrels and large mesocosm leaching tanks). However, two important differences were noted: (a) initial EC levels were higher in the larger mesocosm tanks and (b) the EC in the barrels and mesocosms began to rise again slowly at the end of the study. Thus, presuming we could extrapolate to field spoil valley fill conditions, we would expect that initial EC values for many spoils could be higher than predicted by our columns and that longer term acid-base reactions could potentially prolong elevated TDS release. These possibilities deserve more study. Regardless, we continue to believe that this column leaching procedure gives us a reasonably accurate prediction of the propensity for a given non-acid forming spoil to generate TDS over time and also provides important information about both peak and long-term levels of TDS release.

In contrast to the spoil, the two coal refuse materials studied at two scales (lab columns vs. 200 L barrels) produced very different results for bulk pH, EC, and elemental release response over the leaching period studied. As mentioned above, these refuse materials are much more reactive with respect to S oxidation and carbonate neutralization and dissolution reactions. The refuse materials may also be much more sensitive to sample preparation, final packed size consist, relative aeration pore space and other factors. That being said, the columns and barrels did produce roughly similar EC and elemental release values once the materials progressed beyond their initial two pore volumes, but the variance among replicates in the barrels was much higher and the relative pH values were quite different among the two leaching scales.

As described in the valley fill discharge study (Appendix 1), we are encouraged by the fact that observed levels of SC in the field are quite similar to the peak and average EC levels that we have observed for a wide range of spoils in our column studies. The field fill discharge data also indicate that over the long term, valley fill discharges in the region studied are declining, and we predict a lag time of approximately 20 years for the average fill to decline to < 500 µs/cm. This extended lag time (vs. our column results) is presumably due to their very large volumes, long water percolation/transport times, development of preferential flow paths, common mixtures of widely differing reactivity of spoils, and other complex factors beyond our ability to simulate in our columns or larger mesocosms. However, we stand by our conclusion that in the absence of (a) inclusion of strongly sulfidic/acid-forming materials and (b) acid seepage contributions from

adjacent deep mines, that the TDS discharge from valley fills in this region should be expected to significantly decline over long periods of time (e.g. decades).

One of our original objectives in this study was to test a wide range of simple static lab tests of spoils such as total-S, saturated paste EC, CCE and others against the column data (particularly EC) to determine which test parameter(s) would be the best predictor of (1) peak EC levels, (2) long term quasi-equilibrium EC levels, and (3) the amount of time (or leaching water) elapsed between peak and stable EC elution. This portion of the work was designed to be specifically applied to hard rock spoil materials and not refuse. For the spoil materials tested here, both total-S and CCE were relatively strong predictors of EC levels. Parallel and ongoing work by our group has indicated that saturated paste EC may be a reliable predictor for peak initial EC levels and that some combination of conventional acid-base-accounting parameters or ratios may be predictive of longer term EC levels. However, we were limited in this effort by the relatively small number of spoils (5) tested for this program and by the fact that our parallel work with the much larger ARIES data set (>45 spoils) was drastically curtailed in mid-2013. This combined project is being completed, however, and we are in the process of combining our leaching column data from all materials (> 50) vs. their matching static lab testing parameters to build and test a predictive model.

It is important for us to reiterate our conditional statement from earlier reports that while we do believe that column leachate trial results such as these can be used as a general predictor for how hard rock spoils will behave within an environment such as valley fill, the concentrations of many elements of concern (e.g. Se) that elute from the columns may not reflect those expected at field discharge points. Our results do not take field attenuation processes into account and thus at best should be regarded as internal source estimates for these various constituents.

Finally, we need to note that our data sets continue to reinforce the fact that overall TDS production and trace element release from coarse coal refuse is a much larger concern than from hard rock coal mine spoils. Refuse materials are much more reactive and more enriched in sulfides and trace element host minerals than are coal spoils and they tend to produce a much wider range of leaching responses over time.

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Appendix 1. Evans et al. (2014) Abstract for Journal of the American Water Resources Association

Long-term trends of specific conductance in waters discharged by coal-mine valley fills in central Appalachia, USA.

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Abstract

Anthropogenic salinization of freshwaters is a global concern. Coal surface mining causes release of dissolved sulfate, bicarbonate, calcium, magnesium, and other ions to surface waters in central Appalachia, USA, through practices that include mine rock disposal in valley fills (VFs). This region's surface waters naturally have low salinity, with specific conductance (SC, a salinity indicator) generally <200 μS/cm, and aquatic impacts have been found when SC exceeds the 300 to 500 μS/cm range. We analyzed SC in waters emerging from 137 VFs over periods of 1 to 23 years. Mean SCs for these VFs ranged from 227 to 2,866 μS/cm, generally rose during and immediately following construction, but often declined during latter portions of longer monitoring records. Seventy-four of 103 VFs with postconstruction data had SC trends that fit negative quadratic forms. Of the 16 revegetated VFs with at least five years of SC data past the quadratic maximum, the mean quadratic maximum was 1,464 (±696) μS/cm and the model projected time required to approach natural conditions (by declining to <500 μS/cm) was 19.6 (±6.6) years after VF construction initiation, indicating long-lasting but not permanent aquatic impacts due to elevated (>500 μS/cm) SC.

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