Long-Term Mine Soil Weathering and TDS Release: Do Topsoil Substitutes Really Mimic Natural Soils?

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Introduction and Background

The Surface Mine Control and Reclamation Act (SMCRA) of 1977 contained a number of contentious provisions including return to original contour (AOC), long-term liability bonding periods, and return to "equal or better" post-mining land use conditions. However, one of the more stealthy provisions was SMCRA's allowance for use of pre-selected overburden materials as topsoil substitutes when (A) the native A+E horizon materials are less than 6 inches thick, and (B) 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 six inches 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.

In 1982, the USDI Office of Surface Mining and the Powell River Project co-funded the installation of the Controlled Overburden Placement (COP) experiment to objectively assess the viability of the topsoil substitute concept and to determine whether or not organic amendments would be beneficial. In one component of the COP experiment we are directly comparing five mixes of sandstone:siltstone (SS:SiS) overburden while in a separate experiment we are following the effects of topsoil return, sawdust addition and four incremental loading rates of biosolids. All treatments are replicated four times and the plots are split between herbaceous (dominantly tall fescue) and forest (red oak following pine) vegetation. We intensively monitored those two side-by-side experiments through the late 1980's, and our results can be reviewed at the PRP web site and at http://www.cses.vt.edu/revegetation/minereclam.html. In summary, we found that (A) properly selected and placed spoil materials provided an outstanding soil medium for tall fescue production and allowed vigorous invasion of native herbaceous species; (B) higher pH spoils such as the siltstone strata employed were deleterious to pine tree growth; and (C) higher rates of biosolids amendments drove high fescue production while suppressing the pines. The COP experiment remains the longest intact and continuously monitored study of mine soil genesis in the World. Follow-up studies by our group at other sites in the 1990's and early 2000's also characterized the wider effects of biosolids applications and the nature of inherent variability in mine soil properties in the Research & Education Center. However, very little detailed soil analyses have ever been performed on the native pre-mining soils in the Research & Education Center area for direct comparison.

Over the past decade, the concept of topsoil substitution has been directly and indirectly criticized from a number of perspectives. First of all, advocates of the return of Appalachian mined lands to native forest covers have pointed to the lack of topsoil salvage and the inclusion of higher pH unweathered spoils as directly inhibiting effective reforestation. These objections have been raised by citizens and certain well-trained scientists alike. Secondly, the fact that relatively unweathered spoils (such as those employed in the COP study) release significant total dissolved solids (TDS) loads to drainage waters over time has been implicated as a component of mining related surface water degradation under both low and moderate pH conditions. In fact, it now appears that mining discharges will be directly regulated for TDS (or by proxy by EC – electrical conductance) over time and reducing bulk TDS may be a much more difficult water treatment proposition for the coal industry than limiting more conventional parameters such as total Fe and Mn. Finally, the ability of these mine soils to accumulate organic matter, maintain a stable and viable microbial biomass and available nutrient pools, and overall productivity potentials beyond the requisite five-year performance liability period is also questioned by many citizens' groups.

In 2007, we proposed to directly address a number of these challenges by initiating a new program of mine soil sampling and analysis utilizing our established baseline experiments at the Research and Education Center, and at other locations where long-term baseline data sets are available, that will allow us to study changes in mine soil properties and productivity relationships over prolonged periods of time. Furthermore, we will directly compare mine soil properties for a range of important parameters (e.g. pH, organic matter content, P-forms, microbial biomass) with a suite of unmined native soils forming out of the same rocks. Thus, by a combination of direct and differential analysis, we originally proposed to meet the following objectives:

Research Objectives

1. To determine the long-term (20+ years) effects of overburden rock type and surface treatments on important mine soil morphological, physical, chemical and microbiological properties.

2. To directly compare the properties of weathering mine soils of varying age with unmined native soils formed from the same strata.

3. To measure the net TDS elution potential of a range of fresh, partially weathered and well-weathered topsoil substitute materials.

4. To predict the ability of selected overburden materials to weather and transform into mine soils suitable for the support of native hardwoods and hayland/pasture vegetation, and to estimate the rate of transformation.

Methods and Procedures

Overall Approach

We are fortunate to have an array of well-characterized, documented and "preserved" research sites throughout the Powell River Project Research & Education Center area and the surrounding region. These include the COP experiment, areas to the north of Powell River that have been minimally disturbed since 1990, and certain limited locations south of Powell River that have not been re-mined since 1990. While much of the 1990 aged mine soil surface received uniform treatment of biosolids+compost, there are significant areas of that surface that did not. By differentially sampling across these contrasting treatment areas, we will be able to directly determine the net effect of organic matter additions on long term soil development process and important mine soil productivity parameters.

Furthermore, the recent re-mining activity to the south of Powell River will allow us to sample and "pair up" mine soil pedons that are very young (1 to 10 years) with much older mine soils (25+ years) to the north that formed out of identical parent materials. Finally, we also have access to a range of relatively intact native forest soils in the overall Powell River area that occur between mining disturbances.

We are now completing the third year of this study. In year one, we focused field work on collecting a wide range of unweathered and weathered spoil types in the region and on sampling pedons within the immediate vicinity of the Research & Education Center as described above. In year two, we worked with Jim Burger and other collaborators to locate additional pedons where we can be assured of good "control" of spoil age, type, and treatments, and where we have access to archived original spoil samples or original data sets to determine rates of change of various mine soil properties. In the laboratory we focused on characterizing the chemical and physical properties of these soils, as well as on initiating column leaching studies to characterize the potential leaching behavior of various mine spoil materials pH, EC/TDS, and cations and anions related to acid-base reactions (Ca, Fe, HCO_3^-, and SO_4^{2-}). In the third year, we focused on completion of the column leaching studies. As discussed later, we still have several study components that we intend to finish over the fall and winter of 2010/2011 which include the description, sampling and analysis of the 28 year-old mine soils in the COP experiment and several more natural forest soils from the Wise County area.

Progress to Date (August 2010)

In year one of this study fifteen samples representing fresh, partially weathered and well-weathered topsoil substitute materials were collected from PRP and other mines in southwest Virginia and east Kentucky. These samples represent a variety of spoil types including sandstone, siltstone and shale in different proportions and at various degrees of weathering. Some geologic, chemical and physical characteristics for ten spoil samples used in the leaching studies are presented in Tables 1 and 2. During year two, an eight month leaching column study allowed characterization of element release from three spoil materials including sandstone (OSM 1), a mudstone (OSM 2), and a mix of materials (OSM 11). The leaching columns were built from PVC pipe with a diameter of 7.6 cm and a length of 40 cm. The samples were run in triplicate under saturated and unsaturated conditions (6 columns per sample), and were leached and sampled twice a week using a simulated rainfall solution (pH 4.8). In year three, the columns were re-established with nine additional spoil samples (OSM 3, OSM 4, OSM 6, OSM 7, OSM 10, OSM 12, OSM 14, COP SS, COP SiS) to more completely represent the various spoil types at various degrees of weathering. The second leaching column study lasted one year, and the leachate samples were analyzed for pH, electrical conductivity (EC), Al. Ca, Fe, K, Mg, Mn, Na and S.

Table 1. Geologic description and associated information for 10 mine spoils used in column leaching studies.

Lab-ID	Material	Geologic Description	Geologic formation	Coal Seam	Particle size %	
					< 1 cm	> 1 cm
OSM 1	Mine spoil Unweathered	98% unweathered, gray and orange, medium to coarse grained, feldspathic sandstone; 2% unweathered gray silty mudstone. (No coal apparent.)	Norton	Raven1	23	77
OSM 2	Mine spoil Unweathered	93% dark gray carbonaceous silty mudstone; 6% unweathered, gray, fine-grained sandstone/siltstone; 1% coal.	Four Corners Formation; Breathitt Group	Hazard #7 and Hazard #8	60	40
OSM 3	Mine spoil Partially-Weathered	50% highly weathered, gray and orange, fine grained and medium to coarse grained, feldspathic sandstone; 30% unweathered gray silty mudstone ; 10% unweathered feldspathic sandstone; 8% unweathered gray silty mudstone; 2% coal.	Middle Wise	Kelly/Imboden	87	13
OSM 4	Mine spoil Weathered	98% weathered, reddish-brown silty mudstone; 1% weathered sandstone; 1% coal.	Lower Wise	Clintwood/Blair	85	15
OSM 6	Mine spoil Unweathered	90% minimally weathered gray clayey siltstone; 10% brown silty mudstone; trace coal.	Lower Wise	Clintwood/Blair	79	21
OSM 7	Mine spoil Weathered	85% weathered brown-gray silty mudstone; 13% unweathered gray silty mudstone; 2% weathered sandstone. (No coal apparent.)	Middle Wise	Kelly/Imboden	62	38
OSM 10	Mine spoil Unweathered	97% unweathered gray silty mudstone; 2% coal; <1% unweathered sandstone; <1% brown shale.	Upper-middle Wise	Phillips	72	28
OSM 11	Mine spoil Weathered	99% weathered sandstone; 1% silty mudstone; trace coal.	Upper-middle Wise	Taggart	68	32
OSM 12	Mine spoil Unweathered	98% unweathered, gray, medium grained sandstone; 1% weathered sandstone; 1% silty mudstone.	Upper-middle Wise	Taggart	45	55
OSM 14	Mine spoil Weathered	80% weathered, gray and orange, feldspathic sandstone; 20% gray silty mudstone. (No coal apparent.)	Lower Wise	Clintwood/Blair	65	35

Table 2. Selected chemical properties of the 10 mine spoils used in column leaching studies.

	2:1	Saturated paste		PPA[1]	CCE[2]	Total S
Lab-ID	**pH**	**pH**	**EC dS m^{-1}**	**Tons CCE / 1000 Tons**	**%**	%
OSM 1	7.98	6.88	1.27	0	2.7	0.06
OSM 2	7.14	7.04	3.48	0	4.6	0.23
OSM 3	5.24	6.93	0.94	3.58	1.3	0.07
OSM 4	5.22	6.46	0.29	0.22	1.6	0.03
OSM 6	7.02	7.26	1.40	0	2.1	0.14
OSM 7	7.03	7.66	0.20	0.12	4.7	0.03
OSM 10	8.14	7.85	0.66	0	6.0	0.11
OSM 11	5.24	6.28	0.56	0.28	3.7	0.03
OSM 12	8.64	7.84	0.40	0	5.3	0.12
OSM 14	5.74	7.49	0.36	0.12	3.4	0.03

[1] Potential Peroxide Acidity (PPA). Values shown represent net acidity/lime demand.
[2] Calcium Carbonate Equivalent (CCE)

Characterization of Chemical Properties

The saturated paste pH (Table 2) of these samples was generally in the neutral to alkaline range which is typical of fresh, relatively unweathered materials from this region due to hydrolysis reactions involving broken primary mineral grains and carbonate dissolution. The soluble salt content, indicated by EC (Table 2), produced by most fresh spoils was relatively low (< 1.0 dS m^{-1} or 1000 µS/cm), although a few values ranged up to 3.5 dS m^{-1}. Elevated EC values appeared somewhat related to total S and/or CCE (Table 2). While these values are quite typical for soil:water systems, any mine site effluent/leaching levels in excess of 0.5 dS m^{-1} (500 µS/cm) would pose significant regulatory concern. Total S content was relatively low, ranging up to 0.23%, which is not unusual for the region sampled. Correspondingly, PPA values (Table 2) were low (< 3.6 tons $CaCO_3$/1000 tons material) due to low S content in combination with moderate CCE values.

A comparison of the pH values determined by saturated paste (pH_{sp}) versus in a 2:1 water:sample mix ($pH_{2:1}$; Table 2) indicated lower pH values by the 2:1 method for the samples at $pH_{2:1}$ < 7.0. This may be due to the difference in equilibration time (much longer for the saturated paste method) allowing alkaline mineral surfaces to react with acidic components. As expected, weathered mine spoils tended towards lower pH. Only one weathered sample (OSM 7) was neutral ($pH_{2:1}$ = 7.03), while the other weathered samples had $pH_{2:1}$ values between 5.22 and 5.74. Among the mixed partially weathered/unweathered mine spoils those with higher percentages of weathered material generated lower pH.

Leaching Column Trial

The data presented in Figures 1-11 report results from 45 leaching events over the initial 22 week period. The data are presented in groupings to contrast the results from weathered versus unweathered materials and saturated versus unsaturated conditions. We highlight pH, EC, sulfate, bicarbonate and other elements particularly relevant to acid-base reactions. All data presented below represent the mean observations from three replicate columns. Detail on column replicability (which was outstanding) can be found in Daniels et al. (2009).

pH: For most materials used in this study, leachate pH (Figs 1-2) from the first leaching events was substantially lower than the initial saturated paste pH data on the fresh bulk materials (pH_b). This difference was more readily observed in weathered than in unweathered materials, and was least apparent for unweathered sandstone. With few exceptions, leachate pH increased over the first few leaching events, and achieved a relatively stable equilibrium within 10 to 20 leaching events. The unsaturated columns were usually higher in pH than for the same material when saturated. Under saturated conditions, only samples OSM 1, OSM 2, and OSM 11 equilibrated to pH values near pH_b, while the other saturated samples maintained pH values that were approximately 0.3 to 1.0 pH unit less than pH_b. The higher pH levels from unsaturated conditions could be due to the effects of CO_2 partial pressures on carbonate dissolution in the unsaturated columns or perhaps siderite ($FeCO_3$) formation in the saturated columns.

Electrical Conductance (EC): Analyses completed on the first set of columns indicated a high correlation coefficient (r = 0.98) between EC and TDS, as expected, indicating that EC can be used as an effective proxy for TDS (Daniels et al. 2009). Leachate EC from unweathered mine spoil (Fig. 3-4) was consistently higher than from partially oxidized and weathered samples of similar geology. This difference was more pronounced for mudstone than for sandstone. For most samples, EC values dropped quickly achieving a steady state within 10 to 20 leaching events and maintained relatively low levels for the remainder of the leaching trial. However, OSM 2 and 6, both unweathered mudstones, maintained values greater >1.0 dS m^{-1} through the first 10 leachings. These high EC values may indicate a highly reactive sulfide phase (framboidal?) that while present in relatively low amounts (0.23% and 0.14% S), reacted quickly with substrate carbonates to produce prolonged sulfate release.

Bicarbonate: Bicarbonate analysis was completed only on the first set of columns which included OSM 1, OSM 2, and OSM 11. The release of bicarbonate (Fig. 5) reflected the effects of saturated versus unsaturated conditions more than any other measured parameter in this study with vastly more bicarbonate released under saturated conditions. The lower levels from the unsaturated columns presumably reflect acid neutralization reactions, even when relatively low amounts of S were present.

Sulfate: Sulfate release patterns (Fig. 6-7) reflect the acid-base reactions discussed above which are due to fundamental differences in the geology/mineralogy of these materials such as total-S content (Table 2), degree of "pre-oxidation" via weathering and trace carbonate content. In SW Virginia, the majority of strata within the Pennsylvanian system are low in pyritic-S. Many of the massive sandstones that dominate the Lee, Norton, and Wise formations contain secondary carbonate cementing agents (Howard et al., 1988) which offset the relatively minor amounts of sulfidic minerals found in most geologic sections. Significant accumulations of sulfides do occur in coal seams and underclays throughout the region; however, these seams are relatively thin (< 3 m). Also, several relatively minor sections of overburden in Virginia (e.g. the Standiford seam interburden of the middle Wise formation) generate spoils with significant (>20 Mg/1000 Mg) levels of potential acidity (Orndorff & Daniels, 2004). For most spoil samples used in this study

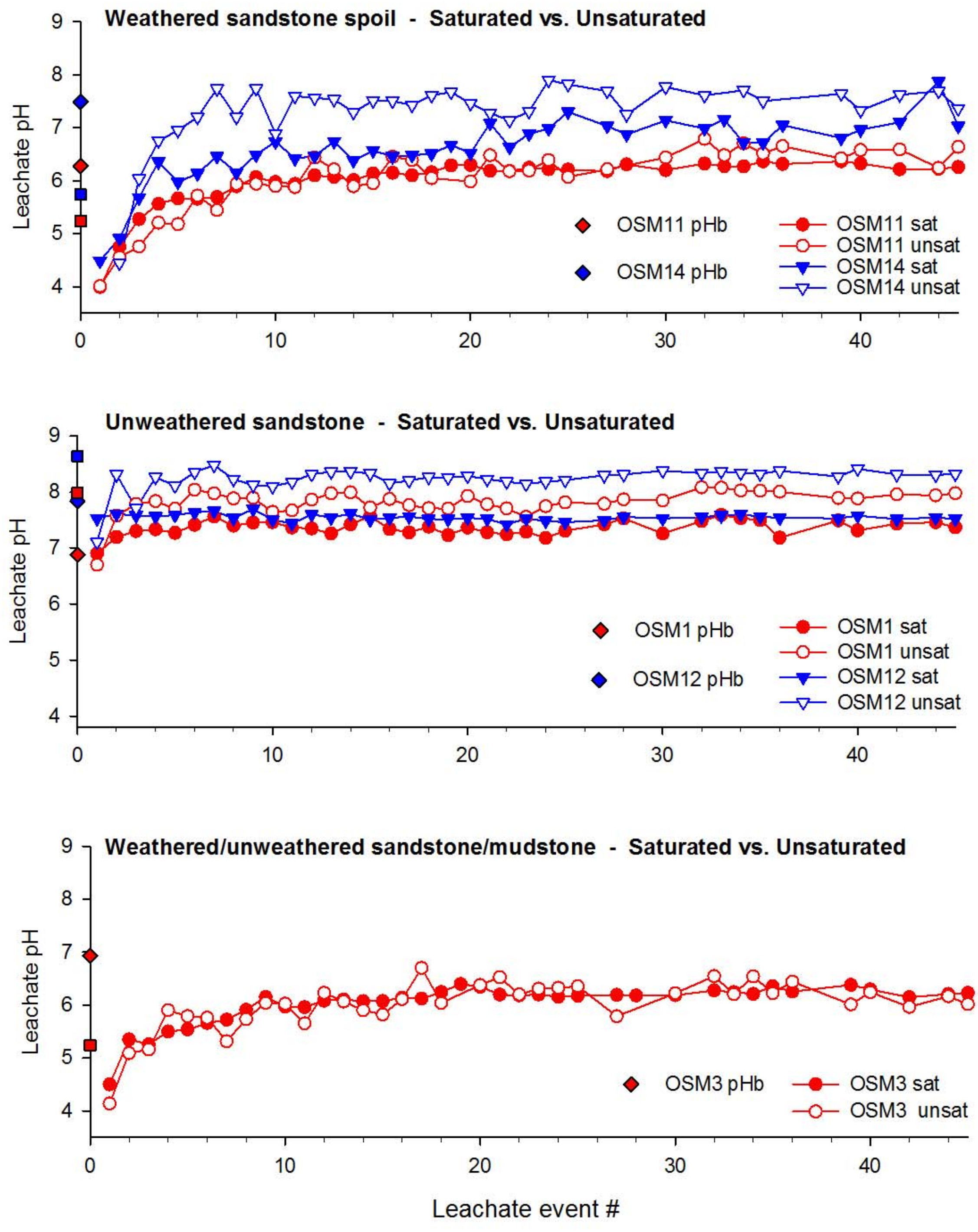

Figure 1. Leachate pH from weathered and unweathered sandstone spoil and mixed spoil material under saturated and unsaturated conditions. Saturated paste pH of the initial bulk material (pH_b) is indicated by symbols on the Y axis. The 45 leaching events occurred over 22 weeks.

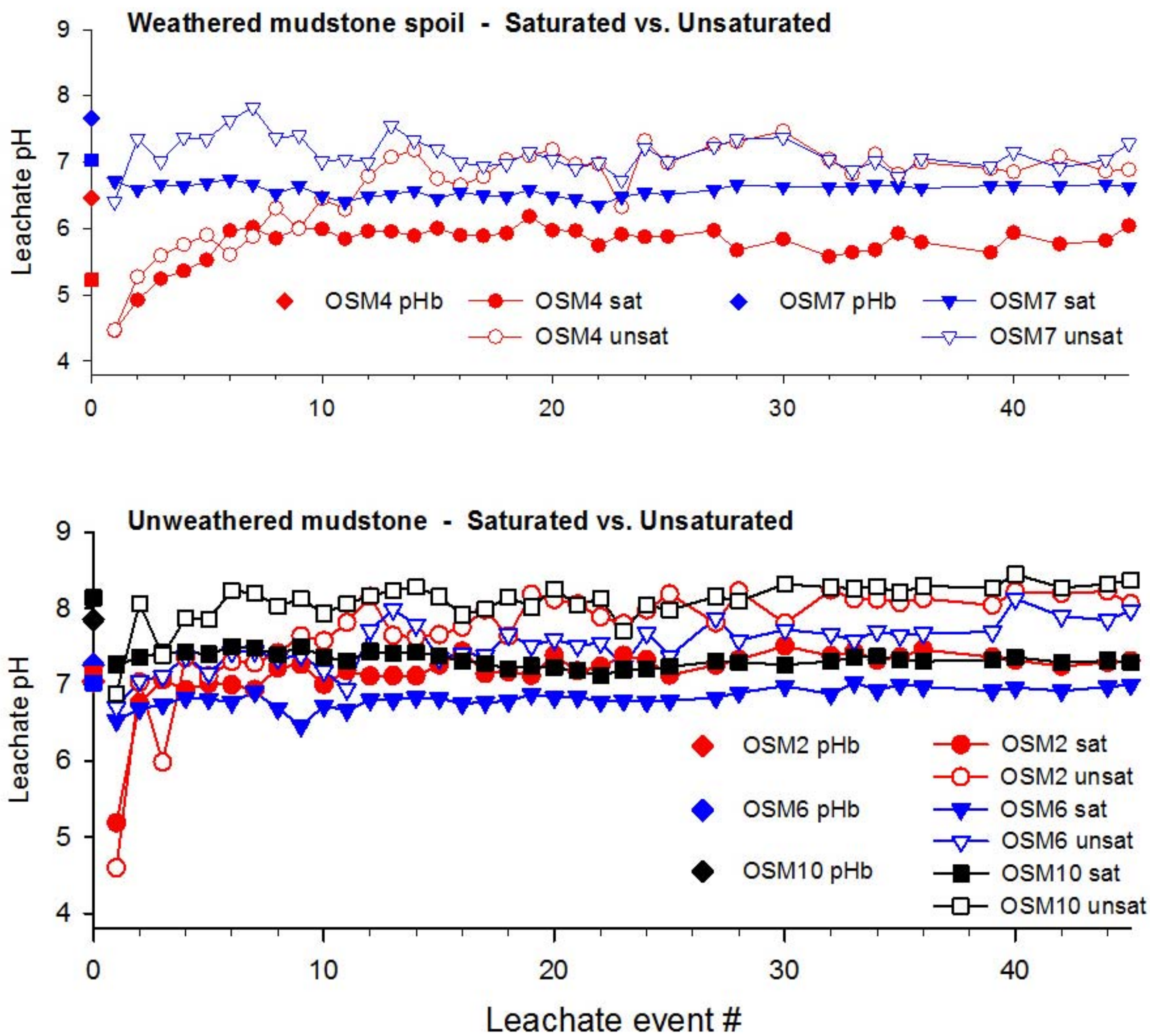

Figure 2. Leachate pH from weathered and unweathered mudstone spoils under saturated and unsaturated conditions. Saturated paste pH of the initial bulk material (pH_b) is indicated by symbols on the Y axis. The 45 leaching events occurred over 22 weeks.

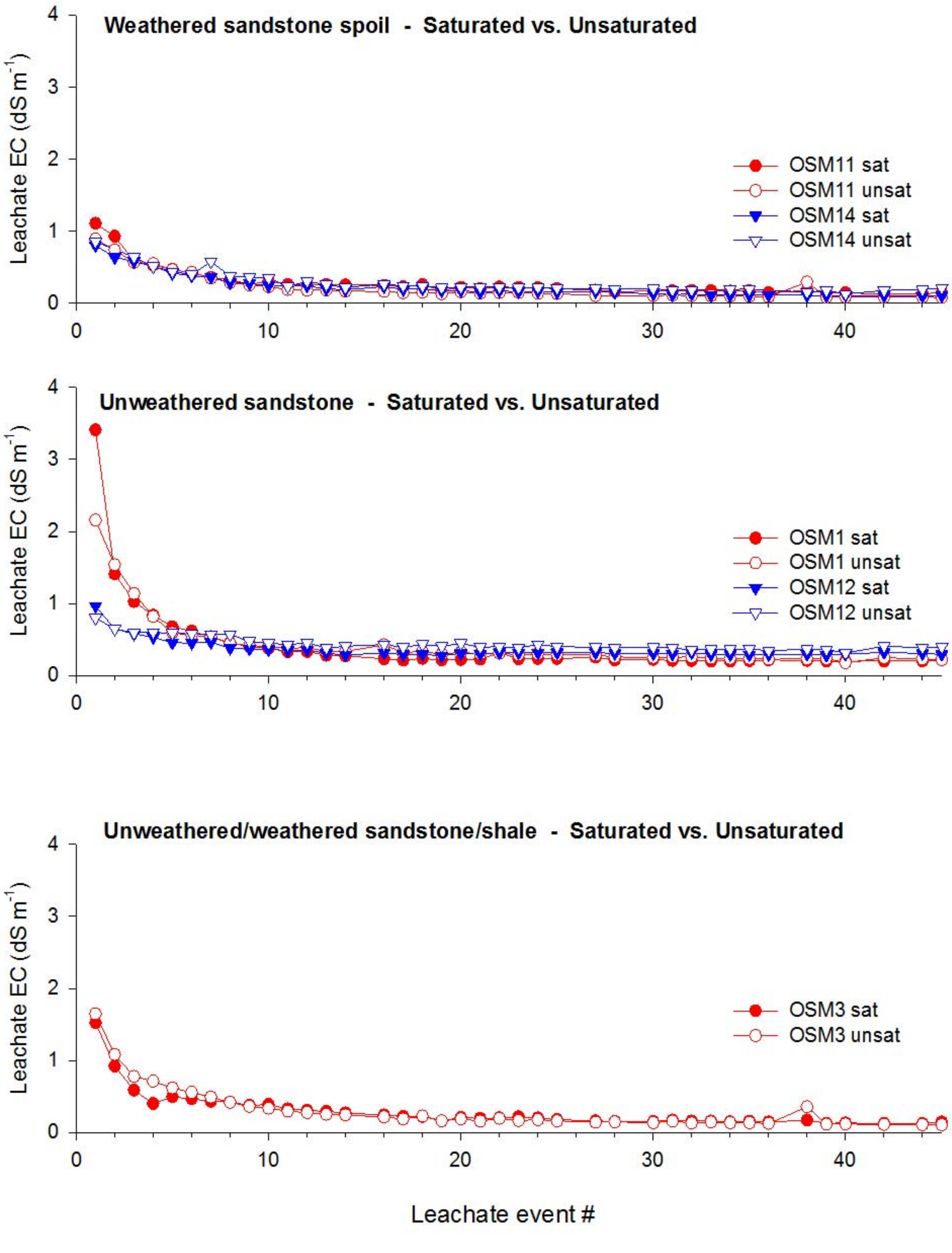

Figure 3. Leachate EC from weathered and unweathered sandstone spoil, and mixed spoil material, under saturated and unsaturated conditions. The 45 leaching events occurred over 22 weeks.

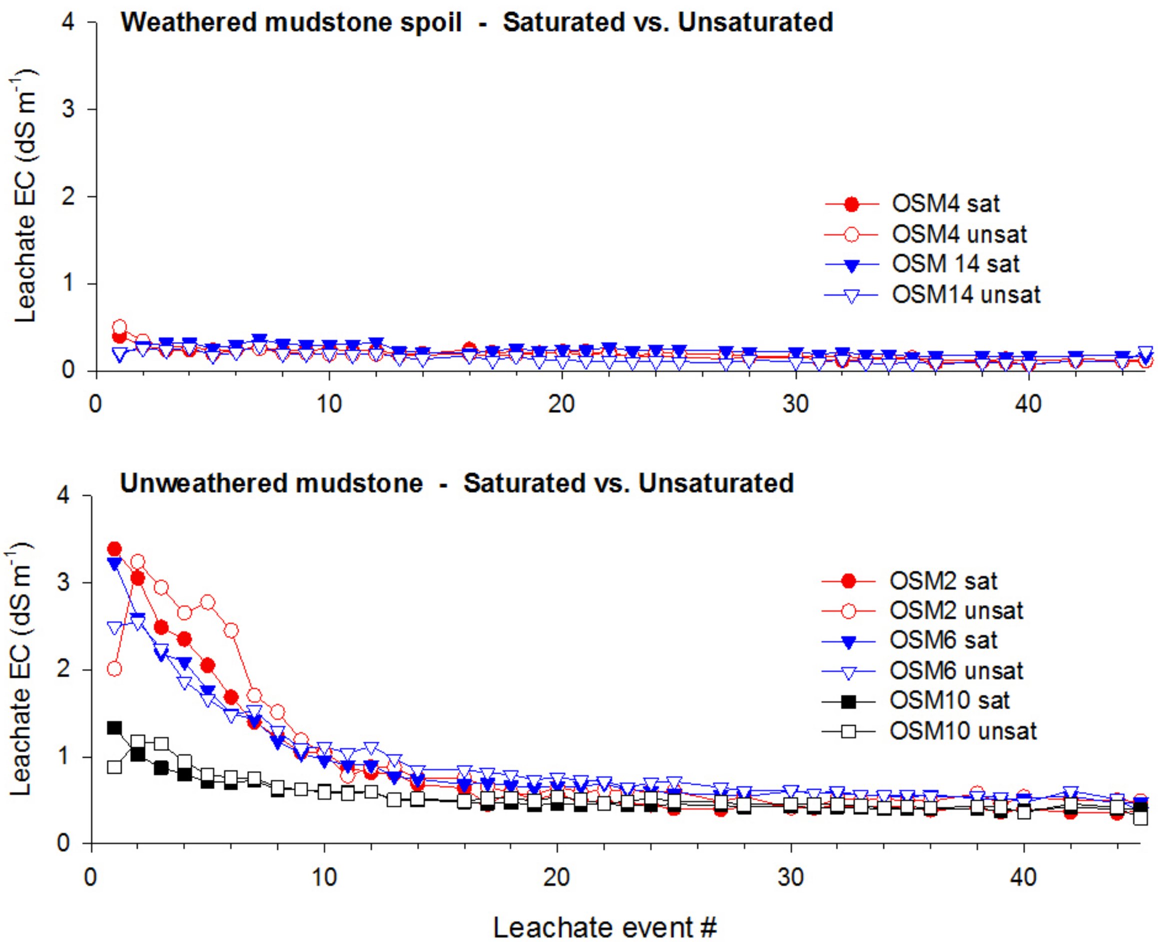

Figure 4. Leachate EC from weathered and unweathered mudstone spoil under saturated and unsaturated conditions. The 45 leaching events occurred over 22 weeks.

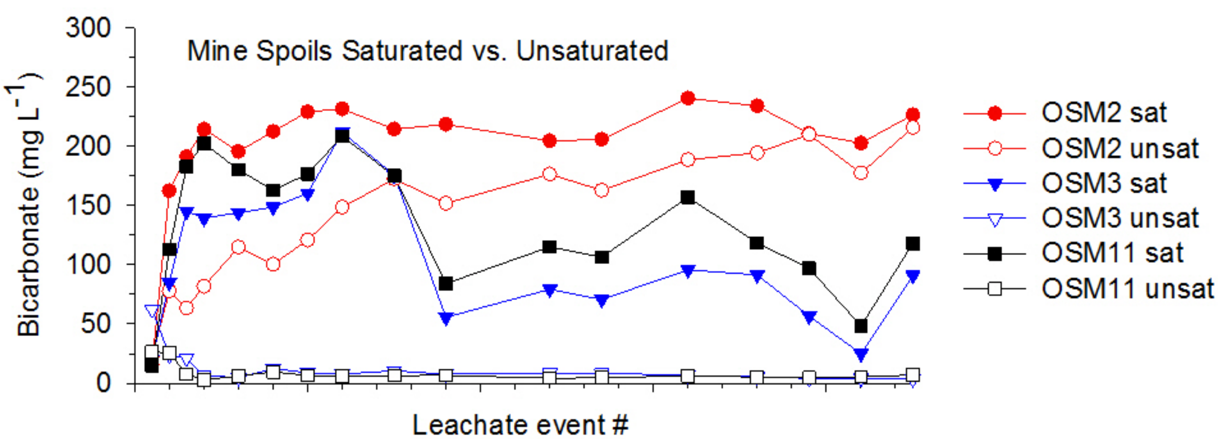

Figure 5. Bicarbonate leached from selected mine spoils under saturated and unsaturated conditions. The 45 leaching events occurred over 22 weeks.

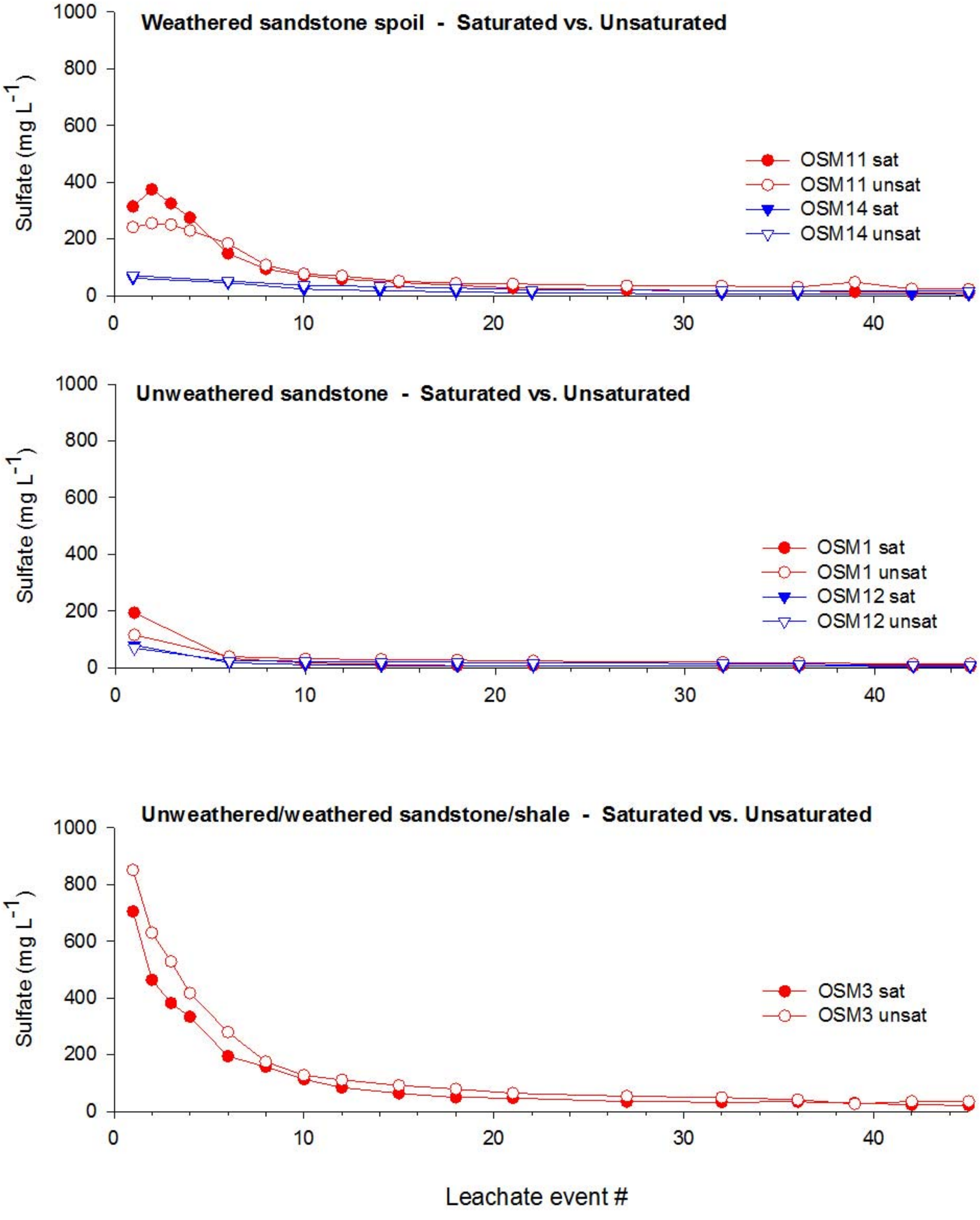

Figure 6. Sulfate leached from weathered and unweathered sandstone, and mixed spoil material, under saturated and unsaturated conditions. The 45 leaching events occurred over 22 weeks. Note: for Sulfate graphs Y-axis ranges from 0 – 1000 mg L^{-1} for Fig. 6 and 0 – 3000 mg L^{-1} for Fig. 7 (below).

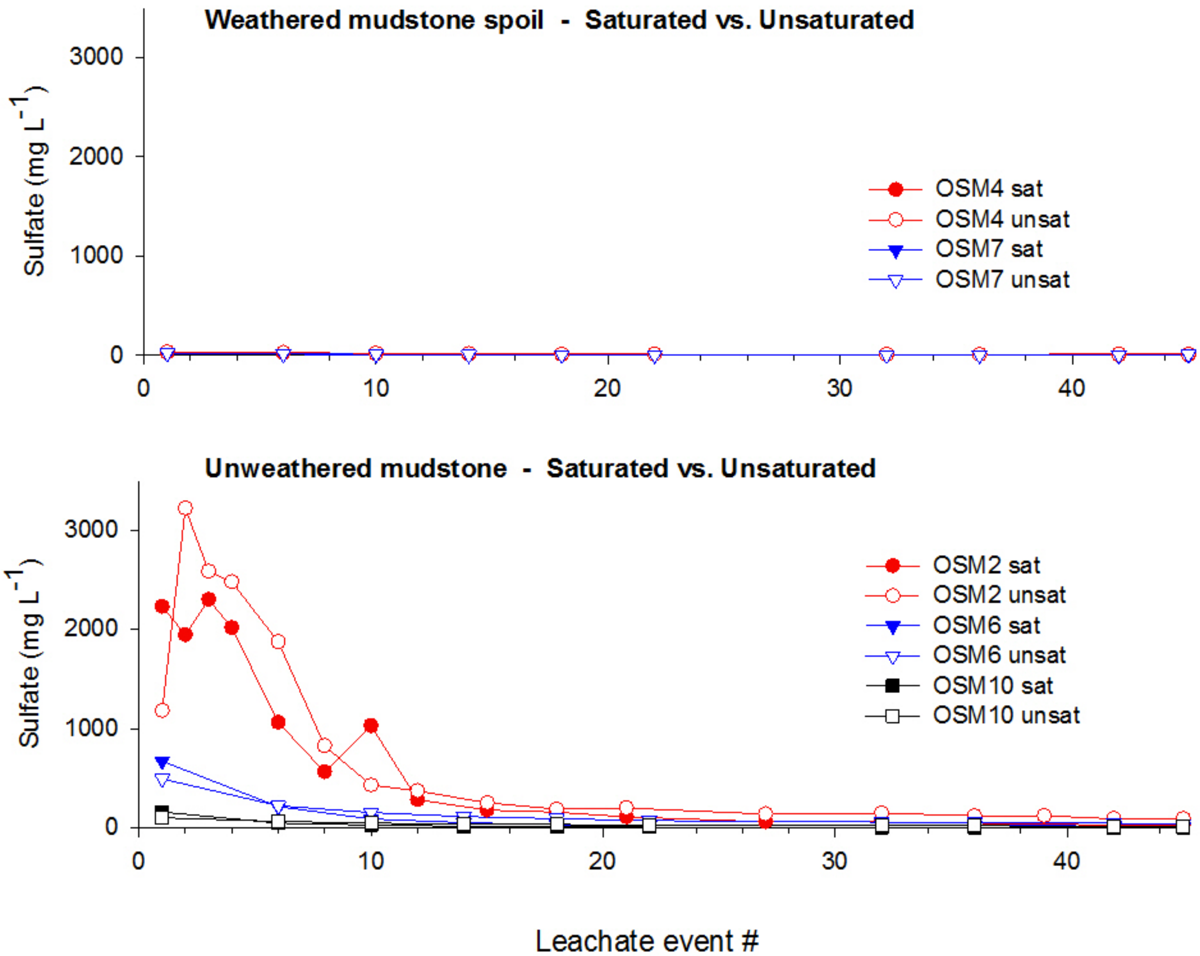

Figure 7. Sulfate leached from weathered and unweathered mudstone under saturated and unsaturated conditions. The 45 leaching events occurred over 22 weeks. Note: for Sulfate graphs Y-axis ranges from 0 – 1000 mg L^{-1} for Fig. 6 (above) and 0 – 3000 mg L^{-1} for Fig. 7.

the majority of sulfate release occurred within the first month (10 leaching events or over approximately one pore volume of total elution). The greatest sulfate release occurred from OSM 2, a mudstone from the Breathitt Formation (eastern Kentucky) which has been noted and studied for its acid forming potential (Barnhisel and Massey, 1969).

Calcium (Ca), Iron (Fe) and Manganese (Mn). Calcium leaching patterns (Figs. 8-9) for the mine spoils followed the pattern of sulfate very closely. As expected, unweathered spoil materials released greater amounts of Ca than did the weathered materials. Iron release patterns (Fig. 10) did not mirror other pyrite oxidation reaction products such as sulfate. Most samples released low concentrations of Fe over the course of the study. Due to the relatively high pH of the leachates, the vast majority of Fe was precipitated and retained within the columns in various oxy-hydroxide forms. The relatively high release of Fe from one saturated weathered mudstone spoil (OSM4) and one saturated weathered sandstone spoil (OSM 11) is notable and may be the result of reduction of original Fe-oxides to soluble Fe^{+2} over time.

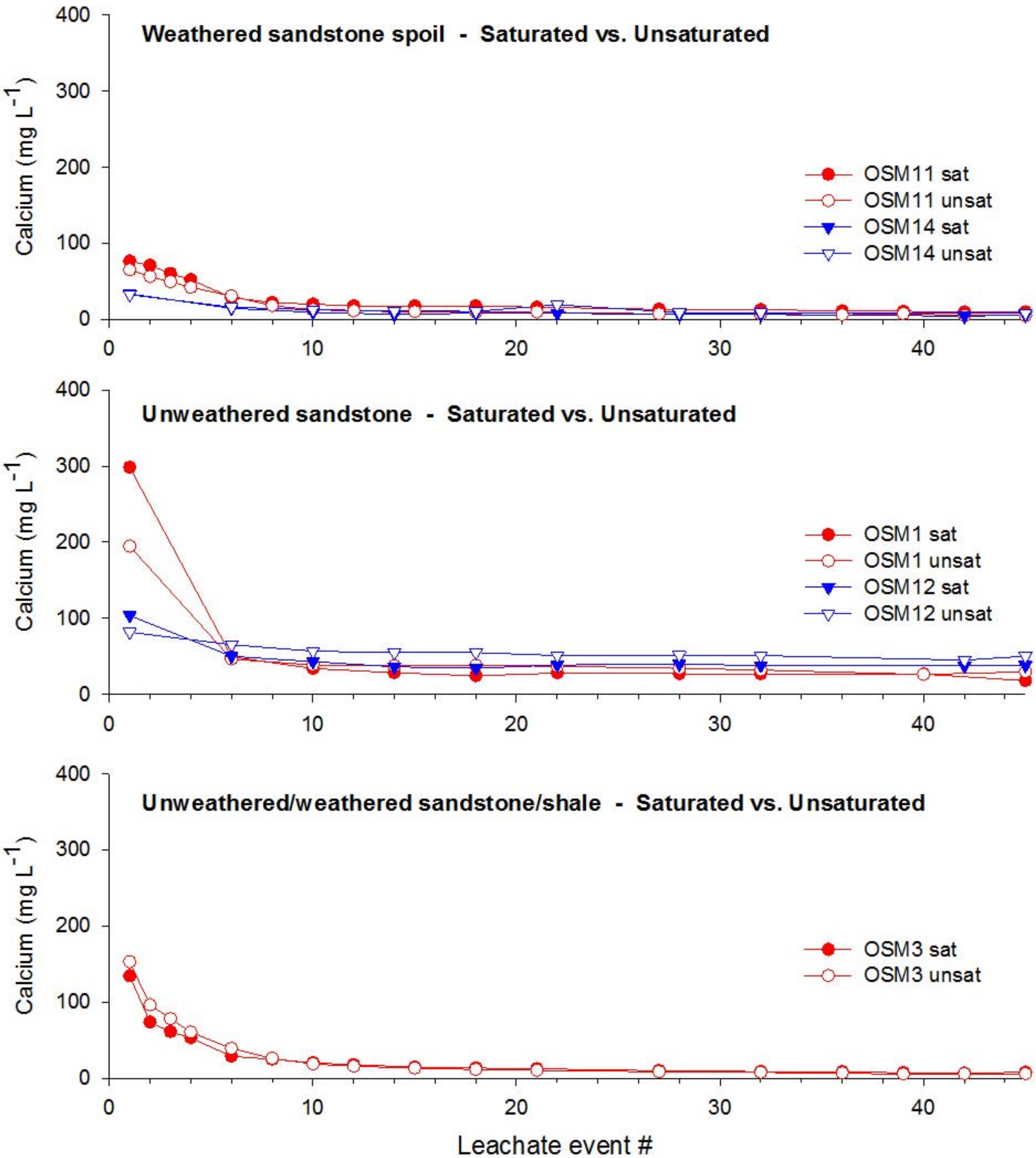

Figure 8. Leachate Ca from weathered and unweathered sandstone spoils under saturated and unsaturated conditions. The 45 leaching events occurred over 22 weeks. Note: for Ca graphs Y-axis ranges from 0 – 400 mg L^{-1} for Fig. 8 and 0 – 800 mg L^{-1} for Fig. 9 (below).

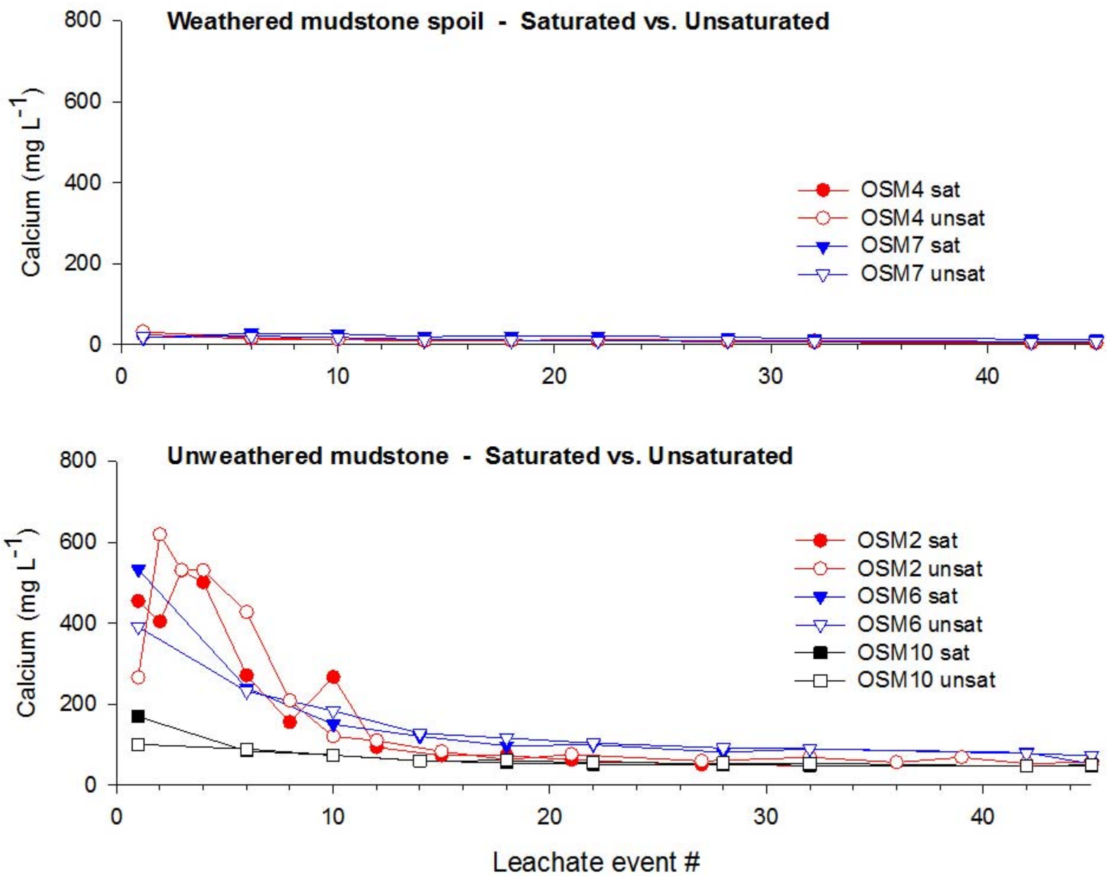

Figure 9. Leachate Ca from selected weathered and unweathered mudstone under saturated and unsaturated conditions. The 45 leaching events occurred over 22 weeks. Note: for Ca graphs Y-axis ranges from 0 – 400 mg L^{-1} for Fig. 8 (above) and 0 – 800 mg L^{-1} for Figs 9.

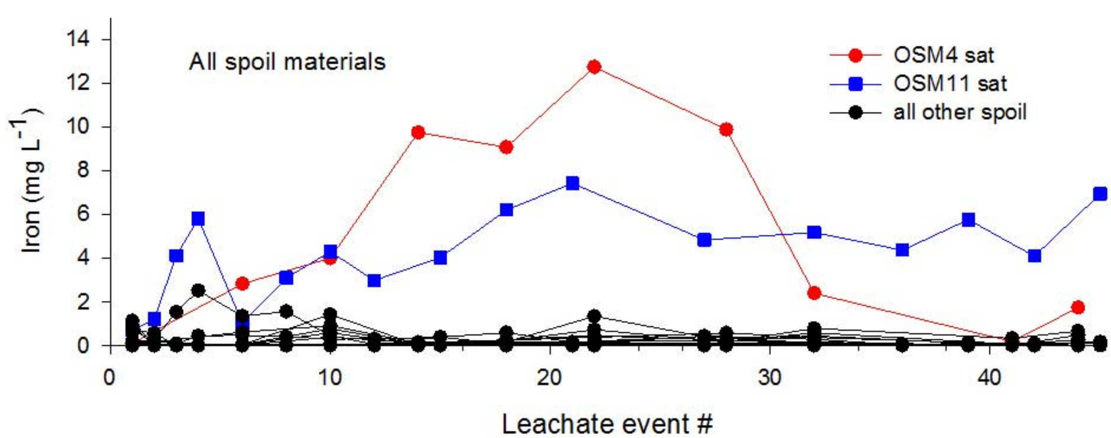

Figure 10. Leachate Fe from all spoil materials under saturated and unsaturated conditions. The 45 leaching events occurred over 22 weeks.

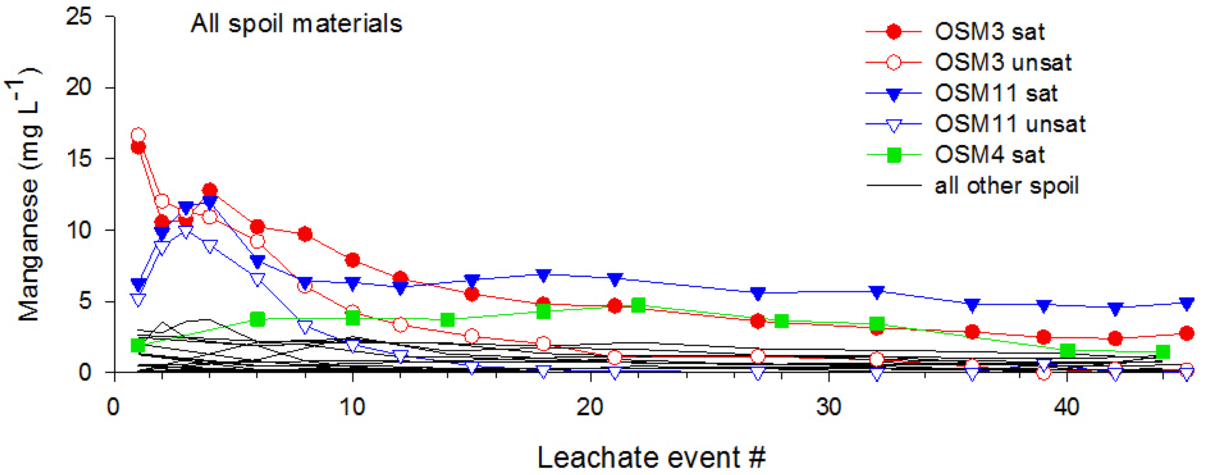

Figure 11. Leachate Mn from all spoil materials under saturated and unsaturated conditions. The 45 leaching events occurred over 22 weeks.

Leachate Mn concentrations typically were higher than Fe due to the higher solubility of Mn than Fe in this pH range (Fig. 11). Furthermore, Evangelou (1995) pointed out that poorly crystalline Mn^{+4} oxides may serve as an alternative electron acceptor (oxidizing agent) in moderate pH sulfide oxidation environments which can lead to large amounts of water soluble Mn^{+2} being mobilized. For some samples, particularly OSM 1 and OSM 3, Mn release patterns were closely related to Ca and sulfate, however, the opposite was true for the Kentucky shale (OSM 2). This is presumably due to differences in the inherent Mn oxide forms in the differing spoils. For both Mn and Fe, the most notable releases occurred under saturated conditions.

Data Analysis, Synthesis and Expected Results

Our combined results from the mine spoil characterization and column leaching components of this program clearly point out that differences in (A) mine spoil strata/origin and associated mineralogy interact very strongly with (B) the extent of *in situ* pre-mining weathering to profoundly influence the bulk chemical properties of resultant mine soils and their potential to generate TDS to contact waters (e.g. leachates). Thus, it is clear that the mining industry should isolate and utilize oxidized and pre-weathered (e.g. brown) materials whenever possible for their topsoil substitutes if their long term management goal is establishment of forest vegetation. This practice will also result in a minimization of TDS release to surface runoff waters. Our results indicate that many partially or non-weathered (e.g. gray) spoils in our region have the potential to produce substantial leachate TDS levels, particularly over their initial leaching cycles. However, our data also clearly indicate that these elevated leachate levels will drop dramatically over time to levels below current regulatory concern (e.g. 500 µS/cm) for most materials. At this point in time the critical question seems to be: *Just how long will it take for TDS levels to drop in a field setting*? We believe that it should be possible to predict TDS elution behavior for a given spoil material based upon a combination of analyses such as routine acid base accounting, hydrogen peroxide potential acidity, saturated paste EC, and other relatively quick lab procedures. These rapid tests will need to be "calibrated" against column data, however, and then appropriate scaling factors will need to be developed to relate the output results to expected field conditions to answer the critical question posed above.

Collectively, it is also clear from our data set that TDS elution is driven by fundamental acid-base reactions in the spoils (e.g. pyrite oxidation coupled with carbonate dissolution/ neutralization) and that these leachates will commonly be circumneutral in pH and relatively low in Fe, Mn and other metals of concern. Spoil leachate TDS levels are driven principally by acid-base reactions products, primarily sulfate and calcium. Thus, when large volumes of these materials are placed into valley fills and highwall backfills and allowed to freely interact with infiltrating water, significant TDS elution should be expected. Alternative fill designs that limit water infiltration into (and percolation through) these materials need to be developed and tested.

To date, we have completed approximately 85% of our originally proposed work plan, but we still need to complete the sampling and analysis of the COP experiment and several more natural and fully weathered forest soils from the SW Virginia region that correlate with our bulk spoil sampling events from 2007. This delay was due to the fact that it became very clear to us by mid-2009 that we needed to focus our attention on TDS elution prediction. However, we do intend to complete this work over the fall/winter of 2010/2011 as an in-kind contribution to the project. Once this final aspect of our work is completed, we will be able to directly determine and report the relative effect of rock type and surface treatments in the COP experiment on 25+ years of mixed herbaceous vegetation and tree growth. Similarly, by comparing the properties of the biosolids treated and untreated areas of nearby 15 year-old Taggart mine soils, we will be able to confirm overall rates of important mine soil transformation such as pH reduction and organic matter accumulation in an initially high pH sandstone system. By then comparing the bulk salt and acid extractable nutrient+metal data for each pedon with depth, we will be able to estimate the mass "TDS leaching potential" of each mine spoil material and assess how much of the TDS load appears to have leached over 15 to 25+ year time spans and from what depth. These data and findings will be reinforced by our spoil leaching column trials. Finally, we will directly compare and contrast all mine soil pedons with nearby natural soils over the same strata.

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