Long-Term Mine Soil Weathering and TDS Release
2010/2011 Powell River Project Annual Progress Report

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Introduction and Background

The Surface Mining 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 interesting 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. One of the unintended secondary effects of this practice has been the intentional selection and placement of topsoil substitute materials derived from deeper unweathered strata that are higher in pH and extractable nutrients than near-surface weathered strata. As discussed later, many of these otherwise suitable topsoil substitutes are also generate significant ionic loads to runoff and leaching waters as they weather over time.

Over the past decade, the concept of topsoil substitution has been criticized from a number of perspectives including potential effects on water quality. Regulation and monitoring of coal mine discharges to surface and ground-waters in the central Appalachian coalfields (WV-VA-TN) have traditionally focused on pH, Fe, and Mn. However, the leaching of both mine spoils and refuse materials is also a primary source of total dissolved solids (TDS) discharges which may affect surface water quality in mined areas. Common ions comprising TDS include, but are not limited to, HCO_3^-, SO_4^{2-}, Cl^-, Ca^{2+}, K^+, Mg^{2+}, and Na^+. Since ion concentrations control electrical conductivity (EC) in water, EC can be used to directly estimate TDS. Several recent studies (Chapman et al., 2000; Goodfellow et al., 2000; Pond et al., 2008; Timpano, 2011) have addressed the issue of TDS as a major stressor upon receiving streams in mined watersheds. The release of TDS has been implicated as a component of mining related surface water degradation under both low and moderate pH conditions. It now appears that coal mining discharges will be directly regulated for TDS over time (USEPA, 2011) and reducing bulk TDS is a much more difficult water treatment proposition for the coal industry than controlling more conventional parameters such as pH and total Fe and Mn. The recent EPA guidance is based on the belief that mine discharges with EC levels <300 μS/cm generally will not cause significant degradation of the aquatic ecosystem while in-stream conductivity levels >500 μS/cm are likely to be associated with significant adverse impacts on the aquatic ecosystem. The proposed guidelines suggest that projects expected to increase conductivity to levels >300 μS/cm should require adaptive remedial action to prevent conductivity levels from rising to levels that may contribute to water quality degradation and that sites with discharges >500 μS/cm should not be allowed to continue to operate.

In 2007, we proposed to directly address a number of challenges associated with topsoil substitution by initiating a new program of mine soil sampling and analysis while incorporating our established baseline experiments at the Research and Education Center and other locations. We originally proposed to meet the following 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.

However, by 2009, it became obvious that we needed to focus our work on TDS prediction in association with our originally proposed mine spoil weathering objectives. Thus, for the past two years, we have focused most of our research effort on Objective 3, while continuing related parallel work on the other three objectives.

Overall Approach

We are now completing the fourth 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 Powell River Project Research & Education Center. 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, extent of their pre-weathering, and associated acid-base weathering reactions on leachate pH, EC/TDS, and cations and anions (Ca, Fe, HCO_3^-, and SO_4^{2-}). During the third and fourth years, in response to the proposed EPA TDS guidelines, our efforts focused on column leaching studies to evaluate TDS potential from a variety of spoil materials. As discussed later, we still have several other study components that we intend to finish including the field 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 (Aug 2011)

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. For ease of sample classification, samples which are dominantly fine-grained (i.e. siltstones and/or shales) are collectively referred to here as mudstones. During years two and three, leaching column studies allowed characterization of element release from 12 spoil materials. The leaching columns were built from PVC pipe with a diameter of 7.6 cm and a length of 40 cm. Each column holds a sample volume of ~1200 cm^3. 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). Leachate samples were analyzed for pH, electrical conductivity (EC), Al. Ca, Fe, K, Mg, Mn, Na and S. We previously reported preliminary leaching results, along with relevant geologic, chemical and physical properties for 10 samples. Below we present leaching results including pH, EC and selected ions over the full leaching periods for all 12 spoil materials.

During the past year we completed leaching column analysis on an additional 14 spoil materials obtained from two drill cores from the vicinity of Buchanan and Dickenson Counties. Six composite samples were collected from Core-1, and 8 were collected from Core-2. Each composite sample was collected as a weighted average representing all strata within the defined section of the core. The samples were run in triplicate as described above, but only under unsaturated conditions. All leachate samples were analyzed for pH and electrical conductivity (EC). Samples were analyzed every 2 to 3 weeks for, Al. Ca, Fe, K, Mg, Mn, Na, S, Cl and HCO_3. Due to equipment difficulties Cl and HCO_3 analyses did not commence until several weeks into the study.

Leaching characterization for initial 12 spoil samples

The data presented in Figures 1-4 report results for 12 spoil samples, run for leaching periods up to 52 weeks (104 leaching events), under unsaturated conditions. The data are presented in groupings to contrast the results from weathered versus unweathered materials and sandstone vs. mudstone material. We highlight pH, EC, sulfate and calcium which are 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:. With few exceptions, leachate pH (Fig. 1) increased over the first few leaching events, and achieved a relatively stable equilibrium within 10 to 20 leaching events. We have seen this behavior in most SW Virginia overburden samples tested to date and believe this is due to the dissolution of carbonates from the near-surface interstices of the overburden fragments. The initial pH is somewhat lower due to the initial reaction pH of the fragment's surface, particularly when the materials are pre-oxidized to any extent to contain Fe and Mn oxides. Of course, the leaching water is acidic (pH 4.80), but it is very weakly buffered. Once the system "wets up" and the partial pressure of CO_2 increases within the column leaching environment, the carbonates in these spoils rapidly buffer the pH upward towards their equilibrium of 8.30. For both sandstones and mudstones, unweathered materials typically equilibrated at higher pH's than their weathered counterparts. This is to be expected since the weathered materials are essentially "pre-leached" which would promote acid-generating reactions while removing alkaline-generating components such as carbonates. For samples tested to date, we have not observed significant differences between mudstones and sandstones (at similar degrees of weathering) in terms of equilibration pH.

Electrical Conductance (EC): Leachate EC from unweathered mine spoils (Fig. 2) was consistently higher than from partially oxidized and weathered samples of similar geology. As above, this is to be expected since the weathered samples have already been subject to loss of soluble materials. Differences between weathered and unweathered samples were more pronounced for mudstones than for sandstones. 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. In terms of the proposed EPA guidelines, all sandstone samples equilibrated to leachate EC ≤500 uS/cm after ~10 leach events, and all were ≤300 uS/cm by the end of the full leaching period (several achieved this state within the first 30 leach events). The weathered mudstones generated EC ≤300 uS/cm within the first 10 leach events. Of the three unweathered mudstone samples, only one achieved an equilibrium ≤300 uS/cm (by leach # 17). The other two unweathered mudstone samples equilibrated to EC levels ≤500 uS/cm within ~40 leach cycles.

Sulfate and Ca: Sulfate and Ca release patterns (Figs. 3 and 4) reflect fundamental internal acid-base reactions within the leaching columns as they weather over time. Due to the nature of these reactions (pyrite oxidation coupled with carbonate dissolution and neutralization) the sulfate and Ca release patterns are almost identical. Variation among samples is due to fundamental differences in their geology/mineralogy such as total-S content, carbonate content, and degree of "pre-oxidation" via long-term pre-mining weathering in the field. Sulfate and Ca release was greater from unweathered materials (vs. weathered material of similar geology) and for mudstones (vs. sandstones). For most spoil samples used in this study, the majority of sulfate release occurred within the first month (e.g. 10 leaching events or about two pore volume of total elution). Interestingly, the greatest overall sulfate release occurred from an unweathered mudstone from the Breathitt Formation (eastern Kentucky) which has been noted and studied for its acid-forming potential (Barnhisel and Massey, 1969).

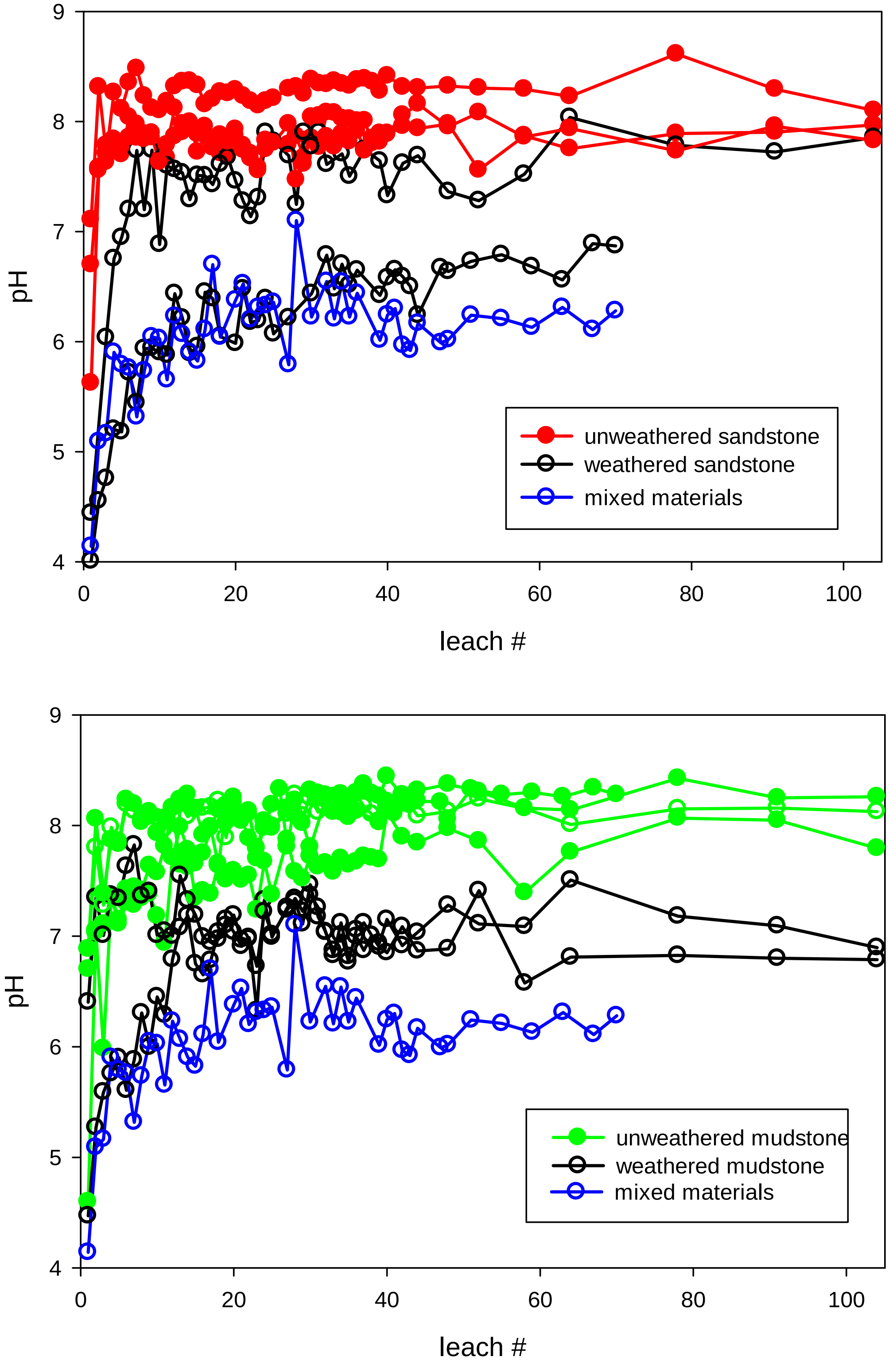
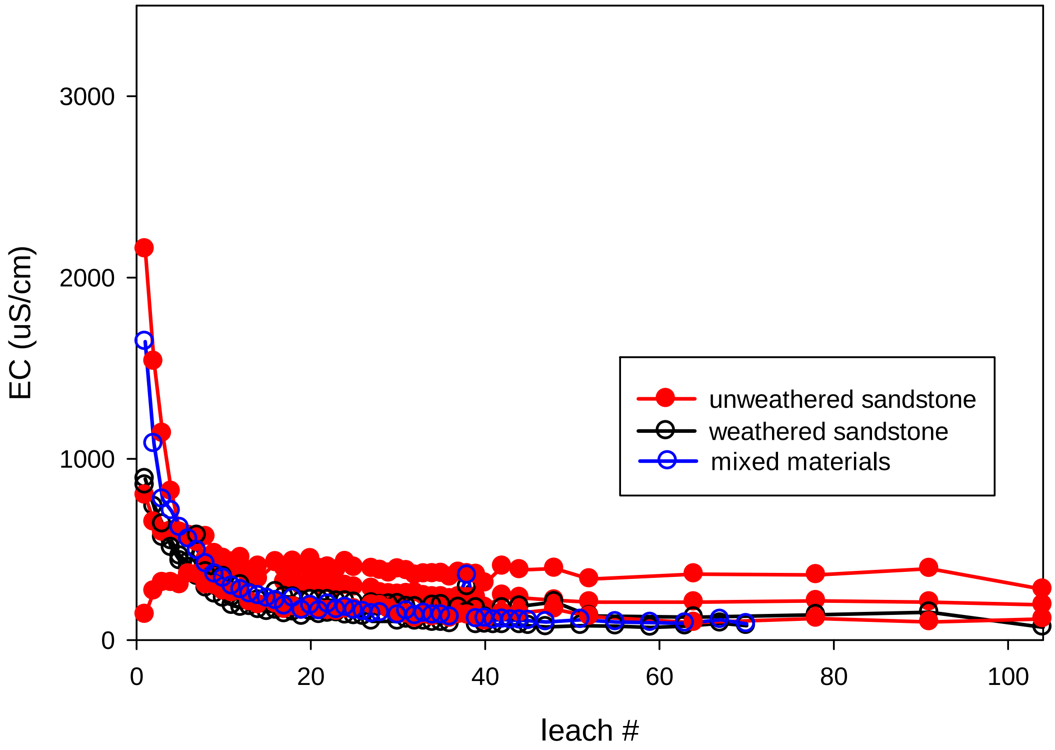


Figure 1. Leachate pH over time (2 leach cycles per week) under unsaturated conditions for 12 spoil materials.



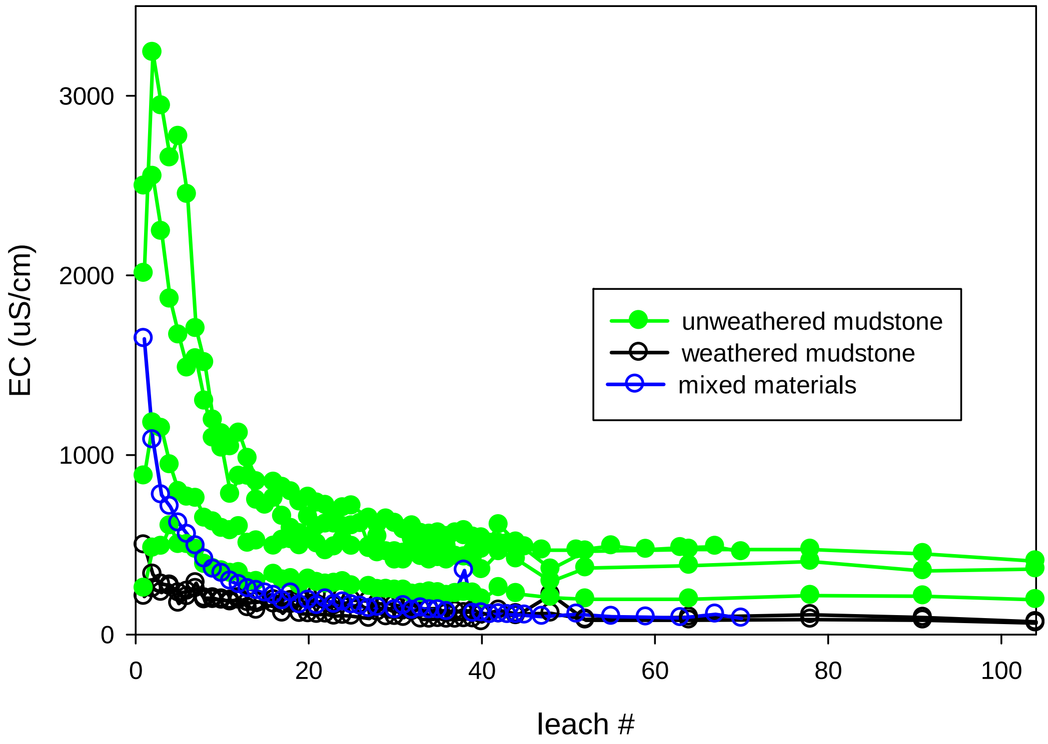


Figure 2. Leachate EC over time (2 leach cycles per week) under unsaturated conditions for 12 spoil materials.

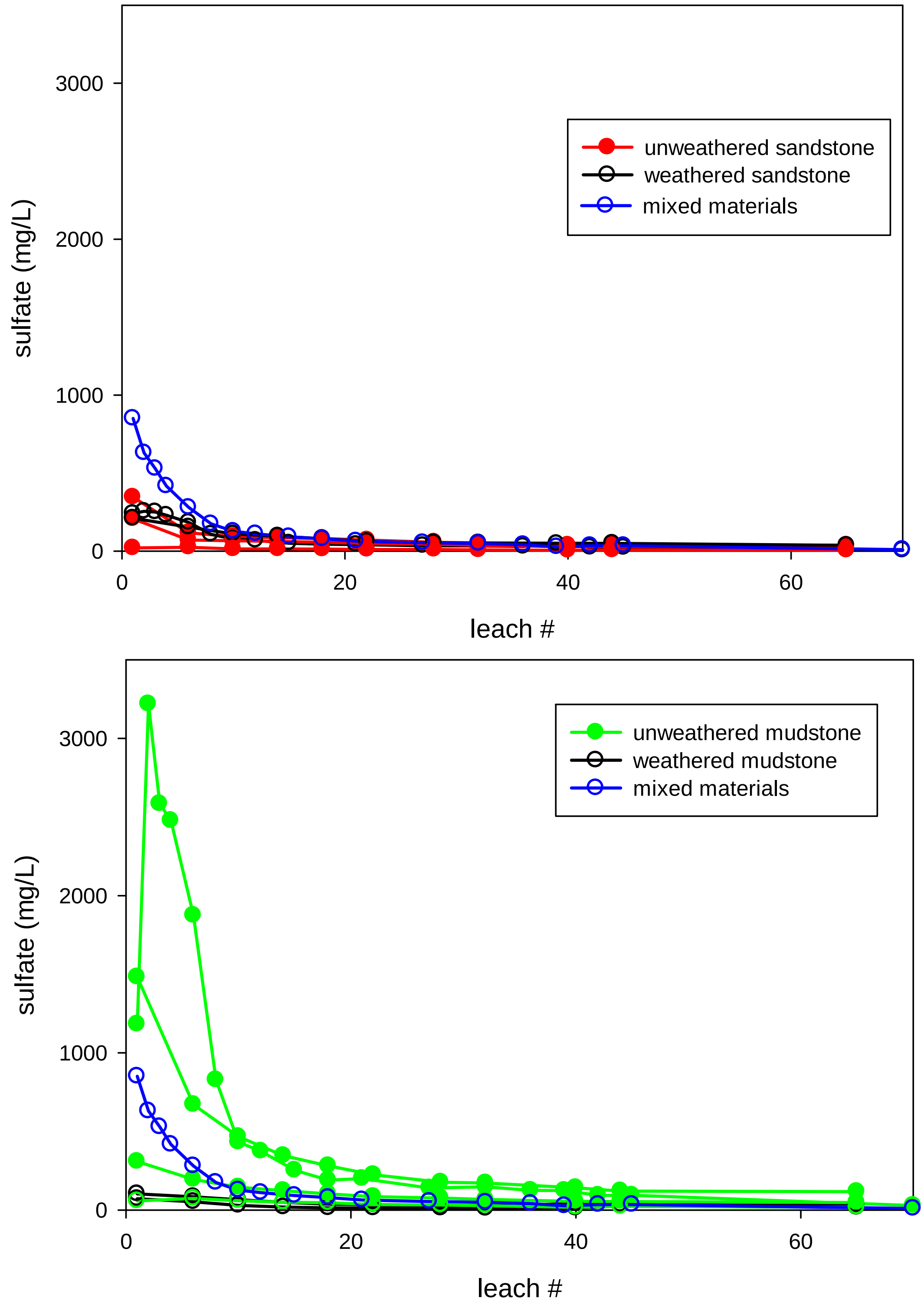


Figure 3. Leachate sulfate over time (2 leach cycles per week) under unsaturated conditions for 12 spoil materials.

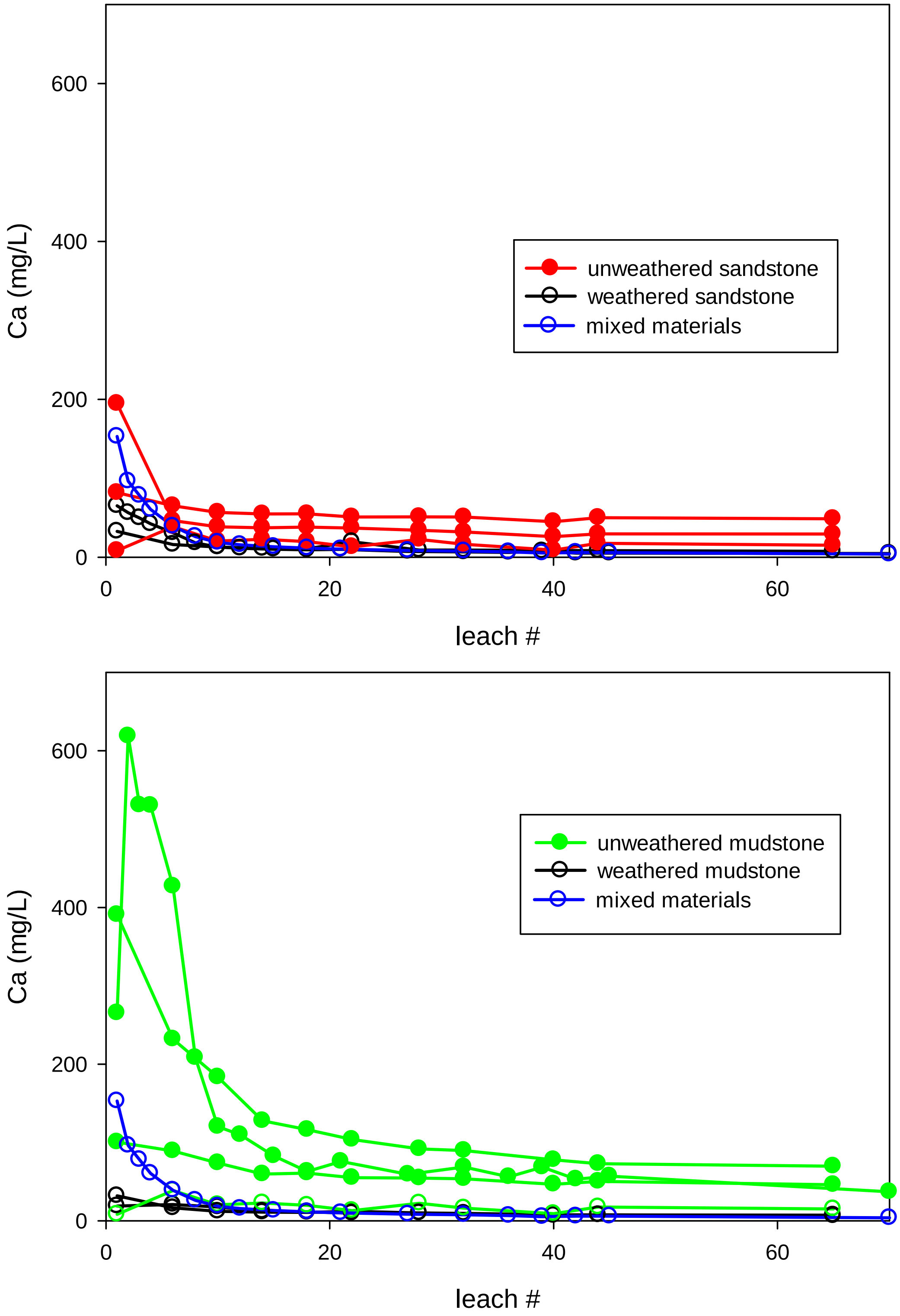


Figure 4. Leachate Ca over time (2 leach cycles per week) under unsaturated conditions for 12 spoil materials.

Characterization and leaching results for 14 spoil samples from Core-1 and Core-2

For the 14 drill core samples, some chemical properties, sample depth, basic geologic composition and associated coal seam information are presented in Table 1. The saturated paste pH of these samples was alkaline which is common for 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 saturated paste EC, produced by these materials was relatively low (< 1.2 dS m^{-1} or 1200 µS/cm). While these EC values are quite typical for soil:water systems, as mentioned earlier, mine site effluent/leaching levels in excess of 0.5 dS m^{-1} (500 µS/cm) would pose significant regulatory concern. Total S content for most samples was relatively low (< 0.13%), which is not unusual for the region sampled, although a few samples contained higher levels (0.43 to 1.02%).

Leaching column results: The data presented in Figures 5 - 11 report results from 40 leaching events over a 20 week period. The data are presented in groupings by drill core. We highlight pH, EC, sulfate, bicarbonate and other elements particularly relevant to acid-base reactions. The graphs are coded so that red indicates highest sandstone content, green indicates highest shale/mudstone content, blue indicates mixed materials, and black (Core-2 only) indicates dominantly weathered material. All data presented represent the mean observations from three replicate columns.

pH: For Core-1, leachate pH (Fig. 5) was initially lowest for the samples highest in sandstone content, which were lowest in the overburden column. Only one sample (1-1) generated an initially acidic (< pH 6.50) leachate while all others were at or above pH 7.0. For Core-2, leachate pH (Fig. 5) was lowest for sample 2-1 which contained weathered sandstone and was highest in the overburden column. This was the only sample that initially generated an acidic (< pH < 6.5) leachate. Samples high in unweathered sandstone produced leachate with lower pH than samples high in unweathered shale, as also seen in Core-1. It should be noted that the upper section of the overburden column for Core-2 included samples which contained noticeable quantities of weathered materials (i.e. brown sandstone) whereas samples from Core-1 were collected from greater depths and contained minimal (if any) amounts of pre-weathered materials.

As seen with previous spoil leaching analyses, the leachate pH of all materials increased sharply within a short period of time (< 2 pore volume; 7 to 9 leaching cycles). As discussed above, this is likely due to dissolution of carbonates which rapidly buffers the pH upward towards an equilibrium of 8.30. In some instances, particularly when traces of Na are present in the system, the pH is buffered to values approaching or exceeding 8.50 as is seen with samples 1-4 and 1-5 (high shale content). The shallowest and most weathered sample (2-1) appears to be largely depleted of carbonates and therefore stabilized at a slightly lower pH (7.50).

Table 1. Basic geologic composition and associated information for 14 samples from Core-1 and Core-2 used in column leaching studies.

ID	Depth (ft)	Saturated paste		Total S (%)	Geologic Composition	Coal Seam
		pH	EC dS m^{-1}			
1-1	462-520	8.50	0.29	0.00	gray sandstone (100%)	Hagy
1-2	415-460	8.38	0.35	1.02	gray sandstone (37%); gray shale (31%); gray sandy shale (31%)	Glamorgan
1-3	376-408	8.72	0.69	0.00	gray sandstone (66%), gray sandy shale (23%), gray shale (10%)	Blair
1-4	290-375	8.22	0.71	0.43	gray shale (83%), gray sandy shale (15%), minor sandstone (2%)	Clintwood Upper Eagle Lower Eagle
1-5	211-290	8.61	0.89	0.43	gray shale (50%), gray sandstone (26%), gray sandy shale(24%)	Clintwood
1-6	160-211	8.24	1.21	0.07	sandy shale (54%); gray sandstone (43%); brown sandstone (3%)	Clintwood
2-1	44 - 87	8.22	0.52	0.00	brown sandstone (87%), black and gray shale (13%)	Raven 3
2-2	87 - 115	8.20	0.75	0.05	gray shale (66%), weathered gray shale (23%), gob (12%)	Raven 2
2-3	115 - 127	8.20	0.52	0.00	gray sandstone (62%), gray shale (38%)	Raven 1
2-4	127 - 153	8.25	0.44	0.00	gray sandstone (34%), brown sandstone (32%), gray sandy shale (19%), gray shale (13%)	Jawbone Rider
2-5	153 - 181	8.30	0.37	0.00	mixed sandstone (41%), gray sandstone (38%), gray shale (21%)	Jawbone Rider
2-6	181 - 257	8.40	0.34	0.13	gray shale (80%), gray sandy shale (16%), gray sandstone (4%)	Jawbone Rider
2-7	257 - 299	8.43	0.35	0.00	gray sandstone (98%), gray shale (2%)	Jawbone
2-8	299 - 333	8.35	0.30	0.10	gray sandstone (89%), gray shale (10%)	Tiller

Electrical Conductance (EC): Leachate EC values over time are presented in Figure 5. For Core-1, the data indicates that several materials within this overburden column (e.g. 1-1 and 1-3) would elute short-term leachates less than 500 µs/cm and that all samples would be expected to stabilize at or under the critical 500 µs/cm level in terms of longer term release. However, these data also point out that each strata tested has a unique temporal profile and that 4 of the 6 materials tested would be expected to produce a leachate EC of 500 µs/cm or greater with their initial wetting and leaching events. Interestingly, sample 1-1, the deepest strata section tested, eluted the lowest levels of EC overall. For Core-2, the data indicates that some of the materials tested would be expected to produce a leachate EC ≥500 µs/cm with their initial wetting and leaching, but the majority of materials within this overburden column would also be expected to stabilize at or under the critical 300 µs/cm level in terms of longer term release. Interestingly, sample 2-1, which we assume was the most "pre-weathered" material present, did elute significant EC over the first few leaching cycles before dropping dramatically. We assume this is due to flushing of sulfates and other reaction products accumulated over long periods of time pre-disturbance. The next strata down in the core, 2-2, eluted the highest levels of EC observed (> 600 µs/cm), but also dropped rapidly to 300 µs/cm or lower within several pore volumes. The most interesting response was that of 2-6, which increased dramatically between cycles 6 and 10, and then dropped again over time to approximately 400 µs/cm. This section (2-6) appears to have a much higher proportion of shale which may contain more reactive mineral surfaces. Sample 2-8, the deepest strata section tested for Core-2, eluted the lowest levels of EC through the majority of the leaching period. It is important to point out that all samples continued to decline in EC over the latter phase of leaching indicating that no "time lagged" increase in EC should be expected from any of these materials.

Ion concentrations: The concentrations of the dominant TDS constituent ions are presented in Figs. 6 - 11. Sulfate is generally considered to be the dominant ion of regulatory concern in circumneutral coal mine discharges and often constitutes more than 50% of total TDS mass. This sulfate is produced by the oxidation of trace pyrites in the overburden with simultaneous neutralization by carbonates. Thus, we expect to see increased sulfate, Ca, and Mg release associated with this process. This behavior was evident for samples 1-2, 1-4, 1-6, 2-1 and 2-2 (Figs. 6 and 7), which were also the samples that produced initially high EC as discussed above. Thus, we conclude that this initial "flush" of TDS is due primarily to the rapid oxidation and neutralization of trace pyrites in these strata. However, as discussed above, samples 1-1, 1-3, and 2-6 are a little more perplexing. Since sulfate elution is largely unchanged over the period of time that EC increased sharply (cycles 7 to 10) it is unlikely that pyrite oxidation was involved here. However, Ca+Mg elution did increase steadily for these samples (Fig. 7) indicating that carbonates were reacting or dissolving actively over this period of time. We did evaluate Cl levels in these leachates and they were negligible. Higher initial Na in sample leachates (Fig. 8) would also shift the carbonate/bicarbonate equilibrium to favor higher pH and EC, particularly for the high shale strata (1-4 and 1-5). Finally, it is apparent for both cores that the deepest overburden strata generated the least amount of overall sulfate leaching risk.

Potassium (Fig. 8) was generally low in all materials tested, particularly the more weathered near-surface strata (i.e. 2-1). Similarly, Mn release (Fig. 9) was low overall but highest for the pre-weathered near-surface strata (2-1 and 2-2) which may have been due to the important coupling that occurs between pyrite oxidation and Mn reduction in these systems. Iron was also eluted in low concentrations due to the high pH of these materials and the fact that any Fe generated by pyrite oxidation would be retained as Fe-oxides in the column. It is interesting to note the short-term spike of Fe eluted by sample 1-1 that appeared to precede the short-term peak in EC for that sample as discussed earlier. Unfortunately, due to equipment failure, we were unable to analyze for bicarbonate in these solutions for the first several leaching cycles. Analysis from later leaching events (Figure 6) confirmed that the highest bicarbonate levels were associated with higher Ca+Mg and EC elution as discussed above.

The overall ion balance for major cations and anions at weeks 12 and 19 (Core-1) and weeks 8 and 20 (Core-2) is presented in Figures 10 and 11. As expected, sulfate-S and bicarbonate are the dominant ions present and account for approximately 2/3 of the TDS mass over time. The cations are typically present as Ca>Mg>K> Na. One final positive note from these data is the fact that bicarbonate is found in higher concentrations than sulfate-S in several strata leachates over time (particularly for lower EC producing materials like 1-1 and 1-3) which would further support their use in areas of re-graded surface spoils in direct contact with surface water or for limiting EC in fill drainage.

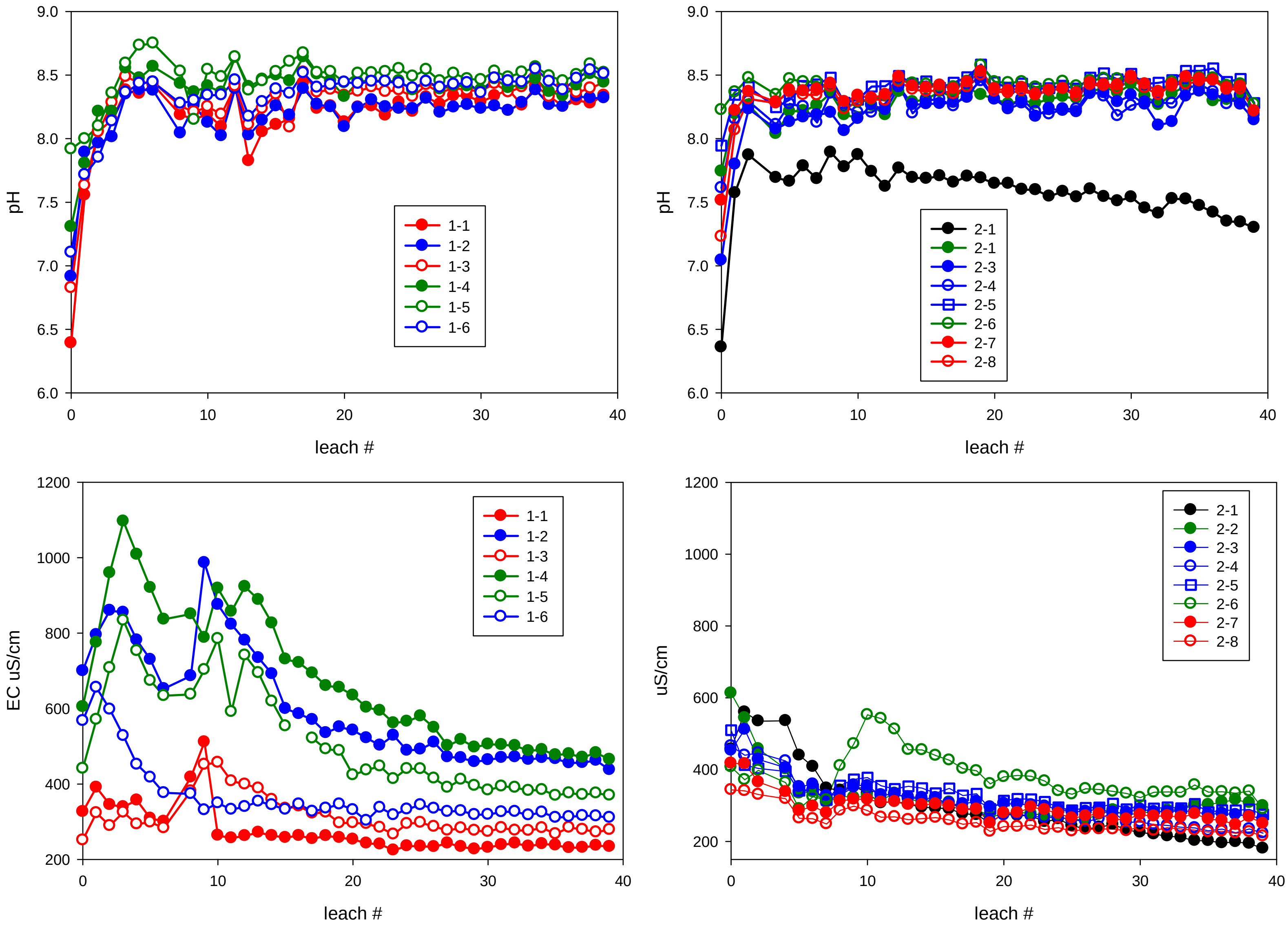


Figure 5. Leachate pH (top) and EC (bottom) over time (2 leach cycles per week) for Core-1 (left) and Core-2 (right).

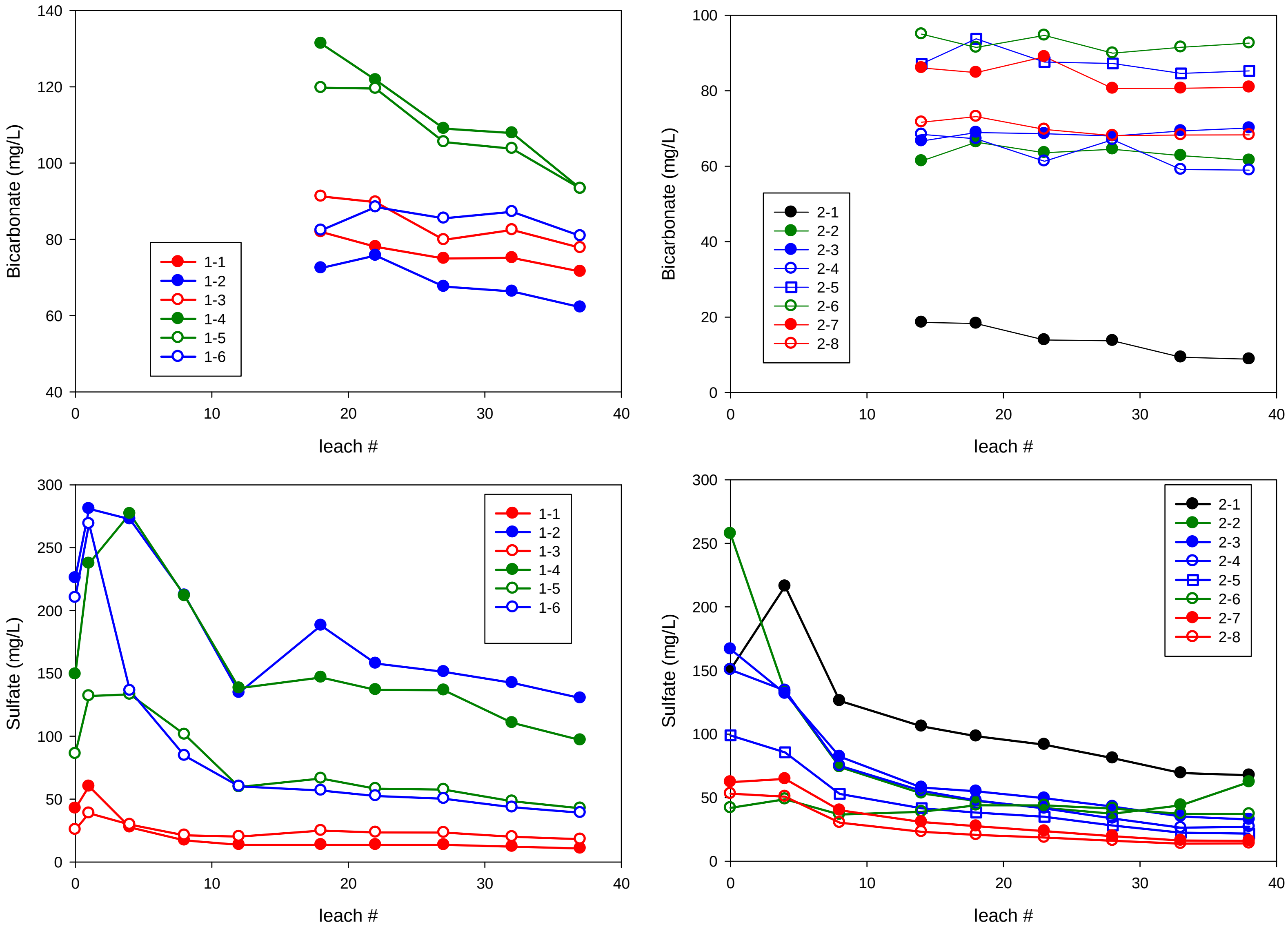


Figure 6. Leachate bicarbonate (top) and sulfate (bottom) over time (2 leach cycles per week) for Core-1 (left) and Core-2 (right).

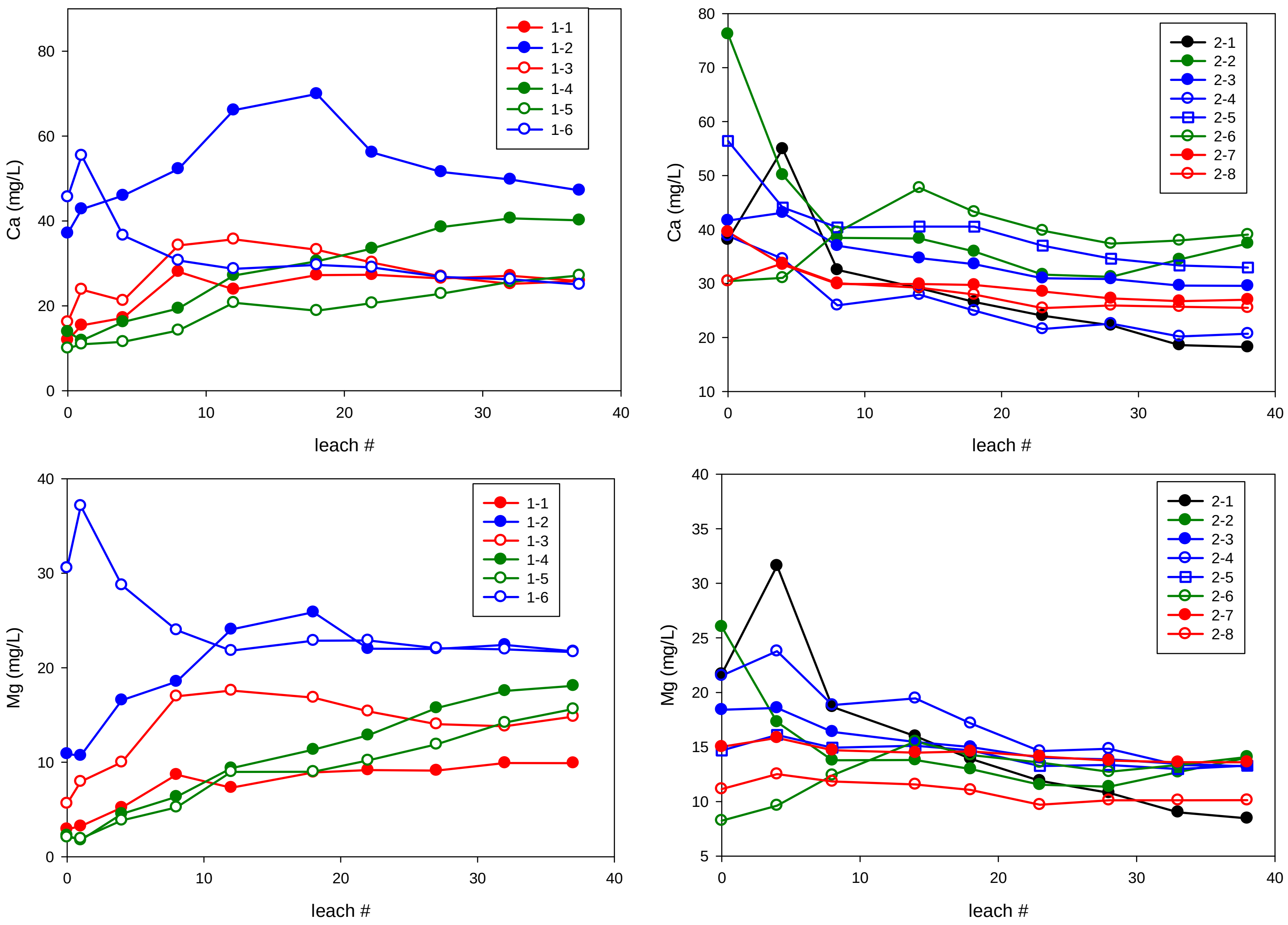


Figure 7. Leachate Ca (top) and Mg (bottom) over time (2 leaching cycles per week) for Core-1 (left) and Core-2 (right).

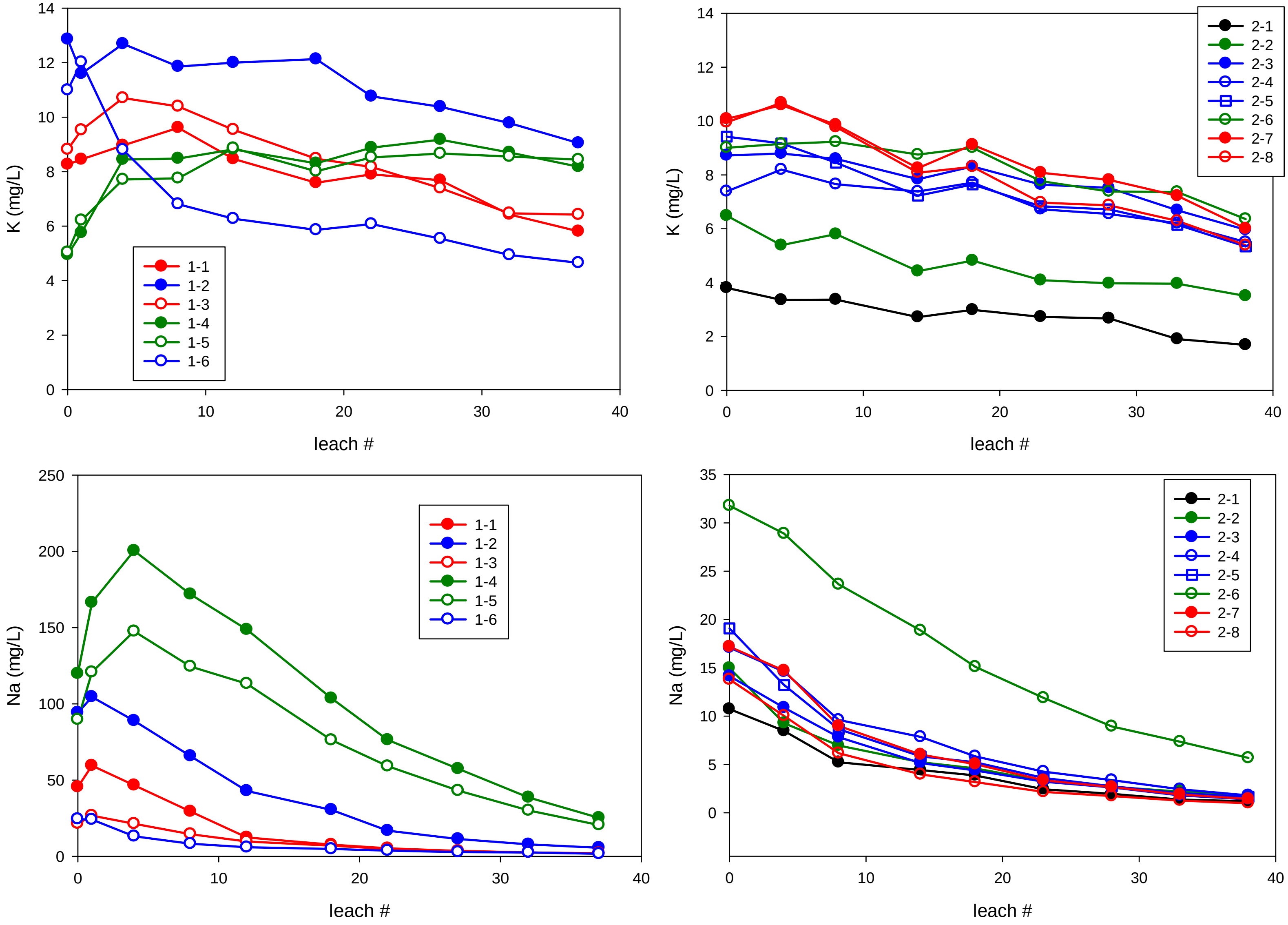


Figure 8. Leachate K (top) and Na (bottom) over time (2 leaching cycles per week) for Core-1 (left) and Core-2 (right).

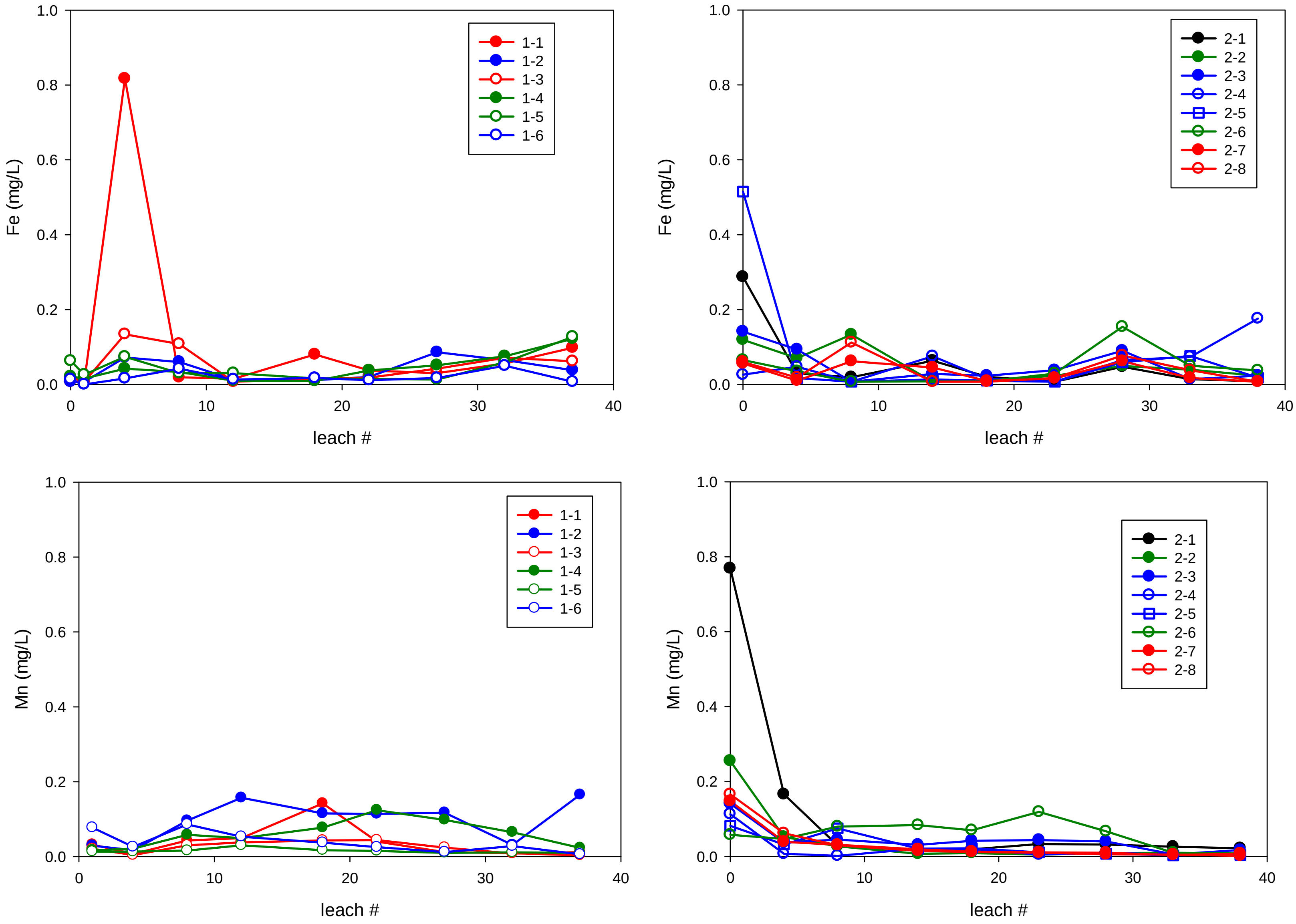


Figure 9. Leachate Fe (top) and Mn (bottom) over time (2 leach cycles per week) for Core-1 (top) and Core-2 (bottom).

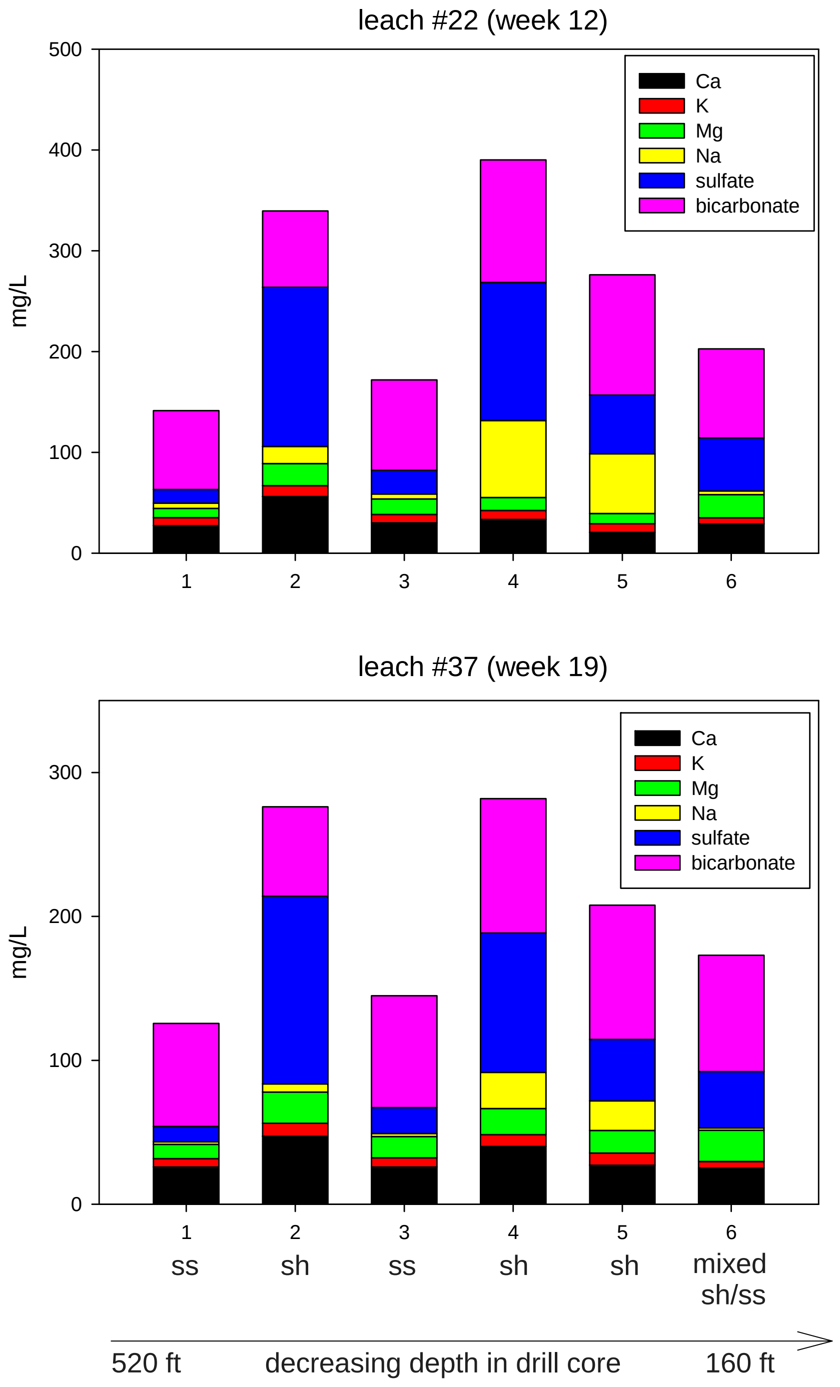


Figure 10. Dominant elemental composition of TDS as determined by ICP-AES analysis of leachates at leach #22 (week 12) and leach #37 (week 19) for 6 composite samples Core-1. Dominant geology indicated (ss=sandstone; sh=shale).

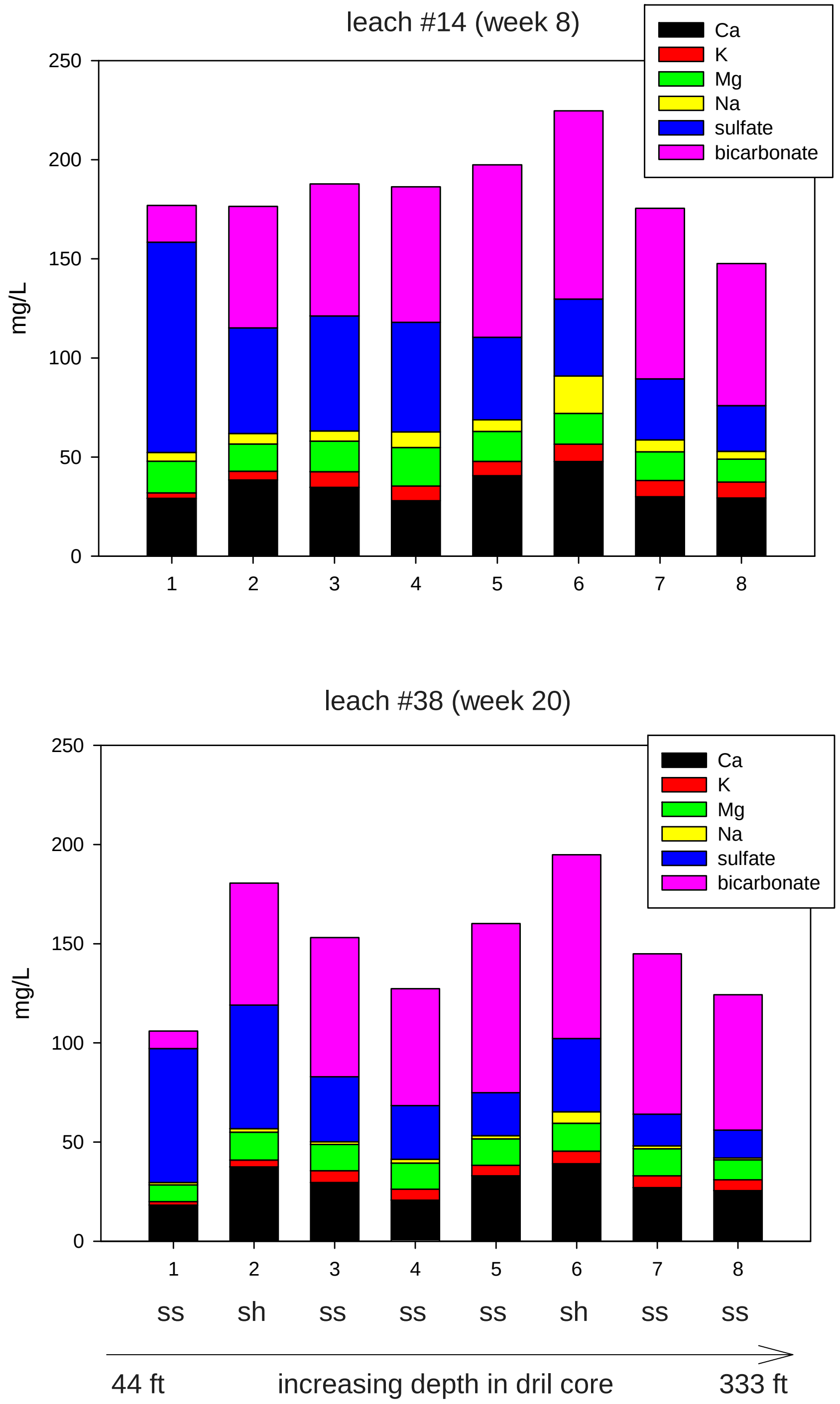


Figure 11. Dominant elemental composition of TDS as determined by ICP-AES analysis of leachates at leach #14 (week 8) and leach #38 (week 20) for 8 composite samples from Core-2. Dominant geology indicated (ss=sandstone; sh=shale).

Data Analysis, Synthesis and Expected Results

After two years of intensive study, our column leaching results continue to point to the fact that the potential for a given spoil material to generate TDS will be directly controlled by differences in (A) mine spoil strata/origin and associated texture/mineralogy that then interact very strongly with (B) the extent of *in situ* pre-mining weathering to profoundly influence their potential to generate TDS to contact waters (e.g. runoff or leachates). Over the past two years, for the strata studied, it is clear that finer textured mudrocks and shales have a much higher probability of significant TDS release. Thus, we continue to recommend that 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. We also firmly believe that this practice will result in a minimization of TDS release to surface runoff waters. Furthermore, the industry should consider the use of these pre-weathered materials for any portion of the mine in direct contact with surface waters, assuming their geotechnical stability (slaking etc.) would allow their use.

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 (> 1000 µS/cm), 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. 300 to 500 µS/cm) for most materials. To date, virtually all of the materials that we have tested have dropped below 500 µS/cm very quickly (several pore volumes) and most of the coarser textured spoils have equilibrated at long-term TDS release levels below 300 µS/cm. That being said, the extent of pre-weathering has a stronger influence on TDS release than does rock type.

At this point in time the critical question continues 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. Over the coming years, we expect to address this challenge directly through cooperative research funding provided by the newly established Appalachian Research Initiative on Environmental Studies (ARIES) and it is important to note that the underpinning research supported here by the Powell River Project was fundamental to the development of many ARIES objectives.

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. 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 90% of our *originally* proposed work plan, but that plan was significantly altered in 2009 to allow for a more direct focus on TDS characterization and prediction. Thus, we still need to complete the sampling and analysis of the COP experiment to allow direct evaluation of the effects of 30 years of field weathering on bulk mine spoil properties, plant growth potentials and TDS elution potentials. Over the coming project year, we also intend to focus our field sampling and analysis on sites where we can adequately sample the entire weathered soil-saprolite-oxidized-reduced rock strata sequence. Our goal will be to find and sample at least six sites for this detailed characterization. Once we can compare the chemical, physical and mineralogical properties of these differentially weathered zones against their associated TDS elution potentials, we will be much better able to prescribe depth cut sequences for the purpose of either minimizing TDS runoff/leaching or for using certain depths of materials for reconstruction of mine soils for reforestation.

References

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

Daniels, W.L., M. Beck, M.J. Eick and Z.W. Orndorff. 2009. Predicting contaminant leaching potentials for Central Appalachian overburden and coal refuse materials. Final Research Report to the OSM Applied Science Research Program, Pittsburgh, December 2009. http://www.techtransfer.osmre.gov/NTTMainSite/appliedscience.shtm

Chapman, P.M., H.B. Bailey, and E. Canaria. 2000. Toxicity of total dissolved solids associated with two mine effluents to chironomid larvae and early life stages of rainbow trout. Environmental Toxicology and Chemistry, Vol. 19(1), pp. 210-214.

Goodfellow, W.L., L.W. Ausley, D.T. Burton, D.L. Denton, P.B. Dorn, D.R. Grothe, M.A. Heber, T.J. Norberg-King and J.H. Rodgers, JR. 2000. Major ion toxicity in effluents: a review with permitting recommendations. Environ. Toxicol. Chem. 19: 175-182.

Pond, G. J., M. E. Passmore, F.A. Borsuk, L. Reynolds, and C. J. Rose. 2008. Downstream effects of mountaintop coal mining: comparing biological conditions using family- and genus-level macroinvertebrate bioassessment tools. J. N. Am. Benthol. Soc. 2008 27(3):717–737.

Timpano, A.J. 2011. Levels of dissolved solids associated with aquatic life effects in headwater streams of Virginia's Central Appalachian coalfield region. M.S. thesis.

USEPA, 2011. July 21, 2011 Final Memorandum: Improving EPA Review of Appalachian Surface Coal Mining Operations Under the Clean Water Act, National Environmental Policy Act, and the Environmental Justice Executive Order. http://water.epa.gov/lawsregs/guidance/wetlands/mining.cfm#memo20100401.