2019-2020 Research Report

Long-Term Effects of Rock Type, Amendments and Weathering on Mine Soil Properties and TDS Potentials

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Executive Summary

In the early 1980s, the USDI Office of Surface Mining (OSM) and the Powell River Project (PRP) cooperatively funded the construction and establishment of the Controlled Overburden Placement (COP) experiment in 1982. This research project is the longest running of its kind in the world and has generated over 50 journal and proceedings articles to date. Results from these plots have largely underpinned regional protocols for topsoil substitute selection since the mid-1980s. Our current research program is completing determination of long-term (30+ years) effects of overburden rock type and surface treatments on important mine soil morphological, physical, and chemical properties. In our last research report (March 2019), we reported results from our parallel lab-based work to evaluate total dissolved solids (TDS) elution potential (in lab columns) from fresh spoil samples taken in 1982 vs. weathered rock fragments from the surface of the current (2016) plots. In our third related study component, we continued our long-term monitoring of mine spoil leaching mesocosms at the Virginia Tech Turfgrass Research Center and those findings are also integrated into this annual report, which is focused on our results obtained from mid-2019 through the early fall of 2020. Our Previous reports and data sets can be viewed at https://powellriverproject.org/reports/

During the 2017-2018 project year, we completed basic chemical and physical analyses on the COP soil pits that were sampled in the fall of 2016. Initial details on the morphology of these profiles were provided in our last annual report and are expanded upon in this report along with insights into changes in physical and chemical properties over time. The morphology of these 30+ year-old mine soils is striking. Profound physical x chemical weathering of the rock spoils was noted, particularly in the higher siltstone spoils. Well aggregated ^A horizons have formed to depths > 10 cm and most subsoils contained moderately well-developed cambic ^Bw horizons. Surface horizons in general have declined in pH, exchangeable bases, and acid-extractable cations over time (30 years). However, the surface soils do show evidence of bioaccumulation of cations and associated higher levels of electrical conductance vs. subsoil horizons. The long-term influence of sawdust and biosolids additions in the surface treatment experiment is still apparent in darker colors, stronger aggregation and higher ^C than the untreated control plots. Perhaps most surprising is the apparent development of compacted subsoil layers in the lower ^B and ^C horizons. Since all vehicle traffic has been excluded, we can only hypothesize that these layers are being formed by a combination of (a) net physical illuviation of finer textured soil sized materials downward, and/or (b) physical weathering/slaking of larger weatherable rock fragments leading to collapse of bridging voids and long-term settling and compaction. This finding has significant long-term management implications.

In this report, we present a much more detailed description and analysis of the chemical and physical properties of the mine soils in the Rock Mix (RM) and Surface Amendment (SA) experiments. Our last report (March 2019) presented summary data on these materials, which now have been much more thoroughly analyzed to determine both relative treatment and depth (by horizon) effects in both experiments. Generally, nutrients, metals, and C and N levels were higher in the surface ^A horizons compared to the subsurface (^Bw and ^C horizons) across treatments and these trends were similar for both the RM and SA experiments. Organic matter accumulation and the effects of higher biological activity in the surface has significantly influenced pH (lower), soluble salts (higher), and CEC (higher) in the ^A horizons. Certain treatment effects are more evident in the RM experiment, mainly due to the higher degree of initial pre-weathering of the sandstone (SS) vs. siltstone (SiS) overburden materials when originally placed in 1982. Subsurface soil properties (^Bw and ^C) within each experiment are much more similar to the original parent materials while surface soil (^A) properties tend to more uniform in the RM experiment due to weathering, OM accumulation and pedogenesis. In the SA experiment, treatment effects were only evident for a few extractable nutrients/metals in the ^A horizons, particularly P. The Sawdust treatment had higher K than the control, the Biosolids 112 Mg/ha treatment was higher in P than the other surface amendments (i.e., Topsoil/Sawdust), while the Biosolids 112 Mg/ha treatment was higher in Cu, Fe, and Al. Soil texture in the RM experiment was clearly still controlled by the original spoil rock type in both the surface and subsurface horizons. For the SA experiment, surface soil (^A) texture was influenced by the different amendments, particularly the Topsoil. Only minor variations in subsurface texture (^Bw and ^C horizons) were observed in the SA experiment.

The combined results from the COP column leaching studies coupled with the long-term (8-year) Harlan spoil leaching field mesocosms reconfirm that while our lab column protocol is a relatively accurate predictor of peak vs. long-term leachate specific conductance (SC; a proxy for TDS), it probably under-predicts peak winter seasonal ion release in younger reactive materials. We continue to see what appears to be a continued gradual decline in TDS elution from the field mesocosm tanks along with a slight seasonal “bump” each winter associated with leaching of accumulated weathering salts from the preceding summer. These results generally support our earlier predictions (e.g. Evans et. al, 2014) of the expected timeframe (15 to 25 years) for field scale valley fill discharges to fall below current levels of regulatory concern for SC (e.g. 350 µs/cm). However, the facts that (a) the deeper spoils in the COP experiment still appeared to be only slightly weathered after > 30 years and (b) the recent apparent increase in leachate SC from the mesocosms demands that such estimates be made with caution.

Currently active work efforts include (a) determination of Fe-oxide content vs. depth in the COP mine soils and (b) bulk density of the compacted layers from original intact “clod samples” taken in 2016. We also continue to study and contrast the 1982 vs. 2016 soil chemical and physical data sets. Finally, we are also attempting to classify these mine soils using the existing NRCS Soil Taxonomy (2014) criteria along with the recently approved criteria for a new soil order (Artesols) that will become effective within two years. If funds are available for additional studies (2021/2022), we will complete more detailed lab analyses on C forms (humus vs. coal vs. carbonates) on COP samples from 1982, 2008 and 2016 to quantify organic matter accumulation (C-sequestration) rates. This would also allow us to complete full statistical comparisons of our recent data sets (2008 and 2016 sampling) against the original primary 1982-1984 data.

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 important 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 (15 cm) 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 (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.

In 1982, the USDI Office of Surface Mining and the Powell River Project (PRP) 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 mid 2000's and our results can be reviewed at the PRP web site and at https://landrehab.org/. The original installation and early results are summarized by Roberts et al. (1988 a,b,c) and Haering et al. (1993), who reported on the initial development of soil morphology as observed from soil pits. More recently, Nash (2012) sampled the surface and subsoil layers in both experiments and reported on long-term changes in chemical and physical properties along with an initial attempt to quantify actual rates of C-sequestration. In summary, our past reporting had concluded 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 various PRP researchers at other sites in the 1990's and 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 area (Haering et al., 2004).

Over the past several decades, 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. 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. Very few studies have been published to date that detail the expected variations in TDS due to spoil type and age/leaching regime since placement. Finally, the ability of these mine soils to accumulate organic matter, maintain a stable and viable microbial biomass and available nutrient pools, and possess overall productivity potentials beyond the requisite five-year performance liability period is also questioned by many.

Progress to Date and Future Research Plans

This program was originally proposed and funded by PRP in 2016/2017 as a one-year intensive project with the understanding that beyond that initial year, subsequent funding might not be available. However, PRP has been fortunate to receive additional allocation of funding for the past several years (2018/2021) and we have been able to extend our efforts and objectives as described below. During the 2016-2017 project year, we completed the detailed morphological description of soil profiles from three selected treatments in the rock mix experiment and five treatments from the surface amendment experiment. Bulk soil/rock samples were taken from all morphological horizons and then every 10 cm with depth. Our interpretations of overall morphology and mine soil weathering processes were summarized in our 2017 Annual Report (https://powellriverproject.org/reports/) and we completed all initial physical and chemical analyses of those soil samples as reported in last year's 2018 Annual Report.

During the second and third years (2017/2018/2019), we also developed a new column leaching protocol to evaluate differences in TDS leaching potentials on original samples archived from the pre-treatment May 1982 plots vs. 2016 rock samples extracted from the upper 25 cm of selected treatments. We also utilized a portion of these funds to continue the limited long-term monitoring of the field spoil leaching mesocosms at the Virginia Tech Turfgrass Research Center (VTRC) which were described in previous reports and by Ross (2015). We were also fortunate to receive funds for the past project year (2019/2020), which allowed us to complete a wide range of lab analyses on samples from multiple depth increments in the COP pits along with manually transcribing historic/archived data sets from the early 1980's into electronic records. We also continued periodic monitoring of pH and SC from the leaching mesocosms at the VTRC.

Currently (2020/2021), our active work efforts include (a) determination of Fe-oxide content vs. depth in the COP mine soils and (b) bulk density of the compacted layers from original intact "clod samples" taken in 2016. We also continue to study and contrast the 1982 vs. 2016 soil chemical and physical data sets. This includes completing a full statistical comparisons of our recent data sets (2008 and 2016 sampling) against the original primary 1982-1985 archived data. Finally, we are working to classify these mine soils using existing NRCS Soil Taxonomy (2014) criteria along with the recently approved criteria for a new soil order (Artesols) that will become effective within two years. If funds are available for additional studies (e.g. 2021/2022), we will complete more detailed lab analyses on C forms (humus vs. coal vs. carbonates) on the COP bulk and soil pit samples from 1982, 2008 and 2016 to quantify organic matter accumulation (C-sequestration) rates.

Once all study components are completed, we will combine our findings from all 30+ years of the experiment to produce a model of long-term soil development, weathering processes and resultant changes in mine soil physical and chemical properties. In parallel, the combined TDS leaching data from our lab columns (on COP samples) and the VTRC mesocosms will allow us to confirm and validate our recent literature predictions (Daniels et. al, 2016; Evans et. al, 2014) on the temporal pattern of TDS release. Finally, we will combine our findings 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 better quantify their rate(s) of transformation.

Thus, by a combination of direct and differential analyses, we are currently working to meet the following objectives:

Research Objectives

1. To determine the long-term (30+ years) effects of overburden rock type and surface treatments on important mine soil morphological, physical, and chemical properties.

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

3. To estimate the actual rate of organic matter accumulation (C-sequestration) in these mine soils and to compare the properties of these now relatively well-developed mine soils to local native soils.

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 their rate(s) of transformation.

Overview of Field and Lab Methods and Procedures

This project is focused on the analysis of a combination of current and past data sets and mine soil samples from the Controlled Overburden Placement (COP) experiment established in 1982. For the results reported here, we excavated, sampled and described three pedons in late September 2016 from each of the pure SS, 1:1 SS:SiS, and pure SiS treatments in the Rock Mix experiment along with three pedons each from the Control (2:1 SS:SiS), Topsoil, 50 T/Ac (112 Mg/ha) Sawdust, and 25 T/Ac + 50 T/Ac (56 and 112 Mg/ha) Biosolids plots in the Surface Treatment experiment.

At each pit location we carefully described mine soil morphology, rooting features, and spoil packing/settling patterns using standard soil survey protocols. We took photographs and at a later date we will superimpose a grid to allow better volumetric quantification of rock amount/size, coarse rooting and other important features. We then incrementally sampled the mine soils with depth by morphological horizon (e.g. ^A-^Bw-^C), in 10 cm increments from 0 to 50 cm, and then again from 50 to 75 cm and 75 to 100 cm to allow quantification of changes in physical and chemical properties with depth. Finally, representative rock fragments were sampled from the upper 0-25 cm, 50-75 cm and from the lowest portion (~1.5 m) of each pit for future TDS related studies (e.g. the column leaching studies reported in earlier reports).

Figure 1. Soil observation and sampling pit being excavated by Dan Early in a pure siltstone (SiS) plot in the Rock Mix Experiment in September 2016. Excavator traffic was limited to the alleyways between plots and the soil pit face was aligned to allow for optimal photography.

A total of 370 separate samples were collected for laboratory analysis. These samples were air-dried in our greenhouse at Virginia Tech and then rock fragments (> 2 mm) were separated away from soil fines for each bulk sample. This was an extremely laborious process and took approximately three months to complete. The fine earth fraction (< 2 mm) was then transported to our laboratories where the following analyses are being performed over time:

pH and total titratable/exchangeable acidity
Saturated paste electrical conductance and soluble salts species (cations + anions)
Total organic carbon and Walkley-Black organic matter
Total-N
Exchangeable cations, acidity and cation exchange capacity
Dilute acid extractable nutrients and metals
Extractable Fe- and Mn-oxides
Calcium carbonate equivalence
% Rock fragments
Particle size analysis
Bulk density on intact clods (taken from cohesive subsoil layers from pits)

Over the period covered by this report (2019/2020, we completed the vast majority of the laboratory analyses listed above with the exception of the intact clod bulk density procedure and several of the more intensive chemical analyses (e.g. C forms and Fe-oxides). All remaining lab analyses will be completed by spring 2021. Over the past year, we also completed additional particle size analyses and statistical analyses of temporal changes (2016 vs. 1982) in several previously determined mine soil chemical properties.

Results and Discussion

Overall Mine Soil Morphology and Interpretations of Pedogenesis

In our last two reports (https://powellriverproject.org/reports/), we focused on the morphological properties of these soils as described in September 2016 and we provided images and detailed profile descriptions for two representative mine soils from the Rock Mix Experiment and three from the Surface Treatment Experiment. We refer the reader to those reports for those detailed analyses and interpretations. In this report, we present several additional profiles (Figs. 2 and 3) and descriptive information from the 2016 sampling along with newly analyzed temporal data sets (1982 vs. 2016) for selected chemical and physical parameters.

As discussed in our last report, it is clear to us, from our comparison of morphological descriptions and imagery over time, that these mine soils progress down a very clear pedogenic pathway (Fig. 4) wherein we see ^A horizons forming very quickly within several years and then distinct transitional ^AC horizons developing in the subsoil within several more years. By the time these mine soils are 7 to 10 years old, many of them possess sufficiently well-developed subsoil structure that they clearly meet NRCS criteria for description as cambic horizons (^Bw) even though they may not show quantifiable evidence of illuviation of clay or Fe-oxides at that time. One of our major current efforts is the determination of those parameters (clay/Fe-Ox) on the surface and subsurface horizons and depth increment layers on the 2016 samples.

As described in our previous report (March 2019) the apparent development of compacted subsoil layers in the lower ^B and ^C horizons over time continues to be a surprising finding from this project. Since all vehicle traffic has been excluded, we can only hypothesize that these layers are being formed by either (a) net physical illuviation, saturated flow/creep, and sorting of finer textured soil sized materials downward over extended periods of time, or (b) physical weathering and slaking of larger rock fragments leading to “collapse” of original open bridging voids. The only similar reports of this latter phenomenon are by Haigh and Sansom (1999) and related work in much different (slaking mudstones and shales) spoils and coal refuse in Wales. However, they do report a very similar process and resultant formation of subsoil compacted layers. In this study, these highly compacted layers were not observed in our previous pit studies in 1983 and 1985, although we did observe some moderate increase in subsoil compaction is some profiles in 1989, but those layers were not reported as being root limiting. and we had previously attributed (e.g. Haering et al., 1993, 2004) similar layers to relict effects of compaction from rubber-tired haulers and excessive final dozer grading. That being said, Haering et al. (1993) did observe that deeper rooting appeared to be more limited than observed in the early 1980’s and some profiles did exhibit modest levels of subsoil compaction. While we still believe those mechanisms are major reasons for root-limiting compaction in Appalachian mine soils, these results clearly indicate that natural pedogenic and/or simple long-term settling processes may be active in forming these limiting layers as well.

Figure 2. Soil profile described in 100% sandstone derived mine soil in plot #4. Note the relatively loose nature of the deeper C horizon material with open "bridging voids" along with the linear void below the large gray unweathered rock fragment on the upper right. However, the ^Bw horizon was quite compact relative to original conditions described in the same treatment in the 1980's. The original sandstone spoils that were used were comprised of approximately 2/3 slightly pre-weathered "brown" sandstone and 1/3 hard gray non-weathered rocks that are so prominent in this profile.

Table 1. Soil profile description for Plot #4, 100% sandstone mine spoil placed in 1982.

Date Sampled: 9-22-2016
Described and Sampled by: D. Johnson, J. Buckwalter, K. Haering
Parent Material: 100% Sandstone
Vegetation: Mostly Allegheny blackberry (*Rubus allegheniensis*) and goldenrod (*Solidago altissima var. altissima*). Some native ferns, *Erigeron sp.*, broomsedge and 2 Tulip poplar (*Liriodendron tulipifera*) seedlings. No woody overstory.

Horizon	Depth --cm--	Description
O	4-0	Partially decomposed mixed leaf litter.
^A	0-7	Very dark grayish brown (10YR 3/2) loam; moderate granular structure; friable; many (15) very fine, common (4) fine and (1) coarse roots; 6% rock fragments by volume (6% gravel); low relative bulk density; no packing voids; clear smooth boundary.
^BA	7-15	Dark yellowish brown (10YR 4/4) gravelly sandy loam, with many (25%) very dark grayish brown (10YR 3/2) lithochromic color variegations; moderate subangular blocky structure; friable; common (4) fine and (1) coarse roots; 20% rock fragments by volume (20% gravels); low relative bulk density; no packing voids; clear wavy boundary.
^Bw	15-60	Dark yellowish brown (10YR 4/4) very stony sandy loam, with common (10%) dark yellowish brown (10YR 4/6) and (5%) very dark grayish brown (10YR 3/2) lithochromic color variegations; moderate subangular blocky structure; friable; common (2) fine roots; 50% rock fragments by volume (25% stones, 25% cobbles); high relative bulk density; no packing voids; gradual irregular boundary.
^BC	60-97	Dark yellowish brown (10YR 4/4) very stony sandy loam, with common (10%) yellowish brown (10YR 5/8) and (5%) very dark grayish brown (10YR 3/2) lithochromic color variegations; weak subangular blocky structure; very friable; common (2) fine roots; 40% rock fragments by volume (20% stones, 20% cobbles); medium relative bulk density; few packing voids; clear wavy boundary.
^C	97-125+	Dark gray (10YR 4/1) very cobbly clay loam, with many (25%) yellowish brown (10YR 5/8) and (25%) black (10YR 2/1) lithochromic color variegations; structureless massive structure; firm; few (0.5) coarse roots; 35% rock fragments by volume (20% gravels, 15% cobbles); medium relative bulk density; few packing voids.
Remarks:		Large boulder in upper 50cm of profile.

Figure 3. Soil profile described in 2:1 sandstone:siltstone derived mine soil in plot #26 (Control; no amendments). In this soil, both the ^Bw and ^C were quite compact relative to originally observed conditions in the early 1980's, and the ^C horizon was clearly root limiting and would qualify as a densic layer below 40 cm. The materials in the deeper C horizon were much less compact and still contained some non-collapsed bridging voids.

Table 2. Soil profile description for Plot #26, formed in 2:1 sandstone;siltstone (SS:SiS) mine spoil placed in 1982. This plot was a Control treatment that did not receive any additional amendments other than N-P-K fertilization.

Date Sampled: 9-22-2016
Described and Sampled by: D. Johnson, J. Buckwalter
Parent Material: 2:1 Sandstone:siltstone with no amendment - control
Vegetation: *Lespedeza cuneata* and *Solidago altissima var altissima*, *Clematis virginiana*, *Erigeron* sp. Northern red oak (*Quercus rubra*) and small *Acer rubrum* in adjacent overstory.

Horizon	Depth	Description
	--cm--	
O	5-0	Partially decomposed mixed leaf litter.
^A	0-7	Very dark grayish brown (10YR 3/2) gravelly silt loam; moderate granular structure; friable; common (4) fine and (3) very fine roots; 30% rock fragments by volume (30% gravel); low relative bulk density; no packing voids; clear smooth boundary.
^Bw	19-39	Dark brown (10YR 3/3) very cobbly sandy loam, with common (5%) yellowish brown (10YR 5/8) lithochromic color variegations; weak subangular blocky structure; friable; common (1) very fine and few fine (0.5) and (0.1) coarse roots; 55% rock fragments by volume (30% gravels, 20% cobbles, 5% stones); high relative bulk density; no packing voids; gradual wavy boundary.
^C	105-125+	Dark brown (10YR 3/3) extremely stony sandy loam, with common (5%) yellowish brown (10YR 5/8) lithochromic color variegations; structureless massive structure; very friable; very few (0.1) very fine roots; 65% rock fragments by volume (35% gravels, 30% stones); high relative bulk density; no packing voids.
Remarks:		1% of coarse fragments in ^Bw and ^C horizons (7-125+cm) are carboliths.

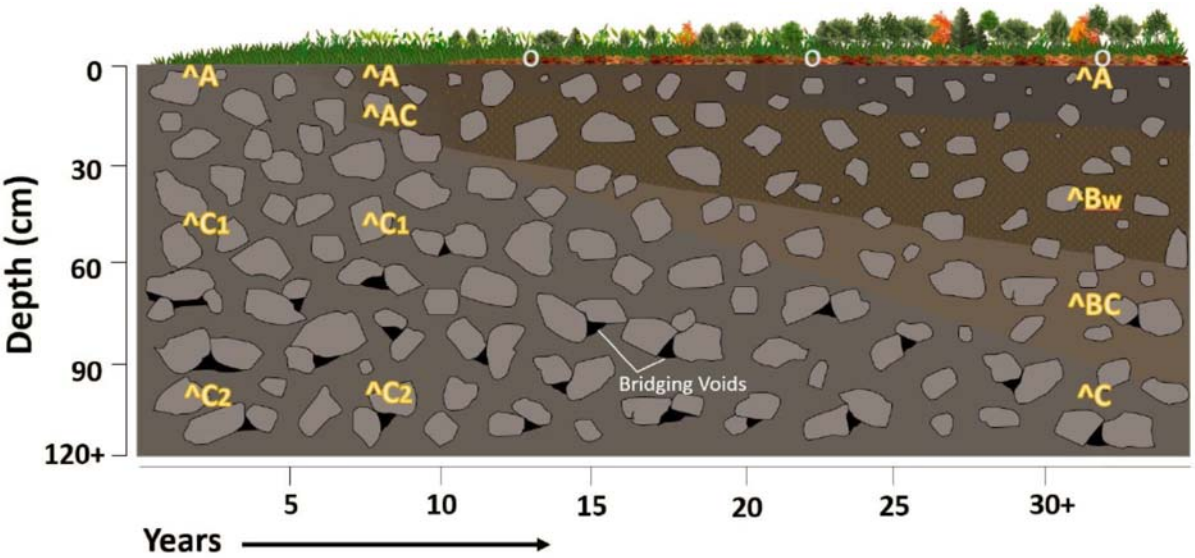

Figure 4. Graphical depiction of the development of major morphological horizons in the Controlled Overburden Placement Experiment mine soils over time. This model based on detailed soil descriptions in 1983, 1985, 1989, and 2016. Figure by Hannah Angel.

Mine Soil Physical and Chemical Properties

Soil Chemical Properties and Texture by Horizons

Horizon properties from the 2016 soil pits were analyzed for treatment effects by aggregated horizon (e.g. ^A vs. ^Bw) and presented in the March 2019 Report. This report presents a much more extensive analysis of these data which includes both treatment and depth effects for selected horizon properties. Three samples were taken per horizon for each treatment from replicate plots in the Rock Mix (RM) and Surface Amendment (SA) experiments. The ^A and ^Bw horizon data were analyzed from the RM experiment and the ^A, ^Bw, and ^C horizon data were analyzed from the SA experiment. Deeper ^C horizons from the RM experiment had several missing samples (or were described as ^BC), but these data will be analyzed and included in a later report. Overall treatment effects provide insight into the influence of different original spoil materials on soil fertility, pH, and the release and/or accumulation of soluble salts, carbon, nitrogen, and other elements over an extended period of time. Comparing soil horizon chemical and physical properties between horizons helps us better understand the soil development (pedogenesis) occurring in these mine spoils as they transform into mine soils. Surface horizons are generated by pedogenic processes that result in different properties compared to subsurface horizons where other developmental pathways occur. Assessing these differences provides insight on the weathering dynamics of complete mine soil profiles. Due to the inherent variation of materials both within and among experimental plots, a paired contrast statistical approach (see below) is most suitable for understanding differences with depth between horizons for mine soils by treatment or across time at a given depth x treatment combination.

Detailed Lab Analysis Methods

The following laboratory analyses were conducted on horizon samples. Soil pH was measured in a 1:1 soil/water slurry with a glass-calomel combination electrode (McLean, 1982). Saturated paste electrical conductivity (EC_e) was determined in a 1:2 soil:water ratio with a conductivity meter calibrated to a 0.01 *M* KCl standard solution (Maguire and Heckendorn 2019). A dilute double-acid extract (Mehlich I) was used to determine P, K, Ca, Mg, Zn, Mn, Cu, Fe, and B by an Optical Emission Spectrometry Inductively Coupled Plasma (ICP-OES) analyzing unit (Donohue and Heckendorn 1996). Exchangeable cations (Ca, Mg, and K) were extracted by 1 *M* NH_4OAc buffered at pH 7 and analyzed by atomic absorption spectrophotometry (Thomas 1982). Exchangeable Al was determined by extraction with 1 *M* KCl and analyzed by titration with 0.1 *M* NaOH to pH 7 endpoint (Barnhisel and Bertsch, 1982). Cation exchange capacity (CEC) was determined as the sum of exchangeable cations + Al or $BaCl_2$-TEA acidity. Total C and N were determined using a controllable combustion elemental analyzer (Nelson and Sommers, 1996). Particle size distribution was determined using the pipette method with removal of organic matter in certain samples by H_2O_2 (Gee and Bauder, 1986).

Statistical Analyses

Variations in properties across treatments in an experiment (RM and SA) by horizon were analyzed using a one-way analysis of variance (ANOVA) followed by Tukey's HSD test for means separation when the overall ANOVA was significant ($p<0.05$). Depth (by morphological horizon) contrasts were analyzed using paired t-tests. The Wilcoxon signed rank test was also used to due to the low sample size (n=6 per paired contrast) of these data. With few exceptions, both analyses generated similar results. A similar approach will be taken to contrast changes in soil properties at given depth vs. time (2016 vs. 1982) for each experiment and some preliminary results are presented below for the RM Experiment.

Results and Discussion

Chemical Properties: Rock Mix Experiment

Total carbon (C) and nitrogen (N) and C:N ratios for ^A and ^Bw horizons are given in Table 3. As expected, total C and N were higher in the ^A horizons versus the subsurface for all treatments ($p<0.05$) due to organic matter (OM) accumulation. The C:N ratio was higher in the ^Bw horizon compared to the surface for all treatments ($p<0.05$), reflecting higher relative levels of geogenic (coal + carbonate forms) C and lower levels of N in the much lower OM subsurface. Geogenic C also contributed to higher overall levels of C that would be expected in the surface horizons for these relatively young mine soils. In the RM experiment, siltstone spoils had higher total C contents compared to SS spoils in the ^A horizon ($p=0.065$), and the 1:1 SS:SiS and SiS spoils were also higher than SS in their ^Bw horizons ($p=0.007$). At this point, it is not clear whether this is due to higher geogenic levels in the SiS or concentration of accumulating organic matter into a much smaller fine earth fraction by volume (e.g. much higher rock fragment content). While there were no treatment differences in the surface horizons for N, the SiS spoils had higher N in their ^Bw horizons compared to SS spoils ($p=0.020$), perhaps due to relatively higher geogenic forms existing within SiS spoils. There were no treatment differences in the C:N ratio for both horizons. Much more detail on the influence of geogenic C and associated complications in interpreting OM levels in these mine soils is provided by Nash (2012).

Table 3. Total C and N and C:N ratio by treatment in ^A and ^Bw horizons in the COP Rock Mix Experiment.

Parameter	Horizon	Sandstone (SS)	1:1 SS:SiS	Siltstone (SiS)
% C	^A	3.48 ± 0.30 Ba*	4.62 ± 0.40 ABa	5.17 ± 0.50 Aa
	^Bw	0.97 ± 0.20 Bb	1.76 ± 0.1 Ab	2.09 ± 0.03 Ab
% N	^A	0.23 ± 0.03 Aa	0.31 ± 0.02 Aa	0.34 ± 0.05 Aa
	^Bw	0.04 ± 0.01 Bb	0.06 ± 0.00 ABb	0.07 ± 0.00 Ab
C:N Ratio	^A	15.2 ± 0.7 Ab	14.9 ± 0.6 Ab	15.6 ± 1.3 Ab
	^Bw	25.7 ± 0.8 Aa	27.7 ± 2.6 Aa	27.9 ± 1.2 Aa

*****Different uppercase letters denote treatment differences across a given horizon and different lowercase letters denote differences between horizon pairs with depth for a given treatment ($p<0.05$, Tukey's HSD).

Dilute acid extractable nutrients and metals are presented in Table 4. However, it is important to point out that interpretation of conventional soil testing extract data (e.g. Mehlich I) is notoriously difficult for these materials since they tend to dissolve large amounts of P and certain other elements from acid soluble cementing agents and mineral phases that are not "plant available" per se (Daniels & Amos, 1982). Thus, it is difficult to separate whether certain differences noted in this section are actually due to treatments, pedogenesis, or background weathering/mineral dissolution effects.

Acid extractable nutrients and metals in the RM experiment were generally higher in the surface ^A horizons compared to the subsurface ^Bw or cambic horizons across treatments, indicating accumulation in the surface via nutrient cycling and associated OM accumulation. For SS spoils, P, Cu, and Fe were not different between horizons, indicating that the abundance of these elements was still largely controlled by spoil type. The other major elements in SS spoils, K, Ca, Mg, Zn, Mn, B, and Al were all higher in the ^A horizon (p=0.086, p=0.004, p=0.008, p=0.005, p=0.017, p=0.006, p=0.029, respectively). For the 1:1 SS:SiS spoils, Cu and Fe were not different between horizons. Additionally, in 1:1 SS:SiS spoils, P was higher in the ^Bw horizon (p=0.033) and K, Ca, Mg, Zn, Mn, B, and Al were higher in the ^A horizon (p=0.013, p=0.015, p=0.014, p=0.004, p=0.049, p=0.065, p=0.029, respectively). For siltstone spoils, Ca, Mg, Mn, and Cu were not different between horizons. Additionally, in SiS spoils, Fe was higher in the ^Bw horizon (p=0.018) and P, K, Zn, B, and Al were higher in the ^A horizon (p=0.058, p=0.012, p=0.018, p=0.041, p=0.010, respectively).

Variations by treatment were noted for most elements in both surface (^A) and cambic (Bw) horizons, but were more common for cambic horizons as discussed below (Table 4). There were no treatment differences in the ^A horizons for K, Ca, Zn, Mn, Cu, Fe, B, and Al. In ^A horizons, P was significantly higher in SiS spoils (p=0.001) which were also higher in Mg than

SS spoils (p=0.049). There were no treatment differences in ^Bw horizons for K, Zn, Fe, and Al. However, P was higher in SS and 1:1 SS:SiS spoils (p=0.013) in Bw horizons and Ca, Mg, Mn, and B were higher in SiS spoils (p=0.002, p=0.011, p=0.001, p=0.020, respectively). For Cu, the 1:1 SiS spoils were higher than SS spoils in ^Bw horizons (p=0.044). Differences in elements by treatment are likely due to sustained weathering release from the parent rock spoils (e.g., Ca, Mg, P are higher in SiS; Daniels and Amos, 1982). Furthermore, the influence of pH and the presence of carbonate cements and rapid increases in Fe-oxides in the weathering spoils are controllers of the availability of certain nutrients and metals, particularly P. For example, low pH generally increases P solubility while carbonates and free Fe/Mn oxides will lead to P fixation at high and low pH levels, respectively (Howard et al. 1988). As stated above, these factors may explain many of the treatment differences for extractable P.

Table 4. Mehlich-1 extractable nutrients and metals by treatment and ^A and ^Bw horizons in the COP Rock Mix Experiment.

Element (mg/kg)	Horizon	Sandstone (SS)	1:1 SS:SiS	Siltstone (SiS)
P	^A	18 ± 2 Ba*	20 ± 3 Bb	39 ± 2 Aa
	^Bw	69 ± 7 Aa	54 ± 8 Aa	15 ± 11 Bb
K	^A	138 ± 53 Aa	95 ± 12 Aa	78 ± 6 Aa
	^Bw	31 ± 3 Ab	35 ± 2 Ab	40 ± 3 Ab
Ca	^A	890 ± 70 Aa	1196 ± 153 Aa	1622 ± 261 Aa
	^Bw	319 ± 69 Bb	619 ± 53 Bb	1713 ± 255 Aa
Mg	^A	227 ± 21 Ba	314 ± 30 ABa	388 ± 48 Aa
	^Bw	138 ± 14 Bb	191 ± 9 Bb	551 ± 120 Aa
Zn	^A	3.7 ± 0.1 Aa	4.7 ± 0.3 Aa	5.3 ± 0.7 Aa
	^Bw	1.3 ± 0.2 Ab	2.3 ± 0.3 Ab	2.2 ± 0.1 Ab
Mn	^A	39 ± 6 Aa	39 ± 3 Aa	56 ± 7 Aa
	^Bw	19 ± 3.7 Cb	30 ± 0.9 Bb	52 ± 0.3 Aa
Cu	^A	0.9 ± 0.1 Aa	1.3 ± 0.4 Aa	1.9 ± 0.4 Aa
	^Bw	1.1 ± 0.2 Ba	2.7 ± 0.5 Aa	2.0 ± 0.2 ABa
Fe	^A	46 ± 2 Aa	39 ± 8 Aa	36 ± 4 Ab
	^Bw	32 ± 9 Aa	41 ± 2 Aa	39 ± 4 Aa
B	^A	0.3 ± 0.0 Aa	0.3 ± 0.1 Aa	0.6 ± 0.1 Aa
	^Bw	0.1 ± 0.02 Bb	0.1 ± 0.00 Bb	0.2 ± 0.01 Ab
Al	^A	118 ± 9 Aa	98 ± 9 Aa	94 ± 3 Aa
	^Bw	74 ± 8 Ab	68 ± 1 Ab	68 ± 2 Ab

*****Different uppercase letters denote treatment differences across a given horizon and different lowercase letters denote differences between horizons for a given treatment (p<0.05, Tukey's HSD).

Saturated paste electrical conductivity (EC_e) indicates the level of soluble salts in a soil. EC_e values by treatment and horizon are given in Figure 5. There were no significant treatment differences in the ^A horizons, but SiS spoils had significantly higher EC_e in the subsurface ^Bw horizons compared to the other two treatments ($p=0.002$). Additionally, EC_e was significantly higher in ^A horizons vs. underlying Bw horizons across all rock types ($p<0.05$).

Originally, SiS spoils were less weathered than the SS spoils and contained higher levels of trace carbonates and weatherable primary minerals in finer and more reactive mineral grains. This difference in EC_e was therefore more evident in the less weathered subsurface. In contrast, original differences in ^A horizon EC_e levels due to rock type have been minimized due to 30+ years of weathering, leaching and OM accumulation processes. However, it is clear that these combined weathering and nutrient cycling processes have led to a significant accumulation in soluble salts in the surface ^A horizons. Conductivities in 2016 were relatively low when compared to known plant growth limiting levels or leachate water quality issues (e.g. TDS drainage). Future COP data analyses, as discussed later, will focus on comparing soil EC_e values to locally unmined native soils and analyzing changes in EC_e over the course of 34+ years to better understand mineral weathering and leaching dynamics.

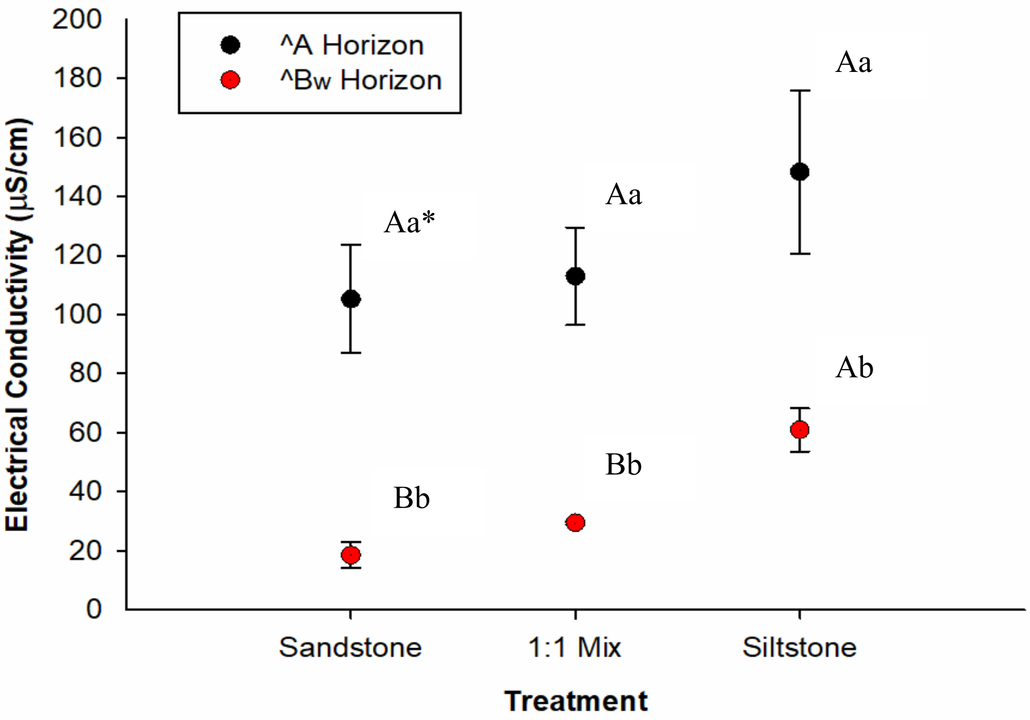

Figure 5. Saturated paste electrical conductivity (mean ± SE) by horizon and treatment in the COP Rock Mix Experiment. *Different uppercase letters denote treatment differences across a given horizon and different lowercase letters denote differences between horizons vs. depth for a given treatment ($p<0.05$, Tukey’s HSD).

Soil pH values by treatment and horizon are presented in Figure 6. Siltstone spoils had higher pH in the ^Bw horizons (p=0.001) and higher pH compared to SS spoils in the ^A horizons (p=0.0155). Soil pH was lower in the ^A horizons compared to the subsurface ^Bw horizons for the 1:1 SS:SiS spoils (p=0.030) and pure SiS soils (p=0.002). There were no differences in pH between horizons for SS spoils. As discussed above for EC, treatment differences reflect initial differences in the weathering status and carbonate content of the parent rocks. Siltstones, being less weathered originally, contained a greater amount of base cations (Ca^{2+} and Mg^{2+}) compared to the SS spoils, which were originally lower in pH due to the greater extent of leaching and oxidation within the mix of SS spoils used in 1982 to build the experiment. Over time, weatherable mineral phases in surface horizons rapidly dissolved and degraded as the surface accumulated OM due to litter deposition and rooting additions. The subsequent turnover of OM likely generated carbonic and organic acids and complexing agents that further enhanced weathering and lowered pH. This led to the larger difference in soil pH between the ^A and ^Bw horizons for the less weathered and more reactive 1:1 SS:SiS and SiS spoils vs. the SS spoils. The fact that the pH of the pure SiS spoils remained above 8.0 indicates that carbonates were still present in the material at the time of sampling, even after 30+ years of weathering and leaching.

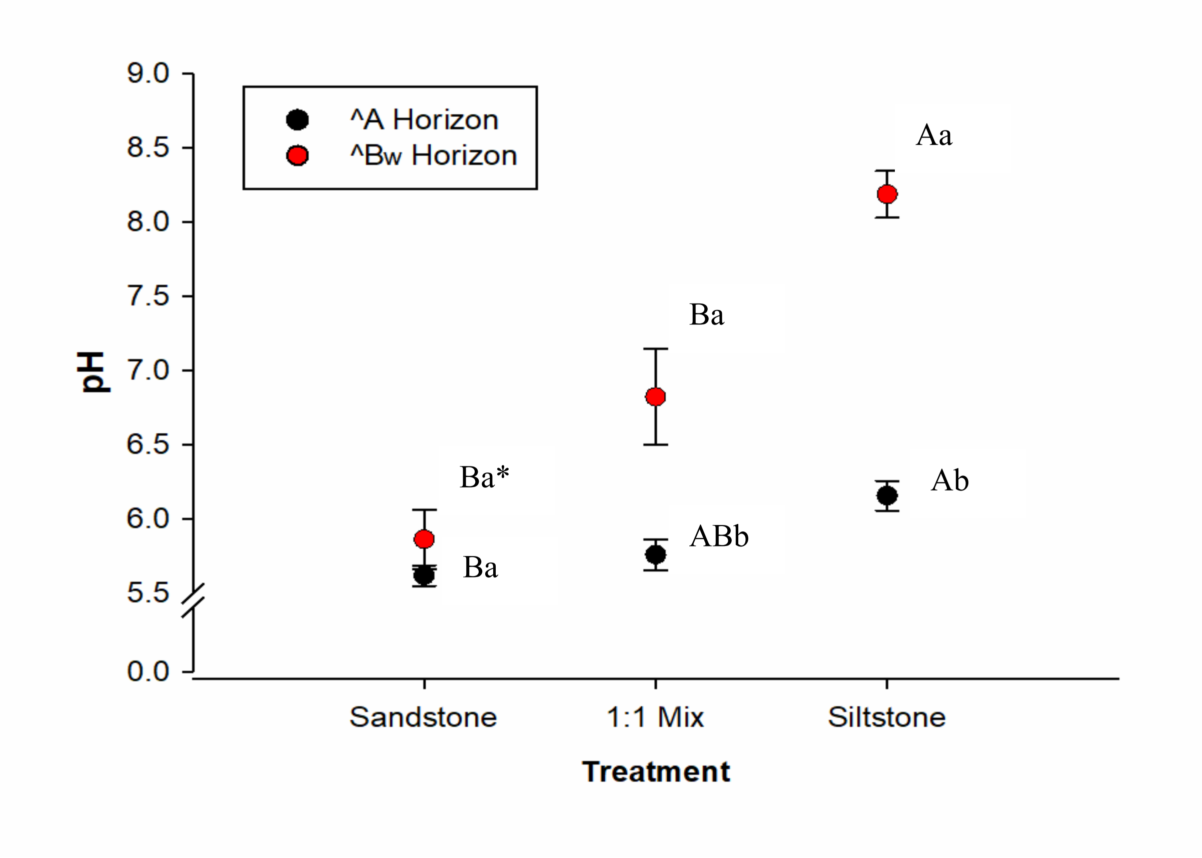

Figure 6. pH (mean ± SE) by horizon and treatment in the COP Rock Mix Experiment. *Different uppercase letters denote treatment differences across a given horizon and different lowercase letters denote differences between horizons vs. depth for a given treatment ($p<0.05$, Tukey's HSD).

Cation exchange capacity (CEC) values are shown by treatment and horizon in Figure 7. For this project, CEC was estimated as the sum of total exchangeable Ca, Mg, K, Na, and Al expressed as $cmol_c$/kg soil. CEC was higher in the ^A horizons compared to the ^Bw horizons across treatments ($p<0.05$), primarily due to OM accumulation, but weathering and accumulation of Fe-oxides and 2:1 minerals may also have affected this. Siltstone spoils were higher in CEC in the ^Bw horizons ($p=0.004$) than other spoils, most likely due to higher silt+clay content and 2:1 minerals in the silt fraction. The pH of the 1:1 SS:SiS and SiS spoils were at moderate levels (5.6-6.3) and therefore likely able to generate comparatively higher pH-dependent charges in the surface via the dissociation of H^+ from accumulating Fe-oxides and OM. However, the higher CEC in SiS spoils may be a product of the CEC method used (1 N ammonium acetate extraction), which is known to enhance dissolution of carbonates in the samples.

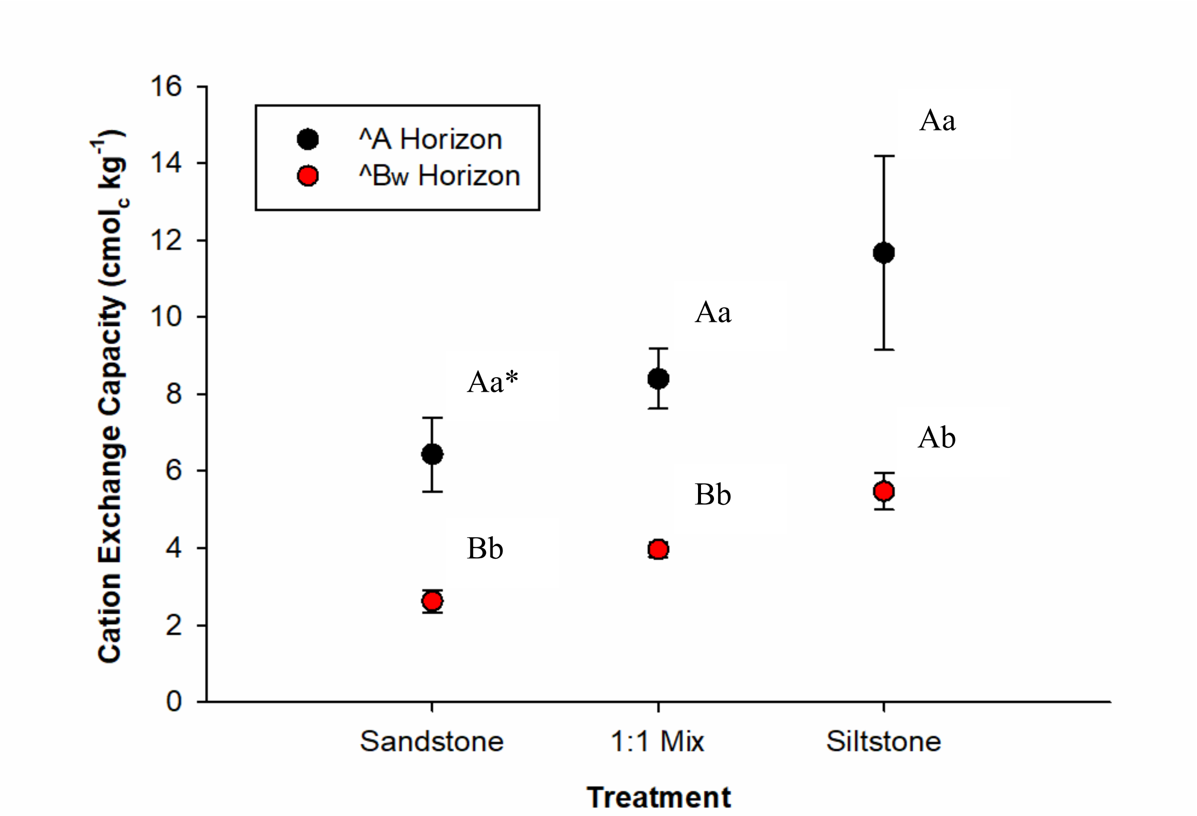

Figure 7. Cation exchange capacity (mean ± SE) by horizon and treatment in the COP Rock Mix Experiment. *Different uppercase letters denote treatment differences across a given horizon and different lowercase letters denote differences between horizons for a given treatment ($p<0.05$, Tukey's HSD).

As mentioned earlier, one of our major efforts during the current project year (2020/2021) was the statistical evaluation of changes in mine soil chemical and physical properties between the original bulk rock spoils as placed in 1982 vs. materials sampled from the same plots in 2016. An example of that effort is presented below (Fig. 8) where we compare CEC in the ^A horizons of the Rock Mix Experiment. The CEC of the 1982 materials was relatively low, as expected, but appeared to increase with SiS proportion at both dates; however, the within-treatment variation and low sample number did not allow separation at $p<0.05$. Nonetheless, the dramatic increase in CEC over time is clearly apparent, and, as discussed above, likely due to combined weathering and OM accumulation processes.

The inset photo in Figure 8 also demonstrates the difference in relative pre-weathering extent of the two spoils used in 1982. The SS spoil used in the RM experiment had a significant component of partially weathered brown materials, but did contain approximately 1/3 unweathered gray clasts that remain visible in the mine soils today (see Fig. 2). On the other hand, the SiS spoil was unweathered, gray and much higher in rock fragment vs. fine earth fraction than the original SS spoil. It is also important to point out that the SS spoil used for the SA experiment (discussed later) contained a much lower proportion of brown weathered SS and was dominantly gray, non-weathered materials.

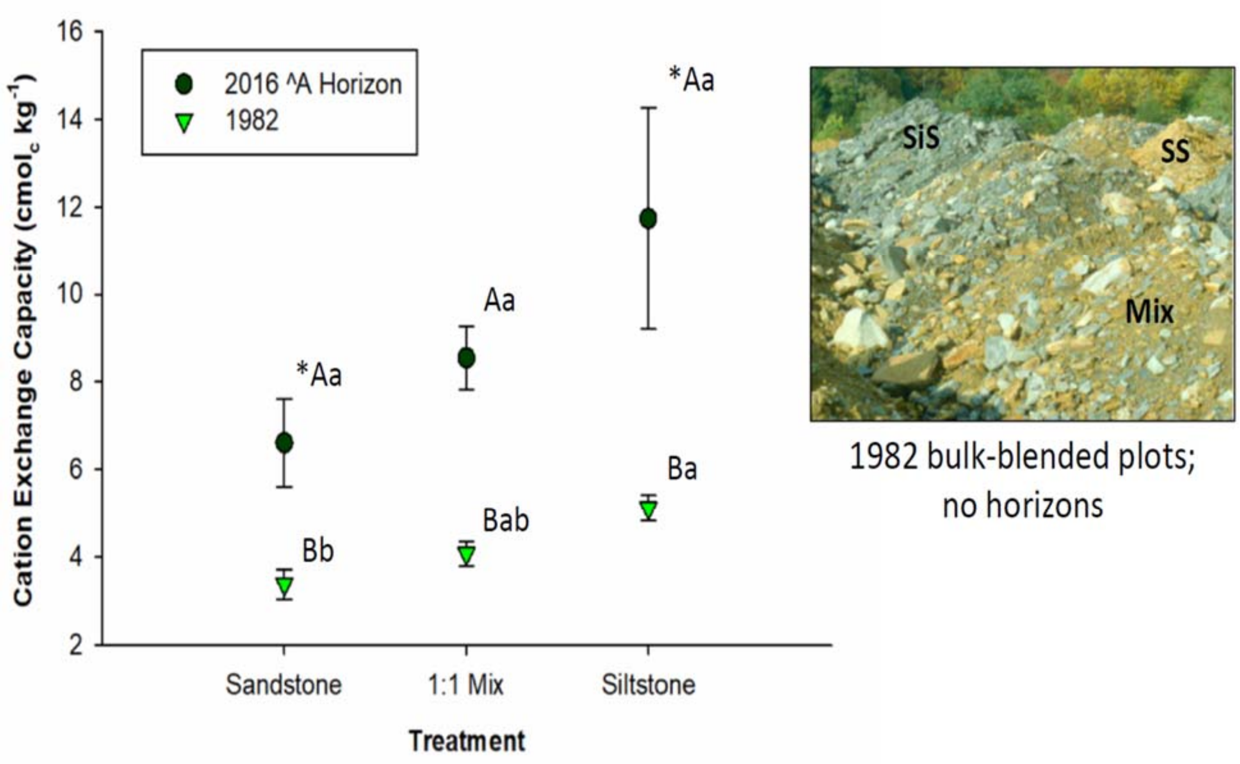

Figure 8. Cation exchange capacity (mean ± SE) in ^A horizons in 1982 vs. 2016 in the COP Rock Mix Experiment. Note the strong differences in color among the treatments due to higher "pre-weathering" of the sandstone (SS) spoils. *Different uppercase letters denote treatment differences across a given horizon and different lowercase letters denote differences between horizons for a given treatment over time ($p<0.05$, Tukey's HSD).

Chemical Properties: Surface Amendment Experiment

Total carbon (C) and nitrogen (N) and C:N ratios for major horizons in the SA experiment are presented in Table 6. Similar to the Rock Mix Experiment, C, N, and C:N ratios were significantly higher in the surface horizons compared to the subsurface horizons across treatments ($p<0.05$). The Topsoil treatment had slightly higher N content in the ^Bw horizon compared to the ^C horizon, but the difference was only moderate (p=0.076) Similarly, the Biosolids 112 Mg/ha had higher C content in the ^Bw horizon compared to the ^C horizon, but at a higher p-value (0.095). Other treatments did not differ among subsurface horizons for any parameters. However, as would be expected, C, N, and C:N ratio varied by treatment across the ^A horizons. Total C was higher in the Sawdust treatment compared to the control, while the remaining treatments were similar (p=0.030). Nitrogen was higher in the Sawdust treatment compared to the Control and Topsoil treatments (p=0.012). The C:N ratio for the Control treatment was higher than the Sawdust and both rates of biosolids (p=0.004). As discussed in detail by Nash (2012), C and N levels were very different across treatments in the ^A horizons in the early years of the experiment, but these differences were minimized over time via net C-sequestration in the Control and Topsoil treatments coupled with net losses of C back to the atmosphere from the Sawdust and Biosolids treatments.

Table 6. Total C and N and C:N ratio by treatment and ^A, ^Bw, and ^C horizons in the COP Surface Amendment Experiment.

Parameter	Horizon	Topsoil	Sawdust	Control	Biosolids 56 Mg/ha	Biosolids 112 Mg/ha
% C	^A	2.84 ± 0.16 Ba*	4.63 ± 0.17 Aa	3.86 ± 0.50 ABa	3.91 ± 0.41 ABa	3.92 ± 0.12 ABa
	^Bw	1.62 ± 0.14 Ab	1.70 ± 0.34 Ab	2.13 ± 0.10 Ab	1.42 ± 0.16 Ab	1.78 ± 0.06 Ab
	^C	1.61 ± 0.22 Ab	1.39 ± 0.16 Ab	1.70 ± 0.53 Ab	1.34 ± 0.19 Ac	1.32 ± 0.40 Ab
% N	^A	0.18 ± 0.02 Ba	0.31 ± 0.02 Aa	0.20 ± 0.03 Ba	0.27 ± 0.03 ABa	0.27 ± 0.03 ABa
	^Bw	0.05 ± 0.003 Ab	0.05 ± 0.008 Ab	0.06 ± 0.004 Ab	0.04 ± 0.005 Ab	0.05 ± 0.006 Ab
	^C	0.04 ± 0.004 Ac	0.04 ± 0.006 Ab	0.05 ± 0.012 Ab	0.04 ± 0.005 Ab	0.04 ± 0.008 Ab
C:N Ratio	^A	15.8 ± 0.96 ABa	14.7 ± 0.33 Ba	18.9 ± 0.49 Aa	14.4 ± 0.16 Ba	14.7 ± 0.94 Ba
	^Bw	35.4 ± 1.50 Ab	32.6 ± 4.97 Ab	33.1 ± 0.77 Ab	34.3 ± 1.59 Ab	35.0 ± 3.31 Ab
	^C	37.7 ± 1.45 Ab	33.5 ± 1.50 Ab	35.7 ± 2.41 Ab	33.3 ± 0.48 Ab	33.4 ± 4.55 Ab

*Different uppercase letters denote treatment differences across a given horizon and different lowercase letters denote differences between horizons for a given treatment (p<0.05, Tukey’s HSD).

With respect to acid extractable (Mehlich I) nutrients and metals in the SA experiment (Table 7), treatment differences were only noted for the ^A horizons, which makes sense given that 1982 amendments were only applied to the surface. That being said, it is notable that certain effects were still apparent after 30+ years. The lack of subsurface (^Bw and ^C) effects was due to the uniform nature of the 2:1 SS:SiS spoil used to construct all plots in the experiment. Phosphorus was higher in the Biosolids 112 Mg/ha treatment compared to the Topsoil and Sawdust treatments (p=0.050). Potassium was higher in the sawdust treatment compared to the control, but the separation was not significant (p=0.098). Similarly, Mg was also higher in the sawdust treatment compared to the Biosolids 112 Mg/ha treatment, though again the differences were not significant (p=0.095). Zinc and Cu were both significantly higher in the Biosolids 112 Mg/ha treatment compared to the Topsoil, Sawdust, and Control treatments (p=0.004 and p=0.003, respectively) due to their enrichment in the original biosolids. Iron was also higher in the Biosolids 112 Mg/ha treatment compared to the Topsoil treatment (p=0.015).

Horizon (depth) effects were noted for all treatments (Table 7). Generally, surface horizons had higher elemental contents than subsurface (^Bw and ^C) horizons. For the macronutrients, particularly for P, the Biosolids 112 Mg/ha, Control, and Topsoil treatments had higher contents in the ^A versus ^Bw horizons (p=0.077, p=0.012, p=0.094, respectively). The Biosolids 112 Mg/ha treatment also had higher P in the ^Bw versus the ^C horizons (p=0.0248), indicating some downward migration of the original high P biosolids materials and/or leaching of complex P forms. As expected, both biosolids treatments had higher P in the ^A vs. ^C horizons (p=0.081 and p=0.053, respectively). For K, all treatments (Topsoil, Control, Biosolids 56 Mg/ha, and Biosolids 112 Mg/ha) had higher contents in the ^A vs. ^Bw horizons (p=0.044, p=0.024, p=0.076, p=0.019, and p=0.050, respectively). The Topsoil and Biosolids 56 Mg/ha treatments had significantly higher K in the ^C versus ^Bw horizons (p<0.05). The Topsoil, Sawdust, and Biosolids 56 Mg/ha treatments had higher K in the ^A vs. ^C horizons (p=0.058, p=0.017, and p=0.016, respectively). Calcium contents were significantly higher in the ^A versus ^Bw horizons for both biosolids treatments and the Sawdust and Topsoil treatments (p<0.05). Topsoil had higher Ca in the ^C versus ^Bw horizons (p=0.070). All treatments except the control had significantly higher Ca in the ^A versus ^C horizons (p<0.05), and the Mg extractable levels were significantly higher in the surface ^A horizons compared to the two subsurface horizons (p<0.05). The Biosolids 56 Mg/ha and Topsoil treatments had higher Mg content in ^C versus ^Bw horizons (p=0.069 and p=0.067, respectively). Most of these differences were clearly due to differences in the original organic treatments applied and relative weathering and nutrient release with depth over time. However, it is important to reiterate that the dilute double acid extractant used here is unreliable as an index of relative plant availability due to its differential attack on carbonates and other acid soluble minerals in these still relatively non-weathered spoil materials.

For the extractable metals (Table 7), Zn contents were higher in the surface ^A horizons compared to the two subsurface horizons for the Sawdust and both Biosolids treatments (p<0.05) due to enrichment in the original amendments. The Control had higher Zn content in the ^Bw versus ^C horizons (p=0.059). For Mn, levels were higher in the ^A versus ^Bw horizons for the Sawdust and Biosolids 112 Mg/ha treatments (p=0.063 and p=0.072, respectively). The Topsoil and Biosolids 56 Mg/ha treatments had higher Mn levels in the ^Bw vs. ^C horizons (p=0.054 and p=0.032, respectively). Furthermore, the ^A horizons were higher in Mn compared to the ^C horizons for the Topsoil, Sawdust, Control, Biosolids 56 Mg/ha and Biosolids 112 Mg/ha treatments (p=0.054, p=0.008, p=0.010, p=0.097, and p=0.018, respectively). For Cu, the 56 and 116 Mg/ha Biosolids treatments had higher levels in the ^A vs. ^Bw horizons (p=0.084 and p=0.084, respectively). The Control had higher Cu in the ^Bw vs. ^C horizons (p=0.029), and

Table 7. Mehlich-1 extractable nutrients and metals by treatment and ^A, ^Bw, and ^C horizons in the COP Surface Amendment Experiment.

Element (mg/kg)	Horizon	Topsoil	Sawdust	Control	Biosolids 56 Mg/ha	Biosolids 112 Mg/ha
P	^A	24 ± 12 Ba	26 ± 2 Ba	34 ± 1 ABa	37 ± 7 ABa	91 ± 30 Aa
	^Bw	45 ± 5 Ab	37 ± 10 Aa	55 ± 3 Ab	39 ± 4 Aa	39 ± 8 Ab
	^C	40 ± 3 Aab	38 ± 5 Aa	46 ± 15 Aab	30 ± 4 Ab	33 ± 11 Ab
K	^A	64 ± 12 AB a	86 ± 13 Aa	49 ± 10 Ba	63 ± 4 ABa	50 ± 2 ABa
	^Bw	27 ± 0.5 Ac	31 ± 0.3 Ab	27 ± 1.4 Ab	27 ± 4.3 Ac	33 ± 3.9 Ab
	^C	34 ± 1 Ab	30 ± 2 Ab	36 ± 5 Aab	32 ± 3 Ab	110 ± 68 Aab
Ca	^A	779 ± 91 Aa	1292 ± 34 Aa	962 ± 253 Aa	1082 ± 152 Aa	1087 ± 105 Aa
	^Bw	607 ± 58 Ac	502 ± 58 Ab	562 ± 34 Aa	558 ± 29 Ab	563 ± 92 Ab
	^C	628 ± 63 Ab	511 ± 30 Ab	576 ± 119 Aa	575 ± 9 Ab	537 ± 95 Ab
Mg	^A	208 ± 21 ABab	296 ± 15 Aa	228 ± 31 ABa	232 ± 25 ABab	202 ± 20 Ba
	^Bw	197 ± 14 Aa	186 ± 9 Ab	188 ± 6 Aa	182 ± 11 Aa	202 ± 16 Aa
	^C	223 ± 25 Ab	176 ± 8 Ab	200 ± 15 Aa	196 ± 5 Ab	200 ± 7 Aa
Zn	^A	2.7 ± 0.1 Ba	5.5 ± 0.4 Ba	3.8 ± 0.8 Bab	10.6 ± 2.5 ABa	20.1 ± 5.1 Aa
	^Bw	2.6 ± 0.2 Aa	2.3 ± 0.2 Ab	2.4 ± 0.3 Aa	2.4 ± 0.2 Ab	3.2 ± 0.6 Ab
	^C	2.8 ± 0.04 Aa	2.2 ± 0.3 Ab	2.0 ± 0.4 Ab	2.1 ± 0.4 Ab	2.6 ± 0.7 Ab
Mn	^A	32 ± 6 Aa	42 ± 2 Aa	36 ± 10 Aa	28 ± 5 Aa	24 ± 3 Aa
	^Bw	27 ± 1 Aa	26 ± 5 Ab	25 ± 2 Aab	21 ± 2 Aa	18 ± 4 Ab
	^C	22 ± 2 Ab	22 ± 4 Ab	19 ± 4 Ab	15 ± 2 Ab	15 ± 2 Ab

Table 7 (continued). Mehlich-1 extractable nutrients and metals by treatment and ^A, ^Bw, and ^C horizons in the COP Surface Amendment Experiment.

Element (mg/kg)	Horizon	Topsoil	Sawdust	Control	Biosolids 56 Mg/ha	Biosolids 112 Mg/ha
Cu	^A	0.9 ± 0.4 Ba	1.4 ± 0.3 Ba	1.7 ± 0.2 Bab	2.5 ± 0.5 ABa	4.1 ± 0.5 Aa
	^Bw	1.7 ± 0.1 Aa	1.8 ± 0.1 Aa	1.9 ± 0.1 Aa	1.6 ± 0.1 Ab	2.1 ± 0.6 Ab
	^C	1.6 ± 0.2 Aa	1.4 ± 0.1 Aa	1.3 ± 0.3 Ab	1.5 ± 0.2 Aab	1.5 ± 0.4 Ab
Fe	^A	35 ± 4 Ba	51 ± 9 ABa	51 ± 15 ABab	84 ± 11 ABa	100 ± 16 Aa
	^Bw	44 ± 4 Aa	40 ± 7 Aa	45 ± 1 Ab	38 ± 2 Ab	37 ± 9 Ab
	^C	43 ± 2 Aa	39 ± 7 Aa	30 ± 7 Aa	32 ± 4 Ac	33 ± 8 Ab
B	^A	0.17 ± 0.05 Aa	0.33 ± 0.02 Aa	0.27 ± 0.14 Aa	0.24 ± 0.06 Aa	0.25 ± 0.03 Aa
	^Bw	0.09 ± 0.02 Ab	0.08 ± 0.01 Ab	0.06 ± 0.01 Aa	0.07 ± 0.01 Ab	0.08 ± 0.01 Ab
	^C	0.08 ± 0.02 Ab	0.07 ± 0.02 Ab	0.07 ± 0.02 Aa	0.10 ± 0.03 Aab	0.07 ± 0.01 Ab
Al	^A	85 ± 11 Ba	125 ± 13 Ba	99 ± 17 Ba	160 ± 21 ABa	241 ± 45 Aa
	^Bw	79 ± 9 Aa	73 ± 4 Ab	62 ± 4 Aab	67 ± 5 Ab	64 ± 8 Ab
	^C	72 ± 11 Aa	70 ± 6 Ac	57 ± 2 Ab	65 ± 7 Ab	65 ± 6 Ab

*Different uppercase letters denote treatment differences across a given horizon and different lowercase letters denote differences between horizons for a given treatment ($p<0.05$, Tukey's HSD).

The Biosolids 112 Mg/ha treatment had higher Cu in the ^A vs. ^C horizon ($p=0.001$). For Fe, the 56 and 112 Mg/ha Biosolids treatments were higher in the ^A vs. ^Bw horizons ($p=0.018$ and $p=0.061$, respectively) and in the ^A vs. ^C horizons ($p<0.05$). The Control and Biosolids 56 Mg/ha treatments had higher Fe in the ^Bw vs. ^C horizons ($p=0.090$ and $p=0.092$, respectively). For boron (B), the Topsoil, Sawdust, and 56 and 112 Mg/ha Biosolids treatments had higher levels in the ^A vs. ^Bw horizons ($p=0.065$, $p=0.008$, $p=0.035$, and $p=0.019$, respectively). Topsoil, Sawdust, and the 112 Mg/ha Biosolids treatments had higher B in the ^A vs. ^C horizons ($p=0.099$, $p=0.008$, and $p=0.022$, respectively). For Al, the Sawdust and 56 and 112 Mg/ha Biosolids treatments were higher in the ^A vs. ^Bw horizons ($p<0.05$). Sawdust was higher in Al in the ^Bw versus ^C horizons ($p=0.096$). Iron was higher in the ^A vs. ^C horizons for the Sawdust, Control, and 56 and 112 Mg/ha Biosolids treatments ($p=0.048$, $p=0.068$, $p=0.027$, and $p=0.023$, respectively).

Soil pH, EC_e, and CEC did not significantly differ between treatments for any given horizon (Table 8). There were, however, significant depth effects for each parameter. For example, the ^A horizons were all significantly lower in pH compared to the subsurface horizons ($p<0.05$), likely due to the organic matter turnover and leaching processes discussed earlier. Also, ^C horizons were higher in pH compared to the ^Bw horizons in the RM experiment for the same reasons. For soil EC_e, the ^A horizons were all significantly higher compared to the subsurface horizons ($p<0.05$) due to OM accumulation and salt concentration related to nutrient cycling. For CEC, the ^A horizons were higher than the ^Bw horizons for the Topsoil, Sawdust, Biosolids 56 and 112 Mg/ha treatments ($p=0.076$, $p=0.085$, $p=0.006$, and $p=0.071$, respectively). There were no differences between the ^Bw and ^C horizons. For the Biosolids 56 Mg/ha treatment, the ^A horizon was higher in CEC compared to the ^C horizon ($p=0.0030$), while there were no A vs. C horizon effects for the remaining treatments.

Table 8. Soil pH, saturated paste electrical conductivity (EC_e), and CEC by treatment and ^A, ^Bw, and ^C horizons in the COP Surface Amendment Experiment.

Parameter	Horizon	Topsoil	Sawdust	Control	Biosolids 56 Mg/ha	Biosolids 112 Mg/ha
pH	^A	5.2 ± 0.20 Ac*	5.1 ± 0.15 Ac	5.5 ± 0.13 Ac	5.1 ± 0.15 Ac	5.2 ± 0.04 Ab
	^Bw	7.2 ± 0.26 Ab	6.6 ± 0.34 Ab	6.8 ± 0.16 Ab	7.3 ± 0.07 Ab	7.0 ± 0.54 Ab
	^C	7.7 ± 0.23 Aa	7.4 ± 0.20 Aa	7.5 ± 0.25 Aa	7.8 ± 0.12 Aa	7.7 ± 0.06 Aa
EC_e (μs/cm)	^A	199 ± 29 Aa	322 ± 86 Aa	147 ± 26 Aa	252 ± 28 Aa	208 ± 46 Aa
	^Bw	29 ± 3 Ab	30 ± 4 Ab	31 ± 2 Ab	33 ± 4 Ab	28 ± 6 Ab
	^C	29 ± 3 Ab	25 ± 1 Ab	27 ± 5 Ab	28 ± 1 Ab	27 ± 3 Ab
CEC[ǂ] ($\text{cmol}_c\ \text{kg}^{-1}$)	^A	9.4 ± 1.8 Aa	12.5 ± 4.4 Aa	9.5 ± 3.1 Aa	15.2 ± 1.2 Aa	8.6 ± 1.8 Aa
	^Bw	4.8 ± 0.2 Ab	4.9 ± 0.8 Ab	4.9 ± 0.6 Aa	5.0 ± 0.3 Ab	4.0 ± 0.2 Ab
	^C	6.5 ± 3.0 Aab	5.4 ± 0.7 Aab	8.4 ± 4.0 Aa	5.0 ± 0.4 Ab	8.6 ± 3.7 Aab

*Different uppercase letters denote treatment differences across a given horizon and different lowercase letters denote differences between horizons for a given treatment with depth ($p<0.05$, Tukey's HSD).
[ǂ] Cation exchange capacity (CEC) is the sum of total exchangeable Ca, Mg, K, Na, and Al.

Particle Size Analysis (Soil Texture)

Soil texture by treatment and horizon in the Rock Mix Experiment is reported in Table 9. For SS spoils, the sand content was lower in the A^ horizon ($p=0.047$) and silt content was higher ($p=0.058$) than the pure SiS treatments. For sand content in the ^A horizons, SS was higher than SiS spoils ($p=0.034$). In the ^Bw horizons, sand was highest in the SS spoils followed by the 1:1 SS:SiS and SiS spoils ($p<0.05$). The reverse trend was true for silt contents – the SiS spoils had higher silt compared to SS spoils in the ^A horizons ($p=0.023$) and in the ^Bw horizons, silt was highest in the SiS spoils followed by the 1:1 SS:SiS and SS spoils ($p<0.001$). There were no differences in clay content between horizons or treatments, but there is a numerical difference that was not significant at ($p<0.05$). Thus it is clear that after 30+ years, differences in sand and silt contents are still strongly linked to the original parent rock materials, even in the fine earth fraction. It is also likely that the SS and SiS coarse fragments (> 2 mm) are physically weathering to release more sand and silt sized particles, respectively, at a faster rate than the release/neoformation of clay sized minerals. Furthermore, there may be greater physical weathering occurring within surface horizons of the SS spoils, due to their more pre-weathered nature of the original SS spoils (see Fig. 8).

Table 9. Particle size analysis on the fine earth fraction (< 2 mm) by treatment in ^A and ^Bw horizons in the COP Rock Mix Experiment.

Soil Separate	Horizon	Sandstone (SS)	1:1 SS:SiS	Siltstone (SiS)
% Sand	^A	66 ± 1 Ab*	59 ± 4 ABa	43 ± 7 Ba
	^Bw	73 ± 1 Aa	58 ± 1 Ba	37 ± 1 Ca
% Silt	^A	23 ± 1 Ba	28 ± 3 ABa	43 ± 6 Aa
	^Bw	16 ± 1 Cb	29 ± 2 Ba	49 ± 1 Aa
% Clay	^A	11 ± 1 Aa	13 ± 2 Aa	14 ± 1 Aa
	^Bw	11 ± 1 Aa	13 ± 1 Aa	14 ± 0 Aa

*Different uppercase letters denote treatment differences across a given horizon and different lowercase letters denote differences between horizons for a given treatment ($p<0.05$, Tukey's HSD).

In the SA Experiment, differences in sand, silt, and clay were evident by treatment (applied to a 2:1 SS:SiS rock mix) and by horizons with depth within a given treatment (Table 10). For sand, there were no treatment differences in the ^Bw or ^C horizons due to the uniform nature of the original 2:1 SS:SiS spoil utilized and lack of weathering at depth. However, for the surface ^A horizons, Topsoil was significantly higher in sand content in the ^A horizon (p=0.001) due to the sandy nature of the originally applied materials. For the silt fraction, Topsoil also had significantly higher levels in the ^A horizon compared to the Sawdust and Control treatments (p=0.010). There were no differences in silt content across the ^Bw and ^C horizons. There were few differences in silt and clay content across treatments, but some minor differences were observed with depth, particularly between ^A and ^C horizons as discussed further below. These results reconfirm that the greatest differences in texture are expected to occur in the ^A horizons where different surface amendments were applied to a 2:1 SS:SiS rock mix, thus leaving the subsurface relatively homogenous across the various amended treatment plots.

Table 10. Particle size analysis on the fine earth fraction (< 2mm) by treatment and depth in ^A, ^Bw, and ^C horizons in the COP Surface Amendment Experiment.

Soil Separate	**Horizon**	**Topsoil**	**Sawdust**	**Control**	**Biosolids 56 Mg/ha**	**Biosolids 112 Mg/ha**
% Sand	^A	69 ± 1 Aa	58 ± 1 Bb	59 ± 1 Bb	63 ± 1 Bb	61 ± 1 Ba
	^Bw	65 ± 1 Aa	65 ± 2 Aa	61 ± 1 Aa	66 ± 2 Ab	61 ± 1 Aa
	^C	66 ± 1 Aa	65 ± 2 Aa	64 ± 3 Aab	68 ± 2 Aa	65 ± 2 Aǂ
% Silt	^A	20 ± 1 Bb	30 ± 3 Aa	29 ± 1 Aa	25 ± 2 ABab	26 ± 1 ABa
	^Bw	24 ± 1 Aa	24 ± 3 Aab	28 ± 1 Aa	24 ± 1 Aa	26 ± 2 Aa
	^C	25 ± 0 Aa	23 ± 1 Ab	26 ± 4 Aa	22 ± 1 Ab	25 ± 2 Aǂ
% Clay	^A	11 ± 0 Aa	12 ± 1 Aa	12 ± 2 Aab	12 ± 1 Aa	13 ± 1 Aa
	^Bw	10 ± 0 Ab	11 ± 0 Aa	11 ± 1 Aa	11 ± 1 Ab	13 ± 1 Aa
	^C	9 ± 1 Ac	11 ± 1 Aa	10 ± 1 Ab	10 ± 1 Ab	10 ± 0 Aǂ

*****Different uppercase letters denote treatment differences across a given horizon and different lowercase letters denote differences between horizons by depth for a given treatment (P ≤ 0.05, Tukey’s HSD).
ǂNot enough sample to conduct a paired test for depth contrasts.

For the Topsoil treatment, differences among horizons were evident only for silt and clay textural separates (Table 10). Silt content was higher in the subsurface (A vs. Bw p=0.085; A vs. C p=0.041). Overall, clay content differed with depth among all horizons (A vs. Bw p=0.002; Bw vs. C p=0.072; A vs. C p=0.020). For the Sawdust treatment, differences among horizons were evident only for sand and silt. The sand content was higher in the subsurface (A vs. Bw p=0.086; A vs. C p=0.008) and silt content was higher in the surface (A vs. C p=0.043). For the Control treatment, differences among horizons were evident only for sand and clay. Sand content was higher in the ^Bw horizon versus the ^A horizon (p=0.062) and clay content was higher in ^Bw horizon versus the ^C horizon (p=0.056). For the Biosolids 56 Mg/ha treatment, differences among horizons were evident for all textural separates: the ^C horizon had higher sand content than the ^A and ^Bw horizons ($p<0.05$), the ^Bw horizon had higher silt content than the ^C horizon (p=0.084), and the surface ^A horizon had clay higher content than both subsurface horizons ($p<0.05$). Collectively, these differences and trends may reflect the texture of the initial surface amendment and how it influenced weathering over time (e.g., Topsoil and 56 Mg/ha Biosolids showed higher differences in clay content with depth).

Summary of Changes in Mine Soil Properties Over Time

Generally, nutrients, metals, and C and N contents were higher in the surface ^A horizons compared to the subsurface horizons across treatments. These trends were similar for both the RM and SA experiments. Organic matter accumulation and the effects of higher biological activity in the surface has significantly influenced pH (lower), soluble salts (higher), and CEC (higher) in the ^A horizons. Certain treatment effects are more evident in the RM experiment, mainly due to the degree of initial weathering of overburden materials (i.e., SS spoils being more pre-weathered versus SiS spoils in 1982). Subsurface soil properties (^Bw and ^C) within each experiment are much more similar to the original parent materials while surface soil (^A) properties tend to be more uniform in 2016 than 1982 across spoil rock types in the RM experiment due to weathering, OM accumulation and pedogenesis . In the SA experiment, treatment effects were only evident for a few extractable nutrients/metals in the ^A horizons, particularly P. The Sawdust treatment had higher K than the control, the Biosolids 112 Mg/ha treatment was higher in P than the other surface amendments (i.e., Topsoil/Sawdust), while the Biosolids 112 Mg/ha treatment was higher in Cu, Fe, and Al. Soil texture in the RM experiment was clearly still controlled by the original spoil rock type in both the surface and subsurface horizons. For the SA experiment, surface soil (^A) texture was influenced by the different amendments, particularly the topsoil addition. Only minor variations in subsurface texture (^Bw and ^C horizons) were observed in the SA experiment.

Ongoing Laboratory and Data Analyses

Time Comparison of Soil Properties

One ongoing goal of the COP research program is to conduct a statistical analysis using historical and recent datasets to assess changes in mine soil properties over time and to determine a relative rate of weathering. This work is currently in progress. Select incremental samples from the soil pits in 2016 are currently being analyzed in our laboratories for dithionite-citrate-bicarbonate–extractable Fe to allow comparisons to historical data sets. Additionally, we are analyzing selected 10 cm depth increment samples from the 2016 soil pits (rather than by horizon) for 1:1 soil:water pH and electrical conductivity, extractable nutrients, total C and N, cation exchange capacity, and particle size analysis. Additional C samples that were not originally processed (from the RM side) are also being analyzed, and will be compared to previous ^C horizon datasets.

In particular, data from the 20-30 cm incremental samples from the 2016 pits will allow us to directly compare soil properties to subsurface (25-30 cm) data from 1982, 1983, and 1985. While these are not the exact same depths, they align most closely. Samples taken at the surface in 2016 (^A horizons and 0-10 cm incremental samples) will be compared to historical datasets for the surface 0-5 cm that was sampled consistently in the past (i.e., 1982, 1983, 1985, 1987, 1988, and 2008). Morphological horizon data from 2016 is also being compared to morphological data from May 1983, October 1985, and August 1989. The statistical methods for these temporal contrasts will be a repeated measures analysis of variances which will allow us to compare parameters at multiple dates (sampling year). The approach is set up similarly to a paired t-test in the sense that data are compared on a paired plot-by-plot basis to minimize covariance issues.

Bulk Density Laboratory Procedure

In 2016, a few dozen intact clod samples (3 to 4 cm diam.) were carefully sampled from the subsurface of various rock mix and surface amendment pits where intact aggregates were available. Over the 2020/2021 year, we will assess bulk density on these clods using the coated clod method, which is based on Archimedes' principle. This method works by immersing a coated clod in a known density of liquid and recording clod weights before and after submersion to determine the volume of the displaced liquid along with the displacement weight differential, and thus the clod density (Blake and Hartage, 1986). Clods may be sealed in substances such as saran and wax mixtures to waterproof the samples. For this method, we are using paraffin as the coating substance as it is more readily available. To correct for rock fragments, we are using the removal procedure outlined in Hirmas and Furquim (2006), who used a similar coated clod method on rocky soil samples. Compact and rocky natural soil clods will be used initially to practice the method. Bulk density data via the clod method exists from the 1980s and is currently being assessed. This data will be numerically compared to values derived from the 2016 clod samples.

TDS Release Over Time by a SW Virginia Sandstone Spoil – Mesocosm Results

In December of 2012, we initiated a field mesocosm study (Ross, 2015) focused on determining the multi-year total dissolved solids (TDS) elution behavior of a typical SW Virginia sandstone mine spoil (Harlan Fm.) in comparison to our column leaching method prediction method (Orndorff et al., 2015; Daniels et al., 2016; Clark et al., 2018.). To accomplish this, we constructed large "leaching tanks" (mesocosms; see Fig. 9) at the Virginia Tech Turfgrass Research Center (VTRC) in Blacksburg and filled them bulk fresh mine spoil collected from the Harlan Formation at the Red River Coal active mine above the Powell River Project field site. This stratum is similar to the unweathered SS component originally utilized for the COP experiment, but occurs higher in the stratigraphic column. The bulk spoils were loaded by hand into the mesocosms and barrels (Fig. 9) to assess the relative influence of size consist on TDS leaching behavior vs. original column predictions as described in our last Annual Report. Materials placed into the barrels were < 15 cm in diameter, while all materials up to ~50 cm in diameter were loaded into the mesocosms. Leachates were drained from below the mesocosms into separate belowground receiving containers and sampled monthly during the winter leaching season and/or following major precipitation events during the growing season. Local rainfall was also collected for analysis. All samples were analyzed for pH and SC in our labs within several hours of field collection.

Figure 9. Harlan spoil leaching mesocosms (left) and barrels (right foreground) at Virginia Tech Turfgrass Research Center (VTRC) in November 2012. Leachates were collected monthly or following significant precipitation events and analyzed for pH and specific conductance. Ion composition was also monitored periodically (not reported here).

In general, analysis of the collective leachate pH data (through 2018) produced by the lab columns matched up well against that observed in the field from both the barrels and mesocosms (Fig. 10) when compared by leachate volumes produced. Similar to many SW Virginia unweathered spoils, these materials are high in pH, most likely due to trace carbonates and other reactive alkaline weathering components like feldspars and metamorphic lithic fragments (Clark et al., 2018). The pH vs. time behavior for the mesocosms (Fig. 11) through early fall 2020 reveals a continuing strong seasonal effect, with pH (and presumably total alkalinity) increasing in the cooler winter months through 2019, most likely due to the slight but positive effect of decreasing temperature on pH, CO_2 partial pressures, and the associated carbonate/bicarbonate equilibrium. The drop in pH over the first two years of the local rainfall (labeled as “blank” in figures) is notable and more than likely indicates that some neutralization must have occurred in the rainwater collection system due to an unknown interaction with the plastic barrels utilized.

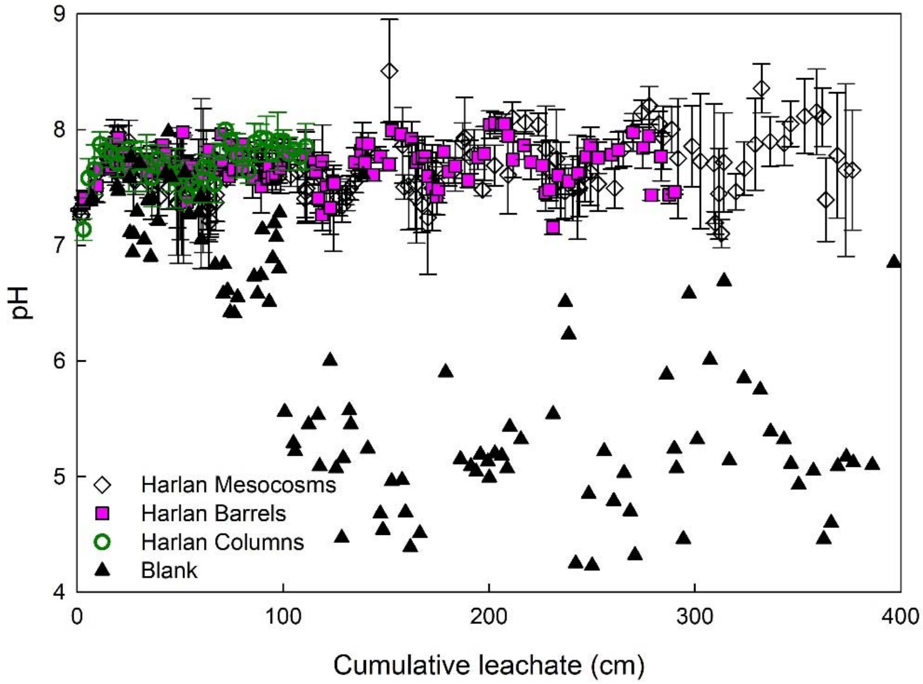

Figure 10. Leachate pH vs. cumulative volume (through 2018) for Harlan mesocosms, barrels and columns. The column technique only evaluated 40 x 2.5 cm leaching cycles. Blank refers to an onsite, and presumably clean, barrel collecting ambient rainfall.

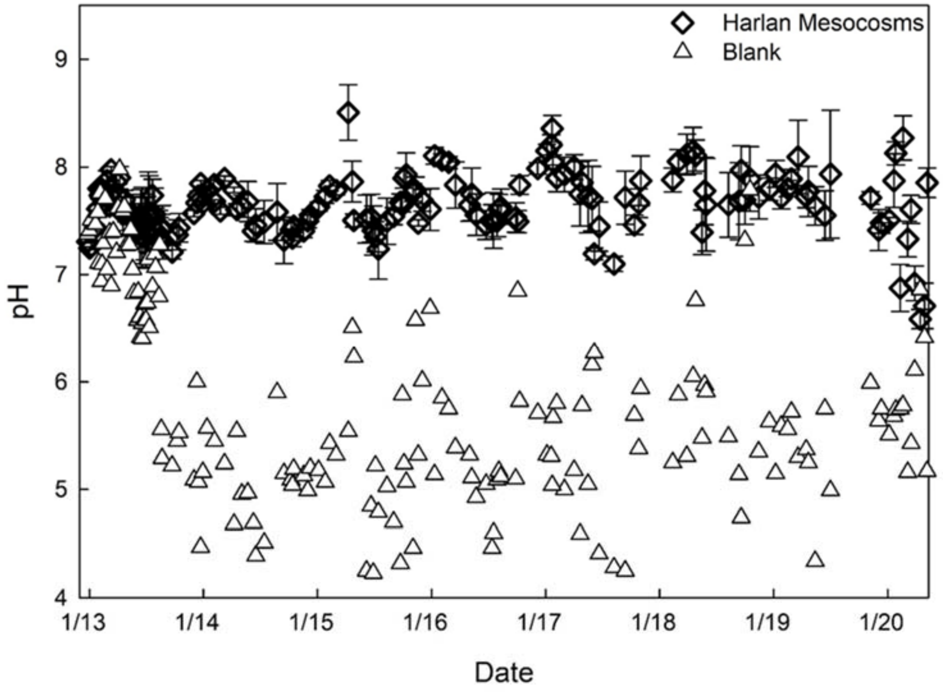

Figure 11. Leachate pH vs. time for the Harlan mesocosms through early fall 2020. Note the pH drop in late 2020 along with the high variability in ambient rainfall pH (4.2 to > 7.0). Blank refers to an onsite, and presumably clean, barrel collecting ambient rainfall.

The longer term rainfall pH ranged from 4.5 to 6.5 as expected. The pH data from 2020 also appear to indicate a significant decrease in pH over the summer months indicating that the inherent neutralizing capacity of the spoil may be finally depleted.

The influence of leaching scale/method on measured SC (Fig. 12) indicates that, while the lab column method did predict the overall shape and initial high vs. longer term SC elution behavior of this spoil, it did not concur with the first winter's seasonal spike as noted in the field barrels and mesocosms (Fig. 13). The longer-term data set indicates that (a) leachate EC/SC fell to ~ 300 µs/cm by the end of the second full year of leaching, but that (b) the seasonal winter increase continued to occur through 2018, with lower amplitude each year. However, it is interesting to note that the winter high SC observed in 2019/2020 and the early fall of 2020 (Fig. 12) subsequently increased relative to previous years, which could indicate the onset of more rapid acid metal hydrolysis reactions (Fe and Mn) as the spoils continued to weather and leach, while at the same time neutralizers were depleted and pH dropped (as discussed above). It is important to note that the mesocosms have been kept unvegetated, so organic matter turnover reactions are not responsible for any changes in pH or SC.

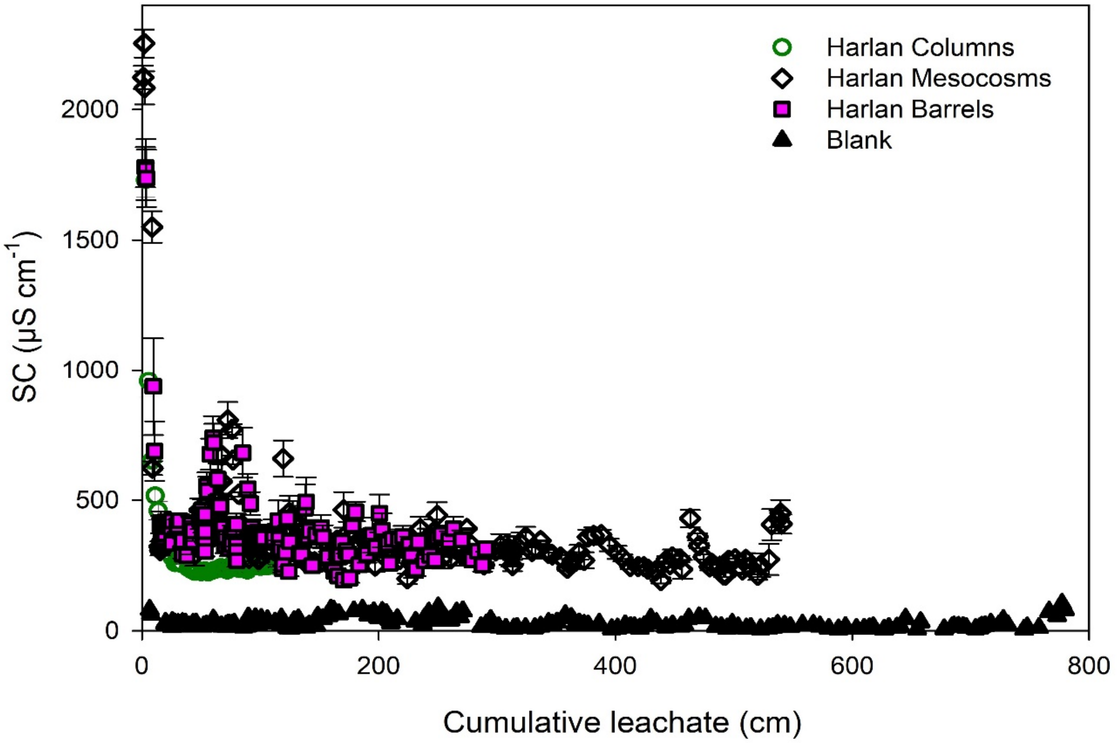

Figure 12. Leachate SC vs. volume for Harlan mesocosms through mid-2020. The column technique only evaluated 40 leaching cycles. Blank refers to an onsite, and presumably clean, barrel collecting ambient rainfall.

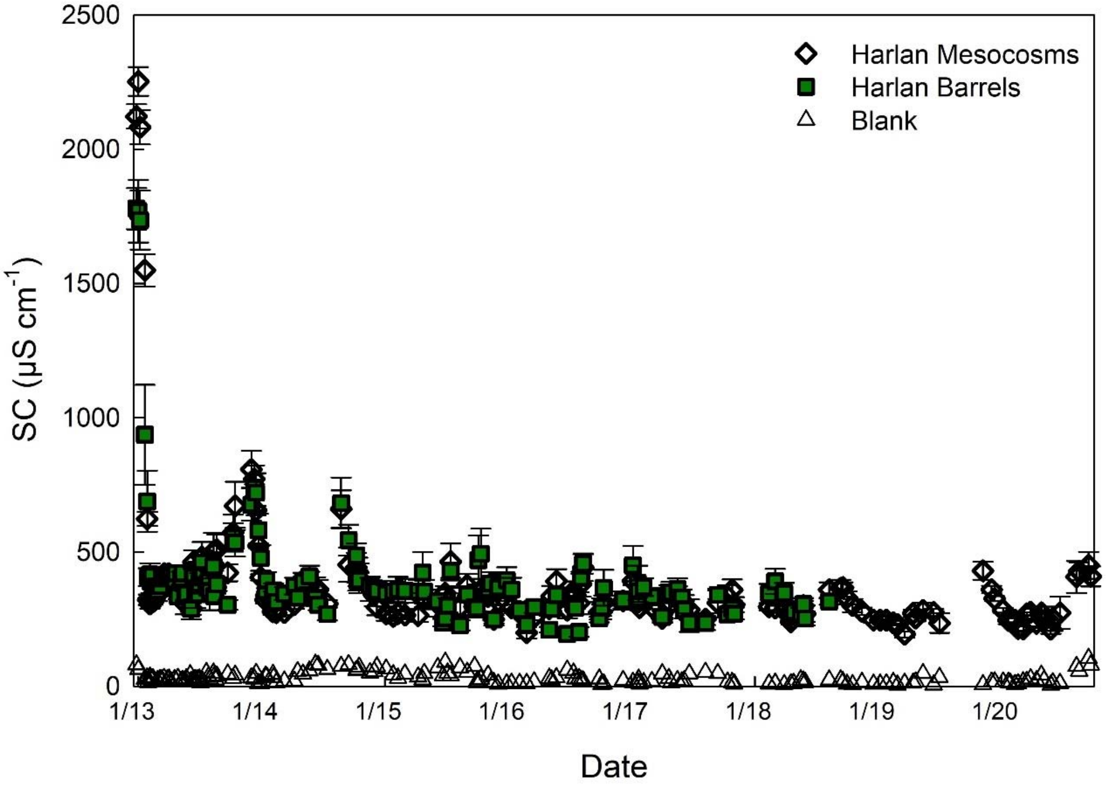

Figure 13. Leachate SC over time volume for Harlan mesocosms through mid-2020. Column technique only evaluates 40 leaching cycles. Blank refers to an onsite, and presumably clean, barrel collecting ambient rainfall.

The relatively large increase in SC over the first full winter leaching season (2013/2014) may indicate that mechanisms other than simple CO_2 partial pressure and carbonate/bicarbonate equilibrium may be involved. It is likely that highly reactive feldspars and other oxidizers and hydrolyzed mineral surfaces generated reaction salts that accumulated over the drier preceding summer months. These salts then dissolved and were flushed from the system under much wetter winter leaching conditions. This process would also account for the diminishing "winter flush" observed over time as highly reactive phases were consumed.

Finally, the fact that the long-term average SC for the mesocosm leachates dropped below 350 µs/cm over time has important regulatory implications as current federal/state guidance and related PRP research findings (Timpano et al., 2018) for TDS release from Appalachian coal mines indicates that 350 µs/cm is an important threshold for limiting impacts to aquatic macroinvertebrates. That being said, recent increase in late fall/winter leachate SC may temper that finding.

Overall Summary and Conclusions

Once we have completed all final physical and chemical analyses on the primary morphological horizon and depth increment samples, we will statistically evaluate them to reconfirm the extent of chemical and physical weathering in these materials over the past 30+ years. However, our detailed morphological studies, coupled with physical and chemical lab analyses to date, clearly indicate that significant pedogenesis has occurred over a relatively short period in these mine soils, resulting in well-developed profiles, including readily discernible cambic (^Bw) subsoil horizons. Thus, while the vast majority of these soils were classified as Entisols by U.S. Soil Taxonomy in the 1980s, they would now all be classified as Inceptisols.

The long-term influence of varying surface treatments (topsoil, sawdust and biosolids) is still readily apparent in the surface ^A horizons of these mine soils, but does not appear to have consistently affected subsoil morphology or physical/chemical properties. While the influence of long-term weathering and leaching on the surface horizons is clear, deeper (e.g. > 75 cm) spoil materials appear to be very similar to original 1982 unweathered spoil properties. Our more detailed analysis of chemical and physical properties over this reporting period clearly reinforces our conclusion that while initial spoil properties dominate surface mine soil quality with respect to plant growth in young soils (e.g. < 15 yr.), organic matter accumulation coupled with significant physical and chemical weathering processes tends to lessen initial parent material influences and leads to more homogenous ^A horizons over the longer term studied here.

The finding that significantly more compact and apparently root-limiting subsoil layers appear to be forming in these mine soils via combined pedogenic processes over a decadal timeframe is an important and novel finding. To our knowledge, this result has not been reported in the USA scientific literature to date, but has been noted in a different mining/spoil environment in Wales (UK), albeit in much more weatherable and fissile shales and coal refuse materials. Recognizing this process may be important for developing management practices (e.g. ripping for forest establishment) on older mined lands, even where rough grading and other initial soil reconstruction practices to limit compaction were followed originally.

The combined results from our previously reported COP column leaching studies and the long-term (8-year) Harlan spoil leaching mesocosms confirm that while our lab column protocol appears to be a relatively accurate predictor of peak vs. long-term leachate specific conductance (SC; proxy for TDS), it probably under-predicts peak seasonal ion release events in younger reactive materials. It is also notable that even though analyses of the mesocosm leaching data over a six year period indicated a consistent and gradual overall decline in TDS elution to levels lower than the presumed 350 µs/cm critical level for instream biotic effects, more recent data indicates the potential for a subsequent rebound in SC and associated lower pH levels.

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