2020-2021 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 for both forestry and forages 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 had formed to depths > 10 cm and most subsoils contained moderately well-developed cambic ^Bw horizons. Surface horizons in general have declined in pH, while exchangeable bases, and acid-extractable cations increased over time (> 30 years). However, the surface soils do show evidence of bioaccumulation of cations and associated higher levels of electrical conductance (soluble salts) vs. subsoil horizons. The long-term influence of sawdust and biosolids additions in the surface treatment experiment is still apparent in darker colors and stronger aggregation 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 (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 important changes over time (1982 to 2016) in the chemical and physical properties of the mine soils in the Rock Mix (RM) and Surface Amendment (SA) experiments. Our last report (February, 2021) presented summary treatment and depth effects on physical and chemical data on these 30+ year-old mine soils. In this report, we summarize important findings regarding changes with time between original bulk mine soils sampled in the spring of 1982 vs. the samples taken from our detailed soil pits in the fall of 2016 from selected treatments.

Overall time, most spoil types generally decreased in sand content while silt + clay content increased, but initial spoil type still controlled mine soil texture after 30+ years. Other temporal trends were similar between experiments, such as the fact that pH generally decreased in the surface with time, while CEC increased due to the accumulation of organic matter over time. Additionally, simple paired t-tests showed that electrical conductivity (EC) dropped in the subsurface across all RM and SA plots due to long-term sustained leaching effects. However, the original EC values were maintained in the surface due to the effects of plant cation-cycling concentrating base cations (Ca, K and Mg) and other compounds. Also, there was an overall increase in Fe-oxides and a decrease in extractable P over time. Interestingly, a moderately strong relationship was found between surface Fe-oxides and P contents in the RM Experiment, but we did not include 2016 data due to a difference in laboratory methods for measuring P (Olsen vs. Mehlich I extract). These data may indicate a long-term negative influence of accumulating Fe-oxides on P-availability. This Fe vs. P correlation did not hold for the SA Experiment due to high variability in extractable P in the surface due to the relatively heavy initial loadings of organic amendments (e.g., biosolids and sawdust).

Our estimated net C-sequestration rates for the 34-year period were relatively low (~0.2 to 0.3 Mg ha^{-1} $year^{-1}$) compared to other literature reports from similar mined and undisturbed sites. This is presumably due to the relatively small mass (< 30% by volume) of soil sized (< 2mm) particles in these soils associated with their relatively coarse texture. The data also indicate that the fertilized 2:1 SS:SiS control plots had reached SOC levels similar to heavily organic amended treatments largely through normal long-term C-sequestration processes while the organic amendment plots lost CO_2 back to the atmosphere.

The combined results from the COP column leaching studies coupled with the long-term (9-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). Combined detailed leaching results from 2020 and 2021 indicate that the "seasonal bump" may be decreasing in amplitude as these materials continue to weather, but may have actually increased slightly. 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 small increase in leachate SC from the mesocosms demands that such estimates be made with caution.

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 maintain their overall productivity potentials beyond the requisite five-year performance liability period is also questioned by many.

Progress to Date and Future Research Plans

Our current research 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 through 2018 Annual Reports (https://powellriverproject.org/reports/) and we completed all primary physical and chemical analyses of those soil samples as reported in our 2019/2020 and 2020/2021 Reports.

During the second and third years (2017/2018 and 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 utilized a portion of those funds to continue the 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 fortunate again to receive funds for 2020/2021, 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 for statistical comparisons. We also continued periodic monitoring of pH and SC from the leaching mesocosms at the VTRC. Those results were reported in last year's (Feb. 2021) Annual Report available at https://powellriverproject.org/reports/.

Additional work completed in the past year (2020/2021), included (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 vs. older clod data from the mid 1980's. We also analyzed and contrasted the 1982 vs. 2016 soil chemical and physical data sets. This includes completing 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., 2022/2023) we will focus on a more comprehensive field evaluation of the subsoil compaction features in these soils along with an overall assessment of vegetation and surface soil (0-5 cm) properties in what would then be 40 year-old plots.

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 in relation to plant growth productivity potentials.

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 (Fig. 1), 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 (15- 20 cm), 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 documented rooting patterns and depths. 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. Intact clod samples were extracted from visibly root limiting subsoil layers for bulk density analysis. 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 last year's 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). In the past reporting year (2020/2021) we completed remaining lab analyses for C forms, EC (soluble salts) and extractable Fe- and Mn-oxides. We also focused on statistical analyses of important changes in mine soil properties over time (1982 vs. 2016).

Results and Discussion

Overall Mine Soil Morphology and Interpretations of Pedogenesis

In past 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 earlier reports for those detailed analyses and interpretations. One additional mine soil profile example from the 2016 soil pit studies appears in Figure 2. We also provided summaries of physical and chemical properties in the 2016 samples.

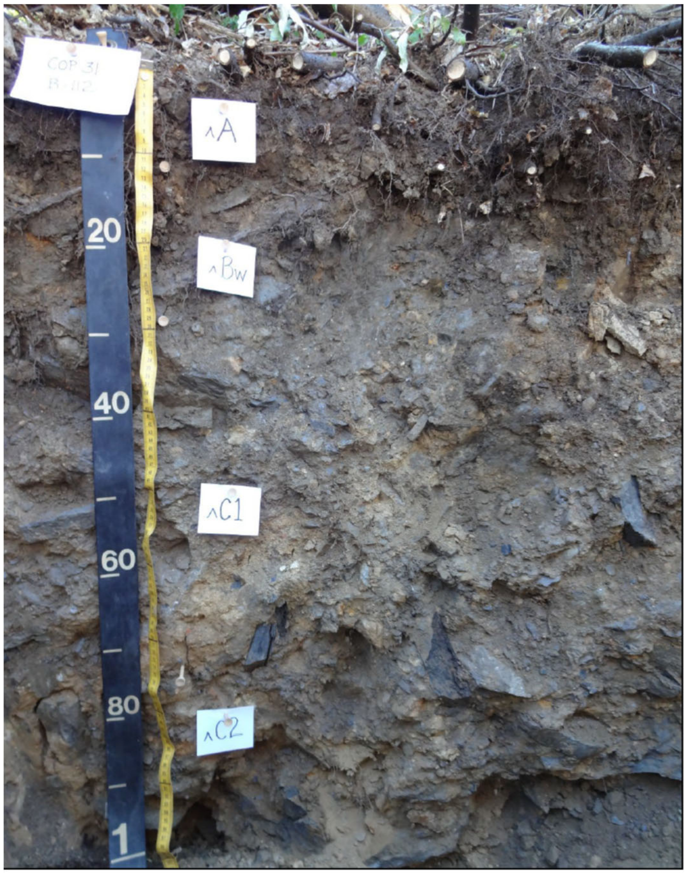

Figure 2. Soil profile from 112 Mg ha^{-1} biosolids treated plot in the Surface Amendment Experiment in the Fall of 2016. Details on overall soil morphology and pedogenesis available in previous Annual Reports https://powellriverproject.org/reports/.

Overview of Temporal Change Analyses

Here we report changes of important mine soil chemical and physical properties as affected by rock type and surface amendments over a period of 34 years. Our goal was to assess long-term soil properties to better understand the rate of weathering processes and soil transformation. Temporal changes were emphasized in the surface soil, where the greatest amount of weathering is expected to occur. We also report clod bulk densities and extractable Fe-oxides across major horizon depths for the 2016 and older mine soil samples since these data have not yet been presented. This study included mine soils from three sandstone (SS) and three siltstone (SiS) treatments within the Rock Mix (RM) experiment, and five treatments from the Surface Amendment (SA) experiment (Table 1).

Table 1. Treatments for RM and SA Experiments. **Bold** indicates treatments sampled in 2016.

RM Experiment Treatment	**Composition**	**Fertilizer†**
Sandstone (SS)	100% SS	N, P, K
2:1 SS:SiS	67% SS: 33% SiS	N, P, K
1:1 SS:SiS	50% SS: 50% SiS	N, P, K
1:2 SS:SiS	33% SS: 67% SiS	N, P, K
Siltstone (SiS)	100% SiS	N, P, K
SA Experiment Treatment	**Composition**	**Other Additions**
Control (No Amendment)	67% SS: 33% SiS	N, P, Kł
Topsoil* (30 cm)	67% SS: 33% SiS	N, P, K + 7.8 Mg ha^{-1} Ag lime
Sawdust (112 Mg ha^{-1})	67% SS: 33% SiS	N, P, K + 336 kg ha^{-1} IBDU^{+}
Biosolids (22.4 Mg ha^{-1})	67% SS: 33% SiS	None
Biosolids (56 Mg ha^{-1})	67% SS: 33% SiS	None
Biosolids (112 Mg ha^{-1})	67% SS: 33% SiS	None
Biosolids (224 Mg ha^{-1})	67% SS: 33% SiS	None

†1120 kg ha^{-1} of 15-30-15 dry fertilizer initially, and 56 kg NH_4NO_3 ha^{-1} annually for three years.

*Includes a mixture of A, E, B, C, and Cr native soil horizons.
$^{+}$Isobutyldiene Diurea, a slow-release N fertilizer.

Methods and Materials

Historical Datasets

Soil surface (0-5 cm) and subsurface (25-30 cm) properties in previous datasets share the same depth intervals, except for the May 1982 bulk samples, which reflected the entire profile (raw untreated spoils). The 2016 morphological ^A horizons ($\bar{x}$ = ~10 cm) were used for analyzing changes over time vs. earlier observations in the 1980's. While the 2016 depth intervals do not exactly match depths used in previous years (i.e., 0-5 cm), they are reasonably similar and were the data available for time comparison analyses. May 1982 archived bulk samples were reanalyzed for EC to compare to the 2016 horizon data, and for soil organic carbon (SOC) to measure accumulation rates over 3 years. To document changes over time for important soil surface (0-10 cm) properties, we used the following datasets: Spring (May) and fall (October) of 1982 and in 1983, 1984, 1987, 2008, and 2016. If one of these years is not featured in the results presented below, it indicates unavailable data for that year. Unless otherwise noted, soil analytical methods outlined below match the methods used for historical COPE datasets in 1982-1984 (Roberts et al. 1988 a,b), 1987 (Haering et al. 1993), and 2008 (Nash et al. 2016).

Laboratory Analyses

Cohesive intact clods were analyzed using a modification of the saran-coated clod method (Shipp and Matelski 1965). Since saran resin is in limited supply, we modified the clod bulk density method by Blake and Hartge (1986) using paraffin wax as the coating substance. Coated clods are immersed in a known density of liquid and clod weights were recorded before and after submersion to determine the volume of the displaced liquid and the displacement weight differential, and thus the clod density. The procedure by Hirmas and Furquim (2006) was used to correct for rock fragments. Clods previously collected from COPE SA plots in 1983 had been partially calculated for bulk density and results were finalized for this study. The 1983 values were numerically compared to 2016 bulk densities. Particle size distribution was determined using the pipette method with removal of high organic matter in certain samples by H_2O_2 (Gee and Bauder 1986). EC was determined in a 1:2 soil:water ratio with a conductivity meter calibrated to a standard 0.01 *M* KCl solution for the May 1982 archived bulk and 2016 horizon samples (Rhoades 1996). Extractable P data were analyzed by 0.5 *M* $NaHCO_3$ at pH 8.5 (Olsen and Sommers 1982). Soil pH was measured in a 1:1 soil:water slurry with a glass-calomel combination electrode (McLean 1982). Exchangeable cations (Ca, Mg, K, Na) were extracted by 1 *M* NH_4OAc buffered at pH 7, and analyzed by atomic absorption spectrophotometry (Thomas 1982). Exchangeable Al which 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). Effective cation exchange capacity (CEC) was determined as the sum of exchangeable cations + Al, and percent base saturation was calculated as the quantity of exchangeable bases divided by CEC. Fe-oxides were extracted using sodium dithionite-citrate-bicarbonate and measured by atomic absorption spectrophotometry (Mehra and Jackson 1960).

Soil organic matter (SOM) was determined using the Walkley-Black method (Walkley and Black 1934) via wet oxidation (Nelson and Sommers 1996). Total-C was determined using a controllable combustion Elementar^{tm} elemental analyzer (Nelson and Sommers 1996). Inorganic C (carbonates) sources were removed using HCl acid fumigation (Harris et al. 2001). To estimate SOC in 2016, we assumed that there was still a significant coal fragment error in these mine soils after 34 years due to the recalcitrant nature of coal. To account for geogenic C sources, we analyzed the bulk May 1982 (pre-treatment application) samples to derive total-C minus carbonate-C, thus representing the "coal-C", assuming the original 1982 samples were devoid of any initial native accumulated organic C. These coal-C values from 1982 were then subtracted from the total-C minus carbonate-C in the 2016 ^A horizon samples, thus representing SOC in the surface. This procedure assumes that the relatively high rank coal fragments/fossils in the spoils are highly refractory and not subject to biological degradation over time. To scale up corrected C values from percent, or mg kg^{-1}, to mass per area (g C per m^2), we used the 0-5 cm soil fines (g) data by Nash (2012) that were volumetrically sampled using a 0.093 m^2 (1.0 ft^2) quadrat given the assumption that there were no appreciable volumetric x mass differences in soil fines between 2008 and 2016. Since the estimated soil fines data by Nash (2012) were based on 0-5 cm samples, the 2016 ^A horizons were adjusted on a plot-by-plot basis (e.g., we doubled fines for 10 cm horizons). Sequestration rates were calculated by dividing corrected SOC stocks by 34 years, assuming a linear sequestration rate, and are reported as Mg C ha^{-1} year^{-1}.

Statistics

All analyses were performed in JMP Pro software (JMP®, Version *15.1* SAS Institute Inc., Cary, NC, 1989-2019). To verify assumptions of normality and homogeneity of variance, visual and formal diagnostics were used. Significant differences were interpreted using an alpha = 0.05 for all analyses outlined below. A mixed model that included a random effect for plots was used to determine differences with depth and included major morphological horizon (uppermost ^A, ^Bw, and lowermost ^C) as the fixed effect and plot ID as the random effect, followed by Tukey's HSD test. To analyze the effects of time on surface soil properties by treatment, a mixed model was used, including main effects (year and treatment), an interaction term (treatment x year), and a random effect (plot ID), followed by Tukey's HSD test. Paired t-tests were used for EC time contrasts between the 2016 horizon samples (^A, ^Bw, ^C) and the May 1982 bulk samples. SigmaPlot® 12.5 software was used for curvilinear regression analyses between soil parameters.

Current Soil Properties Related to Pedogenesis

This section reports data that was not covered in the last report and highlights properties (i.e., clod subsoil bulk densities and Fe-oxides) that support morphological field observations and early signs of pedogenesis. In summary, changes over time included: 1) Rock fragments decreased in size and total volume, particularly in the surface; 2) large bridging voids decreased in size and occurrence due to internal spoil self-collapse and weathering; 3) soil structure advanced to stronger grades in both surface and subsurface horizons (e.g., weak subangular blocky, or sbk, progressing into moderate sbk); and, 4) soil color values and chromas were generally lower (i.e., darker) in the ^A horizons, and were generally higher (i.e., brighter) in the ^Bw horizons, particularly for SS-derived mine soils. Figure 3 depicts temporal changes using the pure SiS plots as an example.

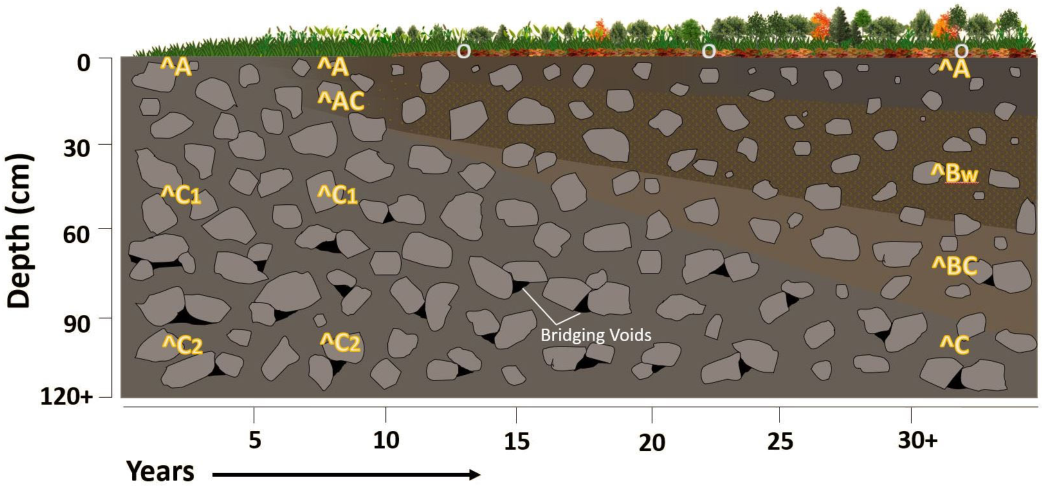

Figure 3. Graphical depiction of long-term morphological development in 100% SiS derived mine soils at the COPE based on detailed soil descriptions made in 1983, 1985, 1989, and 2016.

In earlier reports (1983 to 1984), some evidence of subsoil compaction was noted, but it generally did not limit rooting depth and was presumed to be a result of final plot grading. Compacted zones also were noted in 1985 and 1989, but these observations were generally for the deeper C horizons and not noted as root-limiting. However, in the 2016 profile descriptions, at least one or more subsoil horizon (^Bw and ^C) across the majority of pits were noted as having a higher bulk density relative to overlying and underlying horizons. Overall rooting was restricted in these layers and, where it occurred, was concentrated only along rock fragment faces. Intact cohesive clod samples in 1983 and 2016 were collected in subsoil horizons (25 to 50 cm depths) using similar laboratory methods. Rock-corrected densities in 2016 were 1.26 to 1.61 g cm^{-3}. Clod bulk densities in 2016 were generally higher than clod bulk densities in 1983 when compared numerically on a plot-by-plot basis (Table 2), but were not statistically different due to small sample numbers and variability.

Densification (>1.8 g cm^3) through natural processes has been observed in shale-derived mine soils in Great Britain (Haigh 1992a; Haigh 1992b). Rapid (within 1-year) physical settling of rock-derived mine soils was also documented in Kentucky (Miller et al. 2012). Common large “bridging voids”, or air-filled open gaps between overlapping rock fragments, were documented in earlier (1983 and 1985) profile descriptions at the COPE. We hypothesize that physical weathering of overlying spoil materials, aided by wet-dry and freeze-thaw cycles, led to the well-documented weathering and slaking of rock fragments into soil sized particles. This was then followed by the preferential flow of mixed particle sizes into bridging voids of lower horizons, leading to eventual self-collapse and settling. We further hypothesize that this downward mass movement of fines likely occurred following major precipitation or snowmelt events where ephemeral saturated flow conditions could drive mass slurry flows. Over time, physical settling of spoils presumably filled or reduced the size of bridging voids, while still allowing for the continued infilling and subsequent concentration of finer soil particles in subsoil macropores via percolating waters. Since there were no apparent chemical binding agents in 2016 profiles, the

Table 2. Whole soil and fine earth fraction (< 2 mm) bulk density in 1983 and 2016.

Treatment/ Plot No. ƚ	**1983**		**2016**	
	Whole Soil*	**Fine Earth**	**Whole Soil***	**Fine Earth**
	Bulk density (g cm^{-3})			
Sandstone (SS) #1	-	-	2.04	1.34
1:1 SS:SiS #2	-	-	1.99	1.26
Siltstone (SiS) #9	-	-	2.06	1.38
Topsoil #24	-	-	2.00	1.49
Sawdust #25	1.96	1.42	1.93	1.45
Control #26	1.87	1.45	1.97	1.61
Bios^{+} 56 Mg ha^{-1} #28	1.88	1.27	-	-
Bios 112 Mg ha^{-1} #30	-	-	1.98	1.48
Bios 112 Mg ha^{-1} #31	-	-	2.05	1.52
Bios 112 Mg ha^{-1} #32	-	-	1.91	1.37
Bios 56 Mg ha^{-1} #33	-	-	2.04	1.55
Bios 56 Mg ha^{-1} #34	1.99	1.68	1.92	1.43
Sawdust #35	-	-	1.80	1.41
Control #36	-	-	2.03	1.39
Topsoil #39	1.88	1.18	1.94	1.37
Control #43	-	-	1.94	1.42
Sawdust #44	-	-	1.82	1.34
Topsoil #46	-	-	2.04	1.39
Bios 56 Mg ha^{-1} #47	-	-	2.09	1.52
Overall Mean†	**1.92**	**1.40**	**1.96**	**1.45**

ƚAverage of two clods per plot in 1983 and a single clod value per plot in 2016;
*Includes soil-sized fraction (< 2 mm) and hard mass rock fragments;
†Mean includes SA experiment only;
$^{+}$Biosolids treatment loading rate.

limited amount of finer clay sized soil particles along with simple interparticle attraction must be serving as physiochemical bridging agents among the tightly packed coarse silt and sand grains, creating an overall dense fabric arrangement.

Goethite (α-FeOOH) is common in the Wise Formation overburden rock strata existing as a single phase or a complex mixture with other minerals such as hematite and magnetite (Howard et al. 1988). The SS derived soils had higher extractable Fe-oxides (Table 3) in their ^Bw horizons compared to other rock types. Higher extractable Fe-oxides were likely due to its somewhat pre-weathered nature as described earlier relative to the gray reduced SiS strata. Compared to other rock types, the SS soils were more vibrant with yellowish brown grain coatings. Depth effects were only evident in the SS spoils, where ^Bw horizon had higher Fe-oxides compared to the ^A horizons, suggesting that Fe-oxides forming within upper horizons had been translocated downward. Slight color differences (e.g., higher value and chroma) were evident in ^Bw horizons vs. underlying or overlying horizons, particularly for the SS spoils. Since soil structure (sbk) was more defined in the cambic ^Bw horizons of SS spoils versus in soils of other rock types, it is possible that Fe-oxides improved aggregation. Also, the sandier textures of SS spoils may have facilitated the movement of Fe-oxides relative to the much siltier SiS textures. In the SA experiment, Fe-oxides were generally lower in the surface and higher in the ^Bw and ^C horizons, except for the sawdust treatment, which had no depth effects. The control had the highest percentage of Fe-oxides compared to the topsoil and two biosolids treatments. Differences were likely a result of pre-weathering influences (i.e., control vs. topsoil) and the influences from the high organic sawdust and biosolids treatments influencing Fe extractability.

Changes in Chemical and Physical Properties Over Time

Soil texture, extractable Fe-oxides and P, pH, CEC, and SOM changed significantly with time, and with the exception of P, were significantly affected by rock spoil type (i.e., treatment; Table 4). Sand and silt contents, Fe-oxides, pH, and CEC showed treatment x year interaction effects, indicating that the relative effect of time on a given parameter was not consistent across rock types for all years; in other words, relative differences varied from year-to-year. For the SA Experiment, soil texture, extractable Fe-oxides and P, pH, CEC, and SOM all significantly changed with time (by year main effects; see Table 5). These parameters were also significantly affected by the treatment main effect, with the exception of clay contents. Sand and silt contents, Fe-oxides, pH, CEC, and SOM showed treatment x year interaction effects. For both the RM and SA Experiments, mean separations for all soil parameters by model level are presented in Appendix A.

Overall time effects across treatments generally showed that sand contents decreased and silt + clay contents increased within both experiments, indicating that the original SS and/or SiS parent material drives changes in soil texture with time. Other temporal trends were similar between experiments, such as pH generally decreasing in the surface with time, while CEC increased due to the accumulation of organic matter. Also, there was an overall increase in Fe-oxides and decrease in extractable P over time. Interestingly, a moderately strong relationship was found between surface Fe-oxides and P contents in the RM Experiment (Fig. 4), though we did not include 2016 data due to a difference in laboratory methods for measuring P (bicarbonate vs. Mehlich extract). These data suggest the negative influence of ferruginous mine spoils on limiting P-availability over time. This Fe vs. P correlation did not hold for the SA Experiment due to high P variability in the surface due to heavy organic amendments (e.g., biosolids and sawdust).

Additionally, simple paired t-tests showed that electrical conductivity (EC) dropped in the subsurface across all RM and SA plots due to long-term sustained leaching effects. However, EC values were maintained in the surface over time due to the effects of plant cation-cycling concentrating base cations and other compounds. Differences in EC values between 2016 and 1982 for both experiments are depicted in Figure 5.

Table 3. Extractable Fe-oxides by RM and SA treatment and major morphological horizon.

	Extractable Fe-oxides (%)		
Major Horizon	**Rock Mix Treatment**		
	Sandstone (SS)	1:1 SS:SiS	Siltstone (SiS)
^A	1.81 ± 0.04 Ab*	1.68 ± 0.11 Aa	1.49 ± 0.07 Aa
^Bw	2.40 ± 0.08 Aa	1.85 ± 0.18 Ba	1.54 ± 0.08 Ba
^C	2.10 ± 0.13 Aab	1.82 ± 0.25 Aa	1.50 ± 0.07Aa

	Surface Amendment Treatment				
	Control	Topsoil	Sawdust	Biosolids 56 Mg ha^{-1}	Biosolids 112 Mg ha^{-1}
^A	2.18 ± 0.06 Ac*	1.85 ± 0.01 Bb	2.05 ± 0.06 ABa	1.90 ± 0.04 Bb	1.86 ± 0.06 Bb
^Bw	2.33 ± 0.05 Ab	2.46 ± 0.10 Aa	2.50 ± 0.06 Aa	2.22 ± 0.09 Aa	2.42 ± 0.17 Aa
^C	2.46 ± 0.03 ABa	2.62 ± 0.08 Aa	2.56 ± 0.15 ABa	2.23 ± 0.01 Ba	2.45 ± 0.03 ABa

*Mean ± SE. Different uppercase letters denote treatment differences across a given horizon and different lowercase letters denote differences among horizons within a given treatment ($P \leq 0.05$).

Table 4. Mixed model p-values for selected mine soil properties in the surface at the Rock Mix Experiment.

Model Source	**Sand**	**Silt**	**Clay**	**Fe-oxides**	**P**	**pH**	**CEC**	**SOM**
	(%)				mg kg^{-1}		cmol$_c$ kg^{-1}	(%)
Year	**<0.0001***	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**
Treatment	**<0.0001**	**<0.0001**	**0.0003**	**0.0023**	0.1211	**<0.0001**	**<0.0001**	**0.0001**
Year x Treatment	**0.0242**	**0.0166**	0.2222	**0.0142**	0.4829	**0.0020**	**0.0049**	0.5806

***Bold** font represents significant differences by parameter x model level ($P \leq 0.05$).

Table 5. Mixed model p-values for selected mine soil properties in the surface at the Surface Amendment Experiment.

Model Source	**Sand**	**Silt**	**Clay**	**Fe-oxides**	**P**	**pH**	**CEC**	**SOM**
	-------------------- (%) -----------------------				mg kg^{-1}		cmol$_c$ kg^{-1}	-- (%)--
Year	**<0.0001 ***	**<0.0001**	**0.0007**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**
Treatment	**<0.0001**	**<0.0001**	0.1199	**0.0035**	**<0.0001**	**<0.0001**	**<0.0001**	**0.0001**
Year x Treatment	**<0.0001**	**0.0014**	0.5203	**0.0072**	**<0.0001**	**<0.0001**	**<0.0001**	**0.0005**

***Bold** font represents significant differences by parameter x model level ($P \leq 0.05$).

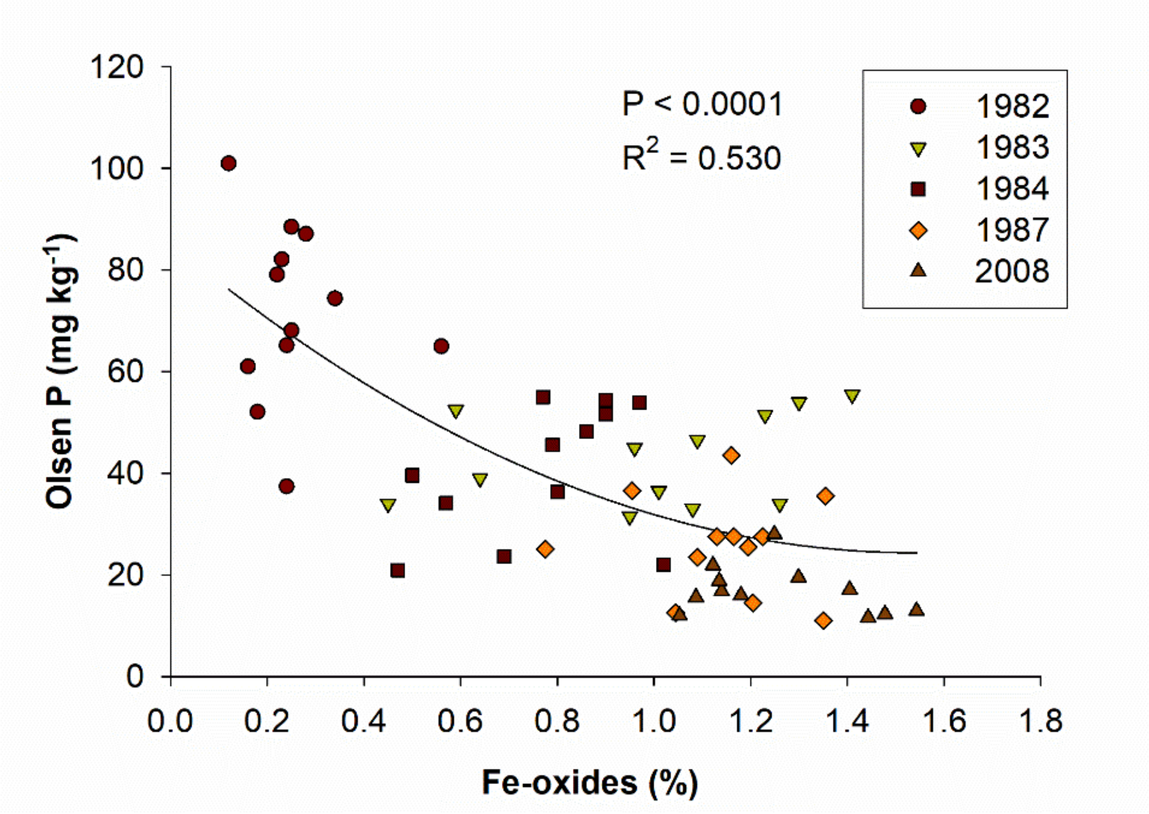

Figure 4. Second order regression of the relationship between Fe-oxides and Olsen-P over time.

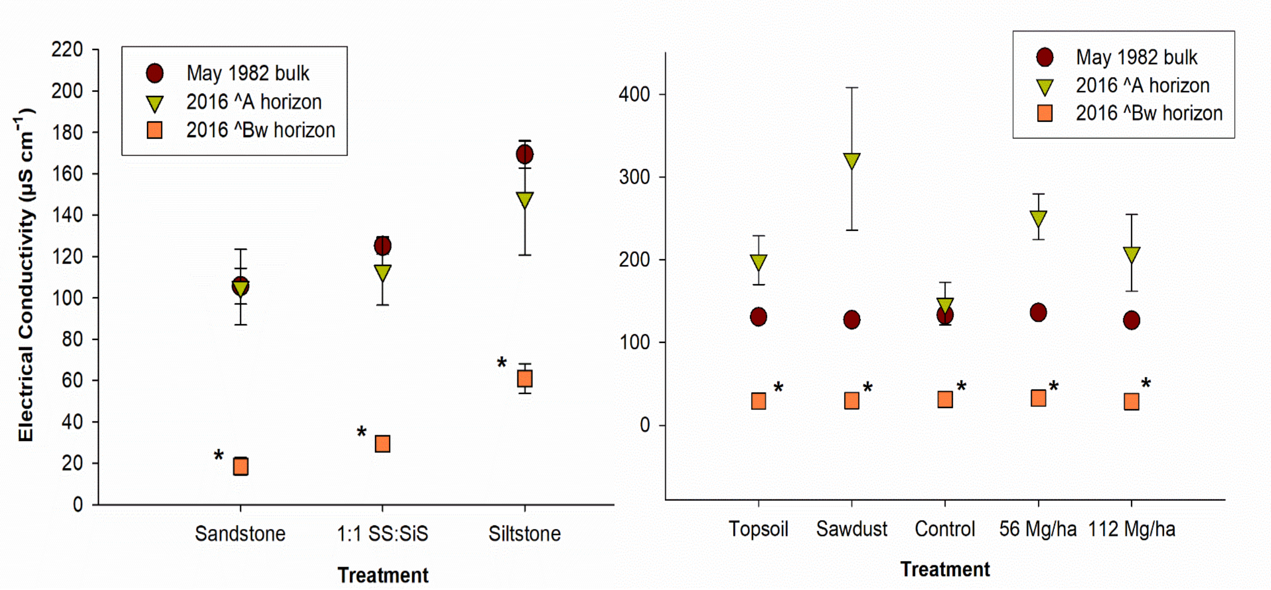

Figure 5. EC (mean ± SE) levels in the original May 1982 bulk spoil samples vs. the 2016 ^A and ^Bw horizons in the RM (left) and SA (right) Experiments. Asterisk (*) = EC lower than May 1982 bulk spoil EC. Delta values were used to test the difference in means between two years for a given treatment and interpreted by two tailed p-value ($\alpha = 0.05$).

Carbon Sequestration Over 34 Years

Soil organic carbon (SOC) accumulation stocks and rates are given in Table 6 and were relatively low (~0.2 to 0.3 Mg ha^{-1} year^{-1}) compared to other literature reports from similar mined sites. There were no significant treatment differences, which was surprising for the organically amended soils. It is important to reiterate from the methods above that these SOC accumulation rates are based on our best available estimates and may be complicated by the fact that it is difficult to obtain accurate soil volume x < 2 mm soil mass estimates in these very rocky materials. Since we used soil fines data collected in 2008 by Nash (2012), we assumed that these data did not substantially change over time and reflected 2016 mass soil fines. Furthermore, our recent 2016 C analyses treated the ^A horizon samples with HCl to test the assumption that carbonate-C had leached from the soil surface, while C data reported by Nash (2012) did not. Hence, our SOC values (~ 0.2 to 0.3 Mg ha^{-1} year^{-1}) are slightly lower than Nash's (2012) estimates. However, we feel confident that, given our approach, the C values in Table 6 reflect the best possible estimations for these mine soils. Sperow (2006) reviewed studies conducted on mined lands and reported an average SOC sequestration rate in KY and WV forested mine soils as 0.58 and 0.56 Mg ha^{-1} year^{-1}, respectively, and an average of 1.4 Mg ha^{-1} year^{-1} in reclaimed pasture mine soils for several Appalachian coal states. Further, Avera et al. (2015) found that within a chronosequence of reclaimed mixed grass and forest stands (5, 11, 21, 30 years) located near the COPE, the 11-year-old forest had the highest SOC rate at 0.7 Mg ha^{-1} year^{-1}. However, the oldest 30-year-old mined stand had a lower SOC rate of 0.33 Mg ha^{-1} year^{-1}, which is only slightly higher than our SOC values reported below (Table 6).

Furthermore, in the earlier years of our study, Roberts et al. (1988c) reported higher overall standing fescue biomass in 1983 vs. 1984 and 1986, indicating that biomass production slowed with time. The higher biosolids treatments (112 and 224 Mg ha^{-1}) generally produced superior biomass production in all early years (1982, 1983, 1984, and 1986) compared to the control, topsoil, and sawdust treatments. Nash (2012) reported no significant differences in biomass production among SA treatments in 2008. Thus, we can attribute relatively lower SOC rates to lower inputs of the aboveground+rooting productivity at our site. Our results also indicate that after 34 years, the fertilized control has reached SOC levels similar to amended treatments through normal C-sequestration processes, despite the fact that the amended plots received relatively high loadings of organic C (biosolids and sawdust) when they were built in 1982.

In summary, our estimated net C-sequestration rates for the 34-year period were relatively low (~0.2 to 0.3 Mg ha^{-1} year^{-1}) compared to other literature reports from similar mined and undisturbed sites. This is presumably due to the relatively small mass (< 30% by volume) of soil sized (< 2mm) particles in these soils associated with their relatively coarse texture. The data also indicate that the fertilized 2:1 SS:SiS control plots had reached SOC levels similar to heavily organic amended treatments largely through normal long-term C-sequestration processes while the organic amendment plots lost CO_2 back to the atmosphere.

Table 6. Soil organic carbon (SOC) and sequestration rates in the surface after 34 years of weathering in rock spoil and surface amendment treatments.

Treatment	**Mean ^A horizon (cm)**	**Mean Soil Fines (g)***	**SOC (mean ± SE)**		
			%†	Mg ha^{-1}	Mg ha^{-1} year^{-1}
	Rock Mix Experiment				
Sandstone (SS)	0-9	2,921	2.01 ± 0.37 Ał	6.71 ± 2.36 A	0.20 ± 0.07 A
1:1 SS:SiS	0-10	3,849	2.42 ± 0.23 A	9.53 ± 2.11 A	0.28 ± 0.06 A
Siltstone (SiS)	0-12	2,834	2.35 ± 0.61 A	5.45 ± 1.41 A	0.16 ± 0.04 A
	Surface Amendment Experiment				
Control	0-8	2,846	1.92 ± 0.39 Ał	6.60 ± 1.41 A	0.19 ± 0.04 A
Topsoil	0-8	4,506	1.20 ± 0.16 A	6.56 ± 1.54 A	0.19 ± 0.05 A
Sawdust	0-12	3,981	2.12 ± 0.09 A	6.73 ± 1.26 A	0.20 ± 0.04 A
Biosolids 56 Mg ha^{-1}	0-10	3,601	2.18 ± 0.52 A	7.88 ± 2.63 A	0.23 ± 0.08 A
Biosolids 112 Mg ha^{-1}	0-10	3,898	1.71 ± 0.18 A	6.55 ± 1.09 A	0.19 ± 0.03 A

†Includes a HCl pre-treatment for carbonates and the "coal correction" from the original May 1982 bulk spoils to account for geogenic C sources.

*2008 soil fines (0-5 cm) adjusted for 2016 ^A horizon depths (7-13 cm RM; 7-14 cm SA).

łLetters denote differences among treatments by experiment ($P \leq 0.05$).

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. 6) 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. 6) 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.

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. 7) 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. 8) through early winter 2021 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.

The longer term rainfall pH ranged from 4.5 to 6.5 as expected. The pH data from 2020 and 2021 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.

Figure 6. 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 (only 2021 data reported here).

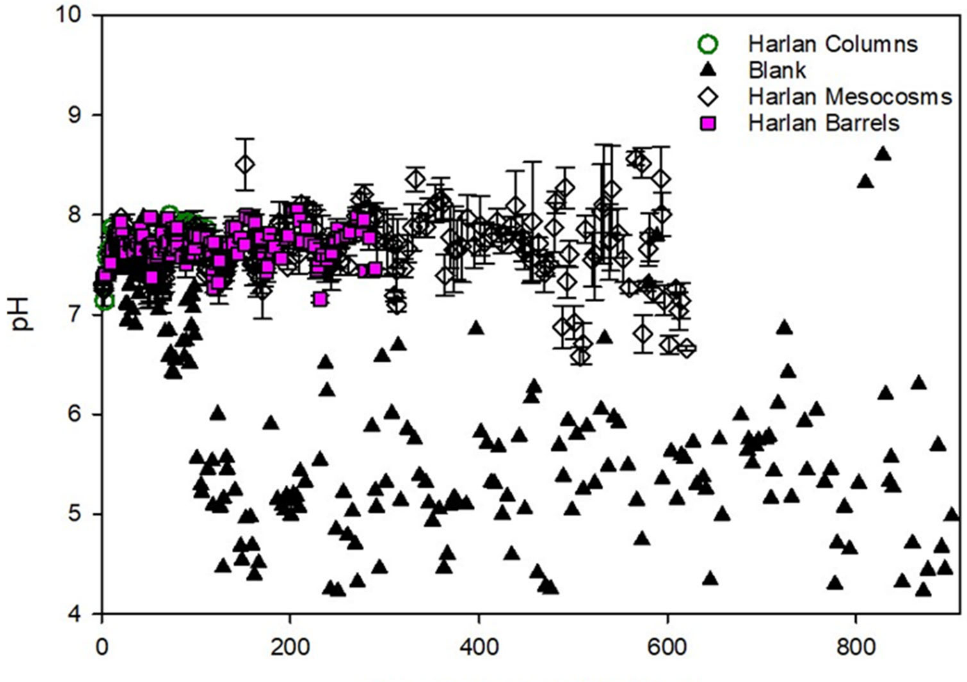

Figure 7. Leachate pH vs. cumulative volume (through 2021) for Harlan mesocosms, barrels and columns. The column technique only evaluated 40 x 2.5 cm leaching cycles. Blank refers to an onsite, and presumably clean, barrel collecting ambient rainfall. Mesocosm volumes lower to due evaporative losses and internal water detention in the spoils over time vs. blanks.

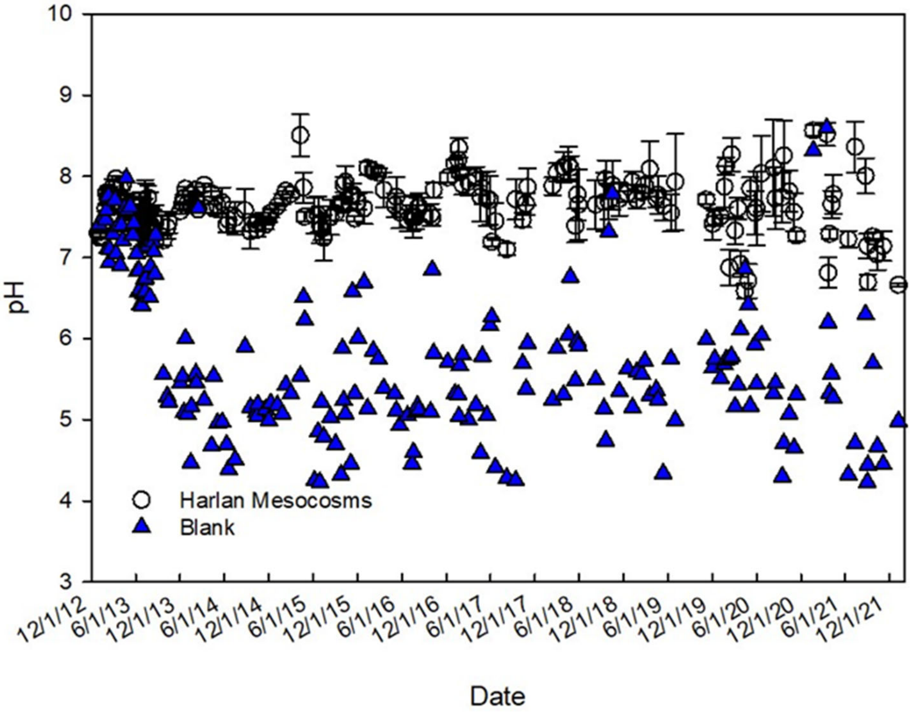

Figure 8. Leachate pH vs. time for the Harlan mesocosms through early winter 2021. Note the pH drop in late 2020 and 2021 along with the high variability in ambient rainfall pH (4.2 to > 7.0). Blank refers to an onsite, and presumably clean, barrel collecting ambient rainfall.

The influence of leaching scale/method on measured SC (Fig. 9) 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. 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 (Figs. 9 and 10) appeared to be increasing slightly between 2019 and 2021 relative to previous years. This 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. A more detailed view of the combined 2020 and 2021 calendar year data sets (Fig. 10) indicates that the amplitude of the "seasonal fall bump" in SC was much lower in 2021 and that SC appears to be slightly increasing again over time.

We periodically analyzed leachate samples for their full suite of soluble ions contributing to SC and those data for one of our 2021 sample events are presented in Tables 7 and 8. We will provide a more comprehensive review of these data over time (9 years) in our next report.

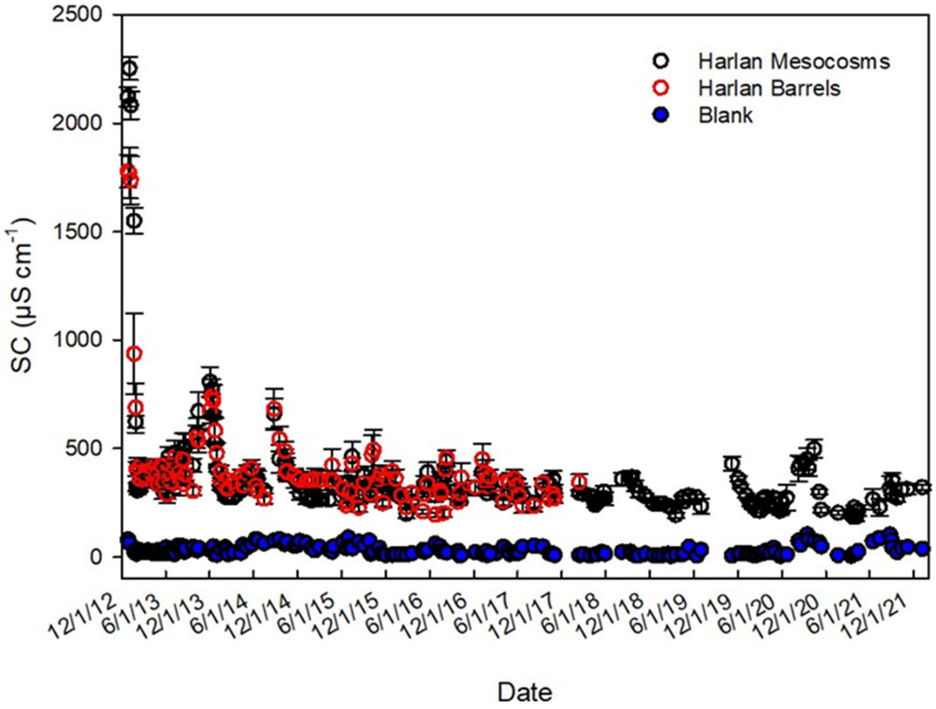

Figure 9. Leachate SC vs. time for Harlan mesocosms through late 2021. The column technique only evaluated 40 leaching cycles. Blank refers to an onsite, and presumably clean, barrel collecting ambient rainfall.

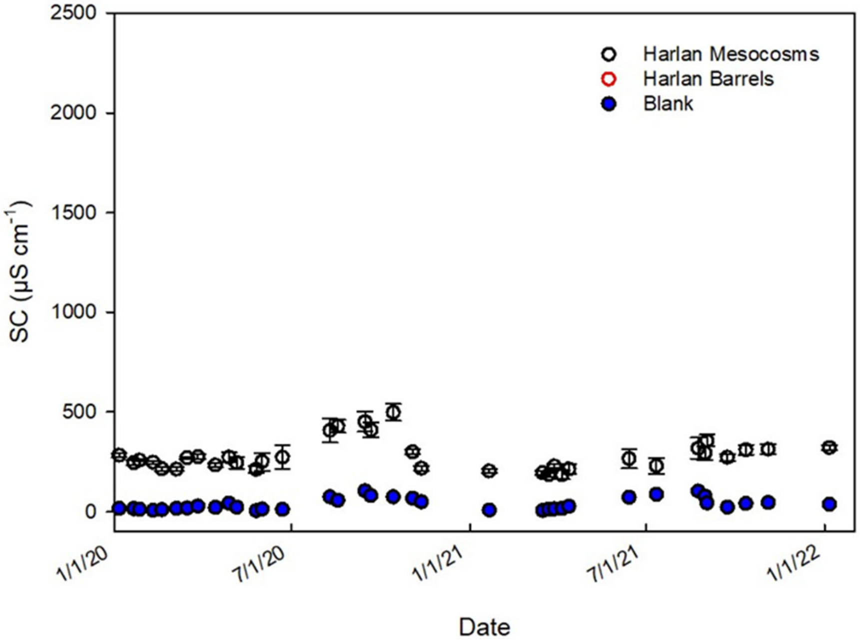

Figure 10. Detail of leachate SC for calendar years 2020 and 2021. Note lack of clear increase with first fall leaching events of 2021, along with what appears to be slow increase in SC over the year.

Table 7. Metals data from January 21, 2021.

		M1	M2	M3	Blank
Al	ug/L	11.08	15.67	10.43	9.30
As		0.12	0.12	0.08	0.07
Cd		<DL*	<DL	<DL	<DL
Cu		0.68	0.97	0.87	0.49
Fe		8.89	8.88	6.92	3.26
Mn		0.73	1.73	30.29	4.03
Ni		0.22	0.14	0.19	0.26
Pb		0.17	0.1	0.12	0.05
Se		0.21	0.19	0.21	<DL
Zn		2.34	3.73	3.06	2.59
Ca	mg/L	25.51	19.89	27.49	0.33
K		3.20	3.10	3.02	0.29
Mg		13.14	11.71	12.55	0.16
Na		0.24	0.19	0.22	0.28
*Below detection limit					

Table 82. Total-S and IC data from January 21, 2021.

	M1	M2	M3	Blank
Inorganic carbon (mg/L)	21.8	18.2	20.8	1.6
SO_4 (mg/L)	16	16	21	2.1

The relatively large increase in SC over the first full winter leaching season (2013/2014) may have indicated 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 (Clark et al., 2018). 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 increases (minor but more variable) in late fall/winter leachate SC may continue to 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.

Further data analysis this past year confirms that field observations over time clearly indicated relative "densification" of subsoil layers and intact clod bulk density values for the 2016 subsoils were generally higher than similar values from 1983. However, these differences were not as great as expected. However, extractable Fe-oxides in 2016 were clearly higher in the pre-weathered SS dominated treatments and increased with depth in ^Bw or ^C horizons in the SS plots and many of the 2:1 SS:SiS plots in the SA Experiment which was taken as an indication of pedogenic translocation.

Overall time effects across treatments generally showed that sand contents decreased and silt + clay contents increased within both experiments, indicating that the original SS and/or SiS parent material drives changes in soil texture with time. Other temporal trends were similar between experiments, such as the fact that pH generally decreased in the surface with time, while CEC increased due to the accumulation of organic matter. Additionally, simple paired t-tests showed that electrical conductivity (EC) dropped in the subsurface across all RM and SA plots due to long-term sustained leaching effects. However, the original surface soil EC values were maintained due to the effects of plant cation-cycling concentrating base cations and other compounds.

We also noted an overall increase in Fe-oxides and decrease in extractable P over time, but this pattern was not consistent across all years. Interestingly, a moderately strong relationship (Fig. 4) was found between surface Fe-oxides and P contents in the RM Experiment, but we did not include 2016 data due to a difference in laboratory methods for measuring P (Olsen vs. Mehlich I extracts). These data suggest the negative influence of ferruginous mine spoils and Fe-oxide accumulation on limiting P-availability. This Fe vs. P correlation did not hold for the SA Experiment, likely due to high P variability in the surface associated with heavily applied organic amendments (e.g., biosolids and sawdust).

Our C sequestration rates were relatively low (~0.2 to 0.3 Mg ha^{-1} $year^{-1}$) compared to other literature reports from similar Appalachian reclaimed coal mine sites. The data also indicate that, after 34 years, the fertilized control has reached SOC levels similar to organic-amended treatments largely through normal C-sequestration processes, despite the fact that the amended plots received relatively high loadings of organic C when they were built in 1982.

The combined results from our previously reported COP column leaching studies and the long-term (8-year) Harlan spoil leaching mesocosms confirm that our lab column protocol appears to be a relatively accurate predictor of peak vs. long-term leachate specific conductance (SC; proxy for TDS), though 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 the first 7 years indicated a consistent and gradual overall decline in TDS elution to levels lower than the presumed 350 µs cm^{-1} critical level for instream biotic effects, more recent data (2021) indicates the potential for a subsequent minor rebound in SC along with associated lower pH levels.

References

Avera, B.N., B.D. Strahm, J.A. Burger and C.E. Zipper. 2015. Development of ecosystem structure and function on reforested surface-mined lands in the Central Appalachian Coal Basin of the United States. New Forests 46: 683-702.

Barnhisel, R. and P.M. Bertsch. 1982. Aluminum. p. 275-300. In: Methods of Soil Analysis. Part 2. 2nd ed. Chemical and Microbiological Properties. ASA and SSSA, Madison, WI. Available online at: https://dl.sciencesocieties.org/publications/books/tocs/agronomymonogra/methodsofsoilan2.

Blake, G.R. and K.H. Hartge. 1986. Bulk density. p. 363-375. In: A. Klute (ed.) Methods of Soil Analysis, Part 1. 2nd ed. Madison, Wisconsin. doi:10.1002/gea.3340050110

Clark, E.V., W.L. Daniels, C.E. Zipper and K. Eriksson. 2018. Mineralogical influences on water quality from weathering of surface coal mine spoils. Applied Geochemistry 91:97-106. https://doi.org/10.1016/j.apgeochem.2018.02.001

Daniels, W.L., C.E. Zipper, Z.W. Orndorff, J. Skousen, C.D. Barton, L.M. McDonald, and M.A. Beck. 2016. Predicting total dissolved solids release from central Appalachian coal mine spoils. Env. Poll. 216 (2016) 371-379. http://dx.doi.org/10.1016/j.envpol.2016.05.044.

Evans, D.M., C.E. Zipper, P.F. Donovan, and W.L. Daniels. 2014. Long-term trends in specific conductance in waters discharged by coal-mine valley fills in Central Appalachia, USA. J. Amer. Water Res. Assoc. JAWRA 2014: 1-12. DOI:10.1111/jawr.12198

Gee, G.W. and J.W. Bauder. 1986. Particle-size analysis. p. 383-411. In: A. Klute (ed.) Methods of Soil Analysis. Part I. 2nd ed. Agron. Monogr. 9. ASA and SSSA, Madison, WI. doi:10.1002/gea.3340050110

Haering, K.C., W.L. Daniels and J.A. Roberts. 1993. Changes in mine soil properties resulting from overburden weathering. Journal of Environment Quality 22: 194-200. doi:10.2134/jeq1993.00472425002200010026x.

Haering, K.C., W.L. Daniels, and J.M. Galbraith. 2004. Appalachian mine soil morphology and properties: Effects of weathering and mining method. Soil Sci. Soc. Am. J. 68:1315-1325.

Haigh, M. 1992a. Degradation of 'reclaimed' lands previously disturbed by coal mining in Wales: causes and remedies. Land Degradation & Development 3: 169-180.

Haigh, M.J. 1992b. Problems in the reclamation of coal-mine disturbed lands in Wales. International Journal of Surface Mining, Reclamation and Environment 6: 31-37. doi:10.1080/09208119208944313.

Harris, D., W.R. Horwáth and C. Van Kessel. 2001. Acid fumigation of soils to remove carbonates prior to total organic carbon or carbon-13 isotopic analysis. Soil Science Society of America Journal 65: 1853-1856.

Hirmas, D. and S. Furquim. 2006. Simple modification of the clod method for determining bulk density of very gravelly soils. Communications in soil science and plant analysis 37: 899-906.

Howard, J., D. Amos and W. Daniels. 1988. Phosphorus and potassium relationships in southwestern Virginia coal-mine spoils. Journal of Environmental Quality 17: 695-700. doi:10.2134/jeq1988.00472425001700040029x.

McLean, E.O. 1982. Soil pH and lime requirement. p. 199-223. In: A. Klute (ed.) Methods of Soil Analysis, Part 2. 2nd ed. Madison, WI. Available online at: https://dl.sciencesocieties.org/publications/books/abstracts/agronomymonogra/methodsofsoilan2/199?access=0&view=pdf.

Mehra, O. and M. Jackson. 1960. Iron oxide removal from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate. 317-327 p. 7th National Conference on Clays and Clays Minerals, Washington. Committee on Clay Minerals of the National Academy of Sciences-National Research Council, Washington, USA.

Miller, J., C. Barton, C. Agouridis, A. Fogel, T. Dowdy and P. Angel. 2012. Evaluating soil genesis and reforestation success on a surface coal mine in Appalachia. Soil Science Society of America Journal 76: 950-960. doi:10.2136/sssaj2010.0400.

Nash, W.L. 2012. Long-term effects of rock type, weathering and amendments on southwest Virginia mine soils. M.S. Thesis. Virginia Polytechnic Inst. and State Univ. Blacksburg, VA.

Nash, W.L., W.L. Daniels, K.C. Haering, J.A. Burger and C.E. Zipper. 2016. Long-term effects of rock type on Appalachian coal mine soil properties. J Environ Qual 45: 1597-1606. doi:10.2134/jeq2015.10.0540.

Nelson, D.W. and L.E. Sommers. 1996. Total carbon, organic carbon, and organic matter. p. 961-1010. In: Methods of Soil Analysis Part 3. Chemical Methods. ASA and SSSA, Madison, WI. Available online at: https://dl.sciencesocieties.org/publications/books/tocs/sssabookseries/methodsofsoilan3.

Olsen, S. and L.E. Sommers. 1982. Phosphorus. Methods of soil analysis: 403-430.

Orndorff, Z.W., W.L. Daniels, C.E. Zipper, M.J. Eick and M.A. Beck. 2015. A column evaluation of Appalachian coal mine spoils' temporal leaching behavior. Env. Poll. 204 (2015) 39-47. http://dx.doi.org/10.1016/j.envpol.2015.03.049

Rhoades, J. 1996. Salinity: Electrical conductivity and total dissolved solids. Methods of soil analysis: Part 3 Chemical methods 5: 417-435.

Roberts, J.A., W.L. Daniels, J.A. Burger and J.C. Bell. 1988a. Early stages of mine soil genesis in a southwest Virginia spoil lithosequence. Soil Science Society of America Journal 52: 716-723. doi:10.2136/sssaj1988.03615995005200030023x.

Roberts, J.A., W.L. Daniels, J.C. Bell, and J.A. Burger. 1988b. Early stages of mine soil genesis as affected by topsoiling and organic amendments. Soil Sci. Soc. Am. J. 52:730-738.

Roberts, J.A., W.L. Daniels, J.C. Bell and D.C. Martens. 1988c. Tall fescue production and nutrient status on southwest Virginia mine soils. Journal of Environmental Quality 17: 55-62. doi:10.2134/jeq1988.00472425001700010008x.

Ross, C.R. 2015. Effect of Leaching Scale on Prediction of Total Dissolved Solids Release from Coal Mine Spoils and Refuse. M.S. Thesis, Virginia Tech, 157 p.

Shipp, R.F. and R. Matelski. 1965. Bulk-density and coarse-fragment determinations on some Pennsylvania soils. Soil Science 99: 392-397. Available online at: https://journals.lww.com/soilsci/Citation/1965/06000/BULK_DENSITY_AND_COARSE_FRAGMENT_DETERMINATIONS_ON.06007.aspx.

Sperow, M. 2006. Carbon sequestration potential in reclaimed mine sites in seven east-central states. Journal of environmental quality 35: 1428-1438. doi:10.2134/jeq2005.0158.

Thomas, G. 1982. Exchangeable cations. p. 159-165. In: Method of Soil Analysis. Part 2. 2nd ed. Agronomy Monograph 9. ASA and SSSA, Madison, WI. doi:10.1002/gea.3340050110

Timpano, A.J., S.H. Schoenholtz, D.J. Soucek, and C.E. Zipper. 2018. Benthic macroinvertebrate community response to salinization in headwater streams in Appalachia USA over multiple years. Ecological Indicators 91: 645-656.

Walkley, A. and I.A. Black. 1934. An examination of the Degtjareff method for determining soil organic matter, and a proposed modification of the chromic acid titration method. Soil Science 37: 29-38. doi:10.1097/00010694-193401000-00003.

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Table A1. Interaction effects (year x treatment) pairwise differences for selected mine soil physical and chemical properties in the surface at the Rock Mix Experiment.

Year	Soil Age (yrs.)	Sandstone (SS)	1:1 SS:SiS	Siltstone (SiS)
		Sand (%)		
May 1982	0	69 ± 1.0 a*	62 ± 1.7 abc	59 ± 4.6 abcd
Oct. 1982	½	71 ± 0.9 a	64 ± 3.6 abc	49 ± 2.2 cde
1983	1	65 ± 3.1 ab	60 ± 0.6 abcd	51 ± 7.1 bcde
1987	5	68 ± 1.9 a	60 ± 2.1 abcd	39 ± 1.4 ef
2008	26	62 ± 0.9 abc	50 ± 0.6 bcde	31 ± 1.2 f
2016	34	66 ± 1.4 ab	59 ± 4.2 abcd	44 ± 6.9 def
		Silt (%)		
May 1982	0	22 ± 0.6 g	28 ± 1.6 cdefg	30 ± 3.9 cdefg
Oct. 1982	½	20 ± 0.8 g	26 ± 3.1 efg	39 ± 1.7 abcde
1983	1	27 ± 3.2 defg	31 ± 0.45 cdefg	38 ± 6.8 bcdef
1987	5	23 ± 1.6 g	30 ± 1.0 cdefg	48 ± 1.2 ab
2008	26	25 ± 1.4 efg	39 ± 2.0 abcd	52 ± 1.7 a
2016	34	23 ± 1.5 fg	28 ± 2.7 cdefg	43 ± 5.9 abc
		Fe-oxides (%)		
May 1982	0	0.52 ± 0.01 ghi*	0.47 ± 0.02 hig	0.27 ± 0.03 ig
Oct. 1982	½	0.35 ± 0.07 hij	0.24 ± 0.00 ij	0.17 ± 0.02 j
1983	1	1.24 ± 0.06 bc	1.08 ± 0.07 cde	0.65 ± 0.10 fgh
1984	2	0.91 ± 0.02 def	0.85 ± 0.06 efg	0.56 ± 0.05 ghi
1987	5	1.19 ± 0.01 bcde	1.20 ± 0.10 bcd	1.03 ± 0.10 cde
2008	26	1.29 ± 0.07 bc	1.31 ± 0.11 bc	1.18 ± 0.08 bcde
2016	34	1.81 ± 0.04 a	1.68 ± 0.11 a	1.49 ± 0.07 ab
		pH		
May 1982	0	5.9 ± 0.4 efg	7.1 ± 0.3 abc	8.0 ± 0.1 a
Oct. 1982	½	5.5 ± 0.3 fgh	6.7 ± 0.2 bcde	7.5 ± 0.1 ab
1983	1	5.0 ± 0.4 h	6.2 ± 0.1 cdefg	6.6 ± 0.0 cde
1984	2	5.3 ± 0.1 gh	6.2 ± 0.2 defg	6.3 ± 0.2 cdefg
1987	5	5.4 ± 0.3 fgh	6.6 ± 0.1 bcde	7.1 ± 0.1 bcd
2008	26	5.7 ± 0.1 efgh	6.1 ± 0.1 defg	6.5 ± 0.2 cdef
2016	34	5.6 ± 0.1 efgh	5.8 ± 0.1 efgh	6.1 ± 0.1 cdefg
		CEC ($\text{cmol}_c\ \text{kg}^{-1}$)		
May 1982	0	3.3 ± 0.3 j	4.2 ± 0.2 hij	5.2 ± 0.2 ghij
Oct. 1982	½	5.3 ± 0.5 ghij	7.5 ± 0.4 defg	8.6 ± 0.3 cde
1983	1	3.7 ± 0.3 ij	5.1 ± 0.2 ghij	5.5 ± 0.3 fghij
1984	2	3.7 ± 0.2 ij	5.6 ± 0.1 fghij	7.1 ± 0.2 efgh
1987	5	5.1 ± 0.8 ghij	8.0 ± 0.1 defg	10.1 ± 0.2 bcd
2008	26	7.7 ± 0.5 defg	10.9 ± 0.4 bc	14.2 ± 0.3 a
2016	34	6.6 ± 1.0 efghi	8.6 ± 0.7 bcdef	11.7 ± 2.5 ab

*Mean ± SE. Different letters show differences among years for a given treatment (columns), as well as differences by treatment within a given year (rows) ($P \leq 0.05$).

Table A2. Main effects (year and treatment) pairwise differences for selected mine soil physical and chemical properties in the surface at the Rock Mix Experiment.

Year	Mean ± SE by Year/ All Treatments	Soil Age (yrs.)	Treatment	Mean ± SE by Treatment/ All Years
Clay (%)				
May 1982	9.9 ± 0.4 c*	0	Sandstone (SS)	9.8 ± 0.4 B
Oct. 1982	10.5 ± 0.6 bc	½		
1983	9.4 ± 0.5 c	1	1:1 SS:SiS	10.3 ± 0.5 B
1987	10.5 ± 0.7 bc	5		
2008	13.7 ± 1.1 a	26	Siltstone (SiS)	13.1 ± 0.6 A
2016	12.6 ± 0.7 ab	34		
P (mg kg^{-1})				
May 1982	4.7 ± 0.7 d	0	Sandstone (SS)	38.6 ± 5.0 A
Oct. 1982	71.8 ± 5.0 a	½		
1983	42.8 ± 2.6 b	1	1:1 SS:SiS	32.6 ± 4.6 A
1984	40.4 ± 3.8 b	2		
1987	25.8 ± 2.8 c	5	Siltstone (SiS)	30.0 ± 5.1 A
2008	16.9 ± 1.4 c	26		
SOM (%)				
May 1982	-	0	Sandstone (SS)	3.9 ± 0.6 C
Oct. 1982	2.3 ± 0.3 d	½		
1984	3.1 ± 0.3 d	2	1:1 SS:SiS	5.2 ± 0.7 B
1987	4.5 ± 0.4 c	5		
2008	9.6 ± 0.6 a	26	Siltstone (SiS)	6.9 ± 0.8 A
2016	7.9 ± 0.8 b	34		

*Lowercase letters show overall differences among years for all treatments and uppercase letters show overall differences among treatments for all years ($P \leq 0.05$).

Table A3. Interaction effects (year x treatment) pairwise differences for sand and silt contents in the surface at the Surface Amendment Experiment.

Year	Soil Age (yrs.)	Control	Topsoil	Sawdust	Biosolids 56 Mg ha^{-1} ǂ	Biosolids 112 Mg ha^{-1}
		Sand (%)				
May 1982†	0	64 ± 0.9 defg*	64 ± 0.8 defg	65 ± 0.8 bcde	-	62 ± 0.4 efg
Oct. 1982	½	62 ± 1.0 efg	73 ± 0.3 a	62 ± 1.4 efg	-	64 ± 1.0 cdef
1983	1	61 ± 0.5 efg	69 ± 1.0 abc	61 ± 0.6 efg	-	59 ± 0.5 g
1987	5	63 ± 0.7 defg	70 ± 0.5 ab	60 ± 1.8 fg	-	60 ± 1.1 efg
2008	26	53 ± 1.5 h	61 ± 1.1 efg	52 ± 1.0 h	-	53 ± 0.9 h
2016	34	59 ± 1.0 fg	69 ± 1.0 abcd	58 ± 1.1 g	-	61 ± 0.9 efg
		Silt (%)				
May 1982	0	27 ± 0.6 cdef	26 ± 0.4 cdef	26 ± 1.0 cdefg	-	28 ± 0.7 cd
Oct. 1982	½	28 ± 0.6 cd	18 ± 0.1 h	28 ± 1.3 cde	-	24 ± 1.1 defg
1983	1	28 ± 0.4 cd	22 ± 0.6 fgh	28 ± 0.3 cd	-	28 ± 0.3 cd
1987	5	29 ± 0.5 bcd	22 ± 0.9 efgh	31 ± 1.0 bc	-	29 ± 0.8 cd
2008	26	35 ± 1.8 ab	28 ± 0.2 cd	35 ± 1.1 ab	-	37 ± 3.2 a
2016	34	29 ± 1.0 bcd	20 ± 1.3 gh	30 ± 2.7 bcd	-	26 ± 0.7 cdefg

†Organic amendments were not applied at the time of May sampling.

*Mean ± SE. Different letters show differences among years for a given treatment (columns), as well as differences by treatment within a given year (rows) ($P \leq 0.05$).

ǂNot enough data available for this analysis.

Table A4. Main effects (year and treatment) pairwise differences for clay contents in the surface at the Surface Amendment Experiment.

Year	Mean ± SE by Year/ All Treatments	Soil Age (yrs.)	Treatment	Mean ± SE by Treatment/ All Years
		Clay (%)		
May 1982†	9.5 ± 0.2 bc*	0	Control	10.0 ± 0.6 A
Oct. 1982	9.9 ± 0.4 abc	½	Topsoil	9.5 ± 0.3 A
1983	10.6 ± 0.4 abc	1	Sawdust	10.7 ± 0.5 A
1987	9.0 ± 0.5 c	5	Biosolids 56 Mg ha^{-1} ǂ	-
2008	11.5 ± 1.0 ab	26	Biosolids 112 Mg ha^{-1}	11.3 ± 0.5 A
2016	12.0 ± 0.5 a	34	-	-

†Organic amendments were not applied at the time of May sampling.

*Lowercase letters show overall differences among years for all treatments and uppercase letters show overall differences among treatments for all years ($P \leq 0.05$).

ǂNot enough data available for this analysis.

Table A5. Interaction effects (year x treatment) pairwise differences for SOM in the surface at the Surface Amendment Experiment.

Year	Soil Age (yrs.)	Control	Topsoil	Sawdust	Biosolids 56 Mg ha^{-1}	Biosolids 112 Mg ha^{-1}
				SOM (%)		
Oct. 1982	½	2.8 ± 0.6 fgh*	1.3 ± 0.2 h	5.4 ± 1.3 cdefg	3.1 ± 0.3 efgh	5.2 ± 0.7 defg
1984	2	3.1 ± 0.1 efgh	1.9 ± 0.1 gh	8.0 ± 0.9 abcd	5.9 ± 0.4 cdef	7.1 ± 0.8 bcd
1987	5	3.2 ± 0.3 efgh	2.3 ± 0.2 fgh	7.2 ± 1.1 bcd	7.9 ± 1.4 abcd	6.6 ± 0.4 bcde
2008	26	8.9 ± 0.9 abc	7.7 ± 0.4 abcd	8.7 ± 0.3 abcd	10.0 ± 1.1 ab	10.9 ± 0.3 a
2016	34	4.8 ± 0.7 defgh	5.2 ± 0.6 cdefg	7.2 ± 0.6 abcd	6.3 ± 0.8 cdef	6.2 ± 0.6 bcdef

*Mean ± SE. Different letters show differences among years for a given treatment (columns), as well as differences by treatment within a given year (rows) ($P \leq 0.05$).

Table A6. Interaction effects (year x treatment) pairwise differences for Fe-oxides and extractable P in the surface at the Surface Amendment Experiment.

Year	Soil Age (yrs.)	Control	Topsoil	Sawdust	Biosolids 56 Mg ha^{-1} ǂ	Biosolids 112 Mg ha^{-1}
		Fe-oxides (%)				
May 1982†	0	0.50 ± 0.02 klm*	0.48 ± 0.05 klm	0.58 ± 0.08 ijklm	-	0.53 ± 0.02 jklm
Oct. 1982	½	0.43 ± 0.01 klm	0.41 ± 0.08 lm	0.37 ± 0.01 m	-	0.35 ± 0.06 m
1983	1	0.97 ± 0.05 fgh	0.96 ± 0.04 efgh	1.04 ± 0.06 defg	-	0.87 ± 0.07 fghi
1984	2	0.92 ± 0.06 fgh	0.70 ± 0.04 hijkl	0.84 ± 0.03 fghij	-	0.80 ± 0.09 ghijk
1987	5	1.28 ± 0.02 cde	1.00 ± 0.02 defgh	1.31 ± 0.05 cd	-	1.12 ± 0.16 cdef
2008	26	1.38 ± 0.03 c	1.00 ± 0.03 defgh	1.42 ± 0.05 c	-	1.10 ± 0.08 cdef
2016	34	2.18 ± 0.06 a	1.85 ± 0.01 b	2.05 ± 0.06 ab	-	1.86 ± 0.06 ab
		P (mg kg^{-1})				
May 1982	0	2.1 ± 0.4 jk	2.0 ± 0.7 k	2.4 ± 0.3 jk	2.4 ± 0.3 jk	2.1 ± 0.4 jk
Oct. 1982	½	60.0 ± 6.5 cdefg	38.1 ± 6.5 efghij	24.0 ± 3.2 ghijk	43.2 ± 4.6 defghi	81.0 ± 14.3 bc
1983	1	50.4 ± 0.9 cdefgh	42.0 ± 7.4 efghi	42.1 ± 6.6 efghi	82.4 ± 10.2 bc	120.4 ± 17.1 a
1984	2	25.2 ± 5.6 hijk	29.1 ± 1.7 fghijk	27.3 ± 4.2 ghijk	50.3 ± 9.6 cdefghi	80.0 ± 6.7 bcd
1987	5	27.1 ± 4.5 hijk	28.0 ± 2.9 fghijk	29.0 ± 3.5 fghijk	70.0 ± 8.7 bcde	81.3 ± 8.8 bc
2008	26	16.3 ± 1.0 ijk	16.0 ± 1.9 hijk	20.2 ± 1.7 hijk	64.3 ± 10.5 bcdef	100.1 ± 4.5 ab

†Organic amendments were not applied at the time of May sampling.

*Mean ± SE. Different letters show differences among years for a given treatment (columns), as well as differences by treatment within a given year (rows) ($P \leq 0.05$).

ǂNot enough data available for this analysis for some datasets.

Table A7. Interaction effects (year x treatment) pairwise differences for pH and CEC in the surface at the Surface Amendment Experiment.

Year	Soil Age (yrs.)	Control	Topsoil	Sawdust	Biosolids 56 Mg ha^{-1}	Biosolids 112 Mg ha^{-1}
		pH				
May 1982†	0	7.3 ± 0.1 a*	7.1 ± 0.2 ab	7.2 ± 0.1 a	7.3 ± 0.0 a	7.1 ± 0.1 abc
Oct. 1982	½	6.8 ± 0.1 abcde	7.2 ± 0.1 ab	6.1 ± 0.3 fghi	7.3 ± 0.0 a	7.0 ± 0.0 abc
1983	1	6.1 ± 0.1 fghi	6.2 ± 0.1 efgh	5.3 ± 0.0 j	6.4 ± 0.0 defgh	6.4 ± 0.1 efgh
1984	2	6.1 ± 0.1 ghi	6.5 ± 0.2 cdefgh	6.0 ± 0.2 ghi	6.3 ± 0.0 efgh	6.0 ± 0.1 hi
1987	5	6.7 ± 0.0 abcdef	7.0 ± 0.1 abcd	6.1 ± 0.1 fghi	6.7 ± 0.1 abcdef	6.6 ± 0.1 bcdefg
2008	26	6.2 ± 0.1 efgh	6.2 ± 0.1 efgh	6.2 ± 0.1 efgh	6.1 ± 0.1 fghi	6.2 ± 0.1 efgh
2016	34	5.5 ± 0.1 ij	5.2 ± 0.2 j	5.1 ± 0.1 j	5.1 ± 0.1 j	5.2 ± 0.0 j
		CEC (cmol$_c$ kg^{-1})				
May 1982	0	3.7 ± 0.0 op	3.9 ± 0.2 nop	3.7 ± 0.1 p	4.0 ± 0.2 op	3.9 ± 0.1 nop
Oct. 1982	½	7.0 ± 0.2 hijklmnop	7.8 ± 0.2 fghijklmnop	10.1 ± 0.5 cdefghij	12.4 ± 0.9 abcdef	15.7 ± 1.8 a
1983	1	4.7 ± 0.0 mnop	5.2 ± 0.2 kmnop	8.0 ± 0.2 fghijklmno	10.6 ± 0.7 cdefghi	12.6 ± 0.9 abcdef
1984	2	5.0 ± 0.2 lmnop	5.3 ± 0.2 jkmnop	7.5 ± 1.0 ghijklmnop	8.7 ± 0.5 efghijklm	13.5 ± 1.2 abcd
1987	5	6.4 ± 0.3 ijklmnop	6.8 ± 0.2 hijklmnop	9.5 ± 0.7 defghijklm	11.3 ± 1.2 abcdefgh	12.2 ± 0.6 abcdefg
2008	26	12.1 ± 0.9 abcdefg	10.1 ± 0.6 cdefghi	13.5 ± 1.2 abcde	12.8 ± 0.3 abcde	14.2 ± 1.3 abcd
2016	34	10.1 ± 2.5 bcdefghijk	10.2 ± 1.2 bcdefghi	14.2 ± 2.8 abc	15.4 ± 1.2 ab	10.3 ± 1.1 bcdefghijk

†Organic amendments were not applied at the time of May sampling.

*Mean ± SE. Different letters show differences among years for a given treatment (columns), as well as differences by treatment within a given year (rows) ($P \leq 0.05$).