

Powell River Project Annual Report (2015 – 2016)
**Characterizing TDS Risk in Appalachian Landscapes: Techniques to
Identify Mine Spoil TDS Generation Potentials**

Daniel K. Johnson and W. Lee Daniels

Graduate Research Assistant and Professor
Dept. of Crop & Soil Environmental Sciences
Virginia Tech, wdaniels@vt.edu; www.landrehab.org

Executive Summary

Surface mining for coal in the Central Appalachians contributes total dissolved solids (TDS) to headwater streams, especially below larger mines and associated valley fills. The objective of this study was to characterize the geochemical properties of a range of surface soils and associated geologic strata from the Central Appalachian coalfields and to relate those properties to simple field indicators, such as color or rock type. We hypothesized that these indicators can accurately predict certain geochemical properties. Thirty-three vertical weathering sequences were sampled from eight surface mines throughout the Central Appalachian coalfields, for a total of 204 individual samples. No differences were found among sites in overall saturated paste specific conductance (SC; used as a proxy for TDS) levels, but significant geochemical differences existed among samples. Sulfate release dominated SC levels, followed closely by Ca and Mg. Surficial soils and sandstones were yellowish-brown in color and low in SC, compared to the underlying grayish to black sandstones, shales, and mudstones. Saturated paste extractable As and P levels were higher in A horizons, whereas Se was significantly higher in unweathered bedrock than in soil or weathered bedrock. Samples generating exothermic reactions with 30% H₂O₂ produced higher SC levels, sulfate, Mg, and Se. In the field, weathered surface materials were frequently abruptly separated from underlying non-weathered strata by thin shale layers or coal seams. In conclusion, the mine spoils studied varied widely in geochemical properties. The simple field indicators presented here, such as color, weathering status, rock type, and H₂O₂ reaction can provide valuable guidance for identifying TDS risk which would greatly improve operator's ability to actively minimize TDS release. We recommend using soil and weathered, yellowish-brown sandstone layers as a source of low TDS spoil material whenever possible. Underlying unweathered bedrock layers should be treated as "potentially high TDS spoils". The H₂O₂ field test is useful for identification of both TDS and Se risk in these layers. Particularly high risk spoils include gray to black mudstones and shales, coals, and coal associated shales, mudstones, and clays directly associated with coal seams. We recommend hydrologically isolating these spoils using techniques similar to those used historically for acid-forming materials.

Background

This report summarizes the findings of our work to date reducing TDS elution from Southwest Virginia surface coal mines to receiving streams. This project was initiated in 2010 with sole support from the Powell River Project. We have had a number of researchers, collaborators, and graduate students involved with the project during the time since. Between 2011 and 2016, we also collaborated with the Virginia Center for Coal and Energy Research and major regional coal producers (Alpha, Arch, Patriot, TECO/Cambrian and others) in a large multi-state research consortium, the Appalachian Research Initiative for Environmental Science (ARIES; <http://www.energy.vt.edu/ARIES>). Between 2012 and 2014, we received significant parallel funding for this program from ARIES to support our collaboration with the University of Kentucky and West Virginia University to broaden the scope to the central Appalachian region while continuing to focus on SW Virginia in more detail. We also collaborated with OSMRE in a separate study funded through OSMRE and ARIES (Daniels et al., 2014) studying leachates from intermediate-sized leaching mesocosms filled with mine spoils. Clay Ross reported the results of the first two years of this simulated field leaching in his M.S. thesis (Ross, 2015). We have utilized part of our current PRP funding for the past two project years (2015-2016) to continue the long-term monitoring of these leaching tanks.

Daniel Johnson's Ph.D. research was funded in part through the PRP over the past five years and concentrated specifically on predicting TDS release from surface coal mine spoils. Preliminary results and reports from past years can be found online on the PRP website at <http://www.prp.cses.vt.edu/Reports.html>. Additionally, Dr. Johnson's results were published in his dissertation, "Field Indicators for the Prediction of Appalachian Soil and Bedrock Geochemistry", which is publicly available at <http://hdl.handle.net/10919/71896>. The discussions and results presented in this report are modified from that work and have been condensed to fit this format; for further details see the full dissertation (Johnson, 2016) at the link above.

Introduction

Historically, acid mine drainage and the lack of approximate original contour (AOC) replacement were the major concerns with surface coal mining in the Central Appalachians, but advancements in reclamation have largely addressed these issues for active operations (Skousen et al., 2002). Over the past decade, focus has shifted to elevated TDS levels in receiving streams affected by surface mining and recent studies, such as Evans et al. (2014) have shown that elevated levels of TDS in receiving streams can persist for decades after mining has ceased.

This is cause for concern because both long-term chronic and short-term acute elevated TDS levels cause negative impacts to stream aquatic life. A number of studies document the negative effects on aquatic life due to elevated stream TDS levels (Chapman et al., 2000; Cormier et al., 2013; Kennedy et al., 2005; Mount et al., 1997; Pond et al., 2008, 2014; Pond, 2010; Timpano et al., 2015). These studies used benthic macroinvertebrates or other aquatic life as proxies for overall stream biological condition and generally concluded that negative impacts to stream aquatic life increased as overall concentrations in TDS levels increased. Furthermore, the specific ionic concentrations making up overall TDS and seasonal spikes in TDS have additionally been shown to impact stream aquatic life (Mount et al., 1997, Timpano et al., 2015). Thus, scientific evidence indicates that chronic and acute elevated in-stream TDS levels generated by surface coal mines negatively impact the Appalachian region by degrading biological conditions in streams.

Contemporary coal-mine water treatment practices do not remove TDS from surface mine effluent effectively and TDS-specific treatment technologies are expensive; prevention is key. By definition, TDS (APHA, 1999) is the sum of the mass of all inorganic and organic filtrate components that will pass through a 2 μm or smaller filter. USEPA (2011) found that the ions responsible for elevated TDS levels in mining affected streams were dominantly sulfate, Ca, and Mg; however, several elements did occur at lower concentrations including Mn, bicarbonate, Se, K, Na, and Cl. Traditional water treatment methods generally use precipitation methods to remove soluble metals, but many TDS components are soluble at very high concentrations (Na_2SO_4 saturation = 110,000 mg L^{-1} ; NaCl saturation = 350,000 mg L^{-1} ; $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ = 1500 mg L^{-1}) and across a range of pH values. Some treatment technologies such as reverse osmosis do exist for specifically removing TDS from coal mine effluents, but are generally expensive (Geldenhuis et al., 2003; Pinto et al., 2016; Tolonen et al., 2015; Ziemkiewicz et al., 2003). Thus, while technologies do exist for reducing overall surface mine effluent TDS, prevention (where possible) would be a better option for mining companies than actual discharge water treatment for TDS.

Rainwater percolating through freshly blasted mine spoils contributes to a significant portion of elevated TDS levels in receiving streams. Freshly exposed geologic materials contribute significant loads via weathering reactions such as hydrolysis and dissolution (Brady et al., 2000). TDS-producing potential varies widely from material to material (Daniels et al., 2016; Orndorff et al., 2015). In particular, oxidized and weathered surficial materials usually produce much lower TDS than unweathered spoils from the same strata. "Fresh" minerals in unweathered mine spoils newly exposed to the surface by mining rapidly weather, releasing a range of constituent ions (Brady et al., 2000). Thus, rainwater percolating through blasted mine spoils, especially unweathered mine spoils that have been moved to the surface from deep below ground, contributes a significant amount of TDS to the receiving streams below.

Saturated paste SC provides a rapid and accurate assessment of TDS generation risk, but requires sample processing and specialized equipment. Some studies (Daniels et al. 2016; Orndorff et al., 2015; Ross, 2015) have used field-scale tanks and bench top columns to study these mine spoil leachates in detail. While these leaching studies provide great details on the materials, they are generally time consuming and expensive. Saturated paste extracts – made by mixing the mine spoils crushed to < 2 mm with deionized water – do, however, provide a faster analysis than the more depth column studies. Saturated paste SC had a very strong correlation with the peak SC of the leachates emitted from 39 mine spoils in a column study by Daniels et al. (2016). Thus, SC is commonly used as a proxy for TDS when measuring the salinity of saturated paste extracts in the lab and the saturated paste SC gives a good idea of the overall TDS generation risk.

Past strategies of identifying acid-forming strata and isolating them from surface and near-surface water flow have been effective at limiting acid mine drainage (Skousen et al., 2002). A similar pre-mining approach to identifying high TDS mine spoils for special handling and isolation may also be effective, but few studies have been published to date on TDS prediction techniques; and no published studies describe TDS prediction techniques that can be used by mine operators and their consultants in the field. Thus, this lack of field TDS prediction methods led to the current study which investigates the geologic sources and geochemical characteristics of TDS in Central Appalachia.

For this study, we hypothesized that a set of simple field and lab indicators could predict certain geochemical properties of the mine spoils in order to approximate TDS generation risk. Identifying the TDS generation risk of individual soil and rock strata in field and pre-mining would allow decisions to be made in the planning stages for TDS risk management. High-risk strata could be identified and isolated from surface and near-surface flow. Materials identified as low-risk would be available for use in reclaimed areas that are expected to have significant contact with surface and near-surface flows, such as drains and waterways. The objective of this study was to develop a set of simple field and lab indicators that would assist field operators, regulators, consultants and researchers in the separation of low and high TDS generation potential mine spoils.

Materials and Methods

Sample Collection and Preparation

Thirty-three vertical weathering sequences were sampled from eight surface coal mines throughout the central Appalachian coalfields (Fig. 1). Twenty-five of these represented unique geologic strata and the remaining eight sequences were replications collected from five of the sites. Sites were selected based on local coal mining companies' willingness to offer site access, but every effort was made to select a wide range of sites throughout the Pottsville and Breathitt groups in the Central Appalachians. Some mining operations covered areas large enough to allow multiple weathering sequences to be collected from different elevations representing different geologic formations, while the size and layout of some operations limited sampling to one weathering sequence. Actual sampling locations at each mine were largely determined by the physical constraints of being able to safely reach the samples. Sites were selected that had been mined within the past five years. In short, samples were collected from recently surface mined areas throughout the Central Appalachians for a total of 33 weathering sequences.

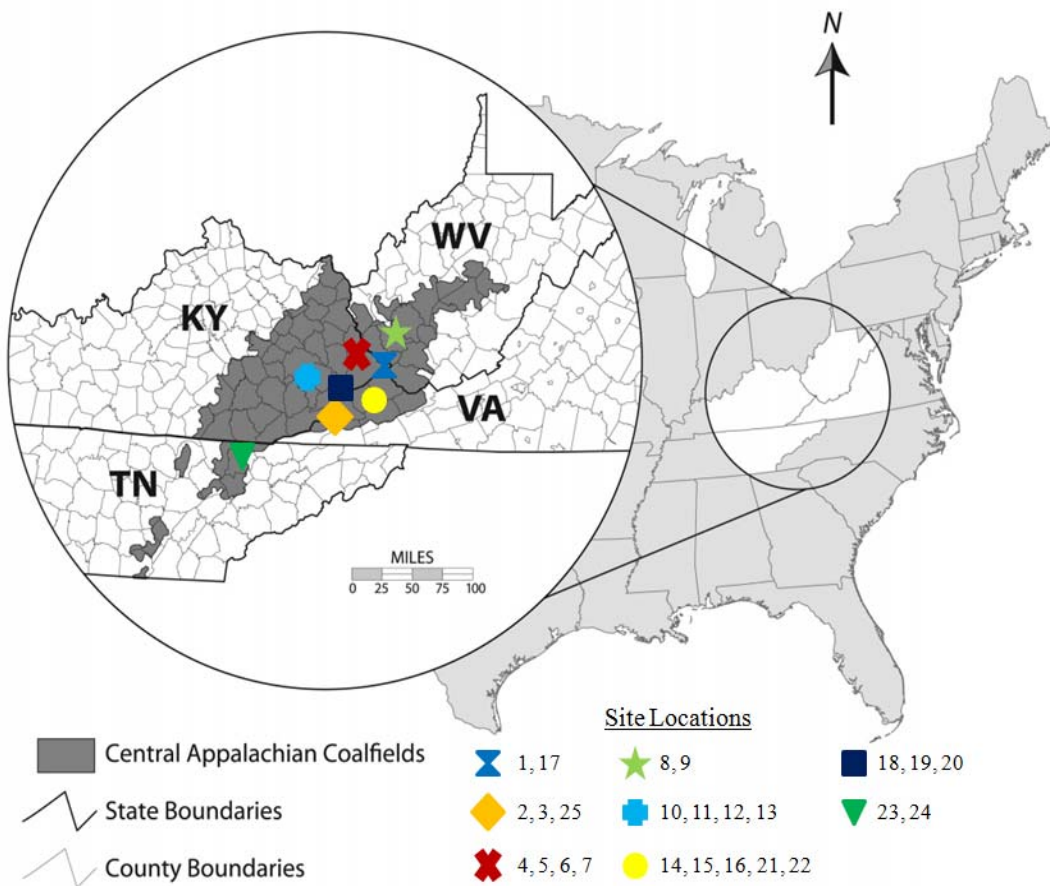


Figure 1. The central Appalachian coalfields with site locations indicated for the current study. Modified from USEPA (2011) and Johnson (2016).

For each "weathering sequence", strata were sampled down through the mining column from the soil surface through fractured, weathered rock into the unweathered lower rock strata. Locations were selected where the native soil and bedrock were still intact and in-situ. Soil samples were dug by hand auger and bedrock samples were removed with a rock hammer from freshly mined highwalls. Sampling generally extended at least 15-30 m below the surface, depending on the physical accessibility of each location. Some weathering sequences were sampled from drill cores (~ 5 cm diameter) rather than from highwalls. In this case, all "rippable" soil and rock layers were bulldozed away before drilling, so the weathering sequences sampled from drill cores did not contain the uppermost soil and rock layers. Each distinct layer was collected from each weathering sequence, for a total of 204 individual samples.

The color and weathering status of each sample was described in the field. All colors were taken using the interior faces of rocks broken open with a rock hammer, being careful to exclude any weathering rinds around the natural rock faces. The Munsell soil color name, hue, value, and chroma of each sample were determined using soil color charts. Nearly all of the samples fit on the "10 YR" color page, so that was generally the only hue page used. The weathering status was also noted in the field. For the purposes of this study, those soil and sandstone samples occurring above the shallowest intact fine-grained shale or mudstone layer at each site were designated as "weathered", while samples occurring below that layer were designated as "unweathered". Highly fractured and weathered shales, mudstones, and coals were included as "unweathered". Thus, color and weathering status were simple traits that were described in the field during sample collection.

Splits of the samples were crushed for further chemical analysis. The samples were mechanically crushed using a swinging jaw crusher and sieved to < 2 mm. This < 2 mm material was then mixed with deionized water to form a saturated paste. After allowing the sample to equilibrate for two hours an extract from the paste was then measured per the method described in Rhoades (1996) to give the saturated paste SC in $\mu\text{S}/\text{cm}$ for each sample. For this study, the saturated paste SC was used to estimate the overall TDS generation potential for each sample. The paste extract was also analyzed for individual ionic concentrations using ICP-MS, but those results are not presented here; see Johnson (2016) for those full methods and results. The < 2 mm samples were also tested for reaction to 30% hydrogen peroxide (H_2O_2). Approximately one to two cm of crushed sample was added to a test tube. Enough 30% H_2O_2 was then added to completely submerge the sample. The sample reactions were recorded as foam, heat, violent, or cold reactions. Samples that boiled, frothed over, and generated extreme heat were labeled as "violent". Samples generating temperature levels below boiling were labeled as "heat". Both samples that produced no bubbles and those that bubbled vigorously, but produced no heat were labeled as "cold". Samples that generated visible amounts of foam, but produced no heat were labeled as "foam". Finally, the

< 2 mm samples were also sent to the Virginia Tech Soil Testing Laboratory (VTSTL; Maguire et al., 2011) for routine soil testing. The VTSTL report generates multiple ratings for each sample, but the Mg rating turned out to be especially useful for separating low and high TDS risk mine spoils. For the Mg rating, the VTSTL rated the samples based on the Mg concentrations present in each sample - based on a low, medium, high, very high ranking system. Thus, the saturated paste SC, 30 % H₂O₂ reaction, and VTSTL Mg rating were three lab tests employed to measure TDS risk that were somewhat rapid and inexpensive compared to other lab techniques.

Results and Discussion

Many of the simple indicators investigated were quite effective at distinguishing low from high TDS generation potential mine spoils; these results provide a valuable field guide to identifying and separating low and high TDS generation potential spoils. Below is an overall description of the various types of soils and geologic materials that were encountered throughout the study area and an associated summary of TDS prediction tools and their potential for field application.

While only partially discussed here, overall saturated paste extract solutions were dominated by sulfate, but Ca and Mg were also significant contributors. Selenium was significantly lower in soil and weathered bedrock than unweathered bedrock. Soil A horizons were significantly higher in As than B horizons, C horizons, or bedrock layers. Magnesium, SC, Se, and sulfate were all significantly higher in samples that reacted with heat or violently to H₂O₂. These results are discussed in more detail in Johnson (2016).

Weathered Mantle

Soils - Low TDS Risk

Weathered native soils in the Central Appalachians are a source of low SC mine spoil for use in reclamation. For this study, soils were differentiated from bedrock when they could no longer be dug through by hand with a shovel and were separated broadly into A (topsoil), B (subsoil), and C (soft, shovel diggable bedrock) horizons. Soil A horizons were significantly higher in SC than B and C horizons, but made up the lowest volume of material (generally < 15 cm thick) overall. Distinct C horizons were only found at a few of the sites and soils generally transitioned from B horizons directly into hard bedrock; few saprolitic materials were found at any of the study sites. On the other hand, B horizons were present at every site and nearly always were the lowest SC material available. The A horizons were generally brownish to blackish in color, while B and C horizons were generally yellowish brown. Thus, while A horizons are somewhat higher in SC than other soils layers, they are generally very thin and all combined soil layers in general are a good source of low SC material.

Brown, Weathered, Near-Surface Sandstones - Low TDS Risk

Brown, weathered, near-surface sandstones, located in situ above any shale or mudstone layers, are also a source of low SC material. Increased exposure to groundwater flow and oxidation of sandstone strata near the surface results in a complex set of colorations in these layers from Fe and Mn staining, soil transportation downward, and the exposure of inclusions in the sandstones, such as lithic fragments. The dominant colors of these materials are yellowish brown, with many individual red, brown, and yellow colors (Figs. 2; 3). Weathered sandstones were found to be significantly lower in SC than any other rock strata studied. Additional studies of selected sandstones in thin section by Dr. Kenneth Eriksson of Virginia Tech revealed both weathered and unweathered sandstones were generally quartz rich subarkoses or sublitharenites. Thus, brown, weathered sandstones found near the surface can reliably be used as a source of low SC reclamation material.

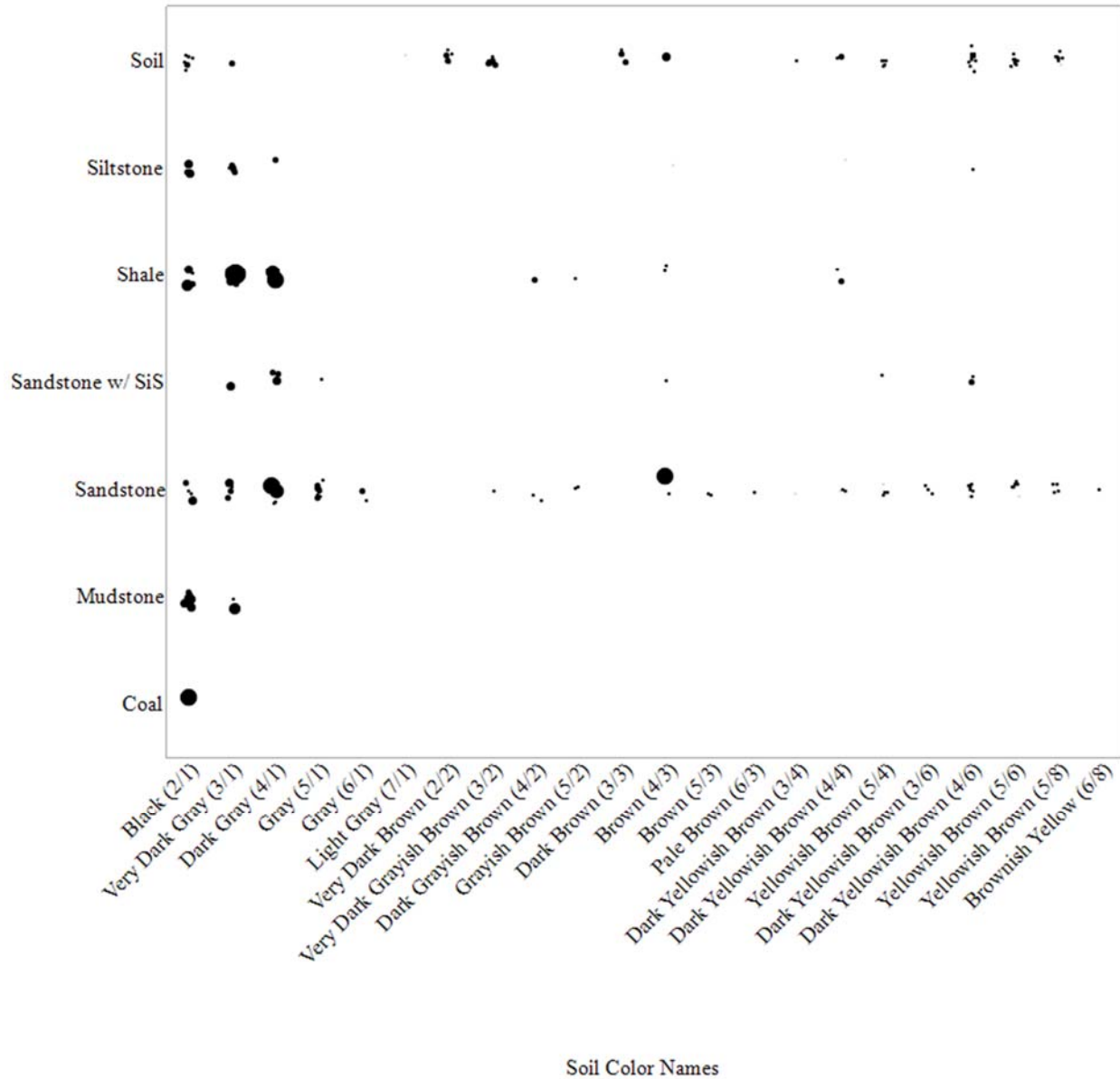


Figure 2. Effects of rock type and Munsell color (value / chroma) for all 204 samples, including outliers. The relative sizes of the bubbles represent relative saturated paste SC (i.e. small bubbles represent low SC samples and large bubbles represent high SC samples). The range of SC was from $23 \mu\text{S cm}^{-1}$ to $4,690 \mu\text{S cm}^{-1}$. The mean and median SC were $503 \mu\text{S cm}^{-1}$ and $204 \mu\text{S cm}^{-1}$, respectively. Black, very dark gray, and gray samples were generally higher in SC than other samples.

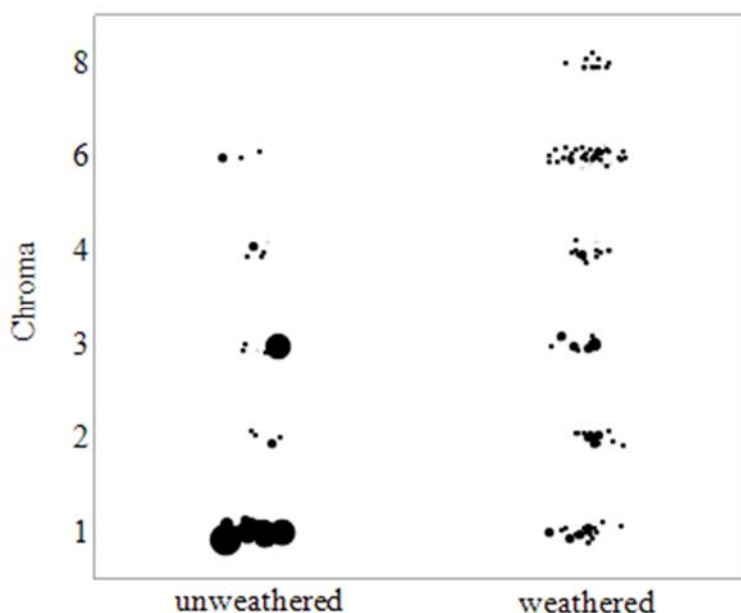


Figure 3. Effect of weathering status and Munsell chroma on saturated paste SC for all 204 samples, including outliers. The relative sizes of the bubbles represent relative saturated paste SC (i.e. small bubbles represent low SC samples and large bubbles represent high SC samples). The range of SC was from $23 \mu\text{S cm}^{-1}$ to $4,690 \mu\text{S cm}^{-1}$. The mean and median SC were $503 \mu\text{S cm}^{-1}$ and $204 \mu\text{S cm}^{-1}$, respectively. Unweathered samples with chroma 1 colors were generally higher in SC than other samples.

Underlying Materials

Gray, Unweathered Sandstones - Potentially High TDS Risk

Sandstones originating deeper below the surface, especially those below an intact shale or mudstone layer preventing downward water movement, were generally gray and potentially high in SC. Hydrologic isolation of these layers resulted in distinctly different properties than the sandstones above. Iron and Mn oxidation was minimal and most colors were uniformly grayish. Gray, unweathered sandstones were significantly higher in SC than weathered sandstones, but some gray, unweathered sandstones also produced low saturated paste SC values. The H_2O_2 reaction test was effective at further differentiating between high and low SC for the unweathered sandstones (Fig. 4); many of the unweathered sandstones producing violent or heat reactions to the peroxide produced high SC while those that produced only bubbles or foam were mostly low in SC. The Virginia Tech Soil Testing Lab (VTSTL) plant available Mg rating was also effective at further differentiating between high and low TDS

risk for unweathered bedrock strata (Fig. 5); nearly all of the unweathered samples that were high TDS risk had a Mg rating of very high (VH). As mentioned above, both weathered and unweathered sandstones were generally quartz rich subarkoses or sublitharenites. Thus, gray, unweathered sandstones in the study area are generally higher in SC than brown, weathered sandstones; however, some unweathered sandstones do produce low SC.

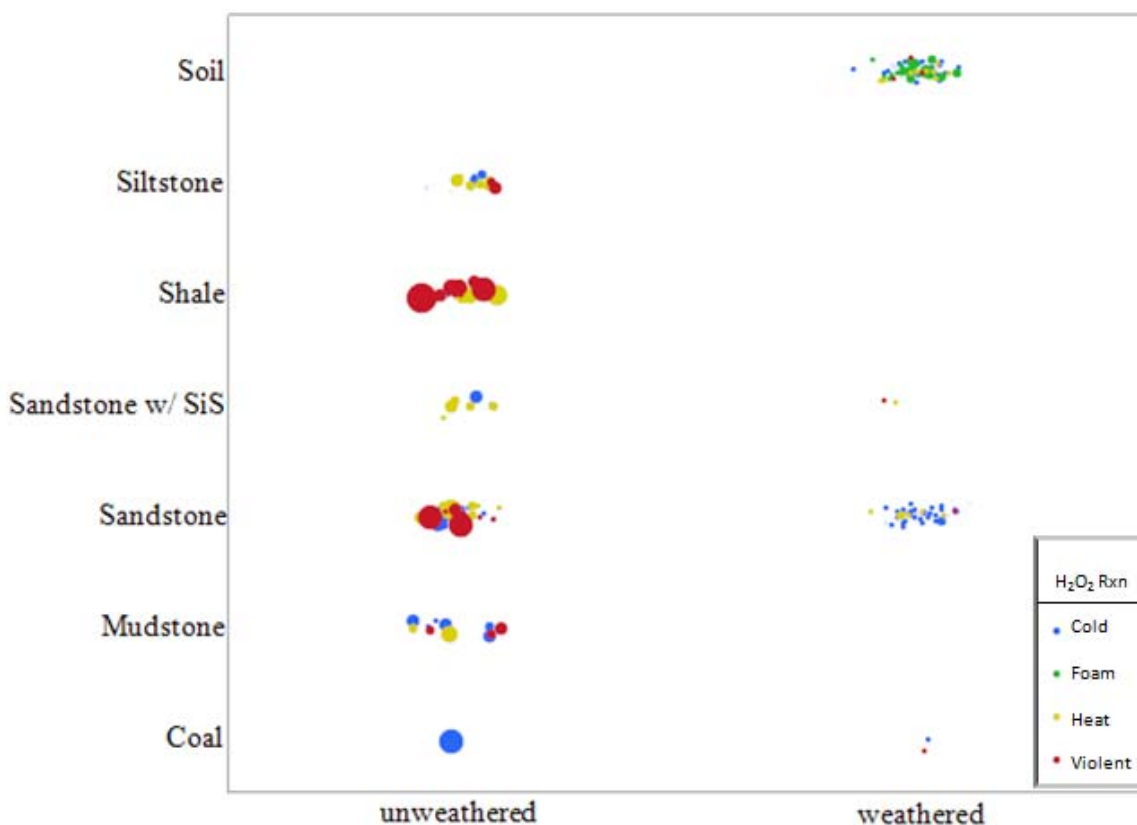


Figure 4. Effect of rock type, weathering status, and H₂O₂ reaction on saturated paste SC for all 204 samples, including outliers. The relative sizes of the bubbles represent relative saturated paste SC (i.e. small bubbles represent low SC samples and large bubbles represent high SC samples). The range of SC was from 23 $\mu\text{S cm}^{-1}$ to 4,690 $\mu\text{S cm}^{-1}$. The mean and median SC were 503 $\mu\text{S cm}^{-1}$ and 204 $\mu\text{S cm}^{-1}$, respectively. 30% H₂O₂ reaction indicated by color; blue= cold, green = foam, yellow = heat, and red = violent. Unweathered samples reacting with heat or violently to the H₂O₂ were generally higher in SC than other unweathered samples.

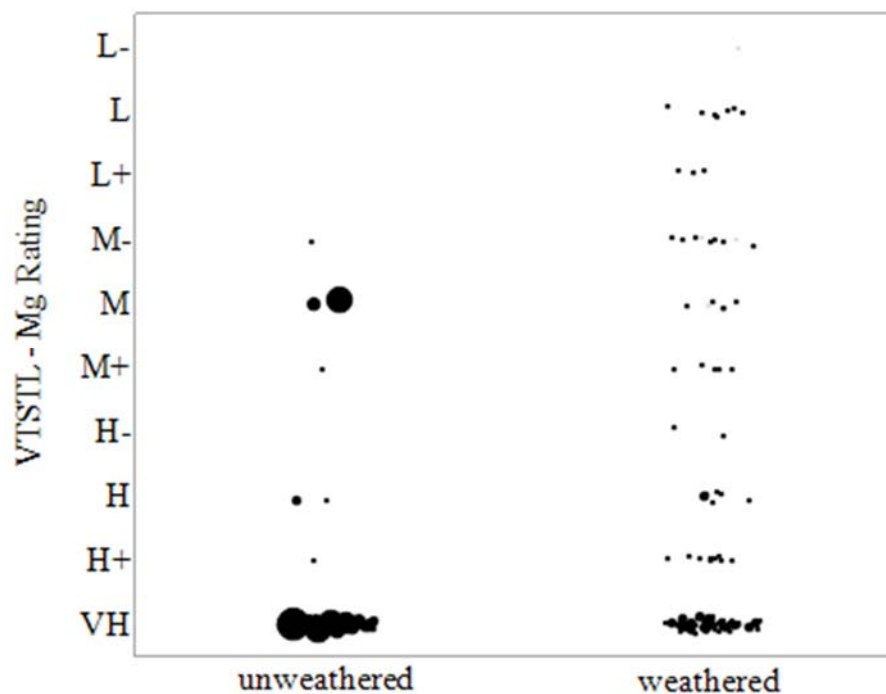


Figure 5. Effect of weathering status and Virginia Tech Soil Testing Lab (VTSTL) Mg rating on saturated paste SC for all 204 samples, including outliers. The relative sizes of the bubbles represent relative saturated paste SC (i.e. small bubbles represent low SC samples and large bubbles represent high SC samples). The range of SC was from $23 \mu\text{S cm}^{-1}$ to $4,690 \mu\text{S cm}^{-1}$. The mean and median SC were $503 \mu\text{S cm}^{-1}$ and $204 \mu\text{S cm}^{-1}$, respectively. VTSTL Mg ratings: L = low, M = medium, H = high, and VH = very high. Unweathered samples rated as very high (VH) for Mg were generally higher in SC than other unweathered samples.

Shales, Siltstones, and Mudstones - Potentially High TDS Risk

Fine-grained rocks produced significantly higher SC levels than sandstones and generally followed the sequence of mudstone > shale > siltstone. Mudstones were either very dark gray or black and significantly higher SC than any of the other rock types (except coal and associated materials). Siltstones were similar in color, often being black, very dark gray, or dark gray, but were moderate in SC. Shales ranged in color and SC, but generally brownish shales were low in SC and black, very dark gray, and dark gray shales were moderate to very high in SC. Some of the fractured, near-surface, fine-grained layers that would have been deemed "weathered", per the convention for sandstones discussed above, had generally weathered to the extent that they were able to be dug by shovel. Therefore, these materials were included as "soil" samples and not reported as siltstone, mudstone, or shale. These

degraded layers formed the only saprolitic C horizons found in the study area and were generally lower in SC than similar rock types in an unweathered state. Thus, brown shales and saprolites are generally low in SC, but most other fine-grained rocks are moderate to high in SC.

Coals, Fireclays, Underclays, Flint Clays, and Other Coal Associated Materials - High TDS Risk

Coal beds commonly occurred in the study area in conjunction with other thin strata, described by many local names, such as fireclay, underclay, flint clay, mudrock, mudstone, or black shale. Coal and all of these associated materials are generally very high SC and should be considered "hot" with respect to SC. The coal associated materials are all dark in color, commonly contain plant fossils, and occur directly above, between, or below coal beds. These layers are often small in volume compared to the total overburden removed, so extra effort focused towards identifying and isolating these layers will be particularly rewarding in the effort to reduce overall mine site TDS elution. In short, coal, fireclays, flint clays, underclays, and associated materials are all very high SC and should be handled separately and isolated from surface or subsurface flow whenever possible.

Conclusions

The central Appalachian mine spoils studied were found to vary significantly in geochemical properties and several of the predictors for TDS evaluated in this study turned out to be quite useful, such as chroma, color, weathering status, VTSTL Mg rating, rock type, and H₂O₂ reaction. Significant differences in overall TDS risk was detected among individual samples, but no differences were found among sites. In general, yellowish-brown sandstones and soil materials were low in saturated paste SC compared to the underlying grayish to black sandstones, shales, and mudstones. Generally all of the soil and weathered sandstones occurring above the shallowest intact shale or mudstone layer can be dependably used as source of low TDS material. However, the extent of rock weathering often changes abruptly immediately beneath the first intact shale/mudstone layer or coal seam encountered in a given weathering profile.

None of the predictors studied here provided an absolute indicator of SC production risk by themselves, but several different combinations of indicators proved quite effective at separating low and high SC spoils. Weathering status and chroma make a simple, but effective combination. Weathering status, rock type, and H₂O₂ reaction also make a reliable combination and improve overall discrimination ability for both SC and Se risk. Weathering status and the VTSTL Mg rating make an even better combination for predicting overall TDS risk, but this would require shipping samples to a soil testing lab. When weathering status is unknown, color and rock type alone make a suitable combination for prediction TDS risk.

Handling techniques similar to those used with acid forming materials are recommended to hydrologically isolate especially high TDS risk spoils and these include gray to black mudstones and shales, coals, and coal associated shales, mudstones, and clays directly associated with coal seams. Yellowish-brown surficial soil and sandstone layers are recommended as a source of low TDS fill for use in areas with significant contact with rainwater or groundwater. Harder, low TDS risk sandstones are recommended (when available) for rock drains and other direct water contact applications.

In summary, there were relatively few high TDS risk materials in the sample set and these originated from strata that were thin in comparison to the overall amount of overburden removed; the field indicators described here were effective at distinguishing those strata. Identification and special handling of high TDS risk strata should be an effective means of reducing overall mine site TDS elution. These results provide a guide for identifying low and high TDS strata pre-mining, which can allow operators to effectively manage materials for TDS risk.

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