



Predicting total dissolved solids release from central Appalachian coal mine spoils[☆]



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ARTICLE INFO

Article history:

Received 14 March 2016

Received in revised form

13 May 2016

Accepted 18 May 2016

Keywords:

Reclamation

Soluble salts

Mountaintop mining

Valley fills

ABSTRACT

Appalachian USA surface coal mines face public and regulatory pressure to reduce total dissolved solids (TDS) in discharge waters, primarily due to effects on sensitive macroinvertebrates. Specific conductance (SC) is an accurate surrogate for TDS and relatively low levels of SC (300–500 $\mu\text{S cm}^{-1}$) have been proposed as regulatory benchmarks for instream water quality. Discharge levels of TDS from regional coal mines are frequently $>1000 \mu\text{S cm}^{-1}$. The primary objectives of this study were to (a) determine the effect of rock type and weathering status on SC leaching potentials for a wide range of regional mine spoils; (b) to relate leachate SC from laboratory columns to actual measured discharge SC from field sites; and (c) determine effective rapid lab analyses for SC prediction of overburden materials. We correlated laboratory unsaturated column leaching results for 39 overburden materials with a range of static lab parameters such as total-S, saturated paste SC, and neutralization potential. We also compared column data with available field leaching and valley fill discharge SC data. Leachate SC is strongly related to rock type and pre-disturbance weathering. Fine-textured and non-weathered strata generally produced higher SC and pose greater TDS risk. High-S black shales produced the highest leachate SC. Lab columns generated similar range and overall SC decay response to field observations within 5–10 leaching cycles, while actual reduction in SC in the field occurs over years to decades. Initial peak SC can be reliably predicted ($R^2 > 0.850$; $p < 0.001$) by simple lab saturated paste or 1:2 spoil:water SC procedures, but predictions of longer-term SC levels are less reliable and deserve further study. Overall TDS release risk can be accurately predicted by a combination of rock type + S content, weathering extent, and simple rapid SC lab measurements.

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1. Introduction

Surface coal mines in the central Appalachian USA region have faced a wide range of public and regulatory challenges since the mid-1970's, including the need to limit acid mine drainage via appropriate application of acid-base-accounting procedures (ABA; Skousen et al., 2002) and other post-mining land use challenges such as re-establishment of native forest vegetation (Zipper et al., 2011). However, a number of recent studies (Pond et al., 2008, 2014; Timpano et al., 2015b) and resultant regulatory proposals

and supporting studies have concluded that relatively low levels of total dissolved solids (TDS) in discharge waters from coal mines as estimated by specific conductance (SC) of 300–500 $\mu\text{S cm}^{-1}$ have negative instream effects to aquatic biota, particularly benthic macroinvertebrates (Cormier 2013a; USEPA, 2011a; Pond et al., 2008; and USEPA, 2011b which is no longer in force as described by Copeland, 2015). The concerns are particularly focused upon mountaintop mining operations with large associated valley fills (Lindberg et al., 2011; Bernhardt et al., 2012) but elevated TDS can also be produced by other forms of coal surface mining and underground mining. Most active coal mines in the region discharge at higher SC levels (commonly $> 1000 \mu\text{S cm}^{-1}$) during and immediately after active operations and elevated SC release continues for extended periods of time beyond mine closure (Evans et al., 2014; Pond et al., 2014). Thus, a clear need has emerged to

[☆] This paper has been recommended for acceptance by Harmon Sarah Michele.

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develop prediction approaches to identify problematic strata and more effective strategies to minimize TDS release from active and post-closure coal mines. Critical to this effort is the ability to predict both short- and long-term TDS release to allow for pre-mine assessment and isolation of high risk spoil materials and to optimize active mine spoil handling and disposal plans.

The dominant constituent ions of TDS released by weathering of central Appalachian mine spoil materials are typically Ca, K, Mg, Na, SO_4 and HCO_3 in circumneutral waters and higher amounts of Al, Fe and Mn in strongly acidified systems (Skousen et al., 2000). All of these components are released by various chemical weathering reactions, particularly when deeper unweathered and unoxidized strata containing sulfides are exposed to rapid oxidation, hydrolysis, hydration and dissolution reactions in reclaimed backfills and valley fills of active coal mines. Even relatively low levels of pyritic-S (e.g. <0.1%) can lead to SC levels >1000 $\mu\text{S cm}^{-1}$ in initial spoil leachates as the reactive sulfides quickly oxidize and are neutralized by carbonates and other neutralizers (Orndorff et al., 2015). Current regulations and mining practices mandate that strongly acid-forming materials (net potential acidity > 5 Mg calcium carbonate equivalent per 1000 Mg spoil by ABA) must be isolated away from significant surface and ground water interactions, presumably eliminating the largest potential source of net TDS release. However, historical application of ABA has sometimes allowed for thinner non-isolated strata containing significant amounts of reactive sulfides to be managed together with thicker adjacent strata higher in carbonates for co-disposal in valley fills such that these co-mingled materials can contribute substantially to TDS loadings (particularly Ca + Mg and SO_4) as they weather over time. Regardless of overall ABA status of strata, it is quite common for high TDS leachates from regional coal spoils to maintain moderate to circumneutral pH conditions (Agouridis et al., 2012; Hartman et al., 2005; Orndorff et al., 2015).

Recent studies of TDS release from southwest Virginia spoils ($n = 15$) in laboratory columns (Orndorff et al., 2015) and from eastern Kentucky spoils ($n = 3$) in large field lysimeters (Agouridis et al., 2012; Sena et al., 2014) have indicated that (a) rock type and extent of pre-mine weathering have a strong influence on overall TDS release risk; (b) leachate SC levels are at their highest immediately after mine-spoil exposure and then drop relatively quickly over time; and (c) initial TDS release is dominated by SO_4 and Ca + Mg, but HCO_3 increases with leaching as sulfate concentration declines over time. In a parallel study to the results reported here, Odenheimer et al. (2014) found that several ABA parameters such as maximum potential acidity (MPA; total-S $\times 31.25$) could reliably predict initial 1:2 spoil:water paste extract SC levels in a large set ($n = 41$) of regional spoils and could therefore presumably be used to predict actual spoil discharge TDS risk.

Historically, ABA has been the dominant set of laboratory static analyses utilized to predict coal mine drainage quality (Skousen et al., 2002). However, many researchers have favored the use of column leaching studies since they presumably offer better prediction of the kinetics of acid-base interactions and temporal change in drainage parameters (Caruccio et al., 1993; Halvorson and Gentry, 1990; Hood and Oertel, 1984). However, column studies generally require replication and high inputs of labor and analytical time and take months to complete. On the other hand, static tests such as those required for conventional ABA (Total-S, neutralization potentials, etc.) are quicker and much less costly. In this study, we collected and analyzed a large set ($n = 39$) of mine spoils from large active coal mines in eastern Kentucky (KY), southwest Virginia (VA) and southern West Virginia (WV) and subjected them to unsaturated column leaching evaluation (replicated $3 \times$ each) coupled with detailed analyses of the spoils via a wide range ($n = 15$) of different static laboratory analytical procedures. Our specific study

objectives were:

1. To utilize unsaturated laboratory leaching columns to determine the overall effects of rock type and pre-disturbance weathering status on TDS production risk for a wide range of regional mine spoils that were actively being placed and managed in large mining fills.
2. To relate laboratory leaching column results to available field TDS/SC leaching or discharge data from the study region to better determine the applicability of the column leaching data to actual measured field conditions.
3. To determine the most effective static laboratory procedures for predicting both initial peak SC levels and long-term semi-stable (tail) SC production risk.
4. To recommend a set of easily applicable and economic laboratory or field procedures for evaluating TDS leaching risk based on our findings.

2. Materials and methods

2.1. Spoil collection and characterization methods

Thirty-nine bulk samples were collected from large active surface coal mines including five southwest Virginia sites, four eastern Kentucky sites, and three in West Virginia (Fig. 1; Table 1). Samples were obtained from freshly blasted and fractured spoils and identified as originating from defined stratigraphic positions within the Pennsylvanian aged Pottsville Group (WV), Breathitt Group (KY), and Norton and Wise formations (VA) which consist of interbedded sandstones, mudstones, shales, and coal. The samples included diverse rock types at different degrees of pre-disturbance (*in situ* pre-mining) weathering, representing the majority of overburden strata associated with large area coal mines in this region. Spoils were classified by weathering status, considering the importance of pre-mine weathering to geochemical mechanisms governing ion release. Materials exposed to near-surface weathering prior to mining have undergone long term geochemical oxidation and dissolution processes not experienced by “unweathered” materials

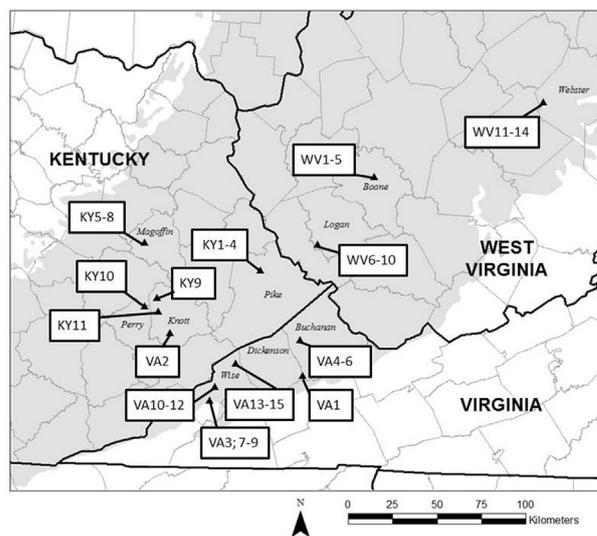


Fig. 1. Location map of spoil sampling locations in Kentucky, Virginia, and West Virginia. The gray coloration indicates the Appalachian coalfield. Sample VA 2 occurred in Kentucky, but was sampled in a previous study along with a wider range of samples from Virginia.

Table 1

Selected geologic and chemical properties of 39 coal mine spoil samples from eastern Kentucky, southwest Virginia and southern West Virginia Pennsylvanian age strata. Abbreviations: R – rock type; W – weathering extent; WV – West Virginia; 1:1 and 1:2 – spoil:water ratio; SC – specific conductance; MPA – maximum potential acidity; CCE – calcium carbonate equivalent; NP – neutralization potential; NNP – net neutralization potential (WV-NP - MPA); PPA – peroxide potential acidity.

| ID | R ^a | W ^b | Geologic formation | WV 1:1 pH | | H ₂ O ₂ pH | WV 1:2 SC | | Sat. Paste SC | H ₂ O ₂ SC | MPA | CCE | WV- NP | Sobek-NP | MPA + Sobek-NP ^c | NNP | PPA |
|------|----------------|----------------|--------------------|-----------|---------------|----------------------------------|---------------------|--------------------|---------------|----------------------------------|-----|-----|--------|----------|-----------------------------|-------|-----|
| | | | | Paste pH | Sat. Paste pH | | uS cm ⁻¹ | g kg ⁻¹ | | | | | | | | | |
| WV1 | ss | uw | Kanawha | 6.3 | 7.05 | 3.51 | 220 | 684 | 514 | 12.0 | 32 | 1.5 | 0.6 | 12.6 | -10.5 | -6.49 | |
| WV2 | ss | uw | Kanawha | 6.6 | 7.13 | 4.75 | 190 | 656 | 334 | 3.6 | 41 | 2.1 | 0.9 | 4.5 | -1.5 | -0.13 | |
| WV3 | ms | uw | Kanawha | 8.0 | 8.19 | 7.05 | 210 | 515 | 286 | 1.5 | 75 | 1.7 | 1.2 | 2.7 | 0.2 | 0.00 | |
| WV4 | ss | uw | Allegheny | 7.3 | 8.13 | 6.48 | 80 | 203 | 185 | 0.4 | 24 | 1.5 | 0.7 | 1.1 | 1.1 | 0.00 | |
| WV5 | ss | uw | Kanawha | 8.1 | 8.27 | 6.96 | 180 | 492 | 218 | 0.6 | 78 | 1.8 | 2.3 | 2.9 | 1.2 | 0.00 | |
| WV6 | mix | uw | Kanawha | 7.3 | 8.02 | 6.69 | 90 | 310 | 217 | 0.6 | 41 | 1.6 | 0.4 | 1.0 | 1.0 | -0.05 | |
| WV7 | mix | uw | Kanawha | 7.6 | 8.02 | 6.60 | 230 | 627 | 263 | 2.0 | 52 | 1.7 | 0.6 | 2.6 | -0.3 | 0.00 | |
| WV8 | ss | mix | Kanawha | 7.2 | 7.82 | 5.06 | 200 | 570 | 461 | 2.0 | 37 | 1.6 | 0.3 | 2.3 | -0.4 | -1.30 | |
| WV9 | ss | uw | Kanawha | 6.9 | 7.52 | 5.53 | 90 | 298 | 191 | 0.8 | 48 | 1.6 | 0.1 | 0.9 | 0.8 | 0.00 | |
| WV10 | ss | uw | Kanawha | 7.8 | 8.09 | 6.63 | 170 | 534 | 236 | 1.7 | 28 | 1.7 | 1.4 | 3.1 | 0.0 | 0.00 | |
| WV11 | ss | uw | Kanawha | 7.1 | 7.69 | 6.08 | 80 | 362 | 231 | 0.6 | 37 | 1.2 | 0.1 | 0.7 | 0.6 | -1.53 | |
| WV13 | ms | uw | Allegheny | 7.2 | 7.64 | 5.97 | 240 | 437 | 278 | 5.4 | 46 | 1.6 | 0.4 | 5.8 | -3.8 | -0.38 | |
| WV14 | mix | uw | Allegheny | 6.4 | 7.06 | 5.85 | 210 | 325 | 188 | 0.6 | 50 | 1.7 | 0.5 | 1.1 | 1.1 | 0.00 | |
| VA1 | ss | uw | Norton | 7.8 | 8.26 | 6.41 | 250 | 742 | 346 | 1.3 | 27 | 1.0 | 0.7 | 2.0 | -0.3 | 0.00 | |
| VA2 | bs | uw | Four Corners | 7.2 | 7.86 | 5.96 | 1010 | 3560 | 1030 | 10.6 | 46 | 1.7 | 1.4 | 12.0 | -8.9 | 0.00 | |
| VA3 | mix | mix | Middle Wise | 4.7 | 4.65 | 4.28 | 210 | 668 | 312 | 2.5 | 13 | 1.7 | 0.0 | 2.5 | -0.8 | -1.50 | |
| VA4 | ms | w | Lower Wise | 5.1 | 5.09 | 5.22 | 100 | 377 | 161 | 0.6 | 16 | 1.7 | 0.2 | 0.8 | 1.1 | -0.13 | |
| VA5 | ss | mix | Lower Wise | 5.6 | 5.31 | 5.00 | 250 | 892 | 282 | 1.3 | 7 | 0.9 | 0.3 | 1.6 | -0.4 | -0.18 | |
| VA6 | ms | uw | Lower Wise | 7.1 | 7.82 | 6.57 | 610 | 2060 | 416 | 3.8 | 21 | 1.3 | 1.2 | 5.0 | -2.5 | 0.00 | |
| VA7 | ms | w | Middle Wise | 7.0 | 7.87 | 6.94 | 80 | 264 | 159 | 0.3 | 47 | 1.0 | 0.6 | 0.9 | 0.7 | -0.09 | |
| VA8 | ms | uw | Middle Wise | 6.7 | 7.01 | 5.51 | 440 | 1532 | 640 | 4.7 | 59 | 1.7 | 0.5 | 5.2 | -3.0 | -0.22 | |
| VA9 | mix | mix | Middle Wise | 7.9 | 8.02 | 6.91 | 200 | 637 | 236 | 2.5 | 59 | 7.1 | 1.2 | 3.7 | 4.6 | 0.00 | |
| VA10 | ms | uw | Middle Wise | 7.8 | 8.22 | 6.97 | 250 | 825 | 404 | 2.8 | 60 | 1.8 | 1.2 | 4.0 | -1.0 | 0.00 | |
| VA11 | ss | w | Middle Wise | 5.5 | 6.62 | 5.19 | 150 | 493 | 255 | 0.6 | 37 | 1.7 | 1.7 | 0.8 | 1.1 | -0.04 | |
| VA12 | ss | uw | Middle Wise | 8.0 | 8.12 | 6.74 | 140 | 425 | 332 | 1.6 | 53 | 0.7 | 1.7 | 3.3 | -0.9 | 0.00 | |
| VA13 | ss | mix | Middle Wise | 7.5 | 8.14 | 7.02 | 120 | 497 | 245 | 0.9 | 47 | 1.0 | 0.7 | 1.6 | 0.1 | 0.00 | |
| VA14 | ss | w | Lower Wise | 6.0 | 7.26 | 5.96 | 90 | 349 | 182 | 0.6 | 34 | 1.7 | 0.2 | 0.8 | 1.1 | -0.13 | |
| VA15 | ms | uw | Lower Wise | 8.3 | 8.44 | 7.60 | 250 | 778 | 387 | 2.8 | 83 | 1.5 | 2.9 | 5.7 | -1.3 | 0.00 | |
| KY1 | ss | w | Princess | 6.8 | 7.52 | 6.33 | 80 | 407 | 242 | 0.3 | 50 | 1.7 | 0.2 | 0.5 | 1.4 | -0.43 | |
| KY2 | ss | uw | Four Corners | 8.2 | 8.09 | 7.14 | 120 | 540 | 296 | 0.5 | 45 | 1.4 | 1.8 | 2.3 | 0.9 | 0.00 | |
| KY3 | mix | mix | Four Corners | 7.8 | 8.16 | 6.88 | 390 | 1213 | 534 | 3.2 | 67 | 5.5 | 1.1 | 4.3 | 2.3 | 0.00 | |
| KY4 | ms | uw | Four Corners | 6.4 | 8.27 | 6.93 | 590 | 1556 | 603 | 3.7 | 61 | 1.8 | 0.9 | 4.6 | -1.9 | 0.00 | |
| KY5 | ms | w | Four Corners | 5.3 | 5.57 | 6.03 | 100 | 525 | 218 | 0.9 | 61 | 1.7 | 0.2 | 1.1 | 0.8 | -0.29 | |
| KY6 | ms | w | Four Corners | 5.5 | 5.04 | 5.53 | 30 | 87 | 144 | 0.5 | 60 | 1.7 | 0.5 | 1.0 | 1.2 | -0.20 | |
| KY7 | bs | uw | Four Corners | 5.4 | 6.37 | 4.11 | 2420 | 7370 | 2790 | 30.2 | 55 | 1.7 | 1.1 | 31.3 | -28.5 | -8.05 | |
| KY8 | ms | uw | Four Corners | 7.0 | 7.28 | 6.25 | 570 | 3040 | 1011 | 6.1 | 45 | 0.7 | 0.6 | 6.7 | -5.4 | -0.36 | |
| KY9 | mix | uw | Four Corners | 5.4 | 6.74 | 4.20 | 1160 | 4040 | 1567 | 7.8 | 36 | 1.5 | 0.9 | 8.7 | -6.3 | -0.48 | |
| KY10 | ss | mix | Four Corners | 4.6 | 5.65 | 3.58 | 860 | 3250 | 1486 | 1.6 | 86 | 1.7 | 0.2 | 1.8 | 0.1 | -0.29 | |
| KY11 | mix | uw | Four Corners | 6.8 | 7.56 | 5.99 | 250 | 837 | 268 | 2.6 | 40 | 1.7 | 0.6 | 3.2 | -0.9 | 0.00 | |

^a bs = black shale; mix = mixed rock types; ms = mudstones; ss = sandstone.

^b mix = mixed weathering status; u = unweathered/gray; w = weathered/brown.

^c Taken as the sum of MPA + Sobek-NP.

deeper in the geologic profile. Highly acid-forming materials were excluded since these materials are required to be identified and isolated by mining operations in compliance with current USA coal mining regulations (SMCRA, 1977). All materials sampled were being disposed in large volumes into active mine valley fills or highwall backfills. Rock types were categorized as sandstone, mudstone, shale, or mixed. 'Mudstone' included non-fissile samples comprised of clay and/or silt-size grains. 'Mixed' samples contained <80% of one given rock type. Weathering was qualitatively classified as unweathered (minimally altered; typically gray), weathered (substantially altered; typically brownish-yellow due to Fe-oxides), or mixed (partially weathered or a mix of weathered and unweathered materials). Three of the samples (KY 1–3) were provided from original sample archives associated with a long-term (9-year) field lysimeter leaching study (Agouridis et al., 2012; Sena et al., 2014) at the Bent Mountain research site in eastern KY. One sample (VA 2) was collected in eastern Kentucky as part of an earlier study, but was included in the Virginia sample set as presented here.

Spoils were air-dried and ground as appropriate for the following procedures. Conventional spoil 1:1 spoil:water pH (WV-pH) was determined and saturated paste SC of a 1:2 spoil:water

(WV-SC) was determined following 15 min of shaking and 1 h equilibration time. Alternative pH (H₂O-pH) and SC (H₂O-SC) analyses were performed on the supernatant portion of a 1:1 spoil:water extract following stirring and 30 min of settling time. For an alternative saturated paste pH and SC (Rhoades, 1982), each spoil was ground to <2 mm, mixed with deionized water to form a glistening paste, equilibrated for ≥ 2 h, then suction filtered and analyzed. To determine whether forced oxidation of sulfides and Fe + Mn species would improve column leachate SC prediction, a similar saturated paste procedure was run using 3% H₂O₂ (H₂O₂-pH, H₂O₂-SC), rather than deionized water. Total-S (%) was determined by dry combustion/infrared analysis using a LECO S-analyzer. Three neutralization potential methods were evaluated including Sobek-NP (Sobek et al., 1978), a modified technique using H₂O₂ additions to minimize positive NP errors due to siderite (WV-NP; Skousen et al., 1997), and calcium carbonate equivalent (CCE; AOAC, 2002). These methods differ somewhat in that for the CCE method, all samples are digested with 50 ml of 0.5 N HCl, and titrated to pH 8.3. With the Sobek-NP and WV-NP, each sample is evaluated by an HCl effervescence test to determine the amount of acid used for digestion, ranging from 20 ml of 0.1 N to 80 ml of 0.5 N HCl, and then titrated to pH 7.0. For acid-base accounting (ABA), maximum

potential acidity (MPA) was calculated as total-S (%) \times 31.25 and net neutralization potential (NNP) was calculated as WV-NP – MPA. All ABA parameters are reported here as g kg^{-1} CCE, which is equivalent to Mg of net CCE surplus or deficit per 1000 Mg spoil (Skousen et al., 2002). Peroxide potential acidity (PPA) was determined by an H_2O_2 oxidation technique (Orndorff et al., 2008) modified from Barnhisel and Harrison (1976); sulfides are oxidized with 30% H_2O_2 and following full reaction (assuming net internal reaction of generated acids with neutralizers) total net acidity is determined by whole sample titration with NaOH.

2.2. Experimental procedures for column leaching

The column leaching method employed here is described in greater detail by Orndorff et al. (2015) and was based upon an earlier design utilized by Stewart et al. (2001) for studying temporal leaching response in coal refuse materials. Leaching columns were built from PVC pipe (inside diameter = 7.4 cm, length = 40 cm) with a concave endcap fitted with a PVC pipe nipple and Tygon tube to drain leachate to a nalgene sample bottle. To minimize preferential flow through the column, rock fragments were crushed to <1.25 cm then back-blended with the finer material. Each column was packed with 1200 cm^3 (mass recorded), and each sample was run in triplicate. To simulate weathering conditions in the Appalachian coalfields, our method maintained unsaturated conditions and twice-weekly dosing/sampling. After initially wetting the material to field capacity, 2.54 cm (125 ml) of simulated rainfall (pH 4.6; Halvorson and Gentry, 1990) was applied twice a week for a total of 40 leaching/sampling events (L0 – L39) over 20 weeks. While the columns varied somewhat in particle size and pore volume, one saturated pore volume was equal to 3 to 5 unsaturated leaching cycles. All leachate samples were analyzed immediately for pH and SC. Leachate data are the means of the 3 replications per spoil material.

2.3. Statistical methods

Statistical differences in column leachate SC between rock types or spoil weathering classes were analyzed graphically; group means separated by ± 2 standard error (SE) for a given leaching cycle were interpreted as different. The primary objective of our statistical analysis was to determine which of the various static lab procedures employed were the best predictors of initial peak SC produced by each material vs. longer term semi-stable SC levels (tail). For this analysis, peak SC was determined as the average of the first two leaching events (0 and 1) and tail SC was determined as the average of the final three events (37–39). First, the entire data set ($n = 39$ spoils with peak SC, tail SC, saturated paste-pH, saturated paste-SC, Total-S, PPA, CCE, H_2O -pH, H_2O -SC, H_2O_2 -pH, H_2O_2 -SC, WV-pH, WV-NP, WV-SC, Sobek-NP, MPA and NNP) was evaluated via correlation analysis (Pearson) with the JMP and SAS statistical packages. Additional combinations of variables (e.g. MPA + Sobek-NP, MPA + WV-NP; MPA + CCE) were also tested. Outliers were identified by a combination of visual analysis and the Cooks D procedure, and correlations were run with and without outliers for certain data sets. Subsequently, step-wise regression was employed to further identify the primary predictor variables and potential data outliers. Additionally, the spoil data set was then split into three groups by weathering status (Mixed = 7; Unweathered = 25; Weathered = 7) and then again into three groups by rock type (Mixed = 8; Mudstone = 12; Sandstone = 17; 2 black shales excluded) for a similar sequence of correlation and regression analyses. Final best fit regression equations were developed following elimination of a limited number (max. $n = 2$) of outliers.

3. Results and discussion

3.1. Spoil properties

The rock type, degree of weathering, and selected chemical properties of the 39 spoils are presented in Table 1 and all ABA parameters are expressed as g kg^{-1} CCE. Overall water and saturated paste pH values were relatively high (most > 6.5) as expected and most MPA values were low (<3 g kg^{-1}). The vast majority (36/39) of samples contained significant levels (>2.0% CCE) of apparent neutralizers such as carbonate cements and reactive feldspars. However, both the WV-NP and Sobek-NP (Table 1) procedures produced much lower neutralization values (<1.0%), indicating that the majority of the CCE values were most likely inflated by the much higher strength of digestion acid of the CCE procedure vs. the two NP procedures as performed. The CCE procedure also titrates to a higher pH (8.3) than the NP procedures (7.0) which also more than likely inflates the values. Samples with NNP values less < -5 g kg^{-1} are considered to be potentially acid-forming materials requiring special handling under current USA coal mining regulations (Skousen et al., 2002). Of this group, only three of the samples (WV 1, VA 2, and KY 7) were predicted to be strongly acid-forming based on combination of conventional ABA and PPA analyses (Table 1) and all but four others had net NNP values of -3 g kg^{-1} or higher. As intended for this study, the 39 materials produced a wide range of saturated paste SC (<200 to >4000 $\mu\text{S cm}^{-1}$), with much higher values associated with black shales and higher total-S, and lower values generally (but not uniformly) associated with significantly weathered strata. The saturated paste SC values were consistently higher than the WV-SC (1:2 spoil:water) values due to the lower spoil:water extract ratio of the latter procedure, but the two were strongly correlated ($r = 0.93$; $p < 0.001$).

3.2. Effects of rock type and weathering on column leachate pH and SC

Orndorff et al. (2015) reported general effects of leaching duration, rock type and pre-mine weathering status on column leachate conductance on a more limited set ($n = 15$) of mine spoils from southwest VA (including one from eastern KY). In this study, we supplemented those original samples with an additional 24 spoils from WV and KY to greatly expand the scope of spoil materials evaluated and to further validate our original findings. As shown in Fig. 2, column leachate pH initially reflected the low pH (4.6) of the simulated precipitation, but increased rapidly due to spoil neutralization potentials. None of the samples produced strongly acidic (<pH 6.0) drainage following the initial equilibration period. The influence of pre-disturbance oxidation, dissolution and leaching reactions is clearly expressed where weathered strata have been previously stripped of neutralizers and stabilized at longer term semi-stable (tail) pH values between 6.0 and 6.6, while unweathered strata were buffered by carbonates to approach 8.0. As one would expect, the mixed samples were intermediate in pH between weathered and unweathered samples, and showed greater variation.

Extent of pre-disturbance weathering also strongly affected leachate SC (see Fig. 3) with pre-weathered spoils generating much lower average peak ($\sim 750 \mu\text{S cm}^{-1}$) and tail ($\sim 150 \mu\text{S cm}^{-1}$) levels than unweathered or mixed and partially weathered strata which produced peak SC levels > $1500 \mu\text{S cm}^{-1}$. Pre-weathered materials typically occurred within 10–20 m of the original soil surface, were usually brown in color due to accumulation of Fe-oxides, and had been exposed to long-term hydrolysis, oxidation and leaching processes. Rock type also significantly affected SC levels (see Fig. 4)

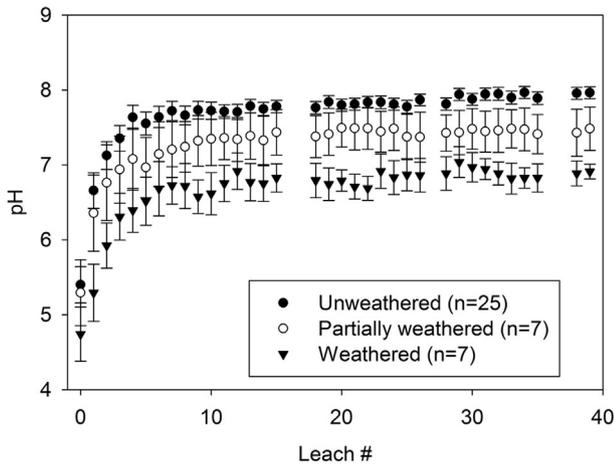


Fig. 2. Effect of pre-mine rock weathering status on leachate pH. Leachates initially reflect low pH (4.6) of the simulated precipitation, but rapidly rise due to spoil neutralization potentials. The influence of pre-disturbance oxidation, dissolution and leaching reactions is clearly expressed where weathered strata have been previously stripped of neutralizers. Data for all 39 samples shown. Bars above/under each point reflect \pm one standard error.

with most finer textured mudstones and mixed sandstone/mudstone samples generating consistently higher SCs throughout the leaching study, but especially at the beginning. It is also important to note that the two black shales (not included in Fig. 4) produced very high initial SC levels ($>3000 \mu\text{S cm}^{-1}$). Overall, the combined SC column leaching analysis reconfirmed the earlier findings of Orndorff et al. (2015), who showed that tail SCs for approximately 90% of the spoils tested fell below the $500 \mu\text{S cm}^{-1}$ level. Pond et al. (2008) suggested a $500 \mu\text{S cm}^{-1}$ level as the threshold for biotic effects. However, the tail SCs of approximately 50% of our samples remained above the proposed chronic aquatic-effects benchmark of $300 \mu\text{S cm}^{-1}$ as suggested by the USEPA (2011a).

3.3. Analysis of lab predictors of peak and tail SC

Initial correlation analysis of the full spoil data set ($n = 39$) vs. the full set of static lab tests indicated that seven static lab

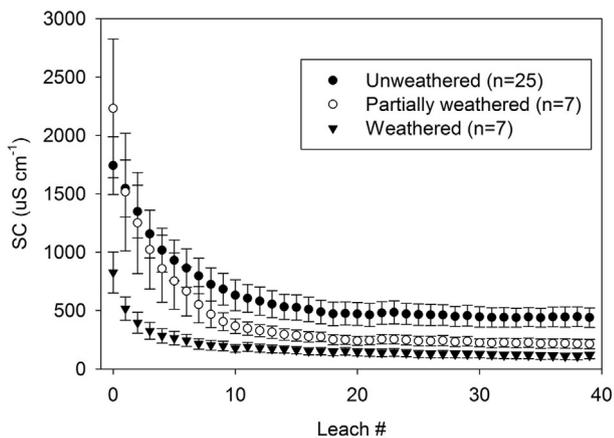


Fig. 3. Effect of pre-mine rock weathering status on leachate specific conductance (SC). Spoils that have undergone significant pre-disturbance oxidation and leaching produce much lower initial (peak) and long-term (tail) SC than unweathered or partially weathered materials. Data for all 39 samples shown. Bars above/under each point reflect \pm one standard error.

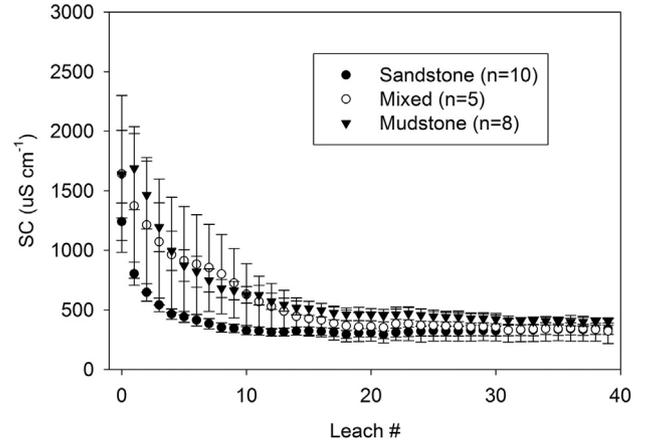


Fig. 4. Effect of rock type on leachate specific conductance (SC) for unweathered spoil samples. In general, finer textured mudstones and mixed sandstone/mudstone samples produce higher peak SC levels, but longer term semi-stable (tail) levels do not differ strongly. Data for all unweathered ($n = 23$) samples shown; weathered and black shale samples excluded. Bars above/under each point reflect \pm one standard error.

predictors (Table 2) were well-correlated ($r > 0.45$ and $p \leq 0.05$) with either peak or tail SC, or both. No combination variables (e.g. MPA + CCE or NP parameters) were well-correlated with peak SC. For peak SC, four different lab SC methods were highly correlated ($r > 0.80$; $p < 0.001$) and both the Sat-SC and WV-SC procedures improved to $r > 0.90$ when two outliers (both black shales) were removed. Total-S (expressed as MPA) generated a lower r -value (0.64; Table 2) for the full data set that was strongly influenced by the two outliers; the r -value fell to 0.44 when they were removed. When the data set correlations were sorted and re-run by weathering status, a relatively slight increase in r -values was observed for certain parameters (e.g. Sat-SC for unweathered spoils increased from $r = 0.91$ to 0.94), but no overall improvement was seen when the correlations were sorted and reanalyzed by rock type. Further efforts to improve peak SC prediction via stepwise multiple regression did not result in significant model improvements beyond the use of one variable (e.g. Sat-SC or WV-SC). The final best fit curvilinear regression model [see Fig. 5; Peak SC = $56.819 + (5.422 \times \text{WV-SC}) - (0.00151 \times \text{WV-SC}^2)$] produced an R^2 value of 0.880 with the two black shale outliers removed and a very similar model [$R^2 = 0.857$; Peak SC = $58.9 + (1.732 \times \text{sat. paste SC}) - (0.000194 \times \text{sat. paste SC}^2)$] was achieved when alternative saturated paste SC (Sat-SC; Rhoades, 1982) was employed as the static lab analysis.

Correlation analysis (Table 2) of the full spoil data set ($n = 39$) for prediction of the longer term semi-stable “tail SC” revealed that both the SC and MPA lab predictors produced relatively strong correlations ($r > 0.84$). However, all of these r -values fell substantially to 0.59–0.67, respectively, when a single black shale outlier was removed from the data set. With one exception (mixed spoils as discussed below), sorting the data set by weathering status or rock type did not improve correlations with longer term semi-stable tail SC levels, nor did stepwise multiple regression improve prediction models beyond one-parameter regression. Figure 6 presents the best fit curvilinear regression [$R^2 = 0.482$; Tail SC = $519.7 \times [1.0 - \exp(-0.003891 \times \text{WV-SC})]$] which is considerably lower in overall prediction strength than the model for peak SC (Fig. 5), and is much less effective at predicting higher leachate SC levels. One additive parameter (MPA + Sobek-NP) was similar in correlation strength ($r = 0.67$) and regression model ($R^2 = 0.56$) to WV-SC, but would require additional lab analyses beyond the simple 1:2 spoil:water extraction procedure. However, correlation

Table 2
Summary of simple correlation results (*r* values) for static lab predictors vs. initial peak and long-term tail specific conductance (SC). Analysis shown for complete data set (*n* = 39) and with strong outliers (peak – 2; tail – 1; *n* = 37) associated with black shale samples removed. PPA = Peroxide Potential Acidity.

| Variable | Peak – SC | | Tail – SC | |
|-----------------------------------|-------------------|--------------------|-------------------|-------------------|
| | Complete data set | 2 outliers removed | Complete data set | 1 outlier removed |
| Sat-SC | 0.891 | 0.908 | 0.845 | 0.629 |
| | <0.0001 | <0.0001 | <0.0001 | <0.0001 |
| MPA | 0.642 | 0.438 | 0.907 | 0.613 |
| | <0.0001 | 0.006 | <0.0001 | <0.0001 |
| PPA | 0.373 | 0.011 | 0.694 | 0.063 |
| | 0.019 | 0.944 | <0.0001 | NS |
| H ₂ O-SC | 0.823 | 0.832 | 0.899 | 0.643 |
| | <0.0001 | <0.0001 | <0.0001 | <0.0001 |
| H ₂ O ₂ -pH | –0.460 | –0.387 | NS | NS |
| | 0.003 | 0.017 | | |
| H ₂ O ₂ -SC | 0.880 | 0.882 | 0.851 | 0.598 |
| | <0.0001 | <0.0001 | <0.0001 | <0.0001 |
| WV-SC | 0.869 | 0.929 | 0.895 | 0.670 |
| | <0.0001 | <0.0001 | <0.0001 | <0.0001 |

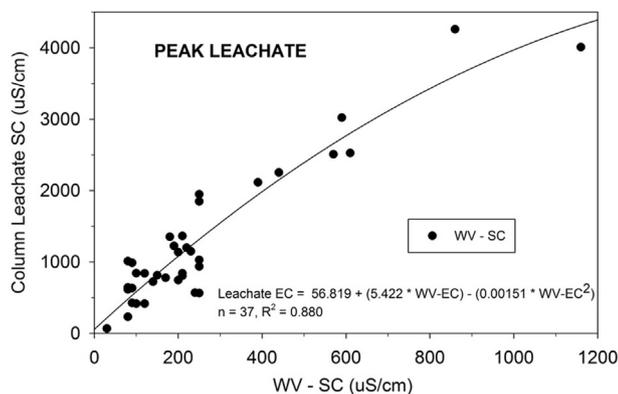


Fig. 5. Best fit regression model for prediction of peak leachate specific conductance (SC) by a simple static lab analysis, 1:2 spoil:water extract specific conductance (WV-SC). A similar predictive model ($R^2 = 0.857$) is achieved with use of a conventional saturated paste SC extract.

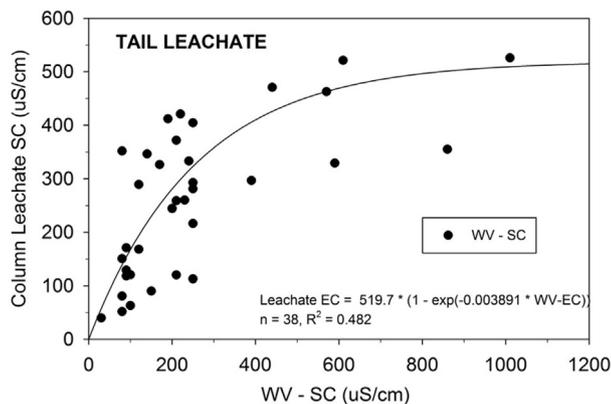


Fig. 6. Best fit regression model for prediction of longer term tail leachate specific conductance (SC) by a simple static lab analysis, 1:2 spoil:water extract specific conductance (WV-SC).

analysis for the relatively limited (*n* = 7) group of mixed spoils revealed that a number of lab static tests (e.g. Sat-SC, CCE, Total-S, H₂O-SC, H₂O₂-SC, and WV-SC) produced highly significant correlations ($r > 0.93$; $p < 0.001$) and associated highly predictive linear regression models (see Fig. 7 for one example). Similar results were

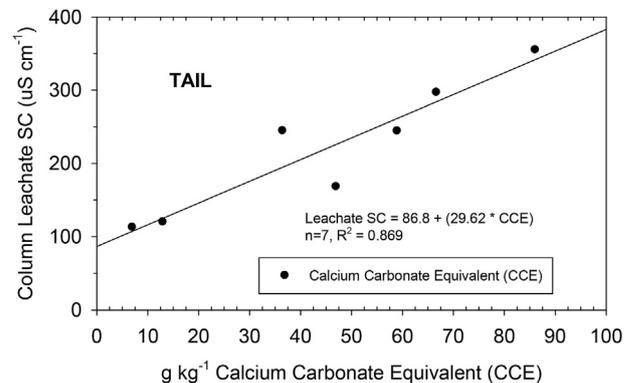


Fig. 7. Simple linear regression model for prediction of long term semi-stable tail leachate specific conductance (SC) for mixed spoils by lab determination of calcium carbonate equivalent (CCE) analysis.

not noted for the other major rock types (mudstone *n* = 12; sandstone *n* = 17) or for differential weathering status. Thus, the utility of this model (mixed spoils) for long-term SC prediction is limited.

Multiple studies cited earlier and our associated leachate analyses (Orndorff et al., 2015) on the VA samples included in this study confirm that bulk leachate SC values from these spoils are dominated primarily by sulfates and Ca associated with rapid and complex sulfide oxidation and carbonate neutralization reactions, but that over extended leaching, bicarbonate becomes more common as sulfate declines. Thus, it is somewhat surprising that total-S alone, or in combination with other variables, was not a strong predictor of peak SC production. We presume this is due to the fact that total-S analysis does not account for S speciation (e.g. sulfides vs. sulfates vs. organic) or size + form (e.g. massive vs. framboidal) and associated differences in reactivity of neutralizers in the spoil matrix. It is also interesting to note that none of the more conventional ABA predictors (e.g. MPA, NNP or PPA), that presumably integrate the net effects of S-oxidation and carbonate neutralization reactions to some extent were effective for predicting column leachate peak SC for this sample set. The combined variable MPA + Sobek-NP did produce a relatively weak predictor for tail SC, however. In a parallel study to ours, Odenheimer et al. (2014) analyzed the same spoil sample set (along with two additional high SC samples from WV; total *n* = 41) and found that MPA could reliably predict ($R^2 = 0.80$) initial saturated paste TDS levels and therefore concluded that overall TDS risk (low, medium and high)

could be approximated by ABA procedures.

Overall, it is highly encouraging that simple, quick and inexpensive laboratory SC procedures can produce relatively reliable predictions of peak SC levels, regardless of bulk spoil rock type (with the exception of high S black shales) or degree of weathering. The relative weakness of the static lab analyses to predict longer term SC production levels, particularly in the range of regulatory concern ($300\text{--}500\ \mu\text{S cm}^{-1}$) is notable, but it is important to point out that either of the SC procedures (saturated paste and 1:2 spoil:water) can be effective at identifying materials likely to produce SC in the lower range ($<300\ \mu\text{S cm}^{-1}$).

3.4. Comparison of column vs. field leaching observations

Another important issue addressed by this study is the relative applicability and accuracy of the column leaching methodology utilized vs. actual observed SC levels and temporal response under field conditions. Directly applicable field studies are limited by the fact that most studies (e.g. Pond et al., 2008, 2014; Timpano et al., 2015b; Vengosh et al., 2013) report SC in receiving headwater streams below valley fills and active mine sites rather than at fill discharge points. Regardless, the typical range of SC values reported for mine affected streams in these regional studies conforms well to those produced by the lab columns in this study.

One directly applicable study (Agouridis et al., 2012; Sena et al., 2014) evaluated large scale (0.4 ha \times 2 m deep each) field lysimeter leachate SC levels as influenced by rock type (primarily weathering extent) over a nine-year period at the Bent Mountain site in KY. Fig. 8 presents a comparison of column leaching SC levels for three original archived samples (KY 1-3) from the Bent Mountain experiment vs. the nine-year field lysimeter SC values. Overall, the relative temporal pattern and levels of peak and longer term tail SC are very similar for both the lab column and field data, particularly for the mixed weathering status (KY 3) spoil materials. The initial SC for the unweathered gray sandstone spoils (KY 2) and the overall SC for the weathered brown sandstone (KY 1) were consistently higher than the column SCs, however. It is also notable that while the columns reached relatively stable levels of SC after 4 to 8 leaching events (one to two pore volumes), the similar time-lagged drop in SC in the field lysimeters took several years. Differences between the time-lag observed for the columns and the field lysimeters were most likely due to (a) the much smaller sized particles of the crushed samples used in the columns vs the field spoils; (b) differences in frequent and consistent leaching cycles and associated high relative humidity conditions for the columns vs. seasonal drying and wetting in the field lysimeters which allowed reaction salts to accumulate and be flushed in higher concentrations; and (c) the shorter leaching path/depth associated with the columns vs the field lysimeters.

Another applicable extensive field study by Evans et al. (2014) in southwest Virginia reports a similar range of SC emanating from a large number ($n > 100$) of valley fills to those produced by our columns. The Evans et al. study also indicated that, for the subset of sampling points with data records of sufficient length to evaluate long-term trends ($n = 16$), the time for discharge SC to drop below $500\ \mu\text{S cm}^{-1}$ was often 10–20 years beyond final closure and revegetation. Similarly, Pond et al. (2014) recently reported continued elevated SC biotic effects in receiving stream with high SC levels in southern WV for 11–30 years following mine closure. The reason for this prolonged time lag in SC decline in the field has not been determined, but is most likely due to a combination of factors including (a) changes in leachate flow paths/macroporosity over time; (b) the heterogeneity of spoils included in valley fills before current concerns over TDS emerged; (c) the thickness of fill materials in valley fill structures, and corresponding lengths of time

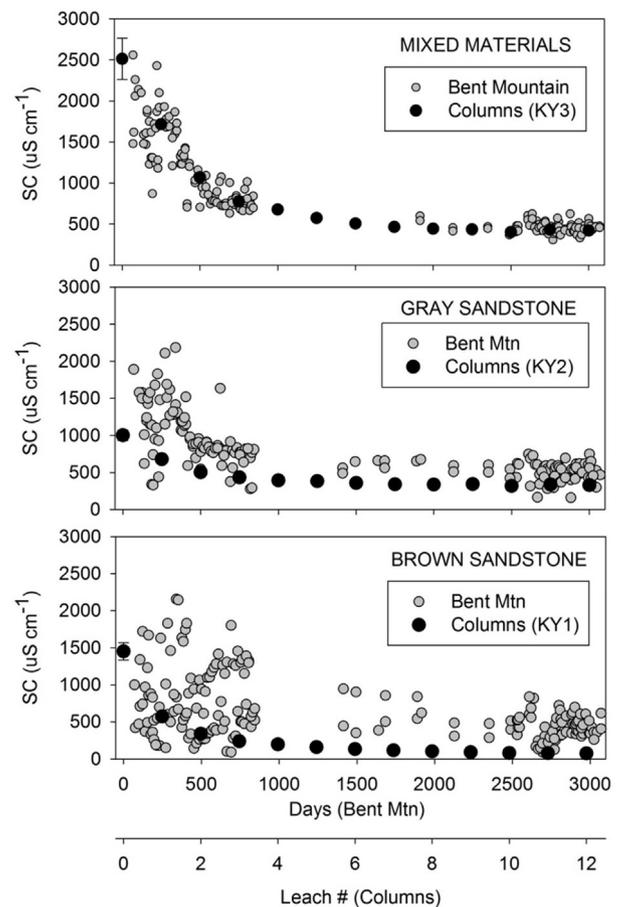


Fig. 8. Comparison of column leaching SC levels with large scale field lysimeter leachate SC levels for three spoil samples from Kentucky (KY 1-3) as reported by Agouridis et al. (2012) and Sena et al. (2014). Column leaching data shown for first 12 cycles; field data collected for over 8 years. The relative pattern and levels of peak and longer term tail SC are similar for both the column and field data, with the exception of somewhat higher initial values for the unweathered gray sandstone (KY 2) and overall higher and more variable SC for the weathered brown sandstone (KY 1). Note that the lab columns appear to achieve relatively stable levels of SC after 4 to 8 leaching events (one to two pore volumes) while a similar response was observed in the field lysimeters over approximately two years.

required for the water supplied by rainfall infiltration to interact chemically with such large material volumes; and (d) contributions from groundwater seepage originating from deep mines and/or surface mine disturbances higher in the watersheds into valley fill drainages.

3.5. Spoil selection guidelines to minimize TDS release risk

Our results indicate that mine spoils can be differentiated based on TDS-production potentials; and that these differences can be detected using relatively inexpensive laboratory procedures. Although the column-leaching procedure utilized here can provide a more robust characterization, the static laboratory tests for pH, EC, and ABA can provide predictions far more quickly and at greatly reduced costs. Hence, these static tests can be applied by mining firms to characterize spoil materials prior to mining disturbance by sampling geologic strata from mineral-exploration drill cores, or during disturbance as long as they are sampled and tested when first exposed, and before their blasting and movement into mine-spoil fills. For example, we suggest that a priori testing of spoil strata with the simple and quick WV-SC procedure (1:2

spoil:water) would allow operators to first eliminate high TDS risk materials ($WV-SC > 250 \mu S cm^{-1}$; Fig. 5) via (a) hydrologic isolation procedures similar to those currently employed for strongly acid-forming materials or (b) heavily compacting them in place to limit their permeability. It also appears that a similar SC test threshold (Fig. 6) would ensure that most strata would produce long-term $SC < 500 \mu S cm^{-1}$ and that the majority of these strata would produce long-term $SC < 300 \mu S cm^{-1}$.

Our results also demonstrate certain principles that can be applied as general guidelines in the field to discriminate among non-acidic mine spoils based on TDS-production potentials. First, unweathered spoils will usually produce higher TDS than those which have been visibly weathered; and second, unweathered fine-textured spoils (siltstones and shales) will often produce higher TDS than those which are more coarsely textured (sandstones). The former guideline appears to be more reliable than the latter, as the weathered spoils in our dataset were uniformly low in TDS production relative to unweathered spoil samples. Although unweathered sandstones were found to produce lower TDS than the unweathered mudstones generally, the dataset also included relatively high TDS sandstones and relatively low TDS mudstones. Hence, a more reliable discrimination of unweathered spoils can be achieved by applying either laboratory or column-leaching tests to representative samples. Our sample set included only two black shales, and both produced higher levels of TDS than any other spoils in our dataset, suggesting that any black shales identified during mining should be isolated, a priori, or tested to determine if isolation is warranted.

These guidelines were derived from analysis of a dataset from dominantly non-acid forming spoil samples as predicted by conventional ABA procedures. When problematic (high-TDS) materials are identified prior to or during mining, operators will be able to place those materials into hydrologically-isolated locations within mine-spoil fills. Extensive experience with acidic spoils (Skousen et al., 2000, 2002) demonstrates that effective hydrologic isolation is capable of greatly reducing the water quality impact of problematic materials. Although operational-scale applications of these TDS-reduction guidelines are limited, experience to date indicates successful reduction of water-discharge TDS levels below those which are typical with conventional mine-spoil fill construction procedures (Zipper et al., 2015; and subsequent unpublished data).

3.6. Implications for long-term SC release to headwater streams

Elevated TDS in mining leachates and related effects in freshwaters are worldwide concerns (Canedo-Arguelles et al., 2013) that are especially acute in Appalachia due to mining's widespread extent (Drummond and Loveland, 2010; Saylor, 2008) and disturbance intensity, (Lindberg et al., 2011; Zipper et al., 2016); and the TDS sensitivity of aquatic macroinvertebrates (Cormier et al., 2013; Pond et al., 2008, 2014). The insights gained here can be applied by industry to reduce TDS in mining effluents, but our results indicate that achieving effluent SCs below the 300–500 $\mu S cm^{-1}$ levels commonly cited as biotic-effect thresholds (Pond et al., 2008; USEPA, 2011a) will be challenging, especially during active disturbance. Only two of our 39 samples, both weathered, produced peak SCs $< 300 \mu S cm^{-1}$; only five $< 500 \mu S cm^{-1}$. However, such levels should be achievable in some watersheds over longer terms, as most tested spoils achieved tail SCs $< 300 \mu S cm^{-1}$.

Many Appalachian streams below coal mined areas have SCs exceeding 500 $\mu S cm^{-1}$ (Bernhardt et al., 2012; Boehme et al., 2016; Hartman et al., 2005; Lindberg et al., 2011; Pond et al., 2008, 2014; Timpano et al., 2015b) which are significantly elevated above natural background levels ($\leq 200 \mu S cm^{-1}$). Our 39 spoil samples

represent regional coal-bearing geologic strata; all exhibited declining SCs with continued leaching. This finding and completed field studies (Evans et al., 2014; Sena et al., 2014) suggest that high TDS levels caused by past mining are likely to decline as in-situ mine spoil leaching and weathering continue. Our results, however, provide no assurance of declines within decadal time scales to levels approaching natural background, generally $< 100 \mu S cm^{-1}$ (Pond et al., 2008, 2014; Cormier et al., 2013; Timpano et al., 2015a, 2015b). Given that regional geohydrology has formed from the same materials that are disturbed by mining, we expect that SC's in mined watersheds will return to background levels eventually but are aware of no research that suggests weathering times or processes to achieve that outcome.

4. Conclusions

Similar to the historical development and application of pre-mine acid-base accounting for coal mine overburden, a new set of integrated procedures to identify and isolate high TDS producing materials has been developed and warrants full scale field testing and application. The unsaturated column leaching procedure utilized in this study produces a similar range and pattern of SC levels to those commonly observed in field discharge and stream impact studies in the central Appalachian region. However, column leaching evaluations are time-consuming and expensive and may not be practical for the evaluation of large numbers of overburden samples from a given mining site(s). As an efficient and economic alternative, our findings indicate that a relatively simple combination of lab procedures (e.g. saturated paste or 1:2 water:spoil SC and total-S) and field indicators (rock type and color) can be used to quickly and accurately identify problematic TDS materials. This protocol should be implemented via improved mine-spoil fill construction procedures that isolate these materials from contact with surface runoff or percolating groundwater.

Assuming excessive amounts of net acid-forming materials are either excluded from valley fills or effectively isolated, the SC of discharge waters for the vast majority of mining fills should decline to $< 500 \mu S cm^{-1}$ over time unless pre-existing acidic seeps or other confounding factors are present. However, our study and others in this region to date indicate that decades following mine closure may be required for this to occur, and that many of these fill discharge SC levels will more than likely remain $> 300 \mu S cm^{-1}$ for longer periods of time.

Acknowledgments

This project was sponsored by the Appalachian Research Initiative for Environmental Science (ARIES). ARIES is an industrial affiliates program at Virginia Tech, supported by members that include companies in the energy sector. The research under ARIES is conducted by independent researchers in accordance with the policies on scientific integrity of their institutions. The views, opinions and recommendations expressed herein are solely those of the authors and do not imply any endorsement by ARIES employees, other ARIES-affiliated researchers or industrial members. The Powell River Project (<http://www.prp.cses.vt.edu/>) and the USDI Office of Surface Mining Applied Research Program also supported portions of this research program. Funding for this work was also provided in part, by the Virginia Agricultural Experiment Station and the Hatch Program of the National Institute of Food and Agriculture, U.S. Department of Agriculture.

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