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Modeling Patterns of Total Dissolved Solids Release from Central Appalachia, USA, Mine Spoils

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Abstract

Surface mining in the central Appalachian coalfields (USA) influences water quality because the interaction of infiltrated waters and O_2 with freshly exposed mine spoils releases elevated levels of total dissolved solids (TDS) to streams. Modeling and predicting the short- and long-term TDS release potentials of mine spoils can aid in the management of current and future mining-influenced watersheds and landscapes. In this study, the specific conductance (SC, a proxy variable for TDS) patterns of 39 mine spoils during a sequence of 40 leaching events were modeled using a five-parameter nonlinear regression. Estimated parameter values were compared to six rapid spoil assessment techniques (RSATs) to assess predictive relationships between model parameters and RSATs. Spoil leachates reached maximum values, 1108 ± 161 μS cm^{-1} on average, within the first three leaching events, then declined exponentially to a breakpoint at the 16th leaching event on average. After the breakpoint, SC release remained linear, with most spoil samples exhibiting declines in SC release with successive leaching events. The SC asymptote averaged 276 ± 25 μS cm^{-1}. Only three samples had SCs >500 μS cm^{-1} at the end of the 40 leaching events. Model parameters varied with mine spoil rock and weathering type, and RSATs were predictive of four model parameters. Unweathered samples released higher SCs throughout the leaching period relative to weathered samples, and rock type influenced the rate of SC release. The RSATs for SC, total S, and neutralization potential may best predict certain phases of mine spoil TDS release.

Core Ideas

- Appalachian mine spoil specific conductance leaching patterns were modeled.
- Weathering type influenced specific conductance at the beginning and end of the leaching period.
- Rock type influenced rates of specific conductance release.
- Considering all mine spoils, RSATs predicted four model parameters.

Increasing soluble salt concentrations in freshwaters are a global concern (Cañedo-Argüelles et al., 2013; Williams, 2001) because such increases have the potential to impact aquatic life at species, community, and ecosystem levels (Cañedo-Argüelles et al., 2013; Pond et al., 2008). Soluble salt increases in freshwaters are exacerbated by numerous anthropogenic activities including agriculture, water use and treatment, urbanization, de-icing road salt applications, and mining (Cañedo-Argüelles et al., 2013; Steele and Aitkenhead-Peterson, 2011). Surface mining methods cause excess soluble salts in stream waters via disturbance of geologic materials, which, on exposure to ambient O_2 and H_2O, undergo geochemical reactions resulting in the release of soluble ions that discharge to surface waters (Li et al., 2014; Orndorff et al., 2015).

In the Appalachian coalfields of the eastern United States, the dominant ion-producing processes occurring in disturbed mining materials, termed *mine spoils*, include pyrite oxidation, feldspar hydrolysis, and carbonate dissolution (Daniels et al., 2013; Orndorff et al., 2015). Appalachian mine spoil exposure to ambient environmental conditions typically releases dissolved SO_4^{2-}, HCO_3^-, Ca^{2+}, and Mg^{2+} to water, as well as lesser amounts of other major cations and trace elements (Pond et al., 2008; Skousen et al., 2000; Timpano et al., 2015). Collectively, the dissolved ions are called *total dissolved solids* (TDS). Electrical conductivity (EC) and specific conductance (SC, which is EC corrected to 25°C), are easily measured proxy variables for TDS (Hem, 1989; Timpano et al., 2010); SC is often measured as a TDS proxy when assessing aquatic ecosystems influenced by Appalachian surface mining (Cormier et al., 2013; Pond et al., 2008).

Typical SC values of Appalachian streams lacking significant anthropogenic influence are <200 μS cm^{-1} (Merricks et al., 2007; Pond et al., 2008; Fritz et al., 2010), whereas mining-influenced waters range from <500 to >3000 μS cm^{-1} (Hartman et al., 2005; Merricks et al., 2007; Lindberg et al., 2011; Evans et al., 2014). Elevated TDS in mining-influenced streams has been linked to altered aquatic macroinvertebrate communities, probably due to organism exposure to excess soluble salts (Hartman et al., 2005; Pond et al., 2008; Timpano et al., 2015), and these community

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Abbreviations: BP, breakpoint; MUD, mudstone; MXR, mixed rock; MXW, mixed weathering; RSAT, rapid spoil assessment technique; SAND, sandstone; SC, specific conductance; TDS, total dissolved solids; UW, unweathered; WX, weathered.

alterations have been detected at SCs >300 μS cm^{-1} (Cormier et al., 2013) and >500 μS cm^{-1} (Pond et al., 2008). Previous studies have shown that mining-influenced streams with elevated SC often have fewer sensitive aquatic taxa present than non-mining-influenced streams (Pond et al., 2008, 2014), and these aquatic community effects have been observed ≥15 yr after mining has ceased (Merricks et al., 2007; Pond et al., 2014).

The ability to predict mine spoil TDS release potentials prior to mining disturbance can aid in the environmental management of mining-influenced landscapes and watersheds. Prior studies have shown that the chemistry of waters produced by Appalachian mine spoils depends on both the rock type and degree of weathering (Evans et al., 2014; Orndorff et al., 2015; Daniels et al., 2016). Central Appalachian mine spoils are typically of clastic sedimentary origin (i.e., sandstones, siltstones, mudstones, and shales) that have been subjected to varying degrees of in situ weathering prior to mining disturbance. Studies to date have indicated that, on weathering and leaching, sandstones typically produce lower SCs than more finely textured clastics, and that mine spoils originating from close to the original land surface that are visibly weathered (oxidized and leached) prior to mining have lower SCs than mine spoils originating from deeper in the geologic column and not visibly weathered (Agouridis et al., 2012; Daniels et al., 2013, 2016; Sena et al., 2014; Orndorff et al., 2015). Furthermore, the SCs of mine spoil leachates are often at maximum values early in the leaching process and decline in subsequent leaching events. Levels of SC in mine spoil leachates may "stabilize" with time but generally remain well above the natural background levels typical of the region's unmined reference streams (Agouridis et al., 2012; Evans et al., 2014; Sena et al., 2014). Although these observations of leaching patterns have emerged from a combination of laboratory and field studies, there is still a lack of knowledge about modeling and predicting the potential SC leaching levels and temporal SC release patterns of Appalachian mine spoils, which have considerable variation depending on rock type and pre-mining weathering status.

Mine spoil TDS release patterns generated by laboratory columns demonstrate a general correspondence with field behavior (Evans et al., 2014; Sena et al., 2014; Ross, 2015; Daniels et al., 2016); however, such studies are time consuming and labor intensive. Methods for characterizing and predicting mine spoil TDS release that are less time and labor intensive are needed. In this study, 39 mine spoil samples collected from central Appalachian surface coal mines were characterized using column leaching and rapid spoil assessment techniques (RSATs). Our specific objectives were to: (i) develop a model of mine spoil SC release patterns; and (ii) examine the relationships between estimated SC model parameters and RSAT results. This research was intended to improve scientific understanding and prediction of mine spoil TDS leaching patterns and to aid development of mine reclamation techniques to minimize TDS elution from mine spoils.

Materials and Methods

Spoil Collection and Classification

Thirty-nine freshly fractured mine spoil samples of known stratigraphic origin were collected from active surface coal mines in Kentucky, Virginia, and West Virginia (Fig. 1). Bulk spoils were characterized by the following weathering types: unweathered, weathered, or mixed weathering (Table 1). Unweathered spoils (UW) are gray in color and originate from beneath weathered strata. Weathered spoils (WX) are visibly altered relative to UW due to the brown coloration of Fe oxides. Mixed-weathering spoils (MXW) have both weathered and unweathered zones within the spoil sample. Spoils were also characterized by the following rock types: sandstones (SAND), mudstones (MUD), mixed rock (MXR), or shales. A classification of MXR implies that a rock has no more than 80% of one rock type (Orndorff

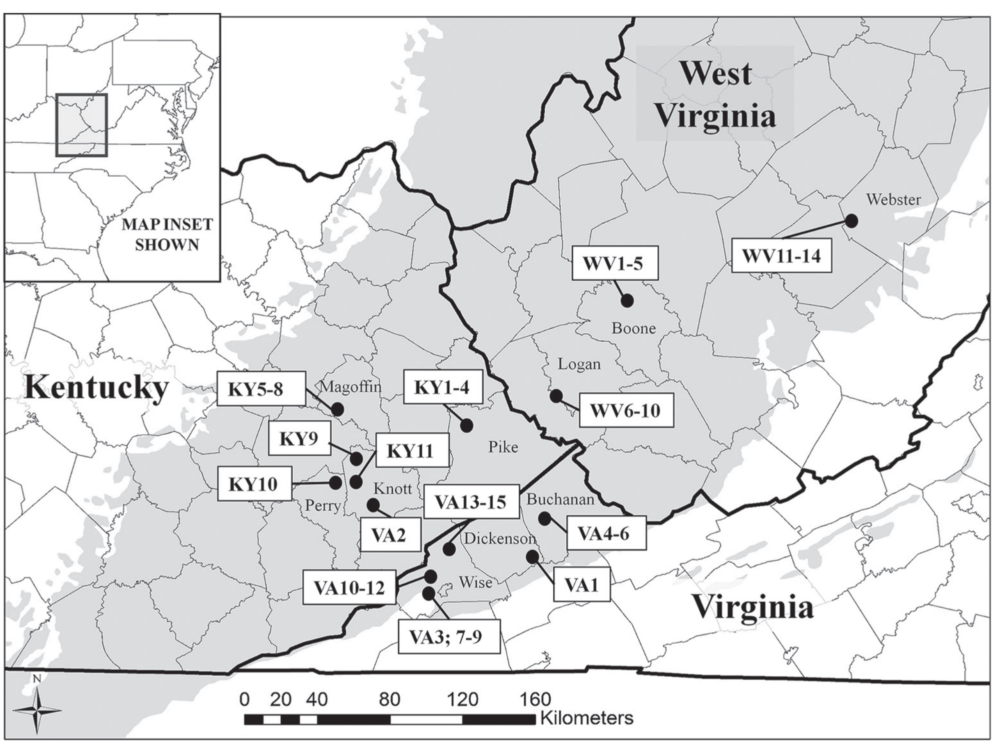

Fig. 1. Location map of the 39 central Appalachian spoils collected in Kentucky, Virginia, and West Virginia. The Appalachian coalfields of the eastern United States are shown in gray.

Table 1. Mine spoil sample numbers by rock and weathering type (n = 39).

Rock type†	Weathering type‡			Total
	UW	MXW	WX	
MUD	7 (1)§	–	4	11(1)
MXR	4 (1)	3	–	7 (1)
SAND	10	4	3	17
SHALE	(2)	–	–	(2)
Total	21 (4)	7	7	35 (4)

† MUD = mudstone, MXR = mixed rock, SAND = sandstones.

‡ UW = unweathered, MXW = mixed weathering, WX = weathered.

§ Numbers of samples excluded from the analyses are in parentheses.

et al., 2015). For further details on the mine spoil properties, see Daniels et al. (2016).

Column Leaching

Spoil samples were ground to <2 mm and back-blended with finer textured spoil materials, then placed into 40-cm-long polyvinyl chloride (PVC) pipes with a 7.4-cm inside diameter. Subsamples of each spoil material were placed into three PVC leaching columns. Reported results are averages of the three replicate samples. The columns were leached with a simulated acid rain (pH 4.6; Halverson and Gentry, 1990). To initialize the column leaching experiment, simulated rainfall was slowly added to the leaching columns until the maximum unsaturated water holding capacity was reached. The first 2.5 cm of leached water was collected and analyzed as Leach Event 0. After the initial leachate was collected, the columns were dosed with 2.5 cm of simulated rainwater (pH 4.6) twice a week, and the eluted leachate was collected and analyzed for SC. The experiment lasted for a total of 20 wk (40 leaching events, Leaching Events 0–39). For a more detailed description of the column dimensions and leaching process, see Orndorff et al. (2015).

Model Development

Previous studies (Orndorff et al., 2015; Daniels et al., 2016) and visual analyses of leachate data found that leachate SC from the column design utilized in this study typically peaked at Leaching Event 0, 1, or 2, then decreased with subsequent leaching events in a decay pattern that appeared exponential. After the decay process, the leachate reached a change point, after which the pattern appeared linear through subsequent leaching events. In response to these observations, the leaching patterns of the 39 mine spoils were used to develop a model for the purpose of quantitatively describing the SC of waters produced during the leaching period.

Exponential nonlinear regression models are often used to model the concentration of a substance during a period of time. A nonlinear regression model has the following form:

$$Y_i = f\left(\mathbf{X}_i, \boldsymbol{\theta}\right) + \varepsilon_i \qquad [1]$$

where Y_i is the response of the ith observation, $\mathbf{X}_i$ is a vector of observed values of the predictor variables for the ith observation, $f(\cdot)$ is a response function that is nonlinear in the parameter vector $\boldsymbol{\theta}$ (Bates and Watts, 1988), and ε_i is the error in the ith observation. It is assumed that ε_i are independent and normally distributed with mean 0 and variance σ^2.

Based on the observation of nonlinear leaching patterns, a five-parameter, nonlinear, segmented regression model was developed (Fig. 2). The segmented regression includes a three-parameter exponential decay function and a linear regression function connected by a breakpoint (BP). The response function f, as a function of the leaching event number x_i (i = 0, 1, ..., 39) and $\theta = (\theta_1, \theta_2, \theta_3, \beta_0, \beta_1, \mathrm{BP})$ is given by

$$f\left(\mathbf{X}_i, \boldsymbol{\theta}\right) = \begin{cases} \theta_2 \exp\left(-\theta_3 x_i\right) + \theta_1, & x_i < \mathrm{BP} \\ \beta_0 + \beta_1 x_i, & x_i \geq \mathrm{BP} \end{cases} \qquad [2]$$

In order for the exponential component and the linear component to be connected at x_i = BP, the relationship is

$$\theta_2 \exp\left(-\theta_3 \mathrm{BP}\right) + \theta_1 = \beta_0 + \beta_1 \mathrm{BP} \qquad [3]$$

and can be rearranged as

$$\beta_0 = \theta_2 \exp\left(-\theta_3 \mathrm{BP}\right) + \theta_1 - \beta_1 \mathrm{BP} \qquad [4]$$

Therefore, the nonlinear response function f used to model SC as a function of time is given by

$$f\left(\mathbf{X}_i, \boldsymbol{\theta}\right) = \begin{cases} \theta_2 \exp\left(-\theta_3 x_i\right) + \theta_1, & x_i < \mathrm{BP} \\ \left[\theta_2 \exp\left(-\theta_3 \mathrm{BP}\right) - \beta_1 \mathrm{BP} + \theta_1\right] + \beta_1 x_i, & x_i \geq \mathrm{BP} \end{cases} \qquad [5]$$

where θ_2 describes the exponential peak, θ_3 is the exponential decay factor, BP is the leaching event at which the decay function changes to a linear function, β_1 is the slope of the linear segment, and θ_1 is the horizontal asymptote associated with the exponential decay segment. The θ_1 values are also similar to the SC associated with the BP leaching event. Parameters of the regression were estimated using nonlinear least squares (Bates and Watts, 1988). All samples were modeled from their peak concentration (i.e., largest SC value of all leaching events). If the peak SC was not at Leaching Event 0 but at Leaching Event 1 or 2, the leaching event(s) before the peak were omitted from the data set, and the sample was modeled from the leaching event with the largest SC value.

Rapid Spoil Assessment Techniques

Rapid spoil assessment techniques (RSATs) are laboratory analyses that characterize mine spoils within a shorter time

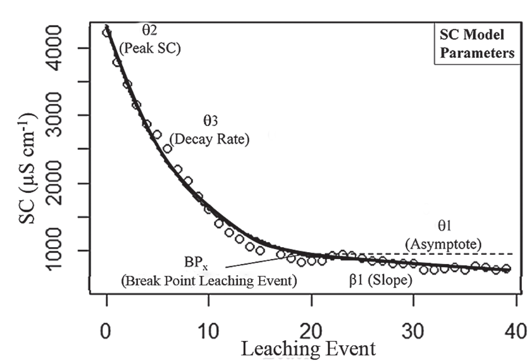

Fig. 2. Diagram of specific conductance (SC) model parameters and the nonlinear regression for the spoil samples.

period and require fewer resources than the column leaching procedure. In total, 14 RSATs were applied to the spoil samples to identify which RSATs may predict SC model parameters; however, two were omitted due to a lack of correspondence with model parameters (H_2O_2 potential acidity and $CaCO_3$ equivalent), and six were omitted because their results were highly correlated with other RSATs. Therefore, six of the original 14 RSATs are presented here. Saturated paste SC (Rhoades, 1982) and pH were measured by mixing ground spoils (<2 mm) with deionized water until a glistening paste formed, then suction filtered after 2 h to extract a liquid, which was analyzed for pH and SC. Hydrogen peroxide SC and pH were determined by reacting a weak concentration (3%) of H_2O_2 with a 1:1 sample/peroxide solution ratio, then analyzed. Total S was measured using the dry combustion technique on a Leco S632 Sulfur Analyzer. Neutralization potential (NP), a test for the amount of neutralizing bases, was measured by adding HCl to the samples, boiling, then back-titrating with NaOH (Sobek et al., 1978).

Statistical Analyses

Model performance was evaluated using the root mean square error (RMSE). The RMSE indicates the difference between measured data and model-predicted values and is calculated as

$$\mathrm{RMSE} = \sqrt{\frac{1}{n-p}\sum_{i=1}^{n}\left(y_i - \hat{y}_i\right)^2} \qquad [6]$$

where y_i and $\hat{y}_i$ are the observed and predicted values, respectively, of n observations considering p parameters.

Mann–Whitney U and Kruskal–Wallis tests were performed using the software R (R Core Team, 2013) to determine statistical differences ($\alpha = 0.05$) between SC model parameters based on rock or weathering type. If differences were found, a Steel–Dwass test for multiple nonparametric comparisons was used to identify rock-type or weathering-type effects. Spearman correlations between SC model parameters and RSATs were calculated.

Results and Discussion

Model Parameters

All samples were successfully modeled; however, model fit varied for different samples, and we recognize that certain mine spoils may not conform to a proposed model due to differences in spoil chemistry, composition, mineralogy, etc. Models with the poorest fits were those producing (i) very high leachate SC and no apparent breakpoint or linear model component (Type I, Fig. 3a), or (ii) a "pseudo-peak" in the initial leaching events followed by a secondary peak later in the leaching period (Type II, Fig. 3b). Two samples (VA2 and KY7) had Type I patterns, and two samples (WV7 and WV13) had Type II patterns; these samples were omitted from further analysis (Table 1). Type I samples, which were both shales, were omitted because 40 leaching events were not adequate to define the model parameters, probably due to high S content in the samples continuing to oxidize throughout the leaching period. Type II samples were omitted because the geochemical drivers for these samples' TDS releases appear to be different than for other samples, probably due to differences in spoil mineralogy or fine particle size coatings affecting mineral reactivity during the leaching and weathering process. Discussion of the results henceforth excludes these four omitted samples, and model parameters are subsequently discussed in order of their appearance throughout the leaching period (Fig. 2).

Peak Specific Conductance

The peak SC parameter (θ_2) ranged from 34 to 4480 μS cm^{-1}, averaging (mean $\pm$ 1 SD) 1108 $\pm$ 161 μS cm^{-1}, and did not differ statistically among rock types (Fig. 4). Among weathering types, the mean peak SC was lower for WX (618 $\pm$ 179 μS cm^{-1}) than for MXW and UW spoils (1737 $\pm$ 534 and 1181 $\pm$ 181 μS cm^{-1}, respectively). Samples with higher peak SCs tended to have significantly higher asymptote SCs (θ_1, Fig. 1) at the end of the leaching study period ($\rho = 0.60$; $p \le 0.001$) and also tended to have more steeply declining linear segment slopes (β_1), ($\rho = -0.43$; $p \le 0.01$) (Fig. 5).

For all samples, the peak SC was positively correlated with the paste SC ($\rho = 0.72$; $p \le 0.001$), H_2O_2 SC ($\rho = 0.70$; $p \le 0.001$), and total S ($\rho = 0.53$; $p \le 0.01$) and negatively correlated with H_2O_2 pH($\rho = -0.39$; $p \le 0.05$) (Fig. 6). Paste SC, H_2O_2 SC, and total S were correlated with the peak SC for most rock and weathering types (Table 2). The peak SC was also correlated with H_2O_2 pH in SAND, UW, and WX spoils.

Pre-mining weathering status had clear effects on the peak SC for individual mine spoils, probably because weathered spoils were preweathered and leached in situ and had smaller pools of potentially leachable soluble ions. Our results suggest that paste SC has a strong predictive relationship with peak SC, probably because paste SC measures easily solubilized ions that contribute directly to the initial SC peak. A related study (Daniels et al., 2016) on mine spoil leachates also found a strong predictive relationship between peak SC and paste SC ($R^2 = 0.85$). Our results suggest that total S also has a predictive relationship with peak SC. Higher total S

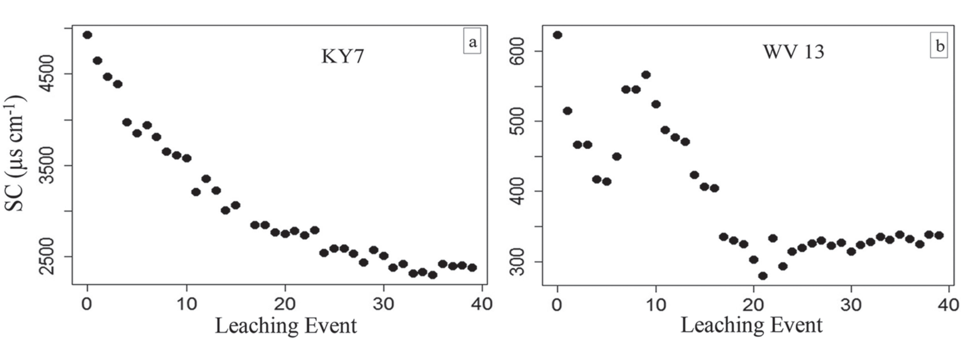

Fig. 3. Examples of spoil samples omitted from analysis due to lack of correspondence with the nonlinear regression due to (a) Type I patterns and (b) Type II patterns.

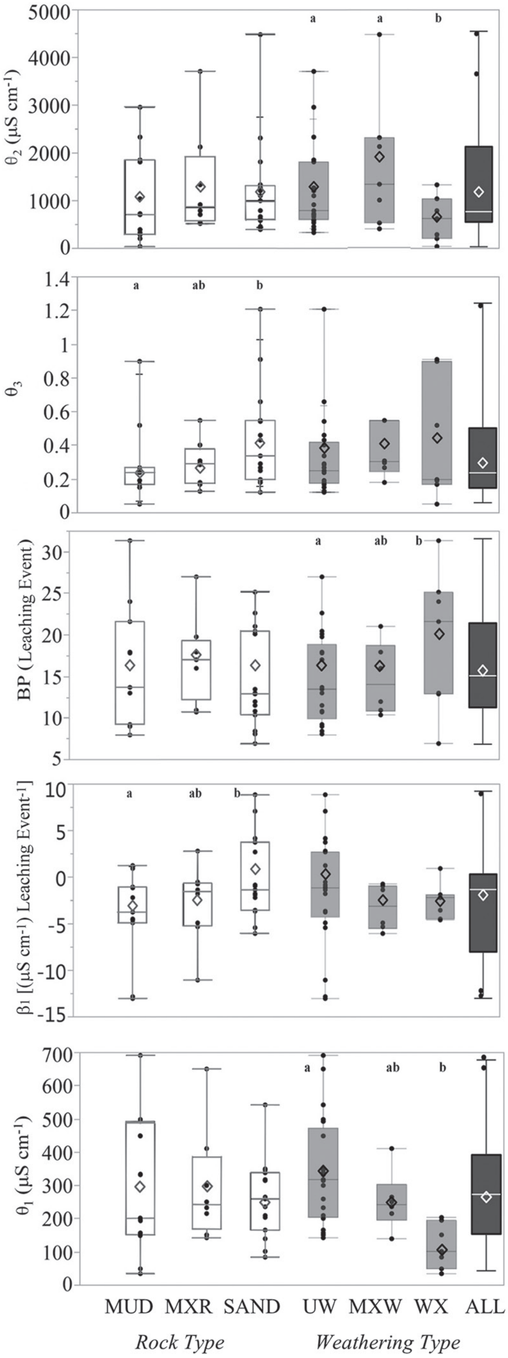

Fig. 4. Box plots of estimated specific conductance model parameters illustrating the range of parameter values. Wide bars represent the minimum, 25th percentile, median, 75th percentile, and maximum values. Diamonds represent means. Mine spoils are classified by rock (MUD = mudstone, MXR = mixed rock, SAND = sandstone) and weathering (UW = unweathered, MXW = mixed weathering, WX = weathered) type. ALL designates all samples. Within each rock or weathering type, box plots with different letters are significantly different ($p \leq 0.05$). Model parameters: θ_2, peak specific conductance; θ_3, exponential decay rate; BP, breakpoint (the leaching event at which the decay function changes to a linear function); β_1, slope of the linear segment; θ_1, horizontal asymptote associated with the exponential decay segment.

typically indicates that a sample may be more affected by S oxidation and offsetting neutralization reactions (Orndorff et al., 2015), hence a higher peak SC.

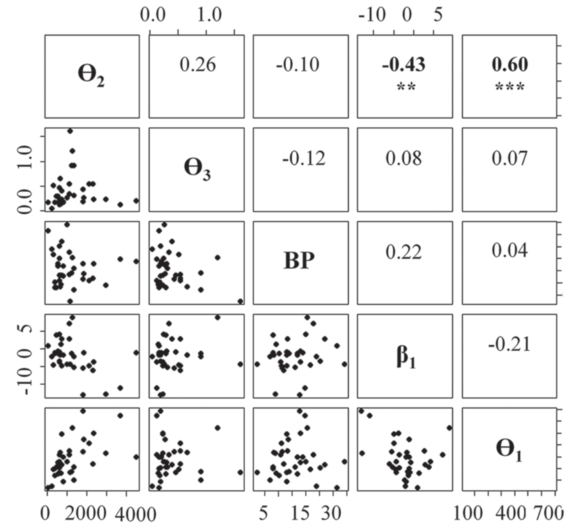

Fig. 5. Correlations among estimated model parameters. Model parameters: θ_2, peak specific conductance; θ_3, exponential decay rate; BP, breakpoint (the leaching event at which the decay function changes to a linear function); β_1, slope of the linear segment; θ_1, horizontal asymptote associated with the exponential decay segment. ***Significant $p \leq 0.001$. ***Significant at $p \leq 0.01$.

Exponential Decay Rate

The exponential decay rates (θ_3) ranged from 0.05 to 1.21 with a mean of 0.36 ± 0.04 (Fig. 4), with relatively high decay rates indicating rapid exponential declines in SC release. Based on rock type, SAND had larger decay rates (0.45 ± 0.08) than MUD spoils (0.27 ± 0.05). The exponential decay rates did not differ statistically among weathering types.

Considering all spoils, exponential decay rates were not correlated with any RSATs (Fig. 6). However, based on rock and weathering type, exponential decay rates were negatively correlated with paste SC, H_2O_2 SC, and total S in UW spoils.

Rock type differences among exponential decay rates were probably influenced by differences in spoil mineralogy and grain size. Larger surface areas associated with smaller grain sizes may result in a more uniform weathering of the MUD and MXR samples, which slows over time as the easily weatherable ions leach out. Comparatively, SAND spoils have different surface areas and greater abundances of primary mineral grains that probably contribute to faster SC decay rates relative to MUD and MXR spoils. Exponential decay rate prediction by RSATs was limited; therefore, other analyses such as mineralogical analyses or specific ion analyses may be necessary to predict spoil exponential decay rates.

Breakpoint

The breakpoint (BP) parameter ranged from Leaching Event 7 to 31 and averaged 16 ± 1. Mean breakpoints for specific rock and weathering types ranged from Leaching Event 15 to 19. Mean breakpoints did not differ by rock type, whereas WX spoils had higher breakpoints (Leaching Event 19 ± 3) than MXW (Leaching Event 15 ± 2) and UW (Leaching Event 15 ± 1) spoils (Fig. 4).

Modeled breakpoints were negatively correlated with both paste pH ($\rho = -0.46$; $p \leq 0.01$) and H_2O_2 pH ($\rho = -0.43$; $p \leq 0.01$) for all samples (Fig. 6). Considering rock and weathering types, paste pH and H_2O_2 pH were negatively correlated with

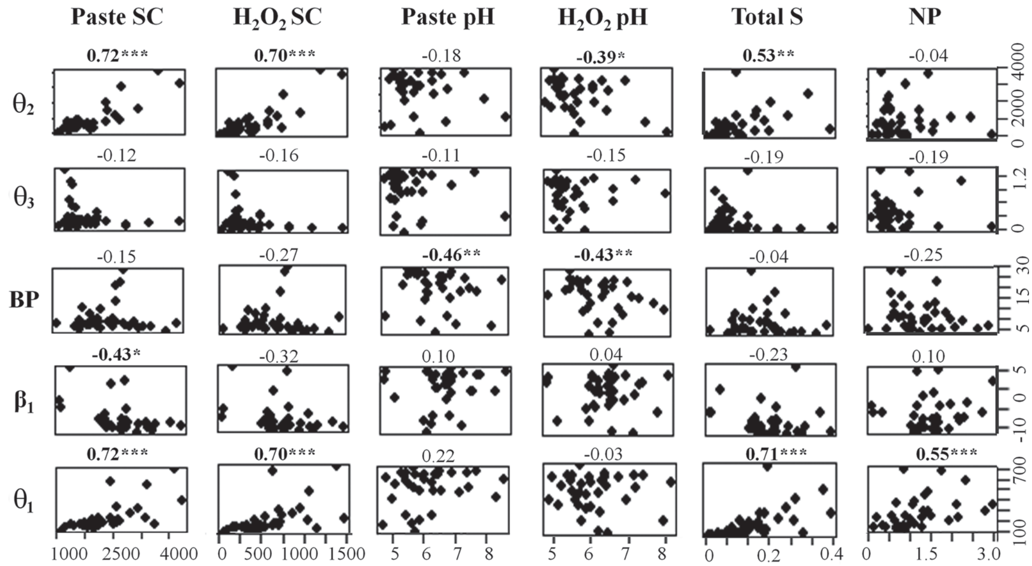

Fig. 6. Correlations between estimated specific conductance (SC) model parameters and rapid spoil assessment tests. NP = neutralization potential. Model parameters: θ_2, peak SC; θ_3, exponential decay rate; BP, breakpoint (the leaching event at which the decay function changes to a linear function); β_1, slope of the linear segment; θ_1, horizontal asymptote associated with the exponential decay segment. ***Significant $p \leq 0.001$. **Significant at $p \leq 0.01$. *Significant at $p \leq 0.05$. Significant correlations are in bold.

the breakpoint for MUD and UW spoils, while paste SC and H_2O_2 SC were negatively correlated for WX samples.

Preweathered samples required four more leaching events on average than UW samples to reach a BP, which may be attributed to WX spoils having less neutralizers and total S overall ($p < 0.01$, Wilcoxon, data not shown). It is likely that the reactions responsible for SC release have already occurred to a larger extent in weathered spoils, thus the breakpoint occurs at a different time in the leaching process relative to unweathered samples. Our results suggest that the breakpoints may be predicted by the initial pH because samples with lower pH values (i.e., less neutralizers) may require more leaching events to reach a BP relative to samples with higher pH values, which contain larger masses of reactive neutralizers such as carbonates that continue to counteract Fe, Mn, and S oxidation reactions throughout the observed leaching period.

Linear Slope

For the post-BP parameters, the linear slope (β_1) parameter values ranged from −13.0 to 8.8 μS cm^{-1} per leaching event, with nine increasing, 21 decreasing, and five slopes not significantly different from zero. The mean linear slope values were negative for all rock and weathering classification types; however, MUD spoils had smaller (i.e., more negative) average

Table 2. Correlation coefficients for significant relationships between estimated specific conductance (SC) model parameters and rapid spoil assessment tests.

Parameter†	Classification‡	Paste SC	H_2O_2 SC	Paste pH	H_2O_2 pH	Total S	NP§
θ_2	MUD	0.91***	0.91***			0.89**	
	MXR	0.86*	0.93*			0.77*	
	SAND	0.52*			−0.52*		
	UW	0.67***	0.64**		−0.59*	0.59**	
	MXW	0.93***			−0.82*		
	WX	0.86*	0.89**				
θ_3	MUD				−0.64*		
	UW	−0.48*	−0.43*			−0.47*	
BP	MUD			−0.75**	−0.61*		−0.69*
	UW			−0.56**	−0.52*		
	WX	−0.82*	−0.86*				
β_1	MXR	−0.79*	−0.93**			−0.79*	
	UW	−0.61*	−0.58**				
θ_1	MUD	0.92**	0.87**			0.89**	
	MXR	0.89**				0.86*	0.79*
	SAND	0.49*				0.52*	0.70**
	UW	0.71***	0.68***			0.58**	

* Significant at $p \leq 0.05$.

** Significant at $p \leq 0.01$.

*** Significant at $p \leq 0.001$

† θ_2, peak specific conductance; θ_3, exponential decay rate; BP, breakpoint (the leaching event at which the decay function changes to a linear function); β_1, slope of the linear segment; θ_1, horizontal asymptote associated with the exponential decay segment.

‡ MUD, mudstone; MXR, mixed rock; SAND, sandstone; UW, unweathered; MXW, mixed weathering; WX, weathered.

§ Neutralization potential.

slopes (-3.7 ± 1.4 μS cm^{-1} per leaching event) than SAND (-0.2 ± 1.0 μS cm^{-1} per leaching event). Samples with more negative linear slopes were correlated with higher peak SCs ($\rho = -0.43$; $p \leq 0.01$) (Fig. 5).

For all samples, the linear slope was negatively correlated with paste SC ($\rho = -0.43$; $p \leq 0.05$). Negative correlations between the linear slope and RSATs for SC also occurred in MXR and UW samples.

Rock type effects on the linear SC release slope are probably influenced by the same factors as the exponential decay rate (e.g., spoil mineralogy, grain sizes). Continuous weathering of finer grained mudstones probably influences the more negative linear slope compared with the relatively constant or increasing linear slope of heterogeneous (i.e., larger primary mineral grains surrounded by cementing agents) sandstones. Paste SC is potentially predictive of the linear phase; samples with higher paste SCs tended to continue declining in TDS release during the linear phase, probably due to a larger availability of weatherable ions during more extended leaching periods. Comparatively, samples with lower paste SCs tended to have constant or slightly increasing linear slopes, indicating that SC release may have reached a near-equilibrium status driven by background mineral weathering rates (Sena et al., 2014).

Asymptote Specific Conductance

The asymptote SC (θ_1) values for all samples ranged from 34 to 690 μS cm^{-1} and averaged 276 ± 25 μS cm^{-1} (Fig. 4). Mean asymptote SC values did not differ by rock type but differed among weathering types. Mean asymptote SC values were the highest for UW (329 ± 33 μS cm^{-1}) and lowest for WX (118 ± 26 μS cm^{-1}). Only three samples, all unweathered, had asymptote SC values >500 μS cm^{-1}, whereas the asymptote SC values of 22 samples (63%) were <300 μS cm^{-1}. Samples with higher asymptote SCs tended to also have significantly higher peak SCs ($\rho = 0.60$; $p \leq 0.001$) (Fig. 5).

The asymptote SC had positive correlations with paste SC, H_2O_2 SC, total S, and the neutralization potential ($\rho = 0.55 - 0.72$; $p \leq 0.001$) for all samples (Fig. 6). Paste SC, H_2O_2 SC, and total S also had strong correlations with the asymptote SC for certain rock and weathering types.

The asymptote SC mimicked the pre-mining weathering status, as samples that had been preweathered generally had lower asymptote SCs and samples that had not been preweathered typically had higher asymptote SCs. The asymptote SC had predictive relationships with the RSATs for SC, total S, and neutralization potential, suggesting that SC release is still influenced, to an extent, by S oxidation and neutralization reactions at the end of the exponential decay period. Typically, samples with lower asymptote SCs also had lower paste SCs (1000–1500 μS cm^{-1}), total S (0–0.1%), and neutralization potentials (0–1.0%) relative to samples with higher asymptote SCs.

Model Error

Model error estimates (RMSE) indicated that model-predicted SCs were under- or overestimated by a minimum of 2 μS cm^{-1}, a maximum of 91 μS cm^{-1}, and a mean of 35 μS cm^{-1} relative to the collected data for all samples (Table 3). The highest overall RMSE occurred in modeling MUD (RMSE 44 μS cm^{-1}) and UW (RMSE 39 μS cm^{-1}) spoils, and the smallest error occurred in WX spoils (RMSE 24 μS cm^{-1}) on average.

Summary of Modeling Results

Overall, the successful modeling of 35 of the 39 central Appalachian spoils revealed clear patterns in leaching behavior. Each model parameter was significantly influenced by rock or weathering type, indicating that such mine spoil classifications are essential to characterizing TDS leaching behaviors. Weathering type only had significant effects on model parameters describing the SC at specific points in the leaching process (i.e., peak SC, breakpoint leaching event, and asymptote). Comparatively, rock type had significant effects only on the rates of SC release in the model (i.e., exponential decay rate and linear slope). Significant relationships between model parameters and RSATs implied that certain phases of the leaching process may be predicted by relatively rapid laboratory-based RSATs. Considering all spoils, four of the five model parameters were significantly correlated with at least one of the six RSATs analyzed; however, different RSATs were correlated with each model parameter.

Model Applications to Laboratory and Field Leaching Behavior

For model validation purposes, relating model results to laboratory and field leaching studies of Appalachian mine spoils may help confirm and improve the understanding of spoil leaching patterns. Considering peak SC (θ_2), exponential decay (θ_3), and the transition from exponential decay to linear SC release (BP), few studies have characterized these phases of the leaching process. In their column leaching study of 15 Appalachian mine spoils, which were a subset of the mine spoils analyzed in this study, Orndorff et al. (2015) found a mean peak SC of 1468 ± 150 μS cm^{-1}, which was slightly higher than the 1108 ± 161 μS cm^{-1} peak SC identified in this study, and also found significantly larger peak SCs in unweathered spoils relative to weathered spoils. A 2-yr field lysimeter study by Agouridis et al. (2012) in Kentucky similarly noted that weathered spoils had significantly lower SC discharges initially (829 ± 68 μS cm^{-1}) relative to unweathered spoils (1032 ± 54 μS cm^{-1}). Prior studies found that three to four leaching events were required for a pore volume and that leaching patterns may cease exponential decay after

Table 3. The root mean square error (RMSE) for model-predicted specific conductance based on rock and weathering type.

Spoil classification†	RMSE	
	Min., Max.	Mean
	μS cm^{-1}	
All	2.1, 91.5	34.8
MUD	2.1, 89.8	44.3
MXR	11.2, 91.5	37.4
SAND	10.2, 80.5	27.1
UW	10.9, 91.5	38.9
MXW	10.2, 80.5	34.1
WX	2.1, 53.2	24.1

† MUD, mudstone; MXR, mixed rock; SAND, sandstones; UW, unweathered; MXW, mixed weathering; WX, weathered.

five to seven pore volumes or approximately 15 to 20 leaching events (Orndorff et al., 2015). In the field, however, many months or years may be required to reach a full pore volume. A study of >130 valley fills by Evans et al. (2014) estimated that 15 to 25 yr on average may be required to complete the exponential decay phase of the leaching process. Under field leaching conditions, the variability of the exponential decay phase is probably influenced by factors such as spoil porosity and volume, preferential flow paths, and weathering front depth.

Laboratory and field studies characterizing the post-BP linear SC release (β_1) and the level at which SC release stabilizes (θ_1) are also limited. A field study on spoil leaching behavior reported that brown (WX) sandstones, gray (UW) sandstones, and MXW spoils had constant TDS release patterns 9 yr after placement, as SC was not decreasing temporally (Sena et al., 2014). Our results suggest, however, that certain spoils may continue to increase or decrease in TDS release, although it is currently unknown if these patterns will continue for a longer period. For SC stabilization levels (θ_1), Orndorff et al. (2015) reported mean SC values of 374 and 129 $\mu S\ cm^{-1}$ for unweathered and weathered spoils, respectively, at the end of the leaching study period. Although not statistically significant, Sena et al. (2014) reported higher SCs in unweathered spoils (564 $\mu S\ cm^{-1}$) relative to weathered spoils (421 $\mu S\ cm^{-1}$) that were leached in the field for 9 yr. The SCs from prior studies and those reported in this study indicate that following the exponential decay phase, mine spoil leachate SCs still remain at levels elevated above natural background for a number of years (Sena et al., 2014; Ross, 2015) and typically stabilize at SC levels above the 300 $\mu S\ cm^{-1}$ benchmark intended to prevent >5% extirpation of aquatic macrobenthic genera (Cormier et al., 2013).

Geochemical Drivers of Specific Conductance Release

Prior studies of Appalachian mine spoils have indicated that rapid oxidation of trace pyrites occurs initially in freshly exposed mine spoils but slows with time (Orndorff et al., 2015), which is probably responsible for the modeled peak SC and exponential decay patterns. Once pyrite oxidation slows, the anion leaching pattern shifts from sulfate dominance to bicarbonate due to neutralization reactions, which may explain the post-BP and linear leaching model segments. Therefore, the interaction of rapid S oxidation combined with kinetically slower carbonate- and feldspar-driven neutralization reactions appears to control the temporal patterns of mine spoil TDS release.

Although certain model parameters had predictive relationships with RSATs, the inability to predict the exponential decay rate (θ_3) parameter indicates that certain phases of leaching were not explained by the RSATs used in this study. Other spoil assessments such as mineralogical analyses and ion chemistry may assist in understanding the SC model parameters that were not predicted in this study.

Conclusions

The leaching patterns of central Appalachian mine spoils were modeled as a continuous nonlinear regression with an exponential phase and linear phase separated by a breakpoint. Each model parameter was significantly influenced by either rock or weathering type, and all but one parameter had predictive relationships with rapid laboratory assessment techniques. Classification of spoil materials by weathering and rock type is essential to understanding the leaching patterns of mine spoils. Future research should focus on improving the understanding of the geochemical mechanisms governing TDS release rates and patterns throughout the leaching process, as well as on relating model predictions and data from laboratory studies to measured field data to evaluate temporal model conformance.

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