

Predicting release and aquatic effects of total dissolved solids from Appalachian USA coal mines

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Abstract Appalachian USA coal mines have been implicated as major stressors to aquatic life in headwater streams via discharge of total dissolved solids (TDS). This paper summarizes column leaching studies of spoils ($n > 50$) and refuse and TDS effects on local water quality and biotic response. The initial pH of most materials is near-neutral. Initial specific conductance (SC) values range from 500–1,000 to $>3,000 \mu\text{s}/\text{cm}$, but 2/3 of materials drop below $500 \mu\text{s}/\text{cm}$ after several pore volumes of leaching. Studies of mining-influenced streams have found altered aquatic life, relative to natural conditions with no mining influence, at SC ranging from ~ 200 to $\sim 700 \mu\text{s}/\text{cm}$ with depressed aquatic life consistently associated with elevated TDS; mechanisms causing such effects are under investigation. We suggest that active mine operations should be modified to place high TDS producing materials in ways that reduce contact with percolating drainage waters.

Keywords Mine spoil · Weathering · Acid base accounting · Water quality · Valley fills

1 Introduction

This paper provides an overview of a critical environmental compliance issue facing the Appalachian USA surface coal mining industry today, the emission of total dissolved solids (TDS) to headwater streams. In this paper we review and synthesize the current literature and associated interpretations surrounding TDS release from coal surface mines and we provide a summary of our related research findings and conclusions to date. This paper is organized into three sections. In the first section, we focus on TDS sources and prediction research. In the second section of this paper we review literature and our related studies of instream aquatic impacts. In the final section, we offer our overall synthesis and conclusions to date.

2 Background on spoil weathering and TDS sources

The USA Surface Mine Control and Reclamation Act (SMCRA) of 1977 contained a number of reclamation provisions including the use of pre-selected overburden materials as topsoil substitutes when (1) the native A + E horizon materials are less than 15 cm (6") thick, and (2) the physical and chemical properties of the proposed substitute spoil materials are deemed suitable. Similarly, SMCRA requires the isolation of acid-forming materials away from contact with surface runoff and isolation away from internal drainage in mining fills. However, where (1) acid-forming strata are thin relative to adjacent net alkaline strata or (2) where they can be blended with sufficient volumes of other net alkaline materials in the blasting-hauling-placement sequence, the industry has relied upon appropriate application of acid-base accounting procedures (ABA; Skousen et al. 2002) to ensure that the drainage from highwall backfills and valley fills is non-acidic and complies with discharge limits for Fe, Mn and pH. Both of these practices (topsoil substitution and acid/alkaline spoil blending) have led to enhanced levels of TDS in Appalachian coal mine discharge waters versus undisturbed pre-

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mine conditions due to a combination of sulfide oxidation, carbonate dissolution and neutralization, and primary mineral hydrolysis reactions that occur very quickly when non-weathered geologic materials are exposed by mining and spoil placement processes.

The dominant constituent ions of TDS released by weathering of central Appalachian mine spoil materials are typically Ca^{2+} , K^+ , Mg^{2+} , Na^+ , SO_4^{2-} 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 are unearthened and exposed to rapid oxidation, hydrolysis, hydration and dissolution reactions in the surfaces and fills of active coal mines. The upper 5–15 m of overburden is typically oxidized to some extent by long-term geochemical weathering (Haering et al. 2004) and leaching of these materials is therefore much less likely to generate significant TDS after blasting and placement. However, deeper strata commonly contain significant amounts of reactive sulfides, carbonates, feldspars and other mineral phases that rapidly produce varying loads of soluble ions to percolating water and runoff, particularly as they interact with their initial pore volumes of bathing waters. Unweathered overburden in the central Appalachians can contain significant amounts (0.5 % to >3.0 %) of complex carbonates (Howard et al. 1988) which occur primarily as secondary cementing agents along with highly variable amounts of reactive sulfides (Sobek et al. 2000). Depending on the distribution and quantity of these minerals, the pH of freshly exposed unoxidized overburden is between 6.5 and 8.2 (Roberts et al. 1988) while that of weathered/partially weathered overburden is generally between 4.5 and 6.0.

Essentially, surface coal mining in the Appalachian region creates a set of “weathering conditions” for disturbed overburden whereby generation of TDS loading to leaching waters and runoff can be significant and certain levels of release are unavoidable. That being said, the fact that current regulations and mining practice mandates that all potentially acid forming materials (potential acidity >5/1,000 tons CCE net acid) must be isolated away from the surface and from significant ground water interaction certainly eliminates the largest potential source of net TDS release. However, many non-isolated strata contain significant amounts of reactive sulfides that are essentially balanced by carbonates in terms of their ABA, such that these materials can still contribute substantially to TDS loadings (particularly Ca^{2+} , Mg^{2+} , HCO_3^- and SO_4^{2-}) as they weather while maintaining moderate to circumneutral pH conditions in that drainage (Daniels et al. 2009). In addition to these acid–base reactions, fresh spoils can also contribute to TDS due to simple dissolution reactions of carbonate cements, hydrolysis weathering of feldspars and other primary mineral grains and traces of entrained Cl salts.

Over the past decade, the concept of topsoil substitution has been criticized from a number of perspectives including potential effects on water quality due to inclusion of higher pH and more chemically reactive overburden in contact with surface water runoff. Similar concerns about elevated long-term emission of TDS from backfills and valley fills have also emerged. In a series of actions between 2009 and 2011, the U.S. Environmental protection agency (EPA) attempted to use its Clean Water Act Section 404 authority that to establish 500 $\mu\text{S}/\text{cm}$ electrical conductivity (equivalent to about 350 mg/L TDS) as a potential or de facto standard, at least within heavily mined watersheds. For example, citing Pond et al. (2008), an EPA official testified to the US Congress that “These dissolved ions are not readily sequestered by the surrounding geology and may ultimately emanate from the fills for decades. ... This impairs the use of the streams and ultimately leads to listing of these streams as ‘impaired water bodies’ in EPA’s water quality reports ...” (Pomponio 2009). Several recent studies (Chapman et al. 2000; Goodfellow et al. 2009; Pond et al. 2008; Timpano et al. 2010) have addressed the issue of TDS as a major stressor upon receiving streams in mined watersheds and are discussed in more detail later in this paper. More recent EPA guidance (issued in 2011; subsequently withdrawn) was based on the belief that mine discharges with EC levels <300 $\mu\text{S}/\text{cm}$ generally will not cause significant degradation of the aquatic ecosystem while in-stream conductivity levels >500 $\mu\text{S}/\text{cm}$ are likely to be associated with significant adverse impacts on the aquatic ecosystem. The proposed guidelines suggested that projects expected to increase conductivity to levels >300 $\mu\text{S}/\text{cm}$ should require adaptive remedial action to prevent conductivity from rising to levels that may contribute to water quality degradation and sites with discharges >500 $\mu\text{S}/\text{cm}$ should not be allowed to continue to operate. While the ability of EPA to directly implement this guidance was rejected in U.S. Federal Court, the decision (Walton 2012) left it open for USEPA, the federal office of surface mining (OSM) and the states to develop and establish TDS regulatory limits based upon the “best available science”.

In addition to the direct acid–base reactions detailed above, hydrolysis weathering reactions involving feldspars and micas can also release substantial amounts of other base cations such as K and Na to percolating waters. Thus, TDS in discharge from coal mines is dominated by HCO_3^- , SO_4^{2-} , Ca^{2+} , K^+ , Mg^{2+} , and Na^+ (Hartman et al. 2005; Orndorff et al. 2010; Agouridis et al. 2012) with SO_4^{2-} and Ca^{2+} dominating the mass of ions released in circumneutral waters. Total dissolved solids is only rarely measured directly due to it being very labor intensive and is generally estimated via electrical conductance (EC) or specific conductance (SC; which is EC corrected to 25 °C). Most studies show correlation coefficients greater than 0.95

between TDS and EC, thus making EC a very effective indicator for TDS for spoil column studies (Hood and Oertel 1984; Daniels et al. 2009). However, it is important to point out that the slope of the EC \times TDS relationship differs depending on the mix of ions present (Evangelou 1995).

Historically, pre-mining overburden analysis to minimize water quality impacts has focused upon conventional ABA (Sobek et al. 2000) since discharge pH, SO_4^{2-} , Fe and Mn levels have been the principal compliance parameters. The seminal study by Skousen et al. (2002) demonstrated that conventional ABA was effective at predicting and limiting strongly acidic discharge from central Appalachian coal mines. However, little if any work has been reported to date on the utility of either ABA or other techniques to predict bulk TDS, primarily due the fact that regulatory pressure on TDS discharge is relatively recent. Several significant recent studies are documented below including the large scale field spoil leaching study by Agouridis et al. (2012) in Kentucky and column leaching studies (Orndorff et al. 2010; Daniels et al. 2013, 2014) on Virginia and central Appalachian region spoils.

Over the past 30 years, many researchers have attempted to gain a better prediction of the complex interactions occurring in weathering mine spoils via a variety of techniques and some of the more notable examples are discussed below. Caruccio et al. (1993) performed an overburden analysis and leachate prediction study comparing acid–base accounting, humidity weathering cells, column tests (large and small), and Soxhlet reactors for the purpose of predicting field leaching conditions. They concluded that the leaching columns provided the best approximations of field weathering conditions. Historically, column leaching studies have been favored for the more accurate prediction of pH/acidity generation via pyrite oxidation, TDS release from mine spoil, and the kinetics of trace metal leaching (Hood and Oertel 1984; Halverson and Gentry 1990; Caruccio et al. 1993; Daniels et al. 2009; Orndorff et al. 2010). However, column leaching studies are labor intensive and take many months to complete while static tests such as the components of ABA (pyritic-S, neutralization potentials, etc.) are completed quickly at much lower relative cost. It is also important to point out that while certain authors (e.g. Vengosh et al. 2013) refer to short-term solution: solid extracts of crushed spoils as “leaching tests”, such procedures are short-term lab extractions and do not provide the kinetic/temporal data of column or field leaching trials.

In a recent column study, Orndorff et al. (2010) found that regardless of leachate pH, samples with significant levels of sulfides release much larger quantities of TDS over extended periods of time. Thus, even circumneutral mine discharges can contain high levels of sulfates as long as sufficient reactive carbonates are present in the source

spoils. On a mass basis, initial TDS mass release is dominated by sulfates under unsaturated flow conditions and by a mix of sulfates and bicarbonate under saturated flow conditions. Furthermore, the anion complement shifts dramatically from sulfate to bicarbonate as leaching progresses for non-acid forming mine spoils. As reactive sulfides are largely oxidized, carbonate dissolution becomes dominant, and TDS emission slows (Daniels et al. 2013). In non-sulfidic materials, leachate EC/TDS values peak within the first few leaching cycles and then drop quickly and eventually level off after 10–20 leaching events (Halverson and Gentry 1990; Hood and Oertel 1984; Orndorff et al. 2010). In the previously mentioned large scale field study by Agouridis et al. (2012), EC levels from unweathered gray sandstone initially exceeded 1500 $\mu\text{s}/\text{cm}$, but approached 500 $\mu\text{s}/\text{cm}$ within 2 years. Additionally, leachate EC is typically higher in leachates from unweathered mine spoil than from weathered materials from the same local strata, and this observed difference is most profound in finer textured mudstones and shales (Agouridis et al. 2012; Daniels et al. 2013).

3 TDS prediction research

For the past two decades, we have focused research efforts on the utilization of a laboratory column leaching procedure to characterize leaching potentials and risks from a wide range of coal mining related materials including coal refuse and fly ash (Stewart et al. 2001; Daniels et al. 2009) and coal mine spoils (Orndorff et al. 2010; Daniels et al. 2013, 2014). In this paper, we summarize our findings with respect to hard rock derived coal mine spoils with reference to coal refuse materials as well.

3.1 Sampling and analytical methods

Major mined lithologies in the region (Kentucky—KY, Virginia—VA, Tennessee—TN, and West Virginia—WV) were sampled (>50 bulk materials) for detailed laboratory analyses. When possible, weathered and unweathered spoils from the same strata were collected. As a part of this process, we largely excluded spoils that were known to be strongly acid-forming (e.g. >5/1,000 tons CCE net acid) since they would presumably be isolated away from drainage. In addition, as part of a parallel study funded by OSM (Daniels et al. 2014), we sampled and analyzed a range of coal refuse materials the same region.

Complete lab analyses included ABA parameters (sulfur analyses to determine Maximum Potential Acidity, Neutralization Potential and CCE, etc.), 1:1 water and saturated paste pH and EC as well as total elemental analysis.

Table 1 Lab pH, saturated paste EC, total S and net neutralization potential for three coal mine spoil and three coal refuse samples from Tennessee, USA. Full characterization data are available in Daniels et al. (2014)

ID	PH	EC ^a (μs/cm)	Total-S (%)	NNP ^b (t/1,000 t)
TN1	7.3	2,250	0.06	29.6
TN4	4.7	1,930	0.08	26.4
TN5	5.8	2,570	0.15	31.8
TNR1	8.0	1,261	0.52	53.5
TNR2	8.0	2,820	1.09	41.7
TNR3	8.1	1,945	1.22	23.3

^a EC electrical conductivity

^b NNP net neutralization potential expressed as 1,000 tons CaCO₃ per 1,000 tons material

Sample analytical parameters for a subset of spoil and coal refuse samples from TN that is used as examples in this paper are provided in Table 1.

Based on the review of field and lab data distributions, we selected over 50 different spoil materials with varying rock type and weathering extent for column (7.5 cm × 40 cm) leaching analyses via methods described by Daniels et al. (2013, 2014).

The columns were leached twice weekly (unsaturated) with 2.5 cm of simulated precipitation (pH 4.6) for 40 leaching cycles or until elution equilibrium for all major TDS constituents was observed. Certain samples were also leached under saturated conditions. Leachates were evaluated for pH and EC and all major components (e.g., SO₄, Cl, HCO₃, Al, Ca, Fe, K, Mg, Na, Se, etc.) by ICP-MS and other appropriate techniques. Similarly, we selected five representative coal refuse materials (Daniels et al. 2014) and leached them via the same procedures.

3.2 Column leaching results

The overall leaching column results from our large regional sample set (Daniels et al. 2013) reconfirmed earlier findings by Orndorff et al. (2010) and Agouridis et al. (2012) that the extent of oxidation and weathering of the mine spoil before mining has a dominant influence on overall TDS release. Initial leachate EC was high (>750–1,000 μs/cm) for most materials tested, but dropped quickly after five to eight leaching cycles (2.5 cm or 1 in. H₂O each) to below 500 μs/cm after 20 leaching cycles for >75 % of the materials tested. Rock type and total-sulfur content strongly influenced overall TDS release as expected. Finer textured shales produced higher TDS than other rock types in general, but high sulfur sandstones also produced higher overall TDS. Two of the Kentucky samples included in the column leaching analyses (Daniels et al. 2013) were derived from the original spoils used by Agouridis et al. (2012) to construct their large

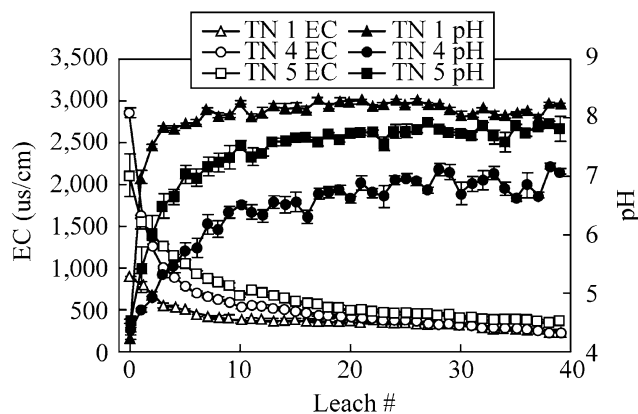


Fig. 1 Column leachate EC and pH from three TN spoils under unsaturated conditions. The columns were leached with simulated acid rain. The 40 leach events occurred over 20 weeks; one pore volume is approximately 3–5 leaching doses. Bars around each point indicate one standard error above and below the mean of 3 replications

field lysimeter study and the column study and comparative overall EC levels and temporal patterns were similar. Complementary work at West Virginia University (Odenheimer 2013; Odenheimer et al. 2013) indicates that both total-sulfur and simple lab extractable EC techniques may reliably predict both short-term maximum and long-term TDS release potentials, but that different predictive functions may be associated with varying initial (low, medium and high) total-sulfur levels.

A detailed example of the leaching behavior for three typical mine spoils of the region is provided in Fig. 1. All of these materials possessed a large excess of neutralizers over potential acidity (see Table 1) and thus were predicted to produce net neutral to alkaline drainage. The initial EC was high (800 to >2,500 μs/cm), but varied widely across materials tested. The initial leachate pH reflected the simulated acid precipitation used, but quickly rose in all three materials to pH 6.0 or higher. All major ions of interest (e.g. As, Ca, Se, SO₄) displayed a similar temporal leaching pattern, with much higher concentrations present in initial leachates and then a rapid drop in concentration once several pore volumes (6–10 leach cycles) had eluted (Daniels et al. 2014). Despite the similarity in overall EC and pH response of these materials, it is important to point out the wide differences in their relative EC and pH among materials.

When three coal refuse materials from TN were subjected to the same leaching column protocol (see Fig. 2), the overall results differed. First of all, coal refuse materials generally contain much more finely divided reactive sulfides than coal mine spoils and are much finer textured (Stewart et al. 2001; Daniels et al. 2009), and therefore produce much higher levels of both initial and long-term EC/TDS. These particular refuse materials are unusual for our region in that all contain a significant surplus of

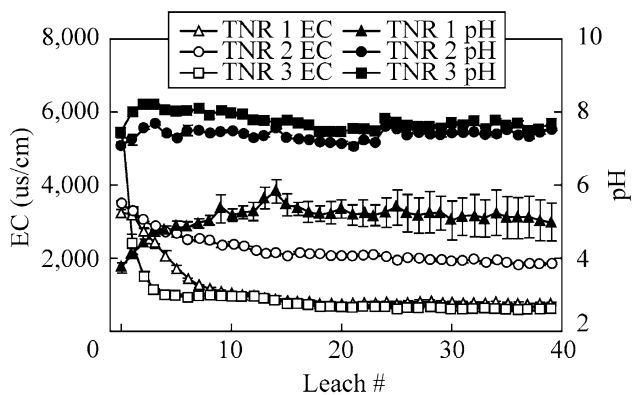


Fig. 2 Column leachate EC and pH from three TN coal refuse under unsaturated conditions. The 40 leach events occurred over 20 weeks; one pore volume is approximately 3–5 leaching doses. *Bars* around *each point* indicate one standard error above and below the mean of 3 replications

neutralizers over potential acidity (Table 1), and all three materials produced moderate (pH 5) to relatively high leachate pH (>7) over time as expected. However, it is clear from this work and other related studies that coal refuse materials pose a much more significant long term source of localized TDS release risk than the vast majority of mine spoils from the Appalachian region. Therefore, the management of effluent discharges beyond disposal facility closure needs to be carefully planned for.

4 TDS effects on aquatic life: summary of field studies

Elevated concentrations of major ions in freshwaters are of worldwide concern (Williams 1987, 2001). Human activities causing freshwater salinization include agricultural irrigation, road salt applications, discharge of treated effluents, and mining (Kaushal et al. 2005; Steele and Aitkenhead-Peterson 2011; Cañedo-Argüelles et al. 2013). Much of the salinization described by the scientific literature is NaCl enrichment, but elevated Na^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} , and HCO_3^- from irrigation in California's San Joaquin river (Leland and Fend 1998); Na_2SO_4 in a South African river influenced by mining (Goetsch and Palmer 1997); and Ca^{2+} , Na^+ , Cl^- , HCO_3^- in a French river receiving industrial discharge (Piscart et al. 2006) are also reported. Mining-related salinization has been studied in Australia (Hancock et al. 2005), Germany (Schreck 1995), South Africa (Goetsch and Palmer 1997), Spain (Cañedo-Argüelles et al. 2013) and the USA. Given the fundamental nature of mechanisms that cause release of mineral salts from rocks exposed by mining, such effects are likely in other world regions. Numerous studies have reported altered aquatic communities in streams with elevated salinity. In their review of world literature, Cañedo-

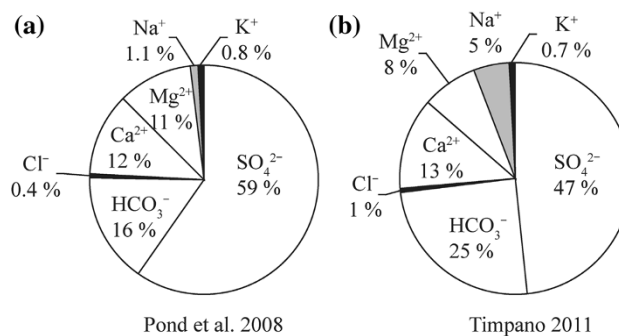


Fig. 3 Mean percentage contributions, by mass, of major ions to total dissolved solids in Appalachian mining-influenced waters, as documented by Pond et al. (2008) (13 West Virginia streams, mean sum of ions = 1,169 mg/L); and Timpano (2011) (63 samples from 21 Virginia streams, mean TDS = 408 mg/L)

Argüelles et al. (2013) state that “In general direct adverse localized effects to freshwater communities are expected to occur if salinity is increased to 1–3 ms/cm” (equivalent to 1,000–3,000 $\mu\text{s}/\text{cm}$) and report a range of effect levels when reviewing individual studies.

4.1 What comprises TDS in Appalachia?

Mining-influenced waters in Appalachia are often elevated in TDS/SC relative to unmined reference waters where SC is often <100 $\mu\text{s}/\text{cm}$ and generally <200 $\mu\text{s}/\text{cm}$ (Hartman et al. 2005; Merricks et al. 2007; Pond et al. 2008; Fritz et al. 2010; Timpano et al. 2010; Timpano 2011; Lindberg et al. 2011; Mack et al. 2013; Petty et al. 2013). Although residential development can also contribute to elevated TDS/SC, studies contrasting mine-influenced waters to those impacted by residential development have found higher TDS/SC levels in the mine-influenced waters (e.g. Pond, 2004, 2010, 2012; Merriam et al. 2011, 2013).

The dominant ion by mass in mining-influenced Appalachian waters is usually sulfate, followed by bicarbonate, calcium, and magnesium. The general composition of stream water receiving mining discharges from ten sites in West Virginia and Virginia is shown in Fig. 3. The relative concentrations of ions are consistent with other literature from the region (e.g. Petty et al. 2013). Chloride can be elevated in some mining-influenced streams that receive deep-mining effluent, but we are not aware of cases where chloride is a significant TDS contributor in central Appalachian streams due to influences by surface mining.

4.2 What are effects of TDS in Appalachia?

A goal of USA federal law, the Clean Water Act, is to “restore and maintain the chemical, physical, and biological integrity of the Nation's waters”. Furthermore, that law requires stream water quality that “provides for the

Table 2 Summary of studies concerning effects by mining-origin total dissolved solids (measured as specific conductance, SC) on benthic macroinvertebrate communities in the central Appalachian coalfield

Study; effect level ^b or finding	Method	Threshold identification	Comment
Green et al. (2000); 426 $\mu\text{S}/\text{cm}$	23–36 sites sampled over 5 seasons. Regress SC versus WVSCI	Regression SC for WVSCI < 70	$R^2 = 0.656$
Pond (2004); 500 $\mu\text{S}/\text{cm}$	85 sites sampled over 5 years, categorized by land use. Data analyzed by land-use category	“Drastic reductions in mayflies occurred at sites with conductivities generally above 500 $\mu\text{S}/\text{cm}$ ”.	Mine-influenced sites tend to have both high SC and poor-quality habitat.
Freund and Petty (2007); 501 $\mu\text{S}/\text{cm}$	46 sites sampled over 1 year	Regression SC for WVSCI < 60.6	Acid mine drainage contaminants were also present and assessed
Pond et al. 2008; 500 $\mu\text{S}/\text{cm}$	27 mined sites and 10 reference sites sampled. Categorical analysis of SC levels versus WVSCI and GLIMPSS	“All mined sites with specific conductance >500 $\mu\text{S}/\text{cm}$ were rated as impaired with the genus MMI (GLIMPSS)”.	GLIMPSS and WVSCI were highly correlated, but GLIMPSS classified more sites as impaired.
Gerritsen et al. (2010); 180–300 $\mu\text{S}/\text{cm}$	Regress SC vs. WVSCI using West Virginia agency data	Regression SC for WVSCI < 68	Several potential thresholds are derived
(Pond 2010). Mayfly richness, abundance are lower at mine-influenced versus Ref. Sites, and have negative association with SC	92 streams each sampled one time in spring. Data (Kentucky agency database) analyzed by land use category	N/A	Mine-influenced sites have both higher SC and poor-quality habitat.
Merriam et al. (2011); 250 $\mu\text{S}/\text{cm}$	41 sites sampled total in Spring; 8 sites along a residential development only gradient, 11 sites along a mining only gradient, remaining 22 sites with combined stressors	Regression and changepoint analysis	Residential impacts also noted
Timpano (2011); 634 $\mu\text{S}/\text{cm}$	8–28 sites sampled up to 4 times each. Regress SC versus VASCI	Regression SC for VASCI < 60 impairment threshold	$R^2 = 0.36$
US EPA (2011) and Cormier et al. (2013); 300 $\mu\text{S}/\text{cm}$	Apply species sensitivity distribution (SSD) approach to WV DEP monitoring data	$\geq 5\%$ of genera are absent in WV streams with SC $\geq 295 \mu\text{S}/\text{cm}$	Sites selected to minimize non-TDS stressors; High variance ($R^2 < 0.5$)
Bernhardt et al. (2012); 308 $\mu\text{S}/\text{cm}$	Regress SC versus WVSCI and GLIMPSS (WVDEP database)	Regression SC for WVSCI < 68 and GLIMPSS < 52	SSD approach had been applied previously only to laboratory data
Pond (2012). Stonefly, caddisfly richness reduced but caddisfly abundance increased at mine-influence sites versus Ref.	94 headwater streams; otherwise as in Pond 2010	N/A	High variance ($R^2 = 0.34$ for WVSCI, 0.48 for GLIMPSS)
Boehme (2013). High-TDS streams’ metrics differed consistently from reference; medium-TDS also differed but not as consistently.	Sampled 12 streams 15 times each; classify by TDS category. Analyzed 12 metrics and VASCI for difference by TDS category	Stream categories are high-TDS (mean SC = 756–1,535 $\mu\text{S}/\text{cm}$); medium-TDS (262–648 $\mu\text{S}/\text{cm}$); and reference (17–142 $\mu\text{S}/\text{cm}$)	Mine-influenced sites have both high SC and poor-quality habitat. Residential impacts also noted
Pond and North (2013). O/E and BC indices are highly correlated with SC	Model as observed versus Expected (O/E) and compositional similarity (BC), West Virginia and Kentucky agency data	N/A	Study sites selected to minimize non-TDS stressor influence (as per Timpano 2011)

^a Multimetric indices are WVSCI west virginia stream condition index; VASCI virginia stream condition index; GLIMPSS genus-level index of most probable stream status; Ref. reference (minimally disturbed or impacted by human activities)

^b 1,000 $\mu\text{S}/\text{cm}$ is equivalent to 1 mg/cm

protection and propagation of fish, shellfish, and wildlife”. Water discharges by coal mining operations, and their effects on the fresh water streams that receive them, are subject to Clean Water Act requirements.

The term “benthic macroinvertebrates” describes a class of non-vertebrate aquatic organisms that live on stream bottoms and are large enough to be seen by the naked eye. Benthic macroinvertebrates are ubiquitous in non-polluted freshwater streams and serve as important components of the food webs that support larger aquatic organisms, such as fish and shellfish. Benthic macroinvertebrates are easily sampled and identified. Hence, benthic macroinvertebrates are often used as surrogates for the full aquatic community in Clean Water Act enforcement. Throughout the USA, government agencies commonly sample benthic macroinvertebrates from freshwater streams, evaluate the taxonomic composition of those samples, and interpret the resulting data to assess those streams abilities to support aquatic life as per Clean Water Act requirements.

Such studies have often observed that benthic macroinvertebrate communities in Appalachian streams receiving coal-mine discharge waters are altered, relative to communities inhabiting streams in unmined areas with no pollution sources. Major questions concerning the influence of TDS from mining on aquatic biota exist. Several studies have been conducted to address those questions (Table 2).

4.3 Interpretations of field studies

When available studies are considered collectively, several observations are apparent. Composition of TDS in non-acidic Appalachian mine-influenced waters is generally consistent, but water chemistry within individual streams may vary from that signature. Dominant ions are generally SO_4^{2-} , $\text{CO}_3^{2-}/\text{HCO}_3^-$, Ca^{2+} and Mg^{2+} . Our scientific review finds few examples of similar water chemistries in other regions that can be drawn upon to illuminate Appalachian mining issues.

Laboratory and field studies support the finding that drawing broad generalizations on toxicity using non-specific measures such as TDS or SC is limited when the ionic composition of the solution is not known. Laboratory studies have demonstrated that the toxicity of dissolved solids to freshwater organisms is dependent upon ionic composition (Mount et al. 1997). However, discrepancies between taxa sensitivities found in laboratory toxicity tests, versus apparent sensitivities derived from field community surveys remain problematic with respect to identification of the mechanism of the potential toxicity.

Researchers have found negative associations of benthic macroinvertebrate community metrics with SC, and that benthic macroinvertebrate samples from mining-influenced elevated-TDS streams consistently lack taxa present in

low-TDS reference streams. We are aware of no studies conducted across a range of independent sites that have produced contrary findings. However, it is also noteworthy that only one of the studies (Timpano 2011) was conducted with data collection and site selection designed to control for other potential stressors associated with mining disturbance and evaluate the effects of major ions (as represented by SC).

Studies assessing individual metrics are consistent in finding *Ephemeroptera* (mayflies) as highly sensitive to TDS/SC (Pond 2004, 2010; Hartman et al. 2005; Pond et al. 2008; Timpano 2011; Boehme 2013). Generally, mayfly relative-abundance metrics are less responsive to elevated TDS than mayfly richness, in large part due to TDS tolerance by certain mayfly taxa (e.g. *Baetidae*) (Pond 2010; Boehme 2013). Also among non-mayfly taxa, richness appears to be more responsive to elevated TDS than relative-abundance metrics (Timpano 2011; Pond 2012; Boehme 2013). However, it is not clear if such findings occur as an artifact of sampling techniques that assess population composition but not population density, or if absolute abundance is less affected by elevated major ions than richness.

It is not clear if the ecological roles of absent taxa are performed by those taxa remaining, or if essential stream functions are also altered in TDS/SC streams. Leaf-litter processing rates are often reduced in mining-influenced streams with elevated TDS/SC, relative to reference streams (Simmons et al. 2008; Fritz et al. 2010; Petty et al. 2013), although it is uncertain if elevated major ions are the causative factor. Two studies have found breakdown rates to be negatively correlated with SC (Fritz et al. 2010; Petty et al. 2013), but both studied limited selections of streams. Other stream functions, such as nutrient uptake, have not been studied sufficiently to draw conclusions concerning how they may or may not be affected by elevated major ions.

Causality for the associations of community indices with SC observed in field studies has not been determined with complete certainty. Field studies are poorly suited for determining toxicological cause-effect relationships. However, studies assessing TDS/SC relationships with aquatic life indicators consistently indicate a likelihood that elevated concentrations of major ions are causing, or contributing to, the aquatic community effects observed in Appalachian mining-influenced streams with elevated TDS/SC (Table 2). Potential causal mechanisms for decreased macroinvertebrate community scores include (1) lethal or sublethal effects to sensitive taxa, (2) voluntary movement of sensitive taxa out of elevated-TDS stream segments, and/or (3) conditions produced by the elevated major ions that influence sensitive taxa only during certain life stages or seasons.

It is also possible that environmental variables associated with elevated TDS are contributing to aquatic

community effects that are being observed in high-SC streams. Such possible contributing (or causal) factors include altered hydrology, given that Appalachian mine sites have been found to have increased runoff during storm events relative to undisturbed sites (Messenger 2003; Wiley and Brogan 2003; Negley and Eshlemen 2006; McCormick et al. 2009), and/or increased sedimentation and unstable stream substrate conditions, which would be affected by altered hydrology. Other factors such as changes in stream temperature and light intensity may also be influencing the suitability of mining influenced stream reaches considered by these studies.

Appalachian SC effect levels derived from field studies (Table 2) are generally lower than the 1,000–3,000 $\mu\text{S}/\text{cm}$ levels cited by Cañedo-Argüelles et al. (2013) from world literature, which agrees favorably with laboratory data. It is unclear whether community effects described herein occur due to the unique ionic signature of Appalachian mine-influenced waters, adaptations of native taxa to the dilute waters produced by this highly weathered landscape, influence by co-variate stressors (see above), greater sensitivity of organisms in field conditions versus laboratory exposure conditions, or some other factor (s).

5 Overall summary and conclusions

Very few studies to date have focused on TDS production by non-acidic spoils, but some general conclusions can be drawn at this time. As expected, mine spoils that are significantly pre-weathered are lower in pH and EC production than unweathered materials of similar geology. Most unweathered spoil samples will produce moderate initial leachate EC levels ($\geq 1,000 \mu\text{S}/\text{cm}$) over their initial leaching cycles. Differences in TDS release appear to be clearly related to sulfide oxidation reactions with subsequent generation of sulfate and other acid–base reaction and carbonate dissolution products. It is interesting to note that the field-scale study of Agouridis et al. (2012) and the column leaching results reported by Daniels et al. (2013, 2014) reached similar conclusions with respect to the overall levels and temporal response of leachate EC to rock type and pre-weathering even though they were conducted independently on different materials. Our subsequent column leaching study using archived sample of the two Kentucky spoils used in the Agouridis et al. study confirmed that the overall column and field-scale leaching results were quite similar. However, more work is needed to determine the actual relationship between column leaching and actual field-scale mine discharge potentials.

While column leaching tests are favored for prediction of mine spoil discharge quality, they are expensive, time-consuming and not a practical alternative for routine mine

planning and permitting. The combination of the efforts reported here indicates that a combination of relatively simple static laboratory procedures for total-sulfur and EC could potentially be used in combination to predict both short-term peak and longer term TDS release potentials. Further effort is needed (and ongoing), however, to investigate the addition of other parameters such as neutralization potential to the prediction models and to compare the relative accuracy of single versus multiple parameter prediction models.

Our column leaching studies combined with the field lysimeter studies of Agouridis et al. (2012) clearly indicate that TDS release potential from non-acid forming spoils should drop quickly once they are exposed to leaching. However, a recent extensive study by Evans et al. (2014) of the actual long-term TDS discharge response of a large number ($n > 100$) of valley fills in SW Virginia indicates that the time for discharge SC to decline below 500 $\mu\text{S}/\text{cm}$ was 10–15 years, on average, beyond final revegetation. The reason for this time lag in field behavior 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 placed in valley fills before current concerns over TDS emerged, (c) the large spoil volumes that have been placed in the valley fills relative to annual rainwater infiltration, and (d) contributions from deep mine influenced groundwater seepage into valley fill drainage. Given that older valley fills in Virginia, such as those studied by Evans et al. (2014) are often smaller than those constructed more recently in other Appalachian mining areas such as southern WV and eastern KY, it is not clear that those estimates represent Appalachian valley fills as a whole. However, geochemical principles and our column leaching studies do indicate that SC/TDS in waters emerging from Appalachian mine sites can be expected to decline, eventually.

With respect to field effects of TDS, reported relationships between SC and benthic macroinvertebrate metrics are highly variable, as studies conducted with regression approaches commonly yield R^2 values of <0.5 . Although most studies have focused on multimetric indices such as West Virginia Stream Condition Index, similar levels of variability are also present for individual metrics (e.g. see Timpano 2011). Some of that variability likely occurs due to variable influence by other stressors at study sites. Other reasons may include “drift” of sensitive organisms from low-TDS waters upstream into the sampling zone, a factor that will vary from site to site. It is also possible that differences among major ion ratios within the general ion-matrix signature of Appalachian mine waters influence macroinvertebrate responses to TDS in a manner that contributes to response variability. Temporal variability of

TDS (and its components) may also play a role if the point-in-time sampling used in studies to date does not adequately characterize the levels that are most influential (Petty et al. 2013). However, research to date has been consistent in documenting depressed benthic macroinvertebrate communities in mining influenced streams, and statistical associations of such effects with measured levels of SC/TDS. Hence, available research strongly suggests that elevated concentrations of major ions in mine discharge waters, measured as SC and TDS, are causing aquatic community alterations.

Overall, results from the studies cited here indicate that identification of high TDS producing strata could potentially be utilized as a part of pre-mine planning and permitting procedures to minimize TDS release to receiving streams. We suggest that active mine operations should be modified to place high TDS producing materials in ways that reduce contact with percolating drainage waters. It is also clear from multiple studies that near-surface pre-oxidized and weathered strata will be much lower in their TDS producing potentials and their use as topsoil substitutes should be emphasized and encouraged. We believe that these practices would minimize TDS of surface runoff waters and associated aquatic life effects in receiving streams.

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