

Predicting release of total dissolved solids from overburden material using acid-base accounting parameters

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Abstract: The Appalachian coal industry has been successful in developing technologies to identify, handle, treat and isolate potentially acid-forming overburden materials at coal mines in the region. Modern coal mining permits have stringent guidelines for reclamation and water discharge limits. Total dissolved solids (TDS) is a new water quality parameter that has been linked to a decrease in survival of aquatic macro-invertebrates in receiving streams. Past techniques to predict acid mine drainage potential to decrease impacts to streams may not accurately predict the release of TDS. The objective of this work was to develop a TDS release index from overburden material that could be used to predict and screen overburden materials that contribute to high TDS concentrations. Forty-one overburden samples containing a range of sandstones and shales were collected from surface mines in West Virginia, Virginia, and Kentucky. Samples were ground to <2 mm particle size and weathered in dilute HNO₃ to determine TDS released. Supernatants were analyzed for pH, electrical conductivity (EC), and other selected ions. Results were compared to Acid-Base Accounting parameters for each sample; i.e. paste pH, maximum potential acidity (MPA), neutralization potential (NP), and net neutralization potential (NNP). Results showed that MPA (sulphur content) had the strongest relationship to TDS release, and low, moderate, and high TDS release indices were developed based on MPA values. Samples with MPA values of 0.0–1.0 g kg⁻¹ gave <150 mg l⁻¹ TDS, 1.0–3.0 g kg⁻¹ gave <300 mg l⁻¹, whereas 3.0+ g kg⁻¹ produced TDS values >500 mg l⁻¹. NPP was also a predictor for TDS, with an NPP ≥ -2.0 g kg⁻¹ likely to produce <300 mg l⁻¹ of TDS and NPP < -2.0 g kg⁻¹ likely to produce TDS concentrations >300 mg l⁻¹.

Keywords: electrical conductivity; surface coal mining; overburden; reclamation; weathering; TDS

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West Virginia is the largest coal-producing state in the Appalachian coal region (U.S. Energy Information Administration 2012). Coal mining has often been at the forefront of controversy concerning human and environmental health and safety because of the prevalence of mining in the state. Environmental impacts caused by the extraction and burning of coal include degradation of aquatic life and streams, deforestation, topography changes, acid mine drainage, erosion, subsidence, and acid rain (Palmer *et al.* 2010). Regulations to control and minimize damage during mining have been passed and adherence to reclamation standards has reduced the environmental impacts.

During surface mining activities, the layers of rock which cover the coal seam, known as overburden material, are blasted apart and moved in order to expose the coal. The broken overburden materials are placed to rebuild the landscape and are subjected to accelerated weathering, which promotes the release of soluble constituents into the environment. Depending on the chemical composition of the rock, weathering of these broken rocks can promote acid mine drainage, alkaline mine drainage (Bernhardt *et al.* 2012), as well as the release of heavy metals, and total dissolved solids (TDS). TDS are defined as the total sum of cations and anions in solution, but also includes any inorganic and/or organic constituent in water that can pass through a 2.0-µm filter (APHA 1992). Common ions are SO₄²⁻, HCO₃⁻, Cl⁻, Ca²⁺, Mg²⁺, K⁺, and Na⁺, but any element that is present in solution will contribute to TDS. Depending on the properties of the disturbed rock, physical and chemical weathering can produce high concentrations of TDS in receiving streams soon after disturbance, which generally declines with time (Skousen & Ziemkiewicz 2000; Skousen *et al.* 2000).

Acid-base accounting (ABA) is the most common method for predicting post-mining water quality (Perry 1985). Researchers at West Virginia University developed the ABA to better understand the chemical production potential of overburden material and to determine potential topsoil substitutes (Smith *et al.* 1974). The ABA procedure is currently utilized to determine the total amount of acidity and alkalinity that may be produced from overburden materials upon weathering (Skousen *et al.* 1997). Overburden cores in areas which are to be mined are extracted and used to gather physical and chemical information about rock layers before they are disturbed (Skousen *et al.* 1990). The geological layers of each core are identified by rock colour, hardness, fizz, and pH, and samples from these layers are then analyzed for total sulphur or maximum potential acidity (MPA) and neutralization potential (NP) (Skousen *et al.* 1987). The acidity or MPA comes from total sulphur analysis, and the alkalinity or NP is a measure of alkaline carbonates, exchangeable bases, and weatherable silicates present in the overburden material. Both MPA and NP are expressed in the unit g kg⁻¹ or parts per thousand parts. Although the ABA has been successful in predicting the release of acidity or alkalinity from overburden and its impact on stream quality (Skousen *et al.* 2002), it is unclear whether ABA will accurately predict TDS release from overburden material.

In recent years, researchers have suggested that TDS are responsible for polluting waterways and harming aquatic insects, which serve as the food supply for fish and other aquatic vertebrates. Several studies (Chapman *et al.* 2000; Goodfellow *et al.* 2000; Pond *et al.* 2008; and Timpano *et al.* 2010) have reported TDS as a major stressor upon receiving

streams in mined watersheds. The US Environmental Protection Agency (USEPA) has issued guidance documents stating electrical conductivity (EC) values (EC being a surrogate for TDS) of $<300 \mu\text{S cm}^{-1}$ (equivalent to 470 mg l^{-1} TDS) will not cause significant degradation of the aquatic ecosystem, but EC levels of $>500 \mu\text{S cm}^{-1}$ (equivalent to 780 mg l^{-1} TDS) are associated with significant adverse impacts on aquatic ecosystems. In order to regulate TDS discharge guidelines, the USEPA, researchers and operators need a better understanding of how TDS constituents are released from disturbed geological materials during mining and after reclamation, and how these constituents enter and impact streams. Unfortunately, no such method currently exists for the prediction of TDS release from overburden material.

The goal of this research was to determine a TDS release index using 41 overburden samples from the Appalachian coal region. Simulated weathering with dilute nitric acid (HNO_3) and ABA analyses for each sample were conducted to determine which parameters were most strongly linked to TDS release. TDS release was then compared to individual cations and anions released during weathering, as well as pH, EC, MPA, NP, NNP, and chroma of the overburden samples.

Materials and Methods

Field overburden collection and sample processing

Forty-one overburden samples were collected in 5-gallon buckets from recently-exposed geological materials at surface coal mines in West Virginia, Virginia, and Kentucky (15 samples from WV and VA, and 11 from KY). Emphasis was placed on collecting samples that represented a wide variety of rock types, such as mudstones, siltstones, and grey and brown sandstones. Initial screening revealed that rocks with high TDS were thought to be those with high sulphur contents and/or high carbonate contents (high MPA and high NP). Rock units with medium TDS potential were thought to be shales or other rocks with moderate sulphur and/or carbonate content. Rocks with low TDS potential were anticipated to be hard sandstones and/or weathered sandstones.

Samples were air-dried in the greenhouse at Virginia Tech and then the entire volume of each sample was crushed and passed through a 1.25-cm (0.5-in) sieve. Approximately 2000 g of each sample were sent to West Virginia University (WVU), where the samples were halved, and then further ground using a BICO pulverizing mill (BICO Inc. Burbank, CA) until all the sample could pass through a 2-mm (0.0787-in) sieve. After preliminary weathering tests involving two overburden sieve sizes (250 μm and 106 μm), we found no statistical difference in the concentrations of constituents released from the two particle sizes (Odenheimer *et al.* 2012). Therefore, we concluded that the current particle size ($<2 \text{ mm}$) was suitable for the weathering experiments.

Laboratory analysis: dilute nitric acid method

Dilute nitric acid (HNO_3) was utilized to determine TDS release from the 41 overburden samples. A solution of 0.0159M dilute HNO_3 (pH of 2) was prepared in the lab by a 1/1000 dilution of trace metal grade HNO_3 (15.9M). A dilute HNO_3 solution of 200ml was combined with 1.00 g of $<2\text{-mm}$ sized overburden material. The solution and overburden were placed in 250-ml plastic Nalgene bottles on a Wrist Action Shaker (Burrell, Model 75, Pittsburgh, PA) at *c.* 200 shakes per minute for a total of 120hs (5 days). Sample bottles were left for 1 hr after shaking to let all solids settle prior to extraction. Aliquots of 20 ml were extracted from

the bottles after 6, 24, 72, and 120 hrs of shaking. About 10 ml of the leachate were filtered and used for analysis of selected cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , P , Fe , Al^{3+} , Mn^{2+}) by inductively coupled plasma atomic emission spectrometry, ICP-AES (Optima DV-2100, Perkin Elmer, Norwalk, CT). A volume of 8ml was used to measure pH and EC using a Mettler Toledo SevenEasy pH meter, and Mettler Toledo SevenCompact conductivity meter, respectively. The remaining 2 ml were analyzed for anions (F^- , Cl^- , NO_2^- , Br^- , PO_4^{3-} , SO_4^{2-}) using Ion Chromatography (ICS-3000, Sunnydale, CA). Simulated weathering using dilute HNO_3 was replicated twice.

To determine paste pH, 5 g of overburden were combined with 5 ml of de-ionized water. The 1:1 mixture was placed on a reciprocating shaker table for 15 mins, then allowed to equilibrate for 1 hr. A Mettler Toledo SevenEasy pH meter was used to take the pH readings. Paste EC was determined by combining 5 g of overburden with 10 ml deionized water. The 1:2 mixture was placed on a reciprocating shaker table for 15 mins, then allowed to equilibrate for 1 hr. A Mettler Toledo SevenCompact Conductivity meter was used to determine EC readings.

Acid-Base Accounting parameters were determined by standard methods. Sulphur analyses were performed by dry combustion (LECO TruSpec S 432 Sulfur Analyzer (LECO Corp., St. Joseph, MI) (Sobek *et al.* 2000). Neutralization potential (NP) was determined by a revised technique using hydrogen peroxide as outlined in Skousen *et al.* (1997). Maximum potential acidity (MPA) was calculated from percent sulphur by multiplying total percent sulphur by 31.25 to get g kg^{-1} CaCO_3 equivalent. Net neutralization potential (NNP) was calculated by combining MPA and NP in g kg^{-1} as CaCO_3 and retaining the sign (an excess of MPA was negative and an excess of NP was positive).

Software programs R and JMP were used to perform statistical analyses to determine significant differences among samples and methods (R Development Core Team, 2013; SAS Institute, Inc., 2005). Analysis of variance (ANOVA) was utilized to determine significant differences in elemental concentrations at different shaking times and means were separated with the Least Significant Difference procedure. Regression was used to examine relationships between TDS and ABA parameters.

Results and Discussion

Dilute nitric acid method

To determine trends of elemental release from these samples with nitric acid, average concentrations for each element were determined across all samples. Concentrations leveled off after 72 hrs of shaking for all samples (Table 1), and showed no significant changes after 72 hrs. Aluminum concentrations ranged from 172 to 2028 mg kg^{-1} in these overburden samples (Table 2). Iron and Ca were released in high quantities: Fe concentrations ranged from 720 to 27,870 mg kg^{-1} ; and Ca concentrations ranged from 279 to 8237 mg kg^{-1} . However, a refuse sample (WV R) was an outlier,

Table 1. Means of elemental¹ concentrations in mg kg^{-1} released with time using dilute HNO_3

Time (hrs)	Al	Fe	Mn	Mg	Ca	K	Na	P
6	368 ^{C2}	3406 ^C	171 ^C	760 ^B	2455 ^A	208 ^B	47 ^A	148 ^A
24	523 ^B	6661 ^B	274 ^B	1023 ^{AB}	2651 ^A	229 ^{AB}	55 ^A	144 ^A
72	707 ^A	8624 ^A	338 ^A	1167 ^A	2725 ^A	281 ^A	52 ^A	142 ^A
120	824 ^A	8630 ^A	332 ^A	1138 ^A	2598 ^A	327 ^A	69 ^A	129 ^A

¹Only cations were utilized to determine significant differences in shaking times.

²Means for each element with different letters signify significant differences at $p=0.05$.

Table 2. Average electrical conductivity, pH, and elemental concentrations from solutions of dilute nitric acid shaking experiments for each of the 41 overburden samples at the end of the 72-hr shaking period

Sample	EC	pH	Al	Fe	Ca	Mg	Mn	Sum	Cl ⁻	SO ₄ ⁻²	F ⁻	PO ₄ ⁻³
	uS cm ⁻¹	s.u.	mg kg ⁻¹						mg l ⁻¹	mg kg ⁻¹		
VA 1	4780	2.0	347	6268	3054	788	286	61	121	986	52	219
VA 2	4140	2.0	441	15143	3214	1894	525	119	155	2251	56	188
VA 3	5210	1.9	838	827	279	387	153	25	216	2243	29	n.a
VA 4	5005	1.9	1549	1168	440	697	387	31	168	1729	33	n.a
VA 5	5195	1.9	641	1273	710	444	297	21	45	788	n.a	73
VA 6	4645	2.0	1379	4344	2985	1175	452	58	47	1143	n.a	138
VA 7	4725	2.0	1967	2086	1500	1186	612	41	50	644	n.a	97
VA 8	4620	2.0	965	8913	1456	810	185	69	44	1079	n.a	264
VA 9	4185	2.0	681	12354	4775	1403	395	104	56	781	92	327
VA 10	4295	2.0	1083	11576	3459	1659	422	96	70	749	n.a	221
VA 11	5190	2.0	957	1105	632	457	378	22	59	690	n.a	89
VA 12	4320	2.0	453	14151	1656	1100	468	95	62	751	n.a	365
VA 13	4990	1.9	405	3326	1874	903	474	40	76	883	n.a	116
VA 14	5195	2.0	767	783	671	563	373	20	66	731	n.a	47
VA 15	3200	2.2	978	21620	8237	3408	584	181	71	836	112	304
WV 1	5340	1.9	199	2295	280	195	26	19	76	749	n.a	n.a
WV 2	3980	2.1	643	21520	2204	1973	520	151	70	3123	n.a	151
WV 3	4970	1.9	432	5552	1415	579	71	47	111	1198	16	n.a
WV 4	4560	2.0	535	10972	1110	771	222	81	213	2207	43	161
WV 5	4810	1.9	204	10939	468	493	365	67	56	877	n.a	n.a
WV 6	4480	2.0	172	16457	690	911	501	99	55	866	n.a	115
WV 7	3140	2.2	2028	27870	4371	2273	550	195	136	1459	40	237
WV 8	5630	2.0	385	8118	760	614	174	55	51	652	n.a	290
WV 9	4135	2.1	365	19376	6423	2580	520	151	126	672	n.a	116
WV 10	5305	1.9	973	6628	1049	499	178	51	93	579	n.a	120
WV 11	5520	2.0	684	8548	1474	753	111	61	37	412	99	n.a
WV 12	6100	1.9	341	2615	952	307	31	26	91	653	n.a	139
WV 13	5915	1.9	852	4604	447	390	121	36	112	637	n.a	79
WV 14	4350	2.0	382	10191	2391	1046	222	75	57	571	n.a	141
WV R	3120	2.3	605	3797	27700	5946	262	211	102	3576	133	n.a
KY 1	6140	1.9	702	893	254	342	117	15	102	568	n.a	n.a
KY 2	5370	2.1	190	7994	4616	1634	193	77	76	579	62	125
KY 3	4915	2.0	365	10014	7446	2018	333	192	5190	9493	893	2551
KY 4	5390	2.0	1141	19657	2233	1122	519	129	76	887	20	67
KY 5	6075	1.7	916	720	496	140	603	18	124	644	n.a	n.a
KY 6	6000	1.8	1153	945	465	547	301	21	114	610	14	n.a
KY 7	5110	1.9	660	10468	3685	1961	641	106	136	3181	n.a	469
KY 8	4510	1.9	500	14401	2167	1344	371	100	135	950	n.a	190
KY 9	5470	1.9	301	10243	1537	1097	336	76	73	1441	n.a	108
KY 10	6005	1.8	287	4122	723	470	226	385	137	1684	n.a	216
KY 11	5425	1.9	528	9686	1421	953	349	70	137	773	n.a	141

releasing 27 700 mg kg⁻¹ of Ca. Magnesium concentrations ranged from 140 to 3408 mg kg⁻¹ with the refuse sample (WV R) releasing concentrations of 5946 mg kg⁻¹. Of the cations measured, Mn was released from the overburden samples in the smallest quantities, with a mean concentration from all 41 samples ranging from 26 to 641 mg kg⁻¹ at 72 hrs of shaking.

For the anions, chloride ion concentrations ranged from 37 to 5,200 mg kg⁻¹ for these samples (Table 2). The overburden samples released sulphate ions ranging in concentrations of 412 to 9493 mg kg⁻¹, roughly double that of chloride. Small amounts of fluoride were released in concentrations ranging up to 893 mg kg⁻¹, which made up less than 10% of the total anion concentration. Phosphate ions were also released from these samples in concentrations up to 2551 mg kg⁻¹. The 41 samples used for this research were chosen based on coal company ABA data and included a wide variety of rock types and stratigraphic positions. Hence, the large range in elemental concentrations released upon weathering for these samples was expected.

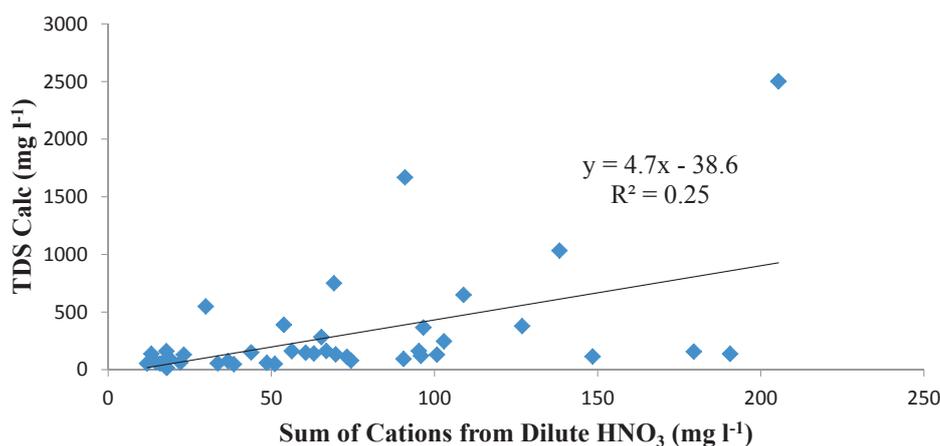
The average pH of the dilute nitric acid stayed constant with a mean of 1.97±0.11 after 72 hrs of shaking for all samples (Table 2). The samples that showed slightly elevated pH values of 2.2 or greater (VA 15, WV7, and WVR) generally had high Ca values, which probably related to higher alkalinity levels in the sample. Electrical conductivity (EC) did not change drastically over the duration of the shaking period (Table 2). The average EC for all 41 samples was 4900±770 uS cm⁻¹ after 72 hrs of shaking. The pH and EC of the dilute nitric acid background solution (2.0 and 6100 uS cm⁻¹, respectively) controlled the pH and EC of the sample solutions during shaking even though some of the samples had significant acid and base components.

Determining a total dissolved solids release index

The sum of cations released from the dilute nitric acid shaking method (Table 2) should provide an indication of approximate TDS release potential, and should ideally correlate well with Paste

Table 3. Values for paste pH, paste electrical conductivity (Paste EC), total dissolved solids (TDS Calc), maximum potential acidity (MPA), neutralization potential (NP), and net neutralization potential (NNP) for each of the 41 overburden samples

Sample	Paste pH s.u.	Paste EC $\mu\text{S cm}^{-1}$	TDS Calc ¹ mg l^{-1}	MPA	NP g kg^{-1}	NNP
VA 1	7.8	252	161	2.2	1.0	-1.2
VA 2	7.2	1013	649	8.0	1.7	-6.3
VA 3	4.7	214	137	1.6	1.7	0.1
VA 4	5.1	98	63	0.8	1.7	0.9
VA 5	5.6	250	160	1.2	0.9	-0.4
VA 6	7.1	610	390	3.7	1.3	-2.3
VA 7	7.0	76	48	0.5	1.0	0.5
VA 8	6.7	442	283	5.0	1.7	-3.3
VA 9	7.9	204	131	2.4	7.1	4.6
VA 10	7.8	253	162	2.6	1.8	-0.9
VA 11	5.5	150	96	0.6	1.7	1.1
VA 12	8.0	145	93	1.4	0.7	-0.7
VA 13	7.5	117	75	1.2	1.0	-0.1
VA 14	6.0	87	56	0.7	1.7	1.0
VA 15	8.3	246	157	2.7	1.5	-1.2
WV 1	7.1	83	53	0.7	1.2	0.5
WV 2	4.1	1555	1034	33.8	0.7	-33.1
WV 3	7.2	235	150	6.3	1.6	-4.7
WV 4	6.4	208	133	1.4	1.7	0.3
WV 5	6.3	221	141	6.3	1.5	-4.8
WV 6	6.6	187	120	4.0	2.1	-1.8
WV 7	8.0	214	137	1.8	1.7	-0.1
WV 8	7.3	78	50	0.8	1.5	0.8
WV 9	8.1	180	115	1.0	1.8	0.8
WV 10	7.3	92	59	0.5	1.6	1.1
WV 11	7.6	231	148	2.3	1.7	-0.6
WV 12	7.2	204	131	2.2	1.6	-0.6
WV 13	6.9	88	56	0.7	1.6	0.9
WV 14	7.8	173	111	1.8	1.7	-0.1
WVR	6.0	3505	2502	213.4	5.6	-207.8
KY 1	6.8	85	54	0.6	1.7	1.1
KY 2	8.2	124	80	0.2	1.4	1.1
KY 3	7.8	386	247	2.8	5.5	2.7
KY 4	6.4	591	378	3.9	1.8	-2.1
KY 5	5.3	104	66	0.4	1.7	1.3
KY 6	5.5	26	16	0.5	1.7	1.3
KY 7	5.4	2415	1669	28.0	1.7	-26.3
KY 8	7.0	572	366	3.7	0.7	-3.0
KY 9	5.4	1157	750	7.3	1.5	-5.8
KY 10	4.6	859	549	3.9	1.7	-2.2
KY 11	6.8	254	162	1.5	1.7	0.2

¹TDS value was converted from EC using Evangelou's (1998) equation.**Fig. 1.** Relationship between the sum of cations released from the dilute nitric acid method and TDS calculated from Paste EC of 41 overburden types.

EC. To make comparisons among parameters, TDS was calculated from Paste EC (called TDS Calc) using equation (1) (Evangelou 1998) (Table 3).

$$\text{TDS} = 640 * \text{EC} \left(\text{dS m}^{-1} \right) \quad (1)$$

When the sum of cations released after 72 hrs of weathering was compared with TDS calculated from Paste EC, an R^2 of 0.25 was found (Fig. 1). Removing the refuse sample (WV R) from the analysis decreased the relationship to 0.09. The lack of relationship provided strong evidence that elements released (sum of cations) from the dilute nitric acid method did not provide a useful TDS release prediction.

Although the sum of cations from nitric acid release (Table 2) did not provide a useful indicator, other rock properties should, such as those measured during the Acid-Base Account procedure. The properties that laboratories measure for Acid-Base Accounting include the reactive rock components such as paste pH, sulphide-bearing minerals and carbonates, all of which should have a strong effect on TDS release upon weathering.

Figure 2 examines the relationship between paste pH and TDS Calc. An inverse relationship was found between pH and TDS because elements in minerals tend to go into solution at lower pH values, thus producing more dissolved solids. But the relationship was not strong ($R^2=0.12$), especially below pH 6.0. The relationship would have been stronger had the three outliers with high TDS been removed from the analysis. Therefore, paste pH was not a strong indicator of TDS release potential.

The relationship between chroma of the material (the oxidized or reduced status of the rock material based on its brown or grey colour, with lower values equating to greyness) and TDS Calc produced a trend (Fig. 3). Overburden samples with a chroma of 1 (grey) tended to produce variable TDS concentrations, whereas samples with a chroma of 4 (brown) produced very low TDS concentrations and very low variation. These results indicate that oxidized samples produced low TDS values, and reduced rock samples (more grey in colour) gave less predictable TDS values.

Neutralization potential (NP) is an important parameter in ABA because it measures the alkalinity or neutralizing capacity of that overburden sample. Carbonates, which are measured by NP, react upon exposure to the environment and high NP was hypothesized to result in high TDS (Table 3). Figure 4 shows the relationship between TDS Calc and NP. The relationship between these two parameters is weak (R^2 of 0.10). Removing the three outlying samples did not improve the R^2 value much, providing evidence that NP was not a suitable predictor of TDS release by itself.

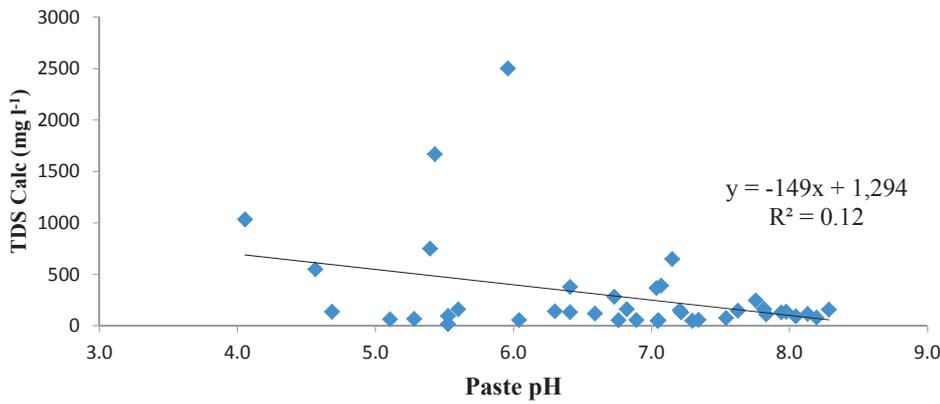


Fig. 2. Relationship between paste pH and TDS for all 41 overburden samples.

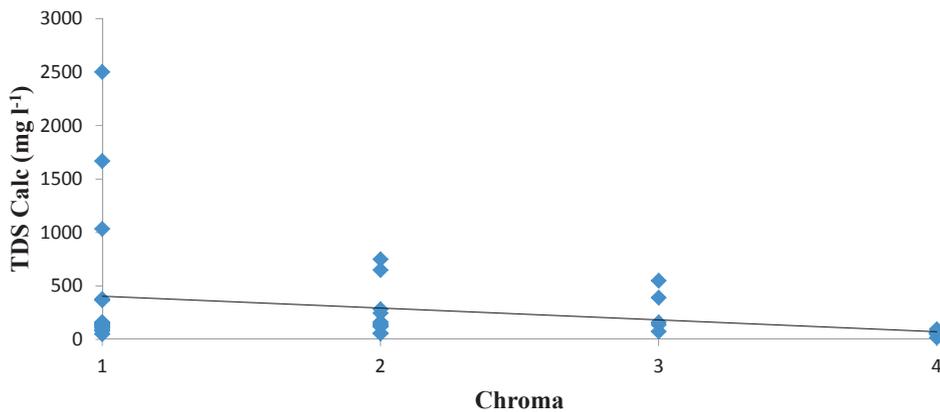


Fig. 3. Relationship between chroma (1 and 2 are reduced and 3 and 4 are oxidized samples) and TDS for all 41 overburden samples.

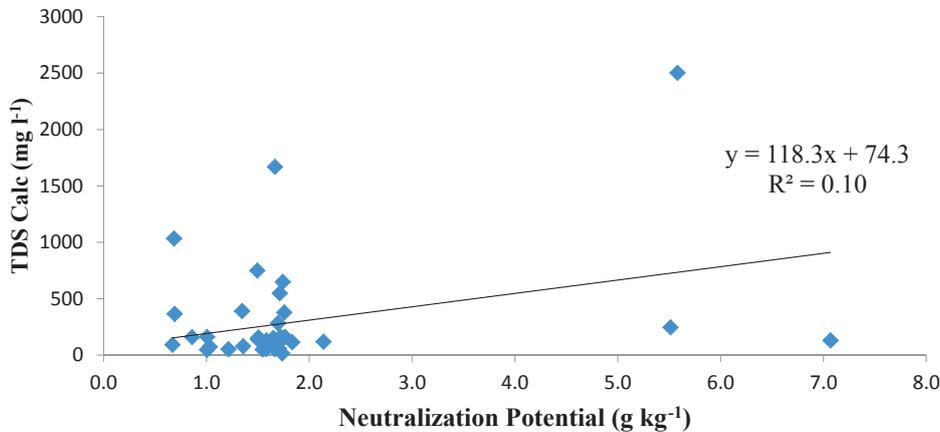


Fig. 4. Relationship between neutralization potential and TDS for 41 overburden samples.

Maximum Potential Acidity is an important parameter of the ABA because it represents the acid potential of that overburden sample due to sulphide minerals. MPA is calculated by multiplying % sulphur by 31.25 (Skousen *et al.* 2000). Maximum Potential Acidity and TDS Calc had a power relationship with an R^2 of 0.80 (Fig. 5). Based on this relationship, overburden samples with MPA values of $<1.0 \text{ g kg}^{-1}$ were categorized in a low TDS potential category because TDS did not exceed 150 mg l^{-1} . Samples with a MPA value ranging from 1.0 to $<3.0 \text{ g kg}^{-1}$ (Table 1.4) produced less than 300 mg l^{-1} of TDS, whereas some rocks with MPA 3.0 g kg^{-1} or greater produced concentrations of TDS that exceeded the USEPA's proposed maximum contaminant limit of 500 mg l^{-1} . This high TDS limit with an MPA $\geq 3.0 \text{ g kg}^{-1}$ is similar to other studies which showed that an MPA value of 5.0 g kg^{-1} or greater is most likely to produce acid mine drainage, and samples with an

MPA $<5.0 \text{ g kg}^{-1}$ are not likely to produce acid mine drainage (Skousen *et al.* 2002).

Subtracting the MPA from the NP yields a net neutralization potential (NNP), which is also in units of g kg^{-1} . A positive NNP indicates potentially acid-neutralizing rock units, and a negative NNP indicates a potential acid-producing rock unit. The relationship of NNP with TDS Calc had an R^2 of 0.73 (Fig. 6), but this was due to the strong pull of the refuse sample outlier (WV R). When removing WV R (-208 NNP , Table 3) and the other two outlying sample points (-26 and -33 NNP , Table 3), the R^2 decreases to 0.49 (Fig. 7). Figure 7 shows, in general, that overburden samples with an NNP value of <-2.0 generated TDS concentrations greater than USEPA's proposed maximum contaminant limit of 500 mg l^{-1} . Overburden samples that had an NNP value of -2.0 or greater generated less than

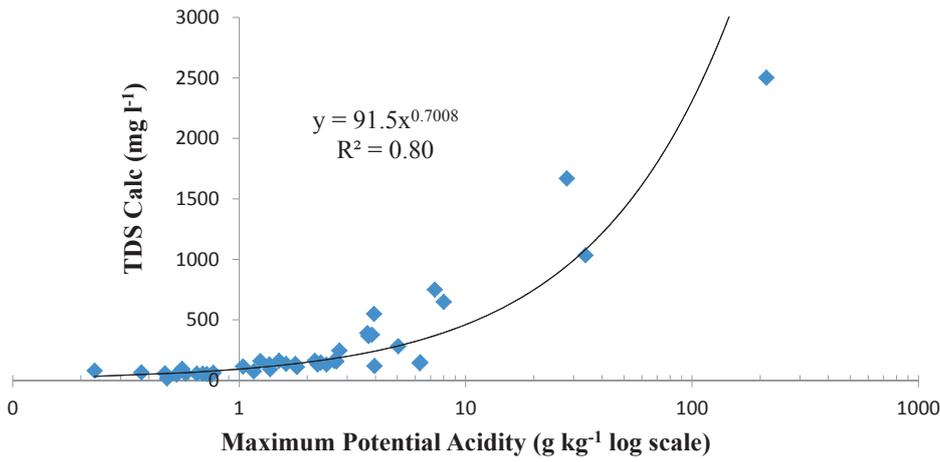


Fig. 5. Relationship between maximum potential acidity and TDS for 41 overburden samples.

Table 4. TDS release index using Maximum Potential Acidity (MPA)

MPA Range g kg ⁻¹	TDS Concentration mg l ⁻¹	TDS Release Index
0.0 to <1.0	<150	Low
1.0 to <3.0	<300	Medium
3.0 +	>500	High

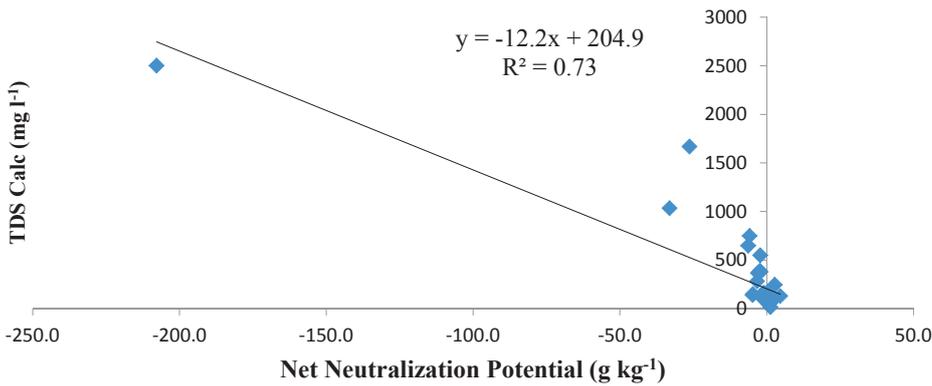


Fig. 6. Relationship between net neutralization potential and TDS for 41 overburden samples.

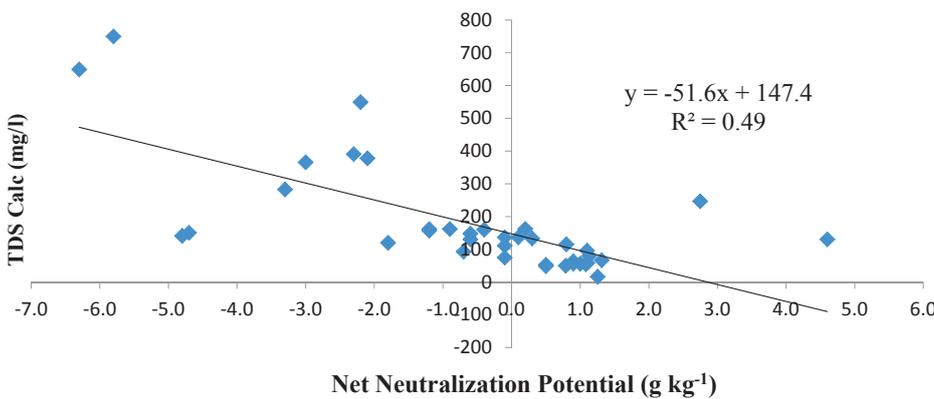


Fig. 7. Relationship between net neutralization potential and TDS (without three outliers) for 38 overburden samples.

Table 5. Net Neutralization Potential (NPP) and its potential release of total dissolved solids

NNP Range g kg ⁻¹	TDS Concentration mg l ⁻¹	TDS Release Index
≥ -2.0	<300	Low
< -2.0	≥300	High

300 mg l⁻¹ (Table 5). According to our results, an NNP value of -2.0 is the threshold for whether or not these particular overburden samples should be further scrutinized for potential TDS concentration concerns.

Conclusion

TDS was calculated from Paste EC for 41 overburden samples collected in the Appalachian coal region and these values were compared to cations and anions released from weathering with a dilute nitric acid solution, as well as to Acid-Base Accounting parameters (paste pH, MPA, NP, NNP, and chroma). The best predictors of TDS were two ABA parameters: MPA and NNP. Based on MPA, a low (<150 mg l⁻¹), moderate (<300 mg l⁻¹), and high (>500 mg l⁻¹) TDS release index was determined using MPA ranges of 0.0 to 1.0, 1.0 to 3.0, and 3.0+ g kg⁻¹, respectively. NNP was also found to predict TDS. An NNP <-2.0 g kg⁻¹ was likely to produce concentrations of TDS exceeding 300 mg l⁻¹, and an NNP ≥-2.0 g kg⁻¹ was likely to produce <300 mg l⁻¹ of TDS. Our results show that MPA and/or NNP can be used to evaluate which overburden samples will likely produce high, moderate, or low TDS concentrations upon weathering, and these routine ABA overburden analyses will provide information to help operators properly treat, isolate and/or handle overburdens in this region to decrease TDS runoff from their sites.

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References

- APHA (American Public Health Association). 1992. *Standard methods for the examination of water and wastewater*. 18th Edition, American Public Health Association, Washington, DC.
- Bernhardt, E., Lutz, D., King, R., *et al.* 2012. How many mountains can we mine? Assessing the regional degradation of central Appalachian rivers by surface coal mining. *Environmental Science Technology*, **46**, 8815–8122.
- Chapman, P., Bailey, H.B. & Canaria, E. 2000. Toxicity of total dissolved solids associated with two mine effluents to chironomid larvae and early life stages of rainbow trout. *Environmental Toxicology and Chemistry*, **19**, 210–214.
- Evangelou, V.P. 1998. *Environmental Soil and Water Chemistry*. New York. John Wiley & Sons, Inc, New York.
- Goodfellow, W.L., Ausley, L.W., Burton, D.T., *et al.* 2000. Major ion toxicity in effluents: A review with permitting recommendations. *Environmental Toxicology and Chemistry*, **19**, 175–182.
- Odenheimer, J., Skousen, J. & McDonald, L.M. 2012. Predicting total dissolved solids release from overburden in Appalachian coal fields. In: Craynon, J.R. (ed) Proceedings, Society of Mining, Metallurgy and Exploration, Denver, CO, February 24–27.
- Palmer, M., Bernhardt, E., Schlesinger, W., *et al.* 2010. Mountaintop mining consequences. *Science*, **327**, 148–149.
- Perry, E. 1985. Overburden analysis: An evaluation of methods. In: Graves, D. (ed) Proceedings of Symposium on Surface Mining, Hydrology, Sedimentology, and Reclamation, University of Kentucky, Lexington, December 9–13.
- Pond, G.J., Passmore, M.E., Borsuk, F.A., Reynolds, L. & Rose, C.J. 2008. Downstream effects of mountaintop coal mining: Comparing biological conditions using family- and genus-level macroinvertebrate bioassessment tools. *Journal North American Benthological Society*, **27**, 717–737.
- R Development Core Team. 2013. *R: A language and environment for statistical computing, reference index version 2.13.0*. R Foundation for Statistical Computing, Vienna, Austria. Available from <http://www.R-project.org> [Accessed 15 February 2013.]
- SAS Institute, Inc., 2005. *SAS user's guide. Version 8*. SAS Institute, Cary, NC.
- Skousen, J.G., Sencindiver, J.C. & Smith, R.M. 1987. *A review of procedures for surface mining and reclamation in areas with acid-producing materials*. WVU Energy and Water Research Center. Publication EWRC 871. Morgantown, WV.
- Skousen, J., Smith, R.M. & Sencindiver, J. 1990. The development of the acid-base account. *Green Lands*, **20**, 32–37.
- Skousen, J., Renton, J., Brown, H., *et al.* 1997. Neutralization potential of overburden samples containing siderite. *Journal of Environmental Quality*, **26**, 673–681.
- Skousen, J.G., Sexstone, A. & Ziemkiewicz, P.F. 2000. Acid mine drainage control and treatment. In: Barnhisel, R.I., *et al.* (eds) *Reclamation of drastically disturbed lands*. Agronomy Monograph **41**. ASA, CSSA, and SSSA, Madison, WI, 131–168.
- Skousen, J., Simmons, J. & Ziemkiewicz, P. 2002. Acid-base accounting to predict post-mining drainage quality on surface mines. *Journal of Environmental Quality*, **31**, 2034–2044.
- Smith, R.M., Grube, W.E., Jr., Sobek, A.A. & Singh, R.N. 1974. Rock types and laboratory analyses as a basis for managing minesoils. In: *Tenth Forum on Geology of Industrial Mineral Proceedings Misc. Report No. 1*. Ohio Department of Natural Resources, Columbus, OH.
- Sobek, A.A., Skousen, J.G. & Fisher, Jr S.E. 2000. Chemical and physical properties of overburdens and minesoils. In: Barnhisel, R.I., *et al.* (eds) *Reclamation of drastically disturbed lands*. Agronomy Monograph, ASA, CSSA, and SSSA, Madison, WI, **41**, 77–104.
- Timpano, A., Schoenholtz, S., Zipper, C. & Soucek, D. 2010. Isolating effects of total dissolved solids on aquatic life in central Appalachian coalfield streams. In: Barnhisel, R.I. (ed.) *Proc. 2010 National Meeting of the American Society of Mining and Reclamation, Pittsburgh, PA, June 5–11, 2010*. ASMR, Lexington, KY, 1284–1302. <http://www.asmr.us>
- U.S. Energy Information Administration. 2012. *Coal explained: Where our coal comes from*. http://www.eia.gov/energyexplained/index.cfm?page=coal_where (Accessed 12 February 2013; verified 16 August 2013.) Department of Energy, Washington, DC.