

# **2014/2015 Powell River Project Annual Report**

## **Developing Field and Lab Predictors of Appalachian Surface Coal Mine Spoil Leachate Geochemistry**

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### ***Introduction***

Release of total dissolved solids (TDS) from Appalachian coal mine spoils to headwater streams has emerged over the past decade as a significant concern for the coal mining industry, its regulatory agencies, and non-governmental organizations. The overall objective of this project is to develop a new set of techniques to reliably predict the amount, ionic composition, and temporal pattern of TDS release from a range of spoil and overlying soil materials from regional coal surface mines. This project was initiated in 2010 with sole support from Powell River Project. Between 2012 and 2014, we received significant parallel funding for this program from the Appalachian Research Initiative for Environmental Science (ARIES) to support our collaboration with the University of Kentucky and West Virginia University to broaden the scope to the central Appalachian region while continuing to focus on SW Virginia in more detail. Therefore, we are utilizing Powell River Project (PRP) funds to focus specifically on the determination of TDS release potentials of soil-saprolite-hard rock sequences in SW Virginia and adjacent counties in eastern Kentucky and southern West Virginia. This information will better allow operators to determine the thickness and availability of low TDS forming strata for use in new and innovative mining and reclamation plans designed to limit TDS release to local streams.

For the PRP portion of this study, we have sampled over 30 different locations in representative SW Virginia strata where we can clearly sample a relatively intact section of weathered surficial soils, underlying oxidized and partially weathered (brown) rock strata, continuing down into unweathered gray strata with depth. Samples are being analyzed for size consist, approximate mineralogy, acid-base accounting parameters, Fe-oxide content, abrasion pH/hydrolysis and total elemental analysis. We are also investigating net TDS release from ground/crushed spoil fractions equilibrated with varying soil:water and soil:H<sub>2</sub>O<sub>2</sub> ratios to develop TDS release indices. The amount and temporal pattern of TDS release for each material will then be related to the chemical and mineralogical analyses described above to determine which field vs. laboratory determined spoil properties are the best predictor(s) of TDS release potentials. In addition to this continuing PRP research effort, we have also been collecting long-term leachate

data from two different sizes of field leaching mesocosms (barrels and leaching tanks); that effort is also discussed in more detail below.

## ***Background***

This report is a continuation of our research over the past decade focusing on TDS release from surface coal mining overburden in central Appalachia (Orndorff et al., 2010; 2015). TDS release from surface coal mining overburden continues to be a major topic of public and regulatory concern (Merricks et al., 2007; Pond et al., 2008) giving rise to the need for further research in the area. Since 2011, we have collaborated with the Virginia Center for Coal and Energy Research and major regional coal producers (Alpha, Arch, Patriot, TECO and others) in a large multi-state research consortium, as the Appalachian Research Initiative for Environmental Science (ARIES; <http://www.energy.vt.edu/ARIES>). The overall ARIES program and scope of work continue to evolve, but our TDS prediction research program was expanded greatly (with ARIES funding) to include significant cooperation with the University of Kentucky (UK - Richard Warner and Chris Barton) and West Virginia University (WVU - Jeff Skousen and Louis McDonald). That expanded program involved a much larger sample set and more detailed analyses than we were capable of addressing with PRP funding. However, the ARIES monies allocated to Virginia Tech were budgeted to support column leaching testing on a much larger (e.g. 40 to 50 spoils) regional sample set, to develop scaling factors for field application of the column data, and to develop a regional spoil testing data base for future statistical analyses and modeling efforts (Daniels et al., 2013).

For the past four years, we have utilized the funds provided by PRP to continue our focused and detailed efforts on sampling combined weathered:unweathered soil:spoil sequences in SW Virginia along with analytical testing of those materials and improved TDS prediction methods specific to our strata. Meanwhile, the ARIES funded collaborations with UK and WVU have enabled us to “farm out” our Virginia spoil samples (> 20) for much more comprehensive lab testing procedures than would have been possible under our original PRP proposal and will allowed us to correlate results with a much wider range of strata from the adjoining region. Thus, the methods and results detailed below remain specific to the work that we are conducting with PRP funds and do not reflect the larger ARIES project per se.

In addition to the TDS prediction research described above, our current funding (2015-2016) is being used to take advantage of the leaching tanks already installed by a separate study funded through OSMRE and ARIES (Daniels et al., 2014). For this study, we are comparing our well-documented, lab-scale leaching columns (Orndorff et al., 2010; 2015) to larger-scale leaching mesocosms. Numerous mine spoil, coal refuse and fly ash materials have been leached in the past using our comparatively inexpensive column leaching techniques (e.g. Daniels et al. 2009; Daniels et al. 2013) but these techniques depend on crushing the hard rock spoil materials to a much smaller size (<1.25cm) than actually found in the field on active mines. Some studies,

such as Agouridis et al. (2012), have constructed large, field-scale lysimeters, but this method is extremely expensive, labor intensive, and requires a large, dedicated and protected physical space to install. For the current study, we constructed intermediate-sized leaching mesocosms from 200 L (55 gallon) barrels and 1.5 m<sup>3</sup> (396 gallon) square plastic tanks to determine the effects of two scales/spoil sizes on spoil leachate chemistry as compared with our leaching column results for the same materials. The results of the first two years of leaching comparisons were recently reported by Ross (2015) in his M.S. thesis. For the current project year (2015-2016), our PRP funds are being used to continue the long-term (>2 years) leachate monitoring of these mesocosms.

### ***2011 to 2015 Field Weathering Indicators Study Objectives***

- 1.** Measure the net TDS elution potential of a range of materials originating from the Pottsville Group in SW Virginia and analyze the difference between (a) fresh relatively unweathered materials at depth; and (b) well-weathered surficial materials.
- 2.** Determine which indicator has a stronger correlation with TDS elution potential in select mine spoils: (a) Previous long-term exposure to the earth's surface, leading to reduction in soluble salts from the long-term leaching effects of percolating water; or (b) variations in the elemental composition of varying geologic strata.
- 3.** Investigate the nature of the boundary between high and low TDS strata in order to determine if: (a) An abrupt boundary exists at some confining layer, such as shale; or (b) the boundary is more diffuse, being more related to distance from the earth's surface; or (c) no discernible boundary exists; variations occur with variations in parent material.
- 4.** Determine if a relationship exists between TDS elution potentials and field description traits such as: HCl "fizz" reaction, H<sub>2</sub>O<sub>2</sub> reaction and/or Munsell color (e.g. gray vs. brown colors).

### ***Field Scale Mesocosm Study Objectives***

- 1.** Measure the long-term variation in spoil TDS at two different leaching scales more similar to field conditions and compare those results to lab column leaching data for the same spoil materials.
- 2.** Determine if a seasonal pattern for TDS release exists that is not seen in column studies and whether it is associated with precipitation frequency.
- 3.** Compare long term, large-scale, field leaching data to small-scale, laboratory column leaching data in an effort to develop better scaling factors.

## *Field Weathering Predictors Study*

### *Past Results*

Our annual reports for the past few years have previously addressed a number of the objectives above (Johnson et al. 2012; 2013; 2014) and detailed our results from various parts of this overall study. Those methods and results are only partially repeated in this report. Preliminary results from this research were presented at the June, 2013, American Society of Mining and Reclamation (ASMR) conference in Laramie, WY, and are available online at: <http://www.asmr.us/Meetings/2013/Wednesday%20S-12/12-1%20Johnson.mp4>.

Our most significant accomplishment this year was the completion of field sample collection. Over the life of this study, thirty-three complete weathering sequence locations were sampled, with a total of 200 individual samples collected for lab analyses. This includes an additional 40 samples from 9 additional sites collected during the past project year (2014-2015). Additionally, all proposed lab analyses are on track to be completed by the end of 2015.

### *Summary of Relevant Methods and Procedures*

Thirty-three vertical weathering sequences were sampled from eight surface coal mines throughout the central Appalachian coalfields. Strata were sampled down through the mining column from the soil surface through fractured, weathered rock into the unweathered lower rock strata. Sampling generally extended at least 15-30 m below the surface at each location. Each distinct layer was collected (for a total of 200 individual samples) and mechanically crushed to < 2 mm. Deionized water was then added to each sample to form a saturated paste, allowed to sit for one hour, stirred, allowed to sit again for thirty minutes, and then extracted using vacuum filtration.

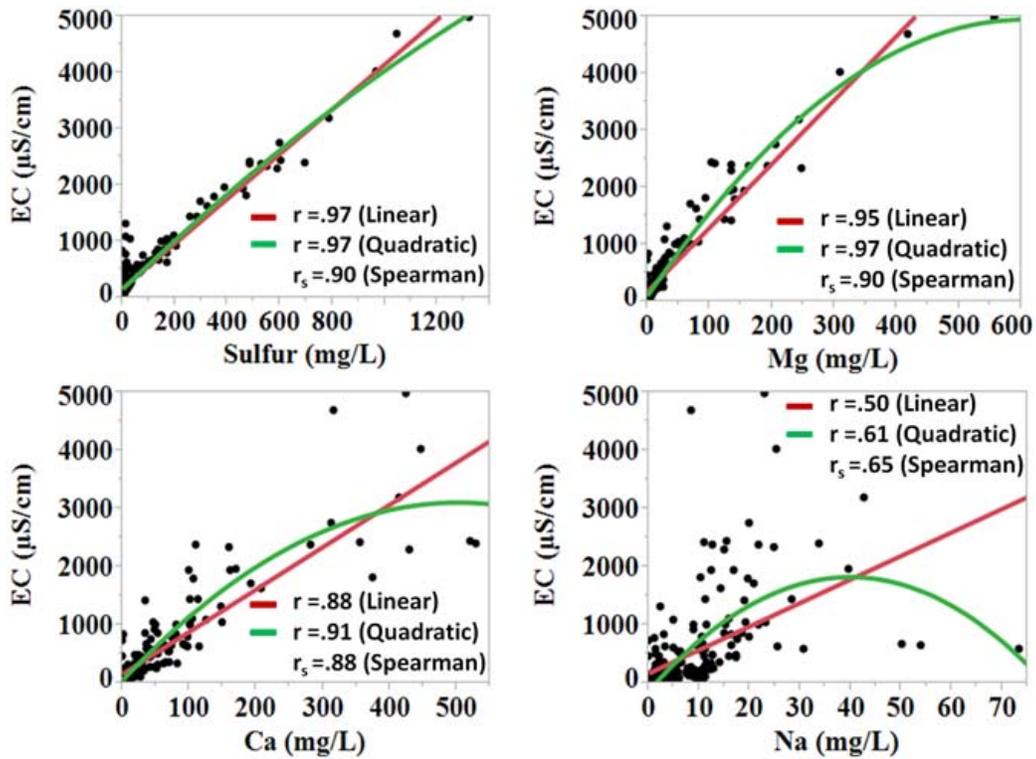
Our major analytical effort this project year was the analysis of the saturated paste extract from these 200 intact soil and directly underlying rock spoil samples. The extract was analyzed for electrical conductivity (EC), total Ag, Al, As, Ba, Ca, Cd, Co, Cr, Cu, K, Fe, Mg, Mn, Mo, Na, Ni, P, Pb, S, Se, Si, Sn, Sr, Ti, U, V, and Zn by ICP-MS, total S by ICP-AES and Cl with a chlorimeter. All solution S was assumed to be in the oxidized form as  $\text{SO}_4^-$  (sulfate). Electrical conductance (EC) was used as a proxy for TDS and samples were grouped as relatively low ( $<300 \mu\text{S cm}^{-1}$ ), medium ( $300\text{-}1000 \mu\text{S cm}^{-1}$ ), or high ( $>1000 \mu\text{S cm}^{-1}$ ) in TDS elution potential in order to compare geochemistry at different salinity levels.

Since several of the assumptions for normal theory correlation analysis were violated (such as unequal variances and the presence of several strong outliers), nonparametric tests were the preferred metrics for statistical comparisons. That being said, many of the parametric and nonparametric tests yielded similar results. Simple linear and quadratic regressions of elemental concentrations versus EC were compared for each element. Spearman's nonparametric rank

correlation coefficient ( $r_s$ ) or “Spearman’s  $\rho$ ” was also used for comparison. A separate forward step-wise procedure was used to determine the most significant predictors of EC from the elements analyzed using SAS. Significant differences between elemental group means were determined on a mass basis using nonparametric comparisons for all pairs using the Steel-Dwass method.

### Results This Year (2014-2015)

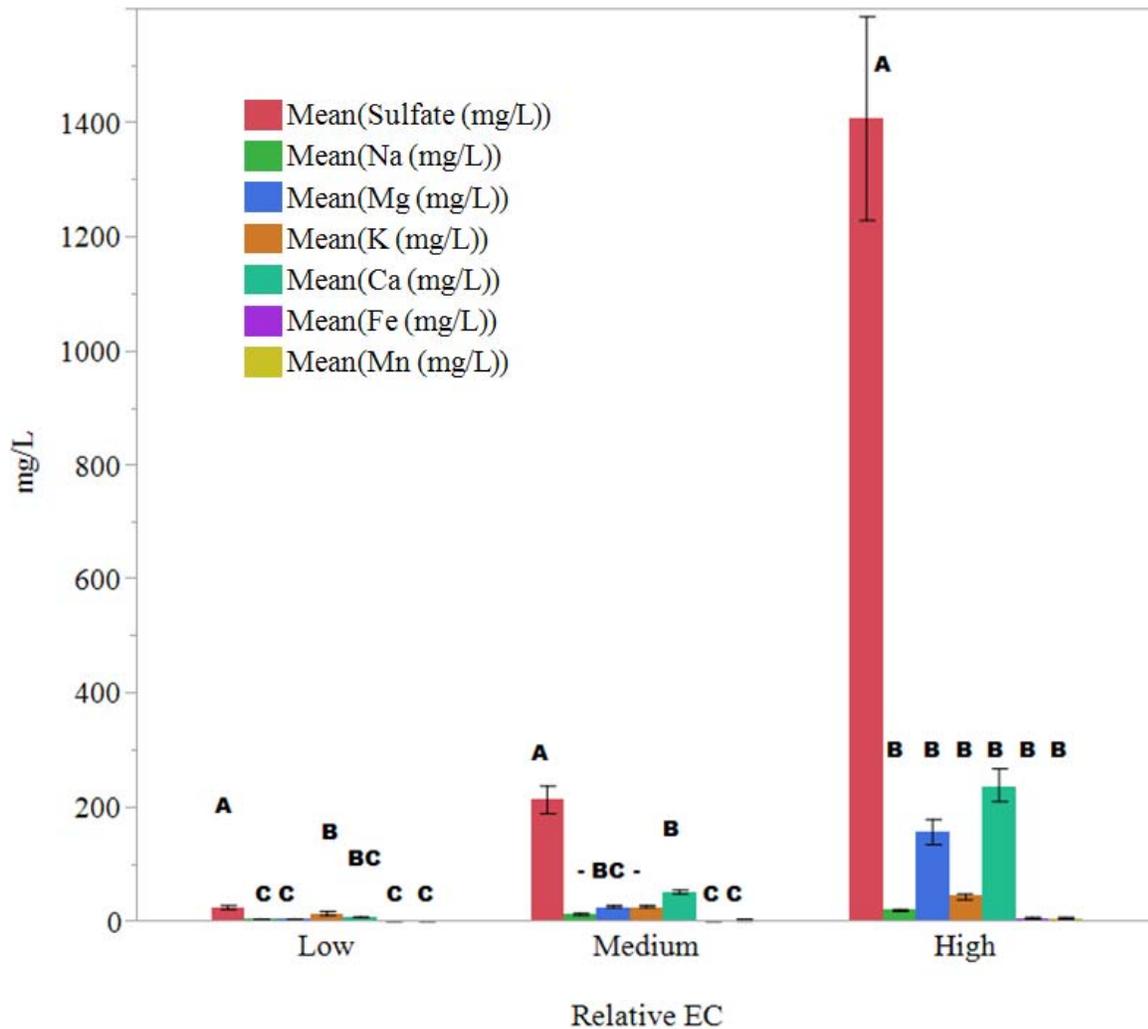
Of the ions analyzed, S, presumably as sulfate, and to a lesser extent Ca, Mg, and Na dominated the saturated paste geochemistry. The ionic concentrations of all four all significantly influenced EC (all p-values <0.001). Increases in S and Mg had the strongest relationship with increased EC; both with  $r_s$  values of 0.90 (See Figure 1). Increases in Ca and Na also had a strong



**Figure 1.** Ionic concentrations of S, Mg, Ca, and Na in saturated paste water extracts of all 200 samples. Graphs of each element versus EC are shown above with simple linear regression (red lines), quadratic regression (green lines), and Spearman's nonparametric rank correlation (no line associated) for comparison.

relationship with increases in EC, with  $r_s$  values of 0.88 and 0.65, respectively. A forward step-wise procedure found S, Mg, and Ca to all be most the significant predictors of EC out of the 29 elements analyzed for by ICP-MS (multiple regression  $R^2=0.98$ ; all p-values  $<0.001$ ). While this data suggests S, Mg, Ca, and Na are all important components of EC, it does not account for the complete mass of the ions present in the extracts.

Nonparametric comparisons of the group means on a mass basis also revealed interesting results. Figure 2 shows comparisons of ranked mean ionic masses across relatively low, medium, and



**Figure 2.** Mean ionic concentrations of saturated paste water extracts for several of the most important ions analyzed. Letter groups above the column groups indicate significant differences between average mean concentrations ( $p<0.05$ ). Samples are grouped as relatively low ( $<300 \mu\text{S cm}^{-1}$ ), medium ( $300\text{-}1000 \mu\text{S cm}^{-1}$ ), or high ( $>1000 \mu\text{S cm}^{-1}$ ) EC ( $n=200$  total samples).

high salinity levels, which were derived using the Steel-Dwass method. The sulfate ion had a significantly higher mass in the saturated paste extracts at low, medium, and high levels, as well as across all samples. This effect is especially apparent at relatively high EC levels. Generally, calcium, followed by magnesium, had the next highest average ionic masses. Iron and Manganese (and the remaining ions tested not shown in Figure 2) generally had little impact on the overall ionic mass. The sulfate ion had a significantly higher mass in the saturated paste extracts at low, medium, and high levels, and across all samples. Table 1 shows the mean, standard deviation, and range of the ionic masses from the extracts across all 200 samples.

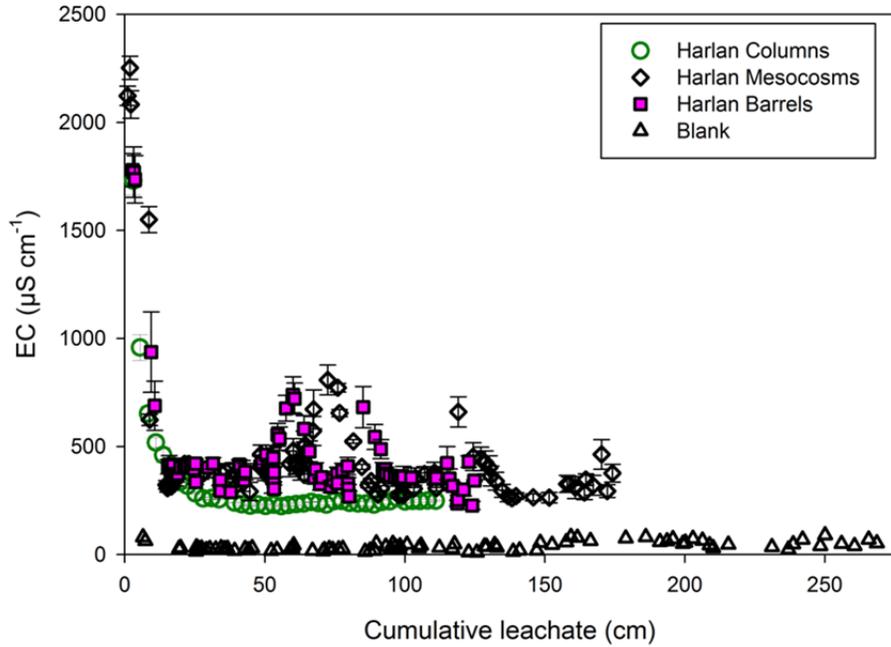
**Table 1.** Mean ionic concentrations for deionized water saturated paste extracts.

<b>Ion</b>	<b>N</b>	<b>Mean</b>	<b>Level</b>	<b>Std Dev</b>	<b>Minimum</b>	<b>Maximum</b>
Sulfate (mg/L)	200	260.0	A	577.5	0.0	3962.6
Na (mg/L)	200	8.6	B	9.7	0.0	73.3
Mg (mg/L)	200	30.4	B	66.8	0.0	557.8
K (mg/L)	200	20.2	B	38.5	0.0	319.5
Ca (mg/L)	200	49.9	B	95.6	0.0	530.0
Fe (mg/L)	200	0.9	B	5.5	0.0	55.6
Mn (mg/L)	200	1.5	B	4.0	0.0	41.5

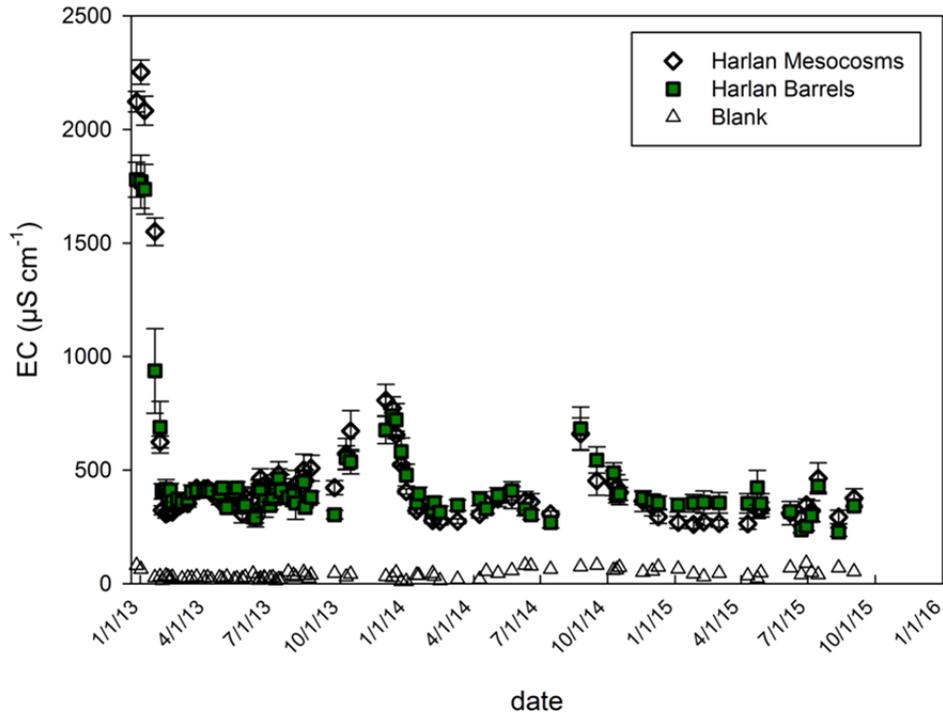
These saturated paste extract data reinforce our column study results (Orndorff et al. 2010; 2015) which indicate that TDS release by these materials is dominated by sulfate and calcium on a mass basis, but that a number of other cations like magnesium and potassium contribute to and differentiate among certain spoil's TDS signatures. Iron and manganese are present only in very low levels, limited by the moderate to relatively high pH of most of the extracts; with manganese maintaining slightly higher solubility, as would be expected. The relatively high ratio of calcium to magnesium in these extracts is also interesting from a scientific perspective. In weathered soils, extractable magnesium is generally present at less than 20% of extractable calcium due to preferential biocycling of calcium by the plant community. In other portions of our related research, we are attempting to determine the source of this magnesium and we presume it must be associated with secondary complex carbonate rock cements.

### ***Scaling Factors for Leachate Prediction Study***

For this portion of the study, several materials and leaching techniques were compared. For detailed methods on the installation of this experiment see Daniels et al. (2014). These trials are also described in detail by Ross (2015). Unweathered sandstone spoil materials from the late-Pennsylvanian age Harlan Formation were simultaneously leached with simulated acidic rain in lab columns and by natural rainfall outside in mesocosm tanks and barrels. Figures 3 and 4



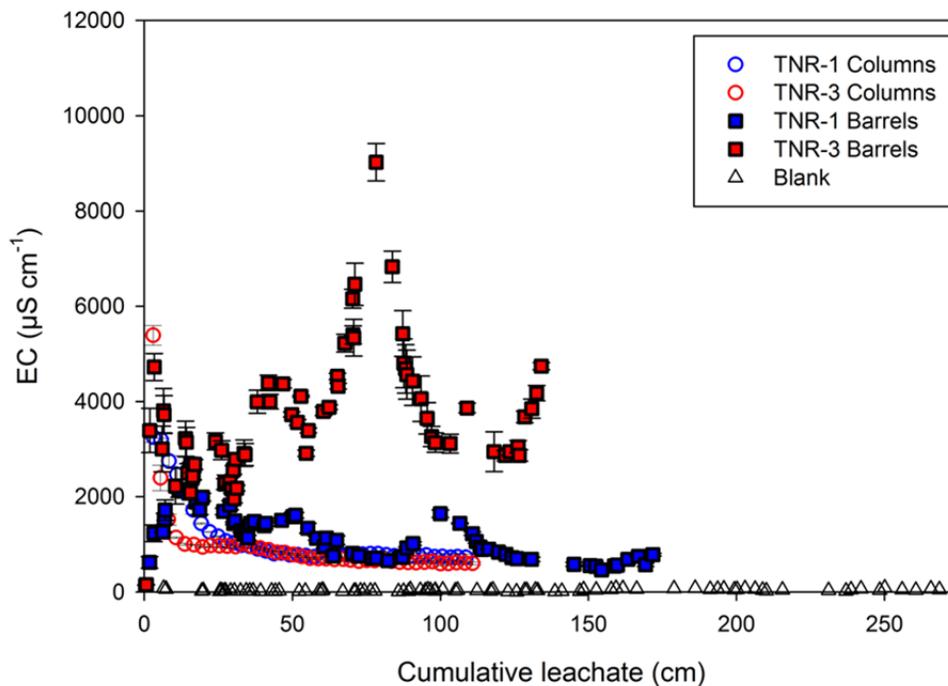
**Figure 3.** Cumulative leachate volume versus leachate EC for field-scale barrels and leaching tanks compared to lab-scale columns for a sandstone spoil originating from the Harlan Formation in southwest Virginia.



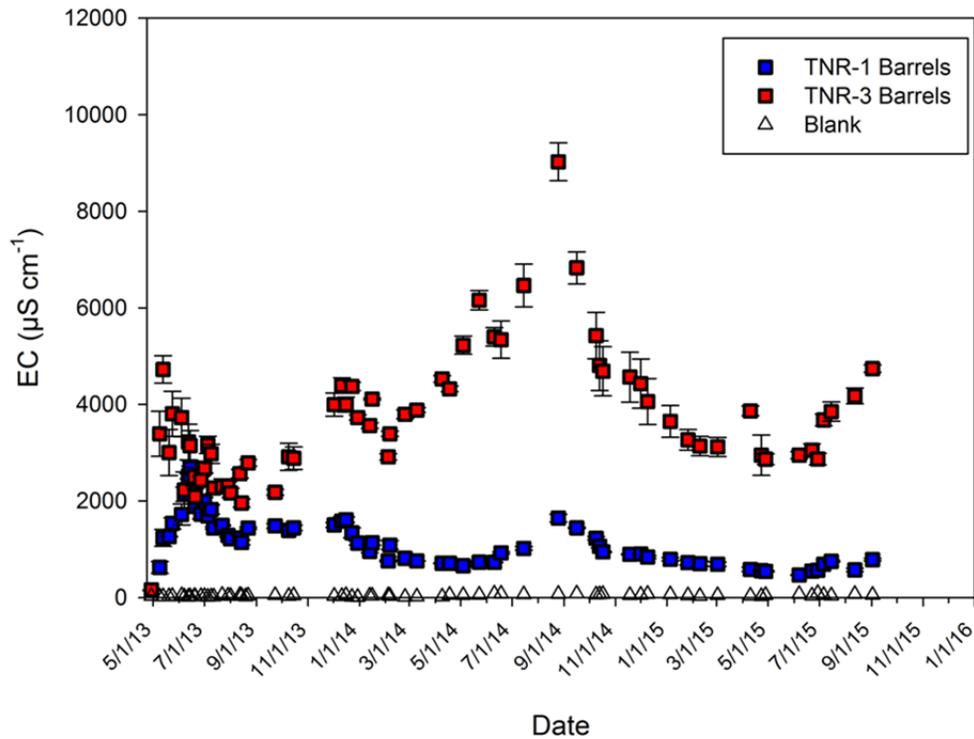
**Figure 4.** Leachate EC by sample collection date for field-scale barrels and mesocosms.

show the average leachate EC for the columns, barrels, tanks and an empty barrel (blank) by cumulative leachate produced and by date, respectively. These figures show that rainfall patterns do produce a temporal effect on the release of TDS that is not observed in the columns. Specifically, EC levels rise somewhat in the fall of each year following the summer dry period. We presume that this is due to accumulation of sulfate salts and other soluble components during the dry period that are then flushed out when sufficiently heavy rains finally occur later in the year. The barrels and tanks also showed a higher initial EC peak, but a similar overall TDS release pattern. So, while summer dry periods do appear to produce somewhat higher fall peak EC from the larger-scale mesocosms, and their peak values do appear to be higher than those produced by their matching columns, the overall pattern and levels of TDS release are fairly similar.

Two coal processing refuse materials are also being leached in sets of columns and barrels and showed comparable results (see Figures 5 and 6). The columns and one of the refuse materials (TNR-1) follow the typical pattern of TDS release we have reported for spoils, with a higher initial peak that declines rapidly with successive leaching events. The other refuse material (TNR-#), however, seems to be producing different, noticeably higher leachates from the barrels compared to the columns. Our 2015 data for the refuse materials also show a recurring spike in



**Figure 5.** Cumulative leachate volume versus leachate EC for two coal refuse materials from field-scale barrels compared to lab-scale columns for two different coal refuse materials.



**Figure 6** - Leachate EC by sample collection date for field-scale barrels and leaching tanks.

leachate EC during the late summer months, similar to the Harlan sandstone spoil. More detail on these results is provided by Ross (2015). Overall, the differences in TDS components observed between the leaching columns and the field mesocosm scales is much greater for the refuse samples than for the Harlan Formation sandstone spoil as described earlier.

### ***Future Plans and Deliverables***

A wide array of additional publications is expected, including additional conference presentations and journal articles along with Daniel Johnson's underlying PhD dissertation. As cited above, L. Clay Ross also published an M.S. thesis this year summarizing results from the column vs. leaching mesocosm studies. Long-term monitoring of the field scale leaching tanks will continue through the 2015-2016 project year in order to gain valuable long-term leaching relationships for both the sandstone spoil and two coal refuse materials.

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