Powell River Project 2019-2020 Annual Research Report

Assessing Flow-driven Effects on Local and Downstream Water Quality in Central Appalachian Headwater Streams Influenced by Surface Coal Mining

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Introduction

Surface coal mining is a common land-use alteration in central Appalachia, affecting more than 3.5% of total land area (Pericak et al. 2018). This form of resource extraction has been implemented in the region for more than a century (Abramson and Haskell 2006) and involves removal of vegetation and bedrock to expose buried coal seams. Fractured waste rock produced during this process undergoes accelerated weathering, thereby releasing increased amounts of major ions (e.g., SO_4^{2-}, HCO_3^-, Ca^{2+}, Mg^{2+}) and trace elements (e.g., Se) to headwater streams (Hartman et al. 2005; Pond et al. 2008; Timpano et al. 2015). Alterations to water chemistry are well-documented (Griffith et al. 2012), along with associated impacts to benthic macroinvertebrates, including the loss of sensitive species (Pond 2010) and communities shifted to more-tolerant taxa (Pond et al. 2008; Timpano et al. 2015, 2018). In addition, surface mining activities can alter the hydrology of headwater streams. For example, headwater streams can be buried under hundreds of meters of waste rock, infiltration can be reduced by soil compaction, and peak flows during storm events can increase (Griffith et al. 2012). Despite the well-recognized impacts of mining on headwater streams, less is known regarding the long-term persistence of these impacts both in headwater streams and in their downstream waters they support.

A component of our previous work assessed long-term trends in dissolved major ions (i.e., salinity) in mining-influenced headwater streams using the reliable salinity surrogate, specific conductance (SC), and found limited declines with time since mining (Cianciolo et al 2020a). However, dissolved ion concentrations naturally vary as a result of streamflow variation, often exhibiting either enrichment or dilution with increased flow (Griffith et al. 2012). Consequently, long-term trend analysis to assess recovery of water chemistry is complicated by this additional driver of water chemistry, requiring statistical methods to indirectly account for it with seasonal-based approaches (e.g., seasonal Kendall analysis; Hirsch at al. 1982). Further, streamwater chemistry sampling is often conducted during baseflow conditions to avoid effects of variable flow associated with storm events (e.g., Timpano et al. 2015, 2018), but this approach limits inferences of water chemistry solely to such conditions. Coincident monitoring of both water chemistry and flow would enable a more direct assessment of long-term trends and potential recovery in mining-influenced headwater streams.

Altered water chemistry in mining-influenced headwater streams may have important consequences for downstream waters. Headwater streams constitute approximately 70% of the total stream network in most landscapes (Leopold et al. 1964) and thus have substantial influence on downstream water quality (Gomi et al. 2002). In the coalfield of Kentucky, Johnson et al. (2019) documented that mean headwater stream (< 15 km^2 watershed area) values for dissolved major ion concentrations can be used to accurately assess concentrations in much larger watershed areas (75–400 km^2). In central Appalachia, headwater stream chemistry is greatly influenced by surface coal mining, but there has been limited research conducted to understand changes in fluxes (or loads) of water-chemistry constituents (e.g., major ions, trace elements, dissolved organic carbon) to downstream waters. Monitoring both water chemistry and streamflow would assess downstream loads of water-chemistry constituents, explore how such loads vary with season and time since mining (Sams and Beer 2000; Cianciolo 2019), and inform monitoring approaches relevant to the total maximum daily load (TMDL) framework (CWA §303(d)(1)(C)).

Salinization resulting from surface coal mining alters community composition of benthic macroinvertebrates (Timpano et al 2015, 2018) and bacteria (Vander Vorste et al. 2019), with likely but unknown consequences for carbon cycling processes and downstream export. Headwater streams play an integral role in landscape carbon processing by capturing, transforming, and transporting carbon (Battin et al. 2009), and in doing so, support complex food webs both locally and in downstream waters. Concentrations and export of DOC in headwater streams influenced by surface mining have not been well-studied, highlighting an additional knowledge gap needed to understand both local and downstream impacts.

Our interdisciplinary research group has continued to be well-positioned to assess local and downstream water quality consequences of surface mining as part of our continued monitoring of 24 central Appalachian headwater streams since 2011. Note that one of the 24 study streams was subjected to extensive recent mining and has been removed from the study. This study is unique in its length of time as well as its breadth of data collection. Specifically, efforts have included 30-minute measurements of SC and biannual sampling of benthic macroinvertebrates and water chemistry. We have also worked in subsets of these 24 study streams to advance scientific understanding of selenium bioaccumulation (Cianciolo et al. 2020b; Whitmore et al. 2018), seasonal changes and improved quantification of benthic macroinvertebrate communities (Boehme et al. 2016; Pence 2019), and stream geomorphology (Drover 2018). With support from the Powell River Project, we have continued this unprecedented study and have addressed new questions about flow-driven variation in water chemistry and the downstream flux of chemical constituents (ions, trace elements, and DOC) that will assist land managers and regulatory agencies in protection of headwater streams and downstream networks.

Objectives

1. Expand temporal scope for sampling of continuous 30-minute SC and seasonal benthic macroinvertebrates and synoptic water chemistry in 23 central Appalachian headwater streams initiated in 2011.
2. Initiate stream water level monitoring and assess flow-driven variation in water chemistry to inform analyses of long-term trends in dissolved major ions and SC.
3. Quantify fluxes of dissolved major ions and trace elements to downstream waters.
4. Evaluate salinity and flow effects on DOC concentrations and DOC export to downstream waters.

Methods

Data Collection

Streamflow

During fall 2019, HOBO U20 water level dataloggers (23 matched by VWRRC, 8 purchased with requested funds) were installed across our 23 study streams to measure stream stage. Dataloggers were placed inside screened wells within each stream to record stage every 30 minutes. Additional dataloggers were installed in streamside areas to collect and account for local barometric pressure variation. We intended to measure flow at a subset of streams and under various conditions using salt tracer additions (Gooseff et al. 2003, Moore, 2005) and response in SC levels (instrumentation described in *Water Chemistry* section below). Rating curves were then to be developed to relate measured flow and stream stage, yielding continuous (30-min) flow estimates. However, sampling was limited to only one round of flow measurements due to the onset of COVID-19 travel restrictions in March 2020.

We conducted salt-tracer-addition experiments to measure flow at six of our stream sites during the summer of 2020. Use of salt addition to study streams was employed to estimate flow by increasing SC, thereby creating a conductivity "salt wave" that moves downstream via longitudinal dispersion. Specific conductance was recorded at 1-second intervals using an automatic datalogger (HOBO Freshwater Conductivity Data Logger, model U24-001, Onset Computer Corp., Bourne, Massachusetts) to measure passage of the salt tracer. Using the known volume and concentration of the salt solution, and stream background SC, stream discharge was estimated from the following equation:

$$Q = \frac{V}{k\Delta t \ \sum_{\mathrm{i=0}}^{\mathrm{n}}[\mathrm{EC(t)} - EC_{bg}]} \qquad (1)$$

where Q is stream discharge (m^3/s), V is the known volume of the injection slug (m^3), k is the calibration constant, EC(t) is the electrical conductivity at time t, and EC_{bg} is background conductivity of the stream (Moore, 2005). Additional salt tracer experiments are planned for the same six streams in the near future so that a stage-flow relationship (i.e., rating curve) can be developed for each stream, yielding sub-daily flow estimates from 30-minute stage data.

Water Chemistry

We continued our long-term monitoring of selected water-quality parameters in the 23 study streams initiated in 2011. In situ SC was recorded every 30 minutes between fall 2019 and summer 2020 using automated dataloggers (HOBO Freshwater Conductivity Data Logger, model U24-001, Onset Computer Corp., Bourne, Massachusetts) that are installed within each stream. Grab samples of streamwater were collected in fall 2019 to assess the ionic composition of streamwater. Samples were not taken in spring 2020 due to COVID-19 restrictions that prevented travel for field work. Vertically mixed water was collected and immediately filtered through a 0.45-µm pore polyvinylidene fluoride filter into pre-labeled sterile polyethylene sample bags. The cation sample was preserved to pH < 2 by adding approximately 0.5% (v/v) of a solution of 1+1 concentrated ultrapure nitric acid and deionized water (USEPA 1996). Samples were stored at 4° C until analysis. Samples were analyzed for total dissolved solids (TDS) by evaporating streamwater to constant weight in a drying oven at 180° C (USEPA 1971). Total Alkalinity was measured by titration of stream water samples with a prepared standard acid (0.02N HCl) using a potentiometric auto-titrator (TitraLab 865, Radiometer Analytical, Lyon, France) (APHA 2005). Calculations of HCO_3^- were made from Total Alkalinity and pH measurements (APHA 2005). Samples were analyzed for major cations/trace elements and SO_4^{2-} by ICP-MS (Thermo iCAP-RQ) (UESPA 1996) and ion chromatograph (Dionex ICS 3000), respectively.

Water chemistry and stage data were used to assess flow controls (indicated by water level variation) on water chemistry variation and also will be used to estimate downstream fluxes of chemical constituents. For example, by relating continuous SC and stage data, we were able to evaluate the degree to which high water level (i.e., high flow) dilutes or enriches the SC signal, thereby allowing a more direct assessment of mining effects on long-term SC trends. Coupling concentrations of water-chemistry constituents with coincident flow estimates will also yield mass fluxes (or loads) to downstream waters and assess how these loads vary across site and flow conditions. This component of our work is also ongoing because of delays in our timetable caused by COVID-19 restrictions.

DOC

As part of the proposed study, we initiated new work to assess DOC concentrations and export in our study streams. Grab samples for analysis of DOC concentrations were collected in Fall 2019 and Spring 2020. However, DOC sampling was limited to these two dates because COVID-19 travel restrictions prevented quarterly DOC sampling as proposed. Vertically mixed streamwater was collected and immediately filtered through a pre-rinsed 0.45-µm pore Polyethersulfone (PES) filter into pre-labeled sterile 40 mL amber glass vials that were acid washed, ashed, and sealed with PTFE/silicone septa and open-holed autosampler cap. Vials were overfilled to prevent headspace contamination and stored at 4° C until analysis. A Shimadzu TOC-V_{cph} Total Organic Carbon Analyzer was used to quantify DOC in each sample. Streamflow estimates will be used to assess flow controls on DOC concentrations and to convert concentrations into mass fluxes of DOC, allowing comparisons of DOC export among sites and between seasons. This work is ongoing because of unexpected COVID-19 restrictions to our sampling regimes for DOC and flow.

Benthic Macroinvertebrates

As has been done since 2011, benthic macroinvertebrates were sampled in fall 2019. However, restrictions due to COVID-19 prevented spring 2020 sampling. Fall 2019 samples were taken in study streams using the semi-quantitative, single-habitat (riffle-run) method established by the Virginia Department of Environmental Quality (VDEQ 2008), which is adapted from U.S. EPA Rapid Bioassessment Protocols (RBP; Barbour et al. 1999) and is comparable to the method used by West Virginia Department of Environmental Protection (WVDEP 2015). Using a 0.3-m D-frame kicknet with 500-µm mesh, a single composite sample (approximately 2 m^2) composed of six approximately 1×0.3-m kicks was collected from separate riffles along a 100-m reach upstream of the SC datalogger. Samples were preserved in 95% ethanol and returned to the lab for sorting and identification.

Macroinvertebrate samples were sub-sampled randomly to obtain a 200 (±10%)-organism count following VDEQ biomonitoring protocols (VDEQ 2008). Specimens were identified to genus using standard keys (Merritt et al. 2008), except for individuals in family Chironomidae and subclass Oligochaeta, which were identified at those levels. Although not completed at this time because of COVID-19 restrictions, we plan to compare macroinvertebrate metrics among sites and between seasons to assess changes that may have occurred since 2011. We also intend to couple these metrics with measured DOC concentrations to provide insights into mining effects on carbon processes that may result from altered macroinvertebrate communities.

Results and Discussion

Streamflow and Water Chemistry

At each of our 23 stream sites, we were able to expand our continuous 30-minute SC and add water level monitoring from Fall 2019 through the summer of 2020 (Figure 1). We found inverse relationships between SC and water level (Figure 2) at all study streams, indicating dilution under high flow conditions. However, the degree of this flow-induced dilution was greater in salinized streams (Figure 2).

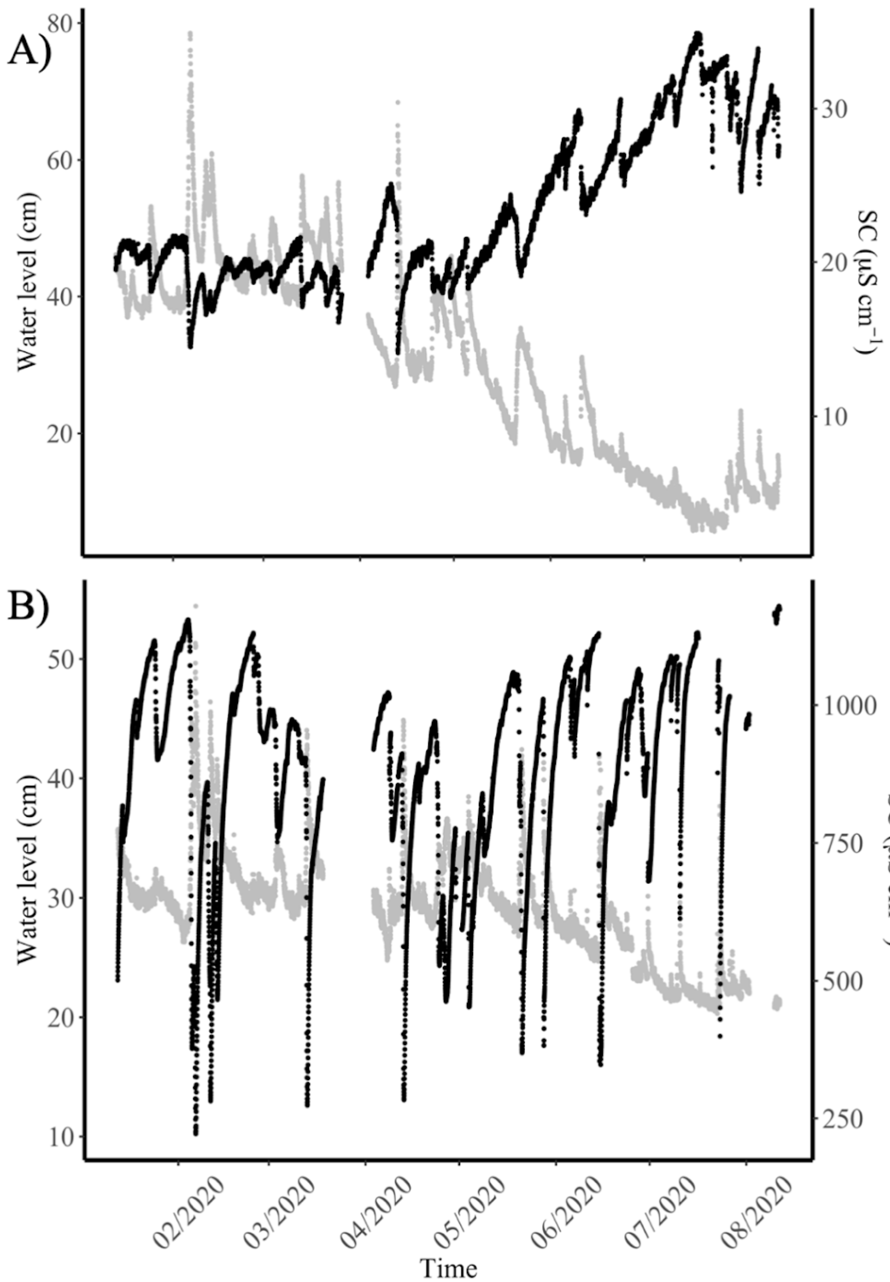

Figure 1: Examples of temporal trends in specific conductance (SC) (black) and water level (grey) at a reference stream (A) and a salinized stream (B).

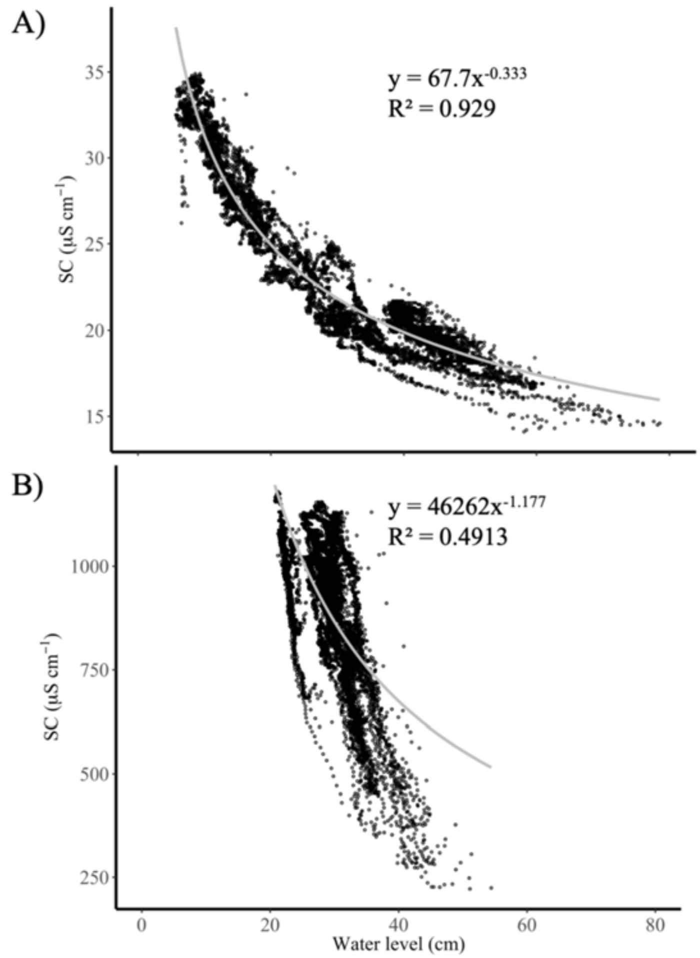

Figure 2: Specific conductance (SC) versus water level in a reference stream (A) and a salinized stream (B) from fall 2019 to summer 2020.

Completed salt tracer experiments at six study streams that spanned a gradient of SC and watershed area established baseline flow measurements for development of stage-flow rating curves. Salt injections resulted in a 25 – 75% increase in salinity from background to produce a "wave" large enough to derive an estimate of stream flow (Figure 3). Flow ranged from 0.7 l/s to 67 l/s across the sampled streams (Table 1). Flow conditions were considered to be baseflow during all salt-tracer experiments. To produce an accurate rating curve, future salt tracer experiments will be conducted across a range of flows. Once an accurate rating curve is developed for each of the six study streams, sub-daily flow estimates can be calculated, enabling load estimates for different water chemistry variables (major ions, trace elements, and DOC).

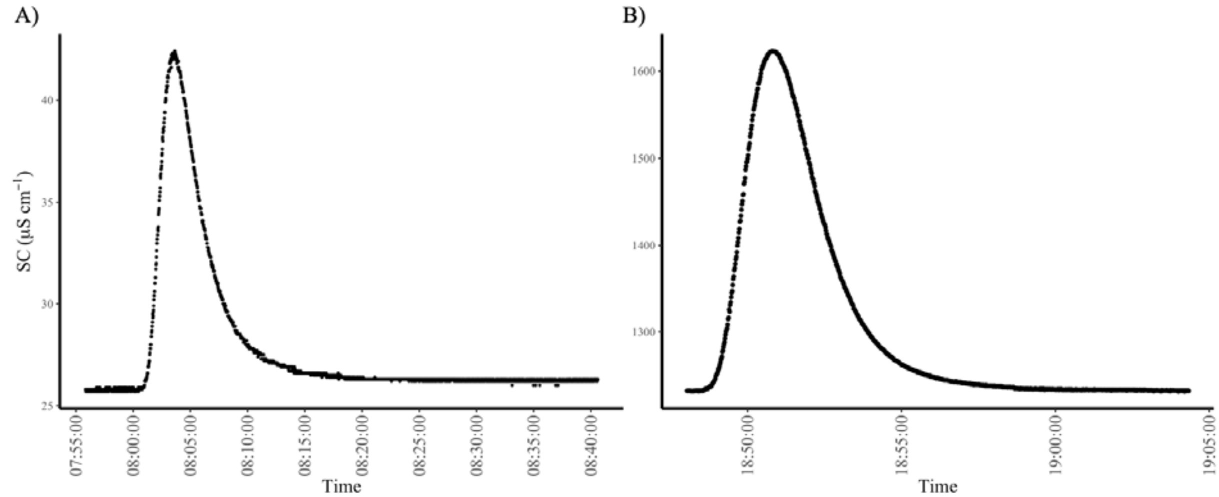

Figure 3: Recorded SC wave created from salt slug additions to a reference stream (A) and a salinized stream (B). The area under the curve is used to calculate stream flow at a given point in time and water level.

Table 1: Initial salt tracer results at six streams. Amount of salt (NaCl) used, mixing length, and time for tracer test to complete varied by watershed area and background SC concentration.

Site	Background SC	Watershed area (km^3)	% Watershed Mined	NaCl (g)	Slug Time (mm:ss)	Mixing Length (m)	Water level (cm)	Flow (l/s)
EAS	26	2.2	0	20	25:00	41	13.9	0.7
HCN	72	6.0	0	100	20:00	70	9.7	8
CRA	424	9.8	NA	200	22:50	85	11.7	67
SPC	506	6.9	2.2	250	45:00	100	19.7	12
MIL	655	2.7	55.3	300	22:00	40	17.7	9
LLW	1205	2.0	27.2	400	21:30	48	11.7	17

DOC

For our two sampling periods, mean DOC was slightly lower in reference streams compared with salinized streams (Figure 4). However, an independent two-sample t-test between reference and salinized streams for each sampling period indicated no significant differences in mean DOC values (Figure 4). Mean DOC in fall 2019 was 1.17 mg/l (n = 5) for reference streams and 1.37 mg/l (n = 17) for salinized streams. Mean DOC in spring 2020 was 0.94 mg/l (n = 5) for reference streams and 1.03 mg/l (n = 17) for salinized sites. Additionally, we found no significant differences in DOC values for reference and salinized streams between the two sampling periods. Last, there was no relationship between stream DOC and SC values when pooling all samples from fall 2019 and spring 2020 (Figure 5).

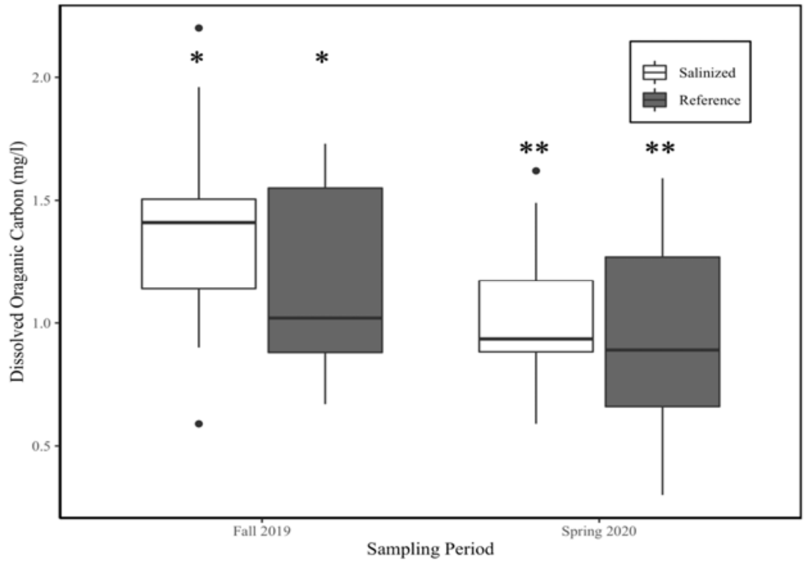

Figure 4: Mean dissolved organic carbon (DOC) at reference and salinized streams from fall 2019 and spring 2020 sampling. There were no significant differences in DOC values between stream types during the two sampling periods ($p > 0.05$) as indicated by matched asterisks for each sampling period.

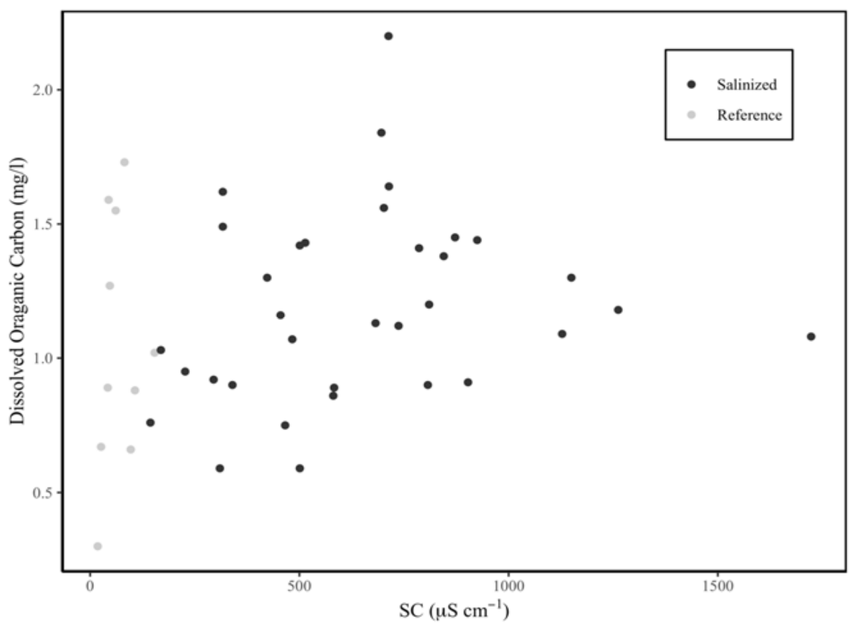

Figure 5: Relationship between specific conductance (SC) and dissolved organic carbon among salinized (n=34) and reference streams (n=10) for all samples taken in fall 2019 and spring 2020.

Conclusions

Although most of our research objectives were affected by unexpected COVID-19 travel and laboratory restrictions during our spring sampling season (March-May), we were able to initiate all of our planned methodologies and conduct preliminary data analyses produced by our sampling protocols. We were able to continue monitoring of SC and initiate stream stage monitoring, and also conducted reduced sampling of DOC and macroinvertebrates in all 23 study streams. Combining SC and stage data demonstrated general dilution of SC with higher stage (and thus higher flow) and will allow us to account for this flow control in future assessment of stream water chemistry recovery. We were only able to conduct one round of streamflow measurements and thus could not develop rating curves between flow and stage; however, we successfully used salt tracer techniques at baseflow at six of our study streams. In doing so, we tested and refined flow measurement protocols, setting the stage for continued measurements needed for development of rating curves. Once these rating curves are completed, we plan to use flow and water chemistry data (SC, DOC, major ions, and trace elements) for novel estimates of downstream export for the suite of water chemistry parameters we have been measuring along with stream stage. With this approach and preliminary data generated here through Powell River Project support, we are pursuing additional funding from OSMRE. Sampling for DOC was only conducted twice and indicates little differences among sites. These data and continued sampling will support a resubmission of a proposal to NSF to understand potential water chemistry effects to stream carbon cycling.

Acknowledgements

Thank you to Dr. Carl Zipper for his contributions to all aspects of this research.

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Cianciolo, T. R., McLaughlin, D. L., Zipper, C. E., Timpano, A. J., Soucek, D. J., & Schoenholtz, S. H., 2020a. Impacts to water quality and biota persist in mining-influenced Appalachian streams. *Science of the Total Environment*. https://doi.org/10.1016/j.scitotenv.2020.137216

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Supporting Data or Appendices

Scholarly Activities

Publications:

Cianciolo, T.R., D.L. McLaughlin, C.E. Zipper, A.J. Timpano, D.J. Soucek, S.H. Schoenholtz. 2020. Impacts to water quality and biota persist in mining-influenced Appalachian streams. *Science of the Total Environment*. https://doi.org/10.1016/j.scitotenv.2020.137216

Cianciolo, T.R., D.L. McLaughlin, C.E. Zipper, A.J. Timpano, D.J. Soucek,, K.M. Whitmore, S.H. Schoenholtz. 2020. Selenium Bioaccumulation across Trophic Levels and Along a Longitudinal Gradient in Headwater Streams. *Environmental Toxicology & Chemistry*. https://doi.org/10.1002/etc.4660

Drover D.R., S.H. Schoenholtz, D.J. Soucek, C.E. Zipper. 2020. Multiple stressors influence benthic macroinvertebrate communities in central Appalachian coalfield streams. Hydrobiologia 847: 191-205.

Drover D.R., C.E. Zipper, D.J. Soucek, S.H. Schoenholtz. 2019. Using density, dissimilarity, and taxonomic replacement to characterize mining-influenced benthic macroinvertebrate community alterations in central Appalachia. Ecological Indicators 106: 105535.

Clark, E.V., K.M. Whitmore, S.H. Schoenholtz, D.J. Soucek, C.E. Zipper. Bioaccumulation of Selected Trace Elements in Appalachian Mining-Influenced Streams. *Environmental Science and Pollution Research*. In review.

Pence, R.A., T.R. Cianciolo, D.L. McLaughlin, C.E. Zipper, A.J. Timpano, D.J. Soucek, D.R. Drover, S.H. Schoenholtz. Comparison of sampling mehods characterizing benthic macroinvertebrate communities and their response to water quality stressors. In prep.

Presentations:

Invited Seminar. T.R. Cianciolo. How Long in Time and How Far Downstream do Surface Coal Mines Impact Headwater Streams in West Virginia & Virginia. Forest Resources and Environmental Conservation department seminar, Blacksburg, VA, 02/14/2020.

Invited Lecture. T.R. Cianciolo. How Long in Time and How Far Downstream do Surface Coal Mines Impact Headwater Streams in West Virginia & Virginia. Watersheds and Water Quality Monitoring - undergraduate course, Blacksburg, VA, 09/12/2019.

D.J. Soucek, A. Dickinson, A.J. Timpano, S.H. Schoenholtz, C.E. Zipper. Disentangling the toxicity of major ions to sensitive freshwater insects. Presentation at 2019 ESA Annual Meeting, Lousiville, KY (August 11-16).

Published Abstracts:
June 2020. Society for Freshwater Science. Does insect emergence decouple from macroinvertebrate biomass in response to mining-induced salinization in Appalachian headwaters? Aryanna James.

Successful grant proposals:

July 1, 2019 - June 30, 2020. Interdisciplinary Seed Grant RFP, Integrative Science and Solutions for Freshwater Systems, Fralin Life Science Institute in support of the Global System Sciences Area at Virginia Tech ($8,400). S.A. Entrekin, E.R. Hotchkiss, D.L. McLaughlin, C.E. Zipper, A.J. Timpano, and T.R. Cianciolo. Using benthic and emergent insect biomass as a metric of stream impairment across a salinity gradient in central Appalachian headwater streams. Grant # 120254

Pending grant proposals:

May 2020. Office of Surface Mining Reclamation and Enforcement ($200,000). Surface Coal Mining Influences on Water Chemistry in Headwater Streams of Appalachia: Temporal Patterns and Contaminant Loadings. A.J. Timpano, T.R. Cianciolo, D.L. McLaughlin, C.E. Zipper, and S.H. Schoenholtz.

September 2020. VT Global Change Center ($24,278) Salty Carbon: Testing the Consequences of Freshwater Salinization on Stream Food Web Dynamics and Ecosystem Metabolism. E.R. Hotchkiss, S.A. Entrekin, S.H. Schoenholtz, and D.L. McLaughlin.

Proposals submitted but not funded:
December 2019. National Science Foundation ($949,706). Salty Carbon: Linking Salinization Effects on Biological Condition to Carbon Processing and Biomass Production in Headwater Streams. S.A. Entrekin, S.H. Schoenholtz, D.L. McLaughlin, C.E. Zipper, E.R. Hotchkiss, and A.J. Timpano.