Assessing Long-term Trends in Specific Conductance, Dissolved Ion Matrix, and Benthic Macroinvertebrate Communities in Central Appalachian Coalfield Streams

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Introduction

Surface-mining activities are a major driver of land-use change in the central Appalachian coalfield region (Sayler 2008). Surface mining activities, including mountaintop removal-valley fill (MTR-VF,) expose buried coal seams to the surface by removing overlaying layers of bedrock using explosives and earth moving machines (USEPA 2011). Consequently, waste rock, or overburden, is deposited into the adjacent valleys of headwater streams, effectively burying stream channels under tens to hundreds of meters of waste rock and affecting downstream water chemistry (Bernhardt and Palmer 2011). Deposited overburden is exposed to air and water, accelerating natural weathering processes and increasing loading of dissolved ions to headwater streams. In central Appalachia, the acids produced by pyrite oxidation are often buffered by neutralizers released from dissolution of carbonates and other associated minerals, resulting in drainage waters that are often alkaline (Clark et al. 2018). The resultant alkaline drainage that flows from overburden deposited from surface mining activities is often enriched in major ions including SO_4^{2-}, HCO_3^-, Ca^{2+}, and Mg^{2+} and has elevated pH, total dissolved solids (TDS), and specific conductance (SC) (Palmer 2010, Pond et al. 2008, Timpano et al. 2015).
Total Dissolved Solids, a measure of nonvolatile dissolved solids in the water column, is elevated in surface mining-influenced streams and can negatively impact aquatic organisms. Specific conductance, a measure of electrical conductivity corrected for temperature, is a reliable surrogate for TDS in coalfield streams (Timpano et al. 2010) and is easily measured *in situ*. Streams that receive discharge from MTR-VF areas can be impacted by elevated SC long after termination of mining and restoration activities (Evans et al. 2014). However, recovery time for water chemistry and its attendant effects on biological conditions is not known.

Numerous studies have documented that elevated salinity negatively impacts benthic macroinvertebrate communities in streams draining MTR-VF (Boehme et al. 2016; Merricks et al. 2007; Pond et al. 2008, Timpano et al. 2015). Streams with elevated salinity have reduced taxon richness and community structures shifted to more tolerant taxa (Pond et al. 2008, Timpano et al. 2015). Sensitive taxa including *Ephemeroptera* (mayflies) can be absent in streams with high salinity (Merricks et al. 2007). Moreover, scraper and shredder functional feeding groups have been documented to have lower richness and abundance in streams with elevated SC compared to reference sites (Hartman et al. 2005).

Central Appalachian states commonly use benthic macroinvertebrate community structure to assess water quality under both the Clean Water Act and Surface Mining Control and

Reclamation Act. The EPA's Rapid Bioassessment Protocols (RBPs) are routinely implemented to assess physical habitat, water quality, and biological conditions relative to reference measures (Barbour et al. 1999) and rely heavily on a suite of metrics that characterize benthic macroinvertebrate communities. Benthic macroinvertebrates are used in such RBPs because they are easy to sample in the field, integrate time-varying water chemistry conditions, and vary in sensitivity to different concentrations of TDS in the water (Barbour et al. 1999). However, improved quantification of associations between measured water chemistry and responses in benthic macroinvertebrate community structure is needed to inform establishment of regulatory standards in headwater streams and improved water resource management (Timpano et al. 2015, Boehme et al. 2016). Moreover, as weathering of mine spoils in closed and reclaimed coal mines progresses with time, it is likely that water chemistry may change in response (Clark et al. 2018) as could its impact on macroinvertebrate communities (i.e. temporal shifts in biota sensitivity), highlighting the need for long-term study of SC and attendant biota response in central Appalachian headwater streams.

Research Goals

The overall objective of this project is to assess long-term changes in SC, dissolved ion matrix, and benthic macroinvertebrate community structure in central Appalachian coalfield headwater streams. To accomplish this goal, the following specific objectives are being addressed:

<u>Field Work</u>

1. Extend 30 minute-continuous sampling of SC through March 2019 in 24 headwater streams in the coalfield region of southwestern Virginia and southern West Virginia.
2. Extend seasonal sampling of TDS and dissolved ion matrix in these streams through fall 2018.
3. Extend sampling of benthic macroinvertebrate community structure in these streams during fall 2017 and spring 2018 sampling seasons.

<u>Data Analysis</u>

1. Evaluate long-term temporal change of SC, TDS, dissolved ion matrix, and benthic macroinvertebrate community structure.
2. Analyze associations between benthic macroinvertebrate metrics and SC to determine if associations change over the duration of study.

Study Sites

Twenty-four headwater streams in the coalfield region of southwestern VA and southern WV (Figure 1) have been identified that meet rigorous assessments of water chemistry and habitat quality (Table 1; Timpano 2011). These streams have been identified to isolate TDS as a stressor to aquatic life. Both reference and test streams have comparable riparian habitat conditions and absence of other possible stressors such as excessive sedimentation, channelization, extreme pH, and low dissolved oxygen within a 100m sample reach. Of our 24 study streams, 19 are test streams influenced by surface coal mining activities. The other five are relatively undisturbed, forested reference sites. All sites are included in the continuing long-term assessment of water chemistry and benthic macroinvertebrate community structure.

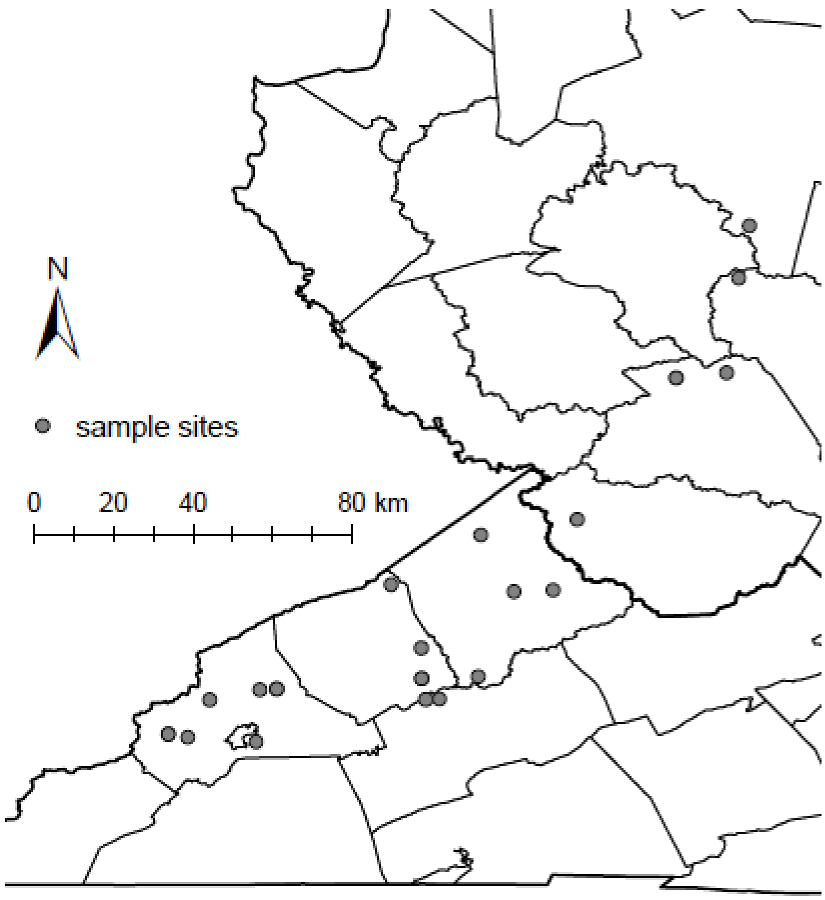

Figure 1: Map showing all 24 study streams across southern West Virginia and southwestern Virginia. Figure produced by Tommy Cianciolo using GPS coordinates of study locations.

Table 1. Abiotic criteria for selection of reference and test streams (Timpano 2011).

Parameter of Condition (units or range)	Selection Criterion[1]
Dissolved Oxygen (mg/L)	≥ 6.0
pH	≥ 6.0 and ≤ 9.0
Epifaunal Substrate Score (0-20)[2]	≥ 11
Channel Alteration Score (0-20)[2]	≥ 11
Sediment Deposition Score (0-20)[2]	≥ 11
Bank Disruptive Pressure Score (0-20)[2]	≥ 11
Riparian Vegetation Zone Width Score, per bank (0-10)[2]	≥ 6
Total RBP Habitat Score (0-200)[2]	≥ 140
Residential land use immediately upstream	None

[1] Parameters and numeric selection criteria (Burton and Gerritsen 2003).
[2] RBP Habitat, high gradient streams (Barbour et al.1999).

Data Collection

Water Chemistry:
In situ SC and temperature measurements are being collected every 30 minutes using automated dataloggers (HOBO Freshwater Conductivity Data Logger, model U24-001, Onset Computer Corp., Bourne, Massachusetts) installed within the 100m stream reach that comprises a study site. Seasonal (biannual) water chemistry monitoring includes standard *in situ* measures of water temperature, SC, and pH via a calibrated handheld multi-probe meter (YSI Professional Plus – YSI, Inc., Yellow Springs, Ohio, USA) and grab sampling.

Grab samples are taken for four different water chemistry analyses; trace metals, TDS, alkalinity, and ion matrix. Water is collected in a clean, plastic bucket below a riffle where stream water has been vertically mixed. Water is drawn into a sterile 60ml syringe and pushed through a 0.45µm pore filter into pre-labeled sterile Polyethylene water chemistry sample bags. 100ml of filtered water is collected for TDS and alkalinity. 50ml is collected for trace metals and ion matrix. Approximately 6 drops of 1+1 trace metal grade nitric acid is added to the trace metal sample to lower the pH below 2. Samples are stored in a cooler on ice and transported to the lab where they are kept in a cold room at 4^{o}C until analysis. (UESPA 1996).

Samples are then analyzed for TDS by evaporating known volumes of sample water in a drying oven at 180^{o}C. Lab duplicates are made for every 10th sample. Total Alkalinity is measured by titration of a field-filtered water sample with a prepared standard acid using a potentiometric auto-titrator (TitraLab 865, Radiometer Analytical, Lyon, France). HCO_3^- and CO_3^{2-} calculations are made from Total Alkalinity and pH measurements. Samples are analyzed for major cations (Ca^{2+}, Mg^{2+}, K^+, Na^+) and dissolved trace elements (Al, Cu, Fe, Mn, Se, Zn) using an ICP-MS. (Thermo iCAP-RQ). An ion chromatograph (Dionex ICS 3000) is used to measure concentrations of Cl^- and SO_4^{2-}.

Benthic Macroinvertebrates:
In fall 2017 and spring 2018, all 24 study streams were sampled using the semi-quantitative, single habitat (riffle-run) method established by the Virginia Department of Environmental Quality (VDEQ 2008). Approximately six, 1-meter riffles located throughout the 100m study reach in each stream were sampled using a 0.3m-wide D-frame kicknet with 500-µm mesh size to achieve a sample area of 2m^2. Riffles were selected to be representative of reach hydrology and have sufficient water velocity to wash dislodged benthic macroinvertebrates into the kicknet. A single composite sample was made from the six riffle kicks in each stream and preserved in 95% ethanol. Samples were returned to the lab for sorting and identification.

Composite samples were washed and cleaned in the lab to remove sediment, leaf material, and detritus using a wash bucket. The cleaned sample was evenly spread on a gridded tray for sub-sampling. The semi-quantitative composite samples were sub-sampled following Rapid Bioassessment Protocol (Barbour et al. 1999), and Virginia Department of Environmental Quality standard operating procedures (VDEQ 2008). The random sub-sample contains a specimen-count of 200 (±20%) individuals and was stored in labeled vials until identification. Sub-sampled individuals are being identified to the genus level if possible.

Data Analysis

Temporal trends in Specific Conductance:

Temporal trends in SC will be analyzed using Theil-Sen slopes and seasonal Mann Kendall analysis. Prior analysis of continuous SC data from fall 2011 to spring 2016 showed that five sites had increasing SC, seven sites had decreasing SC, and the remaining 12 sites had no trend (Timpano et al. 2017). However, magnitude of SC trends, when present, was small. The mean rate of decline for SC at test sites with declining trends was 2.4% of mean SC/year with a range of 0.8% - 4.2%/year. Results from this analysis are summarized in Timpano et al. (2017). Our research effort will build upon these analyses by adding continuous SC data until January of 2019. Additional trend analyses will also be explored.

Temporal trends in Benthic Macroinvertebrate Community Structure:

Biological conditions will be evaluated using a suite of metrics describing benthic macroinvertebrate structure. Analysis to date has shown few significant trends over time in biological metrics. Moreover, these trends do not appear to be related to either increasing or decreasing SC. Sites with increasing SC do not show decreasing biological condition, and sites with decreasing SC show no improvement in biological condition based on assessments of benthic macroinvertebrate metrics (Timpano et al. 2017). Our project will build upon these analyses using fall and spring semi-quantitative benthic macroinvertebrate samples from fall 2016 through spring 2018.

Temporal trends in Ion Matrix:

Ionic composition of stream water will be evaluated using both an anion and cation matrix indicator. Ratio of sulfate to bicarbonate (SO_4:HCO_3) will be used as an anion indicator because laboratory studies have shown that sulfate is the dominant anion early in the leaching process of MTR-VF impacted soils and slowly decreases over time (Orndorff et al. 2015; Daniels et al. 2016). Meanwhile, the relative abundance of bicarbonate slowly increases over time. Therefore, we expect the SO_4:HCO_3 ratio to decline as the overburden ages; indicating recovery from mining conditions (Figure 2). The ratio of calcium to magnesium (Ca:Mg) will be used as the cation matrix indicator because these two ions are found at concentrations greater than all other cations in our study streams and Ca:Mg is altered at test streams relative to reference streams (Figure 2). Analysis of data through spring 2016 shows declines in SO_4:HCO_3 ratios at seven test streams over the study period (2011-2016) (Timpano et al. 2017). Three test streams also showed declines in Ca:Mg. No increases in either ion matrix indicator was found. Our research effort will build upon these analyses using data collected from fall 2016 through fall 2018.

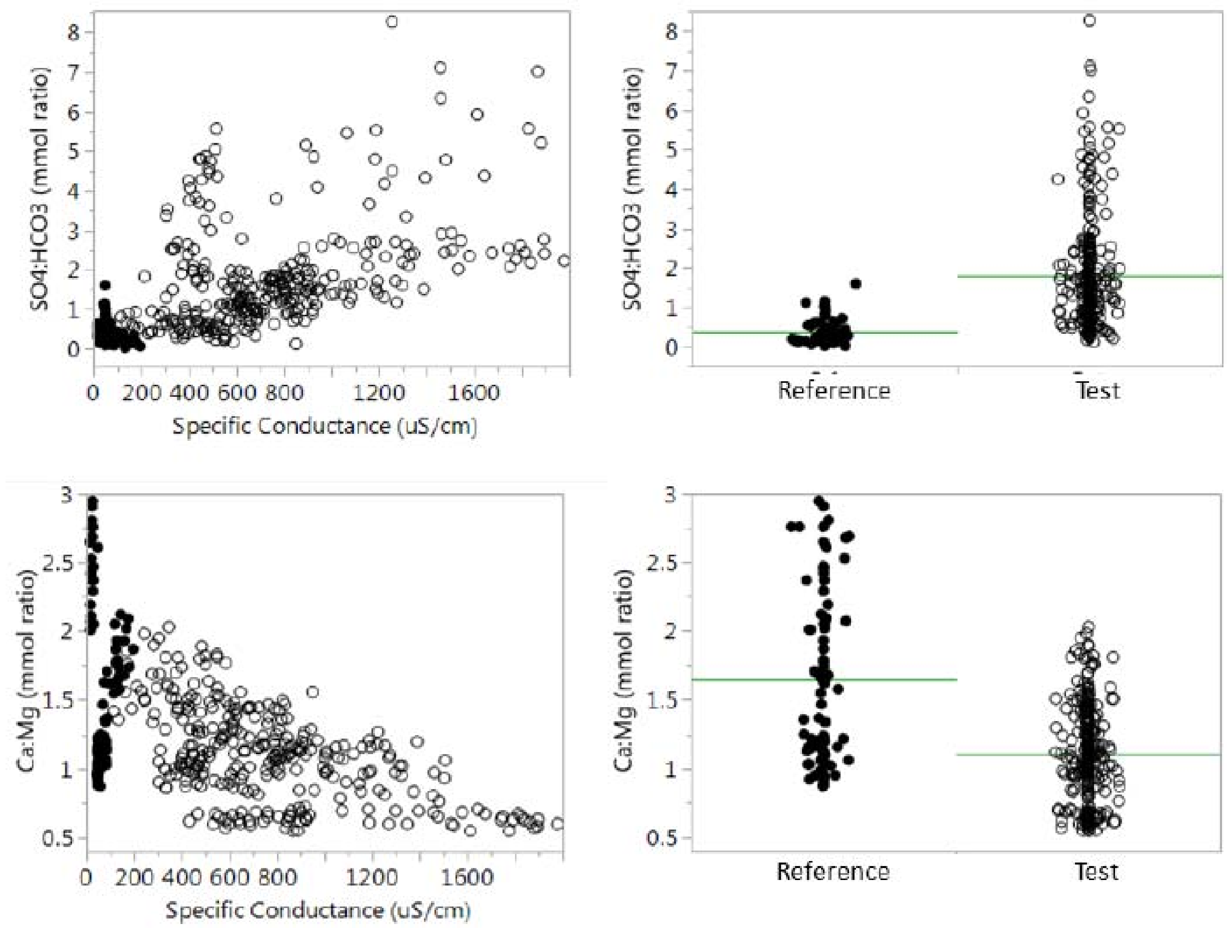

Figure 2: Relationships of SO4:HCO3 and Ca:Mg ion ratios to SC (left); and ratio distributions for reference and test sites (right). Solid symbols are reference sites, and open symbols are test sites (Timpano et al. 2017). Both ratios are altered at test streams. We expect ratios at test streams to move towards reference conditions as fill material ages.

Temporal trends in SC sensitivity:

Analysis of all study streams will examine if macroinvertebrate sensitivity to elevated SC changes over time. Timpano et al. (2017) pooled data from all 24 sites over the entire 2011-2016 study period to model changes in a suite of benthic macroinvertebrate community metrics against a gradient of SC (Figure 3). This analysis yielded the effect magnitude (i.e. slope) and a critical value for SC (SC_{crit}), above which aquatic life is negatively impacted, for each specific macroinvertebrate metric. The critical value was calculated using a reference threshold of the 10^{th} percentile of macroinvertebrate metric value in reference streams and extracted the intersection with the modeled relationship. Instead of pooling all individual years together as done by Timpano (2017), we will repeat this analysis for each year and with the longer-term dataset to determine if SC_{crit} is changing over time. Changes in parameters of the annual fitted models, including slope steepness, inflection points, and start of zero slope, will also be analyzed to further assess temporal trends in aquatic macroinvertebrate sensitivity over time. Additional variables such as year since mining termination and percent mining in the watershed will augment the mixed model to determine if significant effects exist.

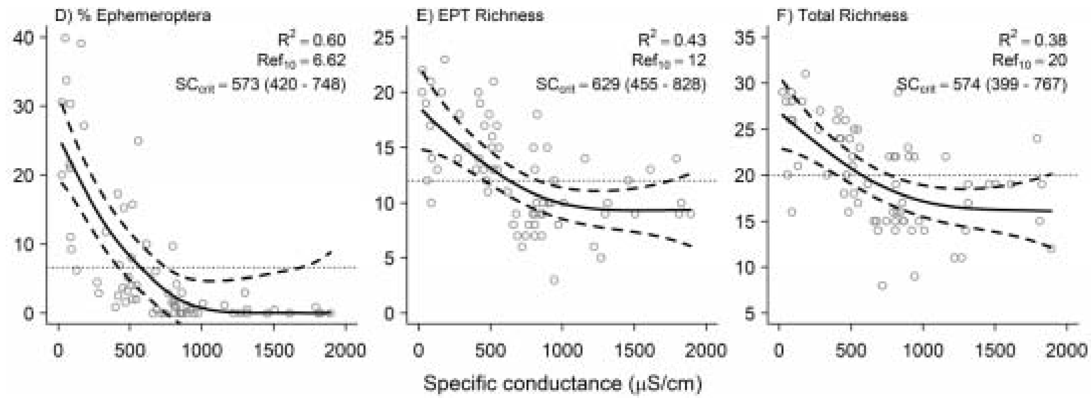

Figure 3: Generalized additive mixed models of SC and community metrics. In situ SC observations (gray circles), with smoothed fit (solid line) and 95% confidence limits (dashed lines). Dotted line is reference threshold (Ref10, the 10th percentile of metric value in reference streams), the intersection of which by fitted lines denotes critical conductivity value, SCcrit (with 95% confidence limits) (Timpano 2017).

Preliminary results

This research effort has added continuous, 30-minute SC data collected from spring 2016 through fall 2017 in our 24 headwater streams. Continuous SC data have now been collected from fall 2011 through fall 2017. This long-term dataset was analyzed for temporal trends using Theil-Sen slopes and seasonal Mann Kendall analysis. These analyses are non-parametric techniques commonly used to analyze water quality data for temporal trends because of their ability to accommodate non-normal data distributions and missing data values while considering data seasonality (Timpano et al. 2017).

We found that all five reference streams had statistically significant temporal trends. Two streams had increasing trends and three had decreasing trends. However, these trends were small ranging from -3.58 μs/cm per year to +1.49 μs/cm per year. These results suggest that headwater streams in central Appalachia vary in SC over time in response to natural factors (e.g. climate patterns). Nine of the 19 test streams (47%) in the study showed decreasing trends in SC over the study period (Figure 4). The mean rate of decline for SC at these test sites was 2.7% of mean SC/year; and the slope range was 0.7% to 5.7% per year. Two test streams showed increasing trends in SC (Figure 5). Eight test streams showed no statistically significant trend (Figure 6). Collection of 30-minute, continuous SC data will continue until spring 2019. Data will be analyzed using the methods described earlier in this report. Additional types of analysis will also be explored.

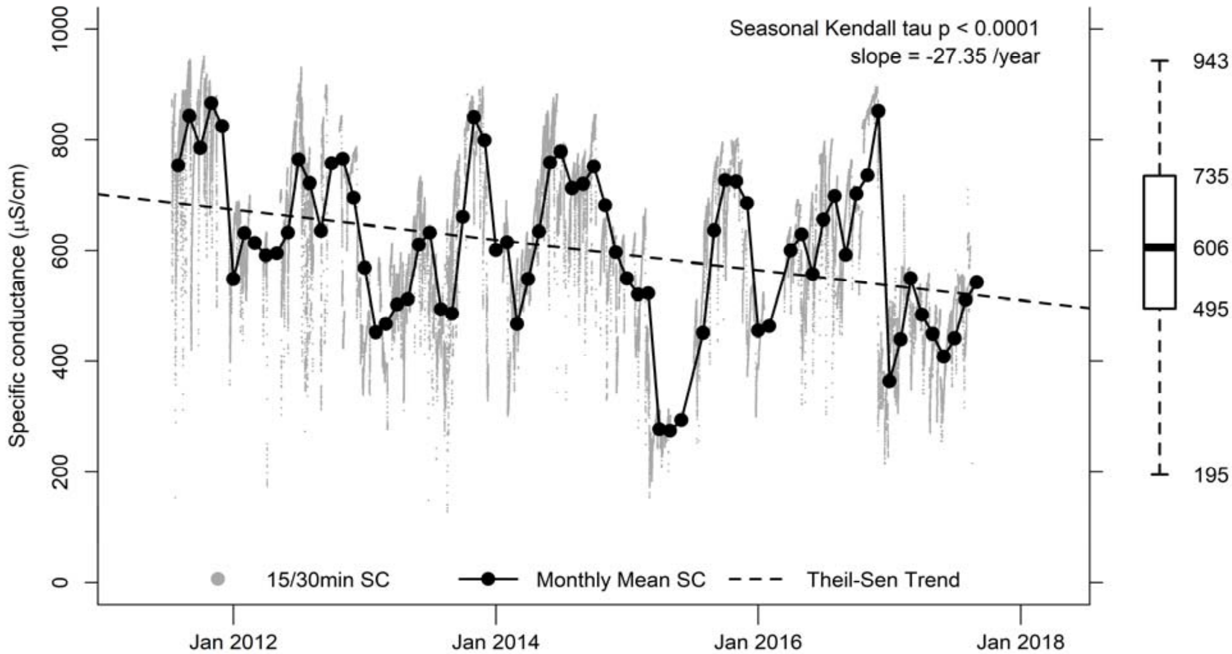

Figure 4: Dashed line is the Theil-Sen slope of SC at the test stream MIL. This site showed a decreasing trend in SC over the study period (Jan 2012 – Jan 2018). The solid black line represents mean monthly SC. The light grey line represents the continuous, 30-minute SC measurements (Data from Timpano et al. 2017 and Tommy Cianciolo fall field work 2017).

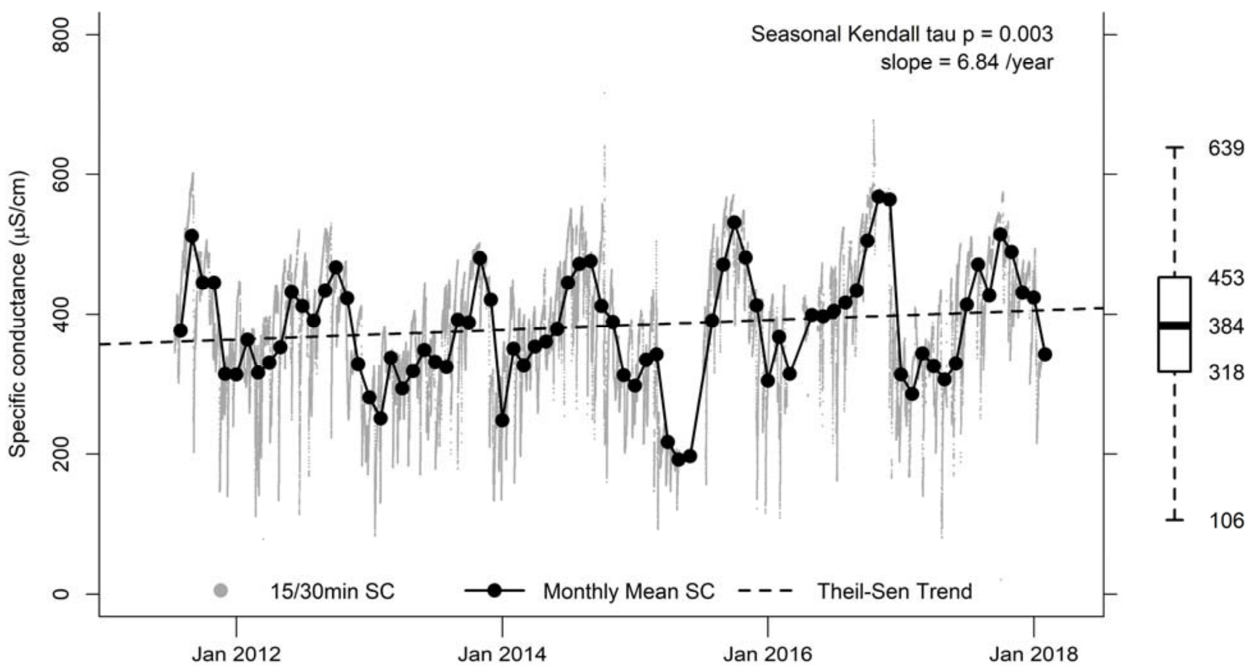

Figure 5: Dashed line is the Theil-Sen slope of SC at the test stream FRY. This site showed an increasing trend in SC over the study period (Jan 2012 – Jan 2018). The solid black line represents mean monthly SC. The light grey line represents the continuous, 30-minute SC measurements (Data from Timpano et al. 2017 and Tommy Cianciolo fall field work 2017).

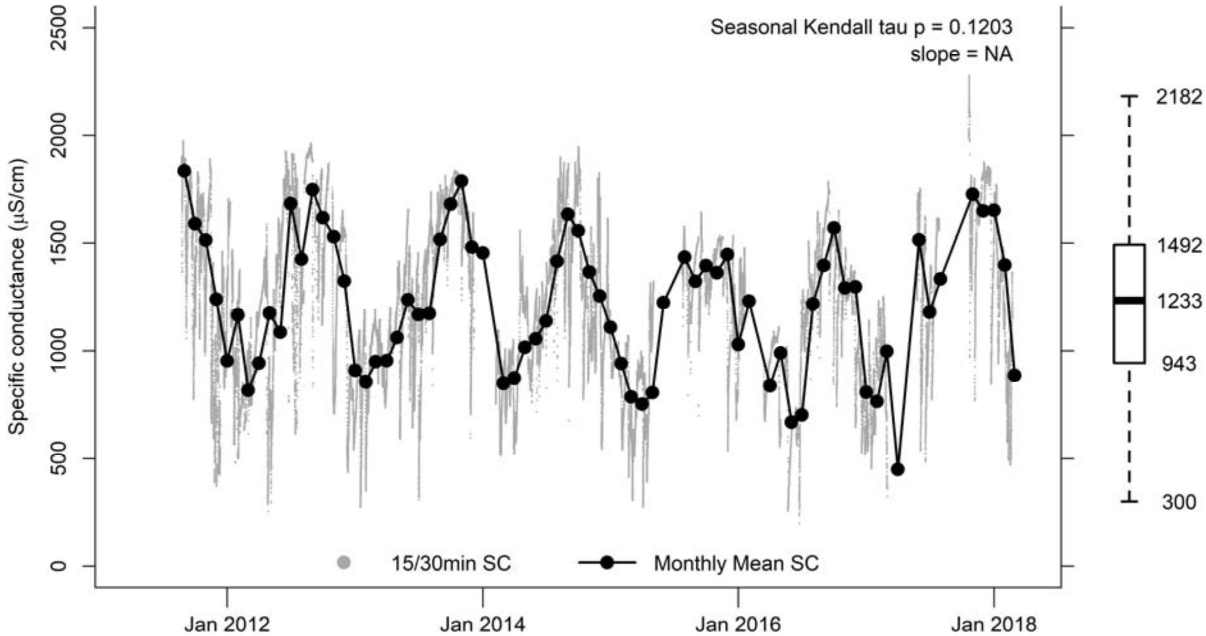

Figure 6: This site showed no statistically significant trend (p value <0.05) in SC over the study period (Jan 2012 – Jan 2018). The solid black line represents mean monthly SC. The light grey line represents the continuous, 30-minute SC measurements (Data from Timpano et al. 2017 and Tommy Cianciolo fall field work 2017).

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