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Characterization of the Major Ions of Coal Creek Near Cedar City, Utah

Jared Bryce Weaver
Southern Utah University, jread.weaver@gmail.com

Christopher Lamb
Southern Utah University, chris.r.lamb3@gmail.com

Kim Weaver
Southern Utah University, weaver@suu.edu

Jason Kaiser
Southern Utah University, jasonkaiser@suu.edu

J. Ty Redd
Southern Utah University, redd@suu.edu

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CHARACTERIZATION OF THE MAJOR IONS OF
COAL CREEK NEAR CEDAR CITY, UTAH

Jared Bryce Weaver[1], Christopher Lamb[2], Kim Weaver[3], Jason Kaiser[4], J. Ty Redd[5]
Department of Physical Science
Southern Utah University
351 West University Boulevard
Cedar City, UT 84720 USA
[1]jread.weaver@gmail.com
[2]chris.r.lamb3@gmail.com
[3]weaver@suu.edu
[4]jasonkaiser@suu.edu
[5]redd@suu.edu

ABSTRACT

The major ions of Coal Creek near Cedar City, in southwest Utah, were measured to determine if there were any differences in ion concentrations in July of 2014 as compared with spring measurements of 2012 and 2013. Past analyses have shown higher ion concentrations in lower regions of Coal Creek despite the apparent lack of water input. This research is aimed to better characterize these abrupt increases in concentration and determine if these trends varied when samples were acquired in the summer vs. in the spring when sample acquisition has occurred in the past. Environmental water samples were collected at evenly spaced locations in Coal Creek from State Route 14 Mile Marker 7 westward to where the creek intersects with Main Street in Cedar City. Ion concentrations were determined in water samples collected every other day for 3 consecutive weeks using Ion Chromatography (IC) and Atomic Absorption Spectroscopy (AA). The spatially intensive sampling revealed two previously unknown low volume springs that are highly concentrated in the major ions and discharge into the creek. Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) was used to characterize trace metal concentrations within the water tributaries, in addition to IC to determine bulk anion content in the creek. The high ion concentrations of springs correlated well with known geologic features near the creek, such as faulted gypsum layers creating springs as well as evaporate deposits, both of which explain the doubling of ion concentrations seen in the examined section of Coal Creek.

KEY WORDS: ion chromatography, atomic absorption spectroscopy, inductively coupled plasma-mass spectrometry, water quality sampling

INTRODUCTION

Environmental testing of surface water is an important practice to ensure that the water quality is safe from high levels of ions, as surface water generally affects ground and drinking water in any community (Alley, *et al.*, 1998). High ion concentrations can cause health hazards to

humans, animals, and/or the environment. This research examined the ion content of Coal Creek, a perennial stream (10 cfs) that runs through Cedar Canyon, east of Cedar City in southwest Utah.

In the spring of 2012, and 2013, students from Southern Utah University conducted similar testing of Coal Creek. Previous testing concluded that sulfate and chloride concentrations increased as the creek water traverses the canyon (Duncan, *et al.,* 2014). This increase of certain ion concentrations of previous years raises questions regarding the source of this increase due to the fact that the only known water tributary of Coal Creek in the study area, Right Hand Canyon Creek, had lower ion concentrations than Coal Creek and did not appear to have a major affect in the prior study. Thus, no explanation existed for past student observations.

A water analysis was completed of Coal Creek to examine if ion concentrations in this local waterway were still rising as the creek flowed down the canyon, and to determine whether any possible ions concentration trends existed. Water samples were collected from Coal Creek and tested for generally prevalent major anions and cations that included: fluoride (F^-), chloride (Cl^-), sulfate (SO_4^{2-}), nitrate (NO_3^-), nitrite (NO_2^-), phosphate (PO_4^{3-}), calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^+) and sodium (Na^+). It is well known that high concentrations of certain ions when ingested have been determined to be hazardous to the health of humans and animals. It is important to understand that most of the anions and cations tested in this research pose little health hazard concerns since consumption of these analytes would have to be at much higher concentrations. Thus, the main part of this research was aimed at understanding the geochemical environment of the water found in Coal Creek in order to explain the increase of certain analytes as the creek flows down the canyon (Duncan, *et al.,* 2014).

EXPERIMENTAL METHODS

Sample Collection

Water samples were collected from nine different locations along Coal Creek during the month of July 2014 (fig. 1). Sample sites were selected starting at UT State Highway 14 mile marker 7 going west down the canyon, sampling at one mile intervals. Mile marker 7 was chosen as the first sampling site (Sample Site 0) for convenience in following ion trends with respect to distance traveled by the creek as it flowed down the canyon. Each subsequent sample collection site was one mile apart following the direction of stream flow down the canyon (except Sample Sites 4 and 5.5 which were 1.5 miles apart) resulting in Sample Sites 0, 1, 2, 3, 4, 5.5, 6.5, and 7.5 (i.e. Sample Site 5.5 was 5.5 miles downstream from the reference, Mile Marker 7). Sample Sites 5.5, 6.5 and 7.5 were chosen (instead of Sample Sites 5, 6, and 7) to allow for comparison of results with earlier studies' sample sites.
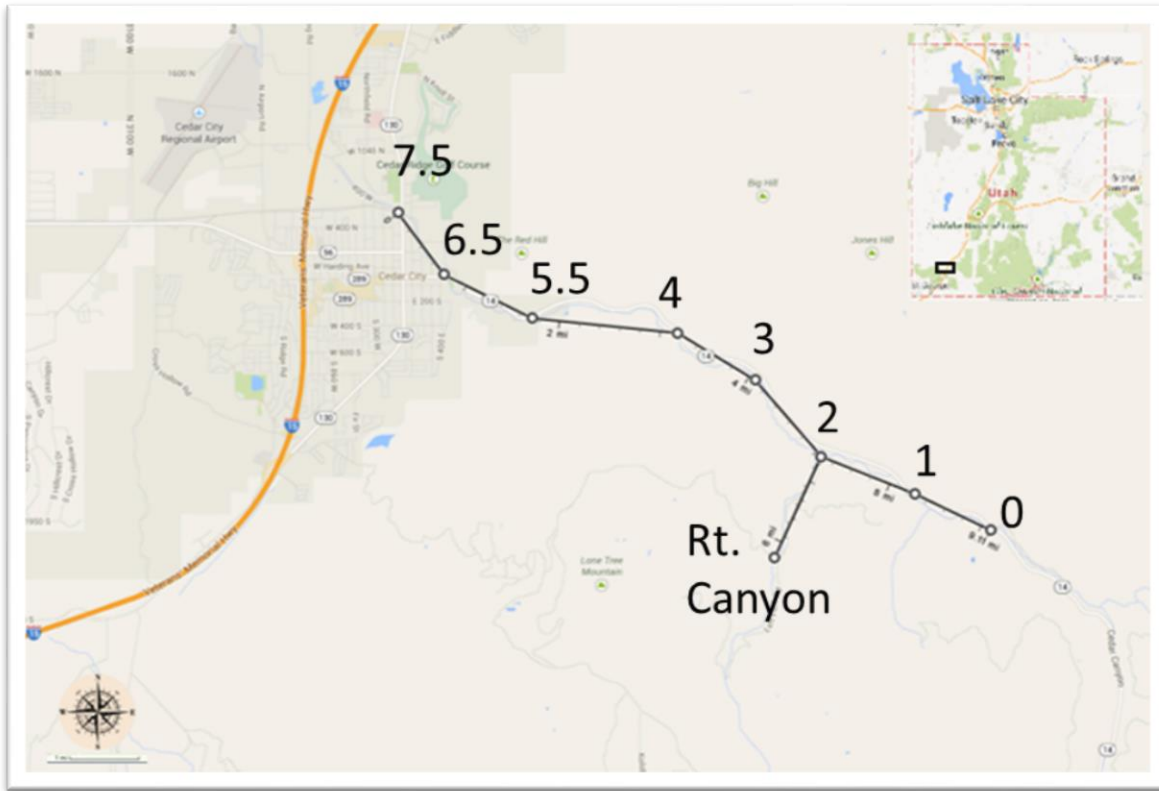
Figure 1. Map and location of sample sites, Mile Marker 7 on UT-14 (along the Cedar Canyon) being the point farthest to the right. Sample site numbering begins at Mile Marker 7 as Sample site 0, the reference point and subsequent sampling sites are labeled by the amount of miles downstream from this reference point. Sampling also occurred in a tributary 1 mile up Right Hand Canyon.

A sample was also taken between Sample Sites 1 and 2, at Right Hand Canyon Creek as the ninth sample site. Water samples were collected every Monday, Wednesday, and Friday for seven days over a 3 week period totaling 63 samples. Water samples were collected every day at approximately the same time (2:00-3:00 p.m.) with a relatively constant flow rate of $8 – 12$ ft^3/s (United States Geological Survey, 2014). Approximately 500 ml of each sample was collected in polyethylene containers from each of these locations and frozen after collection. To ensure that freezing the creek water did not interfere

with anion or cation levels, the first sample collected was split to evaluate the effect of freezing. Half of the sample was frozen and the other half was refrigerated. After collecting all samples, samples were analyzed for fluoride, chloride, nitrite, nitrate, phosphate, and sulfate concentrations via Ion Chromatography (IC). Then, Atomic Absorption Spectrometry was used to determine calcium, magnesium, potassium, and sodium concentrations. Preliminary data showed a dramatic increase in ion concentrations between Sample Sites 4 and 5.5, so an additional set of sample sites was collected,

sampling every 0.3 miles between Sample Sites 4 and 5.5 to more fully investigate this spike in concentration in the creek. This in turn led to future analysis and the discovery of two previously unknown tributaries into Coal Creek. Inductively Coupled Plasma – Mass Spectrometry (ICP – MS) was used to quantify trace metal concentrations in addition to prior analysis techniques to quantify the ion content within these tributaries.   As general trace metal concentrations have been shown to show little deviation of interest (within the scope of this study) along Coal Creek, ICP – MS was only used to analyze water in and around these located tributaries to investigate potentially interesting deviations from normal concentrations.

PROCEDURE
Ion Chromatography.

The environmental samples were tested on a Dionex model DX120 Ion Chromatograph with an auto sampler. Samples were allowed to thaw overnight before testing. A calibration curve was determined by analysis of standards containing 0.25, 0.5, 2.5, 3.75 and 5.0 ppm fluoride, nitrite, nitrate, and phosphate or, 5, 10, 25, 50, 75 and 100 ppm chloride and sulfate (American Public Health Association, 1995).

After the standards were made the 63 different samples were analyzed. This was done in two identical batches, where half of the samples were analyzed each time. The blank was distilled water to ensure that nothing interfered with the column to ruin the samples and to validate the calibration curve. Two additional quality

controls were ran, which consisted of calibration checks of a 50% standard that was placed at the half way mark and a 10% standard which was placed at the end to ensure that there was no drift in the calibration curve throughout the duration of the experiment. An eluent concentration of 1.8 mM carbonate and 1.7 mM bicarbonate was used with a Phenomex STAR-ION A300 ion chromatography column. An auto sampler was used for sample introduction.

Atomic Absorption.

The collected samples were tested on a Perkin Elmer Model 3100 Atomic Absorption (AA) spectrometer for the dissolved metals calcium (Ca), magnesium (Mg), potassium (K) and sodium (Na). The samples had to be individually tested for each element.

The tests for Na^+, K^+, Mg^{2+}, and Ca^{2+} ions were conducted by Standard Methods (American Public Health Association, 1995), measuring absorbance at wavelength of 589.6, 766.5, 285.2, and 422.8 nm, for Na^+, K^+ , Mg^{2+} Ca^{2+} respectively using the appropriate single element Perkin Elmer Hollow cathode lamp. Standards of 5, 10, 15, and 20 ppm sodium were used for calibration of instruments. Likewise, 10, 7.5, 5, and 2.5 ppm standard solutions were used, for potassium and magnesium and 25, 50, 100, and 150 ppm calcium were used for calibration. Lanthanum chloride ($LaCl_3$) was added to all solutions to minimize chemical interferences for calcium and magnesium analysis. The results for analysis are reported below.

Calibration was verified for each metal by analysis of an alternate standard. Also a blank and a calibration check were ran after analyzing every 9 samples, over the course of the analysis of the 63 acquired samples to ensure that the instrument did not drift. Samples for Mg^{2+} and Ca^{2+} analysis were filtered prior to acidification due to carbonaceous sediment containing both analytes.

RESULTS

Anion concentrations gradually increase as water flows down the canyon, between 4 and 5.5 miles down the canyon from mile marker 7 (fig. 1). All fluoride, phosphate, and nitrite concentrations were below the detection limit of the methods used in this paper and were therefore not included in any data. Nitrates were below 0.5 ppm for the bulk of the analyses and no general trend could be noted. A substantial increase in sulfates, chlorides, sodium, magnesium, calcium and potassium concentrations was seen between Sample Sites 4 and 5.5 (Table 1, fig. 2, fig. 3, fig. 4).

In terms of Right Hand Canyon, the only trends seen of any significance were the higher concentrations of sulfate and slightly lower concentrations of magnesium within Right Hand as opposed to before and after the entrance of the Right Hand Canyon inlet into Coal Creek (Table 2). When analyzed further, the increase in chloride and sulfate concentrations between Sample Site 4.0 and Sample site 5.5 was found to be localized in two small regions of the creek.

Inductively Coupled Plasma-Mass Spectrometry (ICP-MS).

All samples were filtered with glass fiber membrane filters and acidified to a final concentration of 1% HNO_3 with trace metal grade concentrate nitric acid prior to analysis on the ICP-MS. Samples were ran using a Semi Quantitative Analysis method on an Agilent Tech ICP-MS 7700 Series spectrometer to find approximate ion concentrations of trace metals (EPA Method 200.8).

Between 4.0 and 4.3 miles sulfates increased 14 ppm and chlorides increased 1.35 ppm and between 5.2 and 5.5 miles, sulfates increased over 22 ppm and chlorides increased 1.80 ppm (fig. 5). All calibration checks performed on the AA and the IC during analysis of cations and the IC showed that the calibration did not drift enough to affect samples by more than 10%. Blanks likewise indicated that sample measurements were not contaminated during the analysis process. The method control (in which the first sample was frozen and refrigerated) showed only a slight decrease in nitrates (to be expected from consumption by bacteria of nitrates even in refrigeration) and deviations of less than 10% in all other analytes except for magnesium (which would likely be due to certain sample preparation precautions that were later corrected among all samples using filtration prior to calcium and magnesium analysis). Analysis of spiked or analyte fortified samples on the IC showed the lack of matrix effect in all anions except for nitrates (which had high standard deviations due to inaccuracy in measurement of such low

concentrations of nitrates by the method used). Alternate standard quality controls ensured the accuracy of prepared standards in sodium and potassium in the AA was lower than 10% discrepancy from known concentrations of alternate standards. Close examination of the creek in these areas revealed two springs emptying into the creek. When the tributaries themselves were analyzed upstream, downstream, and at the tributary, very large relative increases in sulfates and chlorides were found in each (fig. 6). Further analysis of the data showed that almost all of these increases was due to these springs. The concentration downstream of Sample Site 4.0 was higher than upstream of sample site 5.5 because the spring had not completely mixed when the downstream (Sample Site 4.0) was collected. Trace metal analysis in these same regions showed four trace metals which deviated significantly from those along Coal Creek. Barium was relatively lower in concentration in both tributaries. Zinc showed an increase following the tributary (though little zinc was present in the tributary) at Sample Site 4.0, and aluminum and iron concentrations were lower at Sample Site 4.0. Iron and aluminum showed an increased concentration following the water tributary (though little of either was found in the tributary) at Sample Site 5.5 (fig. 7, fig. 8).

			Table 1: Average Analyte Concentrations and Standard Deviations (SD)			
Sample	Na^+ (ppm)	Mg^{2+} (ppm)	Ca^{2+} (ppm)	K^+ (ppm)	Cl^- (ppm)	SO_4^{2-} (ppm)
0	4.6 ± 0.6	21.53 ± 0.35	24.5 ± 7.8	1.54 ± 0.25	6.4 ± 0.5	36.7 ± 3.8
1	5.2 ± 0.2	21.63 ± 0.40	26.4 ± 5.4	1.55 ± 0.17	6.6 ± 0.8	41.3 ± 3.5
2	5.4 ± 0.2	22.13 ± 0.57	25.7 ± 7.6	1.64 ± 0.11	7.1 ± 0.1	41.6 ± 1.2
3	5.9 ± 0.2	21.90 ± 0.82	27.4 ± 11.9	1.71 ± 0.19	7.6 ± 0.8	49.5 ± 1.6
4	5.9 ± 0.2	22.0 ± 1.0	28.9 ± 9.7	1.73 ± 0.19	7.5 ± 0.4	50.5 ± 1.7
5.5	9.5 ± 1.2	24.6 ± 1.2	43.9 ± 10.2	1.98 ± 0.18	11.1 ± 1.6	99.4 ± 16.6
6.5	8.8 ± 1.0	23.8 ± 1.6	37.6 ± 5.1	2.02 ± 0.16	10.3 ± 1.2	94.2 ± 11.2
7.5	8.9 ± 1.0	23.4 ± 1.7	41.3 ± 2.1	2.06 ± 0.12	10.3 ± 1.0	94.1 ± 11.5

*In all tables and figures Sample 0 is mile marker 7 on Cedar Canyon Road, UT 14, all subsequent samples are aquired going west and following the road (using mile markers on the road as points of reference) down the canyon following the direction of surface water flow

Table 1. All ions of significant concentration found via Atomic Absorption Spectroscopy and Ion Chromatography. All other ions not reported were not present in appreciable amounts
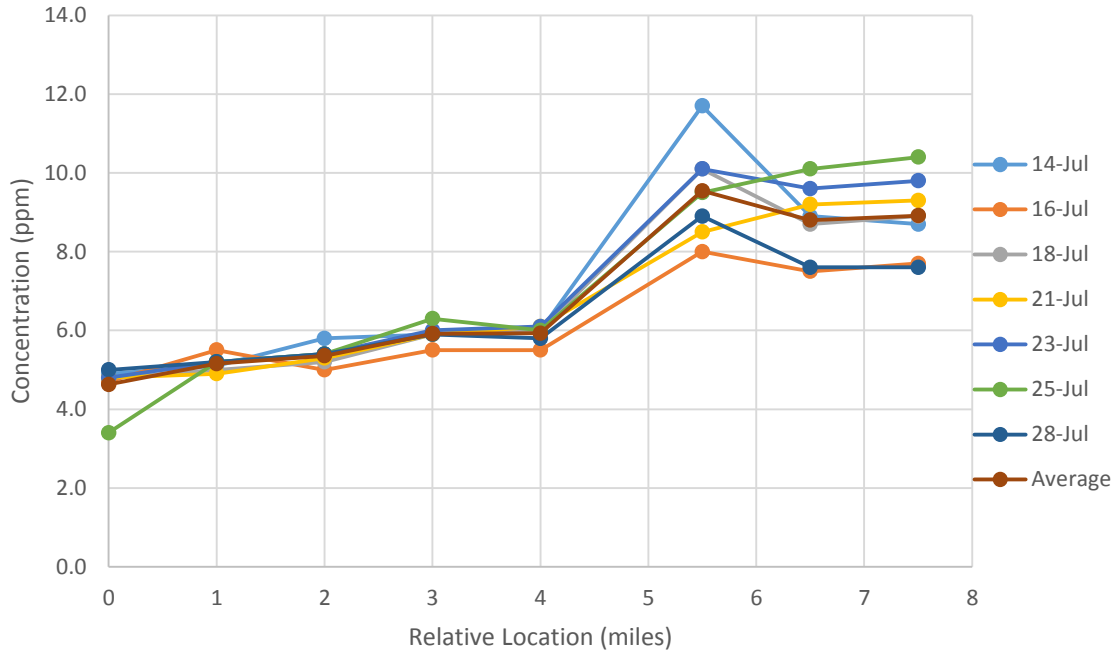
FIGURE 2. Na$^+$ Concentrations per sample site location. Other cations and anions stated in Table 1 follow the same general trends as Na$^+$ in the general increase seen between Sample site 4.0 and Sample site 5.5.
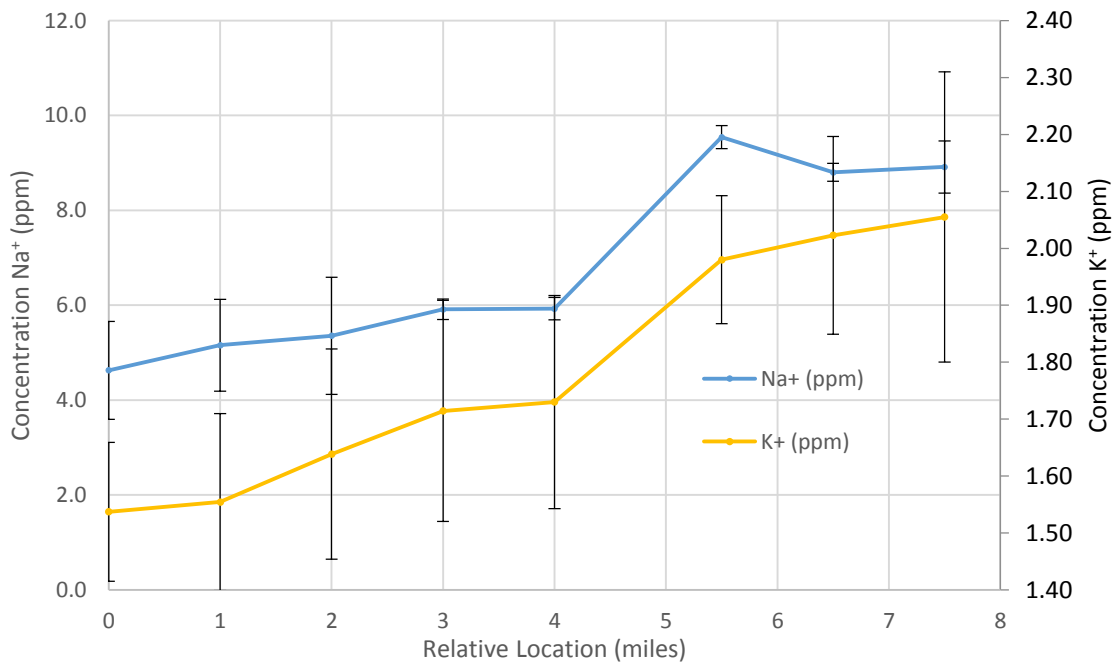

FIGURE 3. Average potassium and sodium cation concentrations. All error bars are made with $\pm$ 1 standard deviation. Ca^{2+} and Mg^{2+} followed similar trends.
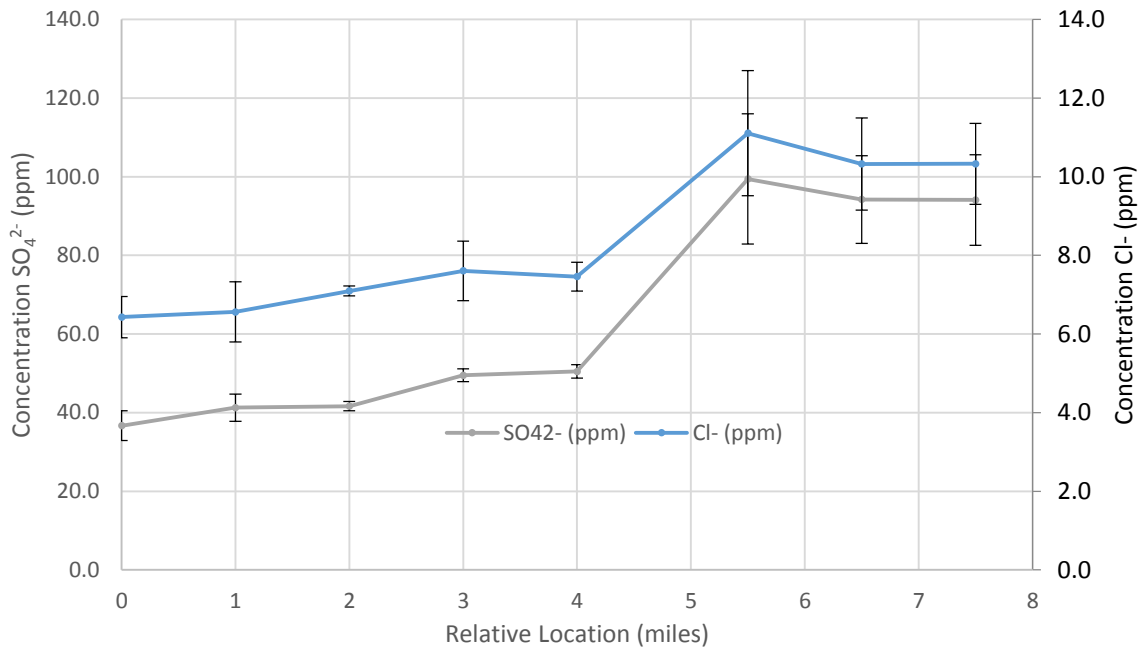
FIGURE 4. Average sulfate and chloride anion concentrations. All error bars are made with $\pm$ 1 standard deviation.

Sample Location	Cl^- (ppm)	SO_4^{2-} (ppm)	Na^+ (ppm)	Mg^{2+} (ppm)	Ca^{2+} (ppm)	K^+ (ppm)
Table 2: Average Anion and Cation Concentrations in terms of Right hand						
Before Righthand	7.1 ± 0.1	41.6 ± 1.2	5.8 ± 0.2	22.13 ± 0.57	25.7 ± 7.6	1.77 ± 0.11
In Righthand	4.9 ± 0.9	62.7 ± 18.6	6.0 ± 0.2	15.8 ± 2.7	37.7 ± 13.6	1.50 ± 0.19
After Righthand	7.6 ± 0.8	49.5 ± 1.6	5.9 ± 1.5	21.90 ± 0.82	27.4 ± 11.9	1.79 ± 0.58

Table 2. All ions of significant concentration found via Atomic Absorption Spectroscopy and Ion Chromatography. All other ions were not present in appreciable amounts. No significant correlation appears among the Right Hand Canyon ion concentrations.
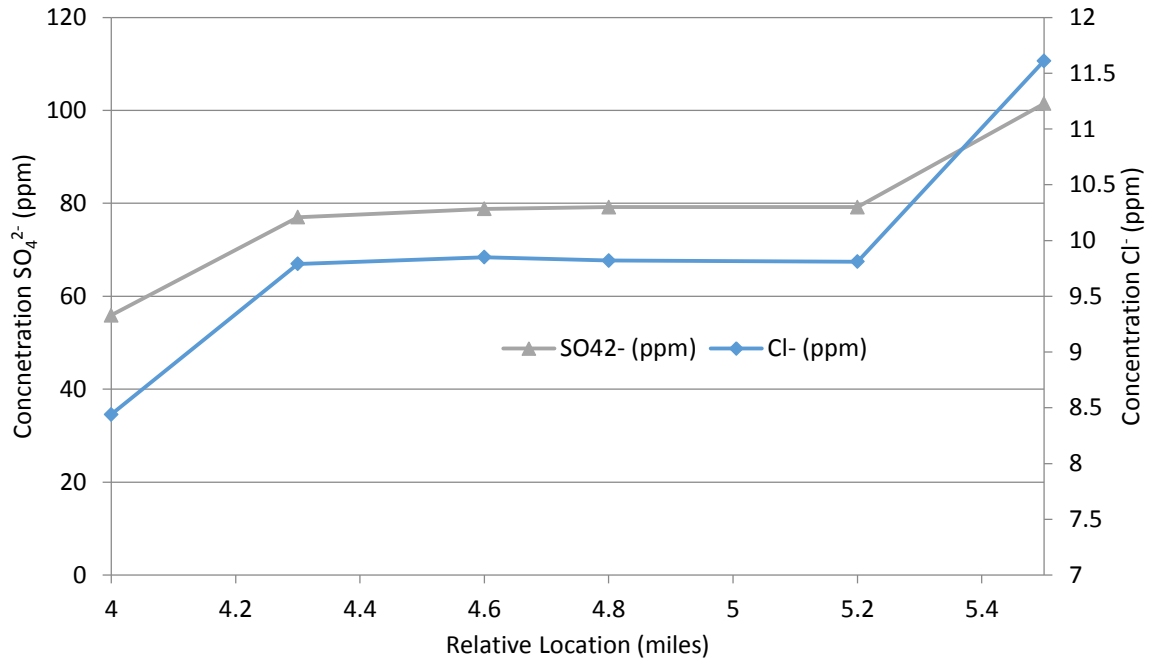
FIGURE 5. Anion concentrations were measured at every 0.3 miles along the area where the nonlinear jump in all ion concentrations was seen.
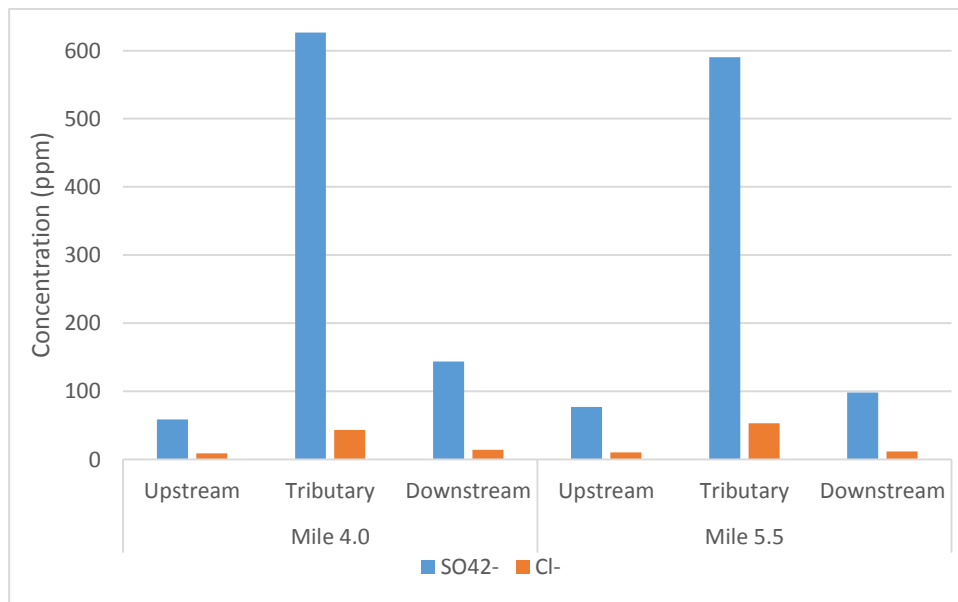

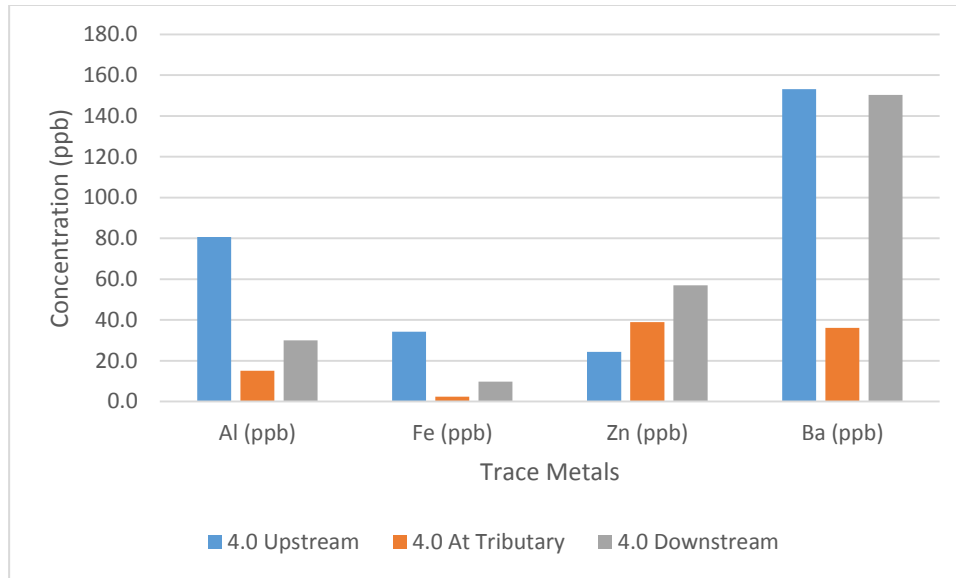**Figure 6.** Major Anion concentrations in and around each found tributary.

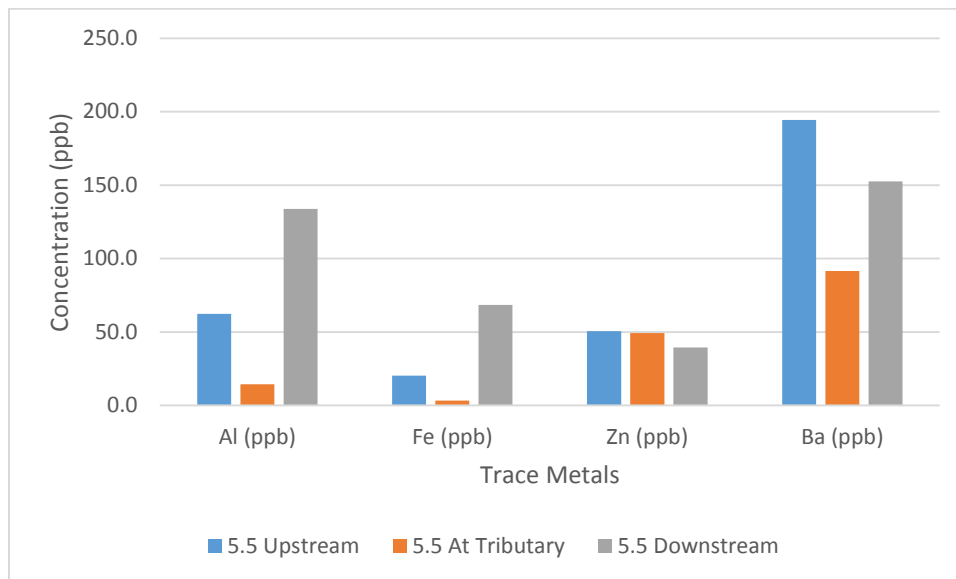**Figure 7.** Trace Metal concentrations at Mile 4.0* Tributary

Figure 8. Trace Metal Concentrations at Mile 5.5* Tributary

GEOLOGY

Coal Creek passes through a Mesozoic section of sedimentary rock east of Cedar City in Cedar Canyon of southern Utah (fig. 9). The creek originates in the Cretaceous units of Brian Head ends up in the quaternary alluvium of Cedar City. The sampled portions of the creek span Triassic limestone and mudstone as well as Jurassic

sandstones and mudstones and limestones. Of particular importance to this study is the Carmel Formation. The Carmel Formation is a Middle Jurassic sedimentary unit with multiple members, all deposited in a shallow inland sea (Sprinkel *et al.*, 2011).

The two most prominent members that crop out along the sampled portion of the creek are the Paria River Member (Jcp, Jcpl, Jcpg on the geologic map of Knudsen, 2014) and the Co-op Creek Limestone Member (Jcc). The Paria River Member consists of a thick upper micritic limestone and a massive lower gypsum bed (Imlay, 1980; Blakey *et al.*, 1983). The Co-op Creek Member consists of micritic limestone, mudstone, and gypsum mapped as a single unit throughout Cedar Canyon (Imlay, 1980; Blakey *et al.*, 1983). Both of these members are notably thick (30-100m) along the cliffs above the creek.

It is interesting to note the location of the units and structures in the canyon relative to the sampling sites and chemical observations. Sample Site 4.0 is located in the Co-op Creek Limestone Member. The sample was taken from a small run-off that runs parallel to Coal Creek within meters of the main channel. It is important to note that this smaller channel flows over loosely packed channel sediment that is interbedded with thin evaporite deposits of gypsum, halite, and calcite that were likely carried by coal creek in times of high flow. As the flow receded, the water would have evaporated leaving the thin, crusty deposits. Sample Site 5.5 is located along the eastern contact of the Navajo Sandstone where is meets the Co-op Creek Member. The

geologic map shows a fault contact (Knudsen, 2014). While it was difficult to confirm this fault contact in the field, a spring with high flow rates at the sample site could mark its location. This fault brings the Paria River Member into direct contact with the ridge-forming Navajo Sandstone and is likely the cause for the spring.

The geologic interpretation for the increased concentrations of sulfates and chlorides differs at the two observed sampling sites. At Sample Site 4.0, a thin carapace of evaporite deposits covers the substrate of both the main Coal Creek channel and the smaller channels. We interpret the cause of the sudden increase in sulfates and chlorides to be the result of the small stream encountering this carapace at the sample site. At Sample Site 5.5, the geology is a bit more complex. The North-South striking thrust fault juxtaposes the limestone and gypsum layers with the more competent sandstone. We interpret this fault to be the pathway for water to flow into Coal Creek as a spring. Along the trace of the fault, groundwater would have come into contact with the limestone and gypsum layers, accounting for the increased concentrations at the sampling site.

State Highway 14 runs along Cedar Canyon and Coal Creek. We interpret the road itself, with a compacted gravel substrate and culverts for runoff, as a natural barrier in some locations and a pathway in others for groundwater to enter Coal Creek. More sampling of Coal Creek at different times of the year could confirm the role that the road plays in allowing groundwater from the North to enter the creek system.
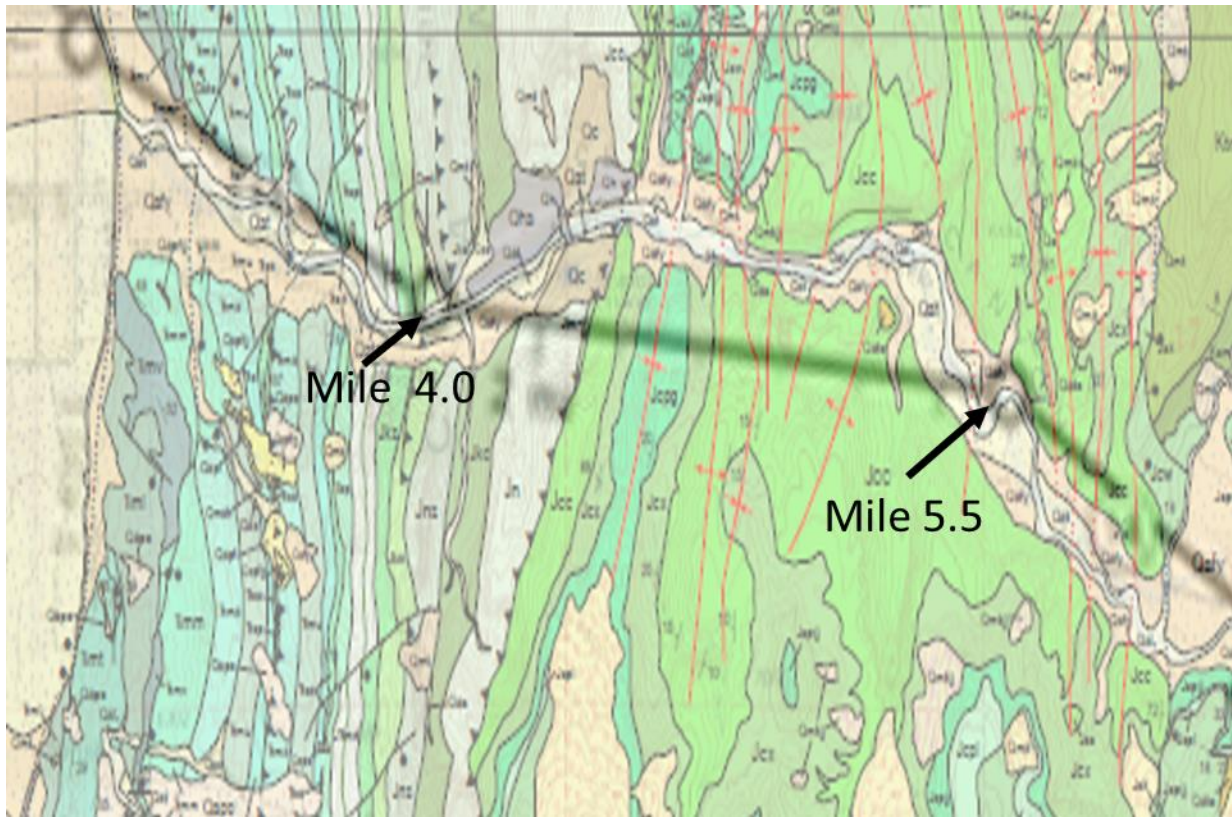
Figure 9. Overlay of the geologic map of Knudsen (2014) on the sampling site locations focusing on water tributaries at Sample site 4.0 and Sample site 5.5.

DISCUSSION

For much of the data, similar concentration levels and trends were seen going down the canyon as those reported in previous years, though concentrations deviated from those supported likely due to experimental error in previous analyses. This is consistent with general ion concentrations of surface water in the Colorado River, which tend to salt load as the body of water travels over more sediment (Hadley, 2012). Unlike previous studies, no concentration differences were seen between Right Hand Canyon Creek and Coal Creek itself. We attribute this discrepancy to collecting samples in the summer instead of the spring.

The most interesting observation was that between Sample Sites 4 and 5.5 there was a significant increase in almost all analytes of observable concentrations. Past analyses concluded that this spike may have been due to sheet flow of melting snow, during the winter. Sheet flow can concentrate ion concentrations as snow melts and solubilizes sediment along its path. This is easily discredited, however, in this summer analysis due to the obvious lack of snow. Further analysis of the this area showed that this spike of concentration was

likely due to at least two sources as evidenced by the two spikes in concentrations. Though first thought to be attributed to differences in sediment composition, analysis of the creek has found two springs, which are the cause of these increases in concentration (fig. 5, fig. 6).

Further analysis of the tributary at Sample site 4.0 revealed decreased concentrations in Fe^{3+}, Al^{3+} and Ba^{2+} ions, likely due to the increased sulfate concentrations. Zn^{2+} showed a large relative concentration increase not due to the tributary (no increased Zn^{2+} present in the tributary) and with no apparent source. Likewise at Sample Site 5.5 decreased concentrations of Ba^{2+} were found, again likely due to the increased SO_4^{2-} concentrations precipitating out the Ba^{2+} ions. Al^{3+} and Fe^{3+} concentrations however, show increases in concentrations which cannot have been due to the tributary, and, likewise, show no immediately apparent source. These unexplained concentration deviations deserve future consideration and analysis.

Finally, spatially intensive sampling proved useful for identifying a high correlation between ion concentrations within the surface water of Coal Creek and the surrounding geology. This high correlation encourages future geology and chemistry interdisciplinary studies and demonstrates that in order to predict future point source contaminations among surface and ground water there is a high need to know both the chemical and geological background of any area. Also, tributaries found entering Coal Creek were unknown to the investigators and relatively unknown to the community in which they were found prior to analysis. Systematic water sampling and analysis proved to be an accurate method to determine unknown sources of water in general as the same trends are likely to continue in tributaries that contribute to surface water in general.

ACKNOWLEDGEMENTS

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