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CAFFEINE AND ACETAMINOPHEN CONCENTRATION AND OTHER WATER QUALITY PARAMETERS ALONG THE MIDDLE TO LOWER BEAR RIVER

by

Autumn Slade

Thesis submitted in partial fulfillment of the requirements for the degree

of

HONORS IN UNIVERSITY STUDIES WITH DEPARTMENTAL HONORS

in

Chemistry in the Department of Chemistry and Biochemistry

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Abstract

Various water quality parameters were measured at seven sites along the Middle to Lower Bear River and compared across the sites, to past data and to set standards in Utah and Idaho. Much of the data was comparable to past data with most state standards being met. However, nitrate was above indicator level for over half of the sites, and turbidity is a problem at the last two sites. Also, chloride and unionized ammonia are at high levels by the last site. Overall, the river tended to decrease in water quality as it moved downstream, with dams like at Cutler Reservoir acting as reset points at times. Pharmaceutical concentration was in the ng/L range, with the highest caffeine value at Alexander Reservoir and the highest acetaminophen value at Oneida Narrows. There were no correlations found between pharmaceuticals and other water quality parameters. However, the pharmaceutical concentration could not accurately be determined due to interferences, bad recovery, and high blanks, which may have affected results.

"For all those I've met along this journey."

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I would like to thank Dr. Stephen Bialkowski and Dr. Michelle Baker for advice and support they have given me throughout this project. I would also like to thank the Chemistry and Biochemistry Department, especially Geri Child, and the College of Science for the help they have given. Lastly, this project would not have been possible without the support given by the Stephen E. Bialkowski Environmental Award. Thank you.

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Introduction

Throughout centuries, water quality has been a concern across the globe, as water is a necessity for civilization to exist. Water quality continues to be an ever-increasing concern as the synthesis and utilization of various compounds such as fertilizers and pharmaceuticals increase in number. To help maintain water quality of rivers, water bodies are given designated uses to determine set standards. This then allows several water parameters are regulated under state or federal laws. A few examples of regulated water parameters including dissolve oxygen (DO), nitrate, ammonia, and water temperature. Depending on designated use, the acceptable values for these parameters will differ.

The Bear River is an important river for agriculture and recreation across three states: Utah, Idaho, and Wyoming. This study focuses on the lower to middle Bear River, ranging from Corrinne, Utah to Soda Springs Idaho. From the Great Salt Lake to Utah-Idaho border, the Bear River, not including the tributaries, is given the designation of 2B, 3B, 3D, and 4 in Utah.^[1] Once Idaho is reached, the Bear River, not including the tributaries, is given the designations of COLD, SS, and PCR from Alexander Reservoir to the Utah Idaho border. [2] The full definitions for these standards are listed below in Tables 1 and 2.

If water quality standards are not met, then humans and the ecosystem can be affected. Unsatisfactory temperatures, pH or DO levels can cause aquatic life to die or potentially replaced by other species. High levels of nutrients from municipal waste or runoff containing fertilizers can cause eutrophication leading to dead zones and fish kills. [3] High levels of certain chemicals can cause symptoms in humans, such as blue baby syndrome in infants caused by high levels of nitrate. [4] Other ions, like chloride and fluoride, are not often associated with negative health effects, but can be indicators of pollution. $[4]$, $[5]$

Recently, pharmaceuticals have become an increasing concern in water quality and are not commonly regulated. ^[6] Pharmaceuticals such as caffeine and acetaminophen can be indicators of waste water, as these chemicals remain relatively unchanged in the environment and many waste water treatment plants do not treat for these compounds. [6], [7] Though the effects of pharmaceuticals on aquatic organisms have not been extensively studied, studies have shown that pharmaceuticals have broad and diverse effects on stream ecologies, including suppressed algal biomass and biofilm respiration, change in preferential food sources, and influence physiology of aquatic invertebrates. [6], [8], [9]

Sample Collection

Seven sites along the Middle to Lower Bear River were selected to measure for various water parameters (Figure 1). These sites were selected based upon available river access and location near sites previously monitored for similar parameters. ^[10] This allows measurements taken to be compared to past data, as well as state water quality standards and each other.

Using a Van der Walls apparatus, water samples were collected at seven sites along the Bear River, which is shown in Figure 1. All samples were collected a few feet from the bank in moving water, except for at Alexander Reservoir, where the sample was collected in the epilimnion layer. Samples were collected on two different days: October 8, 2016 and October 29, 2016. Since the samples were collected in the fall, the flow was lower around base flow. The weather before the first date sampled had been sunny, whereas there had

Figure 1 – Map depicting the seven sampling sites along the Lower to Middle Bear River

been a rain even in Northern Utah before the second date sampled, causing higher water flow.

At each site, one half pint glass mason jar and two approximately 20 mL glass vials were filled with nonfiltered surface water. In another vial, nonfiltered surface water was acidified below pH 2 using a few drops of concentrated H2SO4. Another jar and vial were filled with river sample filtered using ashed Whatman GF/F size 0.7 μm filter paper. All samples were then put on ice and stored at about 2-3^oC until further analysis could occur. [11], [12] In addition, a trip blank and two equipment blanks, one before all samples the other after all samples, were collected for each sampling date. Note that all glass containers were ashed and acid washed before collection occurred.

Site Description

At each sample site, altitude and coordinates were recorded using a GPS, while air temperature was recorded using a thermometer. This data is listed in Table 3. Exact flow was not measured, but flow seemed faster for most sites after the rain event. For most of the sampling, the weather was sunny and clear. A few other items of note were that above Cutler Reservoir, I-34, and Alexander Reservoir had fish jumping, Corinne had geese, and the bottom of Oneida Reservoir was covered in moss.

On Site Measurements

Water temperature, barometric pressure, and dissolved oxygen were collected on site using a YSI optical DO probe. pH was also measured on site using a Vernier pH probe connected to a portable Vernier LabQuest 2 interface system and calibrated between 4.01 and 7.00.

Barometric Pressure

Barometric pressure was between 622.9 and 661.3 mm Hg and had normal linear trends of decreasing pressure as altitude increased. 665.0 660.0 Thus, sites further downstream had lower 655.0 Pressure (mm Hg) 650.0 645.0 barometric pressure. In addition, the pressure 640.0 635.0 630.0 was lower when samples were collected on 625.0 620.0 4000 October 28, 2016 after the rain event.

Water Temperature

Water temperature is an important aspect for any body of water, not only because certain organisms can only live within a certain temperature range, but also because the temperature affects the chemistry occurring in the water. Temperature standards for Utah rivers designated as protected for warm water species has a maximum temperature of 27 °C . ^[1] Idaho, on the other hand, has designated the Bear River for cold water species, making their requirements a maximum of 22 °C with a daily average of no greater than 19 °C. ^[2] The highest temperature measured was 15.0 °C, meaning that at the time sampled, none of the waters were above the maximum temperature. However, it should be noted the samples were collected during the fall, meaning that during warmer months, the water may be above maximum temperature.

Dissolved Oxygen (DO)

Dissolved oxygen (DO) is critical for many aquatic organisms to survive in the water, and thus a lack of DO is what causes many fish kills and dead zones in the environment. Oxygen in the water comes from two sources: the air and photosynthesis. However, it can be used up in many aquatic reactions, such as respiration and redox reactions. The solubility of oxygen in

water is dependent on water temperature, partial pressure of O_2 in the air, and salinity according to Henry's Law. [13]

Figure 3 shows DO in mg/L and as % saturation. Expected mg/L DO was calculated using DOTABLES from the USGS, which used the Benson and Krause Equations. [14] Expected % calculations were then determined using these values. As either salinity or conductivity can be used to determine expected DO, the values shown in Figure 3 are the averages of the values obtained by using the conductivity (at original river temperature) and salinity. Lastly, measured % saturation is only available for the second date sampled, as it was not recorded on the first day.

The DO values seem to increase the further downstream the site is with a large drop between Oneida Narrows and Above Cutler. In additions, the sampling times may have an

influence on DO levels, as photosynthesis causes an increase in DO levels later in the afternoon. However, samples were collected starting downstream, which would cause the opposite trend than that depicted: DO levels would increase going upstream. One explanation for this phenomenon is that increased photosynthesis is occurring further downstream, with a reduction in photosynthesis between Oneida

Figure 3 - Dissolved oxygen content as mg/L and % saturation

Narrows and above Cutler Reservoir due to lack of sunlight penetration as the river becomes more turbid in that area (shown in turbidity section). This increased photosynthesis could be due to an increase of nutrients downstream (supported by nitrate section).

The highest standards in Utah for DO for the designated uses of the Bear River are a minimum of 5.5 mg/L over a 30 day average, 6.0 mg/L over a 7 day average, and 5.0 mg/L at any given time. ^[1] Idaho, on the other hand, requires a DO level of at least 6 mg/L at all times. ^[2] At the times sampled, all the DO levels were above the requirements. However, the DO levels were all above 100% saturation, indicating high levels of biological activity. Thus, at night when photosynthesis is replaced by respiration, there is a possibility of the DO levels decreasing below the standards set.

pH

pH is another important variable for the chemistry occurring within a water body system. For both Utah and Idaho, pH is required to be between 6.5 and 9.0 to meet quality standards. [1], $^{[2]}$ Though the pH was slightly above calibration range, all pH were within standards range on an the alkaline side. In addition, the pH levels recorded seemed to be similar to past data shown, though some values, such as those at above Cutler Reservoir, seem to be slightly lower or on the lower end of the previously reported data (see Table 4). [10]

Alkalinity

Alkalinity is the ability for a body of water to neutralize an acid, which is important in helping to create a buffer that allows pH to be regulated. How alkalinity is expressed is dependent on the endpoint. For example, carbonate alkalinity and total alkalinity are determined by titrating to endpoints $pH = 8.3$ and 4.5 respectively, often using phenolphthalein and methyl orange as indicators.

Within 14 days of collection, carbonate, bicarbonate, and total alkalinity were determined in duplicate by titrating 50 mL of sample from the nonfiltered samples in glass jars to phenolphthalein and methyl orange endpoints with approximately 0.01 N HCl standardized with $25 \text{ mL of } 0.01 \text{ N}$ Na₂CO₃ in triplicate.

As shown in Figure 4, the total alkalinity for the samples ranged from a low of 508.6 mg/L CaCO₃ at the Inlet to A. Reservoir to a high of 642.7 mg/L CaCO₃ at Alexander Reservoir.

Figure 4 - Alkalinity as carbonate and bicarbonate concentrations as mg/L CaCO3

Between the two days, the samples on the later date had a slightly higher total alkalinity, while the samples from the first day normally had a higher alkalinity due to carbonate.

It is interesting to note that some of the samples that were found to contain carbonate had a pH lower than 8.3, which should not be occurring. This may be due to error in pH calibration or during the alkalinity titration. Another explanation is that if any air was trapped in with the sample, there could have been introduction of more carbonate or bicarbonate acid due to $CO₂$ in

the air. However, all of the trip samples had alkalinities lower than $10 \text{ mg/L } CaCO₃$, thus this explanation does not account for all of the error.

Though Utah and Idaho did not seem to have set standards, the EPA has a minimum standard of 20 mg/L CaCO₃ for freshwater water bodies (excluding those with alkalinity naturally under this value). ^[15] In addition, surface waters in Utah and Idaho are naturally high in alkalinity, which can be good for the environment as it allows higher buffering against pH change. Thus, the water samples meet EPA standards and are natural for Utah and Idaho waters.

Solids

Within seven days of sample collection, total dissolved solids and total suspended solids were determined by running 100 mL of nonfiltered sample from the glass mason jar through a weighed ashed Whatman GF/F 0.7 μm filter. The filtrate was poured into a weighed crucible while the filter paper was placed in a separate crucible. The first set of samples were heated to between 100-133 °C for approximately 22.5 hours. The TSS crucibles were transferred into desiccators to cool before weighing, while the remaining TDS crucibles were heated to 176 $^{\circ}$ C for another 15 hours and then placed in desiccators to cool before weighing. The second set of samples were heated to $104-108$ °C for about 40 hours. The TSS crucibles were placed in desiccators, and the TDS crucibles were heated to $177-181$ °C for approximately 12 more hours. All negative weights that were measured are reported as zero.

Turbidity and conductivity were measured from the glass vial filled with nonfiltered sample and values were determined by Vernier sensors and ion-selective electrodes connected to a Vernier LabQuest 2 interface. Turbidity was measured within 48 hours of collection and the turbidity sensor was calibrated using DI water as 0 NTU and formazine as 100 NTU. Turbidity was corrected linearly for slight drift assuming constant drift and time between measurements.

Conductivity was measure within 28 days and the probe was set to 0-2,000 μS range and calibrated with DI water as $0 \mu S$ and a conductivity standard of 99.9 μS .

Total Suspended Solids (TSS) and Turbidity

Total suspended solids (TSS) and turbidity are both indicators of how much solid is suspended in the water. This is important to water bodies as high TSS or turbidity can restrict light penetration, thus decreasing the ability for organisms to photosynthesize and survive in aquatic ecosystems. In addition, high turbidity and TSS can also cause fine sediment to settle on the riverbed, impairing growth of some aquatic life, such as juvenile salmonids. [16] Lastly, sediment can be a transportation mechanism for pollutants that can adsorb to these surfaces.

Turbidity ranged greatly with a minimum at 4.8 NTU at Oneida Narrows to a high of

64.1 NTU at Corinne. TSS also had a large range, with the minimum between 0 ppm at Alexander Reservoir to 20,671 ppm at I-34. The value at I-34 was high due to moss in the water sample. The next highest TSS value was 98 ppm at the site above Cutler Reservoir. Values for TSS and turbidity

tended to trend upward the further downstream the samples were

 $10/8/2016$ = 10/29/2016

collected, with a reset point *Figure 5 – TSS and turbidity results *Negative values for TSS were given value of zero **TSS value for I-34 on 10/29/2016 goes to 20671 ppm*

between I-34 and Oneida Narrows. This is most likely due to sediment dropping out at Oneida Reservoir. Between the two dates sampled, TSS and turbidity values were higher for the samples collected after the rain event, which is likely explained by an increase in sediment due to increased flow and runoff due to rain.

Often there is a correlation made between total suspended solids and turbidity, as they are both a measurement of solids in a sample. However, as shown by Figure 6, there is very little

correlation between the two parameters. This may be due to inaccurate TSS calculation. Another explanation is the fact that turbidity is a measurement of light scattered by the light, and thus is dependent particle color, size and

Figure 6 – Correlation between TSS and turbidity

shape, which can change over the course of the river.

Comparing the collected data with past reported data from 2006-2011 at near collection sites (Table 5), the values for TSS and turbidity were similar, except for the TSS value at I-34 on 10/29/2016. This high value is due to the moss collected in the sample. Both Utah and Idaho have turbidity standards, which are 10 NTU turbidity increase for Utah waters protecting secondary recreation and warm water aquatic life, while Idaho had a maximum 50 NTU instantaneously or no more than 25 NTU for more than 10 days for waters designated for cold water species. All Idaho water samples were below the standard of 25 NTU, but the Utah samples most likely do not meet the standards as all sample values were above 10 NTU with a change greater than 10 NTU between the two sample dates for each Utah site. [1] [2] However,

it cannot be determined for certain whether these samples meet the standards. There were no standards for TSS listed in the Utah or Idaho Administrative Codes for water quality, except a 1200 ppm limit designed for agricultural use in Utah. $^{[1], [2]}$ None of the samples this standard, except for the sample containing moss.

Total Dissolved Solids (TDS) and Conductivity

Total dissolved solids is the measure of all dissolved solids, while conductivity is the measure of all conductive ions in a solution. Though there is often a correlation between the two values, but they are inherently different. Since TDS and conductivity can be caused by numerous ions and molecules, it is not associated with hazards by itself, but can indicate a problem.

As shown in Figure 7, TDS had a larger range than TSS, ranging between 0 ppm at

Alexander Reservoir, Oneida Narrows, and Above Cutler to 540 ppm at Corinne. TDS seems to

show no overall trend across the samples TDS values have no certain trend. However, the TDS data collected in this experiment was low compared to that of past years (Table 6). $[10]$ This is probably due to experimental error. Idaho did not have a standard for TDS.

Total Dissolved Solids (TDS)

To allow for comparison, conductivity values are shown in Figure $\overline{8}$ as conductivity at the measured river temperature and conductivity standardized to 25°C. Conductivity was calculated for these specific temperatures using equation 1 given below:

(1)
$$
C_F = \frac{C_M}{(1+0.02*(T_M-T_F))}
$$

where C_F is the final temperature corrected conductivity, C_M is the measured conductivity, T_M is the temperature that conductivity was measured at, and T_F is the final temperature that conductivity is corrected to.

At river temperatures, conductivity ranged between 463 μS at Inlet to A. Reservoir and 1357 μS at Corinne, whereas when temperature is increased to the standard 25° C, the range moved upward to between 543 μS at Inlet to A. Reservoir to 1561 μS at Corinne. Conductivity also tends to increase the further downstream, but doesn't decrease between I-34 and Oneida Narrows like turbidity, but instead decreased between Cutler and Fife Road. For the two days

Figure 8 - Conductivity at both the temperature of river and standard 25^o C

sampled, conductivity between the two dates was similar for all sites, except Corinne when the conductivity standardized to 25°C is dramatically different. This means that in the river at the time sampled, conductivity was similar, but in reality there were more ions in the river the first day sampled as opposed to the second.

sites, the values for conductivity were similar (Table 6). There were no found standards for conductivity listed in the Utah or Idaho Administrative Codes for water quality. $[1]$, $[2]$ Comparing

conductivity and TDS, there is very low correlation again. Like the TSS vs. turbidity, the second date sampled had a higher correlation than the first. This is most likely due better oven temperatures and measurements.

Ion Selective Electrode Analysis

Nitrate, ammonium, chloride and fluoride were determined by Vernier sensors and ionselective electrodes connected to a Vernier LabQuest 2 interface. Nitrate was measured within 48 hours of sample collection, while the other ions were measured within 1 month**.** Nitrate, chloride, and fluoride were measured from the glass vial filled with filtered sample, while ammonium was measured from the nonfiltered acidified samples. To measure ammonium by probe, the pH was brought back to between 4 to 7 using drops of NaOH and H2SO4. The nitrate, ammonium, and chloride probes were calibrated between 1 and 10 ppm, 1 and 4 ppm, and 10 and 499 ppm respectively with the lowest \mathbb{R}^2 for calibration curves between the two days being 0.9996,

0.9729, and 0.9988. A calibration curve for fluoride was also made between 0.01 and 1 ppm resulting in an R^2 of 0.9872. Un-ionized ammonia concentration was calculated using ammonium determined from an ammonium ion selective electrode and the pH and water temperature collected at each site. Note that ammonium was corrected for slight drift using a linear equation and assuming constant drift over time.

Chloride

Along the Bear River, high chloride concentrations are a concern, because many freshwater organisms cannot live in the water if the saline content is too high. In addition, crop cannot be irrigated with the water if salt content is high.

The maximum chloride concentration was 415.2 ppm at Corinne, while the minimum concentration was 32.6 ppm at the Inlet to Alexander Reservoir. Chloride showed a strong increasing trend the further downstream the samples were collected, with only a small decrease between the site above Cutler and at Fife Road. Converting chloride to salinity using equation 2 below, the salinity ranged between 0.75 to 0.059 ppt.

(2) salinity $(ppt) = 0.0018066 \times Cl^{-}(mg/L)$

Most freshwater streams and lakes have a salinity ranging from 0.001 to 0.5ppt, while brackish waters are often between 1 and 10 ppt. In addition, many freshwater organisms cannot

Figure 10 - Chloride and salinity for water samples

live in salinity levels above 1 ppt. [17] All sample salinity values fell within this normal salinity range for freshwater, except for the 10/8/2016 value for Corinne at 0.75ppt,

which could be considered slightly brackish, making it harder for many freshwater organisms to live there.

The standards listed for chlorine are in total residual chloride, which uses another method to determine chloride. [1], [2] Thus, it cannot be determined whether the chloride in the samples meet the required limit. However, EPA does list a secondary standard for chloride in drinking water, which is 250 mg/L. Chloride above this limit does not appear to be harmful, but gives the water a salty taste. ^[18] Out of all the samples, only Corinne exceeds the secondary standard for chlorine for drinking water.

Fluoride

Fluoride in low concentrations is not generally considered harmful, as it is introduced into tap water. However, in higher concentrations, it can have health effects on fish and organisms. In Utah, the standards for fluoride for domestic sources are between 1.4-2.4 mg/L and are dependent on the temperature of the air. [1] The Idaho Administrative Code did not list a fluoride standard, but the EPA recommends a secondary standard in drinking water at 2.0 mg/L. [2], [18]

Like chlorine, fluoride seemed to increase going downstream. However, the trend is not as clear as chlorine. The concentration of fluoride ranged from 0.353 ppm at Corinne and 0.352

Figure 11 - Fluoride in water samples

ppm above Cutler to 0.192 ppm at Alexander Reservoir. Though the parts of the Bear River that were sampled are not listed as a domestic source, all of the samples met the listed standards.

Nitrate

Nitrate itself is not usually harmful by itself except in very large concentration. However, excess nutrients cause an increase of algae growth, which in turn uses the DO in the water through respiration and decomposition. This in turn creates dead zones and fish kills, as mention in the dissolved oxygen section.

Nitrate-N ranged from a high of 9.1 ppm at Corinne to a low of 1.5 ppm in Alexander

Reservoir. There tended to be an increase the further downstream the sample site was located, but the trend is not largely obvious. Utah administration code has nitrate-N as a pollution indicator set at 4 mg/L for

secondary recreation and wildlife protection, ^[1] while the Idaho administration code does not seem to have any specifics regarding nutrients except that "surface waters of the state shall be free from excess nutrients that can cause visible slime growths or other aquatic growths impairing designated beneficial uses." [2] All the sampling sites in Utah were above the Nitrate pollution indicator point for Utah, while the sample sites in Idaho, except the Oneida Narrows on 10/8/2016, where below Utah's set indicator point. However, the sites at I-34 and especially Oneida Narrows contained moss that might break Idaho's statement regarding excessive nutrients. [2]

Ammonium/Ammonia

In the environment, an equilibrium between aqueous ammonia (NH3) and aqueous ammonium (NH₄⁺) occurs. Ammonia is of more concern than ammonium in surface waters, as it is more toxic to wildlife. As the pk_a of ammonia is 9.25, pH plays a critical role on the amount of ammonium vs. ammonia is in a water body, making more alkaline waters in more danger of having toxic concentrations of ammonia.

Total ammonia is the combination of ammonia and ammonium in a sample. Though only ammonium was measured, all samples were below pH 7, and ammonia levels at $pH < 7.5$ are a very small percentage in comparison to ammonium. Thus, ammonia concentration was assumed negligible and total ammonia – nitrogen (mg/L) was calculated using ammonium and equation (3) below. [19], [20]

(3)
$$
NH_4^+(ppm) * \frac{14}{18} = Total NH_3 \text{ as } N(ppm)
$$

Table 7 shows the calculated total ammonia as nitrogen values in addition to the chronic total ammonia criteria for Utah and Idaho water assuming early fish life. [1], [2] Every site has different standards, as standards are dependent upon the water temperature and pH of the site. In addition,

the chronic standard for water with early fish life was chosen as it has the strictest criteria. The blank measurements of ammonium were similar in concentration to that of the samples, making it impossible to determine if the levels of ammonium are due to ammonium in the sample or contamination. However, most of the samples were beneath the required standards even without correcting for the blank. The exceptions to this are one sample taken from Alexander Reservoir, I-34, and Corinne. Oneida Narrows had one sample that was right on the limit. After correcting for blanks, every sample was below required levels.

In comparison with past data, ammonia levels that were not blank corrected were on the higher end of the ranges or above. However, after blank correction, most of the values were similar to past data, because for

most sites, most samples hand ammonia concentration that was below detection limit.

As ammonia is more toxic than ammonium, un-ionized levels of ammonia are shown in Figure 5 to allow comparison across sites. This form of ammonia was calculated using equation (4), where %NH₃ was looked up using water temperature and pH. $[20]$, $[21]$

(4) Total NH₃ - N *
$$
\frac{\%NH_3}{100} * \frac{17}{14} = NH_3(ppm)
$$

Since blank levels were high, both the concentration with and without correction are shown. Overall, ammonia levels were highest at the inlet to Alexander Reservoir, Oneida Narrows, and Corinne with no overall trend seen from upstream to downstream.

Total Nitrogen

Total nitrogen is composed of nitrate, nitrite, and ammonia. Though nitrite was not measured, it is usually minimal compared to the other two ions. Thus, an estimated total nitrogen using nitrate and ammonia can be

compared decently well to total nitrogen from past data (Table 9). Overall, most sites were found to have a much higher total nitrogen due a much higher concentration of nitrate found than previously reported. This is probably due to an increase in fertilizer use since the data was collected in 2011.

Pharmaceuticals

Within the past few decades, concern over pharmaceuticals has grown exponentially due to better technology and increased globalization. Pharmaceuticals have been found across the environment in ng/L to μg/L concentrations. Though pharmaceutical concentrations are not usually lethal, they still have effects upon the environment, such as changing ecological

behaviors, which can cause more problems up the food web. In this experiment, four pharmaceuticals: caffeine, acetaminophen, acetylsalicylic acid, and diphenhydramine were attempted to be measured. However, only caffeine and acetaminophen were able to be measured to some degree, but still included a lot of interference and bad recoveries.

Methods:

Samples were prepared for pharmaceutical analysis by running 230 mL of the sample collected in the filtered glass mason jar through Discovery DSC-18 3mL/500mg solid phase extraction columns, washing with a few mL water, extracting with 5 mL acetonitrile and evaporating the ACN. All samples were then re-dissolved in 200 μL of HPLC solvent, except for trip blank for 10/8/2016, Corrinne from 10/8/2016, and the blank, 10/8/2016 which were dissolved in 87% H2O, 13% ACN, and 0.01 M ammonium acetate without pH correction. Fife Road from 10/8/2016 was dissolved in pure ACN.

A blank and 0.28 ppb solution of caffeine, acetaminophen, acetylsalicylic acid, and diphenhydramine was also prepared in similarly. Standards containing 1.77, 1.33, 0.884, 0.442, 0.180, 0.135, 0.0902, 0.0451, and 0.0162 ppm caffeine, acetaminophen, acetylsalicylic acid, and diphenhydramine were prepared. In addition, two standard additions for sample E2 were prepared by adding 20.5 μL of 0.884 ppm

HPLC-UV/Vis analysis was run on a Varian 9012 HPLC system connected to Applied Biosystems 783A Absorbance Detector with data collected using SRI PeakSimple Chromatography Data System. The solvent used was made of 87% HPLC grade H_2O , 13% ACN and 0.01 M ammonium acetate buffer acidified to approximately pH 4.7 using glacial acetic acid and set to a flow rate of 1 mL. The column used was an Econosphere C18 5μ 15 cm with the detector set to 274 nm and 0.005 AUFS range, and a 20 μ L sample injection port. [22], [23], [24]

*Figure 14 – Concentration of acetaminophen and caffeine corrected and not corrected for blanks. Any negative values reported as zero. *Alexander Reservoir 10/29/2016 goes to 406 and 389 ng/L for w/o blank correction and w/blank correction respectively.*

A standard curve for acetaminophen and caffeine was determined with R^2 values of 0.9649 and 0.9624 respectively. Acetylsalicylic acid could not be determined as it conflicted with the solvent peak, and diphenhydramine was not sensitive enough at the wavelength measured. The theoretical detection limit [25] for acetaminophen and caffeine was determined to be an absorbance of 0.035 and 0.076, which was below the experimental detection limit of 0.1 absorbance. The theoretical quantitative limit was calculated to be 0.79 and 0.98 absorbance or 0.026 and 0.086 ppm for

acetaminophen and caffeine respectively.

A 0.28 ppb solution of acetaminophen, caffeine, acetylsalicylic acid, and diphenhydramine was run through the procedure, and the % recovery was determined to be 78% and 413% for acetaminophen and caffeine respectively. The acetaminophen is within accepted range of 75-125%, but the caffeine resulted in a much higher recovery.

Results and Discussion

The results for the samples are shown in Figure 14. As the values for the blanks were

high, both values corrected and not corrected for blanks are shown with any negative values

corrected to be zero. In addition to high blanks, the samples showed high interferences, both with peak separation and spike recovery. The sample from I-34 on 10/29/2016 was spiked twice. The first spike contained 50% sample and 50% 0.844 ppm standard, while the second spike contained 50% samples and 0.442 ppm standard. The recoveries are listed in Table 10. Low recoveries may be due to matrix interferences, biological factors, or photolysis or other chemical reactions occurring within the sample.

Overall, the samples showed an increase in acetaminophen going downstream until certain areas, such as between Oneida Narrows, above Cutler, and Fife Road. Caffeine also tends to increase downstream, but the trend is not as clear. The ranges for acetaminophen were between 173 ppt and below detection limit. The range for caffeine was more varied between 406 ppt and below detection limit. The concentration range of caffeine is similar to previously collected data for a few streams in Utah, but the acetaminophen concentration is high in comparison. [26] In addition there was found to be no correlation between acetaminophen and caffeine concentration across the samples as the correlation coefficient was determined to be - 0.0603 with all of the data points, or slightly higher at 0.476 if the Alexander Reservoir data on 10/29/2016 was left out. In addition, there was very little correlation between pharmaceuticals and other values. Due to large interferences and the bad quality control parameters, it must be noted that this procedure is not accurate enough to definitively say what concentrations the samples contained, but rather can be used to give a broad overview and beginning point for further studies.

Conclusion

The water quality at the sampling sites along the Bear River mostly met both Utah and Idaho standards for the parameters measured. Nitrate, however, exceeded Utah's indicator level for all samples from Oneida Narrows downstream. This may be due to either lower flow rates, causing higher concentration, but is more likely an indication of nitrogen inputs from fertilizer from agricultural and urban runoff. Turbidity also becomes a problem past Cutler Reservoir and into Corinne, where high levels of chloride and potential ammonia problems also occurred. Corinne was the worst site with the parameters measured as it had the maximum values for turbidity, TDS, conductivity, nitrate, chloride, total ammonia-nitrogen, and fluoride.

An interesting finding was that between the sampling site above Cutler and on Fife Road, much of the water quality improves. For instance, nitrate, unionized ammonia, fluoride, chloride, and acetaminophen concentrations decrease between these two sites. This is most likely occurring due several variables, including the input of several tributaries into Cutler, change of flow and depth as the river becomes a reservoir, the influence of the dam, and the influence of increased sedimentation shown by an increase in turbidity.

In general, the data indicates that the water quality tends to deteriorate the further downstream the river travels. The data also tends to show that Reservoirs and dams can act as reset points that lower concentration of several water quality parameters, including pharmaceuticals. Throughout the data, there did not seem to be any correlations between pharmaceutical concentrations and other water quality parameters, nor did pharmaceuticals seem to follow any overall trends.

In the end, the pharmaceutical concentration could not be accurately determined due to interferences, bad recovery, and high blanks. A more accurate study on pharmaceutical

concentration would require a better method of analysis and preparation. A solution to this would be to use an LC-MS instrument, as it may help separate out and determine what the interferences are. However, based on the data collected, caffeine and acetaminophen do occur in the Lower to Middle Bear river at ng/L levels, but is not excessively high such that it would indicate serious levels of wastewater contamination or illegal dumping.

Word Count: 6535

Reflective Writing

My project was rife with problems, anxieties, and procrastination. However, I would not trade the experience for anything. My projected started forming in the spring of 2016, when I wanted to come up with a project to apply for the Stephen Bialkowski Environmental Chemistry Award. That semester, in Environmental Chemistry, we did a large water quality project measuring various parameters in water samples we had taken across Utah over Spring Break. In addition, one of the graduate students in the lab I work in was interested in pharmaceuticals along a few of the rivers along the Utah Wasatch Front. Thus, I decided I wanted to see the concentration of select pharmaceuticals along the Bear River, as it is a major water source in several states, and I could find no previous data on pharmaceutical concentrations for it.

I received the funding for my project that spring, but did not start the project until the fall, where I did the research under Dr. Stephen Bialkowski, who is the professor in charge of Environmental Chemistry classes. Luckily, that semester, Fall 2016, I was taking two classes that greatly benefitted my research project. The first was a Water Quality and Pollution class taken through the Watershed Department, while the other was Environmental Quality Analysis taught by the Engineering Department. These two classes helped to further teach me about water quality and how to correctly analyze water samples, which I learned that the way we did it in Environmental Chemistry was technically incorrect, because we did not put the samples on ice, filter them correctly, or analyze certain parameters on time.

At first I felt like the project was going well, though I was a bit stressed at times, learning how to buy supplies from the chemistry store, and making sure everything was ready before I could go sample collecting. When the time came to collect samples, several things went awry. First, I had planned to collect samples along most of the Bear River, sampling at sites that had

been determined previously by a published report containing certain water quality parameters along the Bear River over the course of several years. However, when I drove to those sites, many of the bridges were too high to sample from or there was no access to the river due to the land being private property. Thus, several sites were not sampled at and several more were measured further upstream or downstream where there was easier and public access to the river. I also found that sampling took longer than was expected, and due to time constraints, could only make it to Soda Springs in Idaho, instead of Bear Lake, which is the minimum upstream site that I wanted to collect samples at.

Finding sampling sites was not the only problems that occurred on sampling trips. The first sampling trip I took, I managed to lock my keys in the trunk of my car and had to call the Soda Springs police to help unlock my trunk. To make matters worse, on the second sampling trip, I managed to hit a deer while in Idaho on the way back to Logan. Luckily, my car was not badly damaged, with only slight bumper damage and a headlight out. Coincidently enough, I had pulled over to the side of the road by property that was owned by a USU professor, who was also on his way back to Logan and let me follow him back. I never caught the professors name, but I am very grateful to him.

After collecting the water samples, most of the analysis went well. However, I did have a few problems trying to get the correct temperature in the oven I was using. One of the major problems I had with analysis was trying to analyze pharmaceutical concentrations. Two of the pharmaceuticals I wanted to measure did not have peaks showing up even with the standards, and so, do to time and sample size constraints, I could not analyze for them. In addition, the original procedure I was going to use did not work, thus I had to play around with mobile phases and flow rates. In the end, I never got great results, as I had high blanks and bad recoveries, but I

did learn important skills in dealing with HPLC-UV/Vis. It's also interesting to note that at an environmental engineering seminar I went to this past Spring, one of the graduate students had measured pharmaceuticals in another river in Utah using $LC-MS³$, and though he was using better instrumentation, his recoveries became worse the further downstream he sampled. Thus, there may be an inherent factor, such as bacteria or other matrix effect that causes bad recoveries. This could possibly be a potential research project for future students.

One last anecdote I want to add, is that at the student research symposium, where I was presenting a poster of the data on my research, I had a professor ask why I was doing research on water quality when I was in the Chemistry and Biochemistry Department. I brought up the fact that I was an environmental chemist and loved research that was more interdisciplinary, but he made me reflect upon why I was doing my research. I realized what a great opportunity it is to be able to be funded to do interdisciplinary research and how chemistry is critical in almost every science based major out there, including water quality.

In the end, my advice to future students is do what you love. If you're having fun and interested in the research, then no matter what troubles arise, you will look back and find that even through the anxiety and stress, you enjoyed it. Also, don't think that you need to stick solely to your major when doing projects, because interdisciplinary projects are very informative, and you often discover a new love for your own major when you see it applied to other projects. In addition, I have also found that meeting professors outside of your main department is very beneficial and often have different viewpoints about your own major then what you may find in your department.

Word Count: 1027

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Appendix A - Site Pictures

Appendix B - Data Table

Professional Author Bio

Autumn Slade is a senior in chemistry at Utah State University with math and horticulture minors. For the past four years, she has been an Undergraduate Research Fellow and a part of several university clubs. In April of 2016, she has won the Harris O. and Eleanor Y. Van Orden Award in Physical Chemistry and the Stephen E. Bialkowski Environmental Chemistry Award. Most recently, she has had the privilege of being selected to represent the College of Science on the USU Honors Last Lecture Committee this spring, 2017. She is excited to be graduating this spring and will continue researching in one of her labs this coming summer until she finds a professional chemistry career. After taking at least a year off of school, graduate school may become a possibility. In the long term, Autumn wants to work for the United States Geological Survey to help learn more and protect the environment.