A Geochemical Investigation of the Influence of the Hot Springs on the Fall River in Hot Springs, SD.

By

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Under the Supervision of Dr. Laura Triplett

ABSTRACT

Hot Springs, South Dakota is named for its thermal water features, but little is known about how the hot springs affect the chemistry of the Fall River, which runs through the town of Hot Springs. This study uses chemical and statistical analysis to evaluate water samples from springs and the river to determine the extent to which the Fall River derives its chemistry from the hot springs that feed into it.

Samples were taken from a variety of springs and rivers in the Hot Springs area and tested for water quality parameters such as temperature, pH, specific conductivity, and alkalinity. These samples were also analyzed by ICP-MS for major and trace elements. A variety of descriptive statistics were conducted to evaluate patterns across samples. Ca, Ni, Mn, Ga, Mo, Se concentrations and pH were determined to be statistically different when hot springs and rivers were compared. The variation in concentration of those elements indicates a direct hydrologic connection between the thermal springs and the Fall River. Field observations indicate that several springs, including one that forms the headwaters of Hot Brook, flow into the Fall River as it runs south through Hot Springs, SD.

ACKNOWLEDGEMENTS

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INTRODUCTION

Hydrothermal water features, said to have healing powers, have been of interest to people for thousands of years. Many people flock to hydrothermal springs to soak in the mineral waters and experience the reported health and rejuvenation benefits. These features continue to captivate people today, as many springs boasting thermal waters have been commercialized, and companies are using these naturally warm waters to gain economic profit. However, there are still pristine springs protected, on public land, or unknown on private properties all over the world. Hydrothermal waters, originating deep underground, differ from normal surface waters with respect to temperature and chemical composition. Hydrothermal waters can emerge at the surface in a number of different settings, including superheated pools, geyser, mud pots, and natural hot springs. The most numerous and wide spread of these features are thermal hot springs. Thermal springs can be found in twenty of the fifty states in the United States, and each spring has unique characteristics of discharge and chemical signatures which are affected by the regional geology (Davis and Conway, 1999). Hot spring water coming from deep in rock formations is often mineral-rich. When this water mixes with lower-temperature surface waters, it can leave a distinctive chemical signature and sometimes affect the organisms that live in the resulting mixed waters (Mariner et al., 1982). This study explores the geochemistry of thermal springs located in Hot Springs, South Dakota and their potential effect on the chemistry of the Fall River which runs through Hot Springs (**Figures 1 and 3**).

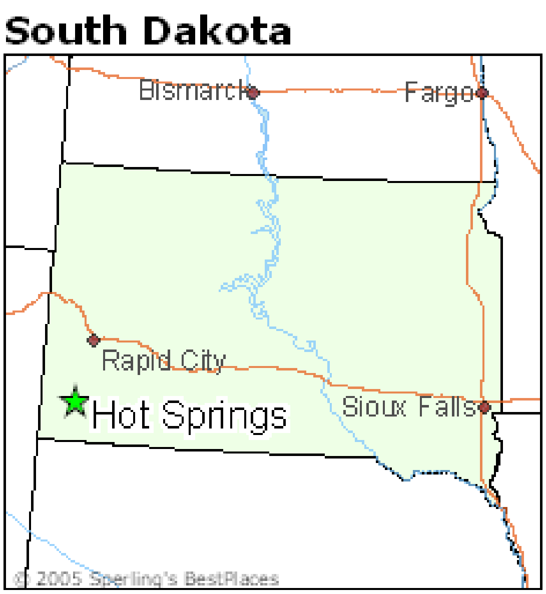


Figure 1. Field work locality highlighted with green star. Hot Springs, South Dakota (Sperling's Best Places).

The Black Hills host five major bedrock aquifers the Deadwood, Madison, Minnelusa, Minnekahta, and Inyan Kara aquifers (Carter et al., 2002). The bedrock geology of the Black Hills region is complex but well studied; a simplified stratigraphic model of the bedrock aquifers can be found in **Figure 2**. These aquifers have been highly described and a detailed description of their geochemical qualities is available as a part of the Black Hills Hydrology Study in a separate report by Naus, Driscoll and Carter titled Geochemistry of the Madison and Minnelusa Aquifers in the Black Hills Area, South Dakota. This work provides a large-scale chemical and hydrologic comparison point for the specific project that I conducted within Hot Springs. Data provided in these studies will be a benchmark for numerical quantities for elemental and water quality data.

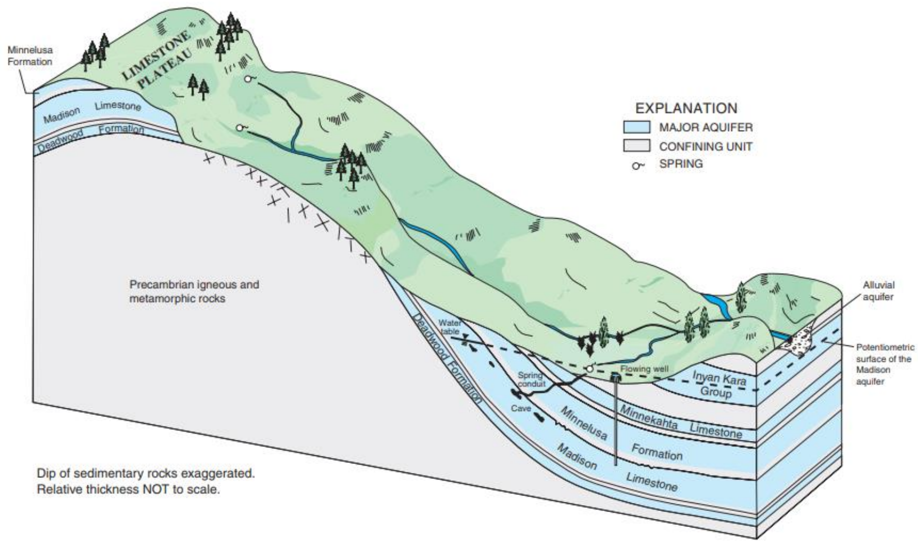


Figure 2. Stratigraphic schematic of the five bedrock aquifers in the Black Hills region (Carter et al. 2002).

Data was gathered from both private and public springs in Hot Springs, SD. The public springs in Hot Springs have known concentrations of elements, but some of the private hot springs had not been tested and the spring owners were unaware of the elemental concentrations. This study aimed to provide trace and major elemental concentrations for each spring sampled, along with additional water quality parameters such as pH, specific conductivity, alkalinity, and temperature.

Work characterizing the water features of this region includes the "Streamflow Characteristics for the Black Hills of south Dakota, through the Water Year 1993", by Miller and Driscol. Miller and Driscol (1998) outlines various types of water features in the western third of the state including the Fall River monitored at Hot Springs. These data were gathered from 1938 to 1993 and do not include chemical analyses of the hot springs. There has been significant development in the town of Hot Springs since this time, which could have introduced many changes to the Fall River at this location since the monitoring has ceased so there are likely changes within the streamflow dynamics of the region. To address the lack of hydrologic data in this area, the South Dakota U.S. Geological Survey (USGS) and South Dakota Department of Environment and Natural Resources (DENR) conducted the Black Hills Hydrology study which kicked off in 1990 and was completed in 2002. This study provided detailed hydrogeologic information in order to help guide management of water resources in the Black Hills area. This study covers the framework hydrogeology in addition to climate, geology, and groundwater and surface water characteristics and trends. Though this study is comprehensive it does not cover the question I am addressed regarding the chemical influence of the hot springs on the Fall River. The Black Hills Hydrology study is used to put the data from this research in context, and assists with interpretations. The direct application of this study is through use of their chemical assessment of the Madison, Minnelusa, Minnekahta, and Inyan Kara aquifers with water quality parameters such as pH, specific conductance, temperature, and alkalinity measured from different gauging stations in the Black Hills area. The aquifer depths, stratigraphic column and Black Hills elemental reports will be used from the Black Hills Hydrology Report by Driscoll et al. 2002.

My study format comparing hot spring chemistry to a nearby river's chemistry was adapted and derived from a similar study completed by Ogawa et al.(2012). In this study the chemical fractionation of various elements is evaluated using Shibukuro and Tama rivers from which the majority of flow and chemistry is hot spring derived. The Obuki hot spring is contributing highly acidic water this river system with a host of other elements for which the authors are measuring chemical behavior and fractionation mechanisms within the rivers. The authors are taking into account the geochemistry of the spring and its effect on the chemistry of the river, and how the chemistry of the rivers changes over time. I have adapted the idea of comparing hot spring and river chemistry based on a variety of sample points from Ogawa et al. to the various hot springs and the Fall River in Hot Springs, SD. This type of study was highly applicable to the Hot Springs area, because thermal spring water forms a majority of the flow of the Fall River, similar to the hydrologic set up in the Tama River watershed in Japan. Fractionation of elements will not be measured but trace and major element data, as well as temperature, alkalinity, pH, and specific conductance will be measured in the Hot Springs study.

Statistical analyses procedures from Yunhui Zhang et al. in "Hydrochemical Characteristics and Multivariate Statistical Analysis of Natural Water System: A Case Study in Kangding County, Southwestern China" such as principle components analysis, were used for data gathered from Hot Springs, SD. Zhang et al. used chemical data from surface water and groundwater systems analyzed by ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry) and titration for alkalinity, which was then statistically analyzed using multivariate analysis and Principle Component Analysis (PCA). For thermal spring and Fall River samples gathered in Hot Springs, SD, Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and titration for alkalinity was used to gather chemical data, and then statistical analysis in the form of a PCA, modeled after Zhang et al., and a Wilcox test were used for the chemical data (Hoang et al., 2010).

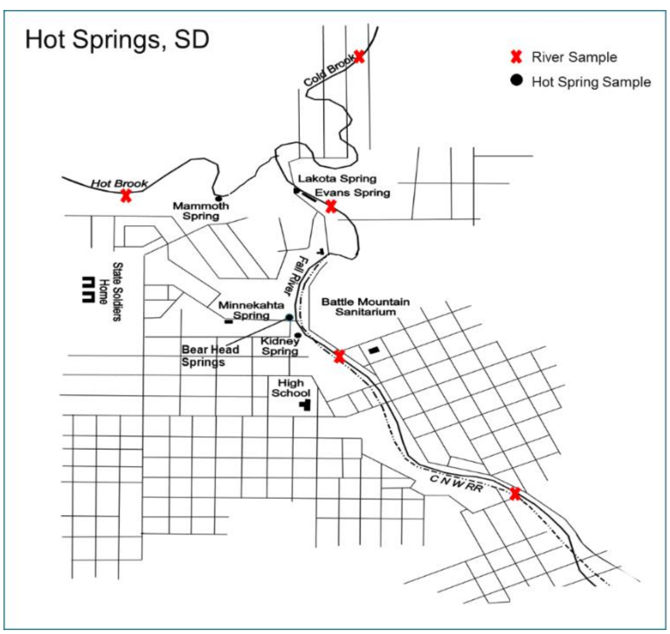


Figure 3. Spatial extent of the city of Hot Springs with sampled hot springs labeled and highlighted (Map adapted from John Lund 1997)

GEOLOGIC SETTING

The Black Hills region of western South Dakota contains rocks from Precambrian silty iron-rich sedimentary rocks to unconsolidated gravels deposited in present day stream beds. Some of the earliest events in the geologic record are the metamorphism and deformation of the silty iron-rich sedimentary rocks around 2.5 billion years ago (Ga). These metamorphic and tectonic events contribute to the current day geothermal conditions in Hot Springs, SD. Precambrian rocks were extensively eroded and uplifted to the surface around 550 Ma. Following this event, shales, siltstones, and sandstones overlay these rocks in a relatively uninterrupted sequence which then was deformed between 65-60 Ma during a regional uplift event that eroded many of the Paleozoic and Mesozoic rocks of the region and exposed Precambrian rocks in the center of the Black Hills. The Black Hills were partially covered by sediments from the highlands to the west 40-35 Ma; however, they have been largely exhumed since then. Erosion continues to modify the landscape today (Dewitt et al., 1986). This series of geologic events is what created the structural dome of the Black Hills.

The source aquifers for the hot springs in Hot Springs, SD are Permian to Cretaceous age sedimentary rocks such as the Minnelusa Formation, which crops out only in the Hot and Cold Brooks of the Hot Springs quadrangle. The rock layers exposed in this area are red brecciated sand stone beds and gray limestone beds. This area is overlain by the Permian and Triassic aged Spearfish Formation, a shale with low permeability that pinches out at the upper north-west corner of the quadrangle (Wolcott, 1967). This is then followed by the Jurassic age Sundance Formation and finally the Cretaceous age Inyan Kara Group. This group includes the Lakota and Fall River formations consisting of limestones and crossbedded fluvial sandstones that interfinger with mudstones (Wolcott, 1967) (**Figure 4**). The Inyan Kara Group forms the main outcropping unit within the town of Hot Springs (Driscoll et al., 2002).

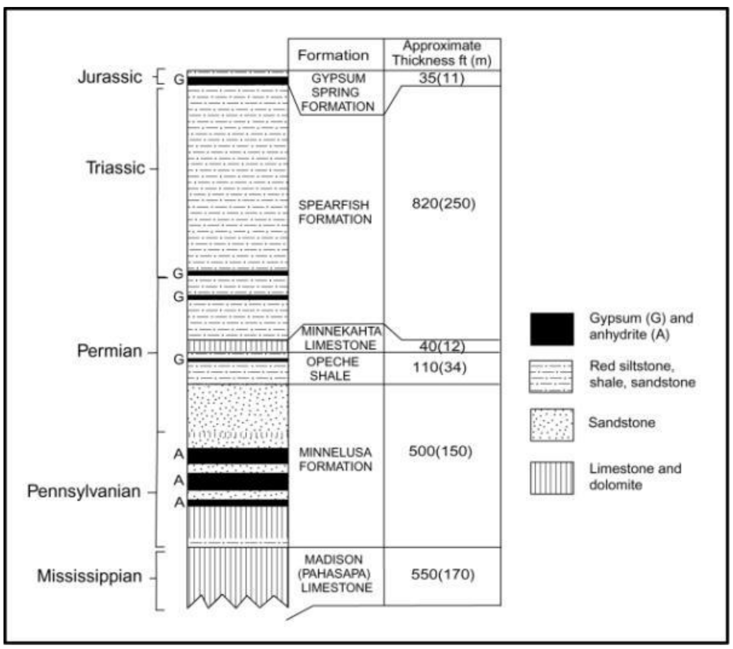


Figure 4. Section of stratigraphy column that is used to describe the Hot Springs quadrangle. The units of Spearfish formation, Gypsum Spring formation, Sundance formation, Unkpapa, and Morrison formation are not outcropping in Hot Springs. The Inyan Kara formation sits atop the Unkpapa sandstone in this area with a thickness of 201.1 m at its thickest point (Driscoll et al. 2002).

Geothermal resources are bound in the strata in the Great Plains, which occurs by both conductive; (transfer of heat through a surface); and advective, (the transfer of heat by flow of a liquid); processes. In these sedimentary basins thick layers of shale with low thermal-conductivity overlie regionally continuous sandstone and carbonate aquifers. Generally, in this basin area, there are high geothermal gradients in the thicker sections of the low-thermal conductivity shales that are producing high temperatures for the aquifers that underlie the shale. In advective areas, gravity-driven flow of groundwater carries heat from the deeper parts of the basin to the edges. Thermally insulating shales and geothermal areas enhanced by advective groundwater flow is mainly located in western area of South Dakota (**Figure 5**) (Lund 1997)

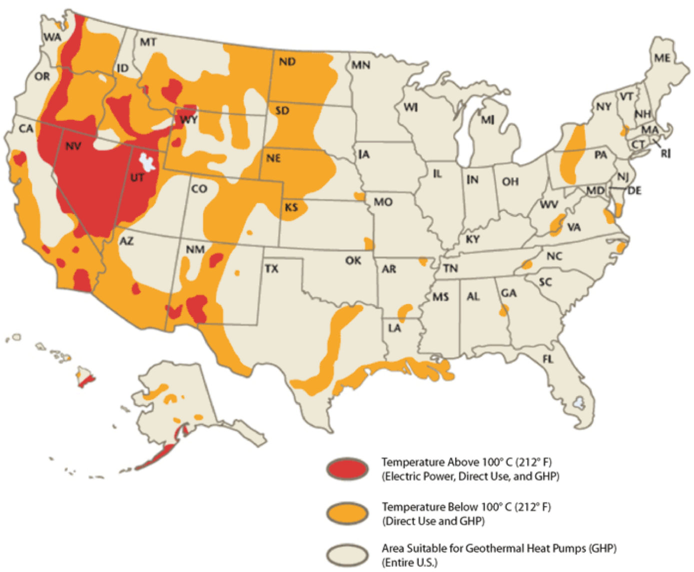


Figure 5. Geothermal energy in the form of ground temperature in thermal belts in the United States (geology.com).

The thermal springs that are located in Hot Springs (**Figure 3**) and around the Hot Springs area originated because the water table is intersecting the ground surface, or alternatively flowing through a spring conduit. The latter is more likely as these conduits have been detected underground in the subsurface in the Madison Limestone and Minnelusa Formations (Darton et al., 1925). The Madison Group comprises a carbonate sequence of rocks Mississippian in age with a thickness varying from zero to 400 m (Lund, 1997). In addition, the Madison Limestone contains water with temperatures that range from 30°C to 112°C with an average porosity of 8%. Recharge for this unit primarily occurs during infiltration of snowmelt and rain, as well as creek beds in the outcrop area in the Black Hills (Lund, 1997).

The surface water hydrology in the Black Hills is mostly controlled by subsurface geology. The Precambrian rocks have generally low permeability; low permeability and the addition of deformation events create fracture systems that provide limited yields from wells (Miller and Driscoll, 1998). The Tertiary rocks in this area contain similar permeability to the Precambrian rock. Many of the sedimentary units within the Black Hills are aquifers (Madison, Minnekahta, Minnelusa, Inyan Kara) to which recharge is largely due to precipitation upon outcrops and stream infiltration (Miller and Driscoll, 1998) Conditions that produce artesian wells generally exist where an upper confining layer is present. Flowing wells and artesian springs that originate from confined aquifers are common on the perimeter of the Black Hills region as can be seen in the case of Hot Springs with the pinching out of the shale Spearfish Formation. The loss of this low-permeability layer allows the spring water to reach the surface.

The Fall River has an average discharge of 25 ft^3/second according to the Fall River Gauging station maintained by USGS. Much of the flow of the fall river can be attributed to Evan's Plunge spring, which discharges 5,000 gal/min into the fall river, which translates to 11.14 ft^3/sec, almost half of the Fall River's average flow (Agenbroad et al., 2005). Half the flow of the Fall River is confirmed to come from Evan's plunge, which means that flow is consistent even in the middle of summer, since the Fall River is groundwater-hot spring fed.

METHODS

A. Sampling methods

Samples were collected from eight hot springs, and 11 river locations to total 19 samples. Samples were taken from hot spring sources using polyethylene bottles, collecting directly from output sources until at least 250 mL was reached within the sample bottle. For Fall River samples, the bottle was filled six inches under water to insure no floating particulates were included within the water sample. Bottles were filled as close as possible to the top. After 250 mL was reached, the cap was put on tightly to prevent further oxidation reactions in the container before samples could be processed. Two sample bottles were filled from each location; one bottle was nitrified with 2.5 mL of 2% nitric acid and the other was left as unaltered for alkalinity analysis.

B.

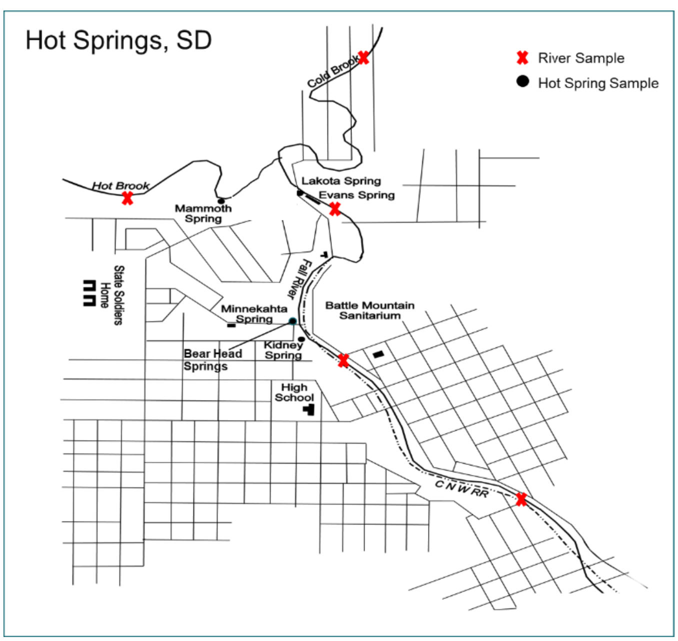


Figure 6. Hot Springs, SD sample sites for hot springs and rivers, three river samples are not listed, and 3 hot spring samples are off the map (adapted from John Lund 1997). See **Figure 12** for a comprehensive map of all sample locations.

At the point of collection, the parameters of temperature, pH, and conductivity were measured using a YSI Pro Plus probe for temperature and pH, and a Hydrolab probe for conductivity. These values were recorded for each sampling location. At each sample location a GPS point was taken and recorded using an Etrex hand held GPS unit.

C. Analytical methods

Non-nitrified samples from each source were titrated for alkalinity using pH (Zhang et al., 2018). Each sample was titrated in triplicate using 25 mL of sample per titration. Samples were agitated before being measured in a graduated cylinder to ensure total mixing. 12M HCl was diluted using a 250 mL volumetric flask, diluting to a concentration of .001M HCl. The .001M HCl was placed in a burette as the titrating agent. The 25mL of sample was placed in a beaker with a magnetic stir bar, that was kept at a constant speed as the sample was titrating to a pH of 4 using a calibrated pH meter. The pH meter was calibrated to a pH of 4 and a pH of 7 before beginning titration. pH was recorded when titration began and ended, as well as total volume of HCl used. The calculation used to determine alkalinity used:

$$\frac{\text{Average volume of HCl used (mL)* .001 M* 50,000}}{\text{25 mL}}$$

For elemental analyses, 1.0 mL of nitrified sample was placed in Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) polyethylene vials with caps along with 8.9 mL 2% nitric acid, and 100 µL of internal standard containing Bi, Ln, Li6, Sc, Tb, and Y. After caps were added, samples were mixed four times to insure the mixing of the internal standard. The elements analyzed were Na, Mg, K, Ca, Co, Ni, Al, V, Cr, Mn, Fe, Cu, Zn, Ga, Ge, As, Se, Rb, Mo, Sb, Cs, Pb, U, and Ti. The first calibration standards that were used 0 ppb, 10 ppb Majors, 30 ppb Majors, 40 ppb Majors, .5 ppb, 1 ppb, 5ppb, 10 ppb. After the samples were run 1 time through, a second batch was run with calibration standards of 10ppb, 20 ppb, 30 ppb, 40 ppb to better match observed concentration range of elements in the samples.

D. Statistical methods

Data analysis was primarily completed using the statistical analysis program R to determine elemental and water quality parameter significance between hot spring and river samples. This was done using a .05 significance level for the Wilcox test in R. The Wilcox test, also known as the Mann-Whitney test is used to test the null hypothesis. We chose a known confidence rate of 95% to determine significant differences between two datasets, in this case between hot spring and river samples for each element (Hoang et al., 2010). Other methods used include Principal Component Analysis (PCA) through PCA diagrams and a PCA biplot. Principal Component Analysis uses orthogonal transformation to convert data values that are potentially correlated into a set of linear variables known as principal components. These plots the data to be seen in different dimensions allowing for maximizing potential groupings of variables (Zhang et al. 2018).

Additional data analysis was done using Excel to generate comparative tables and graphs to display hot spring and river data.

RESULTS

Twenty-seven elements were successfully measured in 8 hot springs and 11 river samples. Data collection methods of ICP-MS and titration for alkalinity yielded numeric results for each of the 19 samples taken in Hot Springs, SD. In addition to these chemical characterization methods, temperature, specific conductivity, and pH were also measured for each sample taken.

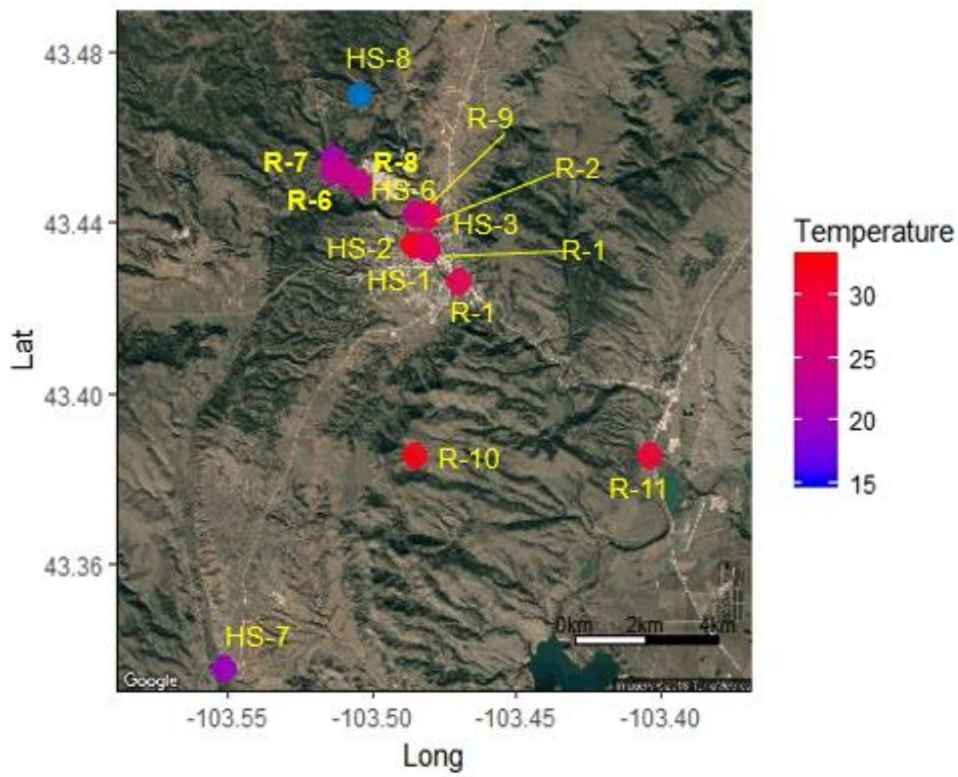


Figure 7. Map locality of Hot Springs, SD and surrounding region with each point representing a sampling location, with a gradiant of colors per temperature in degrees Celsius. While many of the springs range from 22-25°C there is one colder sample site and one very hot sample site on the upper range of the temperature gradient. Spatial maps generated in R overlain on a Google terrain map of Hot Springs, SD.

Temperature trends for samples between hot springs and rivers generally show hot spring samples with higher temperature values than river samples (**Figure 6**). This can further be broken down into distinct groupings of spatially similar samples, broken into different temperature categories. The northernmost grouping includes temperature values from 20-25 degrees Celsius, while the group just southeast contains a combination from 25-30 degrees

Celsius. This trend, with the exception of HS-8 identified as a cold spring (15°C), seems to be increasing in temperature encompassing both hot springs and rivers moving north to south through the town of hot springs. Temperature, in similarity to specific conductivity, contains a wider range of temperature values between hot springs and rivers. Maximum temperature in hot springs was 33.2°C taken from HS-4 with a low of 15°C from HS-8 now classified as a cold spring. The average temperature for hot springs with the cold spring, HS-8, thrown out is 28.8°C while the average temperature for rivers is 25.5°C. River samples 1 and 4 have values close to the average for hot springs at 28.5°C and 28.4°C respectively (Appendix A).

The maximum specific conductivity in hot springs was 1365 µS/cm, with the rivers lying between 505.9 µS/cm and 996.4 µS/cm. The average specific conductivity value for hot springs is 939.1 µS/cm and for rivers is 706.9 µS/cm. Specific conductivity was not measured for HS-7. In contrast with specific conductivity, pH appears stable between hot springs and river samples. The average pH for hot springs is 6.96 and for rivers is 7.65. There is a single outlier within pH for the entire dataset (hot springs and rivers) which is R-11 at a pH of 8.18. The sample R-11 was collected from the Cheyanne River after confluence with the Fall River. These averages computed without outlier samples HS-8, R-10, and R-11 are 6.84 for hot springs and 7.65 for rivers. Average alkalinity for hot springs was 22.6 mEq/L and for rivers was 34.1 mEq/L. These data displayed one outlier with an alkalinity of 34.12 mEq/L given by HS-8 the cold spring. The locations HS-6, R-5, and R-7 were not measured for alkalinity (**Table 1**).

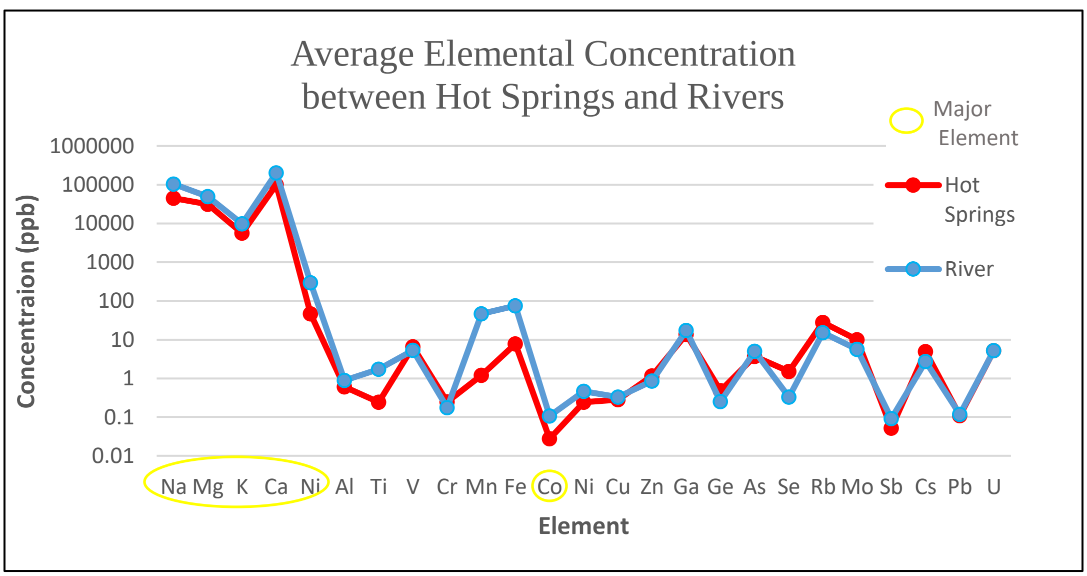
Source	**Sample**	**Alkalinity**	**Temperature**	**pH**	**Spc**
River	R-1-17	27.06	28.5	7.84	966.4
Hot Spring	HS-1-17	20.77	26.8	6.82	1084
River	R-4-17	26.82	28.4	7.05	834
Hot Spring	HS-4-17	20.75	33.2	6.88	1365
River	R-5-17	0	21.2	7.85	599.5
Hot Spring	HS-5-17	20.81	31	6.9	989
River	R-2-17-UNDI	27.06	27.7	7.65	964.2
Hot Spring	HS-2-17-UNDI	19.81	28.6	6.88	1230
River	R-3-17-UNDI	27.13	27.6	7.73	959.4
Hot Spring	HS-3-17-UNDI	20.48	30.1	6.88	1365
River	R-6-17	25.88	23.3	7.37	513.8
Hot Spring	HS-6-17	0	32.2	6.89	988.5
River	R-7-17	0	23.9	7.44	510.2
Hot Spring	HS-7-17	22.07	19.7	6.69	0

River	R-8-17	24.77	24.6	7.82	508.8
Hot Spring	HS-8-17	34.12	15	7.75	491
River	R-9-17	23.12	25	8.18	505.9
River	R-10-17	20.84	32.7	7.6	2296
River	R-11-17	19.43	30.7	7.7	2276

Table 1. Measured values for pH, temperature, specific conductance, and alkalinity measurements per each source.

The minimum value for specific conductivity is 491µS/cm measured from HS-8, the cold spring (T = 15°C). Water quality parameters including Specific Conductivity (spc), temperature, pH and Alkalinity all have differing trends within hot spring and river spatial distribution (**Figure 7**). Spc does not seem to have a distinct trend between having higher values in either hot springs or rivers, which can also be seen from a p-value greater than .05 which is the significance level used for this study (**Table 2)**. pH is relatively uniform between all points with only HS- 2 differing from the average of 7.4 to 7.8. Similar to pH, alkalinity is constant between points, only smaller than 20 g/mL when it is zero as it is for two samples within the study R- 7 and HS- 7 for which non-nitrified samples were not taken. Temperature shows similarity in location groupings with differences in temperature primarily located between different groups and not within individual samples within groups (**Figure 7)**.

Samples had characteristic elemental values, with some anomalies. I considered the elements Na, Mg, K, Ca, Co, and Ni are major elements due to characteristic large concentrations while Ti, V, Cr, Mn, Fe, Cu, Zn, Ga, Ge, As, Se, Rb, Mo, Sb, Cs, Pb, and U are considered trace elements (Appendix A). General trends given by **Figure 7** show high concentrations of majors, and lower concentrations of trace elements. Major element data show elemental Ca for both hot spring and river samples at 100,000 ppb while Ni shows a low with values between 100-500 ppb. Within the trace elements, Mn and Fe have higher concentrations in river samples, nearing 100 ppb. Additionally, Rb and Mo show a higher concentration of approximately 10 ppb in both hot springs and rivers within the trace elements.



An example of an anomaly is the .46 ppb value in HS-5 which is the highest of all samples measured for lead. The same spring with the Pb anomaly also contained the only aluminum detected for the entire data set with a concentration of 4.87 ppb. All values for U are under 6 ppb but generally higher in hot springs than rivers.

The gallium concentration in HS-8 is 70.7 ppb with and average concentration of Ga in springs and rivers combined is only 13 ppb. Additional outliers for Fe include HS5 with a concentration of 42.8 compared to the hot spring average of 2.73 ppb, and R-5 with a concentration of 25 ppb compared to the river average of 6.62 ppb. Considering all elemental data, Co varied the most between its minimum and maximum values within the dataset. The minimum Co value given by HS-1 is 31.4 ppb while the maximum value is 1173 ppb from HS-4. This spread continues for rivers with a minimum of 21 ppb for R-1 and a maximum of 1848 ppb for R-9.

A Wilcox test indicates that Ca, Ni, Mn, Ga, Mo, Se, and pH are significantly different in hot spring and river water ($p < 0.05$) (**Table 2**). A slightly different trend can be seen within Figure 7 as the elemental differences between hot spring and river water are mainly apparent for Ni, Ti, Mn, Fe, and Se. There are only three overlap elements between **Table 2** and **Figure 1**, Ni, Se, and Mn. A second Wilcox test was done without the outlier samples HS-8 (a cold spring), R-10 and R-11 (collected from Cheyanne River). This resulted in 12 total significance values: Ca, Cr, Ge, As, Rb, Cs, U, Ga, Mo, Se and pH and Specific Conductivity as water quality parameters.

Na	.128	Zn	.492	Alkalinity	.300
Mg	.062	Ga	.040**	Temperature	.442
K	.090	Ge	.050	pH	.002
Ca	.020**	As	.206	Specific Conductivity	.432
Co	.544	Se	$2.6461x10^{-5}$**		
Ni	.015**	Rb	.062		
Al	.794	Mo	.025**		
V	.177	Sb	.050		
Cr	.128	Cs	.062		
Mn	.032**	Pb	.237		
Fe	.075	U	.177		
Cu	.716	Ti	.062		

Table 2. Wilcox statistical tests completed for all elements comparing elemental concentrations in hot spring and river sources with p-values given for each element. A Significance value of .05 was used to establish statistical difference and is indicated by **. This grouping of p-values includes identified outliers. Six out of 24 elements were identified as significant, Ca, Ni, Mn, Ga, Mo, and Se as well as pH as a water quality parameter.

Na	.09	Zn	.114	Alkalinity	.055
Mg	.054	Ga	.005**	Temperature	.054
K	.054	Ge	.016**	pH	.0009**
Ca	.011**	As	.041**	Specific Conductivity	.019**
Co	.918	Se	.0002**		
Ni	.071	Rb	.011**		
Al	.313	Mo	.002**		
V	.210	Sb	.090		
Cr	.016**	Cs	.041**		
Mn	.173	Pb	.83		
Fe	.351	U	.001**		
Cu	.757	Ti	.252		

Table 3. Wilcox statistical tests completed for all elements comparing elemental concentrations in hot spring and river sources with p-values given for each element without outlier values of HS-8, R-10, and R-11. A Significance value of .05 was used to establish statistical difference and is indicated by **. This grouping of p-values includes identified outliers. Twelve out of 24 elements were identified as significant, Ca, Cr, Ge, As, Rb, Cs, U, Ga, Mo, Se and pH and Specific Conductivity as water quality parameters.

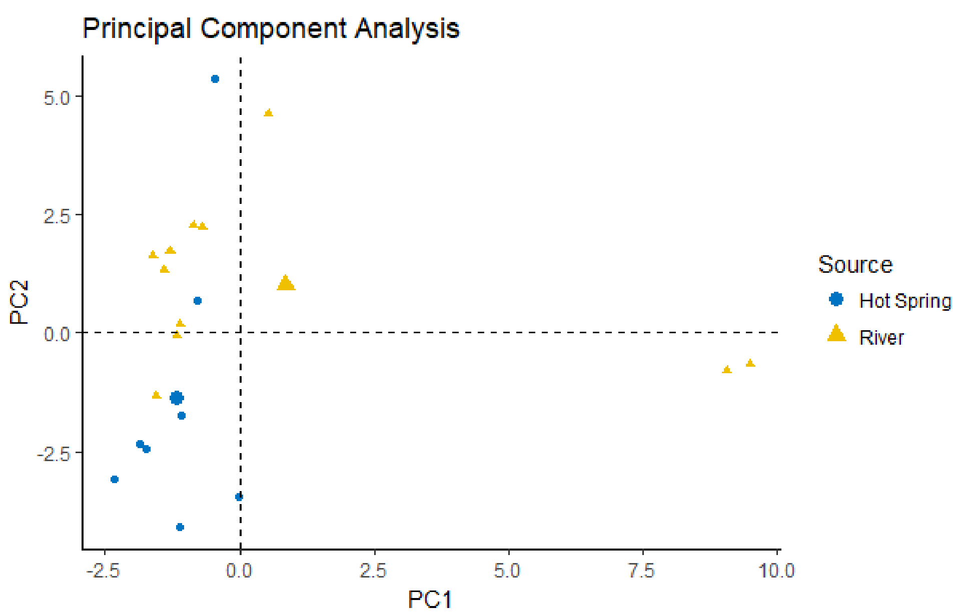


Figure 9. Principal Component Analysis (PCA) for hot spring and river samples. Larger circle and triangle are the averages for hot springs and rivers. There are two distinct outliers to the far right, which are points 18 and 19, or R 10 and R 11 collected from the Cheyanne River.

PCA plots use an orthogonal transformation to convert a data set of potentially correlated variables into sets of values along two principal component axis. PCA essentially works as a grouping variable organizing the data across different components. According to **Figure 8** the majority of the hot spring samples lie together in the negative quadrant for both PC1 and PC2, and river samples occur most often in the positive PC2, negative PC1 quadrant The large triangle and the larger circle show the means of the samples for each water type. The average for rivers is being largely skewed right due to the two outliers seen in the PC1 positive-PC2 negative quadrant.

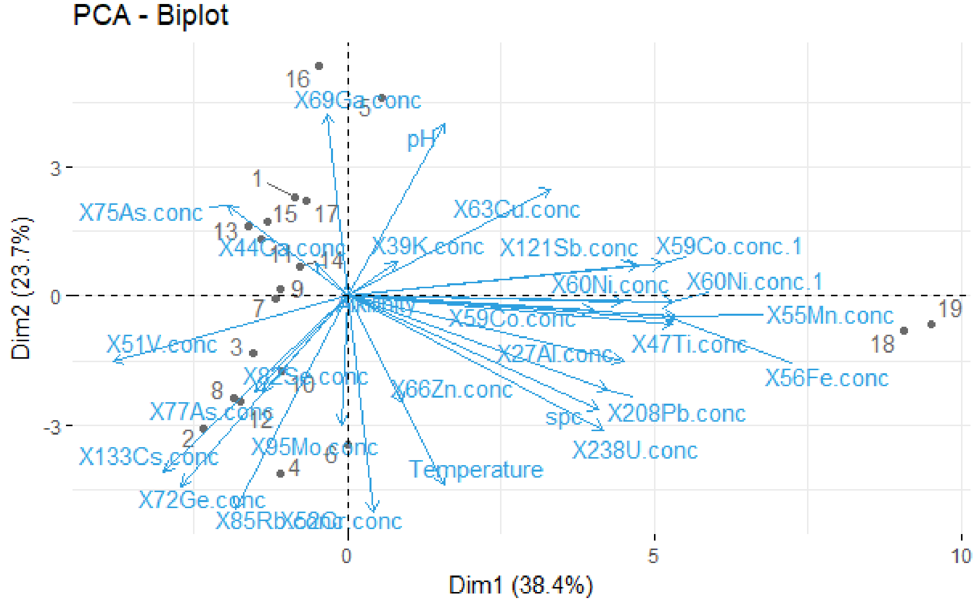


Figure 10. PCA Biplot displaying elemental and parameter trends in dimensional space. Co, Ni, Mn, Fe, Ti, Pb, and U are largely affected by outlier points 18 and 19 representing River sample 9 and 10.

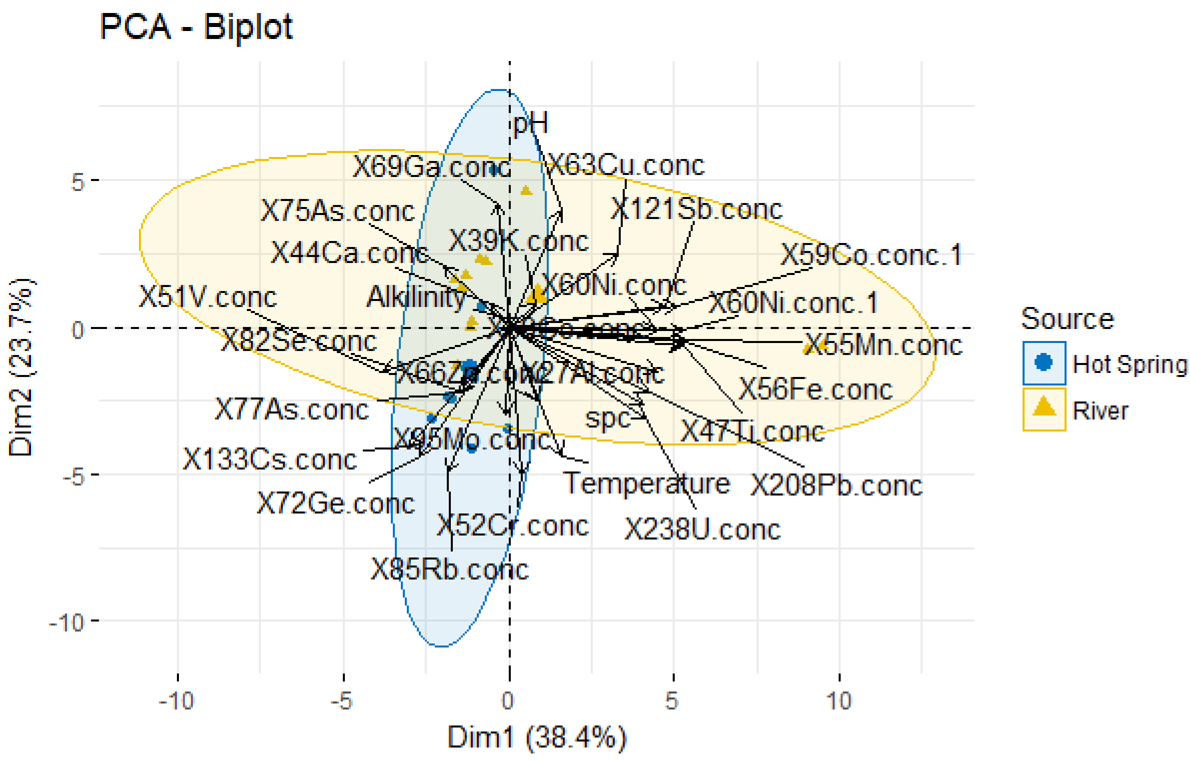


Figure 11. PCA Biplot with ellipses highlighting an east-west trend along the second dimensional axis for river data and a north-south trend along the first dimensional axis for hot spring data within two-dimensional space for hot spring and river data.

The first principal maximizes the variance when data are projected onto a line and the second dimension is orthogonal to it, and maximizes the remaining variance. Using the first two axes should yield the better approximation of the original variables space when it is projected onto a plane. The distribution of data given by **Figure 10** for hot springs is largely along the vertical axis of dimension 1 while the river data are along the horizontal axis of dimension 2. Elemental data is largely influenced by outliers seen first in **Figure 9** but again in **Figures 10 and 11** of which river data trends are largely skewed east-west because of outlier points 18 and 19. This gives elemental concentration trends of Co, Ni, Mn, Fe, Ti, Pb, and U trending towards outlier points in two-dimensional space. Ellipses help to highlight general trends within the two water sources showing that hot springs have elements such as As, Cs, Ge, and Rb trending strongly in direction of hot spring sample points, exerting the strongest influences over the elements within the PCA biplot space (**Figure 11**).

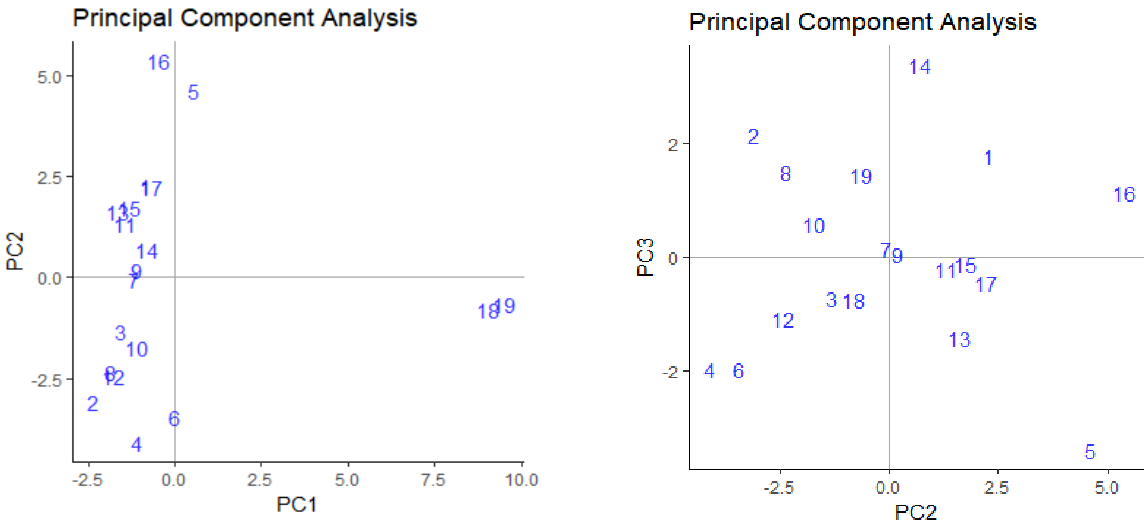


Figure 12. PCA diagrams in combinations of PC1, PC2 and PC2, PC3 showing notable outliers in 18 and 19 in PC1, PC2 and a more even spread within PC2 and PC3. Diagram key: numbers 1,3,5,7,9,11,13,15,17,18,19 are river samples, numbers 2,4,6,8,10,12,14,16 are hot spring samples.

Grouping and location of elements in PCA diagrams gives rise to showing different options for the distribution of samples given elemental similarities and trends, mainly within the PC1, PC2 the distinct outliers of points 18 and 19. Within PC2, PC3 this two-dimensional spaces offers a much more equally spread distribution of both hot springs and rivers, with no distinct groupings within the plot with the exception of potential outliers of 15, and 16.

Sample	Ca (ppb)	Ni (ppb)	Mn (ppb)	Ga (ppb)	Mo (ppb)	Se (ppb)	pH (SU)
HS-1	121,143	37.91	0.16	5.44	9.51	5.84	6.82
HS-4	107,783	174.9	0.23	7.80	9.13	0.62	6.88
HS-5	156,118	42.91	6.57	7.00	7.57	0.67	6.9
HS-2	156,666	40.38	0.22	5.02	11.99	2.65	6.88
HS-3	67,163	23.29	0.31	5.49	12.56	0.60	6.88
HS-6	66,058	10.89	1.67	6.48	7.46	0.53	6.89
HS-7	66,370	15.82	0.20	2.09	18.70	0.56	6.69
HS-8	64,422	28.68	0.18	70.73	2.51	0.60	7.75
R-1	157,079	26.24	0.54	2.79	2.48	0.18	7.84
R-4	159,432	65.29	0.49	8.96	7.43	0.48	7.05
R-5	140,478	56.02	13.24	55.27	3.67	0.19	7.85
R-2	208,168	42.49	1.44	9.72	8.41	0.52	7.65
R-3	263,052	93.64	1.59	9.94	8.48	0.37	7.73
R-6	126,829	29.20	2.96	22.38	4.85	0.39	7.37
R-7	556,665	185.3	0.18	22.32	3.06	0.33	7.44
R-8	83,251	84.01	1.14	22.02	3.56	0.32	7.82
R-9	267,499	587.7	2.39	21.08	4.25	0.29	8.18
R-10	271,702	552.8	259.0	7.1	7.55	0.29	7.6
R-11	336.6	1544.7	228.2	7.51	7.83	0.24	7.7

Table 4. Table of elements and pH values that were determined to be significantly different between hot springs and rivers.

Elements that displayed significance trends between hot springs and rivers were mapped in the Hot Springs area with concentration displayed via an increasing size trend per ppb as noted in the legend in **Figures 8 and 9**. This graphical representation of the locations of concentrations between samples best displays the variation between samples within a close distance. Ga concentration in **Figure 9** is seen to be largest at hot spring 8 which is the only point near to its concentration within the area, and is south of the town of Hot Springs. Other concentrations of Ga are fairly uniform within the remainder of the sample sites. Rivers 10 and 11 have a larger distinctive concentration for Mn, but this is not the case for the concentration of Mo of which river 10 and 11 are uniform size but hot spring 7 stands out as the largest concentration of Mo at the most southern point on the map. Ca shows smaller concentration trends within hot springs, and larger concentration trends within rivers. Nickel concentration is most distinctive at river 11 which is the largest concentration on the map, and seemingly an outlier, which can be verified by **Part 2** in Appendix A.

DISCUSSION

This study shows that hot spring and river samples are generally similar in elemental concentration, which suggests that the Fall River chemistry is largely controlled by the input of spring water. Trends within the data are evaluated in several ways including water quality parameters such as pH, temperature, spc, and alkalinity, followed by elemental trends, and finally national water quality standards. This chemical analysis showed the data had strong elemental similarities within each type of water evaluated (hot spring and river) when the data were analyzed statistically (**Figures 7, 8, and 9**).

Water Quality Parameter Trends (temperature, pH, specific conductance, and alkalinity)

The hydrothermal connection in Hot Springs, SD between hot springs and river samples is evident through the chemical analysis of major and trace elements analyzed with statistical analysis as well as through field data observed on site. Elements that were significant within the dataset included Ca, Ni, Mn, Ga, Mo, and pH as a water quality parameter. Surprisingly, temperature was not significantly different between hot springs and rivers which was probably largely impacted by a few outlier values such as hot spring 8 which had a temperature of 15 degrees Celsius, as indicated by **Figure 6**. This would bring the temperature grouping down for hot springs leading to a lower difference between river values and spring values. Hot spring 8 for sampling purposes was a hot spring, but clearly after temperature data was analyzed it is a cold spring. Thermal water temperatures have range from 15°C upwards of 30°C (**Figure 6**). This range of values for hot springs was being compared to a stable river value where most river samples were around 25 degrees Celsius a few a little warmer. This variation could have been due to the time of year and the weather, as rivers are relatively shallow and have no stable temperature due to exposure to the elements, unlike thermal water which is stored deep underground. It was mid-July and mid-day on a sunny 36°C day when the river samples were taken, so an average effect of warming on the surface water would be expected.

The water quality parameter of pH would be expected to change from hot springs to river as river water is exposed to environmental changes, but spring water has not yet interacted with the surficial environment. A Wilcox test shows a p-value for the pH water quality <.05, indicating that pH in hot springs and river water differ. River water, overall, has a higher pH than the springs, likely because it interacts with surface material, biological activity, and the atmosphere as it moves downstream, while pH of springs was measured from the exact point the spring water was exiting the rock layer.

Alkalinity, a body of waters ability to neutralize an acid, seems to be fairly uniform throughout all measurements according to **Figure 7**. This can be verified by looking at table 5 in Appendix B, as all balance between 20 and 30 meq/L with the exception of hot spring 8, which also had a temperature of 15 degrees Celsius. This value is clearly an outlier and is not part of the same hydrologic suite as the other springs perhaps stemming from a different aquifer. Alkalinity generally communicates how much Mg, Na, K, and Ca is within the water, the higher the amounts of these elements, the higher the alkalinity will be within the water body. This is due to the elements bonding to H+ ions which in effect is neutralizing acid, the definition of alkalinity. Calcium, one the elements that contributes to alkalinity was also statistically significant in terms of differentiating rivers from hot springs. In **Figure 8** there is a clear difference in size between the sample points, more specifically the rivers have an average calcium concentration of 203,136 ppb while hot springs only have an average Ca concentration of 100,716. This difference, similar to pH, could potentially be due to environmental factors and sample location such as taking the sample at the source of the hot spring, the water will not have come into contact with other environmental factors like fresh rock faces, or anthropogenic sources of calcium that water in a surface water source like the Fall River running through Hot Springs may have come into contact with, changing the concentration of the water.

Elemental Trends

The stratigraphy of the Black Hills region likely plays a part in unraveling the significance of the elements determined by the Wilcox test Ca, Ni, Mn, Ga, Se, and Mo. The water of the hot springs in the center of town and north of town is likely from either the Minnelusa or Minnekahta aquifers despite dissimilar water quality parameter measurements between the hot springs and the aquifers (**Table 5**). The spring discharge is likely not from the Inyan Kara group predominantly because this group outcrops in hot springs and is not low enough to be impacted by the thermal gradient, and does not have a low permeability cap rock. The spearfish formation that acts as a cap rock on the Minnelusa and Madison has low conductivity which contains the heat that the groundwater carries from deep underground (Driscoll et al., 2002). The town of Hot Spring's main aquifer for city use is the Inyan Kara aquifer for which most of its flow occurs through the sand stone members of this group. The Inyan Kara group, composed of the Fall River Sandstone and the Lakota interbedded shales, limestones and mudstones. The sandstones in the Inyan Kara group create permeable channels that can carry groundwater up to 66 ft/yr (Rahn, 2014), which could be another avenue, in addition to breccia pipes from the Minnelusa formation that could be carrying springs up to the surface (Naus et al., 2001). The Minnelusa aquifer was sampled to have a specific conductivity of between 500 and 1,500 (ms/cm) for thermal springs in Hot Springs (Naus et al. 2002). This value compared to the average specific conductivity in my thermal spring water samples which were measured to be 1073.2 (ms/cm). This similarity in specific conductance could indicate that the water coming up through the springs originates from the Minnelusa Aquifer. Ultimately, we are unable to say definitively which aquifer the water is sourcing, due to a limited number of samples, short test period, and small test area.

Elementally, R- 9 and R- 10 were the largest outliers, representing points 18 and 19 on the PCA diagrams in **Figure 4 and 5**. These river samples were spatially different enough, and far enough away from the other points to have a significantly different elemental distribution. This skewed the PCA diagrams for PCA1, PCA2 as well as had a large influence on elemental trends when ellipses were applied to the data. Of the five significant elements, two (Ni and Mn) were heavily influenced by these points, noting their trends on the PCA biplot in **Figure 4**. The other three (Ca, Ga, and Mo) largely has trends dominated by hot springs, indicating that the higher concentration of these elements could set apart hot spring water from river water. Due to the outliers and skewedness of the data in terms of river samples, it is unlikely to be able to draw the same conclusions for Ni and Mn, in being able to uniquely identify river water. The presence of hot spring elements such as Ca, Ga, and Mo in the river water, although lower concentrations it was still present, indicates a mixing between hot springs and river water. Perhaps, as the hot springs feed into the Fall River, the hot spring water with larger concentrations of Ca, Ga, and Mo becomes diluted still containing the elements, but not at as notable a concentration as the hot springs. In **Figure 11** the ellipses overlap which means these two water datasets have many chemical similarities.

Furthermore, after the first data set was processed statistically and the outliers HS-8, R-10, and R-11 were found to be outliers skewing the dataset, the data was run again without these values. Once the data was re-analyzed, a Wilcox test showed twelve elements with significant differences between hot spring and river samples, an increase of six from the previous dataset (**Table 3**), despite the fact that the total range of values decreased for most elements. After evaluating the averages for each element numerically within hot spring and river categories, it was determined that for eleven of the twelve elements (Ga being the exception), the concentration of elements is higher in the hot spring samples, suggesting that a more concentrated hydrothermal fluid is being diluted by surface waters. This means that as the water from various hot springs flows into the Fall River, it is experiencing mixing with various other water sources and is becoming more dilute in elemental concentrations (Appendix A).

Minnelusa Aquifer	
Parameter	**Mean**
Specific Conductance	783 µS/cm
pH	7.4
Temperature	16°C
Alkalinity	206 mg/L
Madison Aquifer	
Parameter	**Mean**
Specific Conductance	632 µS/cm
pH	7.4
Temperature	19°C
Alkalinity	203 mg/L

Hot Springs sample Averages	
Parameter	**Mean**
Specific Conductance	1170.25 µS/cm
pH	6.96
Temperature	27.07°C
Alkalinity	20.78

Table 5. Water quality parameters for the Minnelusa and Madison aquifers, compared to data collected from hot springs in this study excluding sample HS-8 (Williamson and Carter, 2001).

Comparison to national water quality standards

Part of this study is in obligation to spring owners to determine chemical constituents within their water in comparison to national water quality standards. All standards used are from U.S. Environmental Protection Agency (USEPA) (1994) (**Table 6**). The state of South Dakota in accordance with the USEPA set limits for contaminant levels in drinking water in 1986 (Williamson and Carter, 2001). For all springs, sampled water quality parameters are well below the maximum acceptable contaminant levels for trace elements in drinking water. In contrast, one Cheyenne River sample was well above the standard for Co at 1848.7 μg/L after its confluence with the Fall River. This high level of Co is may be due to unidentified natural sources in the Cheyenne watershed, or something similar to mining pollution. The concentrations of other metals in this sample including Ni (1,544 ppb), Mn (228 ppb), and Fe (335 ppb) were also very high relative to the other samples in this study (Appendix A). The high concentration of metals is cause for further research in the Cheyenne watershed.

In conclusion, these premiminary results indicate that the thermal springs and Fall River have low concentrations of potentially hazardous metals, through the same cannot be said for the Cheyenne River. This study is based on a relatively small number of samples, over a short sampling period, and water was not analyzed for bacterial components which would be necessary to deem the water completely safe for drinking water.

Parameter/Element	**USGS Water Quality Limits**	**Water samples taken for this study**
pH	6.5-8.5	All pH within interval
Al	50-200 μg/L	Below Standard
As	50 μg/L	Below Standard
Cr	100 μg/L	Below Standard
Co	1,300 μg/L	R-11 is above standard at 1848.7 μg/L
Fe	300 μg/L	Below Standard
Pb	15 μg/L	Below Standard
Mn	50 μg/L	Below Standard
Ni	No current standard	All values are not above 1 μg/L
Zn	5000 μg/L	Below Standard
U	30 μg/L	Below Standard

Table 6. Elements listed in USGS water quality report as elements dangerous in high concentrations that overlap with elements tested in this study. Table does not display a comprehensive list of elements that were tested (Williamson and Carter, 2001).

Conclusion

The hot springs in Hot Springs, SD influence the chemistry of the Fall River, which runs through the town of Hot Springs. This was supported by the statistical difference of only 5 elements and pH between hot spring and river samples. Few of the elements such as Mn were only characterized as significantly different due to outlier data samples that were taken from the Cheyanne River. Samples R-10, R-11, and HS-8 were found to be not a part of the same hydrologic suite as the rest of the samples taken in the study due to extreme differences in elemental values and water quality parameters. Additionally, the data was evaluated statistically a second time without the previously identified outliers, in which 10 elements and two water quality parameters were identified as significantly different. This finding is best explained by dilution within the river water, as every element, with the exception of Ga, had a higher concentration in the hot spring samples than in the river samples.

Both the thermal springs and the Fall river have elemental concentrations lower than USEPA determined water quality standards for all 16 samples taken in this area. The water flowing from the thermal springs could not be sourced directly to an aquifer with the data gathered in this study. Aquifer sourcing is outside the scope of this study but could be a question addressed in a future project in Hot Springs, SD.

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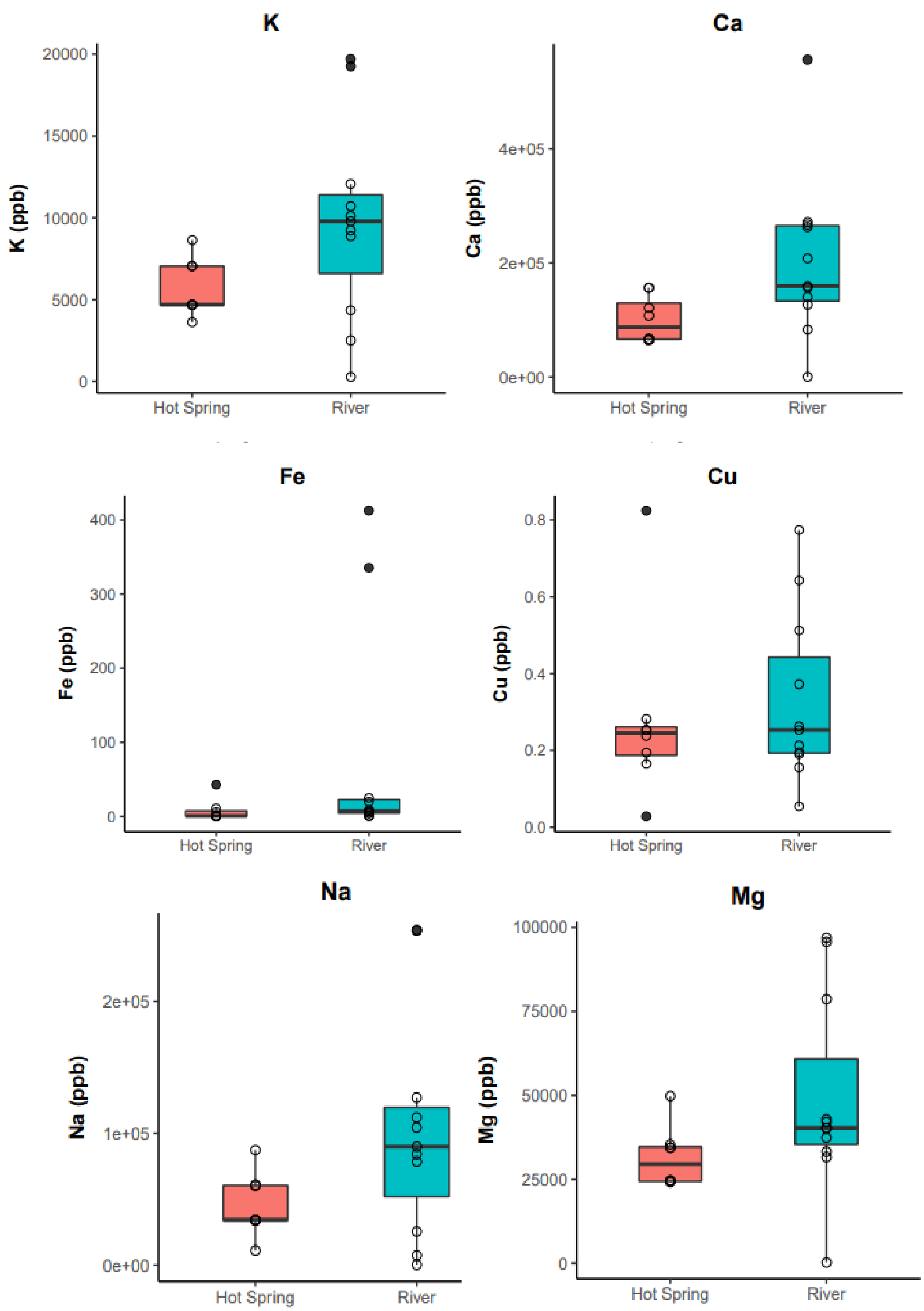
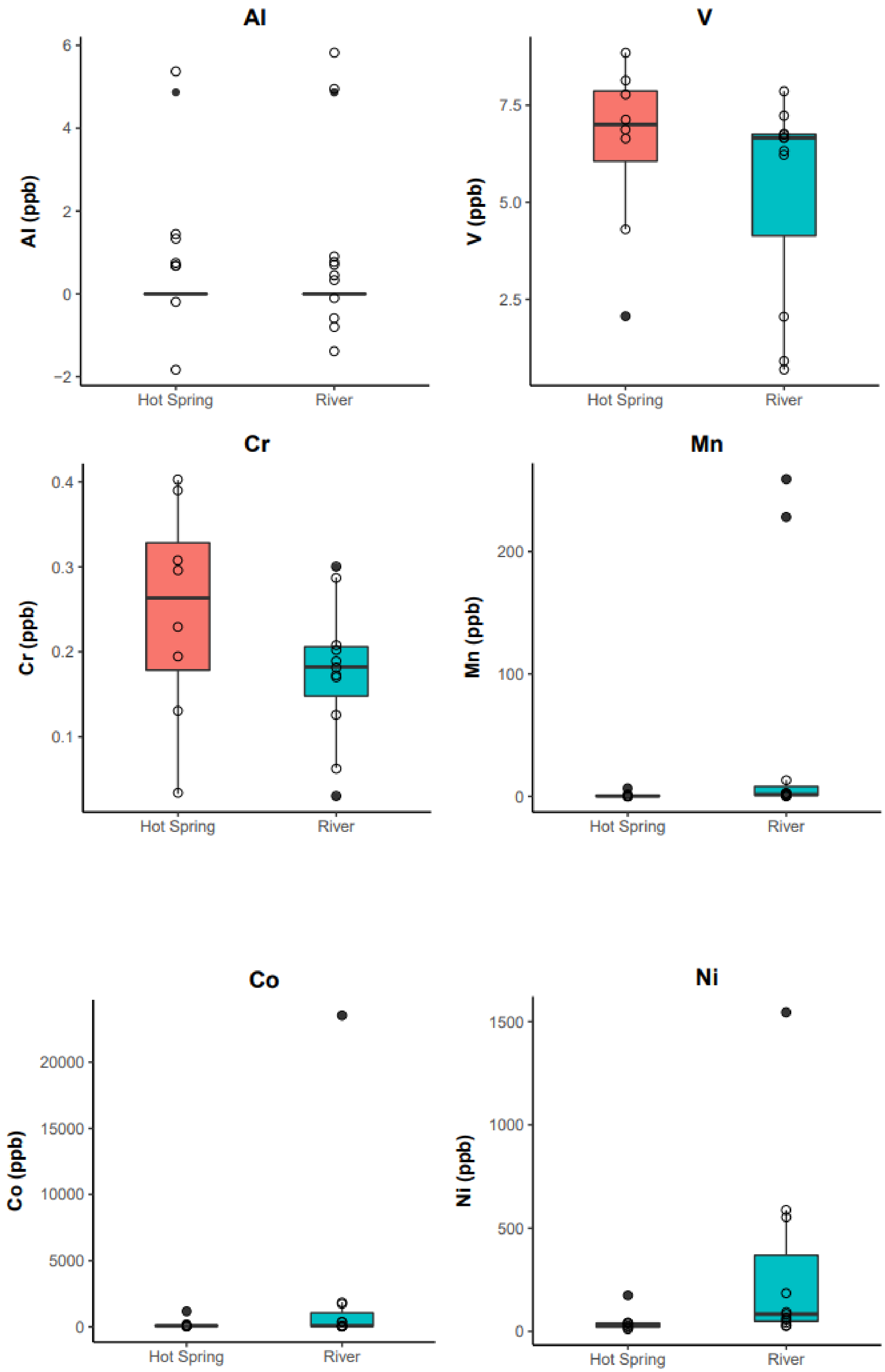
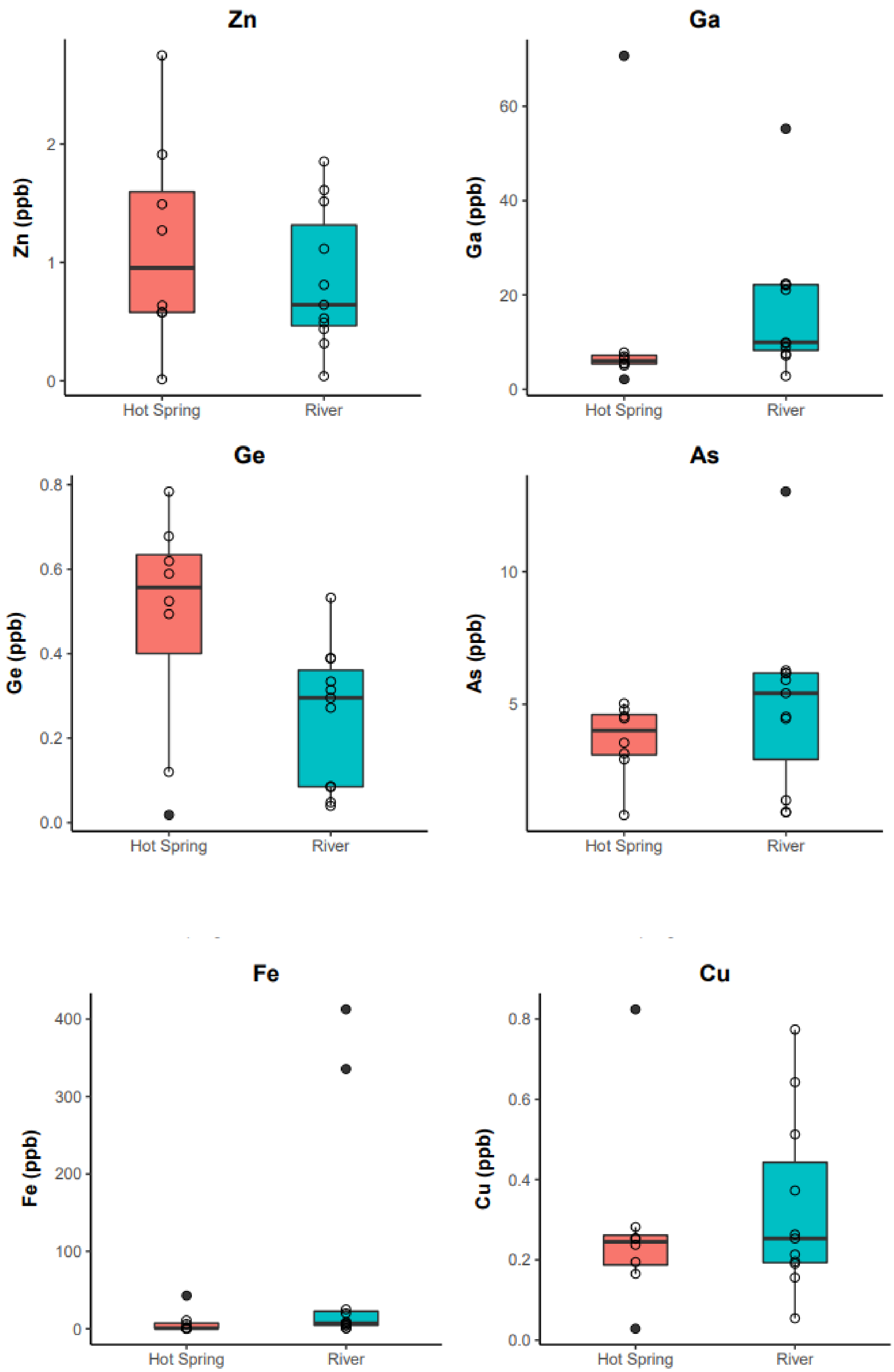
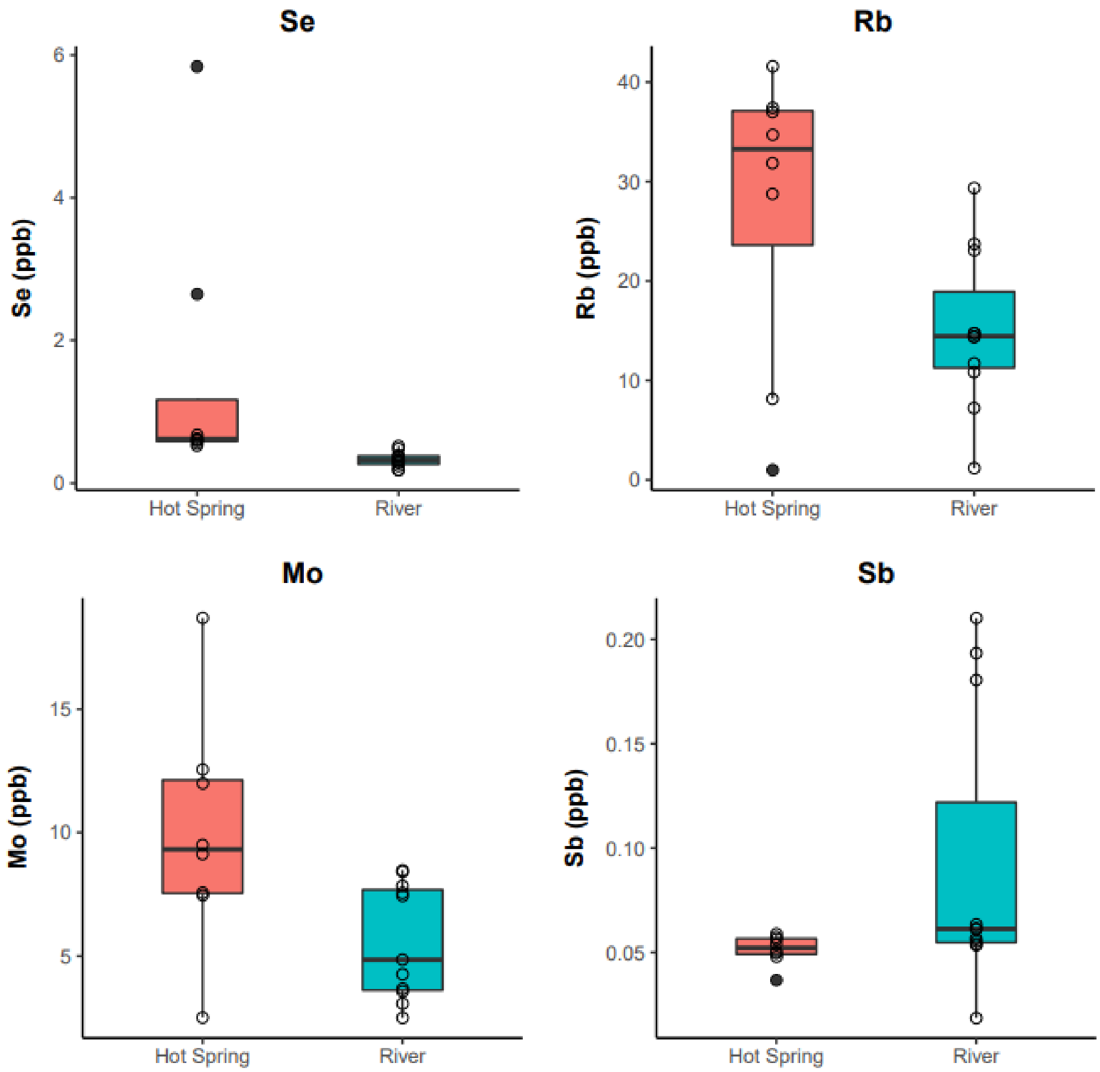
APPENDIX A

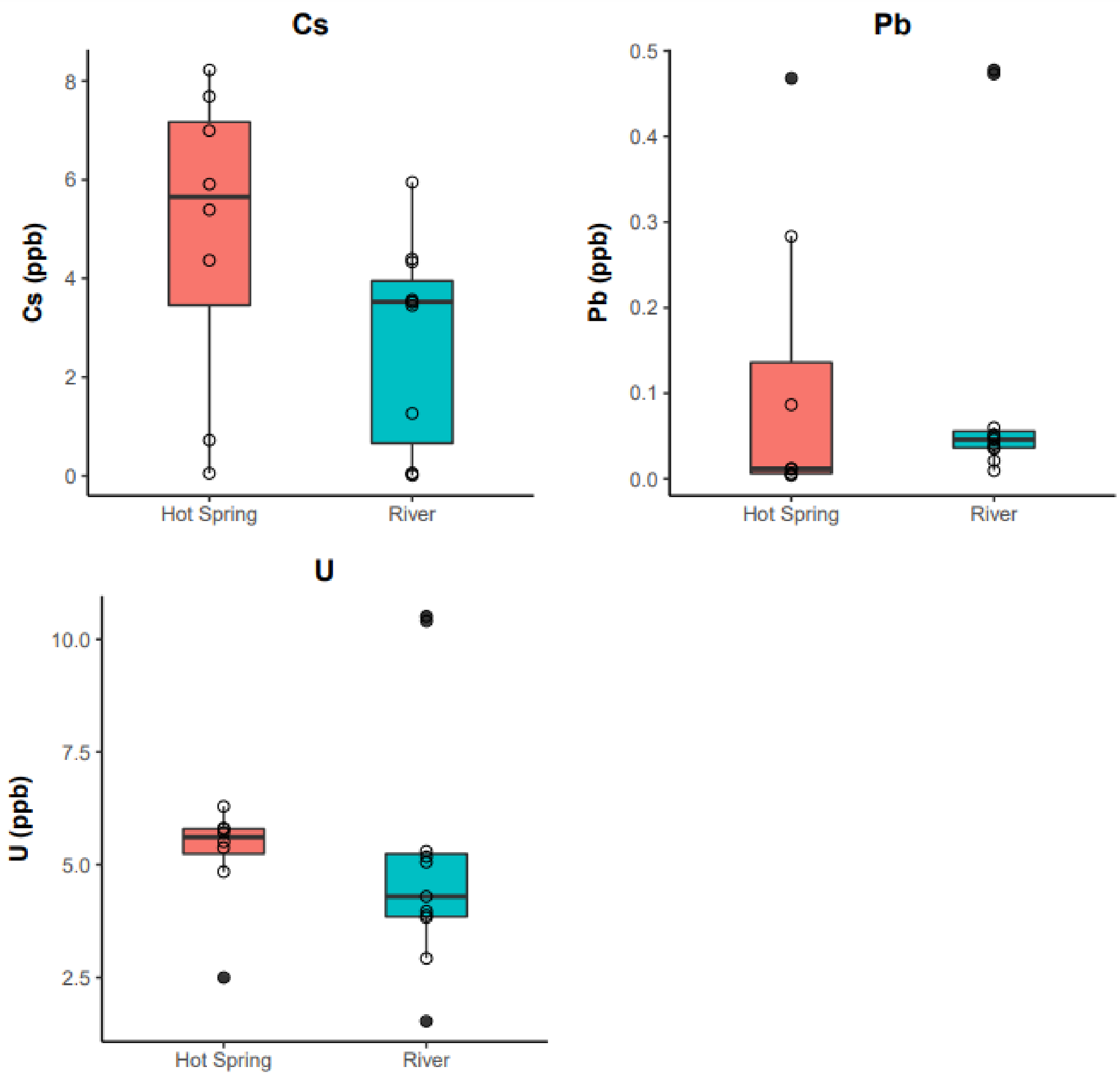
Part 1. All box plots used to visualize statistical significance.




Al
Al (ppb)
6
4
2
0
−2
Hot Spring
River
V
V (ppb)
7.5
5.0
2.5
Hot Spring
River
Cr
Cr (ppb)
0.4
0.3
0.2
0.1
Hot Spring
River
Mn
Mn (ppb)
200
100
0
Hot Spring
River
Co
Co (ppb)
20000
15000
10000
5000
0
Hot Spring
River
Ni
Ni (ppb)
1500
1000
500
0
Hot Spring
River


Zn
Zn (ppb)
Ga
Ga (ppb)
Ge
Ge (ppb)
As
As (ppb)
Fe
Fe (ppb)
Cu
Cu (ppb)
Hot Spring
River


Se
Se (ppb)
Hot Spring
River
Rb
Rb (ppb)
Hot Spring
River
Mo
Mo (ppb)
Hot Spring
River
Sb
Sb (ppb)
Hot Spring
River


Cs
Cs (ppb)
0
2
4
6
8
Hot Spring
River
Pb
Pb (ppb)
0.0
0.1
0.2
0.3
0.4
0.5
Hot Spring
River
U
U (ppb)
2.5
5.0
7.5
10.0
Hot Spring
River

Part 2. Elemental Statistics.

Hot Springs	
Cu	Min: N/A 1st Qu: N/A Median: .245 Mean: .2798 3rd Qu: .261 Max: .824
Zn	Min: .012 1st Qu: .578 Median: .953 Mean: 1.15 3rd Qu: 1.59 Max: 2.74
Ga	Min: 2.08 1st Qu: 5.3 Median: 5.9 Mean: 13.8 3rd Qu: 7.2 Max: 70.7
As	Min: .82 1st Qu: 3.08 Median: 4.0 Mean: 3.6 3rd Qu: 4.6 Max: 5.02
Se	Min: .525 1st Qu: .586 Median: .614 Mean: 1.5 3rd Qu: 1.16 Max: 5.8
Rb	Min: .99 1st Qu: 23.6 Median: 33.2 Mean: 27.5 3rd Qu: 37.1 Max: 41.5
Mo	Min: 2.5 1st Qu: 7.54 Median: 9.3 Mean: 9.9 3rd Qu: 12.12 Max: 18.6
Sb	Min: .04 1st Qu: .05

	Median: .05 Mean: .05 3rd Qu: .05 Max: .05
Cs	Min: .05 1st Qu: 3.45 Median: 5.65 Mean: 4.9 3rd Qu: 7.1 Max: 8.2
Pb	Min: .003 1st Qu: .006 Median: .01 Mean: .109 3rd Qu: .13 Max: .46
U	Min: 2.492 1st Qu: 5.43 Median: 5.6 Mean: 5.23 3rd Qu: 5.795 Max: 6.3
Alkalinity	Min: 0 1st Qu: 20.2 Median: 20.76 Mean: 19.85 3rd Qu: 21.12 Max: 34.12
Temperature	Min: 15 1st Qu: 25.02 Median: 29.35 Mean: 27.07 3rd Qu: 31.3 Max: 33.2
pH	Min: 6.7 1st Qu: 6.8 Median: 6.88 Mean: 6.9 3rd Qu: 6.8 Max: 7.75

Spc	Min: 0 1st Qu: 864.1 Median: 1036.5 Mean: 939 3rd Qu: 1263.8 Max: 1365
River	
Cu	Median: .253 Mean: .329 3rd Qu: .44 Max: .77
Zn	Min: .039 1st Qu: .46 Median: .64 Mean: .85 3rd Qu: 1.31 Max: 1.85
Ga	Min: 2.7 1st Qu: 8.23 Median: 9.9 Mean: 17.1 3rd Qu: 22.1 Max: 55.2
Ge	Min: .04 1st Qu: .08 Median: .29 Mean: .25 3rd Qu: .36 Max: .53
As	Min: .92 1st Qu: 2.9 Median: 5.4 Mean: 5 3rd Qu: 6.1 Max: 13.02
Se	Min: .183 1st Qu: .26 Median: .32 Mean: .32 3rd Qu: .37 Max: .51

Rb	Min: 1.17 1st Qu: 11.2 Median: 14.4 Mean: 15 3rd Qu: 18 Max: 29.3
Mo	Min: 2.4 1st Qu: 3.6 Median: 4.8 Mean: 5.59 3rd Qu: 7.6 Max: 8.4
Sb	Min: .01 1st Qu: .05 Median: .06 Mean: .09 3rd Qu: .12 Max: .2
Cs	Min: .007 1st Qu: .65 Median: 3.52 Mean: 2.73 3rd Qu: 3.95 Max: 5.9
Pb	Min: .009 1st Qu: .03 Median: .04 Mean: .1 3rd Qu: .05 Max: .47
U	Min: 1.5 1st Qu: 3.8 Median: 4.298 Mean: 5.17 3rd Qu: 5.2 Max: 10.51
Alkalinity	Min: 0 1st Qu: 20.2 Median: 24.8 Mean: 20.2 3rd Qu: 26.9 Max: 27.1
Temperature	Min: 21.2 1st Qu: 24.3 Median: 27.6 Mean: 26.7

	3rd Qu: 28.5 Max: 32.7
pH	Min: 7.1 1st Qu: 7.5 Median: 7.7 Mean: 7.6 3rd Qu: 7.8 Max: 8.2
Spc	Min: 505.9 1st Qu: 512 Median: 834 Mean: 994 3rd Qu: 965.3 Max: 2296

Part 3. PCA Diagram Numerical Data

PCA after outliers R10 and R11 were excluded distribution for PC1 and PC2 per elemental distribution.

Element	PC1	PC2
39 K	-0.155	0.059
44 Ca	-0.107	0.048
59 Co	0.298	-0.051
60 Ni	0.294	-0.053
27 Al	0.222	-0.121
47 T	0.299	-0.063
51 V	-0.181	-0.121
52 Cr	-0.031	-0.336
55 Mn	0.301	-0.042
56 Fe	0.301	-0.052
59 Co	0.276	0.068
60 Ni	0.294	-0.003
63 Cu	0.136	0.214
66 Zn	0.001	-0.148
69 Ga	0.012	0.283
72 Ge	-0.140	-0.303
75 As	-0.067	0.140
77 As	-0.077	-0.140
82 Se	-0.073	-0.136
85 Rb	-0.094	-0.334
95 Mo	-0.011	-0.186
121 Sb	0.242	0.065
133 Cs	-0.147	-0.290
208 Pb	0.205	-0.173
238 U	0.194	-0.250
Alkalinity	-0.009	0.013
Temperature	0.033	-0.307
pH	0.097	0.261
Spc	0.189	-0.208

PCA distribution for PC1 and PC2 per elemental distribution

Element		
39 K	0.044	0.055
44 Ca	-0.029	0.053
59 Co	0.219	-0.022
60 Ni	0.246	-0.008
27 Al	0.247	-0.105
47 T	0.291	-0.044
51 V	-0.210	-0.105
52 Cr	0.022	-0.352
55 Mn	0.294	-0.033
56 Fe	0.293	-0.037
59 Co	0.281	0.052
60 Ni	0.291	-0.009
63 Cu	0.182	0.174
66 Zn	0.049	-0.175
69 Ga	-0.018	0.295
72 Ge	-0.419	-0.309
75 As	-0.107	0.146
77 As	-0.082	-0.156
82 Se	-0.076	-0.154
85 Rb	-0.101	-0.345
95 Mo	-0.005	-0.209
121 Sb	0.260	0.051
133 Cs	-0.164	-0.285
208 Pb	0.233	-0.153
238 U	0.229	-0.217
Alkalinity	-0.001	0.019
Temperature	0.087	-0.306
pH	0.086	0.281
Spc	0.225	-0.185

Part 4. Water quality parameters per sample.

Source	**Sample**	**Alkalinity**	**Temperature**	**pH**	**Spc**
River	R-1-17	27.06	28.5	7.84	966.4
Hot Spring	HS-1-17	20.77	26.8	6.82	1084
River	R-4-17	26.82	28.4	7.05	834
Hot Spring	HS-4-17	20.75	33.2	6.88	1365
River	R-5-17	0	21.2	7.85	599.5
Hot Spring	HS-5-17	20.81	31	6.9	989
River	R-2-17-UNDI	27.06	27.7	7.65	964.2
Hot Spring	HS-2-17-UNDI	19.81	28.6	6.88	1230
River	R-3-17-UNDI	27.13	27.6	7.73	959.4
Hot Spring	HS-3-17-UNDI	20.48	30.1	6.88	1365
River	R-6-17	25.88	23.3	7.37	513.8
Hot Spring	HS-6-17	0	32.2	6.89	988.5
River	R-7-17	0	23.9	7.44	510.2
Hot Spring	HS-7-17	22.07	19.7	6.69	0
River	R-8-17	24.77	24.6	7.82	508.8
Hot Spring	HS-8-17	34.12	15	7.75	491
River	R-9-17	23.12	25	8.18	505.9
River	R-10-17	20.84	32.7	7.6	2296
River	R-11-17	19.43	30.7	7.7	2276

Part 5. All Data Values from ICP-MS, concentrations given in ppb.

Sample	Na	Mg	K	Ca	Co	Ni	Al	Ti	V	Cr	Mn	Fe	Cu	Zn	Ga	Ge	As	As	Se	Rb	Mo	Sb	Cs	Pb	U
HS-1	87217	35424.89	8631.6	121143.8	31.05	37.91	0	0.06	7.13	0.3	0.16	0.04	0.17	0.58	5.44	0.59	3.55	26	5.84	34.7	9.51	0.05	5.91	0.01	5.79
HS-4	11058.35	49762.33	3634.78	107783.8	1173.67	174.94	0	0.09	8.85	0.4	0.23	0.45	0.28	2.75	7.8	0.78	5.03	3.56	0.62	41.58	9.13	0.06	8.23	0.28	6.3
HS-5	61046.54	34354	7067.24	156118.7	82.89	42.91	4.87	1.26	8.14	0.39	6.57	42.85	0.25	1.91	7	0.68	4.79	3.24	0.67	37.42	7.57	0.06	7	0.47	5.52
HS-2	60112.79	34450.77	7024.13	156666.4	91.41	40.38	0	0.08	6.87	0.23	0.22	6.05	0.03	0.64	5.02	0.52	2.92	13.92	2.65	31.84	11.99	0.05	5.39	0	5.81
HS-3	34409.64	24759.24	4702.85	67163.27	49.79	23.29	0	0	6.64	0.19	0.31	0.96	0.25	1.49	5.49	0.49	3.14	4.2	0.6	28.75	12.56	0.05	4.37	0.01	5.71
HS-6	33833.66	24240.32	4676.02	66058.69	21	10.89	0	0.26	7.77	0.31	1.67	10.98	0.19	0.58	6.48	0.62	4.54	3.92	0.53	37.01	7.46	0.05	7.69	0.09	5.38
HS-7	34103.86	24446.69	4678.84	66370.8	68.91	15.82	0	0.1	2.07	0.13	0.2	0.39	0.24	1.27	2.09	0.12	0.82	5.27	0.56	8.14	18.7	0.04	0.72	0.01	4.84
HS-8	34203.95	24348.03	4686.5	64422.48	184.21	28.68	0	0.07	4.3	0.03	0.18	0.25	0.82	0.01	70.73	0.02	4.46	3.69	0.6	0.99	2.51	0.06	0.05	0.01	2.49
R-1	104456.2	40274.44	10109.42	157079.3	21.59	26.24	0	0.12	2.05	0.06	0.54	4.22	0.05	0.31	2.79	0.09	1.38	0.79	0.18	7.22	2.48	0.02	1.27	0.04	1.52
R-4	127068	42061.49	12076.18	159432.8	32.02	65.29	0	0.22	7.23	0.29	0.49	0.56	0.2	1.52	8.96	0.53	5.42	2.7	0.48	29.36	7.43	0.05	5.95	0.04	5.31
R-5	112190.9	37493.58	10717.48	140478.7	357.84	56.02	0	0.27	7.86	0.03	13.24	25.11	0.64	1.85	55.27	0.05	13.03	0.83	0.19	1.18	3.67	0.18	0.01	0.05	2.93
R-2	84263.02	40290.03	9234.26	208168.3	30.07	42.49	0	0.11	6.67	0.2	1.44	6.76	0.16	0.64	9.72	0.39	4.45	2.72	0.52	23.73	8.41	0.06	4.4	0.05	5.18
R-3	78590.79	42920.97	8875.32	263052.8	40.12	93.64	0	0.24	6.74	0.19	1.59	7.09	0.21	0.53	9.94	0.39	4.53	2.88	0.37	23.07	8.48	0.06	4.33	0.05	5.05
R-6	89845.48	31655.89	9784.99	126829.1	74.11	29.2	0	0.22	6.32	0.17	2.96	4.67	0.26	1.12	22.38	0.31	6.19	2.24	0.39	14.73	4.85	0.06	3.53	0.02	4.3
R-7	25492.71	78617.84	4347.8	556665.4	82.48	185.32	0	0.06	6.22	0.18	0.18	0.76	0.25	0.44	22.32	0.33	5.91	2.76	0.33	14.43	3.06	0.05	3.52	0.01	3.82
R-8	7371.05	33306.72	2507.34	83251.62	369.21	84.01	0	0.19	6.66	0.17	1.14	8.81	0.37	0.49	22.02	0.3	6.28	2.5	0.32	14.35	3.56	0.06	3.57	0.04	3.88
R-9	253723.6	95651.4	19261.42	267499.9	1848.76	587.76	0	0.52	6.76	0.13	2.39	20.12	0.19	0.04	21.08	0.27	6.16	3.35	0.29	14.75	4.25	0.06	3.45	0.06	3.97
R-10	254201.9	96867.6	19694.97	271702.8	1733.47	552.84	4.87	9.65	0.91	0.3	259.09	412.84	0.77	1.61	7.1	0.08	0.93	1.96	0.29	10.84	7.55	0.21	0.05	0.47	10.51
R-11	324.72	289.16	279.31	336.28	23537.45	1544.72	4.87	7.46	0.69	0.21	228.21	335.65	0.51	0.81	7.51	0.04	0.94	1.78	0.24	11.72	7.83	0.19	0.05	0.48	10.41