

HYDROGEOLOGICAL CONTROLS OF URANIUM AND ARSENIC MOBILITY IN  
GROUNDWATER OF THE PINE RIDGE RESERVATION, SOUTH DAKOTA

by

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## ABSTRACT

This study integrates geochemical modeling, spatial analysis and several statistical methods such as principal component analysis, multivariate regression and cluster analysis to investigate hydrogeologic controls of arsenic and uranium contamination within groundwater of the Arikaree aquifer on the Pine Ridge Reservation (PRR). Located in southwestern South Dakota, geologic strata on the PRR are enriched with uranium and arsenic due to volcanic ash deposits emplaced into the White River Group, which unconformably underlies the Arikaree Group. Groundwater samples were obtained for over 250 wellbores through collaboration with the Oglala Sioux Tribe and Indian Health Service. Cluster analysis was used to delineate differences in these data between groundwater chemistry, and spatial analysis identified four regions, which represent upgradient, intermediate, and downgradient portions of the Arikaree aquifer. Groundwater alkalinity, sodium, and pH levels increase along flowpaths in the Arikaree aquifer despite rising carbonate mineral saturation indices, indicating that volcanic ash may act as a secondary source of alkalinity in the aquifer. Elevated alkalinity and pH levels are the primary drivers of arsenic and uranium mobility within the Arikaree aquifer, indicating that downgradient sections of the aquifer in the northern portions of the PRR are most likely to face impacts from groundwater contamination.

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Dedicated to my late grandmother, Deloris Whitehead, who passed away during the course of this study, but was, and will always remain an inspiration to me.

## CHAPTER 1

### GENERAL INTRODUCTION

Groundwater contamination poses serious risks to human health, especially in rural areas where many people rely on domestic wells tapped into local or regional aquifers. Many domestic wells undergo little to no treatment prior to consumption, leading to chronic exposure through daily intake if contaminants are present in the water. Such contamination can be the result of anthropogenic processes such as mining or industrial activity, as well as natural processes such as heavy metal mineral dissolution and leaching in areas with sizable (above average) bedrock and/or soil concentration. Over 130 million Americans use groundwater as their primary drinking water source and 22% of U.S. groundwater is impaired with contaminants, typically, arsenic, uranium, manganese or radon (DeSimone et. al, 2014). To protect potential drinking water sources, the U.S Environmental Protection Agency (EPA) constructed the Safe Drinking Water Act (SDWA) in 1974 (Tiemann, 2017). The SDWA established Maximum Contaminant Levels (MCLs) as baselines for contaminant concentrations in water that could be hazardous to human health. To date, over 90 MCLs have been established for organic pollutants, heavy metals, inorganic compounds, and disinfectants (U.S. EPA, 2015). However, these standards are only enforceable in public water systems and do not apply to single home groundwater wells.

The focus of this study is assessing controls of uranium and arsenic contamination on the Pine Ridge Reservation (PRR) in South Dakota. The PRR is located in southwestern South Dakota, and is home to the Oglala Sioux Tribe with a population of 18,834 (U.S. Census, 2010). Life on Native American reservations offers a stark contrast from the general United States, as

more than 25% of Native Americans live in poverty—twice the national poverty rate—and poverty rates approach 40% for Sioux and Navajo tribal populations (Ogunwole, 2006). Over 40% of housing on reservations is considered critically substandard, lacking proper sanitation (47%), basic electricity (14%), and/or safe drinking water (9%) (National Congress of American Indians (NCAI), 2017). Across the United States, Native Americans have life expectancy rates that are 5.5 years less than the overall U.S. population (73.0 years to 78.5 years, respectively) (IHS, 2018). Residents of the Pine Ridge Reservation have the lowest life expectancy in the United States at 66.8 years (Dwyer-Lindgren et al., 2017). Residents of the PRR face a number of disparities from health, housing, and environmental factors, and many residents of the PRR are subject to living conditions typically associated with developing world countries.

The Pine Ridge Reservation covers nearly 3500 square miles (~9000 sq. km), and is largely dominated by rural areas with a population density less than 10 people per square mile (U.S. Census, 2010). With such a dispersed population base, many people on the PRR rely on groundwater as their drinking water source through both domestic and small public supply systems (Davis et al., 2014). Much of the PRR is underlain by the Arikaree and Ogallala aquifers, which are both part of the High Plains aquifer system (Gutentag et al., 1984). Volcanic ash emplaced into the basal portion of the Arikaree Group and underlying geological strata acts as a source of uranium and arsenic on the PRR causing elevated levels of both metals in groundwater (Heakin, 1999). However, detailed information on uranium and arsenic occurrence, discrete sources, and hydrogeochemical conditions that alter mobility of these metals within the Arikaree aquifer is generally lacking and few published literature sources currently exist.

Indian Health Service (IHS), an agency within the U.S. Department of Health & Human Services, has funding to install water and sanitation infrastructure for rural homes on the PRR as part of their mission. Since 1990, they have installed over 250 domestic wells on the PRR, and performed water quality tests using established EPA standards on all of the wells they installed to ensure they provide safe drinking water. These water quality measurements were obtained through collaboration with the Martin Field Office of the IHS and the Oglala Sioux Tribe (OST).

The focus of this study was to quantify underlying hydrogeochemical controls of uranium and arsenic contamination on the PRR using various statistical and geochemical methods, characterize spatial trends of uranium and arsenic levels within the Arikaree aquifer on the PRR, and finally develop a conceptual model to aid future risk assessment, planning, and remediation efforts. The results of this project were compiled into a manuscript for submission to the journal *Science of the Total Environment*, presented in the next chapter.

## CHAPTER 2

### HYDROGEOLOGICAL CONTROLS OF URANIUM AND ARSENIC DISSOLUTION INTO GROUNDWATER OF THE PINE RIDGE RESERVATION, SOUTH DAKOTA

A paper to be submitted to *Science of the Total Environment*

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#### **2.1 Abstract**

This study integrates geochemical modeling, spatial analysis and several statistical methods such as principal component analysis, multivariate regression and cluster analysis to investigate hydrogeologic controls of arsenic and uranium contamination within groundwater of the Arikaree aquifer on the Pine Ridge Reservation (PRR). Located in southwestern South Dakota, geologic strata on the PRR are enriched with uranium and arsenic due to volcanic ash deposits emplaced into the White River Group, which unconformably underlies the Arikaree Group. Groundwater samples were obtained for over 250 wellbores through collaboration with the Oglala Sioux Tribe and Indian Health Service. Cluster analysis was used to delineate differences in these data between groundwater chemistry, and spatial analysis identified four regions, which represent upgradient, intermediate, and downgradient portions of the Arikaree aquifer. Groundwater alkalinity, sodium, and pH levels increase along flowpaths in the Arikaree aquifer despite rising carbonate mineral saturation indices, indicating that volcanic ash may act

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as a secondary source of alkalinity in the aquifer. Elevated alkalinity and pH levels are the primary drivers of arsenic and uranium mobility within the Arikaree aquifer, indicating that downgradient sections of the aquifer in the northern portions of the PRR are most likely to face impacts from groundwater contamination.

## **2.2 Introduction**

Native American tribal populations are known to face greater health concerns compared to other population groups in the U.S. (Jones, 2006). Part of this disparity is access to water; community water systems often underserve tribal populations, as many reservations are located in rural parts of the country with a dispersed population base. 8.9% of tribal homes lack access to safe drinking water, compared to 0.6% of non-Native American homes (IHS, 2008). Additionally, contamination is an issue; most tribal lands are located in the western United States, which coincides with the majority of U.S. heavy-metal mineral deposits; up to 75% of uranium mines in the U.S. are within 50 miles of a Native American Reservation (Shacklette & Boerngen, 1984; Blake et al., 2017; Lewis et al., 2017).

Heavy metal mineralization is often dispersed over tens to hundreds of kilometers resulting in non-discrete sources capable of affecting regional water quality (e.g., Colman, 2011; Focazio et al., 1999). Heavy-metal contamination in groundwater is typically attributed to anthropogenic activities such as mining operations and their subsequent industrial use. However, groundwater contamination can also occur by natural mineral dissolution, leaching, and transport in areas with localized high concentrations of uranium or arsenic in bedrock and/or soils (Braithwaite et al., 2008). The U.S. Environmental Protection Agency (USEPA) maximum contaminant levels (MCLs) for uranium and arsenic are 30 µg/L and 10 µg/L,

respectively (USEPA, 2000; USEPA, 2001), as these metals can have adverse health effects on the liver, heart, and kidneys, and are carcinogenic (Milvy & Cothorn, 1990; Smith et al., 1992). Quantifying controls of contaminant mobilization as well as transport pathways are crucial to assessing risk and developing planning and remediation strategies in tribal communities affected by heavy metal exposure.

Here, we explore controls on the mobilization of uranium and arsenic in groundwater on the Pine Ridge Reservation (PRR) in southwestern South Dakota. The PRR encompasses nearly 9000 km<sup>2</sup> roughly 75 km southeast of the Black Hills, the state's most prominent geological feature (Figure 2.1). The PRR is the seventh largest reservation by area in the U.S. and is home to the Oglala Sioux Tribe, which has approximately 19,000 people according to census data from 2010 (U.S. Census Bureau, 2010). The climate of the PRR is semi-arid, and the landscape is marked by rolling fields of prairie grasslands, broken by sandstone buttes in the south and undulating badlands in the north. Most land on the PRR is not suited for farming due to low rainfall and associated droughts, but many of the prairie grasslands are ideal for cattle ranching. Previous studies of water quality on the PRR have found elevated levels of uranium and arsenic in groundwater (Heakin, 1999; LaGarry & Yellow Thunder, 2012), and residents of the PRR have a 40% higher cancer mortality rate than the rest of the U.S. population (Rogers & Peterreit, 2005). Public health research suggests that tribal residents from the PRR are more likely to be exposed to uranium, arsenic, and tungsten than any other demographic group in the U.S. (Pang et al., 2016). Here, we focus on underlying hydrogeochemical controls of heavy metal dissolution and mobility on the PRR for which little to no published research exists. We apply several geostatistical methods to existing geochemical data, and complete geospatial mapping

of those data to assess whether any regions or geologic units are particularly susceptible to contamination impacts from uranium and arsenic dissolution. These analyses are then synthesized to develop a conceptual model for uranium and arsenic dissolution on the PRR based on local hydrogeology and geochemistry.

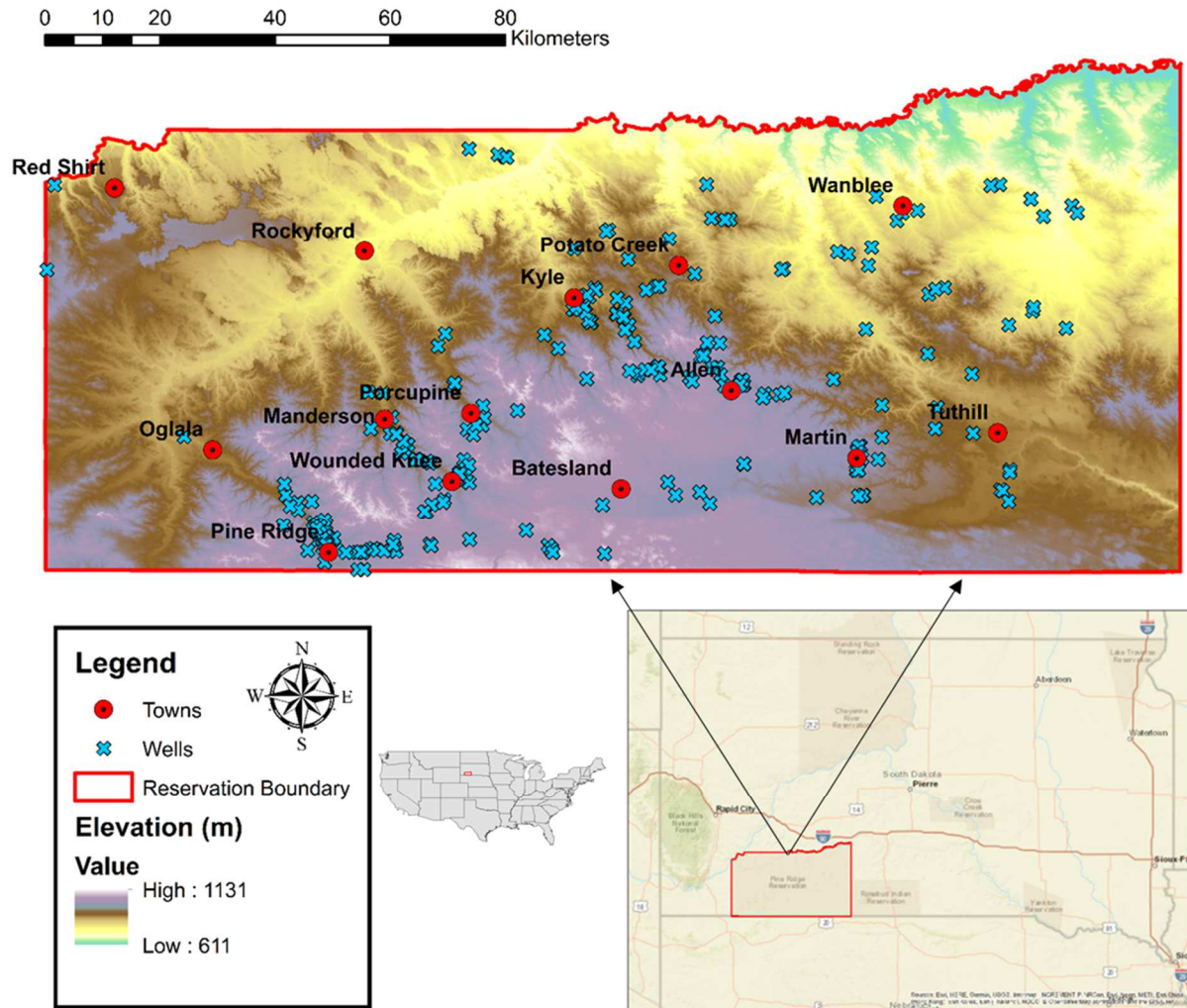


Figure 2.1: Map showing the extent of the Pine Ridge Reservation (PRR) in SW South Dakota. Groundwater well locations, surface elevation and town centers are also detailed on the map.

## 2.3 Background

### 2.3.1 Pine Ridge Reservation Geology

The source of uranium and arsenic on the PRR is mineralization from volcanic ash emplaced into the White River Group and Arikaree Group, which span parts of the PRR and the surrounding area (Figure 2.2; Table 2.1) (Carter et al., 1997; Heakin, 1999; Kipp et al., 2009). The Arikaree Group serves as the primary aquifer for domestic wells, and groundwater generally flows from south to north (Figure 2.2) (Carter & Heakin, 2007). The potentiometric surface of the Arikaree aquifer is controlled by surface topography and major rivers, as the Arikaree Group dips less than 1° (Rahn & Paul, 1975).

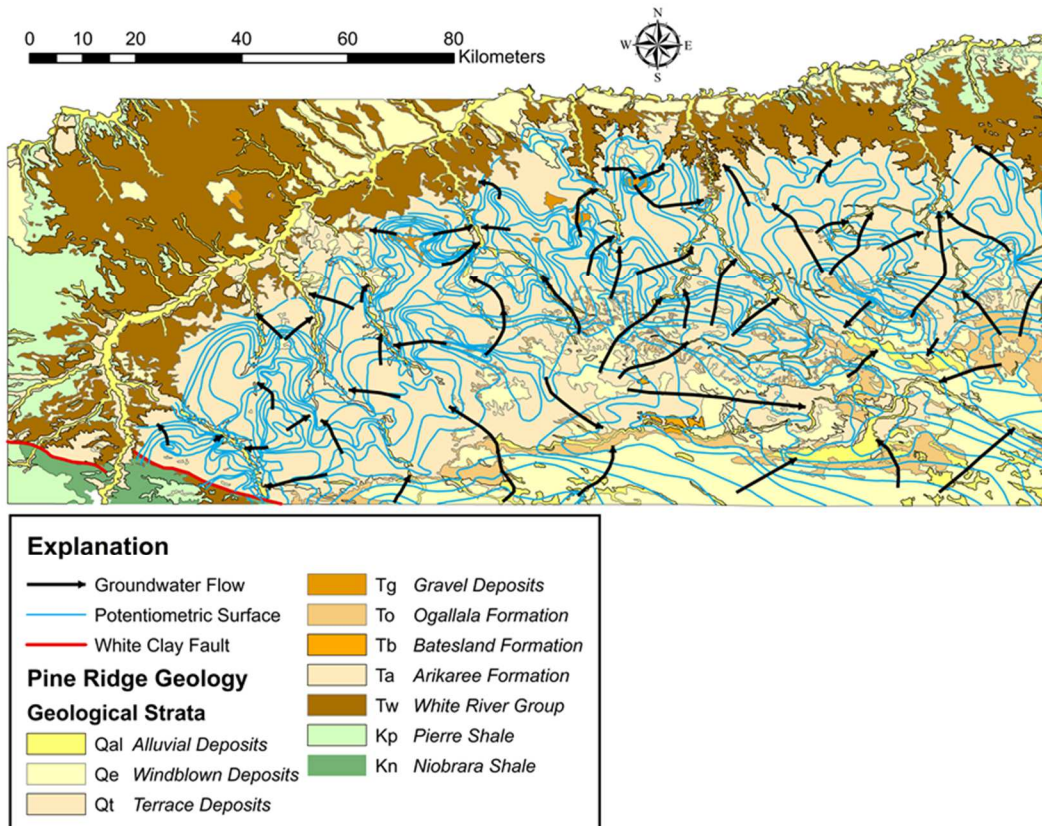


Figure 2.2: Map detailing geologic units of the PRR at a 1:500,000 scale (Martin et al., 2004) overlain by generalized groundwater flow lines for the PRR based on potentiometric contours (contour intervals of 15 m) of the Arikaree aquifer (Carter & Heakin, 2007).

Table 2.1: Stratigraphic column modified from Heakin (1999) detailing geologic formations present on the PRR. Thickness and lithology of the units and subunits (when present) are also noted.

Period:	Epoch:	Unit:	Subunit:	Thickness (m):	Lithology:
Quaternary	Holocene & Pleistocene	Alluvial, Eolian & Terrace Deposits		0-60	Sand, silty clay & gravel
Tertiary	Pliocene	Ogallala Formation		0-60	Tan, fine to medium grain sandstone
	Miocene	Batesland Formation		0-15	Cross-bedded sand interbedded w/ silts, clays & marls
			Arikaree Group	Unit E (Rosebud Form.)	0-72
			Unit D (Harrison Form.)	0-38	Fine, gray sand w/ marl, several pipey and spherical concretions
			Unit C (Monroe Creek Form.)	0-28	Fine grained sandstone & siltstone
			Unit B (unnamed)	0-115	Pinkish tan, consolidated silt and sand w/ limestone lenses and channel sands
			Unit A (Sharps Form.)	0-15	White, tan, & reddish brown volcanic ash interbedded w/ silt
	Oligocene	White River Group	Brule Form.	0-140	Yellow to brown, poorly consolidated siltstone & claystone
			Chadron Form.	0-34	Greenish-gray bentonite clay w/ alternating layers of siltstone
	Cretaceous	Upper Cretaceous	Pierre Shale		0-365
Niobrara Formation				0-100	Gray to tan, calcareous shale

The basal portion of the Arikaree Group is known as the Rockyford ash zone and has significant levels of volcanic ash, which are not sufficiently concentrated in U to be considered economic grade but could impact water quality (McConnell & DiBenedetto, 2012). However, the White River group is primarily composed of bentonite (weathered volcanic ash) and does contains ore-grade uranium mineralization. A major deposit (14 million kg  $U_3O_8$  with a grade in excess of 0.25% U by weight) was discovered in the White River Group near Crawford, Nebraska and this deposit is currently mined via in-situ leaching (Gjelsteen & Collings, 1988; Hansley et al., 1989). On the PRR, uranium mineralization is particularly favorable in paleochannels such as the remnants of the Red River Valley near Red Shirt (Raymond et al., 1976; Dickinson, 1993).

### **2.3.2 Uranium & Arsenic Geochemistry**

Uranium (U) has two oxidation states that are stable in natural environments: U(IV) and U(VI). The U(IV) phase exists under reducing conditions, and is generally considered to be immobile, as it forms insoluble minerals such as uraninite ( $UO_2$ ) (Adler, 1963). U(VI) predominates under oxic conditions, and is much more mobile as it forms several stable aqueous complexes with carbonate, as well as various hydroxyl complexes (Singh, 2010). Additionally, nitrate can mobilize uranium by oxidizing U(IV) to U(VI), particularly in shallow wells where infiltration rates exceed microbial reduction rates (Nolan & Weber, 2015). Coupled reactions with nitrate are especially important in agricultural areas since runoff from farming and ranching is generally high in nitrate. Together, redox chemistry, alkalinity, adsorption, complexation and nitrate levels typically co-control the fate and transport of uranium in subsurface environments (eg. Beaucaire & Toulhoat, 1987; van Berk & Fu, 2017; Zachara et al., 2013).

Arsenic (As) can occur in the environment in several oxidation states, but the most prevalent forms are arsenite (As(III)) and arsenate (As(V)). As(V) is generally more soluble than the more toxic As(III), and also has higher sorption affinity. Both arsenate and arsenite typically exist as oxyanions, and are stable over pH ranges typically found in groundwater in both oxidizing and reducing environments (Nordstrom et al., 2014). Arsenic mobility in groundwater is often controlled by sorption/desorption reactions with iron and manganese oxides, which are common components of sands, silts and clays (Bowell, 1994). As(III) and As(V) can occur together in groundwater due to redox disequilibrium (Bowell et al., 2014). Additionally, As(III) can also form complexes with carbonate in anaerobic conditions, which enhances its subsurface mobility (Lee & Nriagu, 2003). Arsenic mobility is difficult to generalize in subsurface environments given that it can be mobile over both oxidizing and reducing conditions. However, both As(III) and As(V) are influenced by sorption processes which can limit mobility of these species at lower pH levels.

## **2.4 Methods**

Geochemical data and wells logs were compiled from a sampling campaign conducted by the Indian Health Service (IHS) on the PRR. Part of IHS's mission is to provide clean and safe water and sanitation infrastructure to tribal lands, which commonly involves constructing domestic drinking water wells in remote locations. IHS installed over 250 domestic wells on the PRR between 1990 and 2016. Once well construction was completed, IHS then sampled wells for water quality including measurements of gross alpha, arsenic, pH, and major inorganic parameters such as alkalinity, nitrate (NO<sub>3</sub>), sulfate (SO<sub>4</sub>), sodium (Na), potassium (K), magnesium

(Mg), iron (Fe), chloride (Cl), fluoride (F), manganese (Mn), and barium (Ba). Geological strata, well screen depth, and total borehole depth were collected from well logs where available (~75% of wells). Water testing was completed at professional facilities using established USEPA protocol, either the State Public Health Lab in Pierre, SD or at Energy Laboratories in Rapid City, SD. IHS then compared sampling results to USEPA MCL standards, even though MCL standards are not enforceable in private wells. A point-of-use filter was applied to any well water that did not meet MCL standards for uranium, gross alpha, or arsenic.

These water quality reports, well logs (when available), and well GPS locations were obtained through collaboration with the Oglala Sioux Tribe and the Martin field office of the IHS and compiled into a database. Direct measurements of aqueous uranium concentration were only completed in ~40% of the total wells (107 wells); instead, gross alpha, which measures total radioactive decay by alpha emission, was used as a proxy for radionuclide concentration in water. A common assumption is that 2/3 of gross alpha emission (pCi/L) is the result of uranium concentration in water ( $\mu\text{g/L}$ ) (USEPA, 2015); for our dataset, we found simple 2/3 scaling and a linear correlation between gross alpha and uranium were nearly identical in terms of fit (both had a Pearson's  $r^2 \sim 0.6$ ). However, scaling gross alpha by 2/3 predicted lower uranium concentrations and was a more conservative approach. Thus, when uranium concentration was not measured by IHS, we estimated uranium levels by scaling gross alpha concentrations by 2/3. If any geochemical parameters were below analytical detection limits, the concentration was assumed to be one half of the detection limit for statistical analyses (USEPA, 1991).

Once data compilation was complete, the data were analyzed for potentially distinct geochemical environments, groundwater provenance, and how differences in groundwater

chemistry affect subsurface mobility of uranium and arsenic. All parameters were log transformed prior to geostatistical analyses to minimize influences from extreme values. Geochemical measurements are often skewed right, but commonly display log-normal distributions (Helsel & Hirsch, 2002). MATLAB was used for statistical analysis and several approaches were employed such as agglomerative clustering, multivariate regression, and principal component analysis to explore relationships between geochemical variables. Agglomerative clustering was first used to identify potential geochemical environments, and multivariate regression and principal component analysis were then used to help parse geochemical parameters that influence uranium and arsenic mobility on the PRR. Spatial analysis was also completed in ArcGIS to assess whether trends in uranium and arsenic concentration are related to bedrock geology. Finally, geochemical equilibrium modeling was used to quantify mineral precipitation and dissolution rates in each of the distinct geochemical environments, which can affect mobility of uranium and arsenic.

#### **2.4.1 Agglomerative Clustering**

Agglomerative clustering was used to group the borehole geochemical data according to their similarity. Clustering can either be completed to identify natural sample groupings (Q-mode), or variable groupings (R-mode); for example, in water quality studies, Q-mode clustering shows groups that may represent similar geochemical environments, and R-mode clustering shows geochemical parameters that may be interrelated (Meng & Maynard, 2001). Here, Q-mode clustering was used to identify possible geochemical environments using the cosine theta similarity coefficient between different well samples. This method is commonly

employed in Q-mode clustering, and it operates by converting samples into vectors, and measures the cosine of the angle between vectors as shown below:

$$\text{similarity} = \cos(\theta) = \frac{A \cdot B}{\|A\| \|B\|} = \frac{\sum_{i=1}^n A_i B_i}{\sqrt{\sum_{i=1}^n A_i^2} \sqrt{\sum_{i=1}^n B_i^2}}$$

Thus, the cosine theta similarity coefficient is particularly useful in water quality studies as it is only sensitive to proportions between variables rather than absolute magnitudes of the geochemical parameters. This allows water-quality measurements on different scales (i.e. logarithmic pH scale, major ions in mg/L, and trace metals in  $\mu\text{g/L}$ ) to be analyzed together without biasing results from differences in magnitude.

#### **2.4.2 Multivariate regression**

Multivariate regression is a powerful tool in water-quality studies because it considers all possible interactions between geochemical parameter combinations to develop a conceptual model for a given response variable (e.g., Davis, 2002). In this case, a suite of geochemical measurements such as pH, alkalinity, major ions, and metals were used as indicator variables to predict concentrations (responses) of uranium and arsenic in each of the distinct geochemical environments. Multivariate regression was completed on log-normalized data, as its results can be significantly impaired by outliers. Log-normalized data also allowed for more uniform weighting of the multivariate regression to indicate which geochemical parameters have the greatest impact on arsenic and uranium levels. Multivariate regression models have different methods for handling the intercept of the regression. Single intercept models employ only one intercept, similar to bivariate regression, while models with a dynamic intercept have several

intercepts for various parameter and interaction groupings. For simplicity, this study used a single-intercept model, which is a more conservative approach to multivariate regression as the intercept remains quasi-linear rather than changing in high-order dimensions. To avoid overfitting, the Akaike Information Criterion (AIC) was calculated to select the “best” model that employed the fewest parameters. Separate models were developed for uranium and arsenic, as these two metals have varying geochemical controls on speciation, solubility, and mobility in the same environment.

### **2.4.3 Principal Component Analysis (PCA)**

Principal Component Analysis (PCA) is a data compression technique that reduces high-dimension data sets (such as water quality reports) into key components via singular value decomposition (SVD). PCA rotates the original data into a set of new orthogonal variables known as principal components, which are a set of uncorrelated factors ordered so that the first few components describe most of the variation present in the data set (Jolliffe, 2002). This method is particularly useful to identify key parameters in water-quality studies because many variables, such as pH and alkalinity, are often interrelated. Groundwater samples were not split into groups for PCA analysis to allow the analysis to identify any underlying structure of variance within the whole water-quality dataset. Additionally, uranium concentrations were omitted from PCA analysis to avoid autocorrelation with gross alpha measurements. Gross alpha was chosen to represent radionuclide concentrations because it was measured in all wellbores samples in the dataset.

#### **2.4.4 GIS**

Geospatial analysis was completed in ArcGIS 10.5. South Dakota bedrock geology was obtained from the South Dakota Geological Survey, and the Digital Elevation Model was based on a data product from the U.S. Geological Survey (USGS). These maps were produced to show general topography and groundwater flow of the PRR (Figure 2.2). Additionally, distinct well groups found via agglomerative clustering were plotted against bedrock geology of the PRR to determine if any of the groupings related to changes in subsurface geological strata.

#### **2.4.5 Geochemical modeling**

Samples from distinct geochemical environments, indicated by agglomerative clustering, were averaged together. These aggregate samples were used for equilibrium modeling in Geochemist's Workbench (GWB) following methodology from Meng & Maynard (2001). Mineral saturation indices were calculated at 25°C using the thermo.tdat thermodynamic database distributed with GWB to evaluate the potential impact of mineral precipitation and dissolution on uranium and arsenic mobility.

### **2.5 Results**

Clustering, multivariate regression, PCA, and geochemical modeling were used to assess factors that influence subsurface mobility of uranium and arsenic on the PRR. Results for each method are detailed below.

### 2.5.1 Cluster & Spatial Analysis

Agglomerative clustering identified distinct groupings that may represent geochemical environments on the PRR (Figure 2.3). There were four major clusters, and a fifth grouping of outliers with only six wells that was not considered further in any statistical or geochemical methods because of the low number of wellbore samples. Samples from each of the four significant groupings were plotted in a Piper Diagram (Figure 2.4) to delineate major differences in wellbore geochemistry within the dataset. The four geochemical groupings identified by agglomerative clustering have major differences in major ion composition, indicating that the clusters represent distinct geochemical environments on the PRR. Wells from each of the four clusters were then plotted in ArcGIS with bedrock geology of the PRR to assess spatial patterns, and were also spatially clustered (Figure 2.5). Together, these analyses show that agglomerative clustering effectively delineated upgradient, intermediate, and downgradient portions of the Arikaree aquifer. These four regions of the Arikaree aquifer were classified as Regions A-D following flowpaths of the Arikaree aquifer from upgradient (Region A) to downgradient (Region D). Mean values for geochemical and physical parameters in each of the geochemical regions are shown below (Table 2.2), as well as boxplots showing more detailed distributions of all the parameters across Regions A-D (Figure 2.6).

Table 2.2: Mean values representing composite geochemistry for each of the four major geochemical clusters and the fifth outlier group.

Cluster Group	Region A	Region B	Region C	Region D	Outlier Group
Well Depth (m)	64.6	63.4	66.4	54.7	23.1
# of Wells	46	80	67	54	6
U (ppb)	5.0	8.5	9.6	13.0	3.3
As (ppb)	6.1	6.9	11.9	11.6	23.0
Gross Alpha (pCi/L)	6.5	10.6	12.7	15.8	4.9

Table 2.2 Continued

pH	7.8	7.8	8.0	8.1	7.5
Alk (mg/L as CaCO <sub>3</sub> )	172.2	201.9	208.0	252.4	214.8
TDS (mg/L)	269.5	397.1	359.3	373.8	289.7
NO <sub>3</sub> (ppm)	1.4	1.2	0.9	0.9	1.5
SO <sub>4</sub> (mg/L)	20.9	78.1	41.9	34.1	39.4
F (mg/L)	0.4	0.4	0.5	0.5	0.6
Cl (mg/L)	19.6	9.6	9.0	8.6	5.6
Ca (mg/L)	51.9	56.3	36.2	23.5	57.7
Mg (mg/L)	7.6	8.8	4.9	2.0	9.1
K (mg/L)	8.6	11.6	10.0	10.3	10.0
Na (mg/L)	18.8	51.8	70.4	101.1	41.4
Fe (ppb)	36.8	50.2	1658.6	56.3	30.3
Mn (ppb)	24.4	36.6	60.0	13.3	2086.3
Ba (ppb)	205.8	93.6	135.9	46.2	1141.5

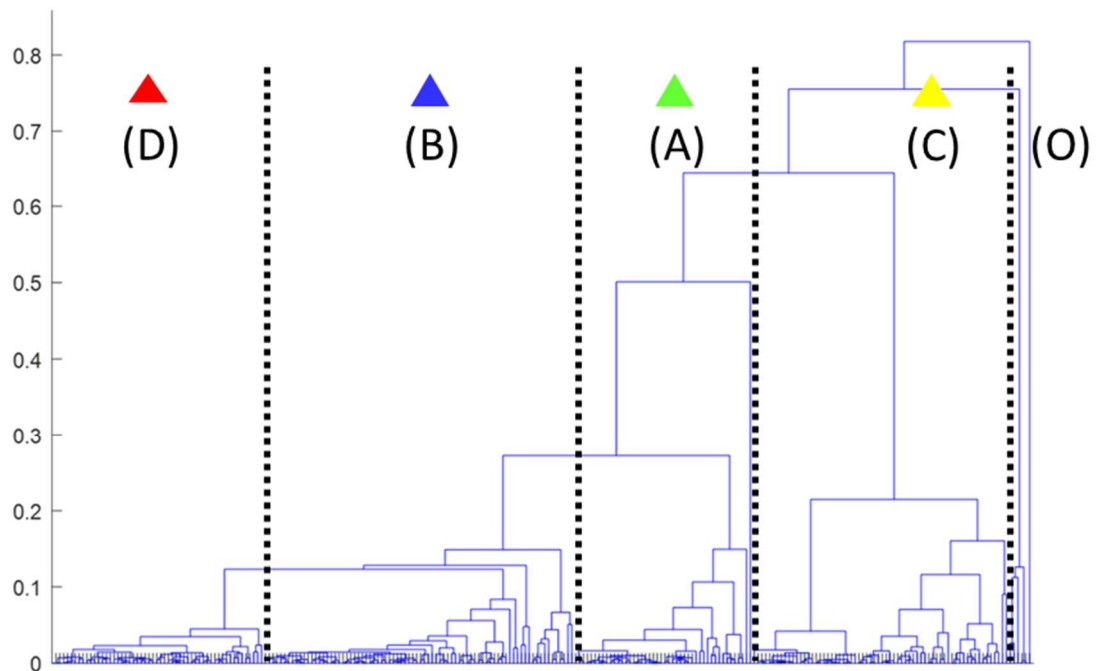


Figure 2.3: Dendrogram of Q-mode analysis of PRR water chemistry. There are five distinct clusters that can be seen in this analysis. Each of the four significant groupings was assigned a color, from left to right: red, blue, green, and yellow. This color scheme was used for further analysis that indicated these groupings are clustered both by major ion geochemistry (Figure 2.4) and spatially (Figure 2.6).

Region A wells are generally clustered in the southern, upgradient portions of the aquifer proximal to contacts with overlying formations and had the lowest TDS levels. Region B had the highest levels of sulfate, and is clustered primarily in the south-central portions of the aquifer. Region C had significantly higher iron levels than any of the other groupings and is located in the central portion of the Arikaree aquifer. Region D is primarily located in the northern, downgradient sections of the Arikaree aquifer and was enriched in sodium, pH and alkalinity.

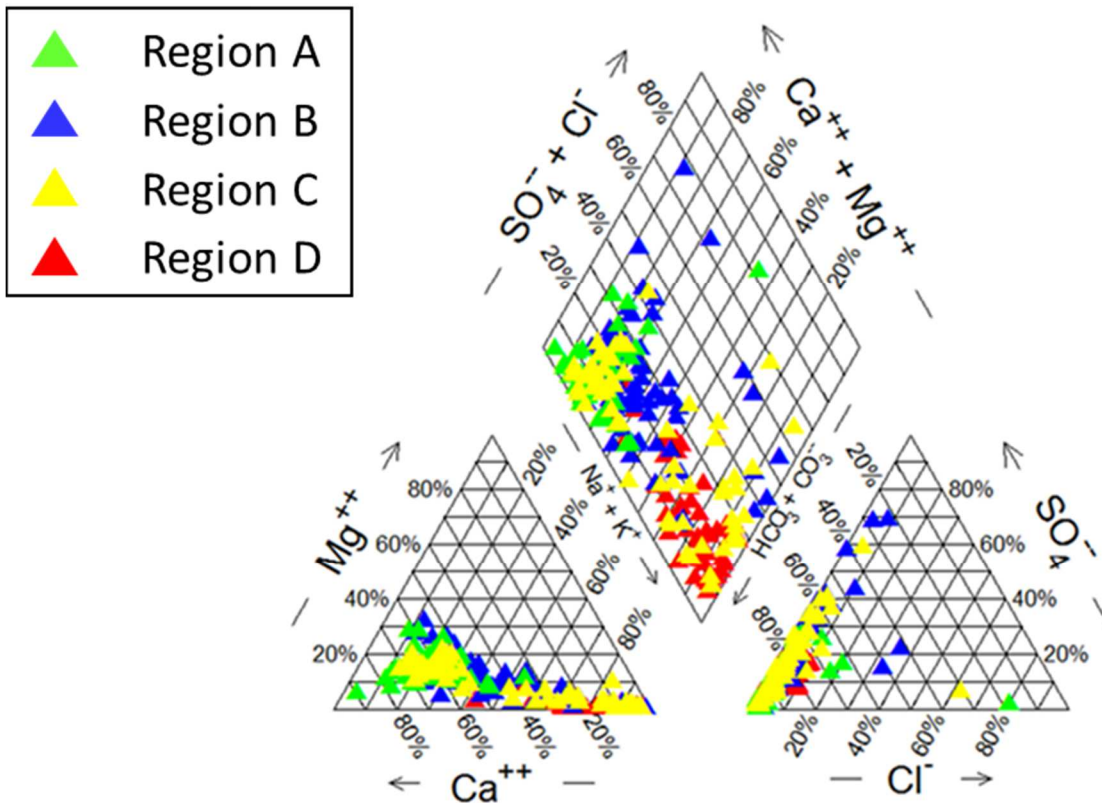


Figure 2.4: Piper diagram showing the relative proportions of major ions in PRR groundwater for the four geochemical regions. Waters are generally rich in  $\text{Na}^+$  or  $\text{Ca}^{2+}$  compared to  $\text{Mg}^{2+}$  and have low relative proportions of  $\text{Cl}^-$  with most waters dominated by carbonate species.

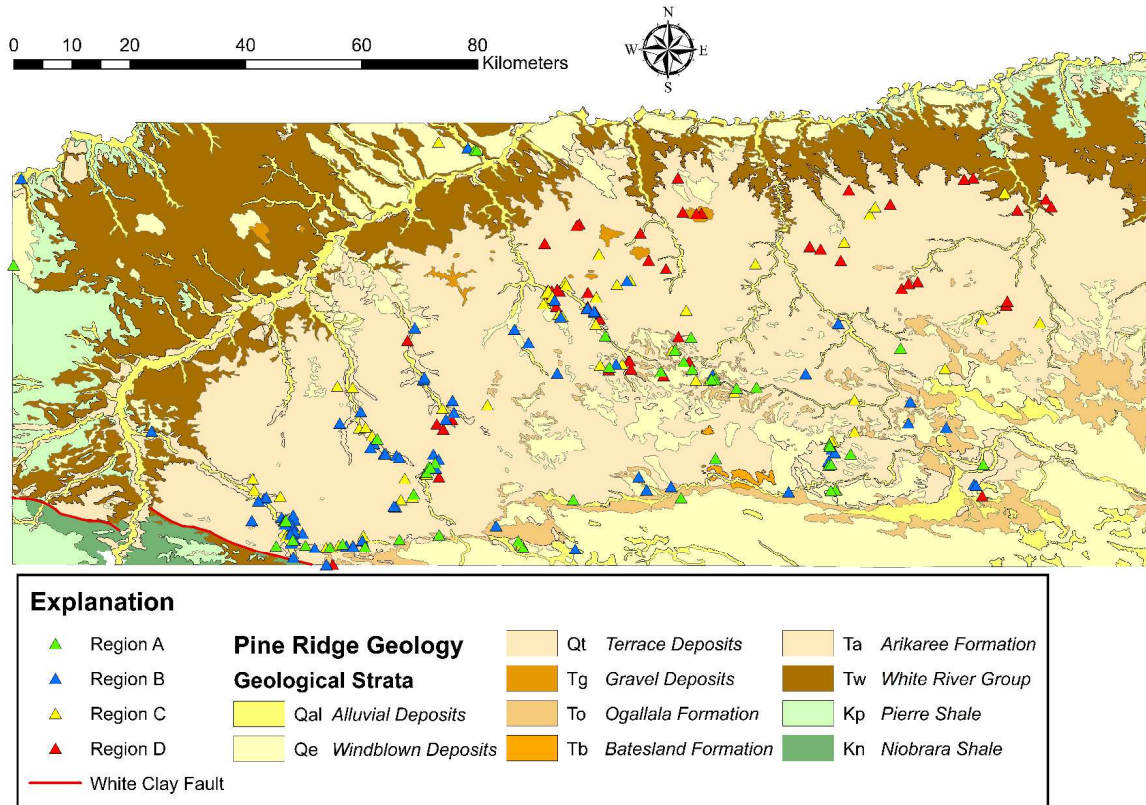


Figure 2.5: Spatial plots of Regions A-D showing their relative position within the Arikaree aquifer.

### 2.5.2 Multivariate Regression

Multivariate regression was used to parse geochemical parameters capable of influencing uranium and arsenic mobility on the PRR in the four major geochemical regions. To find the optimal fit, stepwise regression was used to combine geochemical parameters (i.e. pH, alkalinity, major ions, and trace metals) until the best model that employed the fewest parameters was found according to the Akaike Information Criterion (AIC). In region A, arsenic mobility is enhanced primarily by increasing pH, while uranium mobility positively relates to

alkalinity levels. Fluoride is the strongest multivariate predictor of arsenic levels in regions B, C, and D and could indicate proximity to volcanic ash deposits, which commonly acts as a source.

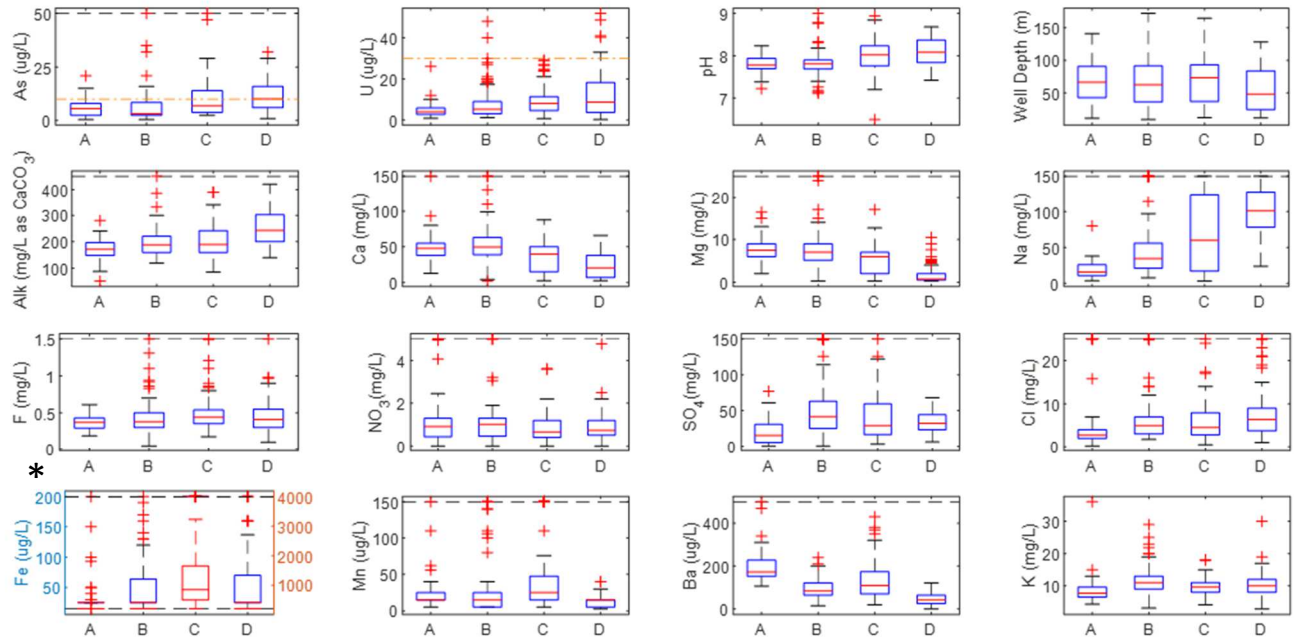


Figure 2.6: Boxplots showing distributions of the various hydrogeochemical parameters for the 4 geochemical regions A-D. MCLs are highlighted for arsenic and uranium using a dashed orange line. The dashed black line indicates the presence outliers greater than the scale shown in the y-axis. Note separate y-axis scales in the iron boxplot: Regions A, B, and D are plotted on the left (blue) scale and Region C is plotted on the right (red) scale.

Table 2.3: Log transformed multivariate regression models for arsenic and uranium concentration in each of the four geochemical groupings

Grouping:	Arsenic (As) (ppb)	Uranium (U) (ppb)
Region A	$As = -7.16 + 9.69*(pH) - 0.251*(NO_3) - 0.199*(Cl) + 0.487*(K) - 0.574*(Fe) + 0.785*(F)$	$U = -1.04 + 0.960*(Alk) - 0.134*(Fe)$
Region B	$As = 1.75 - 0.113*(SO_4) - 0.442*(Ca) + 0.371*(F)$	$U = -1.92 + 1.18*(Alk) + 0.166*(SO_4) - 0.145*(Fe) - 0.230*(F)$
Region C	$As = 1.53 - 0.492*(Ca) - 0.313*(Fe) + 0.253*(Mn) + 0.450*(Ba) + 0.843*(F)$	$U = -0.502 + 0.195*(NO_3) + 0.483*(Ca) - 0.568*(K) + 0.663*(Na) + 0.218*(Fe) - 0.249*(Mn)$
Region D	$As = 4.62 - 4.16*(pH) - 0.128*(NO_3) - 0.292*(SO_4) - 0.330*(Na) + 0.213*(Mn) + 1.21*(F)$	$U = -9.03 + 7.31*(pH) + 0.576*(Ca) - 0.623*(K) + 0.330*(Na) - 0.382*(F)$

The results of the multivariate regression may show a sensitivity to redox processes. Uranium is more mobile in oxic zones, and was positively correlated with nitrate and sulfate, which are prevalent in oxic conditions, seen in Regions B and C. Arsenic concentrations were negatively correlated with nitrate and sulfate in Regions B and D, which could indicate its speciation is primarily arsenite As(III), which is the dominant As species in reducing conditions. Both arsenic and uranium concentrations were negatively correlated with iron levels in Regions A and B, suggesting that sorption of U and As onto iron (hydr)oxides could reduce metal mobility within upgradient portions of the Arikaree aquifer (e.g. Nagorski & Moore, 1999). However, this negative correlation did not hold in Region C, which had significantly higher Fe levels than any of the other groups (Figure 2.6); dissolution of iron (hydr)oxides in a more reducing environment could release adsorbed As and U in this region, leading to higher concentrations.

### **2.5.3 Principal Component Analysis**

Principal Component Analysis was then completed on the log normalized dataset. This dimension reduction technique identified four key principal components that explained 73% of the variation in groundwater geochemistry (Figure 2.7). These principal components were then plotted against one another to further delineate geochemical differences between the various regions of the Arikaree aquifer (Figure 2.8).

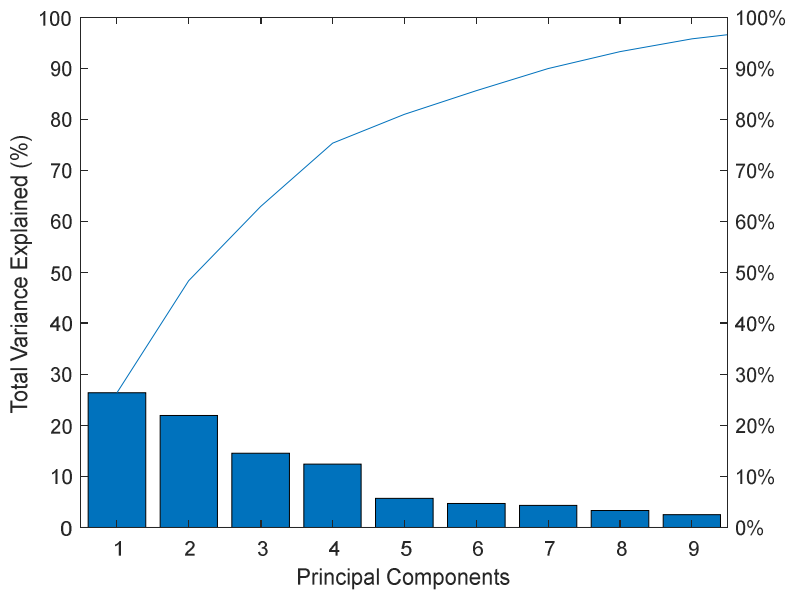


Figure 2.7: Scree plot showing percent explained by principal components (bars), and the cumulative percent explained explained by the line.

Figure 2.8 shows biplots for the four principal components, where PCA-transformed data for each wellbore sample are plotted as dots and vectors for each of the geochemical parameters are plotted as dashed lines. The magnitude of the vector indicates its relative importance on each of the principal components. The first two principal components are most effective at distinguishing boundaries between the four geochemical regions (Figure 2.8a). The first principal component splits PRR groundwater geochemistry into upgradient portions of the Arikaree aquifer, which are characterized by high  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and to a lesser extent  $\text{NO}_3^-$  concentrations, and downgradient portions of the aquifer which are enriched in  $\text{Na}^+$  and  $\text{Fe}^{2+}$ . The third and fourth principal components are controlled by  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{Fe}^{2+}$ , which may be indicative of redox processes within the Arikaree aquifer. However higher order principal components are not as effective at separating the four geochemical regions (Figures 2.8b, c).

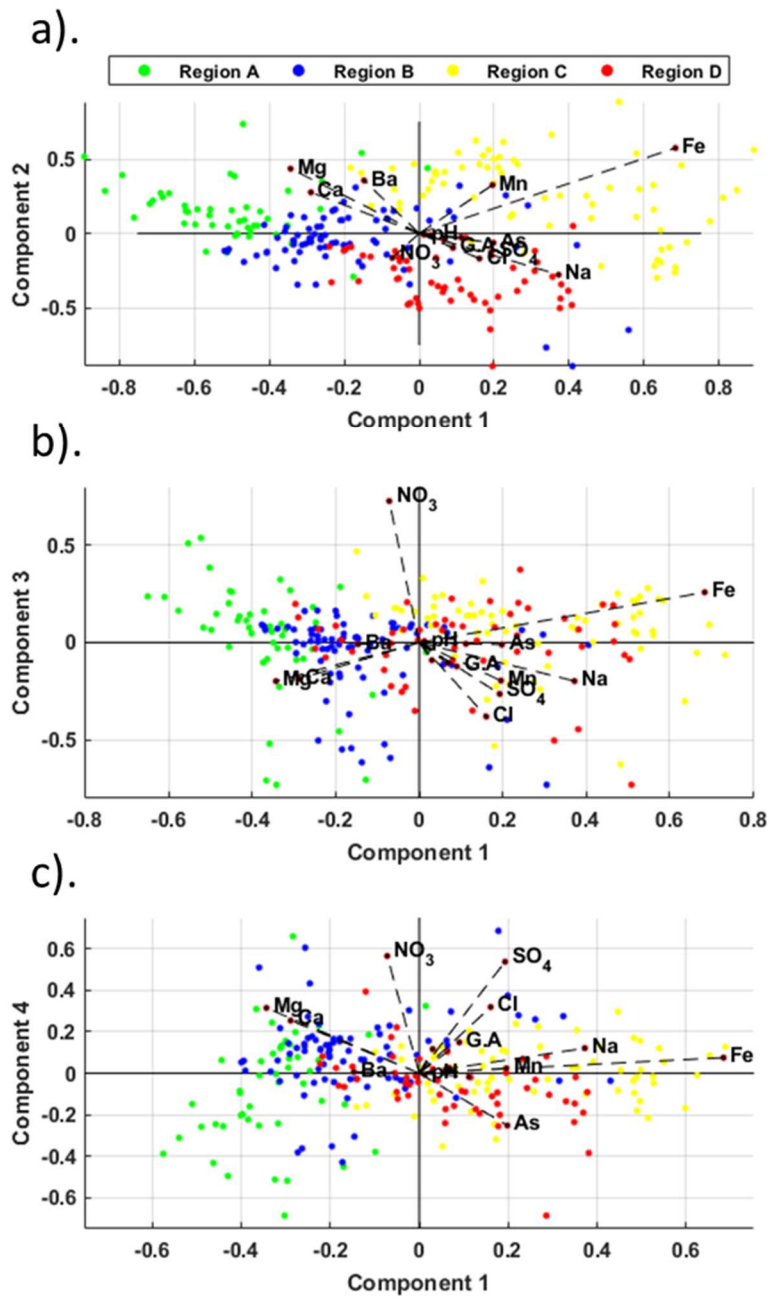


Figure 2.8: Biplots of principal components showing separation of geochemical regions and relative importance of geochemical parameters on delineating geochemical regions (shown by magnitude of parameter vector).

#### 2.5.4 Geochemical Equilibrium Modeling

Equilibrium modeling was used to assess how mineral precipitation and dissolution in the four major geochemical environments may alter metal mobility within the Arikaree aquifer.

Mineral saturation index (SI) was calculated in GWB using composite geochemistry for each major group/region (Table 2.4).

Table 2.4: Saturation indices (SI) of minerals across the four geochemical regions of the PRR. If SI is > 0 minerals will tend to precipitate, if SI < 0 minerals will dissolve if present in the rocks, and dashed lines (--) indicates that the SI was sufficiently small to not be considered (in this case, SI < -3.0).

Mineral:	Region A	Region B	Region C	Region D
Calcite	0.514	0.589	0.65	0.613
Siderite	-0.856	-0.676	1.08	-0.243
Dolomite	-0.211	-0.025	0.034	-0.252
Barite	0.101	0.244	0.381	-0.335
Gypsum	-2.49	-1.94	-2.36	-2.63
Fe(OH) <sub>3</sub>	-----	-----	-1.51	-2.85

Calcite saturation increases along the Arikaree aquifer flowpaths from Region A to Region D, indicating that calcite precipitation likely occurs. Fe(OH)<sub>3</sub> dissolution is predicted to occur more strongly in downgradient Regions C and D, which also have the highest As and U concentrations.

Geochemical modeling may be useful to parse potential transformation pathways. Iron (hydr)oxides are minimally soluble, but may act as a sorption surface for arsenic and uranium,

limiting their subsurface mobility. In downgradient portions of the Arikaree aquifer, such as Regions C and D, groundwater has higher alkalinity and pH, which may decrease sorption affinity of arsenic and uranium while simultaneously making complexation with ligands more favorable, enhancing arsenic and uranium mobility via formation of stable aqueous complexes. Complexation reactions and sorption/desorption kinetics may be an important factor for arsenic and uranium mobility in downgradient portions of the Arikaree aquifer.

## **2.6 Discussion**

The statistical, spatial and geochemical analyses indicate that there are four distinct hydrogeochemical environments within the Arikaree aquifer. These four environments reflect evolution of groundwater geochemistry along flowpaths. Differences between these four geochemical regions are detailed here.

### **2.6.1 Region A (n of wells = 46)**

Region A had the lowest pH, mineral SIs, alkalinity, and sodium levels and was spatially clustered in the upgradient, southern portion of the Arikaree aquifer, or proximal to contacts between the upper extent of the Arikaree and overlying sediments. Wells in this region had an average depth of 64.6 m. PCA and Piper diagram analysis show groundwater samples from Region A are enriched in  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  (Figure 2.8). This upgradient, recharge-dominated portion of the Arikaree aquifer had the lowest levels of arsenic and uranium, suggesting that recharge processes may limit As and U mobility in this portion of the aquifer due to input of low pH, low alkalinity water, as well as limited water-rock contact time.

### **2.6.2 Region B (n of wells = 80)**

Wells in Region B are generally drilled to a similar depth as in Region A (mean depth = 63.4 m), and in the southern or central portions of the Arikaree aquifer. Groundwaters sampled from these wells are characterized by low pH and moderate alkalinity. Mineral saturation is typically higher compared to Region A, and dolomite saturation increases to near equilibrium levels in Region B, indicating that precipitation of a mixed  $Mg^{2+}$  -  $Ca^{2+}$  carbonate phase may begin to appear in this intermediate portion of the Arikaree aquifer. PCA shows that Region B is similar to Region A but has slightly higher  $Na^+$  and  $Fe^{2+}$  levels. Arsenic and uranium levels remain relatively low in Region B, and this region likely represents a transition from the upgradient portion of the aquifer where influences from recharge decrease and mineral dissolution becomes a stronger influence on solute concentrations as water-rock contact time increases.

### **2.6.3 Region C (n of wells = 67)**

Wells in Region C are generally slightly deeper than Regions A and B (mean depth = 66.4 m) and drilled into the central to northern portions of the Arikaree aquifer. Sodium and pH levels rise in this region of the aquifer, while alkalinity remains moderate. Iron levels in Region C are over an order of magnitude greater than any of the other geochemical regions (Figure 2.6), and siderite ( $FeCO_3$ ) saturation indices are positive, indicating possible precipitation of an  $FeCO_3$  phase. Calcite and dolomite saturation increase compared to Region B suggesting that carbonate precipitation becomes more favorable, which could act as a sink for aqueous carbonate species. PCA suggests that Fe and Mn are the distinguishing factors for Region C, as

well as Na and As to a lesser extent. Both As and U concentrations increase in this region of the Arikaree aquifer, and average arsenic concentrations are above the MCL (~12 µg/L). Dissolution of iron (hydr)oxides and release of adsorbed metals may enhance uranium and arsenic mobility in this region.

This region has the greatest mean well depth, and may screen wells in the basal portion on the Arikaree aquifer which is enriched in Fe hydr(oxides) and volcanic ash. The spatial extent of subfacies within the Arikaree aquifer such as the Sharps Formation and Rockyford ash zone (Table 1) are poorly characterized on the PRR, but could explain the major discrepancy in iron concentrations in this region.

#### **2.6.4 Region D (n of wells = 54)**

Wellbores in Region D have the highest pH, alkalinity, and sodium levels as well as the highest arsenic and uranium concentrations. Wellbores in this region likely represent a downgradient endmember within the Arikaree aquifer, where mature groundwater has become enriched in carbonate alkalinity and sodium due to mineral dissolution, ion exchange, and/or leaching of volcanic ash along flowpaths of the aquifer which drives up pH. This region is generally clustered in the northern, farthest downgradient section of the Arikaree aquifer and had the shallowest mean well depth (54.7 m) of all the hydrogeochemical groupings. PCA analysis shows that sodium has the strongest loading on Region D (Figure 7). Carbonate SI's remain supersaturated in this region, suggesting that precipitation of carbonate minerals may influence groundwater chemistry, acting as a carbonate sink and reducing carbonate alkalinity. However, this downgradient portion of the Arikaree aquifer is proximal to volcanic ash deposits

in the basal Arikaree and White River Group. Groundwater in this region is enriched in alkalinity, indicating volcanic ash in this basal portion of the aquifer may act as a secondary source of alkalinity. As groundwater flows downgradient in the Arikaree aquifer, pH and alkalinity increase making complexation more favorable than sorption, which enhances uranium and arsenic mobility, indicating that groundwater residence time and formation water maturity in the Arikaree aquifer may be a key control of arsenic and uranium mobility.

## **2.7 Conclusions**

Here, we explored underlying controls to uranium and arsenic mobility in 253 groundwater chemistry samples from the PRR using various geostatistical and geochemical methods. Our results were compiled into a conceptual model, indicating water quality degrades along the flow direction of the Arikaree aquifer. The southern, upgradient sections of the Arikaree aquifer are influenced by recharge of meteoric water that keeps groundwater pH and alkalinity relatively low, which limits As and U mobility. As groundwater flows through the Arikaree aquifer, pH and alkalinity rise due to mineral dissolution and potentially leaching of volcanic ash from the basal portion of the Arikaree aquifer, which increases As and U mobility. Human health impacts from high As and U levels are more likely in the downgradient sections of the Arikaree aquifer, such as the northern extent of the PRR. The dataset obtained from IHS indicated that 32% of wells exceeded the MCL for arsenic, 8% exceeded the uranium MCL, and 23% exceeded the MCL for gross alpha highlighting critical need for further investigation as thousands of people on the PRR rely on the Arikaree aquifer as their drinking water source.

## CHAPTER 3

### FUTURE WORK

This work successfully identified several controlling factors of uranium and arsenic mobility on the PRR, however, there are still several persistent questions: how does redox potential vary throughout the Arikaree aquifer, and what affect does that have on uranium and arsenic mobility on the PRR? Does heterogeneity within the Arikaree aquifer and/or hydrologic connectivity between the basal Arikaree aquifer and the underlying White River Group explain the high variation of iron concentrations within this dataset? Does volcanic ash act as a secondary source of alkalinity within the Arikaree aquifer? Are seasonal variations in hydrologic conditions within the Arikaree aquifer capable of affecting uranium and arsenic mobility?

Uranium and arsenic mobility in groundwater are both highly dependent on redox processes, which were not measured in the IHS dataset. Future work should include detailed mapping of redox sensitive parameters such as dissolved oxygen (D.O.) and redox voltage (Eh) throughout the Arikaree aquifer. Residence time and well depth of the Arikaree aquifer appear to be key predictors of uranium and arsenic concentrations, and other studies have shown that these factors influence redox processes at the regional scale in other aquifer systems (e.g. Edmunds et al., 1982; McMahon & Chapelle, 2008). Thus, quantifying the link between redox, residence time, and metal mobility may have applications on the PRR as well as other regions.

This work also highlights the need for field access and lack of currently available research instrumentation that creates a barrier to conducting research on U.S. Tribal Lands such as the PRR. Established research sites are a rarity on U.S. reservations, making access to

field scale sites on reservations difficult or impossible to find. This severely limits the potential for scientific research to address critical needs of tribal communities. Future work is needed to foster collaboration with tribal government entities and colleges, and to develop research sites on reservations to support interdisciplinary research projects. Many tribes rely on institutional review boards (IRB's) to ensure research within tribal boundaries is conducted ethically, and tend to be strict with research approval until a project proves it has tangible benefits for the tribal population or lands being studied. Building relationships with tribal professors, government officials and staff members is vital to gain insight into relevant problems facing local tribal communities and local expertise is also helpful when navigating a given tribe's IRB process. Further collaboration efforts between tribes and academic universities could help tribal populations on reservations solve pressing problems, such as impacts from water contamination, while greatly expanding the depth of scientific literature available for such processes on U.S. tribal lands.

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## APPENDIX A

### CONDUCTING RESEARCH ON U.S. TRIBAL RESERVATIONS

This section details the process of gaining permission to conduct research on the Pine Ridge Reservation, and is meant to act as a general guide for conducting research on U.S. tribal reservations. American Indian tribes are federally recognized as sovereign nations, which adds an extra channel of tribal government to traditional federal and state government systems on reservations. Tribes typically have primacy over their land and control what research is allowed to take place within the borders of their reservation. Tribal government structure is typically similar to state government systems, and many tribes have their own departments that oversee environmental protection, land, and natural resource concerns. Many tribes, including the Oglala Sioux Tribe (OST), have research review panels that must approve any research projects before they can proceed and additional permission may be required from other tribal offices.

Collaborating with local professors (from tribal colleges or nearby institutions) who have completed research projects on reservations, and/or tribal officials who have previously supported research efforts can be effective to help navigate the research review and approval process on reservations. This project first gained approval from the OST Land & Natural Resources committee. Our research proposal was added to their monthly meeting agenda after consulting with the OST Environmental Protection Program on conducting research on the Pine Ridge Reservation. Approval was granted to proceed with research once all relevant concerns had been addressed at the meeting. However, research permission was also required from the OST Research Review Board (RRB), which reviews all prospective research studies using

Institutional Review Board (IRB) framework regardless of involvement of human participants. A separate research proposal and several supporting documents were submitted to the OST RRB, and our research proposal was then presented to the OST RRB with full approval granted to begin research in June 2017. Data collection took place in July 2017 at the Indian Health Service Field Office in Martin, South Dakota.

Gaining approval to conduct research on tribal lands is not a straight-forward process, as every research proposal is unique and often requires insight from several tribal offices/departments to ensure that research projects benefit the tribe with minimal risk to its people, land and natural resources. For this study, research approval was required from both the OST RRB and the OST Land & Natural Resources committee. This study would not have been possible without collaboration with the Martin Indian Health Service Field Office and the OST Environmental Protection Program. Research results were disseminated to the OST Land & Natural Resources Committee and the Indian Health Service Field Office at monthly meetings to foster community involvement, which can also aid research efforts on reservations. Building relationships with tribal authorities, fostering community involvement and utilizing expertise of local researchers was critical to the success of this project, and acts as a starting point to navigate tribal government systems and harmoniously conduct research on tribal lands in the U.S.

## APPENDIX B

### MATLAB CODES

#### **B.1: Matlab code for creating hierarchical clusters & dendrogram**

```
%Create a dendrogram of IHS Water Quality data
%Used to parse differences in water quality samples
%Import water quality matrix (253 x 15) from IHS Geochemistry.xlsx
%Water quality matrix referenced as "datamatrix"
%KSB October 2017

%Compute hierarchical clustering using cosine similarity coefficient
z = linkage(datamatrix,'weighted','cosine');
%Visualize dendrogram without compressing lower order nodes
[H,T,OUTPERM] = dendrogram(z,253);
%OUTPERM stores the leaf node number for each sample, used to sort groups
%in excel
```

#### **B.2: Matlab code for Linear Multivariate Regression**

```
%%Linear Multivariate Regression using AIC
%%Import water quality matrix (247 x 15) IHS Geochemistry.xlsx
%%Log transformed data matrix referenced as 'alldata'
%%Variable names stored in string referenced as 'varstring'
%%KSB October 2017

%%Split matrix of predictor variables into four regions
R1=alldata(1:46,1:13);
R2=alldata(47:126,1:13);
R3=alldata(127:193,1:13);
R4=alldata(194:247,1:13);

%%Create Multiple Regression models for uranium in each region
Umod1=stepwiselm(R1,U1,'Criterion','aic','upper','linear','varnames',varstring);
Umod2=stepwiselm(R2,U2,'Criterion','aic','upper','linear','varnames',varstring);
Umod3=stepwiselm(R3,U3,'Criterion','aic','upper','linear','varnames',varstring);
Umod4=stepwiselm(R4,U4,'Criterion','aic','upper','linear','varnames',varstring);

%%Create Multiple Regression models for arsenic in each region
Asmod1=stepwiselm(R1,As1,'Criterion','aic','upper','linear','varnames',varstring);
Asmod2=stepwiselm(R2,As2,'Criterion','aic','upper','linear','varnames',varstring);
```

```
Asmod3=stepwiselm(R3,As3,'Criterion','aic','upper','linear','varnames',varstring);
Asmod4=stepwiselm(R4,As4,'Criterion','aic','upper','linear','varnames',varstring);
```

### B.3: Matlab code for creating geochemistry boxplots

```
%%%Create boxplots for all of the geochemical parameters in each of the
%%%regions
%%%Import boxplot data matrix (80 x 64) from Geochemistry Boxplots.xlsx
%%%Import each geochemical parameter (As, U, Na, etc.) as an 80x4 matrix
%%% "Datalim" is used to focus boxplot on IQR
%%%KSB December 2017
```

```
subplot(4,4,1)
boxplot(As,Groups,'Datalim',[0 50])
ylabel('As (ug/L)')
yticks([0 25 50])
hold on
plot([0 10],[10 10],'Color',[1 0.5 0],'LineStyle','-')
hold off
```

```
subplot(4,4,2)
boxplot(U,Groups)
ylabel('U (ug/L)')
hold on
plot([0 10],[30 30],'Color',[1 0.5 0],'LineStyle','-')
hold off
```

```
subplot(4,4,3)
boxplot(pH,Groups)
ylabel('pH')
```

```
subplot(4,4,4)
boxplot(Depth,Groups)
ylabel('Well Depth (m)')
```

```
subplot(4,4,5)
boxplot(Alk,Groups,'Datalim',[0 450])
yticks([0 100 200 300 400])
ylabel('Alk (mg/L as CaCO_{3})')
```

```
subplot(4,4,6)
boxplot(Ca,Groups,'DataLim',[0 150])
ylabel('Ca (mg/L)')
```

```

subplot(4,4,7)
boxplot(Mg,Groups,'DataLim',[0 25])
ylabel('Mg (mg/L)')

subplot(4,4,8)
boxplot(Na,Groups,'DataLim',[0 150])
ylabel('Na (mg/L)')

subplot(4,4,9)
boxplot(F,Groups,'DataLim',[0 1.5])
ylabel('F (mg/L)')

subplot(4,4,10)
boxplot(NO3,Groups,'DataLim',[0 5])
ylabel('NO_{3}(mg/L)')

subplot(4,4,11)
boxplot(SO4,Groups,'DataLim',[0 150])
ylabel('SO_{4}(mg/L)')

subplot(4,4,12)
boxplot(Cl,Groups,'DataLim',[0 25])
ylabel('Cl (mg/L)')

subplot(4,4,13)
yyaxis left
boxplot(Fe,Groups,'DataLim',[0 200])
ylabel('Fe (ug/L)')
hold on
yyaxis right
boxplot(Fe,Groups,'DataLim',[200 4000],'Colors','r','Symbol','')

subplot(4,4,14)
boxplot(Mn,Groups,'DataLim',[0 150])
ylabel('Mn (ug/L)')

subplot(4,4,15)
boxplot(Ba,Groups,'DataLim',[0 500])
ylabel('Ba (ug/L)')

subplot(4,4,16)
boxplot(K,Groups)
ylabel('K (mg/L)')

```

#### B.4: Matlab code for PCA Plots

```
%%%Plotting Principal Components w/ Colored Regional Groups
%%%Import log transformed data matrix (247 x 14) from PCA_log.xlsx
%%%Data matrix referenced as 'logpca'
%%%KSB March 2018

%%% Compute PCA and store principal component eigenvectors, scores, and
%%% eigenvalues (variance) on log transformed data matrix
[eigvec,score,eigval] = pca(logpca);

%%% PC 1 vs PC 2
z = eigvec(:,1:2);
subplot(3,1,1)
biplot(z,'Score',score(1:46,1:2),'color','g','Markersize',10,'LineStyle','none'); %%%%Group A
hold on
biplot(z,'Score',score(47:126,1:2),'color','b','Markersize',10,'LineStyle','none') %%%%Group B
biplot(z,'Score',score(127:193,1:2),'color','y','Markersize',10,'LineStyle','none') %%%%Group C
biplot(z,'Score',score(194:247,1:2),'color','r','Markersize',10,'LineStyle','none') %%%%Group D
biplot(z,'Varlabels',varnames,'Color','k','LineStyle','--') %%%%Plot black eigenvectors w/ labels
w/ a dashed line

hold off

%%% PC 1 vs PC 3
y = eigvec(:,1:2:3);
subplot(3,1,2)
biplot(y,'Score',score(1:46,1:2:3),'color','g','Markersize',10,'LineStyle','none'); %%%%Group A
hold on
biplot(y,'Score',score(47:126,1:2:3),'color','b','Markersize',10,'LineStyle','none') %%%%Group B
biplot(y,'Score',score(127:193,1:2:3),'color','y','Markersize',10,'LineStyle','none') %%%%Group C
biplot(y,'Score',score(194:247,1:2:3),'color','r','Markersize',10,'LineStyle','none') %%%%Group D
biplot(y,'Varlabels',varnames,'Color','k','LineStyle','--') %%%%Plot black eigenvectors w/ labels
w/ a dashed line
ylabel('Component 3')

hold off

%%% PC 1 vs PC 4
x = eigvec(:,1:3:4);
```

```

subplot(3,1,3)
biplot(x,'Score',score(1:46,1:3:4),'color','g','Markersize',10,'LineStyle','none'); %%%%Group A
hold on
biplot(x,'Score',score(47:126,1:3:4),'color','b','Markersize',10,'LineStyle','none') %%%%Group B
biplot(x,'Score',score(127:193,1:3:4),'color','y','Markersize',10,'LineStyle','none') %%%%Group C
biplot(x,'Score',score(194:247,1:3:4),'color','r','Markersize',10,'LineStyle','none') %%%%Group D
biplot(x,'Varlabels',varnames,'Color','k','LineStyle','--') %%%%Plot black eigenvectors w/ labels
w/ a dashed line
ylabel('Component 4')
hold off

```

```

%%%%%Create a legend, since the groups have varying sizes its easiest to
%%%%%make blank groups and indicate colors manually

```

```

g = zeros(4,1);
hold on
g(1) = scatter(NaN,NaN,36,'go', 'filled');
g(2) = scatter(NaN,NaN,'bo', 'filled');
g(3) = scatter(NaN,NaN,'yo', 'filled');
g(4) = scatter(NaN,NaN,'ro', 'filled');
legend(g,'Region A','Region B','Region C','Region
D','location','northoutside','Orientation','horizontal')
hold off

```