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A characterization of baseline groundwater quality in the New York Southern Tier for Project SWIFT

A Capstone Project Submitted in Partial Fulfillment of the
Requirements of the Renée Crown University Honors Program at
Syracuse University

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and Renée Crown University Honors
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Honors Capstone Project in Earth Sciences

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Abstract

The acquisition of quality baseline groundwater quality in the Southern Tier of New York State has been of concern due to the contention surrounding groundwater quality in areas where hydraulic fracturing for natural gas production has been developed. Little information on groundwater quality is publicly available for the Southern Tier, where natural gas production through hydraulic fracturing is feasible. This Capstone study, as a part of Project SWIFT at Syracuse University, seeks to determine the concentrations of several ionic compounds and elements in the groundwater of the New York counties which are most apt for hydraulic fracturing. Sample sites were determined by adherence to several criteria based on well construction as well as regularly spaced sample distribution throughout the study area. Streams were also sampled, selected according to drainage area. Results showed that groundwater contained higher concentrations of the majority of the compounds analyzed. Only a small number of samples yielded concentrations greater than the Maximum Contaminant Level set by the Environmental Protection Agency. This data will be used to help develop geochemical fingerprinting tool to detect the presence of hydraulic fracturing fluids and associated formation waters in shallow groundwater wells, as goaled by Project SWIFT.

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Acknowledgements

I’d like to thank the team of brilliant scientists working on Project SWIFT for allowing me to participate in many levels of their research. The lessons in data collection and laboratory preparation from Dr. Laura Lautz, Ms. AnneMarie Glose, and Ms. Deb Driscoll are greatly appreciated. Many thanks to the students who supported and advised me during the hours of data entry, GIS analysis, and research required for this project, especially Mr. Greg Wissink and Mr. Pedro Val. I’d also like to thank Dr. Peng Gao for acting as Reader to the written portion of this Capstone. Finally, special thanks are due to project advisor Dr. Gregory Hoke for his guidance, support, and patience throughout every stage of this Capstone project.

Advice to Future Honors Students

“Choose a job you love, and you will never have to work a day in your life.”

-Confucius

1. Introduction

The water quality in New York State has been in discussion as of late, partly due to the controversial topic of production of natural gas in an area known as the Southern Tier of the state. Advancements in hydraulic fracturing and horizontal drilling processes to recover the natural gas in the Marcellus shale have enabled the industry to expand to areas that have been previously disregarded (Arthur 2008). The development of the natural gas industry in many of these areas can change the environmental and socio-economic landscape, through changing economies and environmental practices (Arthur 2008). The controversy revolves around the effects of hydraulic fracturing and supporting actions on regional water supplies (Urbina 2011, Navarro 2012). Some voices in the discussion name hydraulic fracturing as the source of water contamination in some domestic wells (Kappel 2012), while others find the connections between hydraulic fracturing and well-water contamination to be weak or nonexistent (Saba & Orzechowski 2011, Schon 2011). Several known methods for determining the source of introduced contamination exist (e.g. Knuth et al. 1990), but simple tests are less developed. Project SWIFT (Shale-Water Interaction Forensic Tools) at Syracuse University has recognized this need for simple, objective tests that can determine the effects of hydraulic fracturing on regional water supplies.

This study, as a part of Project SWIFT, characterizes present-day water quality in four of the five counties of New York with the greatest potential for hydraulic fracturing of the Marcellus Shale Formation. This information will allow a simple geochemical fingerprinting tool that will provide unambiguous results to be developed by Project SWIFT.

2. Background

Natural gas is a colorless, odorless mixture of light-end, flammable hydrocarbons that burns more cleanly and with fewer undesirable emissions than coal and oil (Arthur 2008, Kappel & Nystrom 2012). Natural gas occurs in both conventional and unconventional reservoirs (Arthur 2008). Conventional oil and gas deposits develop through the migration of fluids from an organic-rich source rock to high permeability reservoirs where stratigraphic and structural configuration of the rocks traps them and vertical or sub-vertical wells are used to extract the resource (Arthur 2008). Unconventional oil and gas deposits are often found in rock where the source and reservoir are one in the same, such as the shale plays found in Marcellus and Utica Shales of New York State[1] (Arthur

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[1] Paleozoic Shale deposits, such as the Marcellus, in the northeastern United States formed from the laminar deposition of clay-sized sediment in a deltaic system (Kargbo et al. 2010). When the sediments were compacted and lithified under pressure and heat, thinly layered shale was formed (Kargbo et al. 2010). The anaerobic breakdown of organic matter in the original clay sediments

2008). In unconventional deposits, the source and reservoir are one in the same. Shales exhibit low permeability, which allows limited flow of natural gas to a traditional vertical well (Arthur 2008). Therefore permeability must be increased in order to retrieve natural gas (Soeder & Kappel 2009). This procedure can be done by drilling into the shale and applying pressure that is greater than the rock's tensile strength, which creates fractures in the rock (Kargbo et al. 2010, Entrekin 2011). The fractures are propped open by the sand and other chemicals in the fracturing fluid (Soeder & Kappel 2009, Kargbo et al. 2010). The chemically-created gel holding the fractures open breaks down quickly and is removed from the well, and the normal geostatic pressure causes the natural gas to flow through the well (Kargbo et al. 2010).

The Marcellus Shale, named for its type locality near Marcellus New York, is part of the Devonian Hamilton Group. The Hamilton Group was deposited in the marine Appalachian basin, adjacent to the ancestral Appalachians during the middle Devonian (Soeder & Kappel 2009). In New York State the rocks of the Appalachian Basin dip to the south. The Marcellus Shale, with its estimated 95,000 sq. mi extent (nearly 246,049 square kilometers), is receiving attention as one of the largest shale plays in the nation (Arthur 2008). Estimates of the amount of potentially recoverable natural gas vary between 363 trillion cubic feet (Tcf) and 489 Tcf. If the United States continues to use nearly 23

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produced the natural gas that can be extracted from the shale by drilling (Kargbo et al. 2010).

Tcf/year of natural gas (Kargbo et al. 2010), then the total volume of recoverable natural gas in the Marcellus Shale alone may sustain the natural gas needs of the nation for 15 to 20 years. The rock column between exploitable Marcellus Shale and "treatable water" or well water is between 2,125 and 7,650 ft. (Arthur 2008).

The process of hydraulic fracturing requires large volumes of water, in some cases up to 3 million gallons of water per well (Harper 2008). This water must be removed from the well before natural gas can be recovered (Soeder & Kappel 2009). In addition to containing human-added chemicals, the returning fluid, called "produced water," or "flowback water" may also contain materials from the rock including brines, radionuclides, and heavy metals (Soeder & Kappel 2009). The high costs of managing this produced water have caused discussion of potential options, including reuse of the water in future wells (Soeder & Kappel 2009, Kargbo et al. 2010). Main concerns involve the unintentional introduction of produced water to drinking water supplies (Entrekin 2011, Urbina 2011).

The Clean Water Act sets guidelines for the removal and handling of the produced water, although debates of state and national regulation are frequent and controversial (Arthur 2008, Urbina 2011). In order to understand the effects of hydraulic fracturing on groundwater, the original groundwater quality must be known. These baseline characterization studies determine the typical variations in the concentrations of ions, elements, and other materials in the groundwater (Knuth et al. 1990, Panno et al. 2006). This information can be used to develop geochemical and isotopic techniques for monitoring change (Knuth et al. 1990, Panno et al. 2006).

3. Study Area

New York State is an ideal location for this study of groundwater quality for multiple reasons. First, parts of the state overlay both the Marcellus and Utica shale plays, which can be accessed for extraction of natural gas. Areas with greatest potential for development of natural gas from the Marcellus shale include Steuben, Tioga, Chemung, and Broome counties in the southern tier of the state and are also known for their contributions to the agricultural economy. New York State is ideal for a study of baseline water quality, because unlike other regions in the USA, the state has place a temporary moratorium on Hydraulic fracturing due to public and environmental health concerns (Pool 2011). This condition provides a control to which post-hydraulic fracturing water analyses can be compared.

4. Goals and Objectives

This Capstone project is included within SWIFT’s mission of establishing publically available baseline water quality data in the Southern Tier of New York State, particularly in Steuben, Broome, Chemung, and Tioga counties. Results are analyzed statistically as well as spatially. Maps created in ESRI ArcGIS software provide visual representations of results for use in a publically available web interface accessible at http://swift.syr.edu.

5. Data and Methods

5.1. Compilation of source data

Several criteria were defined in order to select wells suitable for sampling during this project. Well location, overall depth and depth into bedrock were the most important parameters for well selection. These data for all wells drilled after 2000 are publically available from the New York State Department of the Environment and Conservation (NYS-DEC). Parcel and landowner data were requested and received from county offices. Additionally, parcel centroid data was obtained from the New York State GIS clearinghouse and used for obtaining landowners contact information.

5.2. Sampling rationale

In order to produce results indicative of groundwater quality, wells of sufficient depths were required for sampling. Sufficient depth was determined by the depth of the well into bedrock. This criterion was simply calculated by subtracting the depth to bedrock from the depth of the well, both provided in the NYS-DEC dataset. Wells not drilled into bedrock were automatically excluded from the pool of potential wells. Such wells were eliminated from consideration for this study, as well as water wells penetrating bedrock that are less than 60 ft. total depth.

Wells of sufficient depth were generally clustered across the study area. This spatial arrangement is due to the presence of towns, as well as local geology. In order to create a complete baseline water quality characterization of the southern tier region, samples must have been obtained at regular intervals. In order to select wells at a regular interval, wells were displayed spatially in layout view of ArcMap10. A 7.5 km by 7.5 km grid was then placed over the map. One well from within each grid cell was selected for sampling. When wells did not fit the grid scheme exactly, estimations of the nearest well for each cell were made. Thus, selected wells were regularly distributed across Steuben, Broom, Tioga, and Broome counties.

With appropriate wells selected for sampling, contact with the landowners was initiated through mailers. Tax parcel data from county offices, instead of statewide data, was preferred for specifying landowner name and mailing address. However, inconsistencies with the availability of data limited this strategy. Instead, NYS parcel centroid data from was used to obtain landowner information. Selected wells were joined with the nearest parcel centroid in ArcMap10 in order to match wells to the respective property data. This joining provided a file that contained all of the selected well data as well as the landowner information. Letters explaining the project and requesting permission to sample were sent to each of the landowners of selected wells. Phone calls were also conducted if phone numbers were available. If a landowner responded positively, then further contact was initiated to plan a timeline of sampling.

Figure 1 shows the locations of the landowners that responded to the letters and whose well water was sampled.

Figure 1: Locations of sample sites

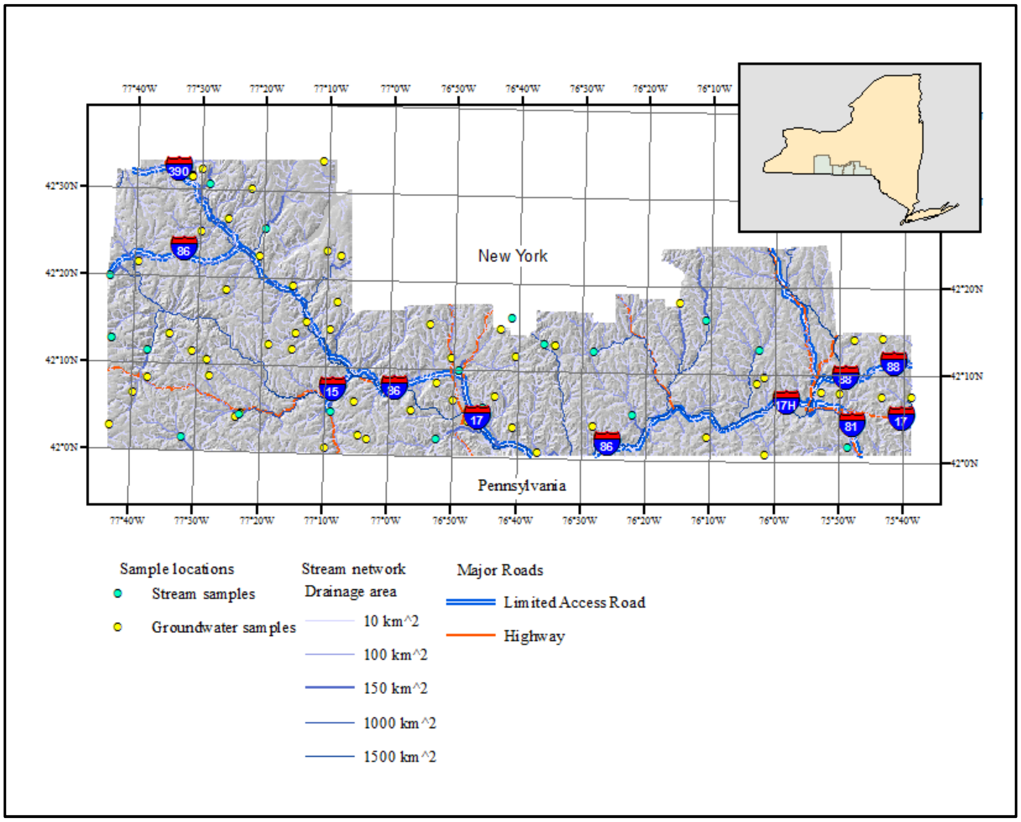

Figure 1 displays the sample area for this study, with groundwater and stream sample sites indicated. Major roads and streams are indicated for reference. A subset of the region within New York State provides coarser-scale spatial reference.

5.3. Sample collection

Two teams collected surface and well water samples in the field. The teams were equipped and trained identically for consistency[2] and each well was sampled using the same procedure. Upon arrival, the best sampling location was decided; in many cases this meant that samples were collect at or before the pressure tank to avoid modification by water treatment devices. After a sampling setup had been arranged, the water was turned on and run for several minutes until the temperature stabilized. This practice was performed to ensure that the water being sampled was groundwater directly from the well, and had not been held at any point in the system. The water was determined to be groundwater when the temperature stabilized. Stabilized temperatures were generally between 9° and 12° Celsius, which is consistent with expectations for local groundwater during the summer months.

All samples were collected wearing nitrile gloves, water was collected in three 250 ml bottles, previously washed in triplicate with distilled water. One 250

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[2] Samples collected in September 2012 had different samplers; however, the September sampling teams had one original sampler on each team to provide consistency.

ml bottle was designated for on-site testing of pH and conductivity using probes and a multimeter. By retaining the probes in one bottle, other water was not at risk from contamination introduced by the probes, although the probes were rinsed with distilled water before and after each use. These in-situ tests provided a simple estimation of the concentration of dissolved solutes in the sample. Water was drawn into a sterile 60ml syringe from the other 250 ml bottles. The water was then passed through a 0.4 µm filter and collected in two 125 bottles previously rinsed in triplicate with distilled water. A small amount of 10 N nitric acid was added to one of the bottles to prevent precipitation of dissolved solutes. Both bottles were then stored on ice until being refrigerated upon return to Syracuse University. Field blanks were also taken in the field, using the same procedure as samples but substituting deionized water in order to confirm the integrity of the sampling procedure and laboratory analyses.

5.4. Laboratory analysis of groundwater samples

A total of 19 stream samples and 59 well water samples were analyzed for major elements and ions. Filtered, acidified samples were analyzed using inductively coupled plasma mass spectrometry (ICP-MS) at State University of New York College of Environmental Science and Forestry. Concentrations of iron, manganese, barium, strontium, phosphorus, lithium, boron, zinc, lead, and selenium were measured.

Filtered samples were analyzed independently of the acidified samples. Non-acidified samples were analyzed using ion chromatography in the laboratory of Dr. Laura Lautz at Syracuse University. Samples were tested for content of ammonium, calcium, chloride, bromide, sodium, potassium, magnesium, nitrate, sulfate, and fluoride.

6. Results

Variations in surface and well water data were explored using descriptive statistics, bivariate plots and geo-statistical analysis in ArcGIS.

Groundwater samples collected from wells showed a greater range in concentrations than stream samples in 19 of the 20 elements and ions analyzed. Additionally, groundwater samples had a higher maximum concentration than stream samples for 95% of the elements and ions tested. Phosphorous was the only element where stream samples showed greater range and a higher maximum concentration than the groundwater samples. Stream samples had a lower minimum concentration than the groundwater samples for 66% of the elements and ions tested. Minimum values for magnesium, calcium, chloride, sulfate, strontium, and selenium were all lower in groundwater samples than the respective minimum values in stream samples. The standard deviation of sample concentrations was greater in groundwater samples for 90% of the elements and ions; only the concentrations of phosphorous and lead showed better grouping in the groundwater samples than in the stream samples.

Comparison of the Project SWIFT samples to the USGS-NURE samples showed marked changes in concentrations for some of the elements analyzed. Magnesium and fluoride showed the greatest percent increase from the USGS-NURE data to the Project SWIFT data, with 80% and 88% increase in median concentration respectively. Chloride showed a 26% increase in median concentration from the USGS-NURE data to the Project SWIFT data. Sodium and bromide both showed a percent decrease in median concentration between the USGS-NURE data and the Project SWIFT data, with 7% and 33% decrease respectively over the past 28 to 39 years.

T-tests were also conducted to quantify the significant variation between the two datasets. These statistical tests showed that the sodium and chloride concentrations did not vary significantly between the USGS-NURE and Project SWIFT data, while magnesium, bromide, and fluoride all showed significant variation between the two datasets. The reader is referred to Charts 3-6 on page 27-28 for details of the T-test values.

6.1 Accounting for skewness

A deterministic factor in data analysis was the degree of skewness of the data. The high skewness first became apparent when conducting basic analysis of our in-situ specific conductivity tests. Potassium was the most skewed of the elements analyzed, with a skewness of 8.79. The high skewness in most of the samples is due to the presence of a small number of high concentrations in each analysis. These few high concentrations, possibly anomalies, greatly affected the averages and other statistical methods. Therefore, some of the anomalies had to be excluded from the data in order to statistically display the other data. Table 1 shows a summary of the statistical results from the elements analyzed at Syracuse University.

Table 1 shows a summary of the basic statistical distribution of the concentrations of elements analyzed in this Capstone study. The ions are listed across the columns. Mean, median, standard deviation, minimum and maximum values are listed each as a row. Each of these concentrations are measured in parts per million.

Table 1: Summary of elements analyzed in SWIFT samples

Ion (ppm) →	Na	NH_4	K	Mg	Ca	F	Cl	Br	NO_3	$S0_4$
Mean	30.544	0.127	1.505	12.682	46.448	0.163	29.116	0.067	3.899	23.488
Median	19.524	0.050	1.373	9.971	44.382	0.160	5.915	0.025	0.129	13.703
Standard Deviation	31.042	0.129	0.608	8.646	25.413	0.089	63.107	0.101	16.994	29.520
Minimum	4.636	0.05	0.617	1.596	0.35	0.05	0.415	0.025	0.025	0.04
Maximum	144.889	0.622	3.809	50.521	138.925	0.586	433.703	0.412	126.057	140.693

6.2. Relationships between ions and specific conductance

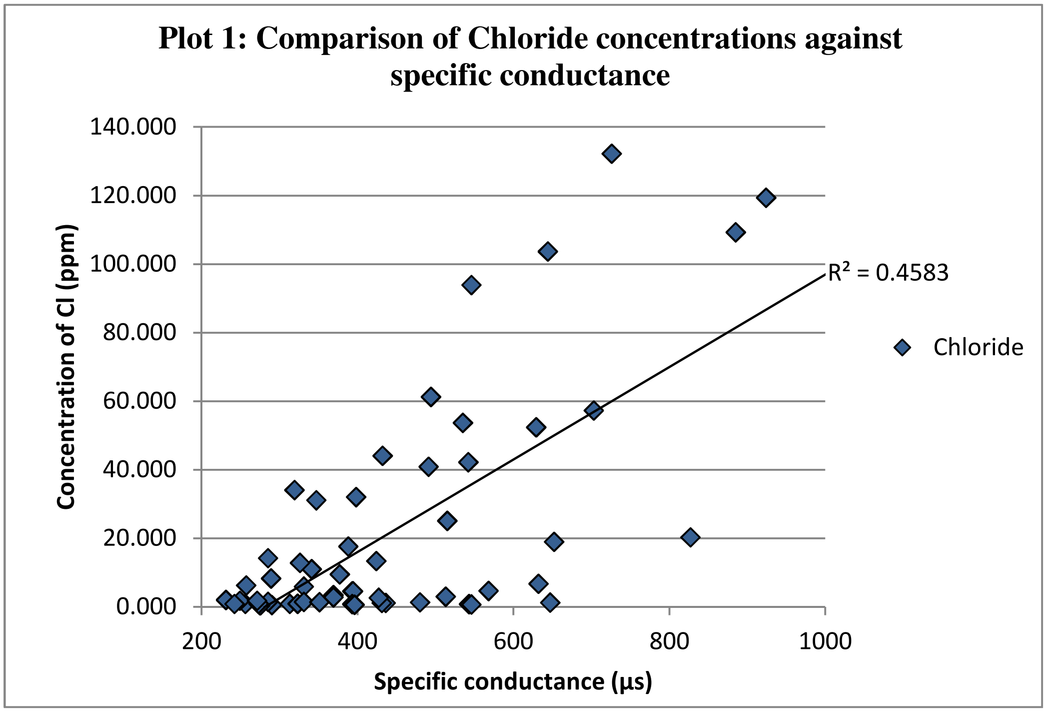
Ions were plotted against specific conductance to determine which ions had a greater effect on the conductivity of the samples (Table 2). A linear regression was created for each ion, and the coefficient of determination (r^2) was established for each. The ion with the trend line of the highest r^2 is indicative of the most consistent relationship between ion content and specific conductance.

Table 2: Coefficients of Determination for ions vs. specific conductance

	Na	NH_4	K	Mg	Ca	F	Cl	Br	NO_3	$S0_4$
r^2	0.10	0.005	0.003	0.47	0.068	0.0003	0.46	0.11	0.004	0.10

The coefficients of determination, or r^2 value, indicate how well each ion correlates to specific conductance. Magnesium shows the best correlation with specific conductance.

r^2 is a metric reflecting the goodness of fit for a given regression model, an exact match between trend line and data would produce an r^2 value of 1, while any thing less shows the percent variability described by the model. Ions analyzed in the SWIFT samples did not yield r^2 values that are conclusive of a direct relationship to specific conductance ($r^2 > 0.5$, a majority of the variability). However, all samples with high conductance must have high amounts of chloride or magnesium, or both. However, the array of chloride content values contained an outlier that had to be excluded in order to properly view the points of lower values. The chloride anomaly, a sample showing a content of 433 ppm, occurred at the greatest specific conductance. Ions with a relatively higher original r^2 were plotted again, excluding the greatest specific conductance value. The r^2 for magnesium decreased by nearly 50% when this point was excluded (although it still showed the most significant correlation) and the r^2 values for other ions likewise did not improve. Therefore, we can deduce that the chloride content in groundwater has the greatest effect on specific conductance of the ions analyzed. However, the low r^2 value even with the anomaly excluded does not strongly support this conclusion



Plot 1 shows the correlation of chloride concentrations plotted against specific conductance. The outlier of 433 ppm is excluded from this plot. The coefficient of determination for the best fit line is 0.4583.

6.3. Spatial patterns in water chemistry

The purpose of this study as a part of Project SWIFT is to provide access to water quality data to the public. While our data is conclusive of a baseline water quality survey, it does not contribute to the dialogue related to hydraulic fracturing-type natural gas production if it is not available to landowners. Therefore, the creation of an interactive online database is in progress.

The goal of the database is to provide the public with relevant data that are accessible both logistically and cognitively. A spatial representation of the results found in the SWIFT study in an interactive interface will allow landowners and other populations interested in the quality of groundwater in the southern tier to explore the data and comprehend the spatial distribution of particular ions.

Sample data, including geographic coordinates, pH, conductivity, and results from laboratory analysis, were compiled into spreadsheets. Surface water data (streams) were separated and interpreted independent of groundwater samples. Coordinates of both groundwater and surface water sampling sites were used to spatially display the data for further interpretation.

Our data were compiled into a shapefile in ArcMap10, an ESRI product. While this may provide sufficient data for those familiar with semiabstract spatial displays, this point format is not well suited for our target audience. A continuous map showing the spatial resolution of the data is easier for a diverse population to understand. This manipulation of data requires estimation of potential values between data points. This estimation is known as interpolation.

There are many different methods of interpolation used in scientific studies. Different methods may produce varying interpolation estimates; therefore, using the best interpolation methods for the dataset is important. Previous studies have used a cross-validation technique to determine the accuracies of the GIS-interpolated estimations. By excluding one data point, interpolating estimations for that site, and comparing the estimation to the real data, the accuracy of the interpolation can be determined (Moral 2010). This method of cross-validation has been widely used in studies gauging accuracies of interpolation estimations between data points.

Most studies show kriging to be the optimal choice for interpolating, and show that kriging can have the lowest error produced in cross-validation. Kriging refers to a set of geostatistical techniques used for interpolation (Zhang 2009). This technique is a more complex and computationally-intensive method than others, due to the requirement of a fitted semivariogram model and development of model parameters (Teegavarapu 2007, Zhang 2009). Kriging is used frequently in geophysical applications, including hydrology (Teegavarapu 2007).

The many variations of kriging may not be accurate for the same set of data. Bazgeer et al (2012) showed that while exponential kriging was the superior interpolation method for one dataset, other kriging methods for the same dataset were notably less accurate. Ashraf et al. (1997) found that while kriging gave the lowest error when cross-validating the interpolation, co-kriging improved the result even further. Additionally, the accuracy of kriging depends on the quality of the fitted semivariogram; accurate estimates cannot be derived from an inappropriate semivariogram (Lu 2008). The computational complexities required for kriging make the technique impractical for this Capstone project.

Polygons are also regularly used in estimating values between data points, especially for precipitation and other variables. Polygons are created around a target value; each point within that polygon must be closer to that target value than to any point in the adjacent polygon (Teegavarapu & Chandramouli 2005). Many studies, including the Tabios (1985) comparative analysis study of interpolation methods, found the creation of polygons to be the least accurate method of interpolation with kriging and IDW to be superior to a polygon method (Tabios III 1985).

Literature shows an inverse distance weighting method (IDW) to be a satisfactory interpolation technique. A grounding theory in related fields assumes that points which are closer in space have a greater influence on each other than on points at a greater distance (Tobler 1970). The concept of IDW, in which known points closer to an unknown point have a greater weight on the unknown, directly reflects this theory (Zhang 2009). Lu (2008) found IDW to be a superior method in interpolating values between point data due to the speed at which estimates can be computed as well as the simple interpretation of the method and results. When Lu (2008) applied their own algorithm to determine the optimal distance weighting, their results were more accurate than kriging the same estimations. Another advantage of IDW is that not all the points of a dataset are required in order to calculate estimation; the operator can choose to include only the neighboring points- which will have a greater weight on the unknown point-or to include all the relevant data points for the study area. The use of an inverse-distance squared method can further improve the accuracy of IDW (Ashraf 1997). IDW methods are limited in that the values estimated between points cannot exceed the maximum or minimum neighboring points to create a smooth surface. This leads to the development of "bulls-eyes" around the data points, which may include inaccuracies at a finer scale than the data points. Many studies show IDW to be satisfactory in estimating soil properties, especially in producing more accurate estimations of interpolated soil organic matter and nitrogen content (Gotway 1996). The simplicity of computations and success in related studies make IDW the ideal interpolation technique for this study.

The first step of using IDW is determining the search radius, or area in which the inclusive points will affect the estimation point. This radius was largely determined by the largest interval existing in the dataset. To approximate an appropriate search radius, Voronoi polygons were created. Voronoi polygons delineate between the data points so that each point within the polygon is closer to its polygon centroid point than to any other point in the dataset. This method allowed for simple visual comparison of the distances between the data points. Once the most remote point was found, the distances between that point and five of its closest neighbors were measured. The largest of those distances represents the search radius necessary to include at least 5 data points in the geostatistical interpolation. 40 km was determined as the optimal search radius and used for the interpolation in the spatial display of this data. Maps 1 through 7 in the appendix of this Capstone show the spatial patterns of the ion concentrations of the Project SWIFT samples.

8. Temporal Comparison

Our study of baseline water quality in the Southern Tier of New York State is not the first study of its kind. A study examining many of the same variables was conducted from 1977 through 1984 (Smith 2006). This data set, known as the National Uranium Resource Evaluation under the United States Geological Survey (USGS-NURE)[3], provides a temporal comparison to the results found in our study for the bromide, chloride, fluoride, magnesium, and sodium content. These ions and compounds have been associated with hydraulic fracturing and produced water. Therefore, understanding the changes in these materials before hydraulic fracturing will help to develop a geochemical fingerprint of produced water

The SWIFT data was compared to the NURE data using statistical methods. A t-test was performed for each ion analyzed by both studies to

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[3] This dataset was compiled in exploration of uranium concentrations in the United States. The dataset includes concentrations of tens of analyzed compounds, in addition to well data. The data collected in the same study area as Project SWIFT was collected during the summer and fall months of 1977 and 1978. This dataset may occasionally be abbreviated as “NURE” in this Capstone.

determine if the datasets were statistically different from one another. Percent change relative to the NURE data was also calculated for each of the selected ions. Percent change was calculated twice; once using traditional mean, and again using the median of each array to account for large anomalies.

Charts 4 through 6 show the temporal changes of elements analyzed in the USGS-NURE study as well as the Project SWIFT study. Each chart contains a comparison of the basic statistic calculations is shown in each chart, the results of a T-test to show the statistical significance of the differences in the dataset, and the percent change, calculated using both the average value and median value for each set. Percent change is calculated with respect to the USGS-NURE dataset.

Chart 3: Summary of temporal changes in Na concentrations			
NURE		SWIFT	
Mean	32.22	Mean	30.54
Standard deviation	40.93	Standard deviation	31.04
Maximum	357.9	Maximum	144.89
Minimum	0	Minimum	4.64
T-Test:		0.73	
Percent Change:		Average	-5.2
		Median	88.61

Chart 4: Summary of temporal changes in Br concentrations			
NURE		SWIFT	
Mean	0.16	Mean	0.07
Standard deviation		Standard deviation	0.1
Maximum	4.63	Maximum	0.025
Minimum	0	Minimum	0.41
T-Test:		2.68E-08	
Percent Change:		Average	-58.57
		Median	-33.33

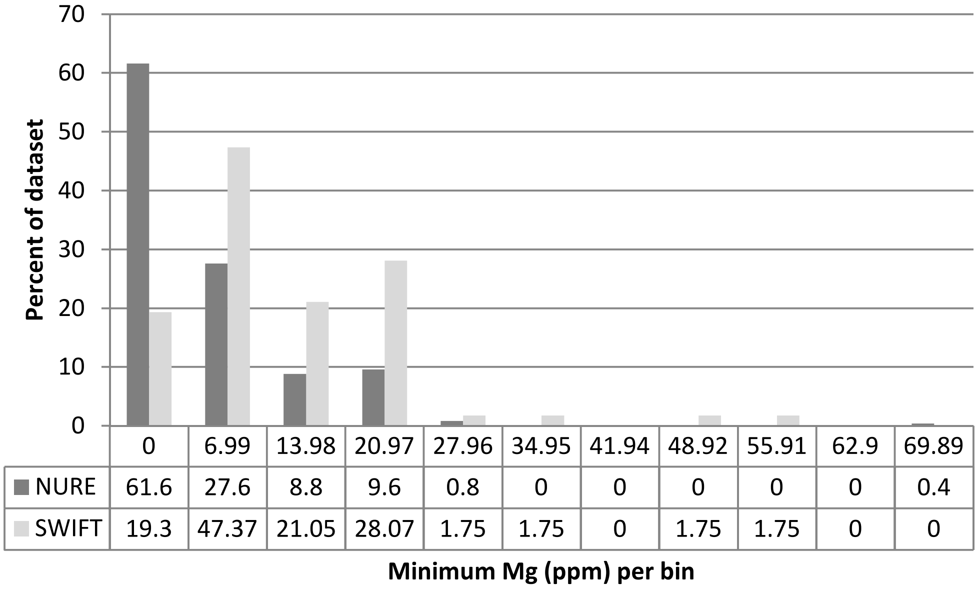
Chart 5: Summary of temporal changes in Cl concentrations			
NURE		SWIFT	
Mean	21.72	Mean	29.12
Standard deviation	53.51	Standard deviation	63.12
Maximum	527.7	Maximum	433.7
Minimum	0	Minimum	0.42
T-Test:		0.42	
Percent Change:		Average	34.03
		Median	26.068

Chart 6: Summary of temporal changes in Mg concentration			
NURE		SWIFT	
Mean	6.72	Mean	12.68
Standard deviation	7.05	Standard deviation	8.57
Maximum	74	Maximum	50.52
Minimum	0	Minimum	1.6
T-Test:		6.73E-06	
Percent Change:		Average	-7.25
		Median	80.8

Chart 6: Summary of temporal changes in F concentrations			
NURE		SWIFT	
Mean	0.1	Mean	0.16
Standard deviation	0.08	Standard deviation	0.089
Maximum	0.814	Maximum	0.586
Minimum	0	Minimum	0.05
T-Test:		1.37E-46	
Percent Change		Average	71.51
		Median	88.19

Regardless of the minute differences between percent change using average and median, the percent change relative to NURE data in magnesium is still robust, and requires closer analysis. To numerically discern where the changes occur, the data can be charted onto a histogram. Using the same interval to display both NURE and SWIFT data allows visualization of the different distributions. Plot 3 contains the histograms of NURE and SWIFT data, and shows that the magnesium contents have generally increased since the NURE data was collected.

Plot 3: Histogram of Mg (ppm) in NURE and SWIFT datasets



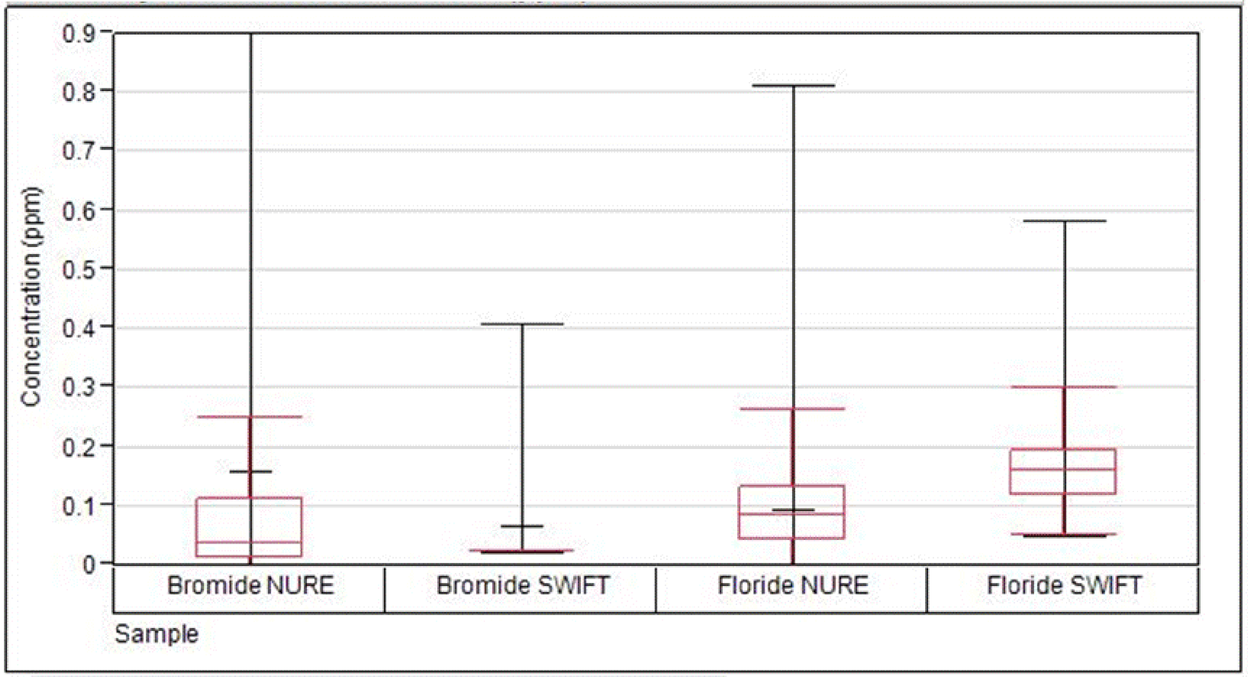
	0	6.99	13.98	20.97	27.96	34.95	41.94	48.92	55.91	62.9	69.89
■ NURE	61.6	27.6	8.8	9.6	0.8	0	0	0	0	0	0.4
□ SWIFT	19.3	47.37	21.05	28.07	1.75	1.75	0	1.75	1.75	0	0

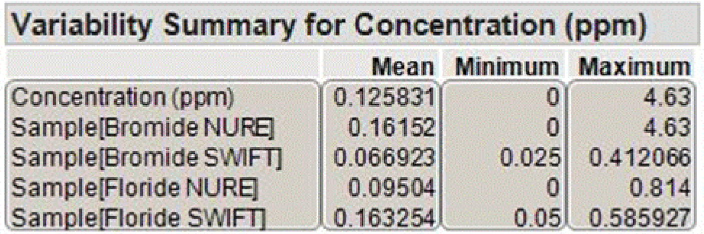
Plot 3 shows a histogram of the magnesium concentrations in the USGS-NURE and Project SWIFT datasets. The NURE data is comprised of 250 samples, and the SWIF data is comprised of 57 samples.

The NURE and SWIFT data can also be compared using box plots. Plots 4 and 5 compare the NURE and SWIFT data for selected elements, separated into two plots for reasonable scales. The first and third quartiles are show with the minimum, maximum, and mean values. These plots include the 250 NURE samples and the 57 SWIFT groundwater samples.

Plots 4 and 5 display the distribution of sample concentrations for Bromide and Fluoride (Plot 4) and Chloride, Mg, and Na (Plot 5) in both the Project SWIFT and USGS-NURE datasets. The degree of skew is made apparent in these plots. The attached tables provide reference for the plots.

Plot 4: Distributions of Bromide and Fluoride in NURE and SWIFT data

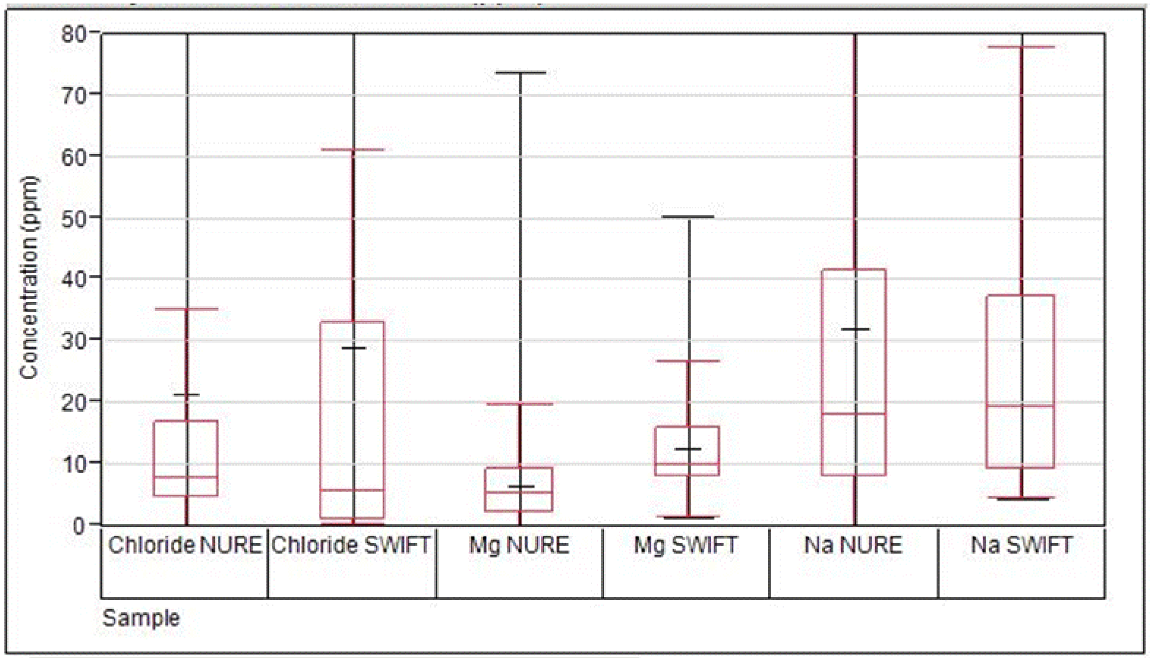


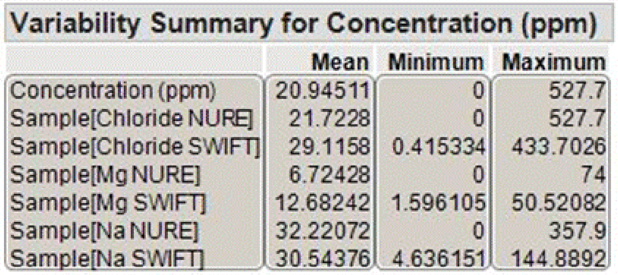


Variability Summary for Concentration (ppm)

	Mean	Minimum	Maximum
Concentration (ppm)	0.125831	0	4.63
Sample[Bromide NURE]	0.16152	0	4.63
Sample[Bromide SWIFT]	0.066923	0.025	0.412066
Sample[Floride NURE]	0.09504	0	0.814
Sample[Floride SWIFT]	0.163254	0.05	0.585927

Plot 5: Distributions of Cl, Mg, and Na in NURE and SWIFT data





Variability Summary for Concentration (ppm)

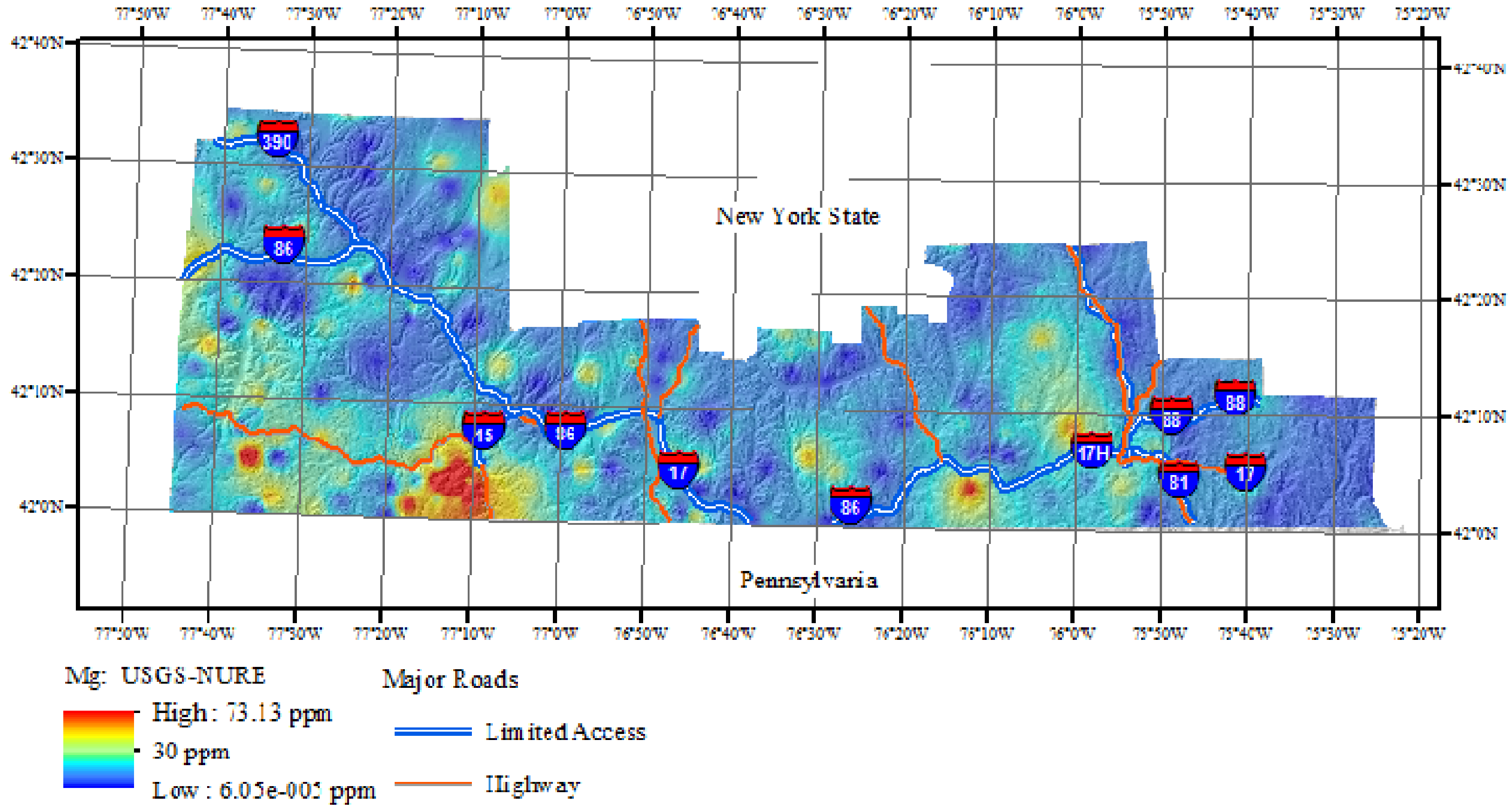
	Mean	Minimum	Maximum
Concentration (ppm)	20.94511	0	527.7
Sample[Chloride NURE]	21.7228	0	527.7
Sample[Chloride SWIFT]	29.1158	0.415334	433.7026
Sample[Mg NURE]	6.72428	0	74
Sample[Mg SWIFT]	12.68242	1.596105	50.52082
Sample[Na NURE]	32.22072	0	357.9
Sample[Na SWIFT]	30.54376	4.636151	144.8892

The NURE data set was spatially processed in the same manner as the SWIFT data. Interpolated surface maps of elements analyzed the SWIFT study were generated using the same search radius and technique as the SWIFT data. Displacement of concentration peaks or other concentration migration can be visually analyzed in comparison of SWIFT and NURE maps. This comparison can provide visualization of the changes in magnesium, as shown in Maps 7 and 8.

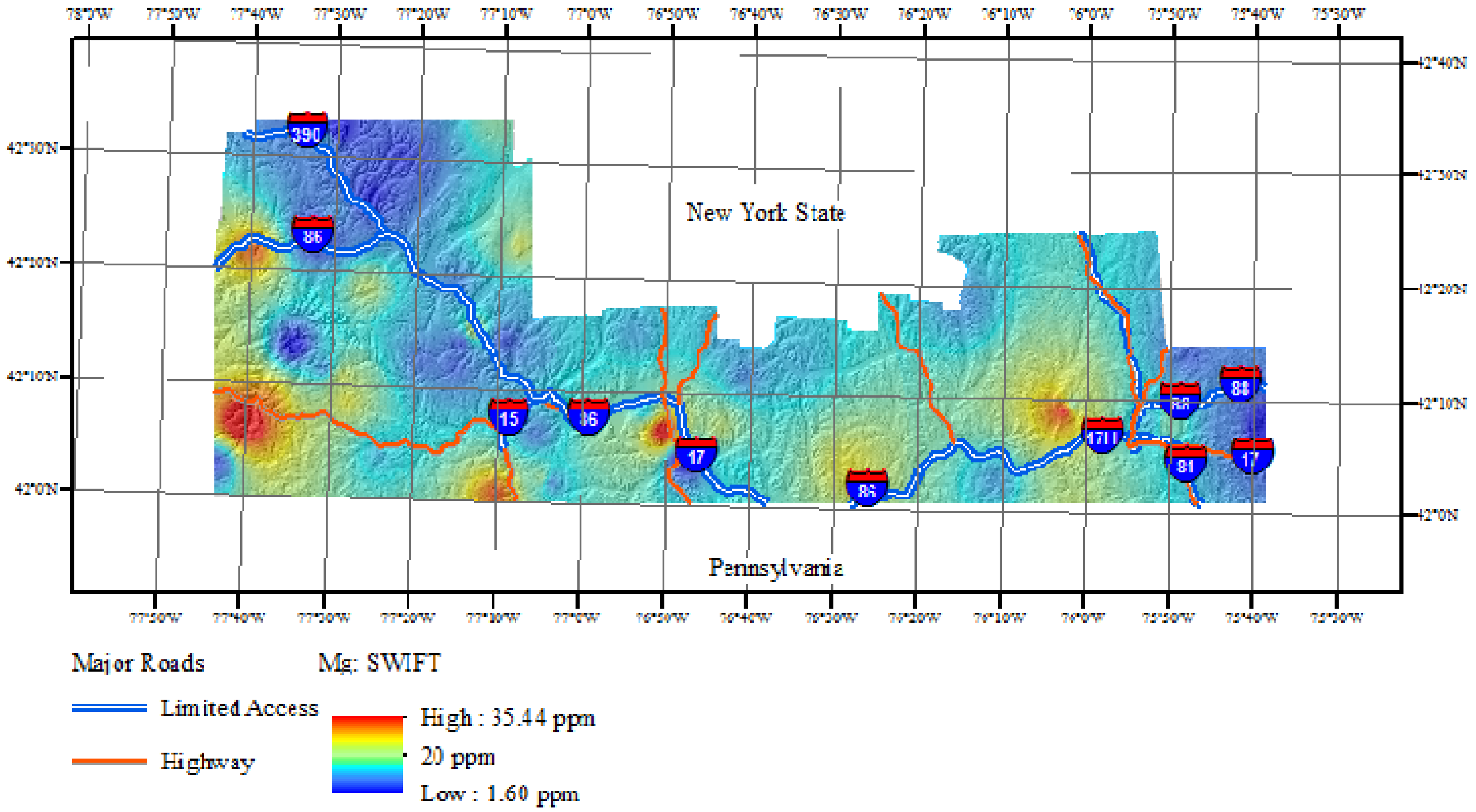
Map 8 shows the spatial patterns of magnesium concentrations in the USGS-NURE study. Map 9, showing the spatial patterns of magnesium concentrations in the Project SWIFT study, immediately follows Map 8 for visual comparison of the changing patterns over several decades. Map 10 shows the calculated difference between the NURE and SWIFT data, as computed and displayed in ArcGIS. This subtraction technique provides a more accurate gauge of changing concentration patterns.

Maps 11 through 14 in the appendix of this Capstone show the difference maps for chloride, bromide, fluoride, and sodium concentrations.

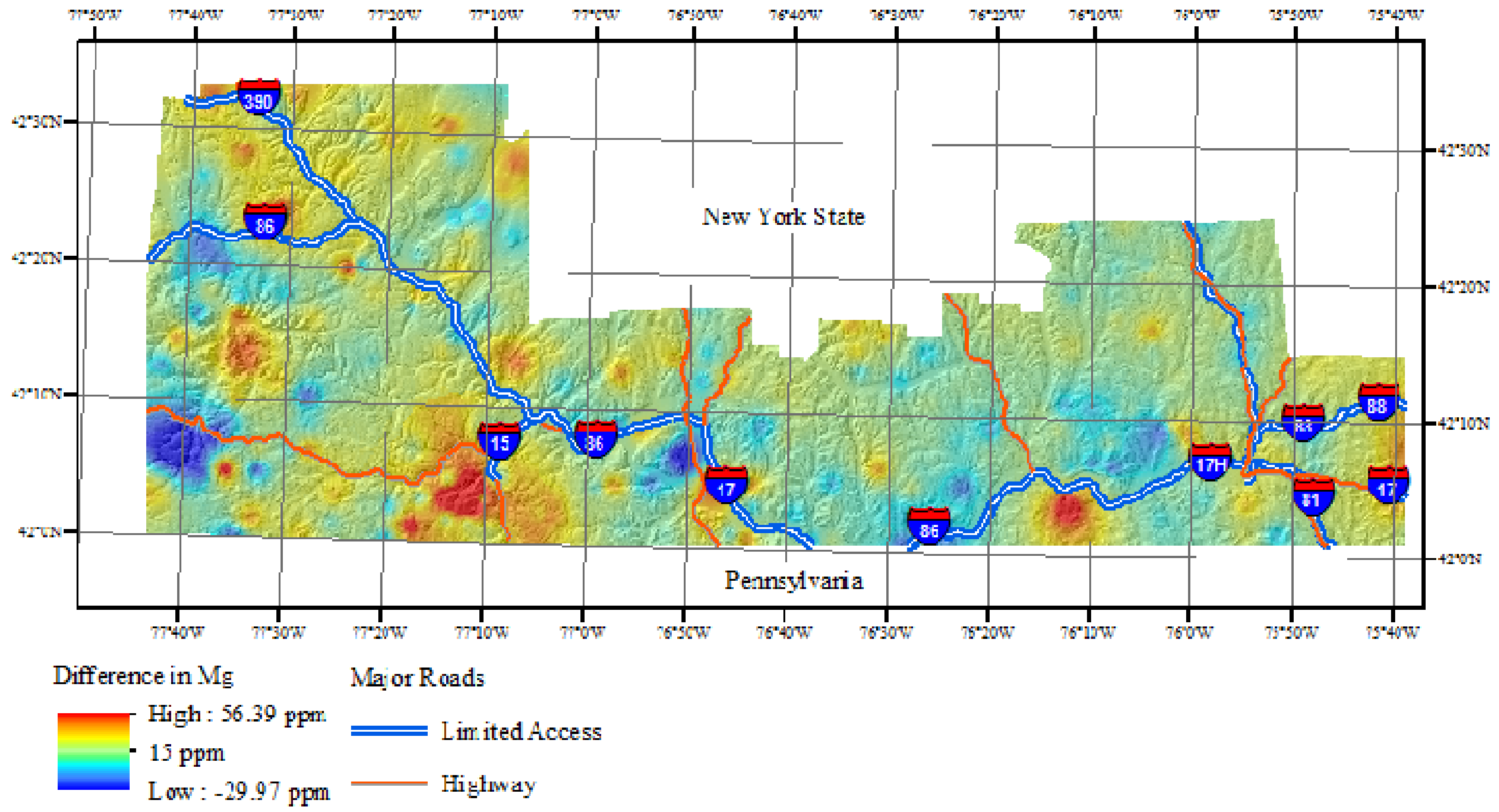
Map 8: Concentrations of magnesium in NURE samples



Map 9: Concentrations of magnesium in SWIFT samples



Map 10: Difference in magnesium concentrations from NURE to SWIFT data



Discussion:

The increase in magnesium seen in the SWIFT data could be attributed to several causes. Most simply, the changes in magnesium content in the groundwater could be caused by changes in land use, including a movement away from agriculture that would otherwise bind the magnesium into the surface and limit magnesium movement to the groundwater. Chapman (1997) found that magnesium concentrations can vary in relation to the divalent cations from groundwater. Increased interaction with the divalent cation-rich groundwater can increase magnesium concentrations; therefore, if groundwater flowpaths have changed to provide more contact with particular groundwater since the NURE data was collected, then our samples may show different results (Chapman 1997).

Another cause of the changing ionic contents of the water could be more anthropogenic. A 28-acre, unlined landfill called the Old Bath Landfill was operating in the region from 1978-1988 (Trust 2008). Kerfoot (2004) found the landfill to have effects on groundwater. Increased magnesium content in groundwater may increase due to effects of landfill gas (Kerfoot 2004). However, this is unlikely the sole cause of the increase, as the largest difference in magnesium concentration is over 30 km from Bath, NY, and most of the sample sites in Project SWIFT are at a higher elevation due to the well-selection criteria. An anonymous resident of the town of Woodhull, where the greatest increase in magnesium occurs stated during the sampling procedure that the Department of Health has advised the residents in the town of Woodhull not to drink the local well water.

The relatively high percent of Project SWIFT samples that showed a significant percent increase in ion content relative to the NURE data should be noted. The seasonality of the samples, or the meteorological conditions preceding the both the NURE and SWIFT sampling, could greatly affect the concentrations of ions found in the water. Samples for Project SWIFT were obtained at the end of an unusually hot and dry summer in New York, which may cause the ions to be more concentrated than normal. The USGS-NURE data was collected from August through November of 1977 and August through September of 1978. This inclusion of later months may affect relatively more diluted concentrations.

Conclusion

The groundwater samples collected for Project SWIFT shows variation in chemical content of groundwater throughout the Steuben, Chemung, Tioga, and Broome Counties, NY. Knowledge of these concentrations is important in determining simple forensic tools that can trace the effect of hydraulic fracturing on the quality of regional groundwater. The comparison of SWIFT and NURE samples provides a marker of temporal changes for five of the ions analyzed for this study. The degree of percent change that occurred in the groundwater chemical content between the early 1980s and 2012 also gauges how groundwater quality may change in future years, and must be accounted for in the development of a geochemical footprint.

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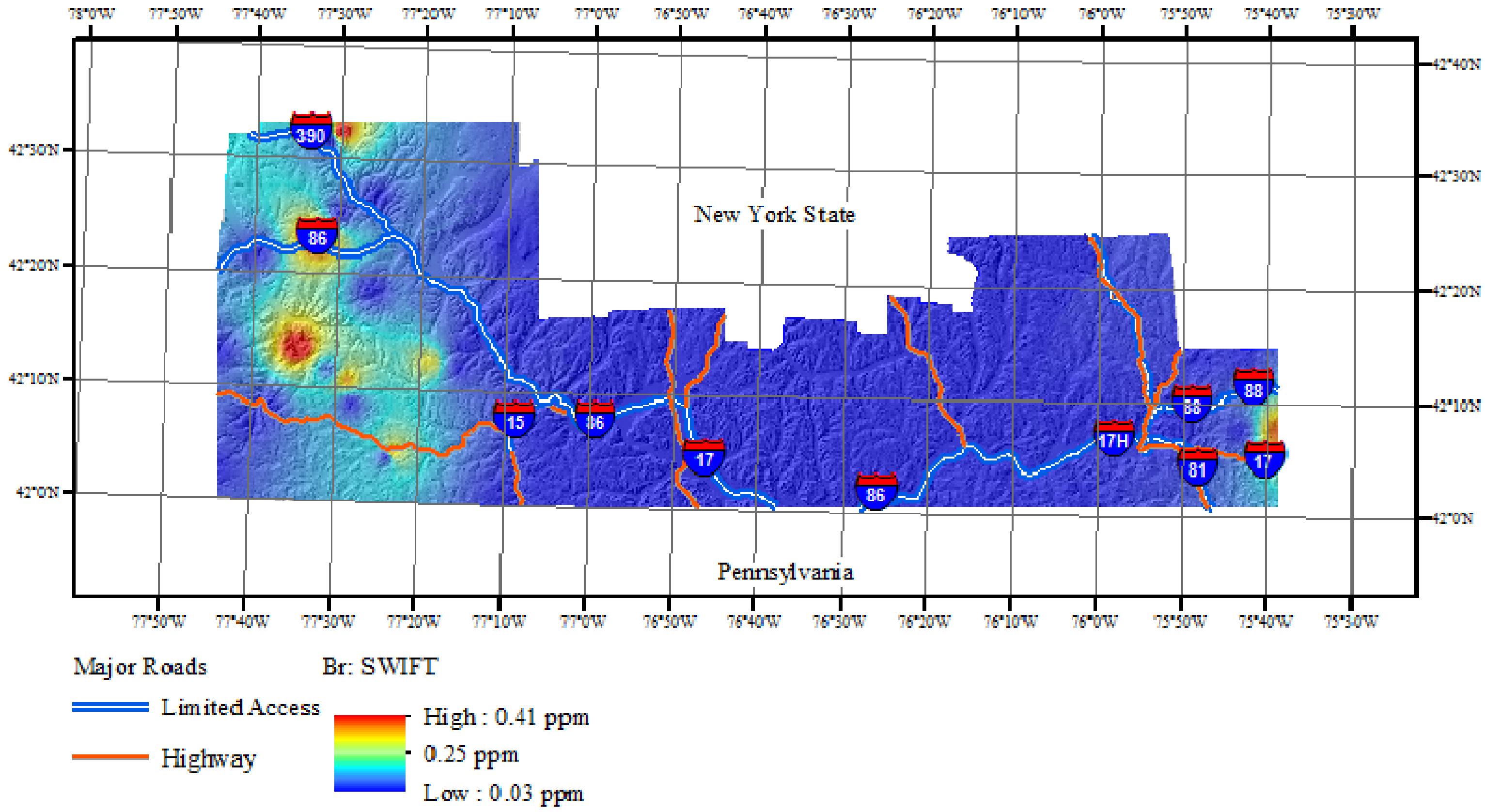
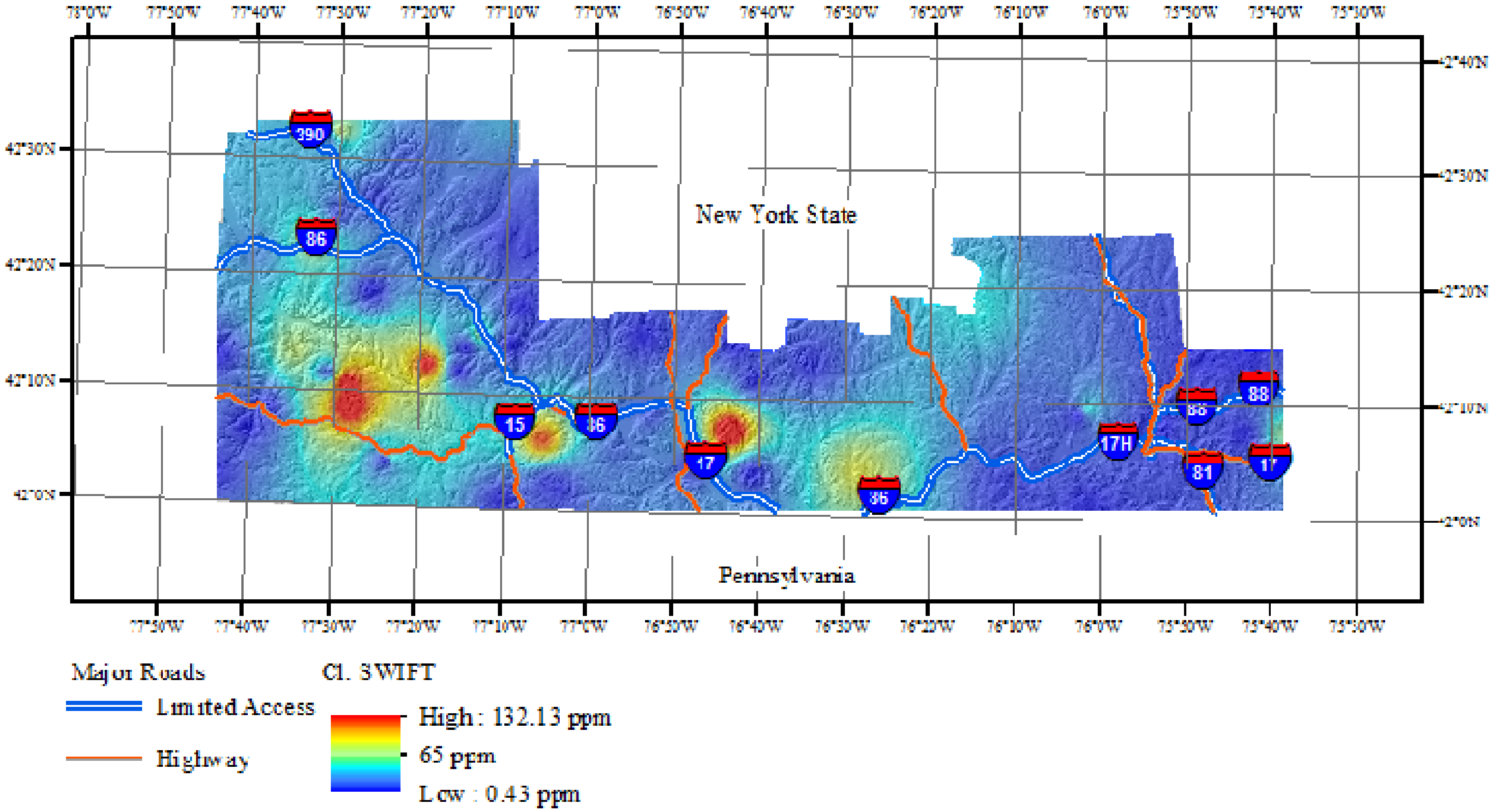
Appendices

Maps 2 through 7 are intended to show the spatial distribution and variation of compounds analyzed in the Project SWIFT data. The colors represent concentration, as indicated in each legend. Major roads are included for spatial reference.

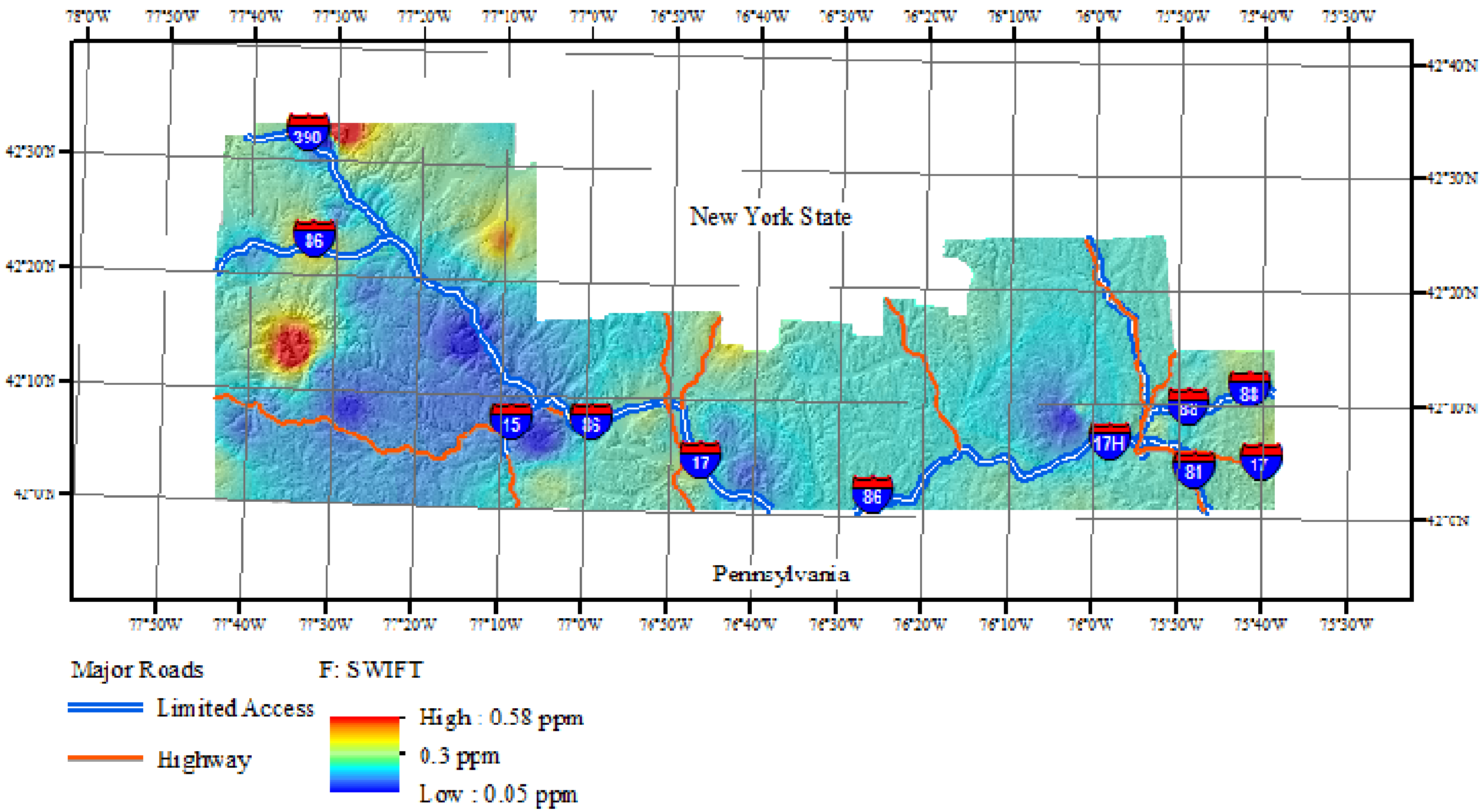
Map 2: Spatial distribution of bromide concentrations in Project SWIFT samples



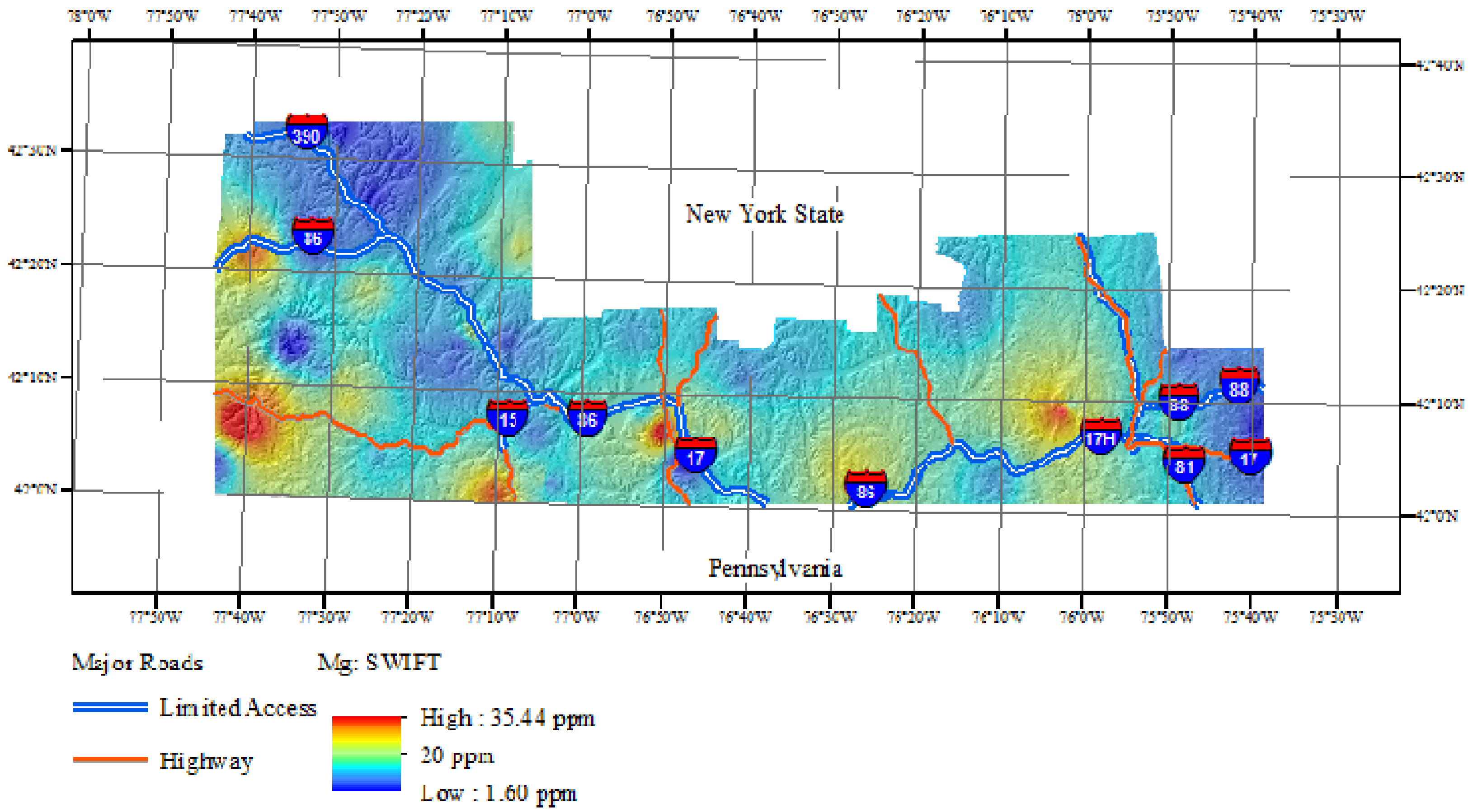
Map 3: Spatial distribution of chloride concentrations in Project SWIFT samples



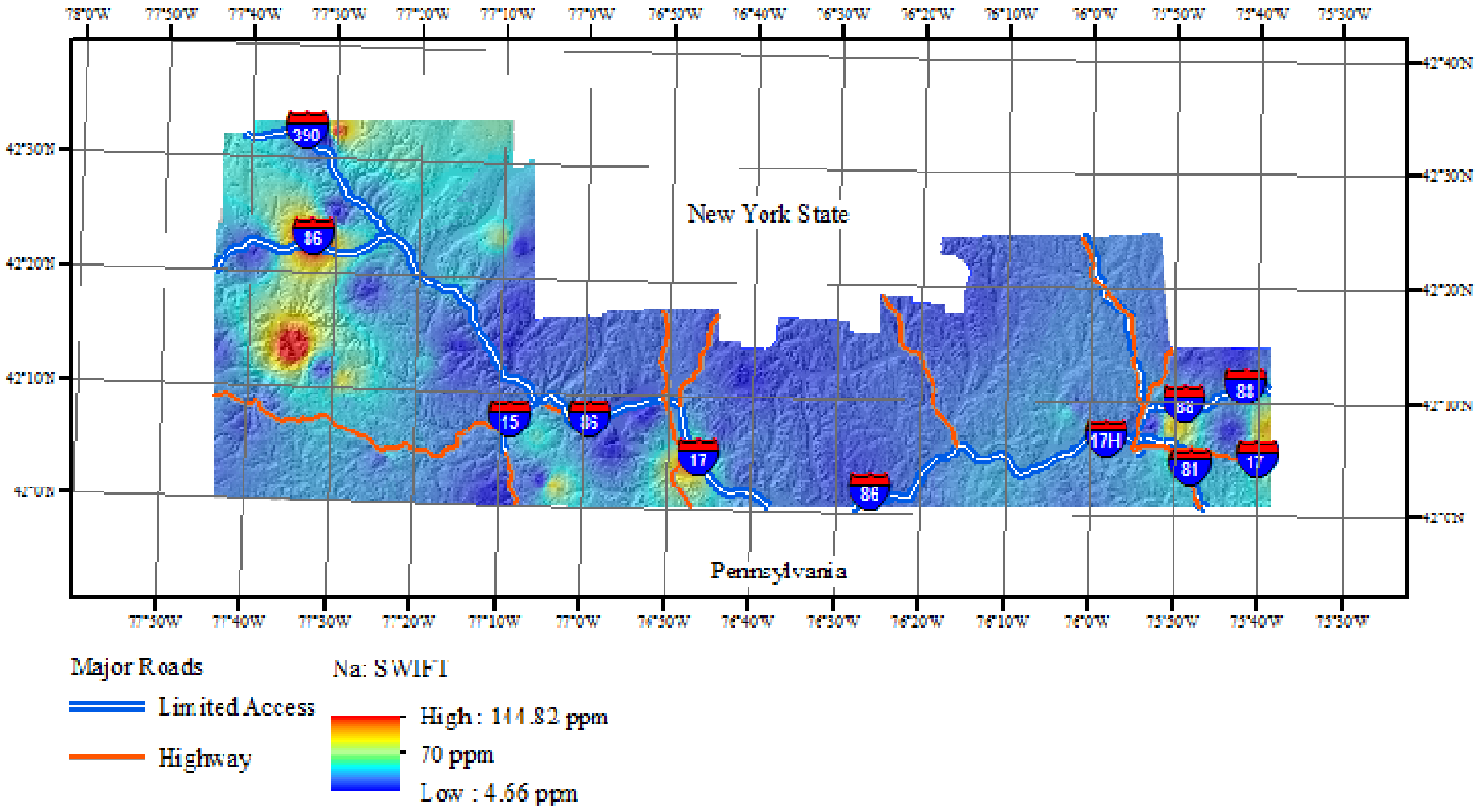
Map 4: Spatial distribution of fluoride concentrations in Project SWIFT samples



Map 6: Spatial distribution of magnesium concentrations in Project SWIFT samples

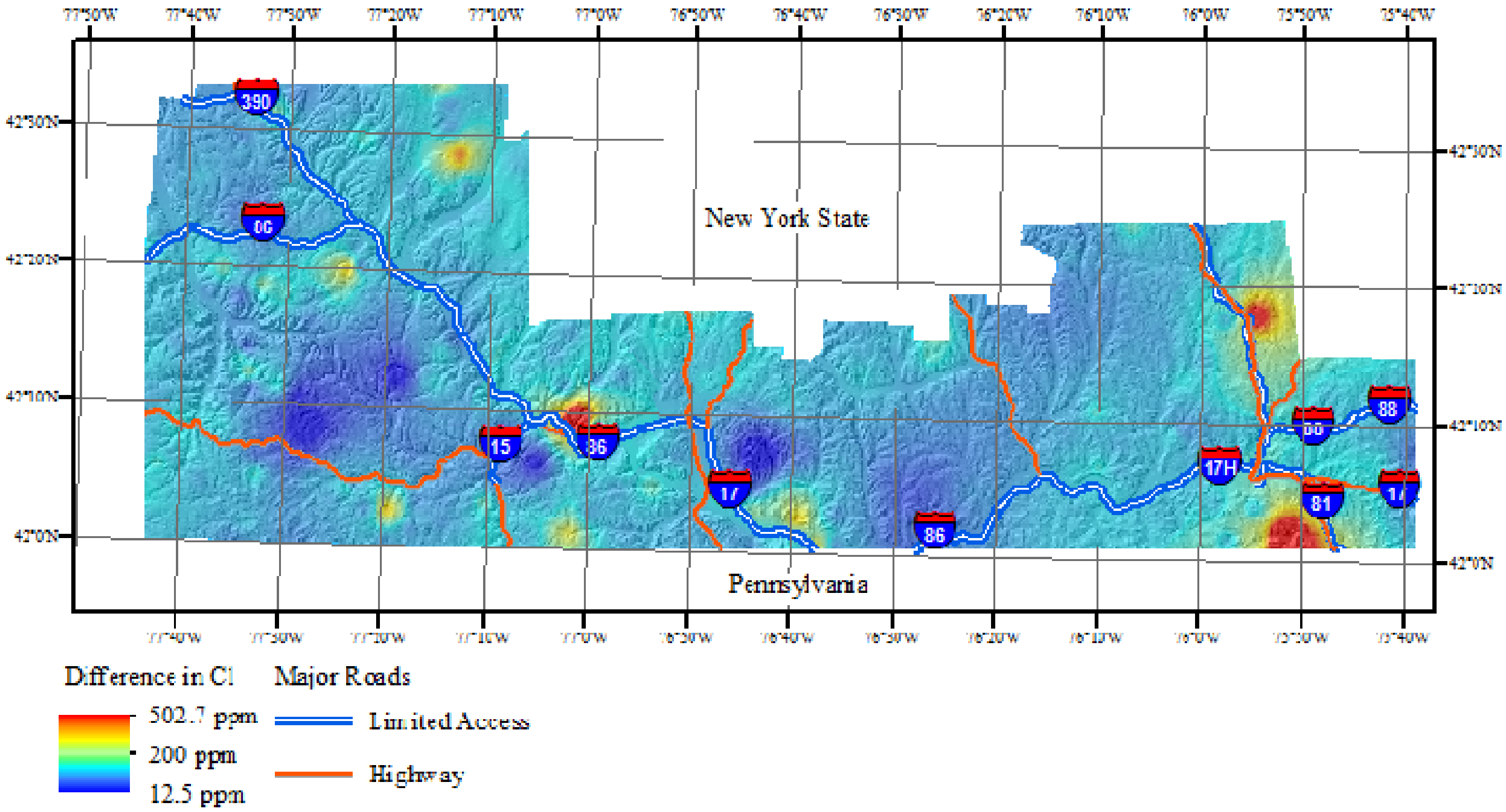


Map 7: Spatial distribution of sodium concentrations in Project SWIFT samples

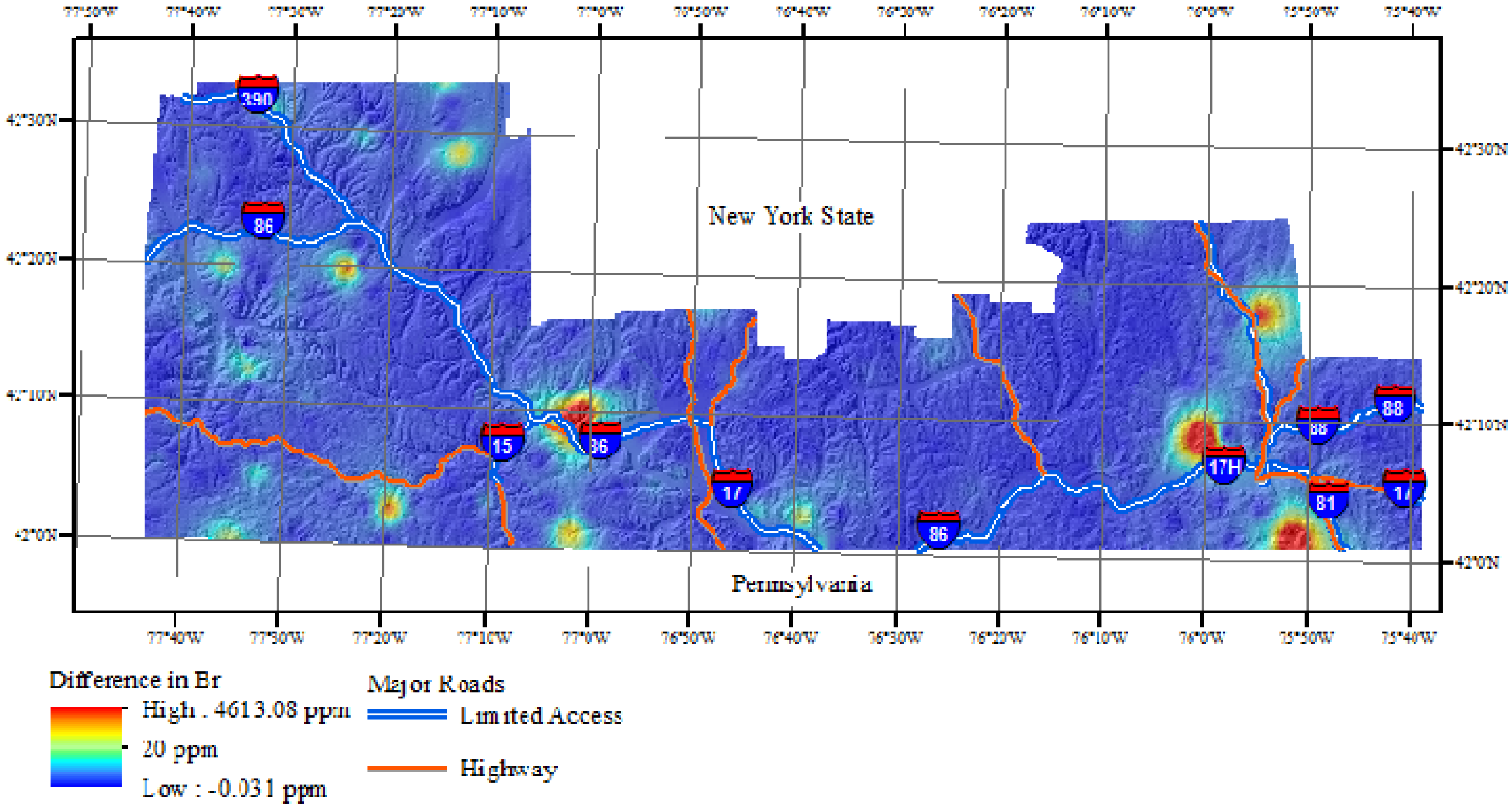


Maps 11 through 14 show the difference between the USGS-NURE data and the Project SWIFT data for mutual analyses. These maps were calculated in ESRI ArcGIS software, and show the difference between pixel-by-pixel comparisons of the two datasets. Major roads are shown for reference.

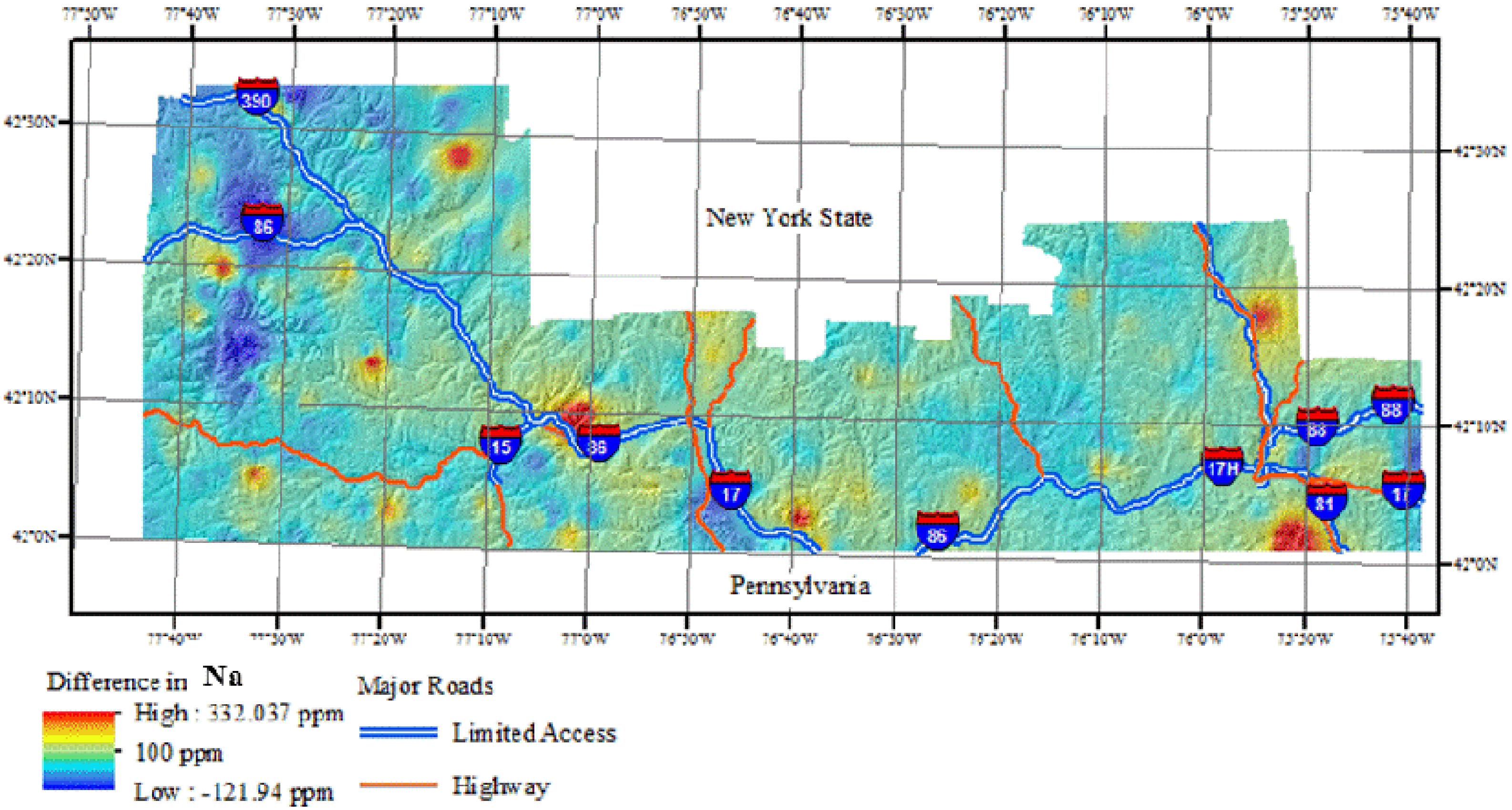
Map 11: Difference in chloride distribution from NURE to SWIFT data



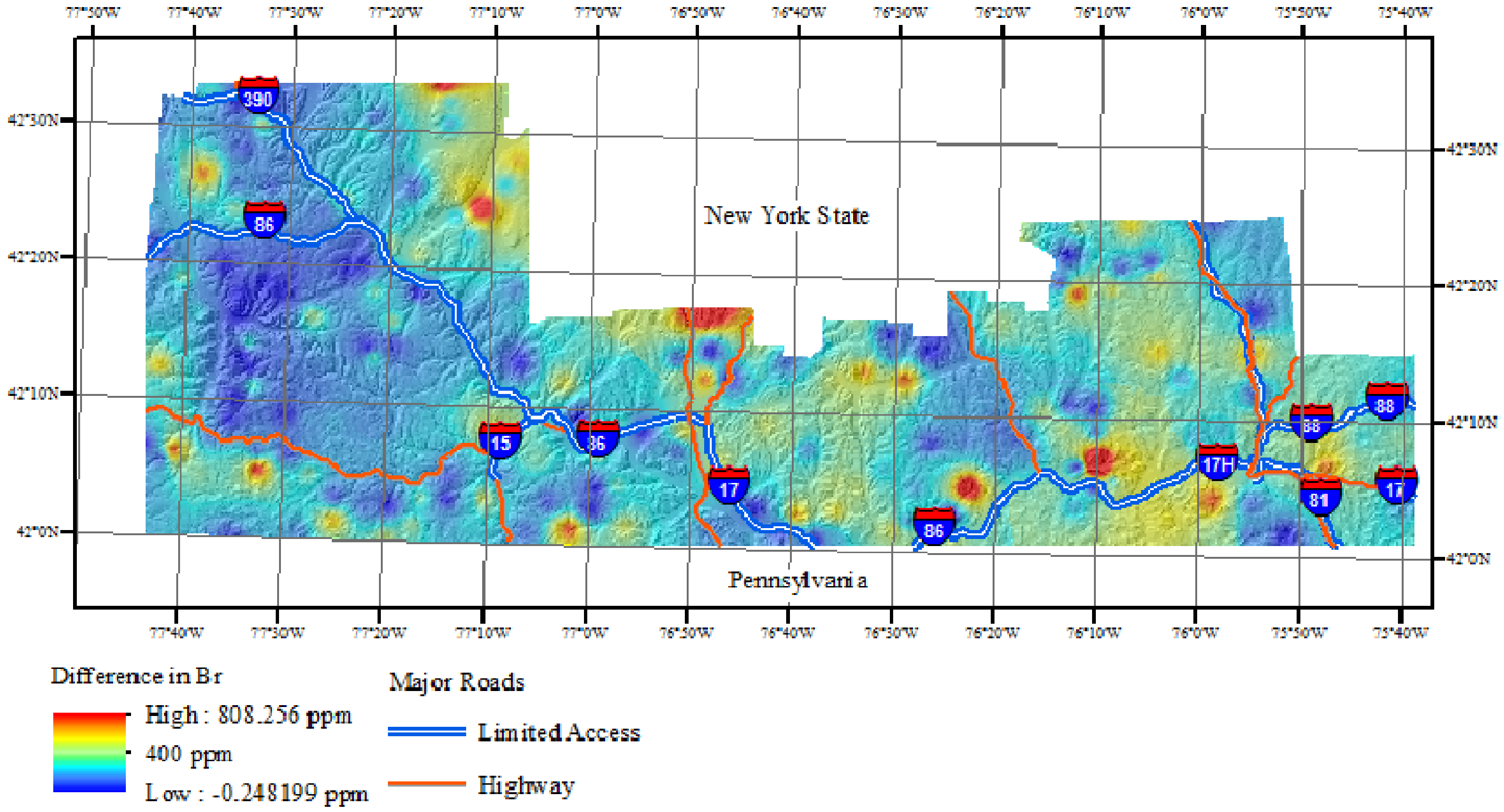
Map 12: Difference in bromide distribution from NURE to SWIFT data



Map 13: Difference in sodium distribution from NURE to SWIFT data

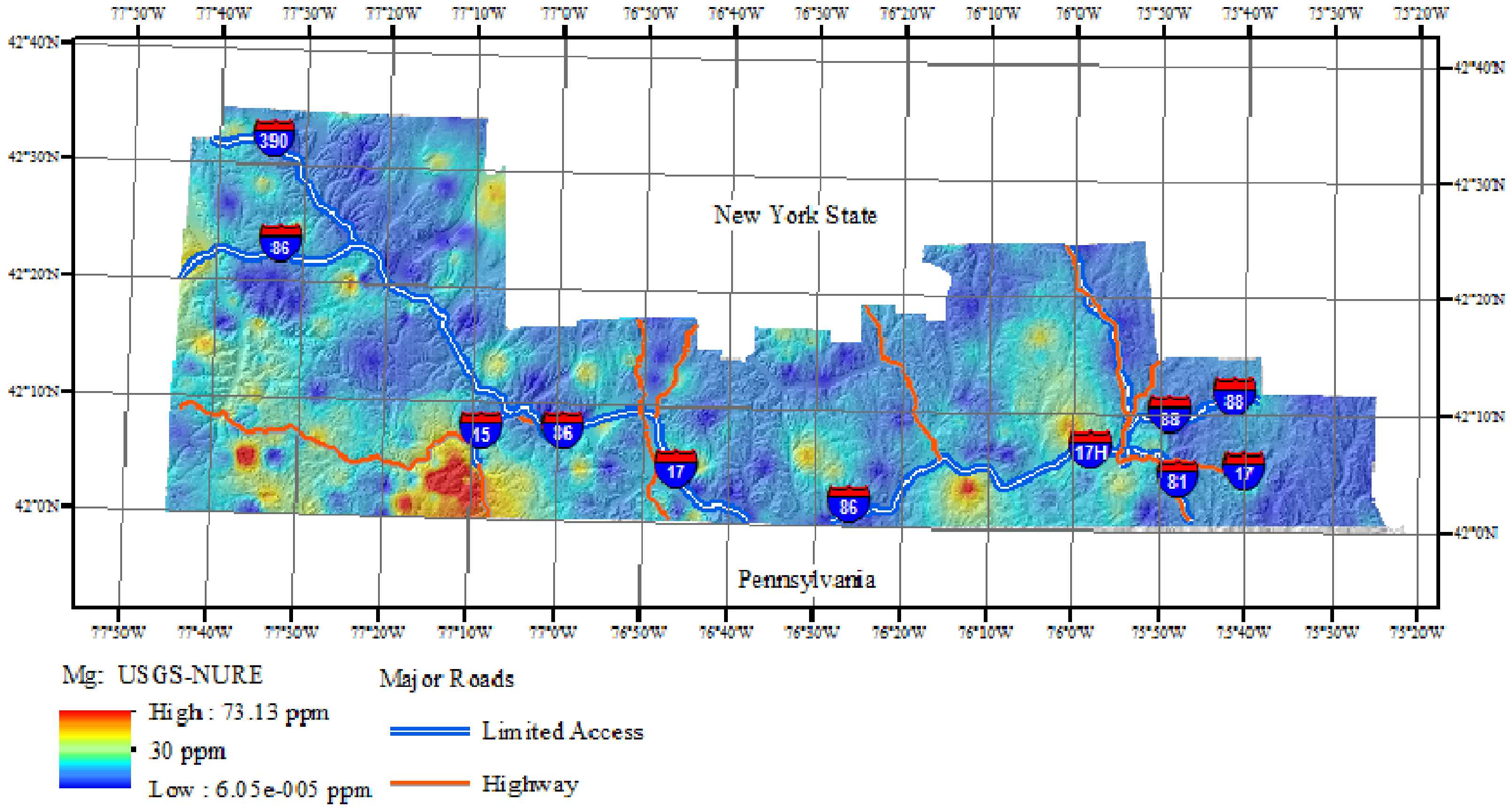


Map 14: Difference in fluoride distribution from NURE to SWIFT data

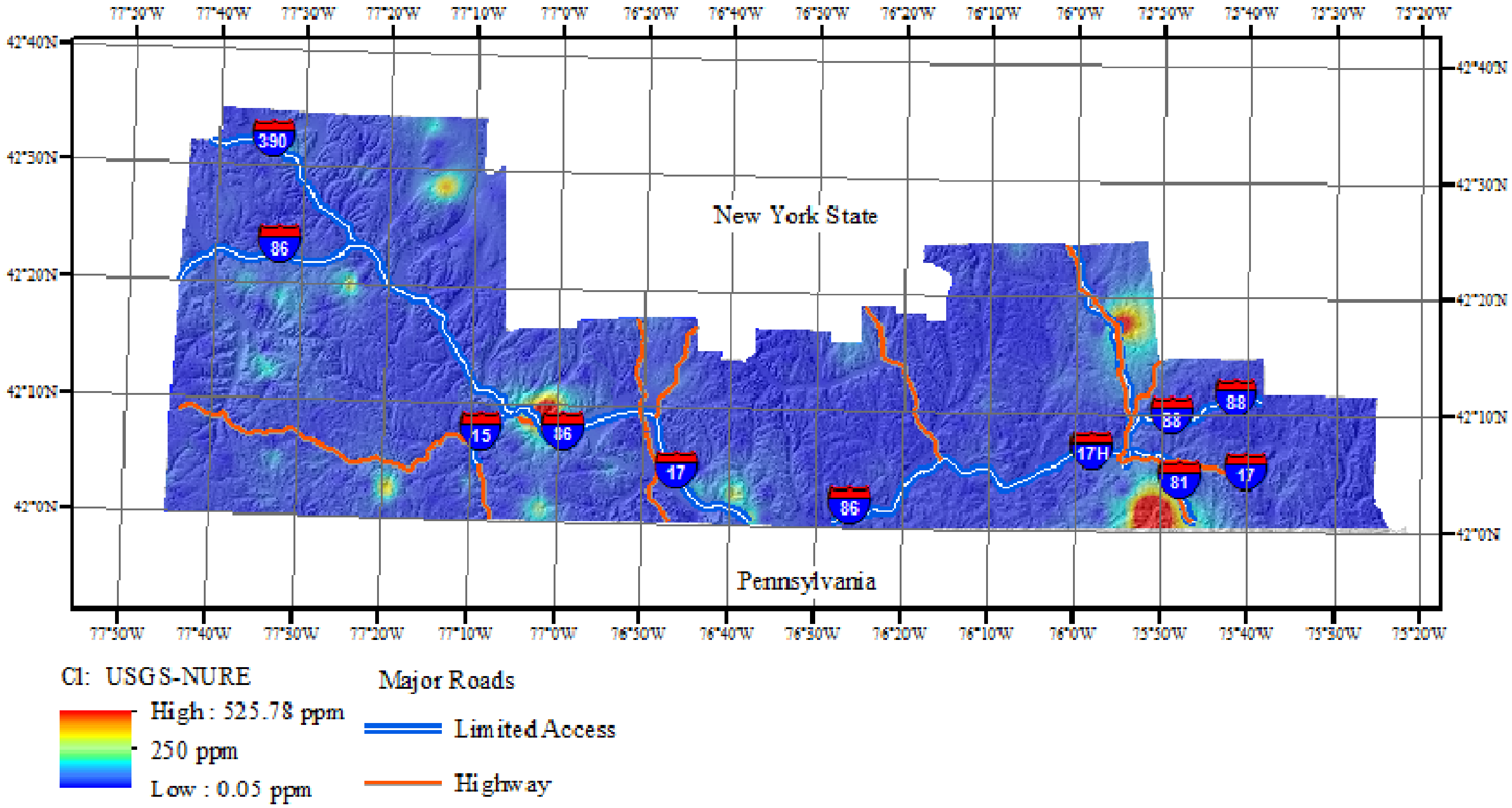


Maps 15 through 19 show the spatial distribution of magnesium, chloride, bromide, sodium, and fluoride in the USGS-NURE data. These were created using the IDW interpolation technique with the same parameters as the Project SWIFT distribution maps. Major roads are shown for reference. These maps are not directly discussed in this Capstone study, but were required for to create Maps 11 through 14.

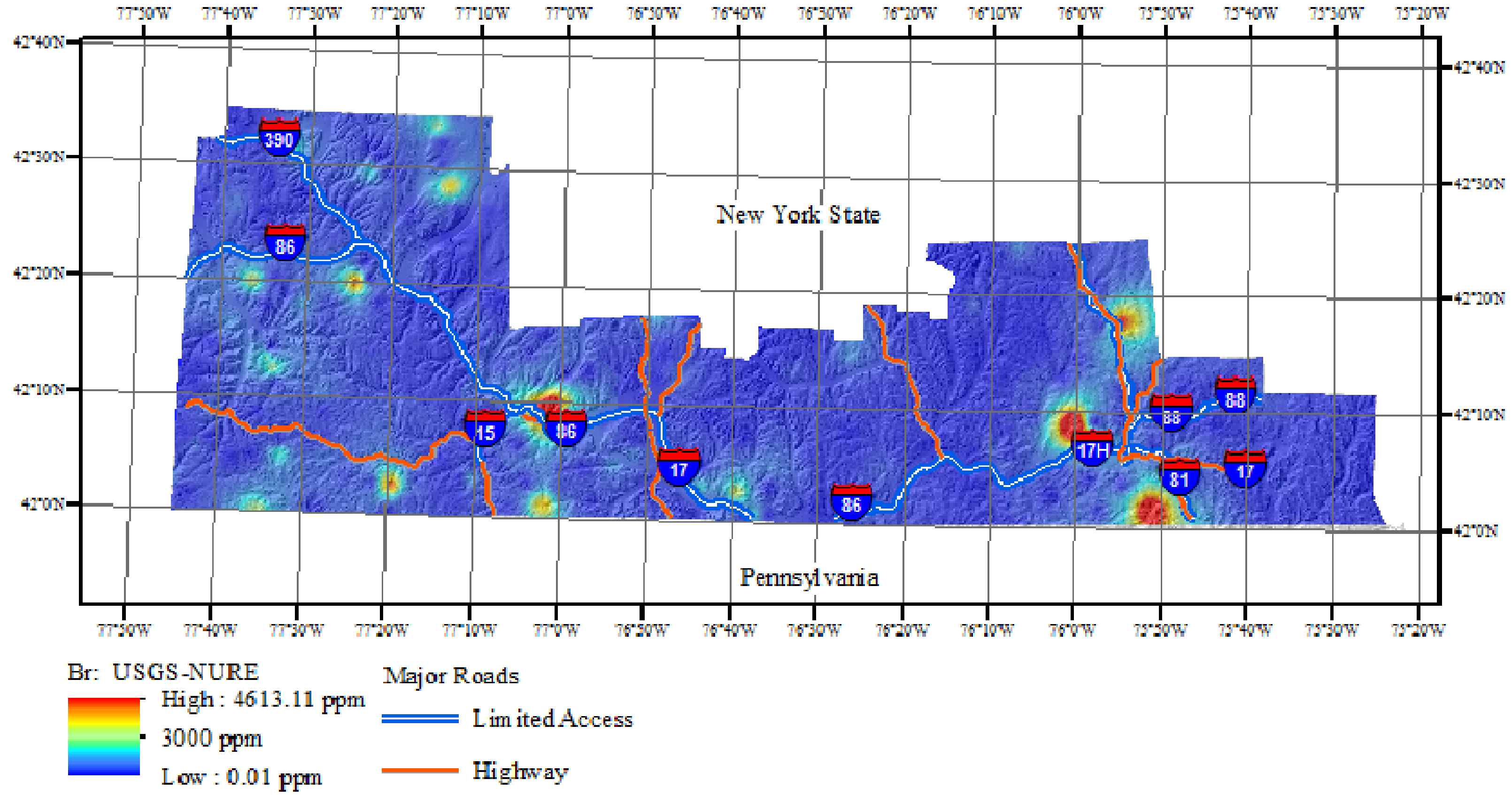
Map 15: Spatial distribution of magnesium concentrations in NURE samples



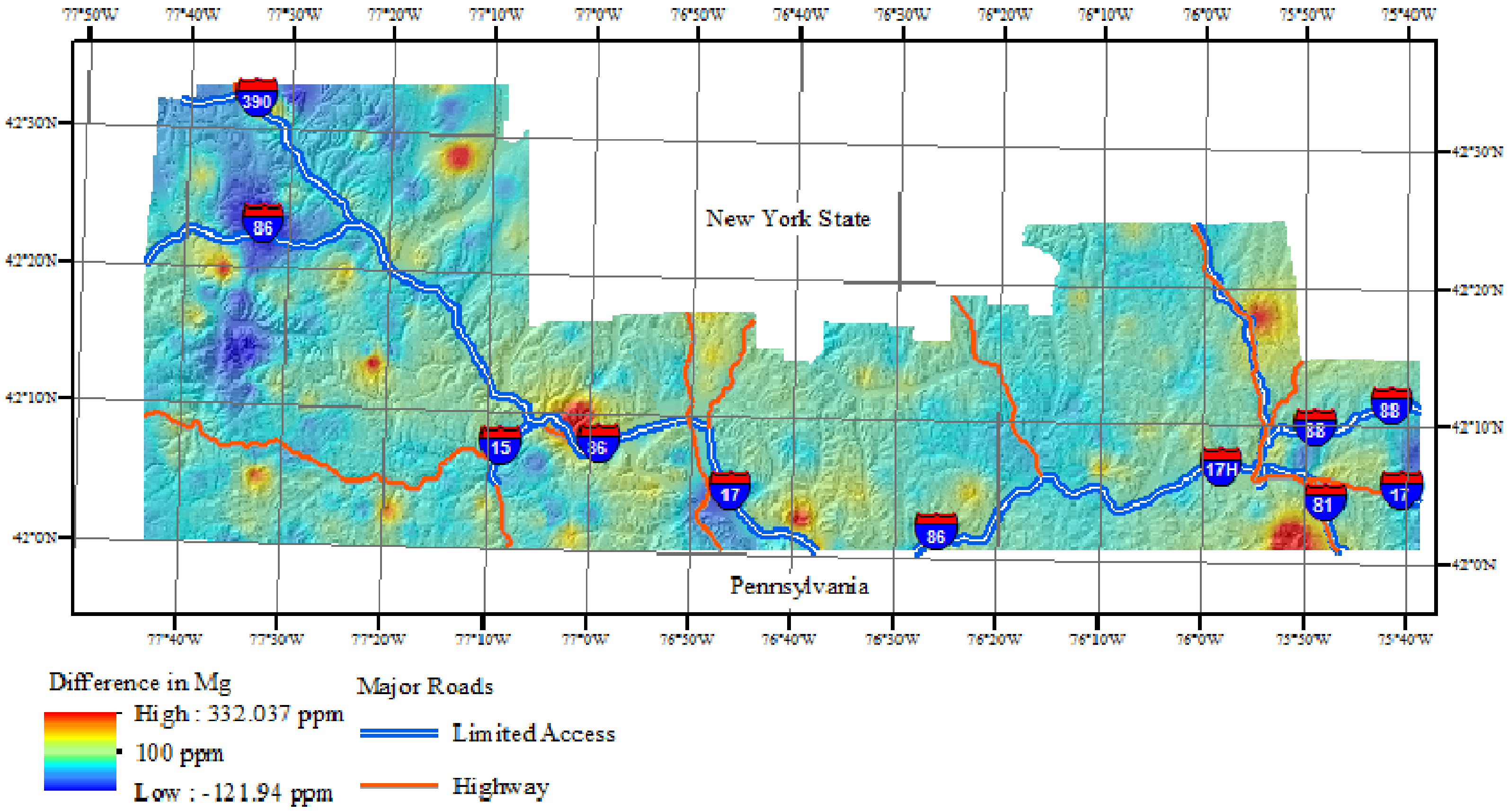
Map 16: Spatial distribution of chloride concentrations in NURE samples



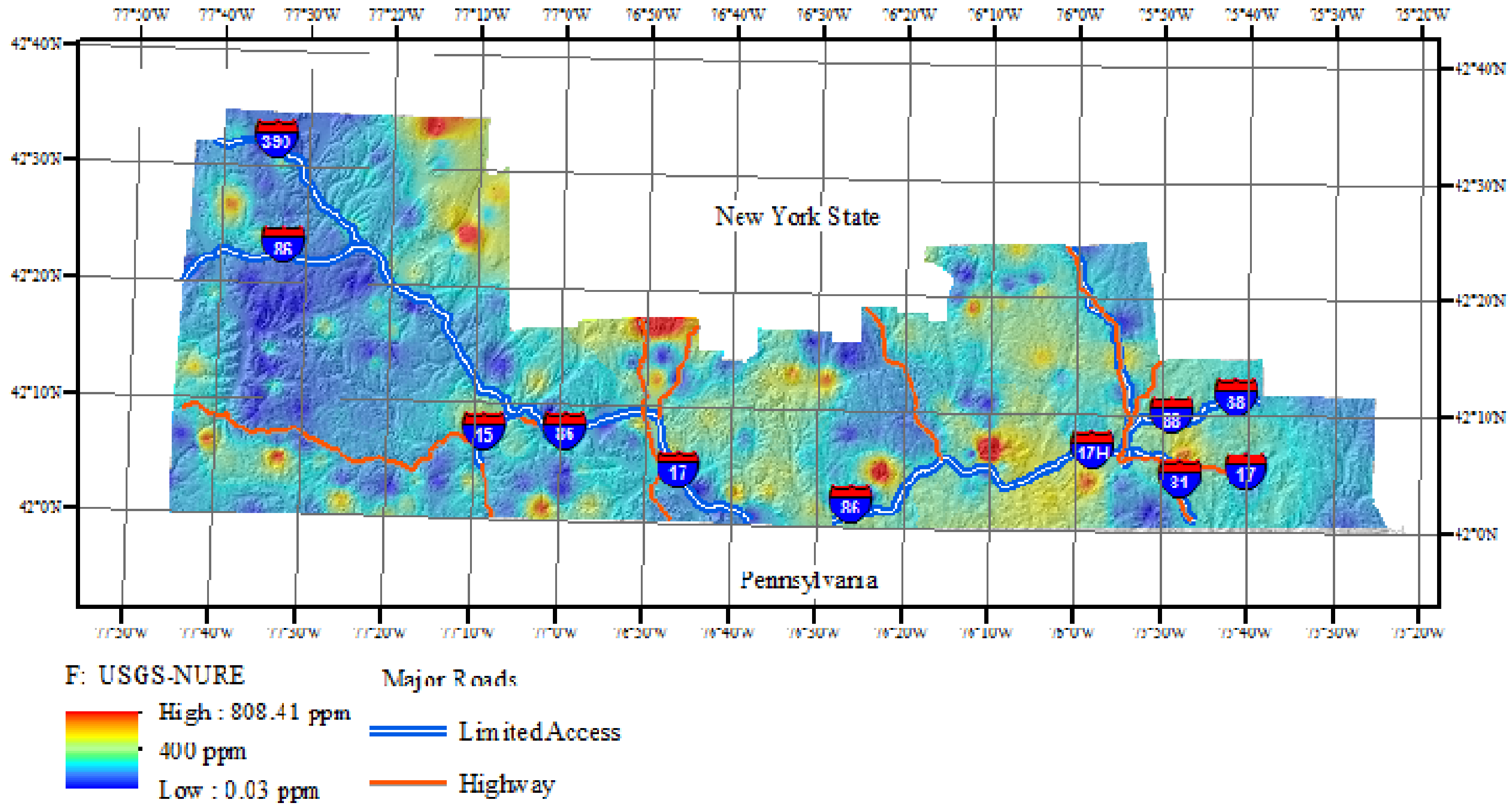
Map 17: Spatial distribution of bromide concentrations in NURE samples



Map 18: Spatial distribution of sodium concentrations in NURE samples



Map 19: Spatial distribution of fluoride concentrations from NURE samples



Summary of Capstone Project

This study provides objective groundwater quality data for an area in New York State that has been targeted for natural gas production. This study characterizes present-day water quality in four of the five counties of New York with the greatest potential for hydraulic fracturing of the Marcellus Shale Formation. This information will allow a simple geochemical fingerprinting tool that will provide unambiguous and publicly-available results to be developed by Project SWIFT at Syracuse University.

Natural gas is a colorless, odorless mixture of light-end, flammable hydrocarbons that burns more cleanly and with fewer undesirable emissions than coal and oil (Arthur 2008). Advances in drilling technology now allow for the hydraulic fracturing of horizontally drilled wells to recover the natural gas have enabled the industry to expand to areas that have been previously disregarded due to cost, such as the Southern Tier of New York (Arthur 2008). This area is considered for natural gas production due to the presence of natural gas in the Marcellus Shale formation. The impermeability of the Marcellus Shale formation has makes traditional drilling inefficient, as only a limited amount of natural gas can flow to a vertical well. Horizontal drilling into the Marcellus Shale greatly increases the yield of natural gas, and makes natural gas production in the region lucrative (Arthur 2008). The technique of horizontal drilling currently practiced in parts of the Marcellus Shale and proposed in areas of New York is called hydraulic fracturing (Boyer 2012). This technique requires the input of several million gallons of water to fracture the shale, allowing the flow of natural gas to the well (Boyer 2012). Chemical additives and proponents such as sand are added to the water for various purposes, including maintaining flow routes through the shale (Boyer 2012). Many of these chemical additives are not regulated by the U.S. Environmental Protection Agency, and the public disclosure of the chemicals is limited (U.S. Environmental Protection Agency, 2004; DEP, 2011). The water that is recovered from the wells contains high concentrations of many of the chemical additives, such as sodium, barium, and strontium (Hayes, 2009). These factors have placed hydraulic fracturing under public scrutiny, especially with concerns about pollution and water contamination. However, few studies utilize simple, objective tests (e.g. Boyer, 2012) that can determine the effects of hydraulic fracturing on regional water supplies. One goal of Project SWIFT is fill this void of scientific procedure. This capstone, as a part of Project SWIFT, identifies the baseline water quality characterization necessary for the development of such tests.

Information about the wells in the study area was obtained from the New York State Department of Environmental Conservation. Certain criteria had to be met for a well to be sampled in this study. Only wells in Broome, Chemung, Tioga, and Steuben Counties were considered for this study. Additionally, wells had to penetrate bedrock in order to be sampled. Wells meeting the criteria were selected to be sampled with even distribution across the study area, based on a 7.5 km-grid spacing. Landowners were contacted to gain permission to access land. Property data, including landowner contact information, were obtained from county offices. If property access was not granted, other nearby wells were selected and the landowners contacted. Streams were also sampled based on drainage area and accessibility.

Temperature, specific conductance and pH were measured onsite during sample collection. Specific conductance is a simple, though not deterministic, indicator of substances in the water (Oram et al, 2010). Two samples from each source were obtained. One sample was filtered and acidified with nitric acid. The other sample was filtered but was not preserved with nitric acid. Both samples were returned to Syracuse University.

Stream and groundwater samples were analyzed in laboratories at Syracuse University and State University of New York College of Environmental Science and Forestry for concentrations of 20 elements and ions.

Data from this study was compared to water quality data from the United States Geological Survey National Uranium Resource Evaluation (USGS-NURE) in the same study area (Smith 2012). The USGS-NURE data was collected between 1973 and 1984, therefore providing a temporal comparison for the Project SWIFT data (Smith 2012). Focus was given to spatial and quantitative variations between the datasets.

The data from both Project SWIFT samples as well as the USGS-NURE samples were displayed and analyzed spatially using a geographic information system (GIS). GIS displays of the data were used to visibly detect spatial trends in both datasets as well as temporal changes in spatiality of elements and ions.

Groundwater was sampled prior to treatment for domestic use. Samplers confirmed the collection of groundwater at each well by allowing water to run until the temperature stabilized. These practices as well as triplicate rinsing of sampling equipment ensure quality data collection. Field blanks, or repeats of the sampling procedure using only deionized water, did not yield any abnormal results, indicating sound data collection and analysis.

Groundwater samples collected from wells showed a greater range in concentrations than stream samples for 95% of the elements and ions analyzed. Additionally, groundwater samples had a higher maximum concentration than stream samples for 95% of the elements and ions tested. Stream samples had a lower minimum concentration than the groundwater samples for 66% of the elements and ions tested. The standard deviation of sample concentrations was greater in groundwater samples for 90% of the elements and ions.

Comparison of the Project SWIFT samples to the USGS-NURE samples showed marked changes in concentrations for some of the elements analyzed. Three of the five compounds mutually analyzed in the USGS-NURE dataset and the Project SWIFT dataset both showed percent increase from 1977-78 through 2012. The remaining two compounds showed a percent decrease.

T-tests were also conducted to quantify the significant variation between the two datasets. These statistical tests showed that the sodium and chloride concentrations did not vary significantly between the USGS-NURE and Project

SWIFT data, while magnesium, bromide, and fluoride all showed significant variation between the two datasets.

The statistical analyses of the ion concentrations show that the groundwater samples generally showed higher variability than the stream samples. While the median specific conductivity levels, which are indicative of dissolved solids, were comparable between the groundwater and stream samples, the greater range standard deviation of the groundwater data shows the greater variation within that data. However, the concentrations of ions groundwater were generally highly skewed, and the dataset for groundwater samples was much larger than that of the stream samples, which may impact the discrepancies unveiled by statistical analyses. Therefore, this occurrence does not lend to conclusions about the groundwater quality in the four counties sampled.

The large majority of wells produced water within the Safe Drinking Water Act quality standards. The Safe Drinking Water Act quality standards are based on maximum contaminant levels (MCLs) (Oram et al, 2010). MCLs are set to be as close to the maximum contaminant level goal (MCLGs) as possible, due to restrictions in measurement, enforcement, and treatment costs (Oram et al, 2010). MCLGs are the highest concentration of a contaminant that can be present without damaging health effects, and are non-enforceable goals (Oram et al. 2010).

Three wells in the Project SWIFT data contained nitrate concentrations that exceeded national standards. Two of the three wells with excessive nitrate were on the same agricultural property. A common source of nitrate contamination of water is agricultural runoff, and could be the cause of contamination on that property (U.S. Environmental Protection Agency, 2012b). The third well that yielded high nitrate concentrations, however, was unrelated to agriculture or the other two wells with high concentrations of nitrate.

The majority of elements and ion concentrations analyzed in the Project SWIFT samples are not regulated by the EPA. While the EPA has not set quality standards for some contaminants, maximum levels have been recommended (Oram et al. 2010). The EPA recommends a maximum contaminant level of 20 mg/L for sodium concentrations for persons requiring a low-sodium diet. 45% of the wells sampled by Project SWIFT exceeded this recommendation (Oram et al. 2010, U.S. Environmental Protection Agency, 2012a). However, sodium is not detectable by taste until concentrations surpass 250 ppm (Oram et al. 2010, U.S. Environmental Protection Agency, 2012a). None of the sampled wells showed sodium concentrations that exceeded this threshold. Strontium is also of consideration to be included in the EPA quality standards. Sources of strontium can be glass production, which is a characteristic industry in the Project SWIFT study site, industrial wastewater, and flowback (Oram et al. 2010). Only one well in the Project SWIFT data exceeded the recommended maximum level of strontium.

The consistency of magnesium, fluoride, and bromide to show significant variation between the USGS-NURE data and the Project SWIFT data as well as the largest percent change in median concentration confirm that the concentration of these elements and ions changed markedly since the USGS-NURE samples were collected.

The groundwater samples collected for Project SWIFT shows variation in chemical content of groundwater throughout the Steuben, Chemung, Tioga, and Broome Counties, NY. Knowledge of these concentrations is important in determining simple forensic tools that can trace the effect of hydraulic fracturing on the quality of regional groundwater. The comparison of SWIFT and NURE samples provides a marker of temporal changes for five of the ions analyzed for this study. The degree of percent change that occurred in the groundwater chemical content between the early 1977-78 and 2012 also gauges how groundwater quality may change in future years, and must be accounted for in the development of a geochemical fingerprint.