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STUDENT SUMMER INTERNSHIP TECHNICAL REPORT

Characterization of Surface Water Dynamics within Fourmile Branch and its Linkages with Groundwater and I-129 Geochemistry

DOE-FIU SCIENCE & TECHNOLOGY WORKFORCE DEVELOPMENT PROGRAM

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EXECUTIVE SUMMARY

This research work has been supported by the DOE-FIU Science & Technology Workforce Development Initiative, an innovative program developed by the U.S. Department of Energy's Environmental Management (DOE-EM) and Florida International University's Applied Research Center (FIU-ARC). During the summer of 2021, DOE Fellow intern, Stevens Charles, spent 10 weeks doing a summer internship at Lawrence Berkley National Laboratory (LBNL) under the supervision and guidance of Dr. Haruko Wainwright from LBNL and Dr. Hansell Gonzalez-Raymat from Savannah River National Laboratory (SRNL). The intern's project was initiated on June 1, 2020, and continued through August 6, 2020, with the objective of characterizing the surface water dynamics in the F-Area of Savannah River Site (SRS) and analyzing the surface water dynamics to find any linkages with groundwater and Iodine-129(I-129) geochemistry.

From 1955 to 1988, low-level radioactive waste solutions were disposed of in three unlined basins which are known as the F-Area Seepage Basins. The contaminants were able to pass through the basins and into the unsaturated and saturated zones. As a result, these contaminants contaminated the groundwater and migrated downstream, resurfacing at outcrops (seep lines) in the adjacent wetlands where some of the contaminants were then able to enter the Fourmile Branch stream system. Groundwater-surface water interfaces are the regions where contaminated groundwater emerges to the surface, which is often one of the major ecological and human health risk pathways. At the F-Area, I-129 is one of the main contaminants of concern appearing at these outcrops/seep lines. To understand the I-129 transport from subsurface to surface, and then to surface water, there must be an understanding of the groundwater - surface water dynamics occurring at the F-area wetlands. These dynamics include water temperature and chemistry as well as flow rate and the impact of precipitation on these controlling variables**.** The goal of this study was to characterize the surface water dynamics and determine if there are any linkages with groundwater and I-129 geochemistry. Focus was given to the spatiotemporal distribution of surface water temperature and chemistry, which are principal factors for consideration at groundwater seepages that may influence contaminant migration from subsurface to surface.

Each parameter was analyzed to determine if any parameters exhibited seasonality. The seasonality of each parameter was then compared to the trend of observed I-129 concentrations in the groundwater and surface water. After each parameter was analyzed, it was discovered that the surface water I-129 concentration that was measured at the stream gauges may be correlated with the seasons in the F-area. During the summer, the I-129 concentration was significantly higher than in the winter. This information will aid in better understanding the seasonal fluctuation of I-129 and its behavior in the wetland system.

The linkage between I-129 concentration and the season was the only correlation that was found during the internship. The time series data provided for the other parameters of interest was scarce, which could account for the inability to establish a correlation between these parameters and I-129 concentration. This study proposes the installation of in-situ sensors at surface water locations to collect continuous data. This would result in better time series records of these parameters, and more access to data that could provide a better understanding of the relationship between the parameters of interest and I-129 behavior in the wetland system.

1. INTRODUCTION

Savannah River Site is a 310 square mile area located in west central South Carolina near the boundary of Georgia that was developed during the middle of the 1950's for use in the production of materials such as tritium, plutonium, and special nuclear materials for national defense, medicine, and space programs. These processes resulted in the release and spread of radiological and other chemical contaminants across the Savanah River Site.

From 1955 to 1988, the F-Area Seepage Basins received low level acidic waste solutions that contained nitrate, metals, and several radionuclides. Some of these contaminants including tritium, uranium isotopes, strontium-90, and iodine-129, over a period, were able to pass through the soils at the bottom of the basins, through the vadose zone and into the saturated zone. Once in the groundwater, these contaminants migrated downstream and resurfaced at seeps in wetland areas associated with Fourmile Branch. Specifically, Fourmile Branch and its associated wetlands have been impacted for more than thirty years by the outcropping of contaminated groundwater coming from the F-Area Seepage Basins.

Since the basins were closed in 1991, several groundwater remedial actions, such as the pump and treat system, were used to lessen contaminants in the groundwater. The groundwater pump and treat system eventually became expensive to maintain and operate, and generated secondary waste that needed to be disposed. As a result, the pump-and-treat was replaced with a more passive attenuation-based remedy in 2004.This passive attenuation-based remedy uses subsurface barriers installed across flow paths in the upper aquifer, forming a funnel and gate system that allow contaminants to be treated within the gates. Base injections are done periodically at the gates to remove U-238 and Sr-90 while silver chloride injection campaigns have been performed just upgradient of the central gate to treat I-129. In the F-Area wetlands, an enhanced monitored natural attenuation (MNA) approach has been implemented, periodically injecting a base solution to increase the sorption of cationic contaminants, making them less bioavailable. While these strategies are successful in sequestering the contaminants of concern, a long-term monitoring strategy is necessary at the zones of vulnerability of Fourmile Branch where there is potential for contaminant remobilization if environmental conditions are favorable. Currently there are three major zones of vulnerability: the F-Area basins, in situ treatment zones, and the wetlands of Fourmile Branch. With long-term monitoring it will be possible to predict contaminant fate and transport by reflecting on the physical parameters or controlling variables that drive contaminant movement

There was a focus on understanding iodine-129 behavior and mobility in the environment during this internship. To understand the contaminant transport from subsurface to surface, and its migration in surface water, there was a need to understand the surface water parameters near the wetland area of Fourmile Branch. These parameters included flow rate, precipitation, water temperature and chemistry. By understanding these controlling variables, it would then become possible to better understand and discover any linkages between the controlling variables and I-129. By the end of the summer internship, the expectation was to be able to predict the concentration and mobility of iodine-129 based on the actions of the controlling variables.

2. RESEARCH DESCRIPTION

Long Term Monitoring

Sites like the F-area where the risk of environmental contamination from heavy metals and radionuclides continues to exist, long-term monitoring is essential. With long-term monitoring, there will be an emphasis on the measure of hydrological and geochemical parameters that control the remobilization of contaminants. By focusing more on the controlling variables, there can be less of an emphasis on the contaminant concentration. This strategy can aid in predicting any change in concentration of contaminants as well as predicting their mobility. Moreover, predicting the behavior of contaminants would provide greater opportunity to take proactive measures rather than remedial actions. Predicting the movement of contaminants would be more beneficial than simply focusing on the contaminant concentration because it will provide an opportunity to avoid lagging results. Instead of reacting to the movement of contaminants, a focus on the controlling variables will provide an opportunity to react before the contaminants remobilize.

Controlling Variables

The long-term monitoring strategy focuses on measuring both hydrological and geochemical parameters. During the summer research, the parameters that were of primary focus included flow rate, water temperature, water chemistry, and precipitation (Seasonality of each of these parameters were also observed). The goal of analyzing these four parameters was to determine if there was a correlation between the trend of I-129 contaminant concentration and the parameters listed. Historical Data from stream gauge FMC-002F, FMC-002H, and FM-2BD was used to evaluate the flow rate, surface water temperature and surface water chemistry. For the flow rate analysis stream gauge FM-A7 was also used to examine the difference in flow rate between the F-Area seepage basins and near the outlet of Fourmile Branch. Groundwater temperature and chemistry were also analyzed during the research. The historical data that was used was taken from groundwater well FSP-2. This well is nearby stream gauge FC-002F so the data between the stream gauge and well could be compared.

Contaminant data was also collected at both the stream gauges and groundwater well. During the data analysis, although there was particular focus on iodine-129, other contaminants were also investigated such as tritium and nitrate. The goal was to examine both the contaminant and the parameter data at the same or nearby gauges and wells and hope to find similar trends during the year that can help in predicting the remobilization of the contaminants by examining the parameters. The flow rate was measured once a month and thus did not always reflect significant precipitation events due to the lag time between the storm events and the time the flow rate data was collected. The other parameters were all collected quarterly. Due to this, most of the data in this report was represented quarterly.

Q1: January, February, March
Q2: April, May, June
Q3: July, August, September
Q4: October, November, December

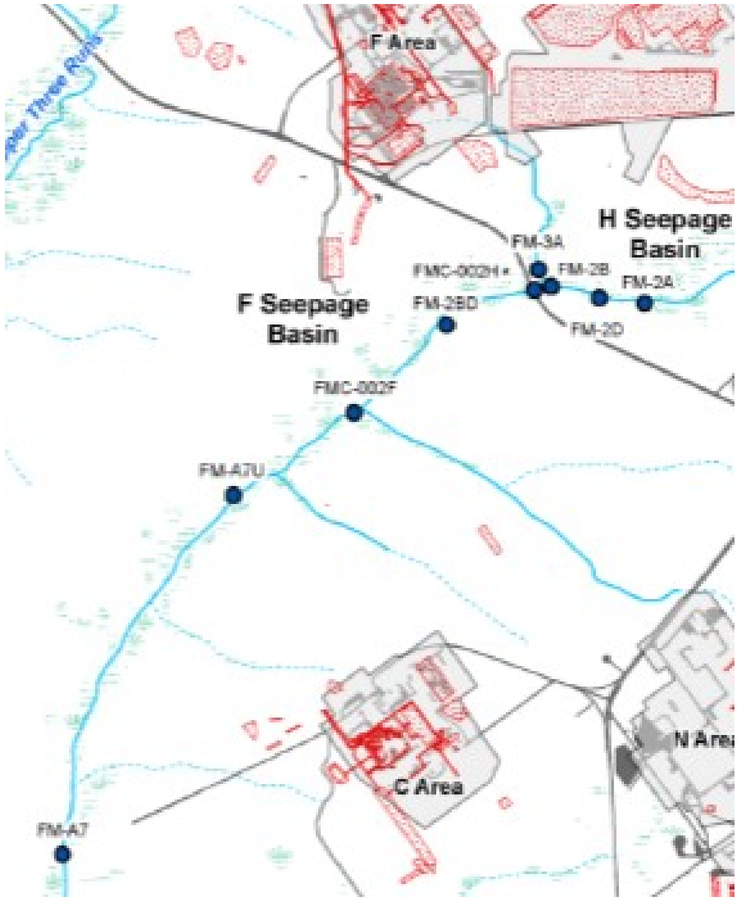

Figure 1. Location of stream gauges near the F-Area used in the analysis of the surface water parameters.

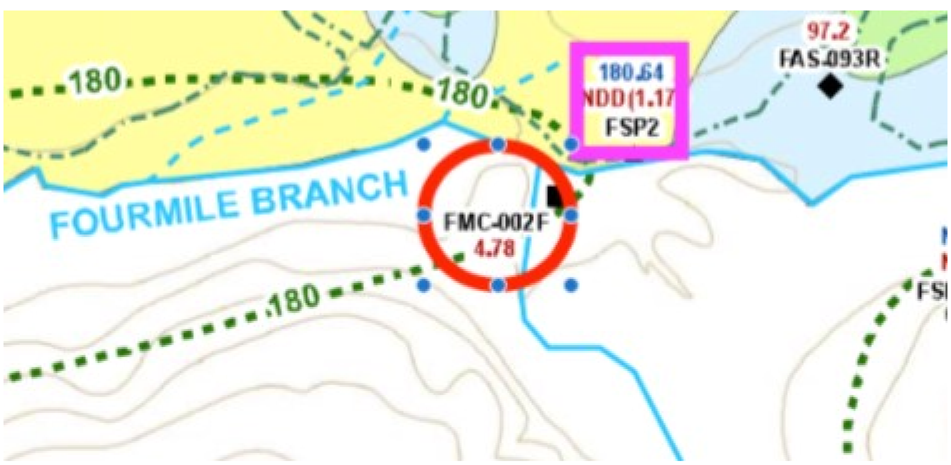

Figure 2. The location of groundwater well FSP2 relative to stream gauge FMC-002F.

3. RESULTS AND ANALYSIS

Flow Rate

The main purpose of this research project was to characterize the surface water dynamics in the F-Area of Savanah River Site. These surface water dynamics, which are also controlling variables of contamination, could then be used as a linkage to the remobilization of iodine-129.

The first parameter that was analyzed was discharge, and that was done by running a statistical analysis on three of the key gauges that are in Fourmile Branch, which were provided in the preliminary analysis. The data was collected between January 2004 and December 2020 for three stream gauges, FMC-002H, FMC-002F, and FMB-2BD. These stream gauges were compared to stream gauge FM-A7 which is towards the outlet of Fourmile Branch. Stream gauge FMB-2BD was not included in the analysis because there was little to no flow recorded at that station.

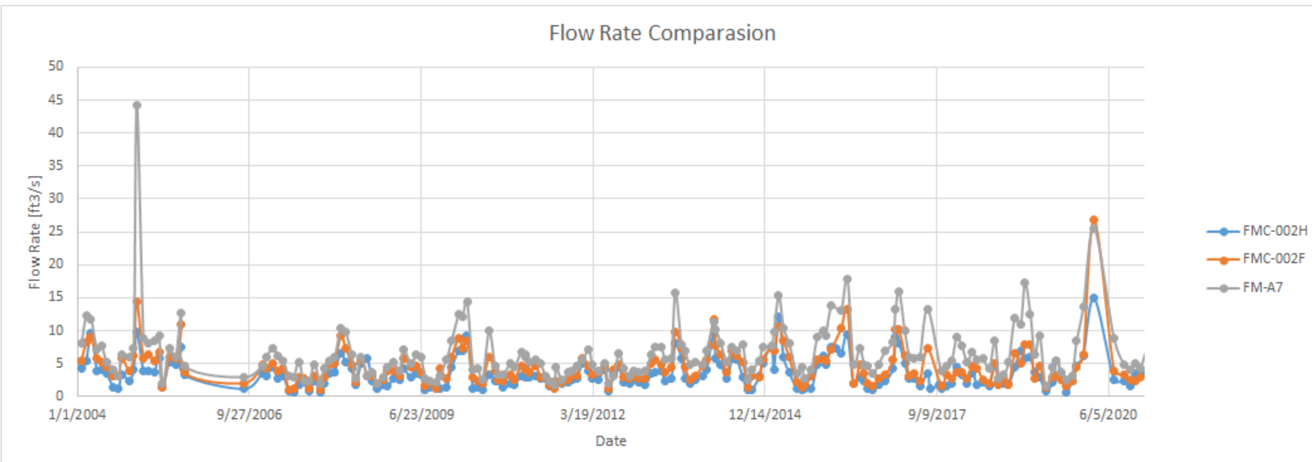

Figure 3.Shows the flow rate of stream gauges FMC-002F, FMC-002H, and FM-A7 which is located near the outlet during January 2004 –December 2020.

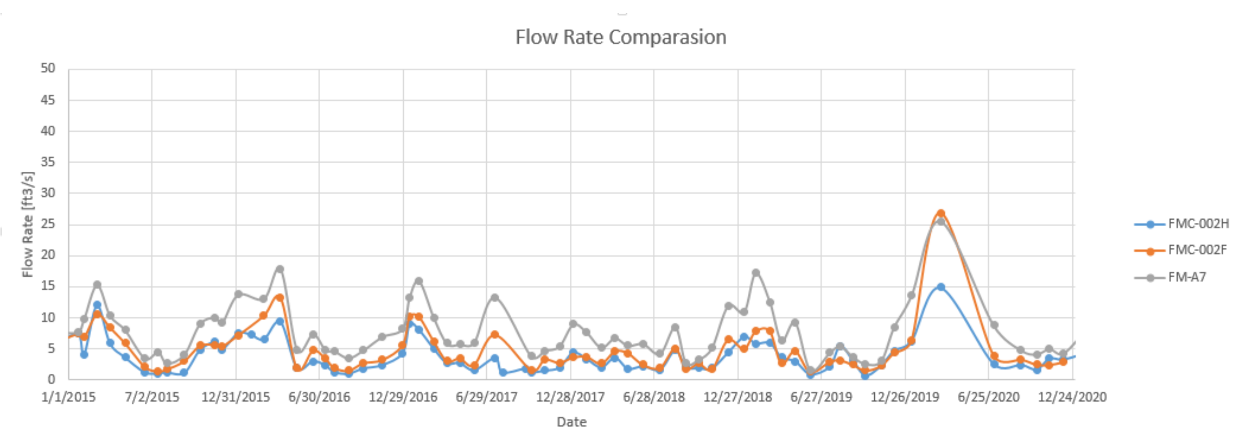

Figure 4. Shows the flow rate of stream gauge FMC-002F, FMC-002H, and FM-A7 which is located near the outlet from January 2015 – December 2020

Stream gauge FM-A7 at the outlet follows a similar trend to the two critical stream gauge in both the historical graph and the quarterly graph. Figure.4 shows the past 5 years of the flow rate. From the figure, the seasonality of the flow rate can be observed. Q1 or the winter months had the highest flow rate while Q3 or the summer months exhibited the lowest average flow rate. It is believed that the low flow rate in the summer is because of high seasonal temperatures and the increase in evapotranspiration during the summer months. Table 8, 9, and 10 in the Appendix provide a statistical analysis of each of the gauges from January 2004 – December 2020.

The precipitation in the F-area was also analyzed. It was anticipated before beginning the research that a relationship between precipitation and flow rate would be evident. However, the flow rate data was collected a few days after storm events. In other words, the storm events would not have any impact on the flow rate due to the lag time between the storm event and the collection of the flow rate measurement. In attempt to find a relationship, a graph between the cumulative monthly precipitation in the F-area, and the flow rate at two stream gauges was created for the time period of January 2004 to October 2019. From the graph, there still was not any clear correlation.

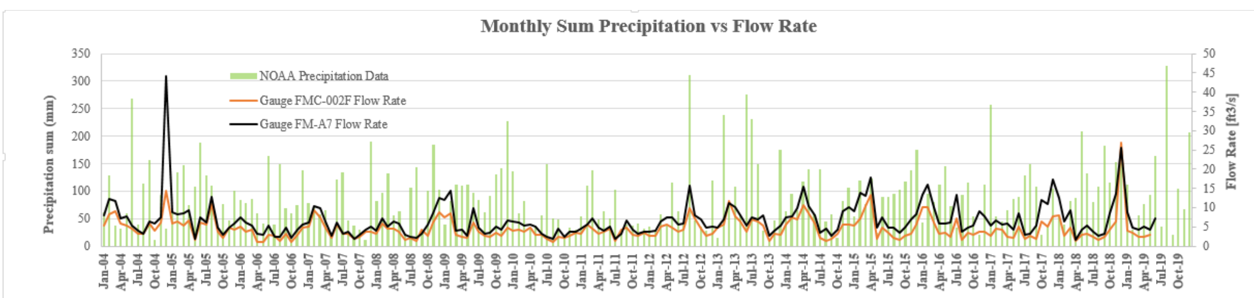

Figure 5. Flow rate at Stream gauge FM-A7 and FMC-002F in relation to the monthly cumulative rainfall in the F-area

Temperature

After failing to find a relationship between flow rate and precipitation, the temperature was the next to be analyzed. The results below.

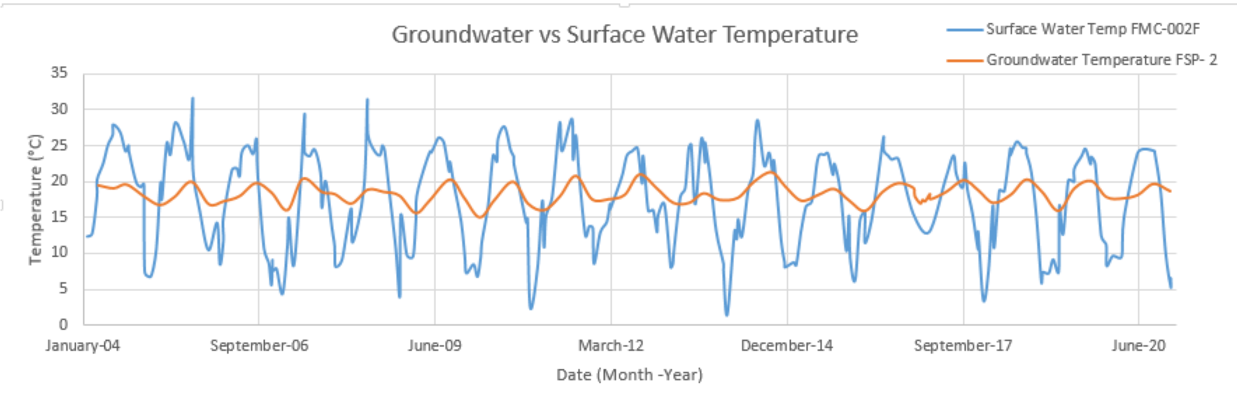

Figure 6. Graphical Representation of water temperature at groundwater well FSP2 and stream gauge FMC-002F from January 2004 to December 2020

Table 1. Quarterly Statistical Analysis of the Groundwater Temperature at Groundwater Well FSP2 Measured in Celsius from January 2004 to December 2020.

.	Q1	Q2	Q3	Q4
Mean	17.09	18.45	19.85	18.11
Max	19.50	20.40	21.30	19.40
Min	15.10	17.10	18.40	16.90
Median	17.20	18.20	20.00	18.00
Count	23	18	17	20

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Table 2. Quarterly Statistical Analysis of Surface Water Temperature Measured in Celsius at Stream Gauge FMC-002F from January 2004 to December 2020.

.	Q1	Q2	Q3	Q4
Mean	11.84	22.09	23.78	12.98
Max	20.30	31.30	31.70	22.90
Min	1.50	8.30	16.40	2.50
Median	11.80	22.60	23.95	12.90
Count	65	59	66	67

Table 1 and Figure 6 show that the groundwater temperatures remain very similar throughout the year. There is not much variability.

With respect to the surface water temperature, Table 2 shows that the surface water temperatures are higher in Fourmile Branch in Q2 and Q3 which are the summer months, and lower during Q1 and Q4 which are the winter months, as expected. In Figure 6, the surface water temperatures show the seasonality.

Analysis of both the surface water and groundwater temperatures is needed because with a thermal camera it is possible to detect groundwater discharge to the surface. For example, during Q1 and Q4 when the groundwater is warmer than the surface water, a thermal infrared camera would be able to detect hotspots (i.e., warmer areas), and thus determine where the groundwater may be resurfacing.

Surface Water Specific Conductance

Specific conductance was the final parameter analyzed. Specific conductance is an indirect measurement of the presence of dissolved ions in solution. In other words, specific conductance is an indicator of groundwater contamination. The higher the specific conductance the higher contamination in groundwater. Analysis began by calculating the mean, median, maximum, and minimum of the specific conductance during each quarter of the year between January 2004 to December 2020.

Table 3. Quarterly Statistical Analysis of the Specific Conductance in µS/cm at FMC-002F between January 2004 to December 2020

Column1	Q1	Q2	Q3	Q4
Mean	56.96	58.22	63.67	67.48
Max	152.30	94.20	193.00	182.30
Min	2.54	34.56	41.00	41.96
Median	54.81	58.05	59.28	63.00
Count	65.00	60.00	65.00	67.00

Table 3 above shows that the specific conductance is higher towards the end of the year in Q3 and Q4.

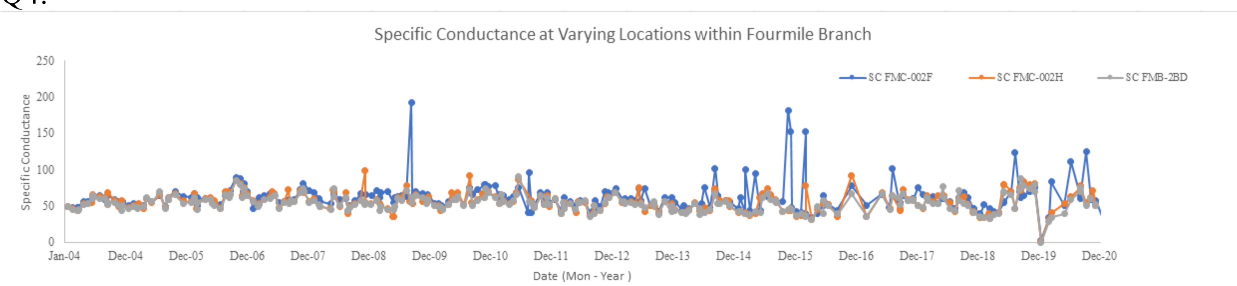

Figure 7. Time series of the specific conductance data at the three critical stream gauges (FMC-002F, FMB-2BD, and FMC-002H) from January 2004 to December 2020

The data collected at the other critical stream gauges all follow similar patterns for a majority of the time. The specific conductance data collected at stream gauge FMC-002F at some points are higher than the other stream gauges but these data points are possibly outliers. However, the overall trend of specific conductance at the three stream gauges are very similar when compared to other stations. Since the trends at these gauges are similar, it possibly means that Fourmile Branch is not affected by the groundwater plumes. The values of specific conductivity at the stream gauges located near Fourmile Branch are also low, meaning that the water that passes through Fourmile Branch is not very contaminated.

Flow Rate vs Specific Conductance

Following this analysis, a time series analysis between the flow rate and the specific conductance was completed. For this analysis, stream gauge FMC-002H was used since there were not as many outliers as its counterpart FMC-002F.

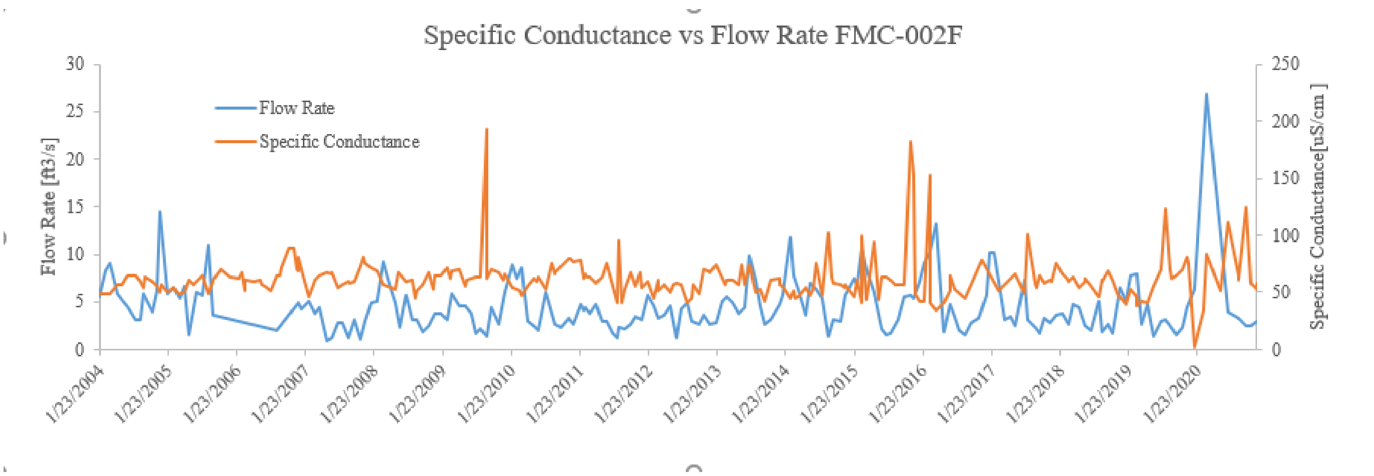

Figure 8. Time series correlation between the specific conductance and flow rate at stream gauge FMC-002H for the period Jan 2004 to December 2020.

By looking at the time series of these two parameters it is believed that the specific conductance and the flow rate are inversely correlated. When the flow rate increases, the specific conductance values decrease, and vice versa. After discussion, this relationship was believed to occur because contamination is constantly migrating to the surface at Fourmile Branch, however, when there is more water (higher flow rate / higher precipitation) dilution of chemical ions occurs resulting in decreased specific conductance.

By looking at both the specific conductance and the flow rate data that was analyzed before, evidence was created to back up the hypothesis that higher flow rate causes lower specific conductance, and vice versa.

Table 4. Quarterly analysis of the flow rate (left) and specific conductance (right) at stream gauge FMC-002F. Both data sets were created based on the data provided from January 2004 – December 2020

FMC-002F Quarterly Flow rate Analysis [ft3/s]				
Column1	Q1	Q2	Q3	Q4
Mean	6.61	4.14	3.58	3.87
Max	26.88	13.24	10.96	14.48
Min	2.66	0.95	1.14	1.08
Median	5.70	4.34	3.08	3.19

.	Q1	Q2	Q3	Q4
Mean	48.50	56.57	57.45	60.58
Median	49.34	55.71	55.40	58.00
Max	78.00	86.20	91.40	99.00
Min	0.83	30.82	36.00	40.77
Count	63.00	58.00	63.00	63.00

The charts above also mimic the pattern that was observed in **Error! Reference source not found.**. The flow rate is greatest during Q1, however during Q1 the specific conductance value is the least. During Q3/Q4 the flow rate values are the least, however the specific conductance values appear to be the highest. In other words, these tables follow the belief that the specific conductance and flow rate are indirectly correlated.

Groundwater Specific Conductance

Table 5. Quarterly analysis of specific conductance at groundwater well FSP-2. These results are based of the data received during January 2004 – December 2020

Quarterly SC Analysis Well FSP-2 (Jan 2004 -Dec 2020)				
.	Q1	Q2	Q3	Q4
Mean	223.7	210.9	217.5	214.7
Median	238.0	201.0	215.0	217.0
Max	308.0	366.0	304.0	305.0
Min	131.0	20.0	134.0	136.0
Count	23.0	18.0	17.0	20.0

Along with analyzing the specific conductance data at the three critical surface water gauges, it was also a priority to focus on groundwater specific conductance. The first thing that was noticed in this analysis was that the groundwater specific conductance is much higher than the specific conductance that was calculated at the surface water stream gauges. This should be expected since the groundwater migrating to the surface is a contributor to the contamination in the surface water.

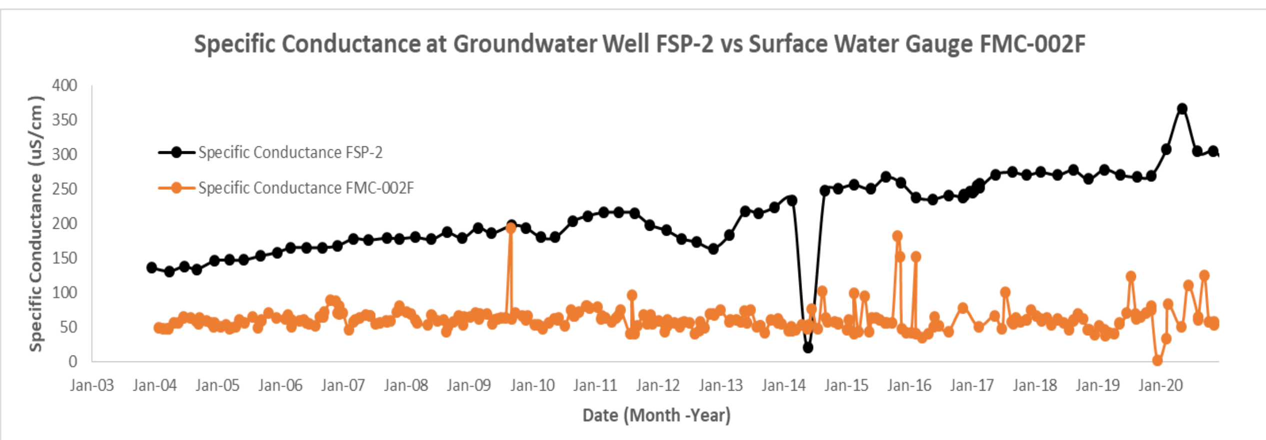

Figure 9. Time series of the specific conductance values of both the surface stream gauge (FMC-002F) and the groundwater well (FSP-2) over the time span of January 2004 – December 2020

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At first glance of **Error! Reference source not found.** we are able to see that during the majority of the time span, the specific conductance values collected at the groundwater well are higher than the specific conductance values collected at the surface stream gauge. It was also noticeable that the specific conductance values at groundwater well FSP-2 continuously increase over the time span, while at the stream gauge the specific conductance for the most part remained constant. This shows that surface water is not being impacted significantly by the contaminated groundwater.

The iodine-129 concentration data was also unsuspecting. With most of the contaminants in the F-Area, the concentration is greater in the groundwater then when compared with the surface water. However, with iodine-129 the opposite occurred. The tables below compare the concentration of iodine-129 at groundwater well (GW) FSP-2 and the surface water (SW) stream gauge.

Table 6. Statistical Analysis of the Iodine-129 Groundwater Concentration (pCi/L) at well FSP-2

GW Iodine-129 Concentration Quarterly Analysis (Dec 2003-Mar 2020)				
.	Q1	Q2	Q3	Q4
Mean	0.76	0.59	0.45	0.19
Max	9.05	2.50	0.95	1.01
Min	-0.35	-0.26	-0.07	-1.36
Median	0.34	0.30	0.42	0.18

Table 7. Statistical Analysis of the Iodine-129 Surface Water Concentration (pCi/L) at Stream Gauge FMC-002F

SW Iodine-129 Concentration Quarterly Analysis (Sept 2004-Jun 2021)				
.	Q1	Q2	Q3	Q4
Mean	2.35	5.75	5.22	3.79
Median	1.71	5.61	5.34	3.27
Max	8.48	14.50	9.14	7.22
Min	0.74	1.23	2.49	1.34
Count	18.00	17.00	19.00	17.00

A graphical representation of the results in Table 6 and Table 7 is available in Figure 10. By looking at both the table and the graph, the seasonality of iodine-129 is able to be observed. The iodine-129 concentration at the stream gauges, specifically, increased during the summer months and decreased during the winter.

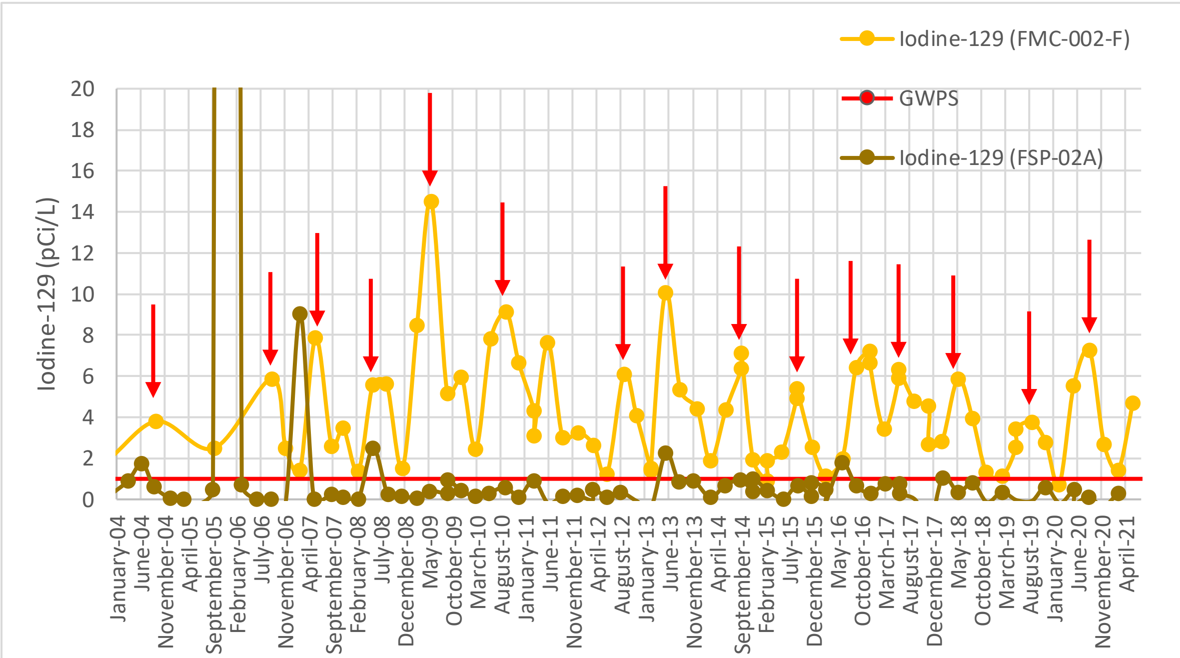

Figure 10. Iodine-129 concentration at both the surface water stream gauge (FMC-002F) and a nearby groundwater well FSP-2.

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The spikes in iodine-129 concentrations observed at surface water stations during the summer suggest that there are processes (e.g., geochemical, microbial, physical) releasing iodine-129 from wetland soils to surface waters.

4. CONCLUSION

The purpose of this research was to characterize surface water dynamics within the F-Area of Savannah River Site, and to find any linkages between the surface water dynamics and the contaminant concentration of iodine-129. These surface water dynamics included the flow rate, precipitation, groundwater/surface water chemistry, and groundwater/surface water temperature. Each of these parameters were analyzed, and during the analysis, each of these parameters were also compared to each other. For example, a possible relationship between the specific conductance and the flow rate at the surface water gauges was found. In another situation, a comparison between the flow rate and precipitation was attempted. However, due to the lack of data, no relationship was found. Many of the parameters had gaps in data, and that made it harder to find linkages with iodine-129. In the future, the implementation of monitoring stations that collect continuous measurements using in situ sensors will be necessary. These sensors would provide more time series data that can be used to characterize the surface water parameters, and possibly provide more information that can be used to predict contamination concentration in Fourmile Branch.

Even with the lack of data, a linkage between the iodine-129 concentration and season was found. During summertime the iodine-129 concentration received a spike at several stream gauges downstream. During the winter/spring months, the iodine-129 concentration decreased from the summertime spike. This spike may be due to certain processes (e.g., geochemical, microbial, physical) that occur in the F-Area. This information can be used to predict the concentration of iodine-129, prepare for the spike in the iodine-129 concentration in the future, and to understand how iodine-129 concentration reacts under conditions in the F-Area of Savanah River Site.

5. REFERENCES

Denham, M. E., Amidon, M. B., Wainwright, H. M., Dafflon, B., Ajo-Franklin, J., & Eddy-Dilek, C. A. (2020). Improving long-term monitoring of contaminated groundwater at sites where attenuation-based remedies are deployed. *Environmental Management, 66*(6), 1142-1161. Doi: 10.1007/s00267-020-01376-4

Denham, M. E., Eddy-Dilek, C. A., Wainwright, H. M., Thibault, J., & Boerstler, K. (2019). A new paradigm for long term monitoring at the F-Area Seepage Basins, Savannah River Site. Doi: 10.2172/1504623

Hitchcock, D. R., Barton, C. D., Rebel, K. T., Singer, J., Seaman, J. C., Dan Strawbridge, J., . . . Blake, J. I. (2005). A containment and disposition strategy for tritium-contaminated groundwater at the Savannah River Site, South Carolina, United States. *Environmental Geosciences, 12*(1), 17-28. doi:10.1306/eg.04120404020

APPENDIX

Table 8. Quarterly Flow Rate Analysis of Stream Gauge FMC-002H (Jan 2004 –Dec 2020)

FMC-002H Quarterly Flow Rate Analysis [ft3/s]				
Column1	Q1	Q2	Q3	Q4
Mean	5.33	3.08	2.77	2.84
Max	14.93	9.41	8.05	9.87
Min	1.70	0.67	0.74	0.69
Median	4.36	2.86	2.27	2.35

Table 9. Quarterly Flow Rate Analysis of Stream Gauge FMC-002F (Jan 2004-Dec 2020)

FMC-002F Quarterly Flow rate Analysis [ft3/s]				
Column1	Q1	Q2	Q3	Q4
Mean	6.61	4.14	3.58	3.87
Max	26.88	13.24	10.96	14.48
Min	2.66	0.95	1.14	1.08
Median	5.70	4.34	3.08	3.19

Table 10. Quarterly Flow Rate Analysis of Stream Gauge FM-A7 (Jan 2004 –Dec 2020)

FM-A7 Quarterly Flow Rate Analysis (ft3/s)				
Column1	Q1	Q2	Q3	Q4
Mean	9.39	5.92	5.14	6.05
Max	25.58	17.89	15.82	44.30
Min	3.94	1.63	1.75	0.20
Median	8.09	5.76	4.39	4.79

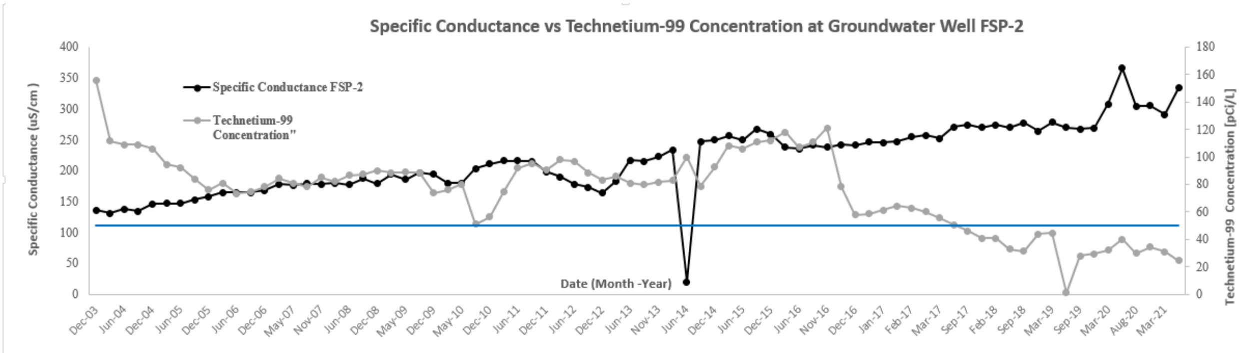

Figure 11. Graph showing a similar relationship where the technetium-99 concentration decreases while the specific conductance continues to increase. This show a similar relation to nitrate concentration.

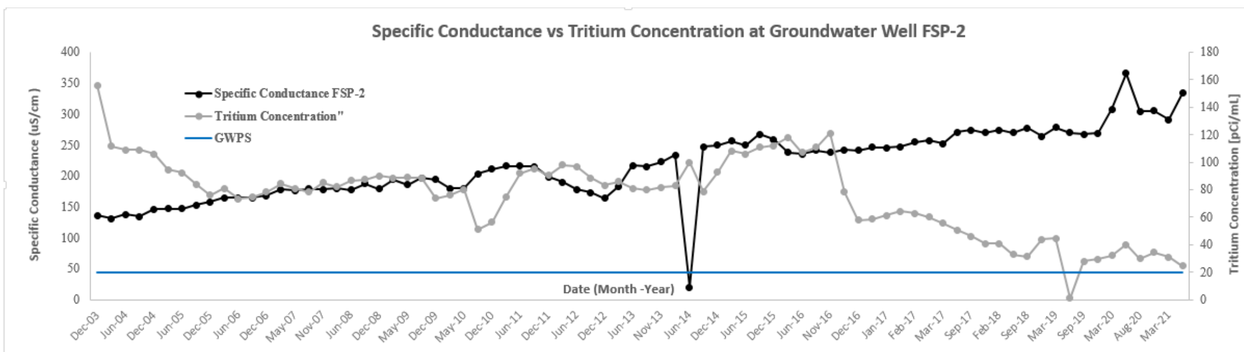

Figure 12. Graph showing similar relation where the tritium concentration decreases while the specific conductance continues to increase. This show a similar relation to nitrate concentration.