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Hydrogeochemistry of Kanuga Fen

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Abstract

Kanuga fen, located outside of Hendersonville, NC, is rare type of wetland found in the Appalachian Mountains. It is inhabited by two federally protected species, *Clemmys muhlenbergii* and *Sarracenia rubra* subsp. *jonesii*. This study examined the water chemistry of samples collected from various sites of the fen during the summer and fall seasons. Major ions were quantified using ion chromatography and alkalinity titrations then plotted on Piper and Stiff diagrams for data comparison. Samples from the summer and fall seasons were similar as they were slightly acidic (pH of 5.7-6.7), had low ionic strength, and consisted of the sodium-bicarbonate type. However, the influence of the water chemistry on these species' preferences has yet to be determined.

1. Introduction

Southern Appalachian mountain wetlands are rare habitats that host a variety of endemic and federally protected species which include the bog turtle (*Clemmys muhlenbergii*) and mountain sweet pitcher plant (*Sarracenia rubra* subsp. *jonesii*).[1] Of the known 722 rare plant species found in mountain wetlands, approximately 1/5th strictly inhabit this habitat type.[2] Previously, fens may have existed in each county of the mountains. However, they are now scarce as less than 500 sites exist in the Appalachian Highlands.[3] Anthropogenic sources are primarily responsible for habitat destruction and decreases in the rare species' population. Urbanization and land development can also introduce toxins into the environment. This alters the habitat and affects the species' ability to survive.[4,5] To better preserve these ecosystems, further knowledge of these habitats is required. Information on these habitats is limited as much comes in unpublished articles and survey forms.[1] Hence, information on the soil chemistry, water chemistry, and water table dynamics—fluctuations in the water table level—are either non-existent or lacking.[1,6] Thus, there is a need for research in this field.

1.1. Rare Species

The bog turtle is listed as a federally threatened species.[7] It inhabits areas with high water table levels, deep mud, and slow-moving water with no deep stagnant areas.[2,6] The reduction in bog turtles is attributed to urban expansion and land modification which results in decreased water levels.[4] Additionally, habitats are becoming more isolated from one another, resulting in no available habitats for the turtles to migrate towards.[2] Bog turtles, despite being federally protected, have also been involved in the pet trade.[2,8]

The mountain sweet pitcher plant is listed as a federally endangered species.[9] It is known to inhabit cataract bogs and valley bottoms that do not flood.[10] Human alteration and destruction of these habitats have contributed to the decrease in their numbers by changing the hydrology, nutrient density, and species that thrive there. Grazing and mechanical trampling of these species in addition to encroachment of invasive species are also concerns that affect the plant population.[11]

1.2. Characterization of Similar Habitats

In a similar study, Dripps et al. studied several groundwater-fed springhead seepages in South Carolina that are inhabited by the endangered Bunched Arrowhead (*Sagittaria fasciculata*). Analysis of the water chemistry via ion chromatography concluded that the wetlands were acidic (pH of 4.5-5.7), dilute (conductivity of 13-52 μs/cm) and contained low concentrations of NH_4^+ (≤0.06 mg/L).[4] In Kentucky, 3 different mountain fens were also examined hydrochemically as pore-water samples were analyzed across different seasons. The fens were acidic (pH of 4.3–5.9) with low Mg^{2+} (0.12-3.4 mg/L) and Na^+ (<1.5 mg/L) concentrations. Ca^{2+} (0–14.6 mg/L) and K^+ (0.22-19.2 mg/L) concentrations varied among the sites.[12] In fens across Virginia, the pH of these habitats ranged from 3.8 – 5.5, and Ca^{2+} was found to be the dominant cation.[13]

1.3. Kanuga Site

In an effort to protect these wetlands, the U.S. Fish and Wildlife Service (USFWS) established the Mountain Bogs National Wildlife Refuge. This refuge will encompass up to 30 wetland sites spanning from Western North Carolina to Eastern Tennessee as shown in Figure 1. By working with the communities and individuals that govern these lands, the goals include the protection and conservation of the few remaining Southern Appalachian wetlands while preventing the extinction of several federally protected species.[14]

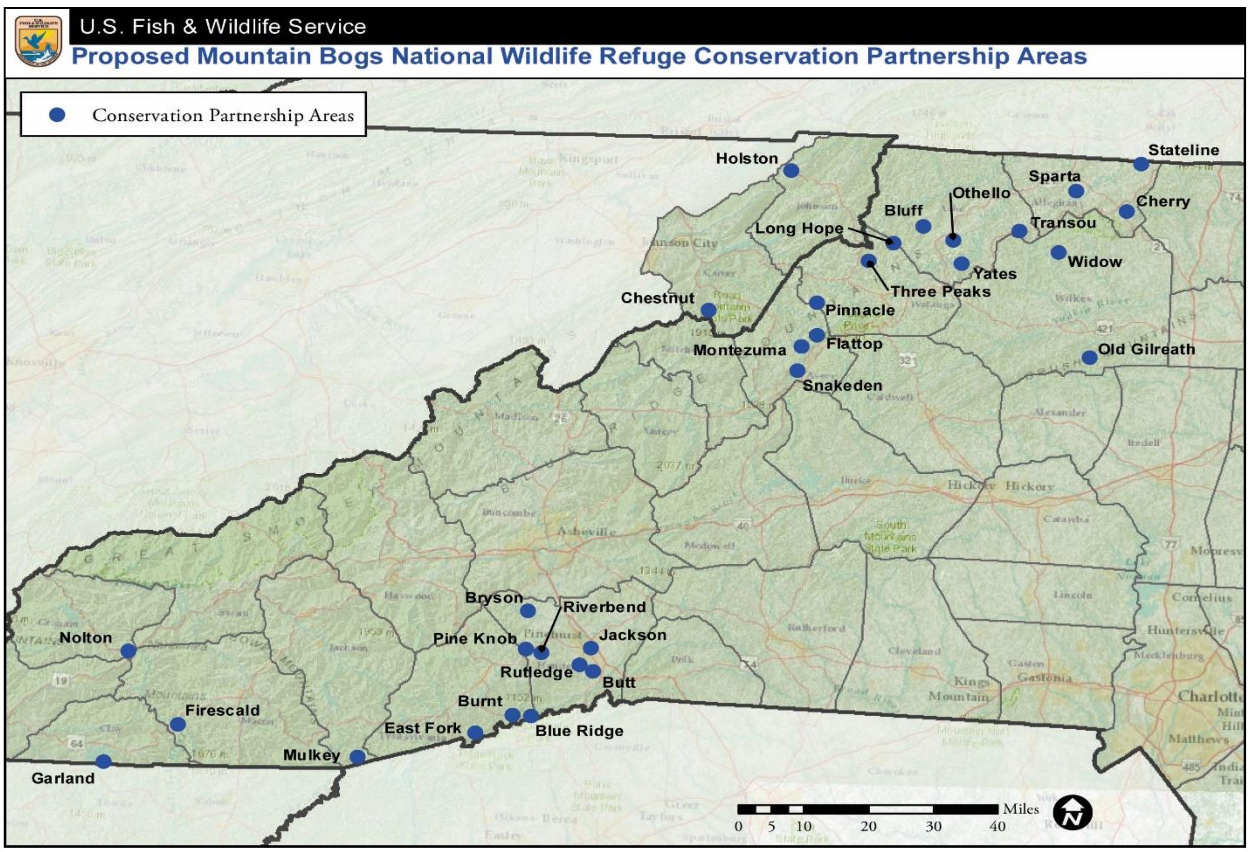

Figure 1. Map of 30 potential sites that the Mountain Bogs National Wildlife Refuge will encompass.[14]

Of the 30 sites, Kanuga fen, located outside of Hendersonville, NC, is inhabited by the mountain sweet pitcher plant and potentially bog turtle. The fen is primarily fed by groundwater but also includes precipitation, stream water, and runoff from flooding/storm water. Precipitation refers to rainfall that has only reacted with the atmosphere; naturally it is slightly acidic due to interactions with nitrogen, sulfate, and carbon dioxide in the air.[15] Precipitation can then result in runoff or infiltrate to groundwater. When precipitation has infiltrated, percolated, and interacted with ions present in the soil, the chemical composition of it can change. When groundwater discharges to the surface, this produces the streams at Kanuga fen. Runoff occurs when precipitation does not infiltrate the ground due to conditions such as oversaturated soil or a non-permeable surface—asphalt or concrete—which can result in a different chemical composition. Figure 2 shows a schematic of these various water source inputs into the fen.

1.4. Objectives

Examination of the fen's water sources was conducted to allow for characterization and better understanding of the habitat's water chemistry. Ion chromatography was utilized to enable identification of the chemical composition of each water source to determine the effects and influences of those sources. Graphical representations of the ion compositions were displayed with Stiff and Piper diagrams to allow for comparison. Stiff diagrams represent the chemical composition and concentrations as polygons. Piper diagrams use a triangular plot to map the percentage of each ionic component of the sample. Samples that are closer to each other on the plot are more similar in their chemical composition. This study was the first to examine the hydrogeochemistry of the Kanuga fen.

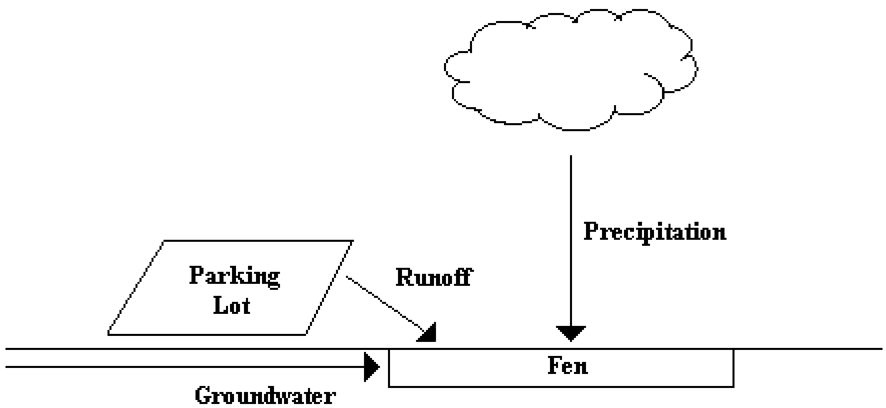

Figure 2. Schematic of the water sources contributing to Kanuga fen.

2. Methodology

2.1. Sample Site

Samples were collected during the summer and fall (July 7 and November 21) of 2014. Figure 3 shows the sample collection sites. Samples 1 and 4 were collected from wells near the pitcher plants; samples 2, 5, and 7 were collected from surface-water streams; sample 3 was collected from the lake; sample 6 was an area where groundwater discharge was visibly seen; sample 8 represented the runoff from the parking lot; sample 9 was collected from a previously installed well; an additional sample was taken for precipitation.

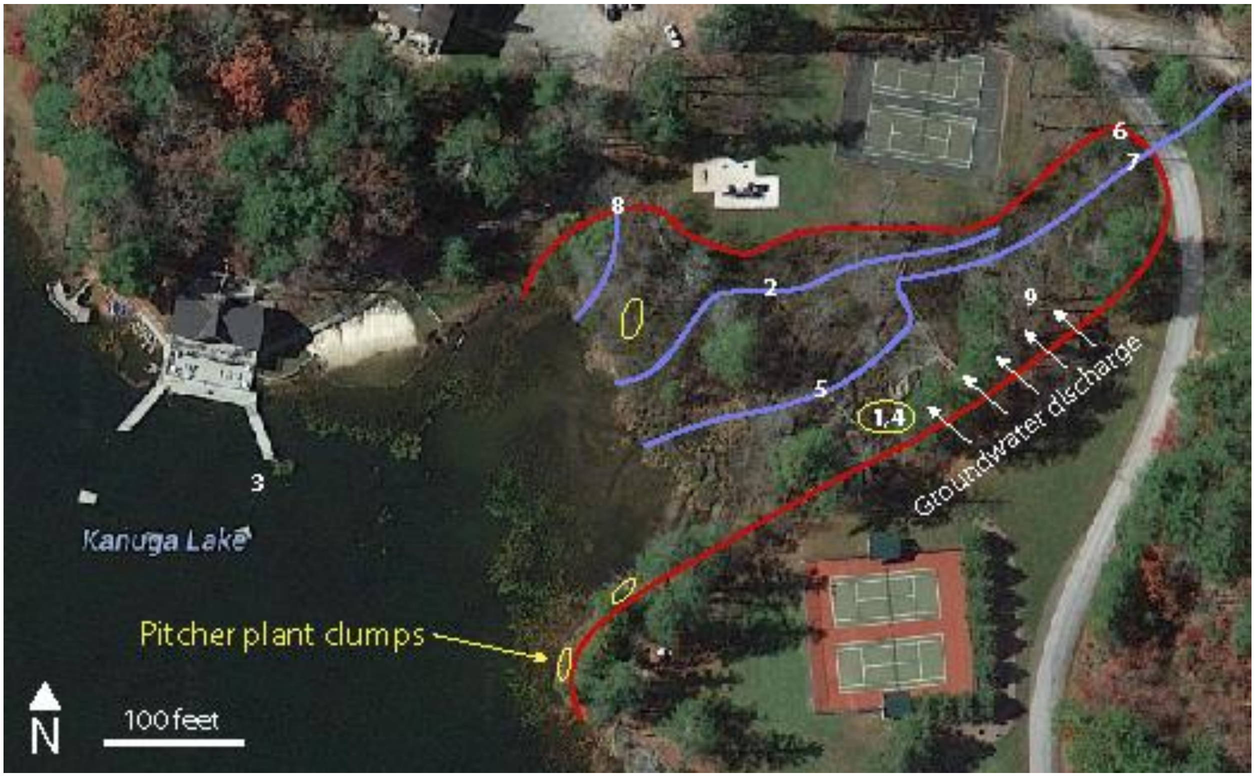

Figure 3. Sample collection sites for summer 2014. Red lines represent the boundaries of the fen; blue lines represent the streams that discharge through fen; yellow areas represent known populations of pitcher plants.

2.2. Sample Collection

Standard methods were employed for water sampling and analysis.[16] Samples were initially measured for conductivity, temperature, and pH using an Oakton Waterproof pH/CON 10 Meter pH meter. All water samples were collected in high-density polyethylene bottles. Collection of surface water consisted of rinsing the bottles three times with the sample before bottling. Groundwater samples were collected from the monitoring wells, and precipitation was collected from a funnel and bottle set-up. Samples were then transported on ice to the laboratory and refrigerated until use.

2.3. Filtration and Preservation

All samples were filtered for sediments and solids using a 0.45 μm nylon filter. Each filtered sample was divided into 3 aliquots. The aliquot for cation analysis was preserved with a drop of concentrated nitric acid. Aliquots for anion analysis and alkalinity titrations were left unpreserved.

2.4. Ion Analysis

Samples were analyzed for the aforementioned ions using a Dionex LC120 ion chromatograph with AS14A and CS12A columns and an ED50 electrochemical detector. Calibration curves were generated for cations (Na^+, K^+, Mg^{2+}, Ca^{2+}, and NH_4^+) and anions (Cl^-, SO_4^{2-}, and NO_3^-) from 0.4 to 7 ppm. Each sample was titrated with 0.012M HCL to calculate alkalinity and bicarbonate (HCO_3^-) concentrations. Ion concentrations were further used to calculate charge balances and generate Stiff and Piper diagrams.

3. Results and Discussion

Among both seasons, water samples from Kanuga fen were slightly acidic with a pH ranging from 5.7 to 6.7. They were dilute with conductivity ranging from 17.8 to 82.9 uS/cm in the summer and 19.2 to 117 uS/cm in the fall. The sum of cations and anions, total dissolved solid (TDS), ranged from 0.27 to 1.30 meq/L for summer and 0.32 to 1.50 meq/L for fall. HCO_3^- was the dominant anion, and Na^+ was generally the dominant cation. Table 1 shows that ion concentrations were predominantly low, but the highest ion concentrations were from the parking lot sample. Because the samples were very dilute, slight errors were high relative to the measured values as seen in summer samples measured for K^+.

Calculation of the limit of detection (LOD) and limit of quantification (LOQ) revealed many values fell below these limits. For example, as seen in the summer samples of Table 1, most of the K^+ and half of the Mg^{2+} concentrations were below LOQ. All of the NH_4^+ and half of the NO_3^- concentrations fell below LOD. Alternative methods of quantifying data, such as the method detection limit (MDL) and minimum level (ML) as reported by the United States Environmental Protection Agency (EPA), could be investigated.[17,18] Alternatively, the instrument may not have the sensitivity required to analyze the ions that are so dilute in solutions. In this case, other instruments may be more precise for future work. For the purposes of this study, values were included as estimated values even if they fell below the calculated LOQ.

3.1. Charge Balance

As shown in Table 2, charge balances for 7 out of 10 summer samples were within 10%, and 2 sampled bordered the 10% margin; Well 4D had a poor charge balance. Most summer samples had negative charge balances. Inversely, all but one of the fall samples had positive charge balances. Seven out of ten samples fell within 10%, and the Well 4D sample bordered the 10% margin; Road Spring and Parking Lot were unbalanced. The consistent all negative/positive charge balances could be due to an error in the alkalinity titration that could have over- or under-accounted for bicarbonate. Because samples had low TDS, a small error in one parameter could have a significant impact on the overall charge balance.

3.2. Stiff Diagrams

Data from Table 1 was used to generate Stiff diagrams in Figure 4 for comparison among individual samples. Among samples in the summer, the polygons of some samples were very similar which indicated a likewise similarity in their composition. Generally, polygons were wider towards the top and slender towards the bottom (Well 4D, Well 4S, Lower E Bridge, Well 1, Lake, and Road Spring). This indicated that the concentrations of sodium and bicarbonate were the highest, demonstrating that the water is of the sodium-bicarbonate type. Deviations from this general shape included more width towards the bottom half of the polygon (Lower W Bridge, 2S, Parking Lot, and Precipitation) as there was a higher concentration of Ca^{2+} and SO_4^{2-} ions in solution. From summer to fall, the shapes generally remained the same. This indicates similar ratios of ions. The width of the polygons during the fall had generally decreased, indicating that the actual amount of ions have decreased—there are fewer ions in the water as it is more dilute.

3.3. Piper Diagrams

For comparison among samples collectively, Piper diagrams were generated as shown in Figure 5. The bottom left triangle indicates the percentage of each cation across the axes. Most samples were grouped towards the lower right quadrant of the triangle, which correlates to a dominance of Na^+ and K^+ ions in their chemical composition. The bottom right triangle indicates the percentage of each anion across the axes. Most samples grouped towards the bottom left of the triangle, which relates to dominance in HCO_3^-. Thus, the majority of the samples consisted of a sodium-bicarbonate ion composition. The center diamond maps both the cations and anions mapped on one plane. In Figure 5a, there are two extremes in this plot: 4D represents groundwater that has interacted with the ions in the soil, whereas precipitation represents water that has not reacted with the soil. Both of these samples lie far from each other, and all other samples lies between them. The parking lot sample is plotted closer to precipitation which indicates that it is more similar to precipitation. This is consistent with the process of runoff—precipitation that drains off a surface. The other samples are plotted closer to the 4D groundwater sample, which is consistent that this is a groundwater-fed fen. In Figure 2b, most of the samples are plotted relatively close to where they were in the

Table 1. ion concentrations (mg/L) ± error of Kanuga samples in Summer and Fall 2014.

Sample	Na^{+}	K^{+}	Mg^{2+}	Ca^{2+}	NH_4^{+}	HCO_3^{-}	Cl^{-}	NO_3^{-}	SO_4^{2-}
Well 1									
Summer	1.49 ± 0.26	nd	0.239 ± 0.069*	0.782 ± 0.086	nd	8.21 ± 0.21	1.02 ± 0.12	nd	0.198 ± 0.065*
Fall	2.12 ± 0.14	0.80 ± 0.19*	0.189 ± 0.093*	0.84 ± 0.14	nd	7.12 ± 0.21	1.04 ± 0.15	nd	0.29 ± 0.18
Well 4D									
Summer	2.07 ± 0.26	0.77 ± 0.30*	nd	0.270 ± 0.086*	nd	8.93 ± 0.21	1.37 ± 0.12	nd	0.339 ± 0.065
Fall	3.33 ± 0.15	1.42 ± 0.19	nd	0.24 ± 0.14*	nd	5.44 ± 0.21	1.66 ± 0.15	0.55 ± 0.14	0.29 ± 0.18
Well 4S									
Summer	1.73 ± 0.26	nd	0.187 ± 0.068*	0.811 ± 0.086	nd	8.93 ± 0.21	1.06 ± 0.12	nd	0.256 ± 0.065*
Fall	2.49 ± 0.14	0.62 ± 0.19*	0.157 ± 0.093*	0.90 ± 0.14*	nd	7.12 ± 0.21	1.72 ± 0.15	nd	0.93 ± 0.19
Lake									
Summer	1.68 ± 0.26	0.64 ± 0.30*	0.348 ± 0.069*	1.233 ± 0.087	nd	8.58 ± 0.21	1.21 ± 0.12	nd	nd
Fall	2.45 ± 0.14	1.08 ± 0.19	0.314 ± 0.093*	1.26 ± 0.14	nd	9.49 ± 0.21	1.44 ± 0.15	nd	0.29 ± 0.18
Parking Lot									
Summer	2.81 ± 0.27	1.13 ± 0.30*	1.479 ± 0.070	7.888 ± 0.136	nd	24.91 ± 0.21	3.45 ± 0.14	1.51 ± 0.16	6.091 ± 0.090
Fall	3.92 ± 0.15	1.53 ± 0.19	2.070 ± 0.097	10.20 ± 0.25	nd	24.87 ± 0.21	3.52 ± 0.16	1.41 ± 0.14	4.38 ± 0.22
Lower W Bridge									
Summer	2.55 ± 0.27	0.79 ± 0.30*	0.647 ± 0.069	2.495 ± 0.092	nd	16.96 ± 0.21	1.20 ± 0.12	nd	0.43 ± 0.065
Fall	3.53 ± 0.15	1.08 ± 0.19	0.703 ± 0.094	2.66 ± 0.15	nd	15.44 ± 0.21	1.46 ± 0.15	nd	0.63 ± 0.19
Lower E Bridge									
Summer	1.55 ± 0.26	0.53 ± 0.30*	0.244 ± 0.069*	0.829 ± 0.086	nd	8.64 ± 0.21	0.91 ± 0.12	nd	0.342 ± 0.065
Fall	2.46 ± 0.14	0.87 ± 0.19*	0.235 ± 0.093*	1.00 ± 0.14	nd	7.66 ± 0.21	1.02 ± 0.15	nd	0.29 ± 0.18
Road Spring									
Summer	1.97 ± 0.26	0.88 ± 0.30*	0.388 ± 0.069	1.478 ± 0.088	nd	12.09 ± 0.21	1.21 ± 0.12	0.52 ± 0.16*	nd
Fall	2.58 ± 0.14	1.22 ± 0.19	0.388 ± 0.093*	1.62 ± 0.14	nd	8.16 ± 0.21	1.34 ± 0.15	nd	0.50 ± 0.18
Well 2S									
Summer	1.42 ± 0.26	1.82 ± 0.31	0.192 ± 0.069*	1.084 ± 0.087	nd	9.46 ± 0.21	1.25 ± 0.12	1.24 ± 0.16	0.400 ± 0.065
Fall	2.26 ± 0.14	1.25 ± 0.19	0.587 ± 0.093	1.43 ± 0.14	1.51 ± 0.21	15.04 ± 0.21	1.14 ± 0.15	nd	0.29 ± 0.18
Precipitation									
Summer	0.68 ± 0.25*	nd	nd	1.814 ± 0.089	nd	4.23 ± 0.21	1.07 ± 0.12	0.74 ± 0.16*	1.738 ± 0.067
Well 2D									
Fall	2.41 ± 0.14	2.85 ± 0.20	0.575 ± 0.093	1.40 ± 0.14	8.09 ± 0.31	40.66 ± 0.21	1.04 ± 0.15	nd	0.80 ± 0.19

nd indicates values below LOD

* indicates values above LOD but below LOQ

Table 2. charge balances for Kanuga samples

Samples	Summer			Fall		
	Cations	Anions	Charge Balance (%)	Cations	Anions	Charge Balance (%)
Well 4D	0.13	0.20	-20.98	0.19	0.15	12.53
Lower W Bridge	0.31	0.32	-1.90	0.37	0.31	9.02
Lake	0.18	0.17	1.43	0.22	0.21	4.06
Well 4S	0.15	0.18	-9.55	0.18	0.19	-1.44
Lower E Bridge	0.14	0.18	-10.71	0.20	0.16	9.59
Road Spring	0.21	0.24	-5.93	0.26	0.19	16.14
Well 1	0.14	0.17	-10.45	0.17	0.16	4.57
Parking Lot	0.67	0.66	0.73	0.89	0.62	17.77
Well 2S	0.21	0.22	-2.31	0.33	0.29	7.34
Precipitation	0.13	0.15	-6.61			
Well 2D				0.74	0.72	1.93

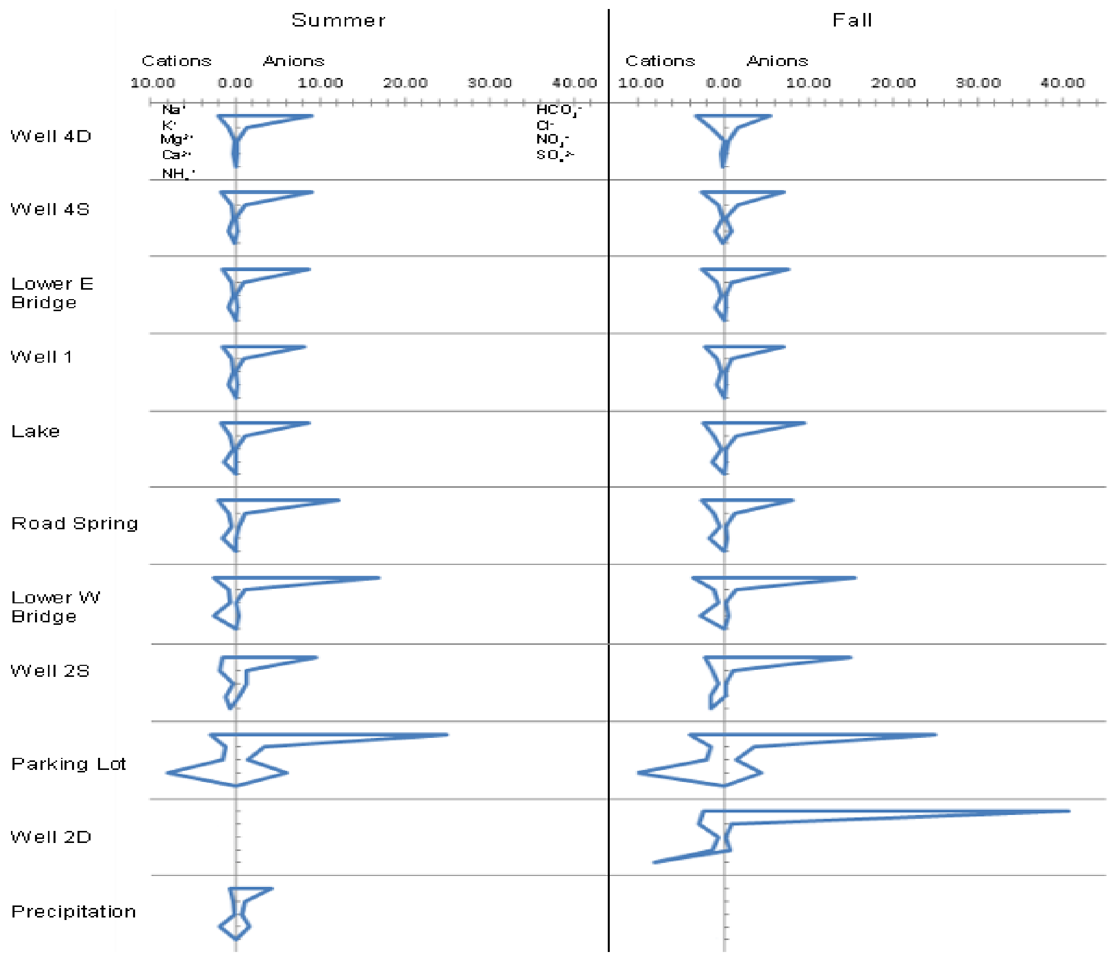

Figure 4. Stiff diagrams of ion concentrations (ppm) represented as polygons of samples from Kanuga fen. The left of the y-axis represents the cations (Na^+, K^+, Mg^{2+}, Ca^{2+}, and NH_4^+), and the right represents the anions (HCO_3^-, Cl^-, NO_3^-, and SO_4^{2-}).

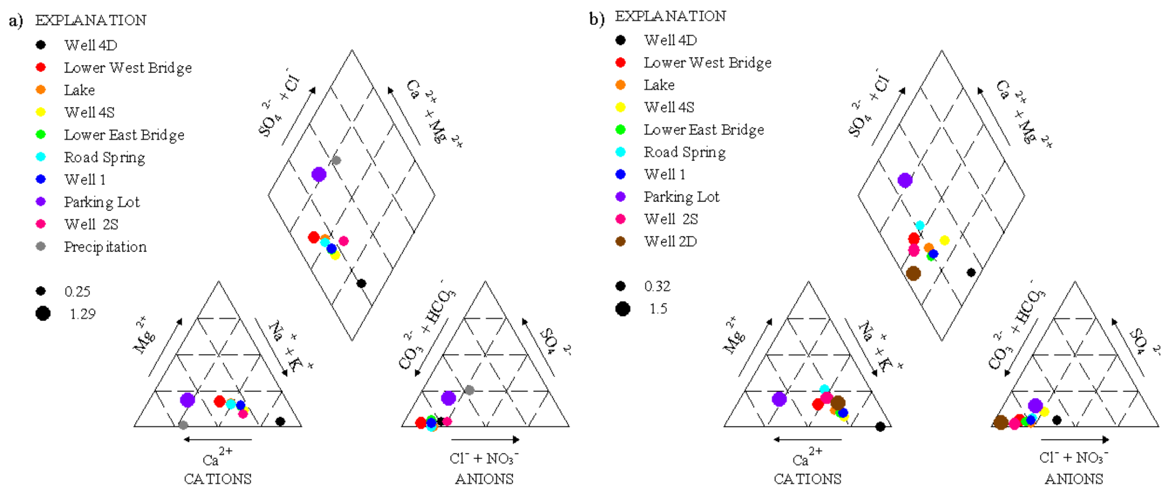

Figure 5. Piper diagram of the fen's ion composition from samples collected during a) the summer and b) the fall.

summer. This implies a stable environment throughout the seasons.

Compared to Dripps et al. (pH of 4.5-5.7), Thompson et al. (pH of 4.3–5.9), and Walbridge (pH of 3.8 – 5.5), samples at Kanuga were not as acidic (pH of 5.7-6.5).[4,12,13] However, in Figure 6, the chemical composition of Kanuga fen was consistent with Dripps et. al. who reported a similar sodium and bicarbonate dominant water chemistry.[4] With the exception of the parking lot, the other samples were dilute. This could be a result of the relatively short travel time between recharge from precipitation and discharge to the fen that would limit the interaction of groundwater with the ions in the soil.

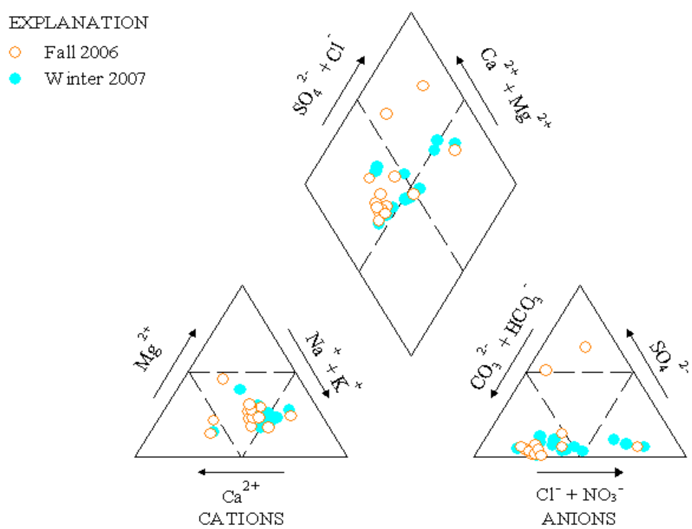

Figure 6. Piper diagram of data from Dripps et. al showing a dominant sodium and bicarbonate chemical composition.

3.4. Other Observations

The parking lot sample contained the highest ion concentrations. This sample was taken from a location downhill of and closest to the parking lot. The parking lot sample was not directly feeding into the fen at all times as a physical barrier separates it from the fen. However, during a storm where runoff from the parking lot adds more ions to the pooling water, water levels rise above the barrier, resulting in overflow and deposition of ions into the fen. While this could potentially affect the fen, it is possible that the additional ions may flow straight to the lake and not disturb the pitcher plants. The effects of this hydrochemically different parking lot sample on the fen warrants further investigation. Preferably, more water samples could be taken during a storm to examine any drastic changes in ion composition after the additional intake from the parking lot.

Most of the fall samples fell under LOD for NH_4^+ with the exception of two samples—both of which are adjacent to each other at the site. It was discovered that a sewer line ran through the site. A tracer test was conducted where a biodegradable red dye was added to the septic pipe from one side of the fen. It was found to reach the opposite side of the fen; thus, confirming that the sewage line ran under the fen. The dye was not observed in the fen's surface water, so it was concluded that the sewer line was not directly feeding into the fen. This implies a possible leak of the sewage line into the groundwater. No NH_4^+ was detected in the surface water samples, therefore if it unclear how this will affect the fen.

4. Conclusion

Samples were collected from Kanuga fen throughout the summer and fall seasons of 2014. The goal was to characterize and better understand the water dynamics of Kanuga fen in order to possibly identify trends among the data and the few previously characterized fens. Thus far, these data and those reported by Dripps et. al share a common trend of a sodium-bicarbonate dominant water chemistry. While it is possible that the water chemistry may not be a prominent factor in the habitat selection of these rare species, it is important to characterize the habitat. Future characterization could be expanded to include soil chemistry, streamflow, and shading.

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6. References

1. Weakley, A. S.; Schafale, M. P. *Water, Air, Soil Pollut*. **1994**, *77*, 359-383.
2. Murdock, N. A. *Water, Air, Soil Pollut*. **1994**, *77*, 385-405.
3. Moorhead, K. K.; Rossell, I. M. Southern mountain fens. In *Southern forested wetlands: ecology and management*; Messina, M.G.; Conner, W. H., Ed.; CRC Press: Boca Raton, 1998; p 379-403.
4. Dripps, W.; Lewis, G. P.; Baxter, R.; Andersen C. B. *Southeastern Naturalist*, **2013**, *12*, 619-637
5. Lewis, G. P.; Mitchell, J. D.; Andersen, C. B; Haney, D. C.; Liao, M. K.; Sargent, K. A. *Water, Air, Soil Pollut*. **2007**, *182*, 303-323.
6. Feaga, J. B.; Haas, C. A.; Burger, J. A. *Wetlands*, **2012**, *32*, 1011-1021.
7. U.S. Fish & Wildlife Services. *Fed. Reg.* **1997**, *62*, 59605-59623.
8. Morrow, J. L.; Howard, J. H.; Smith, S. A; Poppel, D. K. *J. Herpetol*. **2001**, *35*, 545-552.
9. U.S. Fish & Wildlife Services. *Fed. Reg.* **1998**, *53*, 38470-38474.
10. Godt, M. J. W; Hamrick, J. L. *American Journal of Botany* **1996**, *83*, 1016-1023.
11. U.S. Fish and Wildlife Service. Mountain sweet pitcher plant (Sarracenia rubra ssp. jonesii) 5-Year Review: Summary and Evaluation. May 2013. http://ecos.fws.gov/docs/five_year_review/doc4156.pdf
12. Thompson, Y.; Sandefur, B. C.; Karathanasis, A. D.; D'Angelo, E. *Aquatic Geochemistry* **2009**, *15*, 349-370.
13. Walbridge, M. R. *Water, Air, and Soil Pollution* **1994**, *77*, 247-269.
14. U.S. Fish & Wildlife Services. Mountain Bogs National Wildlife Refuge Proposal. May 2012. http://www.fws.gov/southeast/mountainbogs/pdf/2012-Fact-sheet-Overview-FINAL.pdf
15. Teixeira, E. C.; Migliavacca, D.; Filho, S. P.; Machado, A. C. M.; Dallarosa, J. B. *Anais da Academia Brasileira de Ciências* **2008**, *80*, 381-395.
16. Sanders, L. L. *A Manual of Field Hydrogeology*; Prentice-Hall: Upper Saddle River, 1998.

17. U.S. Environmental Protection Agency. *CFR 40* **1984**, *136*, 343-346.
18. U.S. Environmental Protection Agency. *Method 1631: revision B : mercury in water by oxidation, purge and trap, and cold vapor atomic fluorescence spectrometry*; Office of Water: Washington, 1999.