University of North Carolina Asheville
Journal of Undergraduate Research
Asheville, North Carolina
Spring 2024

Using Chemical Fingerprinting to Analyze Stormwater Runoff Patterns in McClure's Bog, North Carolina

Abby Sgan

Environmental Studies - Earth Science
The University of North Carolina Asheville
One University Heights
Asheville, North Carolina 28804 USA
Faculty Mentor: Dr. Jeff Wilcox

Abstract

McClure's Bog, a Southern Appalachian wetland located in Henderson County, North Carolina, has undergone extensive hydrologic remediation efforts since the mid-1990s. McClure's is located downstream from a livestock farm, a source of runoff and excess nutrients that threatens fragile populations of federally protected pitcher plants. To combat this, engineers rerouted runoff around the bog's central area and constructed three water retention cells that serve to collect rerouted runoff during major storm events. This project compared chemical signatures, or "fingerprints", of agricultural runoff to signatures of well and pond water samples in order to analyze patterns of runoff movement throughout the bog. We used ion chromatography to identify major ion concentrations (sodium, potassium, magnesium, calcium, chloride, nitrate, and sulfate), and used alkalinity titrations to determine bicarbonate concentrations. These chemical markers were analyzed in eighteen water samples collected from twelve sampling locations across three dates from late 2023 to early 2024. The samples were compared to previous water samples dating back to 2014. We found that runoff exhibited a distinct chemical signature that expresses lower sodium and potassium concentrations than groundwater, and higher magnesium than both precipitation and groundwater. Using these signatures, we identified when and where runoff contaminants affected bog water

quality. We concluded that runoff is still infiltrating some groundwater-fed areas despite rerouting, although areas with pitcher plants did not appear to be affected by runoff. Investigation into other sources that could be affecting observed chemical signatures is still needed, however, and could be completed through further study.

1.Introduction

McClure's Bog is a Southern Appalachian wetland situated in Henderson County, North Carolina (Figure 1). This particular bog is defined by its extensive remediation efforts and role as a host site to numerous rare species of federally protected flora and fauna including the mountain sweet pitcher plant (*Sarracenia rubra var. Jonesii*). Additionally, the only known variation of the mountain sweet pitcher plant in its yellow form is in McClure's bog. McClure's is also one of the only sites where mountain sweet pitcher plants and purple pitcher plants (*S. purpurea*) are observed to hybridize (Lynch, 1998). *Helonias bullata*, or swamp pink - which is threatened in its Appalachian territory - also grows here. The North American bog turtle (*Clemmys muhlenbergii*) has historically been found at McClure's as well (Lynch, 1998).

1.1. Hydrology and Geochemistry of McClure's Bog

The vitality of Southern Appalachian wetlands and the rare flora and fauna that they host depends greatly on geochemical composition. These wetlands are defined by their characteristically moist, muddy, and acidic soils that are poor in nutrients and oxygen (McGreal, 2016). Excess nutrients encourage increased shrub growth, an area that has historically been of distinct concern (Sutton, 2008). At McClure's, the primary source of intrusive nutrients originates with surface runoff from a livestock farm located directly across the road from the central part of the wetlands and the vulnerable pitcher plant populations. Elevated calcium, magnesium, and potassium concentrations have been observed in samples from ditches adjacent to the livestock pasture (Reberg-Horton, 1996). Nitrate intrusion is particularly common in this area as well, posing a significant threat to the pitcher plants that require nutrient-poor water and soils to thrive (Sutton, 2008). It is therefore essential to monitor nutrient and dissolved ion concentrations throughout the wetland in order to validate remediation efforts and identify potential areas of concern.

The wetland lies on the floodplain of Gash Creek, a tributary of the French Broad river (Merrill and Lynch, 1998), but is primarily fed by groundwater flowing from the upslope area south and west of the wetland.

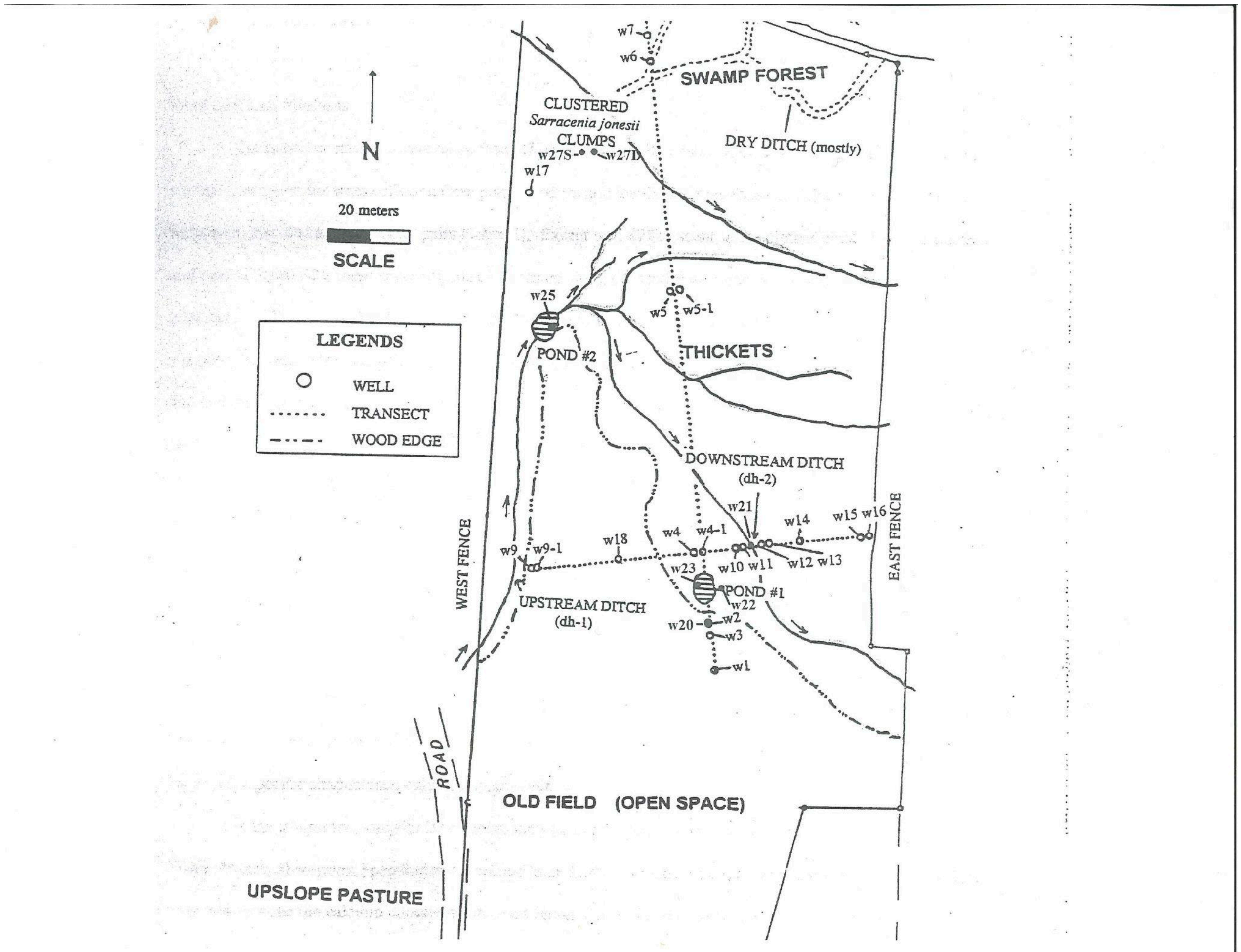

Figure 1. Site map of McClure's Bog, NC provided by The Nature Conservancy. Sampling wells are represented with their corresponding number and depth identification (ex: 27D). Pond #2 is referred to as Overflow Pond and Pond #1 is referred to as Groundwater Pond in this project.

1.2. Restoration

Restoration efforts have been ongoing since the mid 1990s. Initiated by The Nature Conservancy, who acquired the land in 1982, these efforts began with converting the area from a dumping ground and grazing pasture to a saturated wetland (Reberg-Horton, 1996). Approximately one third of the site is former agricultural land, with the majority of previously cultivated land being situated in the bog's southern region. Previous owners also created ditches in multiple areas of the bog in an attempt to drain the bog and keep it suitable for agricultural use (Huang, 1996).

Restoration efforts culminated in 2019 with a large stormwater rerouting project conceptualized by The Nature Conservancy and constructed by Wildlands Engineering and Peak Hydrogeologic, PLLC. Whereas farm runoff originally flowed directly across the road and into the central, pitcher plant-inhabited area prior to rerouting, it now flows around the central area and into three retention cells located south of the main wetland area (Figure 2).

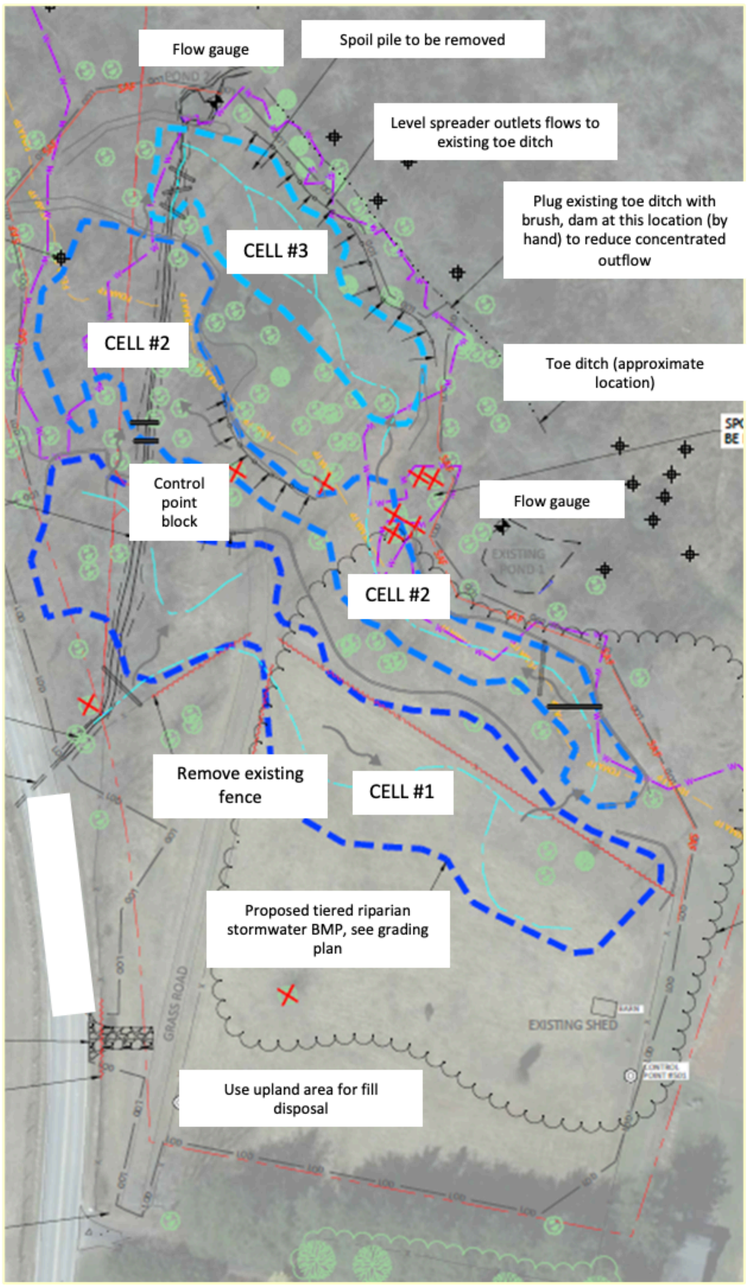

Figure 2. Grading concept map for McClure's provided by The Nature Conservancy. White boxes denote site-specific remediation practices.

1.3. Objectives

This project aimed to assess the effectiveness of stormwater rerouting efforts in McClure's Bog using techniques of chemical fingerprinting. Our goal was to compare chemical signatures of water samples from livestock farm runoff to chemical signatures from groundwater wells and ponds located throughout the property in order to determine if and how runoff was entering the wetland. Doing so will help assess the effectiveness of the 2019 restoration project and identify any areas for improvement in restoration efforts.

2.Methods

Eighteen samples were collected from twelve sampling sites on three dates from 2023-2024: September 3rd, 2023, October 29th, 2023, and January 10th, 2024. Consistent sampling from the same wells across all dates was impossible due to extremely dry conditions in September and October of 2023, and farm runoff was only available for collection after a large rain event in January of 2024. However, all samples were collected and treated using the same methods. Data from previous UNC Asheville undergraduate research projects were also included in this study. The water samples from previous projects used for data analysis in this study were collected in 2015, 2017, 2018, 2019, 2020, 2021, and 2023.

2.1. Sample Collection

Water samples from ponds were collected by hand in 500mL polyethylene bottles, while samples from shallow and deep groundwater wells were collected using a peristaltic pump. All water samples were placed in a cooler during transportation from field site to laboratory and refrigerated until filtration and analysis.

2.2. Sample Filtration and Titration

Samples were filtered using vacuum filtration to remove excess suspended solids and particulate matter. Once filtered, the samples were divided into three subsets of samples. Two 20mL aliquots for major ion analysis. The first aliquot, supplemented with two drops of concentrated hydrochloric acid, would eventually be analyzed for major cations, while the other 20 mL aliquot remained unaltered and was analyzed for anions. The third filtered aliquot was used for alkalinity titrations; approximately 50 ml of each sample was titrated with 0.0255N hydrochloric acid to to determine bicarbonate concentrations.

2.3. Ion Chromatography

We used a Dionex Easion ion chromatograph (IC) to quantify sodium, potassium, magnesium, calcium, chloride, nitrate, and sulfate in water samples. Before samples were analyzed, a series of standards (20 ppm, 10 ppm, 5 ppm, 2.5 ppm, and 1 ppm) were run in the IC to establish detection limits and standard curves for each ion. Sample measurements from the IC were then converted into concentrations of parts per million (ppm) using the standard curves (Table 1).

3.Results and Discussion

We found that farm runoff and groundwater each exhibited a unique cation fingerprint pattern across sampling dates. Runoff from the neighboring farm had higher concentrations of nearly all parameters than samples collected within the wetland (Table 1), and clustered toward the Ca/Mg (middle-left) side of the Piper diagram (Figure 3). Samples comprising primarily of groundwater (Wells 27s and 27d) clustered near the Na/K (lower right) corner, while precipitation sample plotted toward the Ca (bottom left) portion of the Piper diagram (Figure 3).

Samples	Na	K	Mg	Ca	Alkalinity	HCO3	NO3-N	Cl	NO3	SO4
A) McC Gw pond 10/29	1.45	4.11	0.95	3.05	8.2	9.9	0.00	4.47	0.00	0.02
B) McC27D 10/29	1.97	1.52	0.33	2.06	5.5	6.7	0.39	2.85	1.74	0.17
C) McC 29S 9/7	1.62	0.44	0.27	1.31	1.6	2.0	0.07	16.96	0.30	0.28
D) McC 29D 9/7	2.15	1.82	0.36	1.79	7.2	8.8	0.78	2.85	3.45	0.30
E) McC 27S 9/7	1.67	0.36	0.24	1.42	1.8	2.2	0.04	3.22	0.16	0.39
F) McC Leaving Stream 9/7	1.70	2.27	0.70	2.31	8.0	9.7	0.15	5.75	0.65	0.29
G) McC G-Water Pond 9/7	1.44	2.38	0.61	2.26	6.9	8.4	0.03	4.96	0.13	0.02
H) McC 27D 9/7	2.04	1.51	0.34	1.96	6.3	7.7	0.40	2.92	1.76	0.15
I) McC Overflow Pond 9/7	1.09	3.46	0.73	3.58	8.2	10.0	0.07	6.24	0.29	1.31
J) McC 27S 10/29	1.60	0.46	0.18	1.27	1.6	1.9	0.03	2.37	0.12	0.32

K) McC 28S 10/29	1.56	0.33	0.26	1.68	2.1	2.6	0.06	1.75	0.26	0.12
L) McC Cell 1 1/10	0.42	3.51	1.23	2.74	8.1	9.9	1.19	2.39	5.28	1.80
M) McC Overflow Pond 1/10	1.43	4.91	2.13	3.73	7.5	9.1	3.41	6.44	15.11	3.87
N) McC Cell 2 1/10	0.85	3.27	1.51	2.48	7.2	8.8	1.65	3.91	7.31	3.05
O) McC G-Water Pond 1/10	0.92	2.55	0.83	1.76	2.4	3.0	1.31	3.27	5.79	2.54
P) McC Leaving Stream 1/10	0.95	2.49	1.07	1.87	8.2	10.0	1.78	4.16	7.87	2.79
Q) McC Farm Runoff 1/10	1.91	10.58	4.49	9.18	8.2	10.0	11.23	10.52	49.70	7.90
R) McC 27S 1/10	1.24	1.18	0.45	0.19	0.3	0.4	0.09	2.58	0.38	2.29

Table 1. Concentrations of major ions for all samples, expressed in milligrams per liter (mg/L). Samples collected on October 29th, 2023 are highlighted in blue to emphasize abnormally dry conditions; only four locations yielded enough water for a sample. Samples with high nitrate concentrations are highlighted in green to emphasize evidence for runoff intrusion.

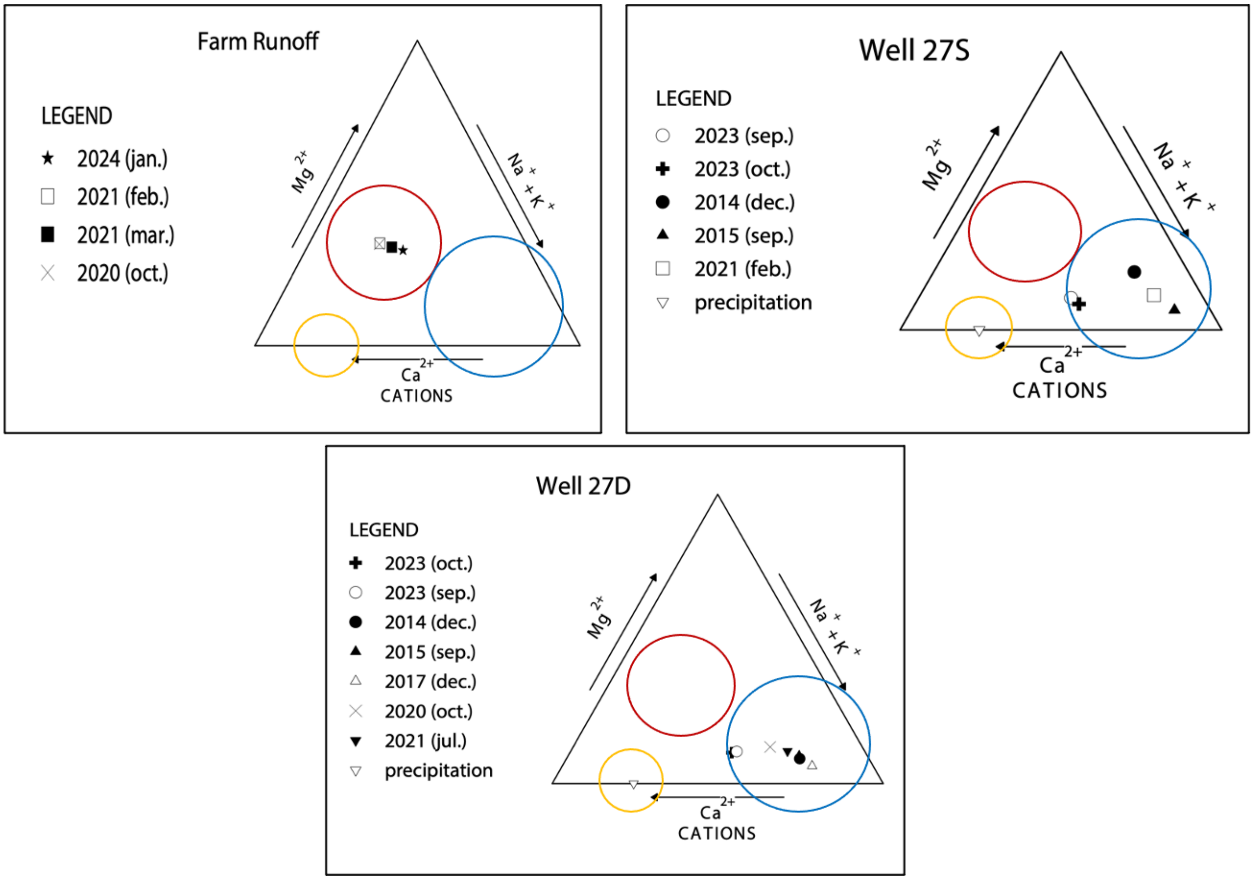

Figure 3. Piper diagrams for farm runoff samples and wells 27S and 27D. Runoff signatures are delineated with a red circle, groundwater signatures are delineated with a blue circle, and an observed precipitation signature is delineated with a yellow circle.

Wetland conditions were extremely dry on two of the sampling dates: September 7th and October 29th, 2023. Samples on September 7th were collected right after a flash storm, but conditions in the wetland were extremely dry leading up to that event. While cation concentrations for the overflow pond plot closer to a precipitation signature than other samples, most of the samples collected align closely with a groundwater fingerprint (Figure 4). This indicates that sampling sites were not significantly affected by that precipitation or runoff.

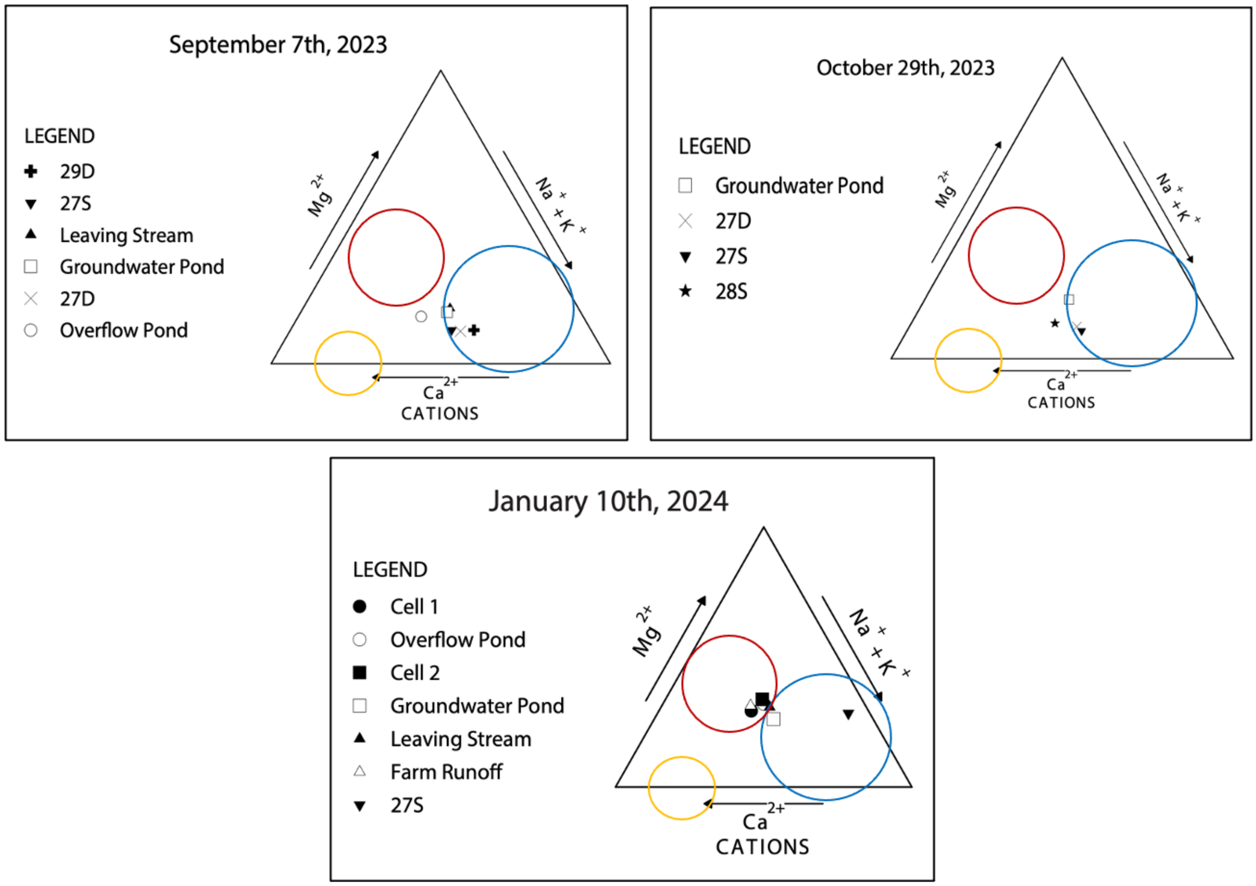

Figure 4. Piper diagrams indicating cation concentrations (mg/L) for the three primary sampling dates: September 7th, 2023, October 29th, 2023, and January 10th, 2024. The relative observed chemical fingerprint for farm water runoff is delineated with a red circle, and the relative observed chemical fingerprint for groundwater is delineated with a blue circle.

The overflow pond was almost entirely dry on October 29th, which is why we couldn't collect a sample. Because of these extremely dry conditions, all samples plotted within the limits for a groundwater fingerprint (Figure 4). Samples collected on January 4th, 2024 were collected the day after a major storm event, allowing for the collection of farm runoff and water from retention cells one and two (see Figure 4). With the exception of well 27S and the Groundwater pond, samples from January 4th were consistent with farm runoff signatures and plotted closely together, indicating these areas were affected by runoff from the neighboring farm. The "Groundwater" pond appears to be more consistent with a groundwater signature, but it still plots closely to other samples, indicating it is being fed by runoff in some capacity. Well 27S is located directly within the pitcher plant habitat and did not plot consistently with any of the other samples on January 4th, signaling that even during periods of increased precipitation and runoff, the pitcher plant habitat is not being contaminated by runoff (Figure 4).

Samples	Cations	Anions	TDS	Charge Balance (%)
A) McC Gw pond 10/29	0.398543	0.289392	0.69	15.87
B) McC27D 10/29	0.254242	0.221947	0.48	6.78
C) McC 29S 9/7	0.16883	0.520366	0.69	-51.01
D) McC 29D 9/7	0.259086	0.286358	0.55	-5.00
E) McC 27S 9/7	0.172386	0.137445	0.31	11.28
F) McC Leaving Stream 9/7	0.304716	0.337475	0.64	-5.10
G) McC G-Water Pond 9/7	0.286591	0.28068	0.57	1.04
H) McC 27D 9/7	0.253265	0.239499	0.49	2.79
I) McC Overflow Pond 9/7	0.374221	0.371364	0.75	0.38
J) McC 27S 10/29	0.159536	0.107017	0.27	19.70
K) McC 28S 10/29	0.181828	0.097885	0.28	30.01
L) McC Cell 1 1/10	0.346019	0.352551	0.70	-0.93
M) McC Overflow Pond 1/10	0.549306	0.655091	1.20	-8.78
N) McC Cell 2 1/10	0.368726	0.435119	0.80	-8.26
O) McC G-Water Pond 1/10	0.260673	0.287165	0.55	-4.84
P) McC Leaving Stream 1/10	0.286545	0.465761	0.75	-23.82
Q) McC Farm Runoff 1/10	1.181096	1.426508	2.61	-9.41
R) McC 27S 1/10	0.130192	0.133374	0.26	-1.21

Table 2. Total cation, anion, total dissolved solids, and charge balance measurements per sample. Charge balance errors greater than 10% are highlighted in orange.

Charge balances were calculated as well (Table 2). Usually, charge balance errors within 10% are indicative of accurate cation and anion measurements. Several samples showed charge balances that exceeded 10%, indicating possible error in sample analysis, or the presence of cations and/or anions that were not tested. Future sampling and analysis may be necessary to determine the cause of larger charge balance errors.

The chemical fingerprints observed in this study allowed us to identify which sampling locations are still being infiltrated by runoff despite hydrologic restoration. It is evident that some sites are still being affected by farm runoff. The overflow pond, the location into which runoff used to flow directly, exhibited signs of contaminated runoff despite the location no longer receiving a direct influx of stormwater (Figure 4). Further, wetland conditions were extremely dry on two of three primary sampling dates, but samples collected on those dates were consistent with a groundwater fingerprint (Figure 4). It can therefore be assumed that the water that was present in Overflow pond on those dates came from groundwater discharge. However, it can be noted that samples from wells 27S and 27D (which are located directly within pitcher plant territory) did not appear to be consistent with runoff fingerprints, even after the large storm event in January 2024. This indicates that the stormwater rerouting project was effective in diverting contaminants from the pitcher plant populations. Additionally, Figure 4 shows that the water collected within retention cells one and two plot very close to the point at which the farm runoff sample plots, further signifying efficacy of rerouting efforts.

4.Conclusions

Runoff and groundwater each demonstrated distinct chemical signatures that allowed for conclusions to be drawn regarding runoff movement throughout McClure's Bog. These signatures demonstrate that runoff is still infiltrating some sampling sites despite stormwater rerouting efforts. This is visible in the ion composition of Overflow pond in particular. However, the rerouting efforts have certainly prevented significant intrusion of contaminated runoff into pitcher plant territory. Long-term monitoring of runoff fingerprints in pitcher plant sampling sites would be beneficial to ensuring this continues to be the case. Investigation into other sources that could be affecting observed chemical signatures is still needed, however, and could be completed through further study. Future studies should also investigate long-term trends in nitrate concentrations and additional sources of runoff contaminants such as sediment, nitrates, phosphorous, and chloride. It may also be helpful to investigate the current state of woody and shrubby plant succession, as this has been an area of concern at McClure's in the past.

Acknowledgments

I would like to thank my advisor, Dr. Jeff Wilcox, for guiding me through this project. Many thanks to The Nature Conservancy for their tireless work preserving this valuable piece of land. And finally, I would like to send a thank you to the UNCA Environmental Studies department and all of Dr. Wilcox's previous student researchers, especially

Matthew McGreal and Mimi Nguyen for their contributions to the research and restoration of McClure’s Bog.

References

Huang, Y.P. 1996. Water Quality Analysis at McClure’s Bog, Henderson County, North Carolina. M.S. thesis, Duke University, Durham, North Carolina.

Kehew, A. E. 2001. *Applied Chemical Hydrogeology*. Upper Saddle River, New Jersey: Prentice-Hall, Inc.

Lynch, M. 1998. Potential Preserve Site Summary. The Nature Conservancy.

McGreal, M. 2016. Hydrochemistry of the Riverbend Bog. B.S. thesis, The University of North Carolina at Asheville, Asheville, North Carolina.

Nguyen, M. 2015. Hydrogeochemistry of Kanuga Fen. B.S. thesis, The University of North Carolina at Asheville, Asheville, North Carolina.

Reberg-Horton, C. 1994. Mountain Bog Management. B.S. honors thesis, The University of North Carolina at Chapel Hill, Chapel Hill, North Carolina.

Sutton, M. 2008. Hydrologic Summary of McClure’s Bog, Etowah, NC. The Nature Conservancy.