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# Characterizing and Assessing the Hydrological Connection of Sawyer Fen to Nearby Bluewater Creek in the Zuni Mountains, New Mexico

Luke Collis

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# **Characterizing and Assessing the Hydrological Connection of Sawyer Fen to Nearby Bluewater Creek in the Zuni Mountains, New Mexico**

**by**

## **Luke C. Collis**

Committee  Dr. Rebecca J. Bixby, Chair  Dr. Laura Crossey  Livia Crowley

A Professional Project Submitted in Partial Fulfillment of the Requirements for the Degree of:  **Master of Water Resources** Water Resources Program   The University of New Mexico   Albuquerque, New Mexico  December 2020 

## **Committee Approval**

The Master of Water Resources Professional Project Report of **Luke Collis**, entitled **Characterizing and Assessing the Hydrological Connection of Sawyer Fen to Nearby Bluewater Creek in the Zuni Mountains, New Mexico**, is approved by the committee:

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#### **Abstract**

Wetlands can hydrologically connect to nearby surface waters allowing for interaction with other landscape elements through spatial and temporal variation. The hydrologic connection of wetlands to surface waters is an important issue due to policies and regulations of the Clean Water Act (CWA) which emphasize the physical connection that wetlands have with nearby surface waters. The goal of this research was to quantify the hydrological connection of Sawyer Fen to a nearby Bluewater Creek in the Zuni Mountains, western New Mexico. Data were collected in the summer through the winter of 2019 at seven locations including Sawyer Fen, Bluewater Creek and adjacent springs. Physicochemical parameters (temperature, pH, total dissolved solids, specific conductivity), major ions (Ca, Mg, Na, K, Cl, HCO<sub>3</sub> and ClSO<sub>4</sub>) and stable isotopes (δ<sup>18</sup>O and δD) were collected to analyze wetland classification, seasonal variation, flow paths, and recharge mechanisms. Results from the physicochemical parameters of Sawyer Fen were indicative of a groundwater fed (rich-fen) wetland in the summer that transitioned to a rain fed (poor-fen) wetland. Hydrogeochemical analysis displayed similar ionic compositions among all locations at the study site with seasonal variability from Sawyer Fen and West Bank Spring and migration from calcium bicarbonate (Ca-Mg-HCO<sub>3</sub>) complex to chloride sulfate (Ca-Mg-Cl-SO4) complex. Stable isotopes showed recharge mechanisms for East Bank Spring proceeded from winter snowmelt while recharge to Sawyer Fen and West Bank Spring came from both winter snowpack and local precipitation. Sawyer Fen appears to be hydrologically connected to Bluewater Creek with seasonal alteration to the water chemistry due to local precipitation and flow paths.

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#### **Introduction**

 Recent rollbacks from the US Environmental Protection Agency (US EPA) and US Army Corps of Engineers (US ACE) have threatened wetlands in the U.S. by removing regulations that protect them and suggesting certain wetlands are isolated from other water systems and therefore are not considered waters of the United States (Christie and Hausman, 2003; Downing et al., 2003) There is currently a widespread recognition of the services that wetlands provide which include habitat for species, protection against floods, water purification, and recreational opportunities (Woodward and Wui, 2001; Barbier, 2011; Bedford and Godwin, 2003; Hansen et al., 2018; Leibowitz et al., 2018; Rains et al., 2016).  Wetlands can also provide these benefits to nearby surface waters, such as lakes and streams, by storing and purifying water through subsurface flow and creating a hydrological connection between the wetland and nearby surface water (Rains et al., 2016; Brooks et al., 2018; Lane et al., 2018; McLaughlin and Cohen, 2013). The hydrological, chemical and biological functions of wetlands affect nearby surface waters (Rains et al., 2016; Fossey and Rousseau, 2016). 

It is important to acknowledge the current policies and regulations regarding wetland management. The most important policy may come the 2001 U.S. Supreme Court's decision in Solid Waste Agency of Northern Cook County (SWANCC) which held that non-navigable waters, such as wetlands, would not be protected under the Clean Water Act (CWA) (Downing et al., 2003). The SWANCC decision is important to understand as it relates to the "significant nexus", or connection between intra-state and isolated waters and is likely to determine whether the water will be protected by the CWA. In other words, wetlands will not be

protected by the CWA unless they have hydrological influence on downstream waters with chemical, physical or biological effects. The hydrological influence under the significant nexus policy includes groundwater connections. As of June 22, 2020 under Trump's administration, a new policy, the Navigable Waters Protection Rule. excludes groundwater and ultimately negates any sort of CWA protections for wetlands or surface waters that were under the premise of significant nexus (reference). The new Navigable Waters Protection Rule opened up an important discussion regarding wetlands and how they are connected to nearby surface waters through subsurface flow. Land management agencies, such as the United States Forest Service (USFS), have a vested interest regarding the protection of wetlands due to their beneficial factors of hydrological connections and have the ability to propose long term management plans for developing future restoration activities on surface waters, such as creeks, lakes, and rivers. The policies concerning wetlands are an important part of land management regulations and it has been proven through recent research that most wetlands have a connection or a significant nexus to nearby surface waters such as streams and rivers (Brooks et al., 2018; US Environmental Protection Agency, 2015; McLaughlin and Cohen 2013; Rains et al., 2016).

Wetlands are important landscape components, hydrologically affecting nearby aquatic systems (Cohen et al., 2016; Leibowitz et al., 2018; Lane et al., 2018). The hydrologic connectivity between wetlands and nearby surface waters has been the focus for many studies in North America (Murphy et al., 2007; U.S. Environmental Protection Agency, 2015; Lane et al., 2018; Leibowitz  et al., 2018). In addition to surface water connectivity, groundwater flow can

connect wetlands with other surface water bodies, with movement that is potentially one kilometer in a two days, especially in unconsolidated sediments like carbonate or volcanic rocks which tend to be more porous allowing water to flow relatively freely (U.S. Environmental Protection Agency, 2015). Many studies have shown that wetlands can connect to groundwater, either receiving groundwater discharge, contributing to groundwater recharge, or both (Mushet et al., 2015; Leibowitz et al., 2018; Winter and Rosenberry, 1995). The magnitude and transient time of groundwater flow from a wetland to other surface waters depends on the properties of the rock or unconsolidated sediments between the water bodies and the intervening distance (U.S. Environmental Protection Agency, 2015). Groundwaterfed wetlands, such as fens or seeps, are considered important sources of  baseflow to nearby surface waters (Morley et al., 2011). Moreover, wetlands can be focal points for groundwater recharge and might contribute to baseflow of other surface waters (Rains et al., 2016). The constant connection of wetlands to nearby surface waters is important to understand because of the effects of the chemical, biological and physical  properties that wetlands have on those nearby surface waters. Although there is important research regarding wetland connections and its influence on surface waters, the identification and classification of different wetlands have an important role in the way the hydrological connection of wetlands interact with the surrounding environment.

Globally, there are many types of wetlands, each having their own unique characteristics, such as water chemistry and hydrology. Wetlands generally include swamps, marshes, bogs and fens and are defined as areas inundated or saturated by surface or ground water at a frequency or

duration sufficient to support a specific type of vegetation typically adapted to saturated soil conditions (U.S. Army Corps of Engineers, 2017). Although several types of wetlands exist, the focus of this research paper will be on fens which are considered minerotrophic (i.e., groundwater fed) opposed to ombriotrophic (i.e., rainwater fed). Because fens require groundwater, their hydrogeologic setting almost guarantees a strong influence on nearby surface waters such as streams or lakes (Bedford and Goodwin, 2003). Defining the hydrology and chemistry of fens is vital in understanding the recharge mechanisms of fens and the temporal and spatial variations in water movement between fens and nearby surface waters.

Fens are a type of wetland where the water table is at or near the surface for most of the growing season during most years, causing saturated and poorly aerated soils (US Department of Agriculture, 2007). Unlike bogs, fens require groundwater inputs and are less influenced by precipitation.  For this reason, fens may be classified as slightly acidic (poor fens) or circumneutral (rich fens), depending on the flow rates and chemistry of groundwater  reaching the plant rooting zone (**Table 1**, Bedford and Godwin, 2003). Fens are defined in many ways by hydrologists, ecologists and geochemists but the distinguishing factor of all fens is that they are groundwater-fed water systems. Poor fens typically have an acidic (pH 4.5-5.5)  peatland  dominated by *Sphagnum* moss, whereas rich fens have bicarbonate (i.e., alkaline) as their dominant anion and calcium as their dominant cation with a pH greater than >6.0 and an abundance of sedges and mosses (Vitt and Chee, 1990). Poor fens may arise because groundwater is moving through geology with low solubility (e.g., gneiss, granite) while  extremely rich fens may arise where calcium carbonate precipitates at the fen surface (Bedford

and Godwin, 2003). Some fens are known to have shallow groundwater connection with an ionic composition lower in chloride, sulfate, magnesium, and sodium but higher in calcium and bicarbonate which can be attributed to the movement of groundwater through base-rich bedrock, such as limestone or dolostone (Komor, 1994). Fens receiving an abundance of calcium-rich water are classified as calcareous fens and support a distinct flora of calcium-loving plant species called calcicoles  (Almendinger and Leete 1998). Calcium concentrations in fen waters can be quite high, especially in rich fens, which tend to have high pH conditions under which  phosphorus (P) is removed (Bedford and Godwin, 2003). Unless enriched in nitrogen (N) by atmospheric deposition, seepage from septic tanks or drainage from fertilized agricultural lands, fens are inherently low in available N and P (Bedford and Godwin, 2003). Defining the chemical characteristics of fen wetlands to help determine the hydrological connections to other water bodies.

To understand the hydrological connection of fens to nearby surface waters it is important to trace groundwater recharge from the fen into nearby surface waters. Delineating groundwater flow patterns around a wetland can be measured through chemical and stable isotope parameters (Haldorsen et al., 1997; Kehew et al., 1998) along with physicochemical parameters. Physicochemical parameters, like temperature and pH, indicate the influence of seasonal precipitation  but also can indicate geochemically stable waters associated with deep groundwater flow paths. Water that is from deeper sources can maintain  stable physicochemical parameters because there is reduced evaporation rates and buffering from freezing temperatures (Frus et al., 2020). Compared to other surface waters, wetlands also

have unique isotopic signatures, resulting from evaporative-enrichment processes which assist in understanding how and when wetlands are contributing to streamflow (Rains et al., 2016; Kehew et al., 1998). The isotopic and chemical composition of shallow ground water around wetlands can be used to temporally and spatially delineate recharge from the wetland or discharge to the wetland (Kehew et al., 1998).  As water evaporates from the wetlands, the heavy isotope remains behind while lighter ones evaporate in the atmosphere, leaving an isotope signature indicating the degree of evaporation (Clark and Fritz, 1997). Major ion concentrations can determine and describe the chemical evolution of groundwater and can also define the patterns of spatial change in water chemistry along geologic units, along a line of section or along a path line (Domenico and Schwartz, 1998). Analyzing major ion concentrations is therefore useful in understanding groundwater flow and water chemistry (Ophori and Tóth, 1990). For a more integrated analysis, a multi-tracer approach (major ion chemistry, physicochemical analysis, δD and  $\delta^{18}$ O isotopes) will not only classify the type of wetland but also quantifies the hydrologic connection between the wetland and nearby surface water. 

#### **Case Study: Sawyer Fen**

Sawyer Fen is proposed to be hydrologically connected to a nearby tributary of Bluewater Creek and the  surrounding springs through subsurface flow. The hydrologic connection from  Sawyer Fen to a tributary of Bluewater Creek and springs is hypothesized to alter the chemistry of Bluewater Creek and provide baseflow via subsurface movement. The results of this study will provide a better understanding of the hydrologic connections in the Sawyer Fen area and will assist the USFS in regards to the protection and preservation of wetlands in the

Cibola National Forest while considering the effects of the new rollbacks by the US EPA and US ACE.

**Objective**: The primary objective of this project is to characterize and assess hydrological connection between Sawyer Fen and Bluewater Creek by analyzing temporal variation using physicochemical parameters, flow paths using changes in ionic concentrations, and recharge mechanisms using stable isotopes.

#### **Site Description**

The focus of this study is at the Sawyer Fen complex consisting of Sawyer Fen, West Bank Spring, Bluewater Creek Downstream, and East Bank Spring (**Figures 1**, **2**). Sawyer Fen is approximately 340 m west of a tributary to Bluewater Creek, termed "Bluewater Creek" in this research. The stream below the fen is a tributary to Bluewater Creek and in this reach, the stream is perennial due to the springs. Above the area where the springs supply water, there is an intermittent reach and above that is the ephemeral reach. Bluewater Creek contains both the Rio Grande Chub and Rio Grande Sucker that are x listed (Rees and Miller, 2005). Peak discharge of Bluewater Creek occurs during the spring snowmelt runoff in March and April (Curtis, 2008). The sub-watershed has a drainage area of 96.5 km<sup>2</sup> (USDA, 2003). Watershed elevation ranges from 2026 m to 2816 m above mean sea level (USDA, 2003). Precipitation varies across the watershed with approximately 30.5 to 58.4 centimeters/yr (Curtis, 2008).

The water supply for Zuni Mountains is primarily stored in the hydrologically connected Permian Glorieta Sandstone and San Andres Limestone (Psg)-confined aquifer (Frus et al.,

2020). Additional aquifers located in the Zuni Mountains store water locally in the unconfined units of the Quaternary alluvium (Qa) (Frus et al., 2020). Recharge mechanisms in the confined aquifer rely on snowpack as the source for infiltration, while unconfined desert aquifer can be recharged through both snow and rain events (Shanafield and Cook, 2014). Recharge to the alluvium is derived from direct precipitation, surface runoff, leakage from streams, spring discharge and upward leakage from San Andres-Glorieta aquifer (Baldwin and Anderholm, 1992). Some of the upland area vegetation consists of pinon-juniper to mixed conifer. Grasses and rabbit brush along the valley bottom are the predominant vegetation (Curtis, 2008). 

The rocks of the Zuni Mountains consist of a Precambrian core flanked by sediments that range in age from Pennsylvanian to recent (**Table 2**).  The highest peaks of the Zuni Mountains consist of exposed 260-million-year-old granites and metavolcanics due to an uplifted basement block (Frus, 2016). The Zuni Mountain Paleoproterozoic basement rocks are unconformably overlain with Paleozoic, Mesozoic, and Cenozoic sedimentary rocks (Heckert and Lewis, 2003). The sedimentary rocks of the Zuni Mountains have been folded, faulted, and eroded since deposition by several regional tectonic events, including Laramide uplift and compression and subsequently the spreading of the basin and Zuni Mountain Range (Aldrich et al., 1986). Sawyer Fen is associated with the alluvium and bedrock outcrops adjacent to the fen while nearby Bluewater Creek is positioned around gneissic granite bedrock (**Figure 3**). The Quaternary alluvium is considered a local resource for storage of groundwater and is the youngest of the geologic formations in West-Central New Mexico formations (**Figure 4**).

#### **Methods**

#### **Field Methods**

Physicochemical parameters, major ions, and isotopes were collected during the months of June-November 2019. Collections were taken once in June, once in July, twice in September, twice in October, and once in November for a total of seven sampling dates, although not all sites were sampled every time (**Table 3**). Samples were taken in Sawyer Fen, Bluewater Creek Upstream, Upstream West Bank Well, Bluewater Creek Downstream (BWD), Downstream West Bank Well, West Bank Spring (WBS), and East Bank Spring (EBS) (**Figure 5**). The focus for this research was on Sawyer Fen, EBS, WBS and BWD; the wells were sampled but because of design and installation issues, data from the wells were not utilized in this project.

Physicochemical parameters included temperature (°C), pH, total dissolved solids (TDS, mg/L), and specific conductance ( $\mu$ S /cm) and were taken from a YSI Professional Plus multimeter.

 The YSI Professional Plus multimeter was used with a Quatro cable that included a specific conductance sensor, a pH glass combination electrode, a field-grade water temperature sensor and a TDS sensor (Frus et al., 2020). Water samples were collected for anions, cations and stable isotopes. Anions and stable isotope samples were collected in a 125-mL polypropylene bottle that was pre-rinsed with sample water three times. The lid was sealed in the field with no headspace. Cation samples were collected in 60-mL bottles that has been rinsed three times with water filtered with a 0.45- um glass fiber filter. New filters were used each time in order to prevent cross contamination. The 60-mL cation bottle was left with headspace and preserved

with 5 drops of concentrated nitric acid (HNO<sub>3</sub>). Both the 60-ml and 125-ml bottle were immediately put on ice to preserve. 

#### **Lab Methods**

The water samples were returned to the University of New Mexico, Department of Earth and Planetary Sciences and refrigerated until analysis of anions, cations and stable isotopes. Anion samples were filtered using 0.45 µm glass fiber filters. The alkalinity was determined using the endpoint titration method (titration with dilute sulfuric acid). Anion concentrations of chloride (Cl), bicarbonate (HCO<sub>3</sub>) and sulfate (SO<sub>4</sub>) were measured using Dionex Ion Chromatography (IC). Inductively Coupled Plasma Optical Emissions Spectroscopy (ICP OES) was used to measure major cations [calcium (Ca), magnesium (Mg), sodium (Na), and potassium (K)]. Isotopologues of water (deuterium δD and δ<sup>18</sup>O) of creek, spring, and fen waters were measured using laser ring-down cavity spectrophotometry. Duplicate analyses were routinely performed on 10 percent of the major ion samples, and external reference standards were used to ensure accuracy.

### **Data Analysis**

Physicochemical parameters were used to determine seasonal variation, wetland classification and as additional support for the results from ionic composition and stable isotopes analyses. Seasonal alteration of physicochemical parameters (temperature, specific conductance, TDS, and pH) is a good indication of local precipitation events while stable physicochemical parameters indicate flow paths from deeper groundwater that are not altered

by local precipitation, such as flow-path springs. The physicochemical parameters of Sawyer Fen were used to indicate whether it was a poor fen with low pH or rich fen with higher pH values.

Results from the major ionic compositions were uploaded to Geochemists Workbench software for assembly of piper diagrams (Bethke, 2007). Piper diagrams are graphical representations of the chemistry of water and can be used to understand flow paths (Drever and Marion, 1998). Comparing the ionic compositions of springs in previous work done by Frus et. al. (2020) to this work at Sawyer Fen can help understand the origins of water from regional aquifers and determine the chemical processes associated with flow paths recharging and discharging from Sawyer Fen. The isotopic signatures of each location were plotted and compared to the Global Meteoric Water Line (GMWL) (Sharp, 2017). A linear relationship (slope of 8, y-intercept of 10) is displayed on the Global Meteoric Water Line (GMWL) for surface water across the globe (Craig, 1961). Isotopic fractionation is dependent on temperature; therefore with the results of  $\delta$ D and  $\delta^{18}$ O isotopes from the groundwater samples, conclusions can be drawn about the recharge of groundwater (Gat, 1996). The delta notation (δ) provides a convenient way to indicate the relative differences in isotopic ratios between samples and standards that are measured by isotopic ratio mass spectrometry (Mook, 2000; Sharp, 2017).  Positive δ values mean that the heavy to light isotope ratio is higher in the sample than in the standard, whereas negative δ indicates the opposite response (Sharp, 2017). Points that are plotted away from the GMWL represent alteration of meteoric water due to evaporation, water-rock interaction, or gaseous exchange (Craig, 1961). Values of most fresh waters fall

along a meteoric water line (MWL) with a slope of  $\approx$  8 in H (as  $\delta$ D) and O isotopic space which is characterized through measurement of the GMWL precipitation samples (Craig, 1961). The MWL establish a reference framework that identifies  source water that contributes to a sample, and can be interpreted as samples from an aquifer, lake or stream (Good et al., 2015). 

Variation in the isotopic ratios of all locations at Sawyer Fen allow for an understanding of recharge mechanisms relating to seasonal variability and flow paths. Natural spatial and temporal variation in stable isotope ratios of H and O (as  $\delta^{18}$ O and δD) is common in most hydrological systems (Good et al., 2015). The variation of isotope ratios arises primarily from changing atmospheric conditions, which affect the transport of heavy and light isotopes in atmospheric moisture to a given region of the continents at a given time giving a better understanding of how certain water systems are recharged (Good et al., 2015). Precipitation derived from ocean water that is closer to the poles is isotopically lighter than precipitation derived from ocean water originating at lower elevations such as Gulf of Mexico (Robertson et al., 2013). Seasonal variation in isotopic composition of local precipitation is likely the result of different sources of winter recharge, predominantly from storms moving into the Pacific Coast (Robertson et al., 2013). The Vienna Standard Mean Ocean Water (VSMOW) is an isotopic standard for samples where water from different points in the water cycle contains molecules with different ratios of isotopes due to different rates of evaporation and condensation. VSMOW is a standard which is easily reproducible and can be compared with other waters. An investigation of the seasonal difference of  $\delta$ D and  $\delta^{18}$ O at locations offer insight into the timing of recharge events.

#### **Results**

#### *Physicochemical* **parameters**

 Discrete physicochemical measurements at all locations indicated that throughout the study, Sawyer Fen and WBS saw greater seasonal variation in temperature, specific conductivity and TDS while EBS and BWD remained relatively stable in their physicochemical parameters **(Table 3)**. Water temperature for Sawyer Fen show the greatest variation (4.6-26.5 °C; average 14.1 °C), along with WBS (7.3-21.9 °C; average 13.1 °C), while EBS shows the least variation (11.7- 16.0 °C; average 14.4 °C). Specific conductivity of all sites stayed below 700 µS/cm with Sawyer Fen having the largest variability (449-668  $\mu$ S/cm; average 563.3  $\mu$ S/cm) along with WBS (397.7-607 µS/cm; average 477.1 µS/cm) (**Figure 6**) but EBS having the least variability (302.5- 306.6 µS/cm; average 304.5 µS/cm), along with BWD (345.8-366.9 µS/cm; average 353.1  µS/cm) from June to November (**Figure 7**). The TDS of Sawyer Fen shows the most seasonal variation (291-433 mg/L; average 374.7 mg/L) along with WBS (258-394 mg/L; average 310 mg/L) while EBS has the least variation (196.5-199.2 mg/L; average 197.17 mg/L) along with BWD (224.7-238.5; average 229.5 mg/L). The pH slightly decreased at all locations from summer to winter with an exception of EBS, which had a relatively stable pH except for October 19 date. Based on the physicochemical parameters, Sawyer Fen is classified as a richfen as the pH never falls below 6.0 in any of the sampling dates but has a decrease in the pH of Sawyer Fen from summer to winter; therefore, more sampling dates for winter might indicate a poor-fen complex due to local precipitation. With the current data, Sawyer Fen is classified as a rich-fen complex with higher than a value of 6.0 that changes to a poor-fen complex with pH values around six.

#### *Ionic composition*

The anions and cations of all sites has seasonal variations that display a calcium bicarbonate (Ca-Mg-HCO3) hydrogeochemical facies **(Table 3)**. Calcium is the dominant cation while bicarbonate is the dominant anion for all locations at the Sawyer Fen site (**Figure 8**). Major ion concentrations analyzed from water samples collected at Sawyer Fen and WBS showed the greatest variation in all ions among  seasons while EBS and BWD showed the least variation among seasons (**Figure 9)**. Ionic composition in EBS and BWD remained relatively stable throughout the seasons opposed to Sawyer Fen and WBS which had seasonal variation. The water in West Bank Spring and Sawyer Fen migrate from (Ca-Mg-HCO<sub>3</sub>) to (Ca-Mg-Cl-SO<sub>4</sub>) hydrogeochemical facies while EBS and BWD remain relatively steady all year and did not appear to vary in ionic composition. A comparison of ionic compositions from springs in previous studies by Frus et al. (2020) showed most springs in the Zuni Mountains have a calcium bicarbonate composition and appear to come from the San Andres-Glorieta or the Quaternary alluvium (**Figure 10**).

*Isotopes*

Isotopic analysis reveals seasonal variation among Sawyer Fen and WBS when plotted on the GMWL and also shows Sawyer Fen and WBS being recharged through both snowpack and local precipitation while EBS and BWD is primarily snow recharge. We can understand the recharge and atmospheric mechanisms of surface and groundwater through isotopes and  $\delta^{18}O$ (Glynn and Plummer 2005). An XY-plot of stable isotopes (δD and-δ<sup>18</sup>O) of the Sawyer Fen sites as well as isotopes from local precipitation events (**Figure 11**) were plotted relative to the GMWL (Craig 1961). A trend line was plotted for the Sawyer Fen and WBS waters as they move away from the GMWL indicating local precipitation while EBS and BWD reside mostly in the winter recharge zone. The seasonal variability of the isotope values in Sawyer Fen and WBS move away from the GMWL.  Samples from EBS appear to be more depleted (minimum – 10.94‰ for δ $^{18}$ O; -81.7‰ for δD) along with BWD (minimum –11.05‰ for δ $^{18}$ O; -80.6‰ for δD), compared to samples from Sawyer Fen (minimum –6.29‰ for δ $^{18}$ O; -59.3‰ for δD) and WBS (minimum –9.32‰ for δ<sup>18</sup>O; -72.5‰ for δD) (**Table 3**). Sawyer Fen appears to have the largest variation in isotope values, with ranges of –22.5‰ for δD and –4.7‰ for  $\delta^{18}$ O, along with WBS, with ranges of -13.9‰ for δD and -2.63‰ for δ<sup>18</sup>O while samples from EBS have the least variation, with ranges of  $-5.4%$  for δD and  $-1.09%$  for δ<sup>18</sup>O along with BWD, with ranges of -5.6‰ for δD and -0.79‰ for  $\delta^{18}$ O. The seasonal isotopic differences of Sawyer Fen and WBS, compared to EBS and BWD, showed that only fall (October) and winter (November) values of Sawyer Fen and WBS were as depleted as EBS and BWD.

#### **Discussion**

#### *Physicochemical* **parameters**

Physicochemical parameters used in this project proposes an alteration in the hydrology between two of the four locations due to seasonal variability while supporting the changes in stable isotopes and ionic compositions and also describes wetland classification that is groundwater fed. Sawyer Fen and WBS lowers in TDS and specific conductivity from summer to winter suggesting a change in the hydrology from a groundwater-fed system with high TDS and specific conductivity to a combination of groundwater and rain fed with lower TDS and specific conductivity. The TDS of Sawyer Fen and WBS decreased from June to November whereas EBS remains steady all year with an average of TDS of 242.55 mg/L  $\pm$  2.62 mg/L from June to November. The variation in the specific conductivity is even more evident of seasonality with Sawyer Fen average of 563.3 ±219.2 µS/cm and WBS average of 477.1± 209.3 µS/cm while EBS has average of 304.5 ± 4.1 µS/cm and BWD has an average of 353.1 ± 21 µS/cm. The changes of TDS and specific conductivity from Sawyer Fen and WBS compared to EBS from season to season means Sawyer Fen and WBS are more susceptible to atmospheric events such as rain or snow while parameters from EBS remains steady in TDS and specific conductivity due to the origins of the water preventing it from being altered by atmospheric events. In areas with dry and wet seasons, conductivity and TDS usually drops overall during the wet season due to the dilution of the water source from rain (Christenson and Li, 2014) which seems to be the case for Sawyer Fen and WBS as both parameters change during the wet season of fall. Normal conductivity and TDS levels usually come from the surrounding geology such as clay soils or granite bedrock (Environmental Protection Agency, 2012) but can be lowered due to rain

events (Christenson and Li, 2014). The seasonal change of TDS and specific conductivity of Sawyer Fen and WBS is more evident of local precipitation when comparing the  isotopologue analysis (**Figure 11**) of all four locations. Sawyer Fen and WBS are plotted along the evaporation line of summer recharge opposed to EBS and BWD which is predominantly recharged through winter snowpack, suggesting a stable water source for EBS and BWD with consistent TDS and specific conductivity values and no alteration to the hydrology from one season to the next.

The temperature results show Sawyer Fen and WBS change with the seasons while EBS does not change and provides additional evidence that Sawyer Fen and WBS are altered by local precipitation opposed to EBS. The temperature of Sawyer Fen significantly changes from 26.5°C in June to 4.9°C in November along with WBS, with ranges of temperature from 21.9°C in June to 8.9°C in November. This difference of temperature change is a result of seasonal local atmospheric temperature change. In contrast, the temperature of EBS does not appear to change with only a range from 16 °C to 11.7 °C  $\pm$  4.3 °C from summer to winter, signifying a relatively stable water source that is not altered by local atmospheric temperatures, due to its direct flow path from the regional confined aquifer. The stable temperature of EBS also reveals a short residence time in the fen and a constant supply of the same water source that is not altered by local precipitation events whereas Sawyer Fen and WBS changes temperature from June to November.  

Results also show Sawyer Fen is groundwater fed and considered to be a rich-fen with high pH values but changes to a poor-fen with lower pH values due to local precipitation. As raindrops fall through the air, they interact with carbon dioxide molecules in the atmosphere, lowering the rain's pH value (Drever, 1997) thus, lowering the pH value of Sawyer Fen which signifies inputs of rain. But, when carbonate minerals are present in the soil, the pH of water stays close to neutral due to the buffering capacity (Drever, 1997). Daily precipitation values from the Remote Automated Weather Station (RAWS)( [https://wrcc.dri.edu/wraws/nmF.html\)](https://wrcc.dri.edu/wraws/nmF.html) indicate large precipitation events during August and September 2019 which correlates to the decrease in pH and specific conductivity values of Sawyer Fen from August and September (**Figure 12**). In general, the average precipitation in the Zuni Mountains is lowest in June and slightly increases each month going into the fall season (**Table 4**); therefore, the lack of precipitation in the summer (June) combined with the steady influx rate of ground water discharge to Sawyer Fen allows for higher pH and conductivities due to longer rock-water interactions from groundwater flow paths. The high pH and specific conductivity are indicative of a rich-fen fed by ground water because deep ground water tends to have higher pH and conductivity values (Komor, 1994; Glynn and Plummer, 2005) as opposed to lower conductivities and pH values from rain water. It is noted water is present in Sawyer Fen all year long which may indicate a constant supply of ground water and therefore classifying Sawyer Fen as a (i.e., rich-fen) wetland due to groundwater with high pH values and slightly changes into a more acidic (i.e., poor-fen) due to the increase in precipitation during the winter and spring seasons.  The change in physicochemical parameters of Sawyer Fen compared to EBS and BWD are a result of local precipitation events due to seasonal variation and also from flow paths originating in the

confined aquifer. EBS has a flow path directly from the regional aquifer that is discharging into Bluewater Creek which stabilizes the water chemistry of BWD whereas Sawyer Fen and WBS has a flow path from the regional confined aquifer that is discharged into the alluvium and then altered by local precipitation and atmospheric events.

#### *Ionic composition*

Comparing the hydrogeochemical facies of this project with Frus et al., (2020) determines flow paths originating from the San Andres-Glorieta aquifer and gives an understanding of how certain processes such as dissolution, precipitation, and ion exchange modify the ionic composition while providing evidence of seasonal variation. Sawyer Fen and WBS waters are a discharge zone from the confined aquifer (e.g., San Andres-Glorieta) to the alluvium (Qa). The flow paths of all locations from the Sawyer Fen complex are shown to originate from the San Andres-Glorieta which can be compared to previous work by Frus et. al. (2020) in which similar water quality analysis of springs and streams in the Zuni Mountains was used. Most of the springs from previous studies in the Zuni Mountains derive from either the alluvium or the San Andres-Glorieta aquifer and appears to have similar ionic compositions as all the locations in this project, thus this work is yielding results consistent with Frus et al.(2020), inferring a flow path from San Andres-Glorieta aquifer. Discharge from the alluvium is by leakage from the San Andre-Glorieta aquifer, evapotranspiration, withdrawal by wells or discharge to streams (Baldwin and Anderholm, 1992) which seems to be case for Sawyer Fen as the subsurface flow paths from Sawyer Fen, located in the alluvium, discharges into WBS and Bluewater Creek. Water can leave the San Andres-Glorieta aquifer through faults and enter the alluvium (Baldwin

and Anderholm, 1992). The direction of groundwater movement through the alluvial aquifer is the same as the direction of surface water (Baldwin and Anderholm, 1992), therefore the location of Bluewater Creek downgradient from Sawyer Fen, indicates a high probability of groundwater discharge from Sawyer Fen to WBS and eventually into Bluewater Creek.

The ionic composition of all locations results from various processes including dissolution, precipitation and ion exchange. The base-rich nature of Sawyer Fen water (e.g., Ca-Mg-HCO3) is attributed to the movement of ground water through or over base-rich bedrock before it enters the fen. A major component of the San Andres-Glorieta aquifer is affected by the concentration of carbon dioxide in water due to the dissolution of dissolved limestone (limestone compromises a big portion of the San Andres). As a result, carbon dioxide-rich groundwater near recharge areas can readily dissolve limestone (Baldwin and Anderholm, 1992; Drever, 1997). Limestone dissolution in the San Andres-Glorieta aquifer could explain the calciumbicarbonate composition. Chloride concentrations are generally smaller than 13 mg/L and the small concentrations could be due to the large amount of precipitation during the fall which infiltrates to the groundwater and lacks the ability to evaporate or could be from smaller amounts of disseminated halite (sodium chloride) in the aquifer (Baldwin and Anderholm, 1992).

The high sodium concentrations may indicate ion exchange, whereby calcium replaces sodium ions on clays (Baldwin and Anderholm, 1992). Halite is undersaturated in the alluvial (Robertson et al., 2013), explaining the higher concentrations of sodium at all the sample locations.

samples with large sodium concentrations indicate longer time in contact with aquifer materials and further along the flow path, conversely samples with low sodium concentrations may be considered to be closer to the groundwater recharge source (Robertson et al., 2013). Aqueous calcium binds to clay minerals due to cation exchange, calcium is therefore not able to bind with bicarbonate and precipitate out solution (Robertson et al., 2013) which might explain the high calcium composition of Sawyer Fen compared to other locations. Additional geochemical modelling could examine sorption equilibria but is beyond the scope of this work.

The change of ionic composition from bicarbonate to sulfate provides additional evidence of seasonal variation among Sawyer Fen and WBS. The cations and anions collected at EBS and BWD varied little between seasons but WBS and Sawyer Fen varied notably over the seasons. Sawyer Fen and WBS migrate from a bicarbonate (HCO<sub>3</sub>) to chloride-sulfate (Cl-SO4) hydrogeochemical facies because Sawyer Fen waters are from the regional confined aquifer that discharges to the shallow alluvium allowing exchange with the atmosphere thereby undergoing evaporation and altering the ionic composition from one season to the next. This change in ionic composition is interpreted to be a result of seasonal recharge to the alluvium in which Sawyer Fen and WBS reside whereas EBS and BWD do not migrate and remain relatively stable all year. Seasonal precipitation varies in quantity and quality which also explains the shift of ionic composition of Sawyer Fen and WBS opposed to EBS and BWD. It is important to note East Bank Spring's visual discharge into Bluewater Creek (**Figure 13**) showing clear discharge from EBS into Bluewater Creek which means alteration of water chemistry to BWD. We expect the water chemistry of EBS to be similar to BWD given the visual analysis.

#### *Isotopes*

The wide range of  $\delta$ D and  $\delta^{18}$ O values from Sawyer Fen and WBS suggest differences in the isotopic composition of recharge water entering the alluvial aquifer consisting of winter snowpack and local precipitation. Isotope samples collected from EBS and BWD varied little across the seasons and were consistently the most isotopically depleted from all the sites which resembles recharge from winter snowpack. Differences in stable isotope composition between summer and winter precipitation occur all over the world and can manifest as snow, rain, hail which is predominantly related to temperature variations affecting evaporation from the Pacific Ocean (Sharp, 2017). The waters collected from Sawyer Fen and WBS varied the most, indicating a water system recharged not just by winter snowpack, but also local precipitation. The weighted mean of isotopic compositions is related to the mean relative humidity of air masses over the oceans which happens to be about 10% lower in the winter (as colder air masses) than in summer, an effect that explains seasonal shifts of isotopic compositions (Sharp, 2017). Sawyer Fen and WBS have larger variations in the weighted mean values of both  $δ<sup>18</sup>O$  and δD compared to EBS and BWD and this could also be a result from EBS having flow paths coming directly from the confined aquifer, preventing the water from evaporating and creating an evaporative signature and the difference of weighted means also suggest Sawyer Fen and WBS are being recharged by both snowpack and local precipitation.

The comparison of sample results with the Global Meteoric Water Line (GMWL) confirms and interpretation of recharge mechanisms of snowpack and local precipitation from Sawyer Fen and WBS. Sawyer Fen and WBS undergo evaporation when plotted on the GMWL. Movement along the GMWL represents fractionation of isotopes of water due to seasonal temperature differences, movement of atmospheric water onto the continent, and movement of atmospheric water to higher latitudes (Craig, 1961). Precipitation that falls during cold seasons tend to be depleted (more negative) relative to precipitation that falls during warm seasons (Craig, 1961) which is why Sawyer Fen and WBS is considered to be recharged by both local precipitation and winter snowpack, due to their location on the GMWL (**Figure 11**). Waters in arid regions commonly have slopes of  $\sim$  5 (Sharp, 2017) which tend to plot to the right of the GMWL. Along with seasonality of recharge and variability of precipitation to Sawyer and WBS, the samples also plot to the right (down) from the GMWL line representing evaporation. Therefore, we interpret the waters in Sawyer Fen and WBS undergoing evaporation during the warmer months due to their flow paths in the alluvium while the water in EBS and BWD remain relatively stable during the seasons due to the direct flow paths from regional confined aquifers contributed by winter snowpack and the short residence time (consistent with the small observed temperature changes described above).

 Analyzing the stable isotopes of EBS and comparing it the stable isotopes of springs from previous work done by Frus et al. (2020) provides additional evidence of a winter snowpack recharge mechanism. The weighted mean values of precipitation, surface waters and spring water isotopologues from the Zuni Mountains are reported (**Table 5)**. Isotopologue  results

from springs and streams in the Zuni Mountains  are plotted on the GMWL and suggests most  of the springs in the Zuni Mountains are recharged by snowmelt (**Figure 14)**. The variation of weighted means of streams in the Zuni Mountains from work done by Frus et. al.(2020) is similar to the variation of weighted means of Sawyer Fen and WBS, which is expected in this region of New Mexico for surface waters deriving from local precipitation. It can be concluded that the comparison of weighted means from previous work in the Zuni Mountains with this project suggests both water have the same hydrologic functions and are thought to derive their source of water from either, solely winter snowpack, or a combination of winter snowpack and local precipitation. Therefore, EBS is recharged primarily from winter snowpack whereas Sawyer Fen is also recharged by winter snowpack but altered by local precipitation. Due to our understanding of ionic and isotopic compositions and the influx of groundwater in the summer to Sawyer Fen, it is understood that Sawyer Fen is retaining the snowpack groundwater in the summer and slowly discharging to the water table which is then hydrologically connected to Bluewater Creek.

### **Conclusion**

This research confirms the hydrological connection of Sawyer Fen wetland and adjacent springs to nearby Bluewater Creek in the Zuni Mountains of the Cibola National Forest. The similar ionic compositions of all locations suggest they came from the same source of the San Andres-Glorieta aquifer and indicate a hydrologic connection. Using our understanding of flow paths, recharge mechanisms, spatial and temporal analyses from physicochemical, major ions, and stable isotope (δD and δ<sup>18</sup>O) parameters, one source of water was identified at the Sawyer Fen

location with temporal variation altering certain water quality characteristics of West Bank Spring and Sawyer Fen. EBS water was found to have very little variability in the proportions of major ion concentrations, physicochemical and stable isotope parameters and is presumed to be primarily recharged by snowmelt from the San Andres-Glorieta aquifer which has limited interaction with the atmosphere. EBS is discharging into Bluewater Creek, providing a constant supply of water during all seasons and an alteration to the water chemistry to BWD. Sawyer Fen and WBS has highly variable stable isotopic, physicochemical and major ion concentrations throughout the seasons, is recharged with both rain and snow events and undergoes evaporation. Sawyer Fen and WBS water is interpreted to originate from the San Andres Glorieta that discharges into the shallow alluvium and eventually flows into Bluewater Creek whereas EBS is interpreted to originate straight from the San Andres-Glorieta and discharges into Bluewater Creek with variation to the water chemistry of BWC from season to season. BWD is then a mixture of flow paths coming from Sawyer Fen, WBS and EBS which supports the idea of a hydrologic connection within the Sawyer Fen complex. Sawyer Fen is a groundwater fed wetland with a high pH and calcium carbonate composition that changes  slightly to a lower pH and chloride-sulfate composition due to local precipitation. Sawyer Fen is classified as a rich-fen with bicarbonate as its dominant anion and calcium as its dominant cation and a pH greater than six that changes into a poor-fen during the fall and winter. 

Wetlands have many benefits including flood control, water purification and recreational activities but one of the most important characteristics of wetlands include their hydrological connection to other nearby surface waters which alters the chemical, physical and biological

parameters (Rains et al., 2016). It is important to know if a wetland has a hydrological connection to other surface waters because of the new regulations of the Clean Water Act (CWA) which state that waters of the United States will only be subject to the CWA if shown that they have a "significant nexus" or an alteration of the physical, chemical, and biological integrity to other waters (Downing et. al., 2003). Because of the dry environment in the southwest and the new regulations of the Clean Water Act, it is especially important for land managers to understand the characteristics of wetlands and the connectivity they have with other surface waters. A geochemical analysis of other wetlands in the Zuni Mountains may provide additional evidence of wetland connectivity to nearby surface  waters and provide rationale and criteria for wetland protection by the Clean Water Act. 

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*Table 1. Classifying poor and rich fens through pH, hydrology and ionic composition. Table taken from Bedford and Goodwin, 2003.*

*Fen (Midwestern U.***S.)—**a grassland on a wet and springy site, with an internal flow of water rich in calcium and magnesium bicarbonates and sometimes calcium and magnesium sulfates as well *Fen (Southeastern U.S.)—*a minerotrophic (''groundwater-fed'') wetland, richer in nutrients and less acid (pH > 4.8) than a bog and usually having a very slow internal drainage through seepage down low gradient slopes

*Fen (Iowa)—*wetland areas with saturated but not inundated soils which are fed by permanent groundwater seepage; sites which have saturated soils, but little or no peat accumulation, are considered fens

*Fen (Canada)—*peatlands that derive their water and nutrient supplies from precipitation and from water that has been in contact with upland soils

*Fen (Midwestern U.S.)—*wetland communities (1) dependent on ground water, which moves through and maintains saturation of the root zone throughout most of the year; (2) that do not experience long-term inundation; (3) that have carbon-accumulating substrates, including histosols ranging from fibrists to saprists, histic deposits, and carbonates such as marl and tufa; (4) that are dominated by non-emergent graminoid vegetation

*Fen (England)—*base-rich wetland with water pH values greater than about 5.5 but generally >6, with high calcium and bicarbonate, and vegetation rich in dicotyledonous herbs and brown mosses; a generic term for both herbaceous and wooded base-rich mires

*Fen—*somewhat less-acidic [than bog], more alkaline peatlands dominated by graminoids, brown mosses, taller shrubs, and coniferous and/or deciduous trees

*Poor fen—*an acidic, non-alkaline (pH 4.5–5.5) peatland dominated by Sphagnum mosses; influenced to some degree by water moving from surrounding uplands as well as precipitation; more similar to bogs than to rich fens in terms of vegetation and chemistry

*Rich fen—*fens having bicarbonate (thus they are alkaline) as their dominant anion and calcium as their dominant cation; pH >about 6.0; characterized by brown mosses largely of the family

Amblystegiaceae, and an abundance of sedges; often used synonymously with calcareous fen *Calcareous fen—*a term used to refer to rich fens with high calcium carbonate in water and soils, with peat or surficial deposits of calcium carbonate (marl) and a distinctive flora of rare calciphilic species, with pH in the range of 6.8–7.8; often used synonymously with rich fen

*Marl fen—*strongly minerotrophic wetlands in which the substrate is a marl bed derived either from lacustrine marl deposits or actively accumulating marl that is exposed at the ground surface, with pH generally higher than 7.5, and vegetation that is often sparse and stunted; because extreme-rich fens often accumulate marl, the two terms are sometimes used interchangeably



*Figure 1. Map displaying the location of Sawyer Fen area in the Zuni Mountains in relation to Albuquerque, New Mexico*



*Figure 2. Pictures of (A) Sawyer Fen (07/13/2019) (B) West Bank Spring (10/19/2019) (C) Bluewater Creek Downstream (06/11/2019) and (D) East Bank Spring (11/02/2019) located in the Zuni Mountains, Cibola National Forest, New Mexico.*

*Table 2. Primary geologic formations, Zuni Mountains, Cibola National Forest, listed from youngest to oldest in the watershed. Figure taken from Curtis, 2008.*





*Figure 3. Geologic map representing the formations in which Sawyer Fen and Bluewater Creek are located. Figure taken from USGS 1966.*



*Figure 4. Stratigraphic columns for West-Central New Mexico displaying the geologic era. Figure taken from Frus, 2016.*

Table 3A. Physicochemical results of all locations at the Sawyer Fen site consisting of temperature (°C), pH, total dissolved solids (TDS, Table 3A. Physicochemical results of all locations at the Sawyer Fen site consisting of temperature (°C), pH, total dissolved solids (TDS, mg/L), and specific conductance (µS /cm) . Blank boxes represent data that was not recorded. mg/L), and specific conductance (µS /cm) . Blank boxes represent data that was not recorded.









*Figure 5. Map of sampling locations at the Sawyer Fen complex. Samples were taken in Sawyer Fen (green), Bluewater Creek Upstream (white), Upstream West Bank Well (light green), West Bank Spring (blue), East Bank Spring (blue), Downstream West Bank Well (light green) and Bluewater Creek Downstream (white).* 

## A. Sawyer Fen



**B.** West Bank Spring



*Figure 6. Seasonal variation in specific conductivity and total dissolved solids (TDS) in (A) Sawyer Fen and (B) West bank spring.*

## A. East Bank Spring







*Figure 7. Seasonal variation in specific conductivity and total dissolved solids (TDS) in (A) East Bank Spring and B) Bluewater Creek Downstream.* 



*Figure 8. Piper diagram showing relative proportions of major ionic concentrations at all sites in the Sawyer Fen complex.*



Bank Spring is related to (D) Bluewater Creek Downstream in seasonal stability. Figure 9. Piper diagram displaying the ionic compositions (A) Sawyer Fen which is related to (B) West Bank Spring in terms of seasonal variability because both migrate in their hydrochemical facies while (C) East



*Figure 10. Piper diagram displaying the relative proportions of ionic compositions of multiple springs in the Zuni Mountains (see Figure 8). The majority of springs represent the regional Permian San Andres-Glorieta (Psg) water bearing aquifer and local alluvium aquifers (Qa) with a calcium bicarbonate (Ca-Mg-HCO3) hydrogeochemical facies. Figure from Frus, 2016.* 



*Figure 11. An XY-plot of stable isotopes (δD and δ<sup>18</sup>O) of Sawyer Fen sites as well as local precipitation events. The δD and δ<sup>18</sup>O values of precipitation behave predictably, falling along the global meteoric water line (GMWL) as defined by Craig (1961). Stable isotope ratios of water are conventionally expressed as per mil (‰*) deviation from VSMOW (Vienna Standard Ocean Water).



*Figure 12. Seasonal change of pH and specific conductivity in late August from Sawyer Fen relates to local precipitation events recorded in August and September from the Remote Automated Weather Station (RAWS) in the Bluewater Ridge, New Mexico region.* 



*Figure 13. Picture taken November 2, 2019 shows discharge of East Bank Spring into Bluewater Creek. Due to atmospheric temperatures, ice forms on the surface of Bluewater Creek and visibly shows flow of EBS water into Bluewater Creek where no ice is forming.*



*Table 4. Annual average precipitation amounts of Zuni Mountains, New Mexico from 2007-2019. Table taken from U.S. Climate Data 2020.*

*Table 5. Sites, dates, and stable isotope concentrations from precipitation samples from West-Central and Central New Mexico. Table from Frus, 2016.*





*Figure 14. X-Y plot of stable isotopes (δ <sup>18</sup>O  and δD) for Zuni Mountain springs (circle) and streams (triangles) as well as west-central and central New Mexico precipitation (squares) in 2014-2016. The Global Meteoric Water Line, the GMWL (Craig, 1961), is plotted to determine if Zuni Mountain waters are altered away from global precipitation events and determined most of the springs in the Zuni Mountains are recharged by snowmelt. Figure taken from Frus, 2016.*