

Geochemical Impacts of Montezuma Well Discharge on Wet Beaver Creek, Verde Valley, Arizona

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I. Introduction

Wet Beaver Creek (WBC) is a perennial stream that drains part of the west side of the Mogollon Rim between Flagstaff and Pine, AZ. The creek has a drainage area of about 560 square kilometers and flows over and through the lithologies commonly found where the southern portion of the Colorado Plateau transitions to the Verde Valley. As water flows from the upper reaches on the rim to the lower reaches in the Verde Valley, it passes respectively through Basalt, Kaibab Limestone, Coconino Sandstone, the Schnebly Hill Formation, Hermit Shale, the Supai Group, and finally the Verde Formation (Blasch et al., 2006). Montezuma Well (MW), a limestone collapse sinkhole and spring contained in the Verde Formation, is located adjacent to WBC, and flows into WBC (Johnson et al., 2011). Each lithology WBC flows through is different and adds a unique geochemical character to its water, but the spring discharge of MW and the carbonates and evaporites that make up the Verde Formation appears to make the greatest change in WBC's water composition.

The upper and middle Verde River watershed lies in the transition zone between the Basin and Range, and Colorado Plateau physiographic provinces. Geologically, the uplands surrounding the valley consists of Precambrian aged volcanic and metamorphic rocks overlain with Paleozoic aged sedimentary strata capped with Cenozoic volcanic rocks. (Woodhouse et al., 2002)

WBC is a tributary of the Verde River in the middle Verde Valley. WBC is sourced in the Coconino sand stone and flows through silicate mineral rocks such as feldspar, $\text{CaAl}_2\text{Si}_2\text{O}_8$, before reaching the Verde Formation downstream approximately 3 km upstream of Montezuma Well (Bills et al., 2002). The Verde Formation is composed of silt, clay, calcite (CaCO_3) and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$).

The purpose of this study is to understand the changing geologic controls on WBC water composition as it flowed from Paleozoic siliciclastic rocks into the limestone, marl, and evaporite rocks of the Tertiary Verde Formation and then mixed with the waters draining from Montezuma Well.

II. Methods

This report documents two studies. One study was synoptic, conducted in October of 2017 and is described first. The second study was a review and synthesis of 10 years of data collected by Northern Arizona University students.

The synoptic study was conducted along Wet Beaver Creek on October 7th and October 14th, 2017. GPS locations of the sample sites are included in Table 1. The containers we collected samples in were acid washed with 10% HCl, and then rinsed three times with distilled, deionized water. Upon reaching a site, containers were rinsed three times with filtered (base cations and anions) or unfiltered (for alkalinity) stream water before collecting our sample. Containers were labeled with sample site number, description, date, and time.

Table 1. Sample site locations and distances between sites

Site	UTM Easting	UTM Northing	Distance to next site (in km)
WBC_Stop_1_USGSweir	438418	3837131	0
WBC_Stop_2_CasnerCanyon	437204	3837718	1.5
WBC_Stop_3_Ranch	436047	3837625	2.65
WBC_Stop_4_PicnicArea	434528	3836619	4.7
WBC_Stop_5_LawrenceCamp	432822	3834825	7.5
WBC_Stop_6_AboveMontezumaWell	431166	3834303	9.6
WBC_Stop_7_SycamorePark	428594	3833524	12.5
Montezuma Well	431136	3834290	Not on creek
FC_Stop_1_WayAbove Falls	444719	3808742	0
FC_Stop_2_AboveFalls	444370	3808318	0.58
FC_Stop_3_Below Falls	444369	3808277	0.62
FC_Stop_4_April	444393	3807950	0.98
FC_Stop_5_Pool	444291	3807906	1.09

*FC_Stop_6_Crossing	443973	3807567	1.65
FC_Stop_7_Irving	443257	3807071	2.65
FC_Stop_8_Bridge	442091	3806052	4.71
FC_Stop_9_Corral/Sallie Mae	440284	3805557	7.15



Figure 1: Wet Beaver Creek Study Sample Sites.

Samples were collected in the highest discharge part of the stream in free-flowing water. Sample bottles were filled completely to the top. At each site we collected one large, 500ml, bottle of unfiltered water to later titrate to find alkalinity. At each site we also collected two smaller, 250ml, bottles of water filtered through 0.45-micrometer paper using a syringe. One of the two smaller bottles from each location was acidified with nitric acid for preservation. Samples were stored in an ice chest or refrigerator until experimentation could be performed. In addition to taking samples at each location, we used Orion temperature-compensating pH meters and conductivity meters to take measurements of temperature, pH, and conductivity.

In order to understand the effects of each lithology, MW, and the surrounding basin have on the aqueous chemistry of WBC, many water samples were collected. Sites were chosen in a

manner to specifically isolate the effects the Verde Formation and MW have on the geochemistry of the creek. Eight sites were selected along the creek from upstream to downstream heading toward Camp Verde. The location of these sites can be seen in figure 1, mapped out along the creek. It is important to note that the site of WBC7 is of Montezuma Well itself before it flows into WBC, while site WBC6 is above where Montezuma's Well flows into the creek. It is also important to note that WBC5 at Lawrence is the first sample taken after WBC flows into the Verde Formation. Samples were collected on multiple occasions along these sites, including Fall 2011, Spring and Fall 2014, Fall 2016, and the Fall of 2017 semesters at Northern Arizona University (NAU). These samples were then analyzed for pH, conductivity, alkalinity, and temperature. Chemical concentrations were also analyzed for chloride $[Cl^-]$, sulfate $[SO_4^{2-}]$, magnesium $[Mg^{2+}]$, calcium $[Ca^{2+}]$, sodium $[Na^+]$, potassium $[K^+]$, and silicon dioxide $[SiO_2]$. This data was then sifted through and compiled on one table, figure 7. This analyzed data was then converted within the table to be reported in the same units, and organized chronologically for ease of reading. Not all parameters measured were able to be found for each set of data, but all data was used within the graphical analysis.

Once the raw chemical data was compiled for all separate time periods along selected sites, chemical models were ran for the samples where sufficient data was able to be found. This ended up being only three of the six datasets compiled within this report. WATEQ4F was used to run chemical speciation models and thermodynamic data models. This was used to calculate mineral saturation indices for calcite ($CaCO_3$), anhydrite ($CaSO_4$), dolomite ($CaMg(CO_3)_2$), gypsum ($CaSO_4 \cdot 2H_2O$), and quartz (SiO_2). The data for each sample was then recorded in figure 7, within the same table. These minerals were selected because of their suspected effect on and

relationship with the aqueous geochemistry of WBC, and were expected to fluctuate between different lithologies the creek encounters.

The data for each site was then averaged for each parameter, including modelled data for saturation indices. This was done in order to get an accurate picture of the characteristics for each site, as well as downstream trends, without being influenced by a temporal component.

For the long-term study, data collected between 2011 and 2017 by NAU undergraduate and graduate students were aggregated. Averaged data and standard deviations were then used to create a series of plots to help understand how WBC water chemistry changes as it flows down gradient and if it changes over time. The measuring tool in Google maps was used to delineate the watershed area that feeds WBC above the last sampling site WBC8 at Rimrock. This was used to help understand the lithologies present within the WBC drainage basin, and to better understand its geochemistry.

Completed analyses were run through the equilibrium speciation model WATEQ4F (Ball and Nordstrom, 1991) to ensure adequate quality assurance using charge and conductivity balances. In addition, saturation indices were calculated for minerals common in the rocks of the study area.

IIIa. Results of October, 2017 Synoptic study

The pH of WBC was relatively steady for both days of observations, with the exception of dip in pH after the confluence with MW (see table 2 and Figure 2). The range in pH for October 7th, not including Montezuma's Well, was 0.28. The range in pH for October 14th, not including Montezuma's Well, was found to be 0.39. The average of these pH ranges is then 0.34.

WBC conductivity increased through MW, then fell back down to a value intermediate between MW and WBC (see table 3 and Figure 3).

WBC alkalinity followed a consistent pattern of increasing through Montezuma's Well and decreasing to pre-MW levels (see Figure 4). There is a noticeable difference in the alkalinity value measured at MW between the 7th and 14th of October. This difference is equal to 2 mL/Eq between the two weeks.

Table 2	pH	[H ⁺] mol/L	alkalinity Equivalents/L	DIC mol/L
WBC1 10-7	8.25	5.62E-09	2.72E-03	2.73E-03
WBC2 10-7	8.29	5.13E-09	2.90E-03	2.90E-03
WBC3 10-7	8.21	6.17E-09	2.40E-03	2.41E-03
WBC4 10-7	8.25	5.62E-09	2.92E-03	2.93E-03
WBC5 10-7	8.21	6.17E-09	3.06E-03	3.07E-03
WBC6 10-7	8.01	9.77E-09	4.62E-03	4.69E-03
WBC7- Mont well 10-7	6.96	1.10E-07	8.00E-03	9.74E-03
WBC8-10-7	8.22	6.03E-09	6.20E-03	6.22E-03
WBC1 10-14	8.13	7.41E-09	2.60E-03	2.62E-03
WBC2 10-14	8.2	6.31E-09	2.65E-03	2.66E-03
WBC3 10-14	8.23	5.89E-09	3.08E-03	3.09E-03
WBC4 10-14	8.13	7.41E-09	2.84E-03	2.86E-03
WBC5 10-14	8.16	6.92E-09	2.80E-03	2.82E-03
WBC6 10-14	8.06	8.71E-09	4.62E-03	4.67E-03
Mont Well 10- 14	7.05	8.91E-08	1.03E-02	1.21E-02
WBC8 10-14	7.84	1.45E-08	5.70E-03	5.84E-03

Table 3	[Ca2+] mol/l	[SO42-] mol/l	IAP of Calcite	IAP of Gypsum	SI of Calcite	SI of Gypsum
WBC1 10-7	5.94E-04	2.08203E-05	1.42E-08	1.24E-08	0.440792461	-3.305
WBC2 10-7	5.94E-04	2.18613E-05	1.65E-08	1.30E-08	0.507888387	-3.284
WBC3 10-7	0.000451597	2.18613E-05	8.67E-09	9.87E-09	0.227841355	-3.404
WBC4 10-7	0.000477545	2.08203E-05	1.22E-08	9.94E-09	0.376606585	-3.400
WBC5 10-7	0.000708583	2.29024E-05	1.73E-08	1.62E-08	0.528991305	-3.188
WBC6 10-7	0.00094486	3.33125E-05	2.22E-08	3.15E-08	0.635460237	-2.900
WBC7- Mont well 10-7	0.000958084	9.57735E-05	3.50E-09	9.18E-08	-0.166020707	-2.435
WBC8-10-7	0.001851547	3.43535E-05	9.39E-08	6.36E-08	1.262643868	-2.594
WBC1 10-14	0.000412675	2.08203E-05	7.16E-09	8.59E-09	0.144630741	-3.463
WBC2 10-14	0.000422405	2.18613E-05	8.75E-09	9.23E-09	0.232012537	-3.433

WBC3 10-14	0.000432635	2.18613E-05	1.12E-08	9.46E-09	0.337224059	-3.422
WBC4 10-14	0.00029491	2.08203E-05	5.59E-09	6.14E-09	0.037057704	-3.610
WBC5 10-14	0.000692365	2.29024E-05	1.38E-08	1.59E-08	0.431128719	-3.198
WBC6 10-14	0.001153443	3.33125E-05	3.03E-08	3.84E-08	0.771551126	-2.813
Mont Well 10-14	0.001728044	9.57735E-05	9.96E-09	1.66E-07	0.288096601	-2.179
WBC8 10-14	0.001851547	3.43535E-05	3.63E-08	6.36E-08	0.850290886	-2.594

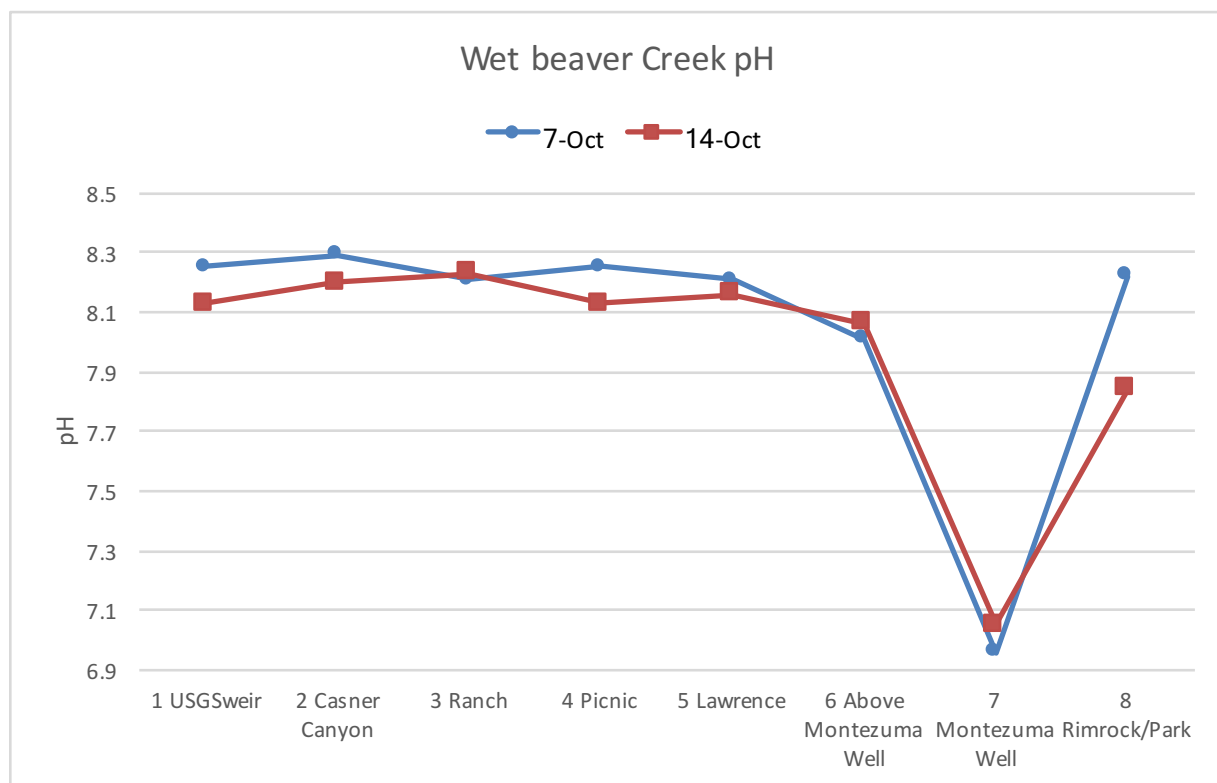


Figure 2. pH of water samples collected along Wet Beaver Creek and at Montezuma Well, 10-7-17 and 10-14-17.

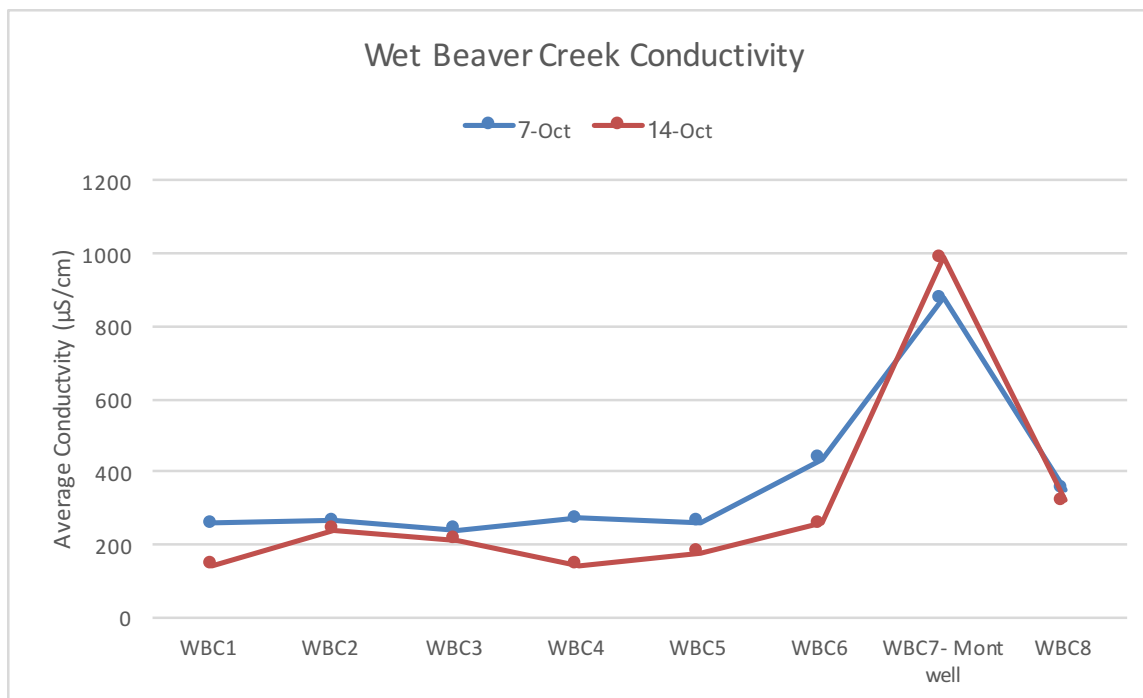


Figure 3. Conductivity of water samples collected along Wet Beaver Creek and at Montezuma Well, 10-7-17 and 10-14-17.

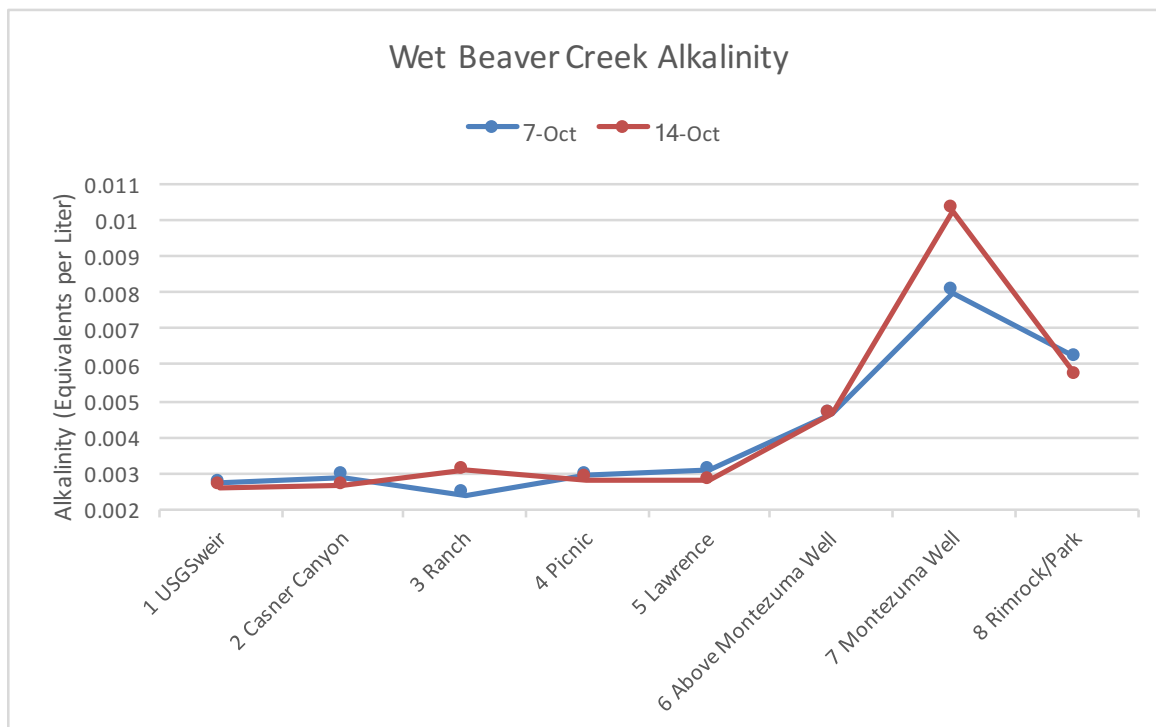


Figure 4. Alkalinity of water samples collected along Wet Beaver Creek and at Montezuma Well, 10-7-17 and 10-14-17.

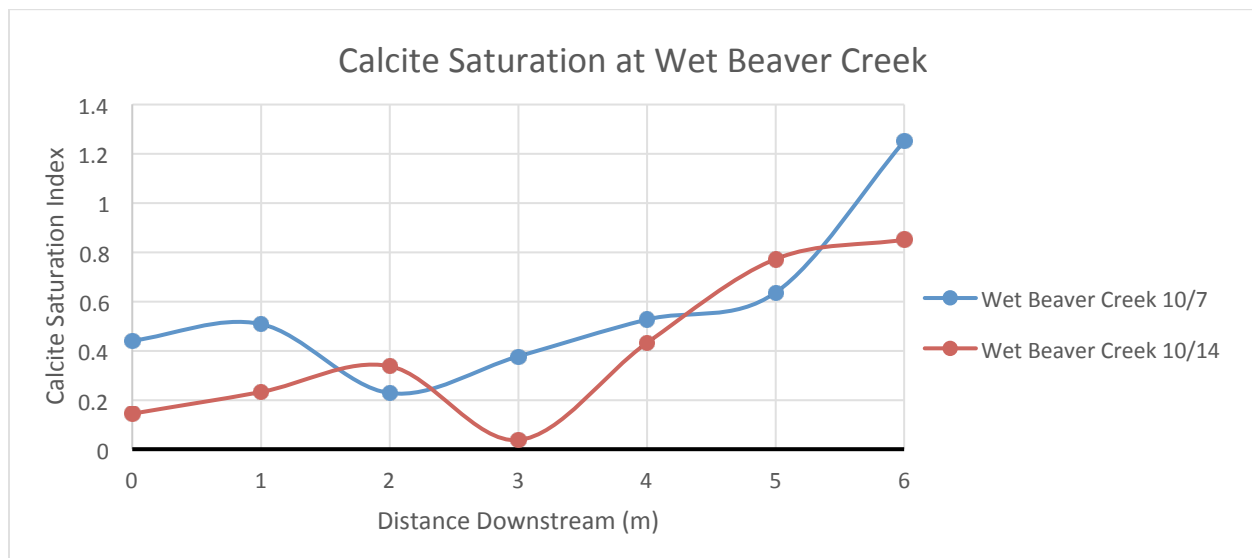


Figure 5: Calcite is oversaturated in Wet Beaver Creek. Moving downstream results in an increase in calcite.

Saturation indices for most rock-forming minerals were below zero, that is under saturated. The exception was for calcite, which shows near saturation or oversaturation for all samples. Because of kinetic inhibitions for calcite precipitation, the potential for calcite precipitation at these levels of super saturation is negligible (Malusa et al., 2003).

IIIb. Results of long-term study

In the first four sampling areas on WBC (Weir - WBC1, Casner - WBC2, Ranch - WBC3, Picnic Area - WBC4) the average pH, conductivity, alkalinity, and saturation indices for calcite, anhydrite, dolomite, gypsum, and quartz remain relatively unchanged. The average pH is slightly basic with values that hover around the 8.1 range, while the pH of MW is more neutral with an average value of 7.21 (see Figure 6 and Appendix A). In the water samples from site WBC1 to site WBC4, the mean conductivity remains very stable at values near 250 $\mu\text{S}/\text{cm}$, while the water in MW averages 866 $\mu\text{S}/\text{cm}$ (Figure 7). This is consistent with the concentrations of dissolved ions measured at these sites (Appendix A).

The average alkalinity in WBC remains very near the 3.00 mEq/L through WBC4, and the avg. alkalinity in MW is 8.74 mEq/L (Figure 6). The concentrations of the cations and anions examined (chloride $[Cl^-]$, sulfate $[SO_4^{2-}]$, magnesium $[Mg^{2+}]$, calcium $[Ca^{2+}]$, sodium $[Na^+]$, and potassium $[K^+]$) also remain stable from WBC1 through WBC4 Appendix A, Figure 8). In the reach before WBC contacts the Verde Formation the concentrations for $[Cl^-]$, $[SO_4^{2-}]$, $[Na^+]$, and $[K^+]$ are between 1 to 6 mg/L, while the $[Mg^{2+}]$ and $[Ca^{2+}]$ concentrations are between 15 and 22 mg/L. The average saturation indices for calcite ($CaCO_3$), anhydrite ($CaSO_4$), dolomite ($CaMg(CO_3)_2$), gypsum ($CaSO_4 \cdot 2H_2O$), and quartz (SiO_2) all remain stable at the first 4 sampling sites (Figure 9).

As the creek passes from the site WBC1 downstream, its composition gradually begins to change, then more rapidly as it flows into the Verde Formation at site WBC5. The pH drops slightly reaching a minimum value of 7.88 just above MW, 7.21 in MW, and rebounding to 8.13 at site WBC8 downstream from the well. The average conductivity of MW is 866 $\mu S/cm$ (Figure 8). The average conductivity of WBC almost doubles between site WBC4 and site WBC6 from values of 263 $\mu S/cm$ to 505 $\mu S/cm$. The average alkalinity again almost doubles from site WBC4 to site WBC6, going from 3.2 mEq/L to 7.11 mEq/L.

All ion concentrations tend to increase as WBC flows beyond site WBC4. Calcium initially has the highest concentration of about 20 mg/L at site WBC4 and upstream, and also shows the greatest increase to an average value of 60.31 mg/L at site WBC8. Magnesium increases from 17.24 mg/L at site WBC4 to 26.55 mg/L at site WBC8. Sulfate, potassium, and sodium have values that range from 1 mg/L to 6 mg/L at site WBC4. Sodium displays the greatest increase in concentration besides calcium; from 5.41 mg/L at site WBC5 to 23.90 mg/L at site WBC8. Chloride also shows a sharp increase; from 3.58 mg/L at site WBC5 to 12.06

mg/L at site WBC8. Sulfate and potassium show milder increases; from values around 1.80 to just above 3 mg/L at site WBC8.

The saturation indices for calcite, dolomite, and quartz tend to be slightly positive from sites WBC1-WBC4; their values range from -0.13 to .33. From sites WBC1 to WBC5, gypsum and anhydrite have saturation index values that range between -4.04 and -3.7.

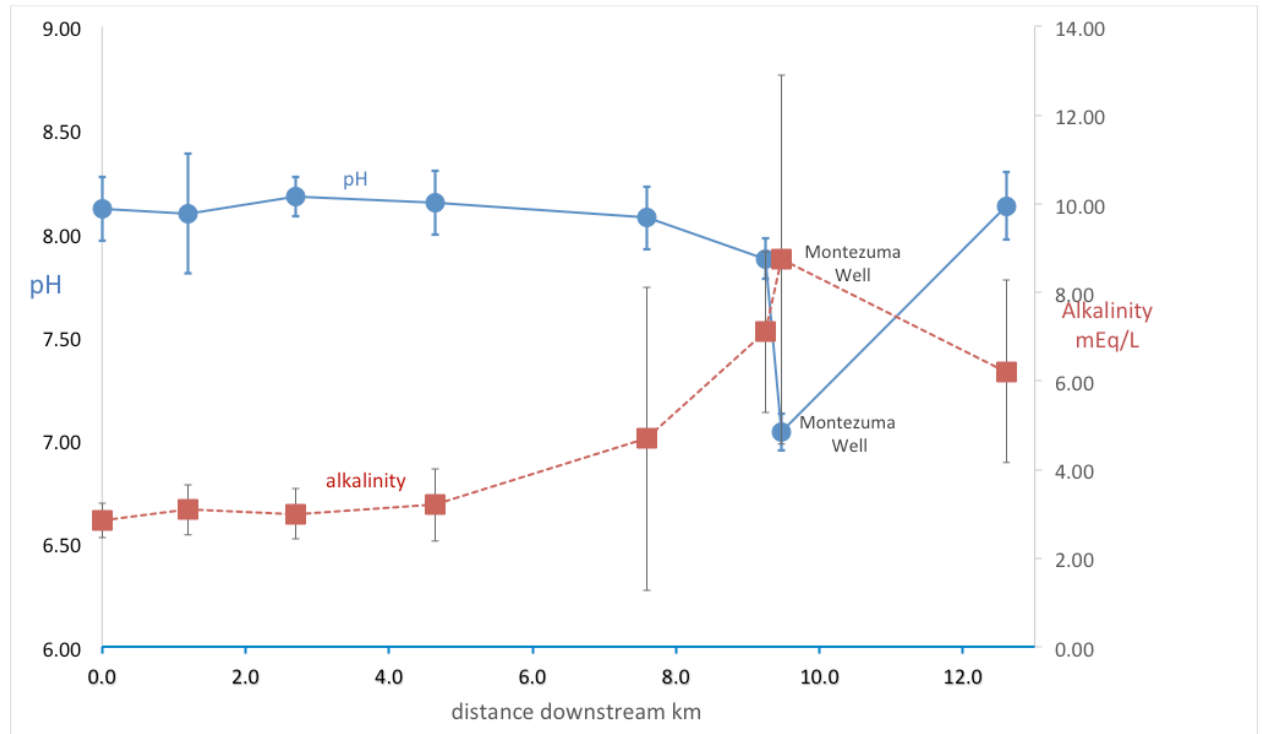


Figure 6. pH and alkalinity of water samples collected along Wet Beaver Creek and at Montezuma Well collected between 4-2011 and 10-2017.

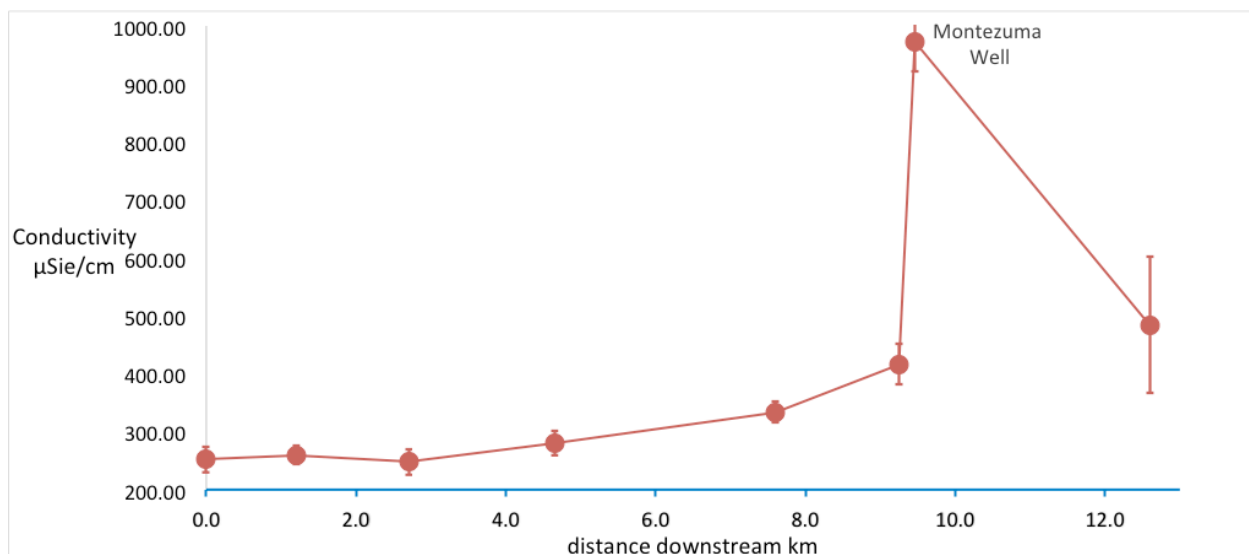


Figure 7. Electrical conductivity of water samples collected along Wet Beaver Creek and at Montezuma Well collected between 4-2011 and 10-2017.

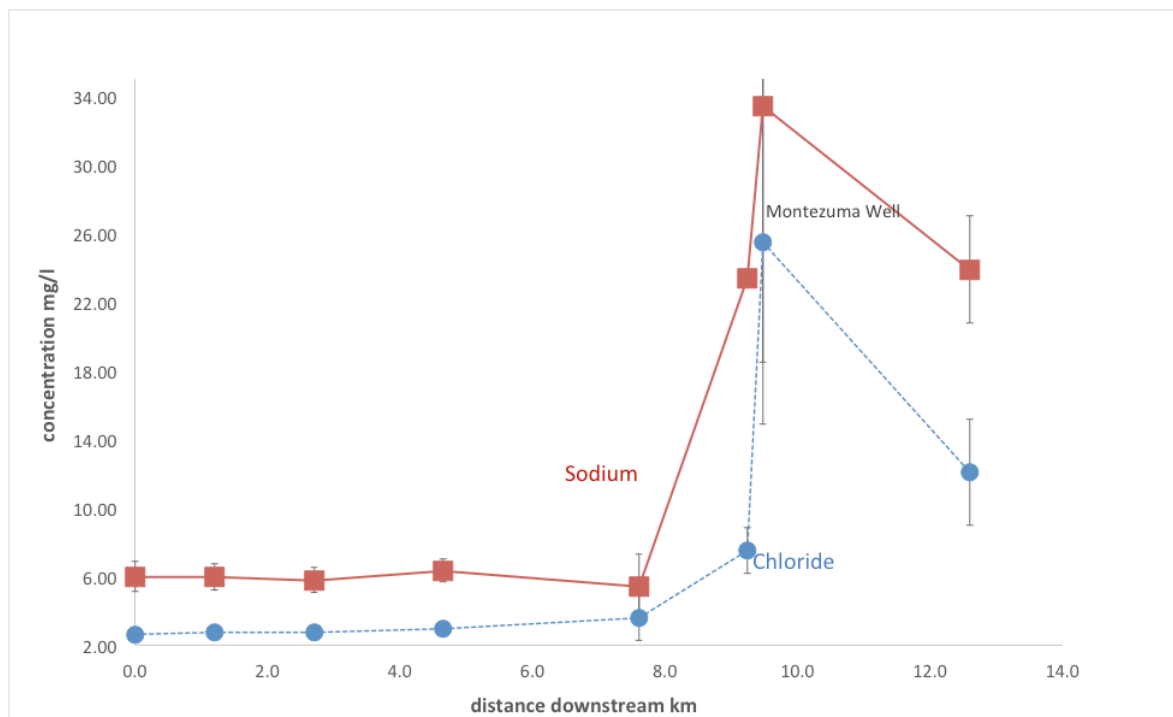


Figure 8. Sodium and Chloride concentrations of water samples collected along Wet Beaver Creek and at Montezuma Well collected between 4-2011 and 10-2017.

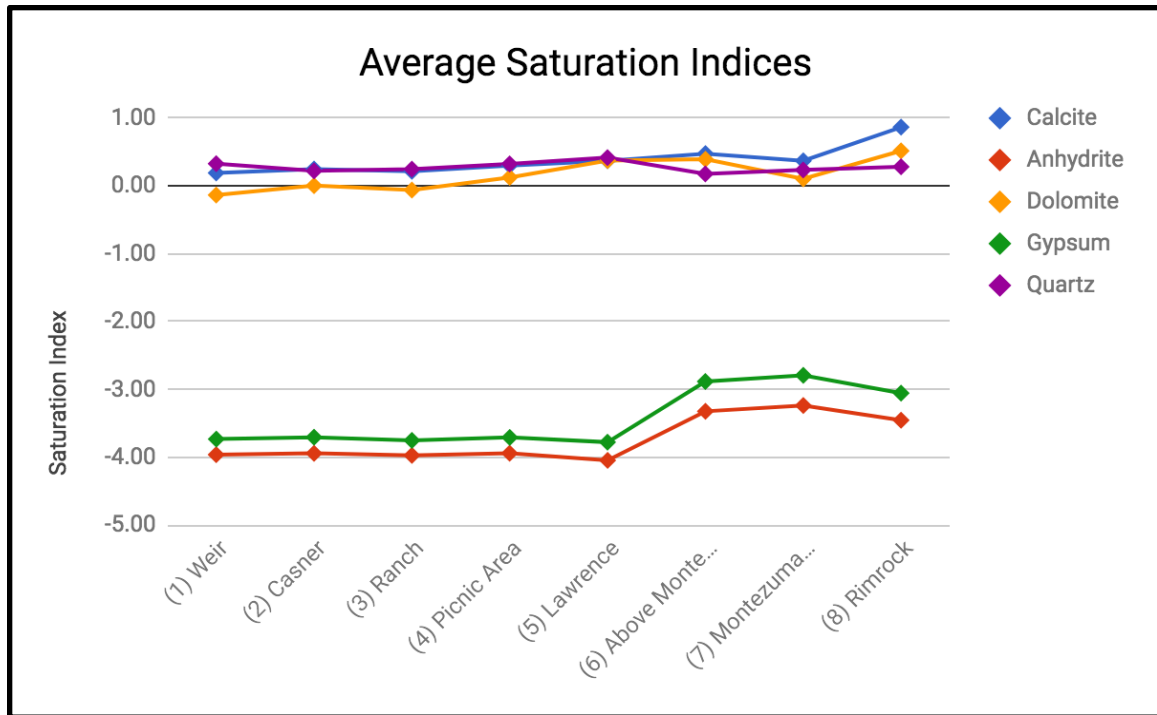


Figure 9. Average saturation indices for several minerals for water samples collected along Wet Beaver Creek and at Montezuma Well collected between 4-2011 and 10-2017. A saturation index of 0 indicates equilibrium, a negative value indicates under saturation, and a positive value indicates super saturation.

IVa. Discussion Short-term study

It was hypothesized that Wet Beaver Creek pH varies with distance downstream, increasing as it moved into the limestone-rich for the formation. However, with the exception of Montezuma Well, the difference in pH between sites is negligible.

Saturation Index was negative for gypsum (see table 4). This means that gypsum was not going to precipitate at all in either formation. However, the Saturation index was positive and for almost every site in WBC indicating that calcite was oversaturated, but not sufficiently oversaturated to cause significant precipitation..

The data from WBC conductivity support the hypothesis that the conductivity at the last site (Redrock/Park Site) would have higher conductivity than the rest of the creek (see Figure 7).

In WBC, there is an evident increase in the alkalinity that is consistent with the sites from the Supai formations and the Verde formations, and after Montezuma Well water flows into the river.

By studying the geology of the area and testing for minerals found in these certain geologies, there is large correlation to be able to say that the geologies of the area influence Wet Beaver Creek and Fossil Creek. From the Coconino Sandstone and Limestone, to the Verde Formation and Montezuma's Well, it is evident that these geological features influence water composition and subsequent water qualities that intersect them.

Limestone has been continuously proved to be an excellent buffer in water systems, and gypsum has been continuously shown to be much less soluble and less contributory to the buffering capacity of water systems.

Ivb. Discussion long-term study

As expected, the chemical parameters measured along WBC remain consistent as it flows downstream, until the creek encounters the Verde Formation and MW. For the mainstem of WBC, between sites WBC1 and WBC4, pH levels maintained around 8.1 with relatively normal dissolved ions between 0-20 mg/L. Once the creek hits the Verde Formation above WBC5, there is a minor decrease of pH, a minor increase in alkalinity, and increased ion concentrations, primarily $[Ca^{2+}]$ and $[Mg^{2+}]$, with a downstream increase of $[Na^+]$ as well at WBC6. This increased concentration corresponds with the doubling of measured conductivity from WBC4 to

WBC6. The Verde Formation consists of mostly evaporitic and carbonate constituents, which are likely the significant agents of the geochemical change. These two sites also show a higher saturation index for dolomite and calcite than previous sites, indicating that this lithology is likely the cause of increased $[\text{Ca}^{2+}]$ and $[\text{Mg}^{2+}]$ concentrations. Evaporites within the formation could also explain the increased $[\text{Na}^+]$ concentrations.

Data from MW shows similar chemical differences as the Verde Formation, but with much more extreme changes recorded in the well itself. This is as hypothesized, since the water from MW spends much more time within the Verde Formation before contact with WBC, which allows it to pick up more of its constituents than the surface water of the creek. MW has a drastically different average pH, average alkalinity, and in anion / cation concentrations than the creek. MW has double to triple the average concentration of cations in most cases, and the same concentrations of anions compared to the creek above WBC5. This increased ion concentration corresponds with a tripling of average conductivity levels. This corresponds with peaks in the saturation indices of anhydrite and gypsum, as ion concentration peaks at these same sites. A drop in average pH from 8.1 to 7.21 in MW is measured along with an increase of average alkalinity levels to a peak of 8.74 (mEq/L). pH levels dropped as expected while cation concentrations increase, especially from the presence of stronger cations like $[\text{Ca}^{2+}]$ and $[\text{Mg}^{2+}]$. This high concentration of 2^+ cations corresponds with high alkalinity observed within MW, with more dissolved bicarbonate in the water.

As the creek flows past MW, the aqueous chemistry equilibrates fairly quickly on its way to returning to base flow geochemistry for WBC. All parameters measured trend towards the baseline established from sites WBC1 to WBC4 except for the saturation indices of calcite and dolomite. The increases in these however does correspond with the decrease of high $[\text{Ca}^{2+}]$ and

[Mg²⁺] ion concentration, as the creek downstream of MW is more saturated in the compounds needed to make these minerals. Calcite downstream is over saturated with a saturation index of 0.87 at WBC8, and precipitation downstream from WBC8 is likely.

As the basic water (pH 8.15 at WBC4) of WBC mixes with the lower pH water of the Verde Formation and Montezuma Well, the pH of WBC is immediately lowered. As the water from the Verde Formation and MW mixes with WBC, the high alkalinity of MW (8.74 mEq/L) is able to quickly neutralize excess hydrogen ions which equilibrates the pH of the creek and brings the pH value back to levels seen above where the creek meets the Verde Formation.

Conclusion

The chemistry of Wet Beaver Creek (WBC) is significantly affected by the Verde Formation, both by flowing through it, and by the direct influence of Montezuma's Well (MW). The creek does equilibrate fairly quickly towards base conditions at the last sample site after flowing past MW. It is, however, hard to fully affirm that WBC returns to its baseline chemistry with only one site below MW, and before the creek itself becomes too dry and influenced by modern human activity and pollutants. The general chemistry of WBC at sites 1-4 (before it enters the Verde Formation) has an average pH of about 8, an average conductivity of about 250 $\mu\text{S}/\text{cm}$, and an average alkalinity of just above 3 mEq/L. The ion concentrations ([Cl⁻], [SO₄²⁻], [Mg²⁺], [Ca²⁺], [Na⁺], and [K⁺]) in this reach range from about 1 mg/L to 20 mg/L. Once WBC encounters the Verde Formation itself, especially from MW, all measured chemical parameters were affected. These samples had double to triple the amounts of average ion concentrations, average conductivities, and average alkalinities compared to WBC, as well as pH being significantly lower at 7.21. All of these parameters were shown to move towards upstream

levels, as the creek equilibrates downstream. As WBC's chemistry continues to equilibrate downstream from MW, the pH returns to 8.13, and will likely remain at values around 8.1. We expect the alkalinity and ion concentrations to remain elevated above the pre Verde Formation contact levels. The negative saturation indices for gypsum and anhydrite indicate that the concentrations of the ions that these minerals are comprised of ($[Ca^{2+}]$ and $[SO_4^{2-}]$) will likely increase as the system moves towards equilibrium.

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