

**Final Report on Geochemistry
of
Bitter Lake National Wildlife Refuge, Roswell, New Mexico**

by

Frederick K. Partey^{1 2}, Lewis Land¹, Bonnie Frey¹, Elizabeth Premo³ and Laura
Crossey³

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¹ New Mexico Bureau of Geology and Mineral Resources, New Mexico Tech, Socorro, NM.

² Current position: Agrium, Inc., Pocatello, ID.

³ University of New Mexico Dept. of Earth and Planetary Sciences, Albuquerque, NM.

Introduction

Water is one of our most important natural resources, and ascertaining its quality is crucial for both human and aquatic life. Water bodies such as the sinkholes, springs and lakes at Bitter Lake National Wildlife Refuge (BLNWR) provide habitat for a number of threatened and endangered species. These features are formed in gypsum bedrock, which serves as a leaky confining unit for an artesian aquifer in the underlying San Andres limestone, and are fed by upward seepage of groundwater from the aquifer (Land and Huff, 2010a; 2010b). However, the processes that control or influence groundwater quality at Bitter Lake are poorly understood. Managers at BLNWR observed that certain aquatic species are restricted to specific springs and sinkholes. Their first hypothesis was that species distribution might be related to the high salt content of some of the water bodies in the area.

Staff of the New Mexico Bureau of Geology and Mineral Resources (NMBGMR) were contracted to construct a conductivity map to aid in determining the relationship between groundwater chemistry and the distribution of aquatic species for the summer of 2008. Water samples were collected for measurements of pH, conductivity and major ions. With these data, diagrams were made to demonstrate the distribution of various salts. For example, Box and Whisker plots have been constructed to show major chemical constituents in water bodies in the study area. Stiff diagrams and Piper Plots for the springs and sinkholes have also been used to classify the water by hydrochemical facies and to indicate the relative proportions of ions. A conductivity map was constructed to show the distribution of electrical conductivity of groundwater in and around BLNWR. Because electrical conductivity is directly related to variations in dissolved solids (mostly mineral salts), other diagrams, such as total dissolved solids, pH and bicarbonate maps have also been constructed to confirm the spatial distribution of conductivity in the area.

Study area

Bitter Lake National Wildlife Refuge is situated on the northeast outskirts of the city of Roswell (Figure 1). The Refuge occupies an area of approximately 158 km² (61 square miles) and includes a number of springs, sinkhole lakes and extensive wetlands that have formed in gypsum bedrock on the west side of the Pecos River floodplain (Land and Huff, 2010b). These springs and sinkholes are fed by ground water from an east dipping, karstic limestone aquifer that is under artesian conditions in the vicinity of the Refuge, and a shallow water table aquifer made up of sand and gravel of the Pecos river floodplain alluvial terraces (McCraw et al., 2007). An important feature present in the artesian aquifer is a freshwater-saltwater interface, which extends roughly northwest-southeast beneath the city of Roswell (McCraw et al., 2007). Numerous depressions and sinkholes occur east of the freshwater-salt water interface, formed by gradual subsidence or catastrophic collapse in gypsiferous carbonate terrane. Most of the work presented here focuses on these sinkholes and the springs that lie within and south of BLNWR. A detailed description of the geology and hydrology of the Bitter Lake Quadrangle has been documented by Land and McCraw and their colleagues (Land, 2005; McCraw et al., 2007; Land and Huff, 2010a; 2010b).

Materials and methods

Spring and sinkhole water samples were collected between May 12 and 16, 2008. Forty-four sites were sampled including one well (Figure 2). Not all the sinkholes sampled in the summer of 2008 were again sampled in the spring of 2009 due to low water levels in those sinkholes. Sampling protocols described by Barcelona et al. (1985) and Claasen (1982) were strictly observed during sample collection. Samples were collected using new certified clean polypropylene containers. Each sample was immediately filtered on site through 0.45 µm filters

on acetate cellulose. Filtrate for metals analyses was transferred into 100-ml polypropylene bottles and immediately acidified to $\text{pH} < 2$ by the addition of Merck™ ultrapure nitric acid (5 ml 6 N HNO_3). Samples for anion analyses were collected into 250-ml polypropylene bottles without preservation. All the samples were stored in an ice chest at a temperature of $<4^\circ\text{C}$ and later transferred to the NMBGMR chemistry laboratory and stored in a refrigerator at a temperature of $<4^\circ\text{C}$ until analyzed (within 1 week).

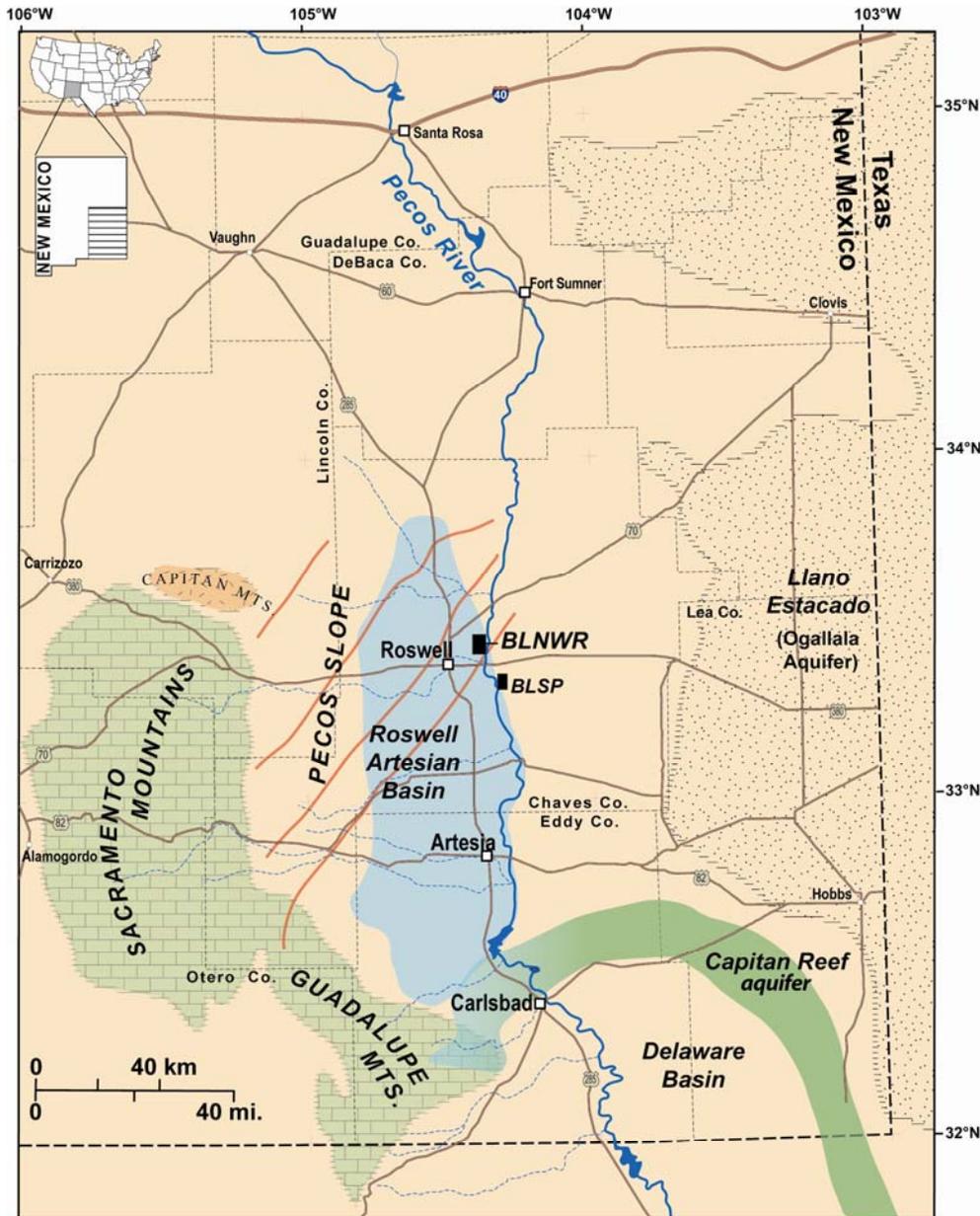


Figure 1: Regional map of southeastern New Mexico, showing location of BLNWR. Adapted from Land and Huff, 2010. BLSP = Bottomless Lakes State Park.

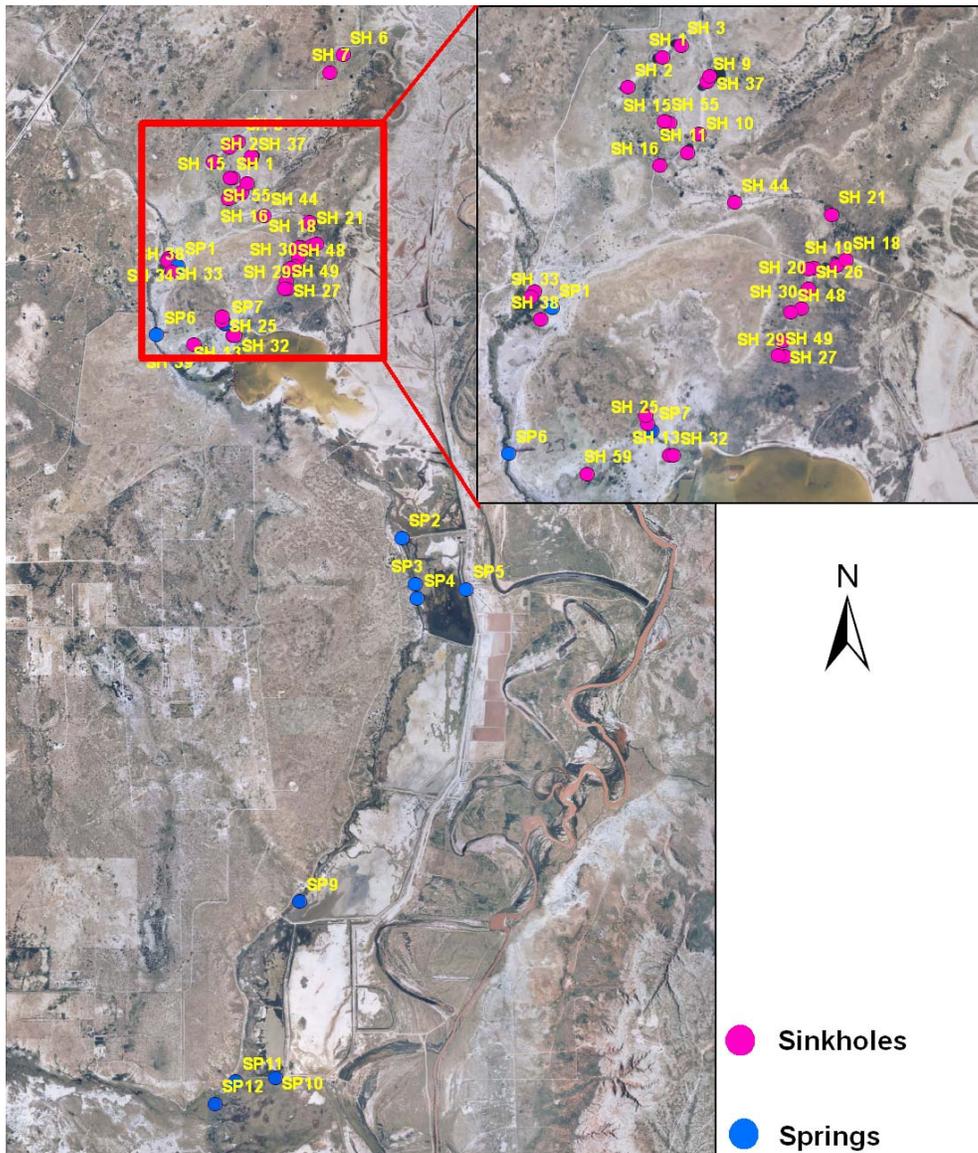


Figure 2: Location map of Bitter Lake National Wildlife Refuge showing sampling points. Enlarged window is an area with high sinkhole density.

Temperature, electrical conductivity, pH and redox potential were determined in the field with portable meters. Before taking readings, pumping was carried out with a peristaltic Geopump until the meter readings were stable for each parameter. The instruments were calibrated before sampling. The pH electrode was calibrated against pH 4, 7 and 10 buffers. Alkalinity (as mg/L HCO_3^-) was determined in the NMBGMR chemistry laboratory by titration with 1.6 N H_2SO_4 to pH ~4.5 using a pipette and a burette.

Chemical analyses for anions (Cl, SO₄ and NO₃) were performed at the NMBGMR chemistry laboratory using a Dionex DX-120 ion chromatograph. Cations (Na, K, Ca, and Mg) were analyzed using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) (Perkin Elmer OPTIMA 5300 DV). The quality of the chemical analyses was carefully inspected by analyzing blanks and duplicate samples, and checking ion balances. The ion balance errors for the analyses were generally within $\pm 5\%$.

Results and discussion

Statistical summaries of chemical parameters measured in the springs and sinkholes for May of 2008 are presented in Tables 1 and 2, where Max is maximum, Min is minimum, AM is arithmetic mean and STD is standard deviation. The symbols in the parameter column are: Ca = calcium, Na = sodium, K = potassium, Mg = magnesium, Cl = chloride, SO₄ = sulfate, HCO₃ = bicarbonate, TDS = total dissolve solids, and cond = conductivity.

A second round of sampling was conducted in February, 2009 with the hope of elucidating any seasonal variations in water chemistry. However, the data were insufficient to make any meaningful statistical analysis of the seasonal changes in chemistry in the sinkholes and springs.

Parameter	Unit	Max	Min	AM	Std
Ca	mg/L	7361	170	960	2434
Na	mg/L	1680	405	1072	388
K	mg/L	12	2.1	7.0	3.2
Mg	mg/L	255	40	133	67
Cl	mg/L	2820	630	1820	689
SO ₄	mg/L	2130	525	1286	505
HCO ₃	mg/L	220	115	168	37
pH		8.0	7.0	7.4	0.3
TDS	mg/L	7361	1830	4854	1687
Cond	uS/cm	10600	1100	7015	2990

Table 1: Statistical summary of parameters determined in the springs (May, 2008).

Parameter	Unit	Max	Min	AM	Std
Ca	mg/L	1165	480	799	177
Na	mg/L	26950	810	6514	5587
K	mg/L	95.0	6.0	31.0	22.0
Mg	mg/L	3200	135	822	606
Cl	mg/L	42910	1260	10779	8907
SO ₄	mg/L	12670	1250	4368	2506
HCO ₃	mg/L	370	70	141	55
pH		9.0	7.2	8.0	0.4
TDS	mg/L	86976	4790	23391	17667
Cond	uS/cm	113300	6600	33253	22755

Table 2: Statistical summary of parameters determined in the sinkholes (May, 2008).

The pH of the springs and sinkholes is typically high and varies from 7.0 to 9.0 with a mean value of 7.0 and 7.2 respectively (Tables 1 and 2). However, the majority of the samples (>99%) fall above the natural water pH range of 4.5–7.0 (Langmuir, 1997). Electrical conductivity (EC) values are extremely high. Minimum and maximum respective values are 1100 and 10600 $\mu\text{S}/\text{cm}$ with a mean value of 7508 $\mu\text{S}/\text{cm}$ for the springs, whereas the sinkholes have minimum and maximum values of 6600 and 113300 $\mu\text{S}/\text{cm}$ respectively with a mean value of 33254 $\mu\text{S}/\text{cm}$. Total dissolved solids in both the springs and the sinkholes follow the same trend as the electrical conductivity.

Major cations (Ca, Mg, Na and K) are also generally high in both the springs and sinkholes. Comparison of concentrations for the springs and sinkholes are illustrated in the Box and Whisker plots (Figures 3 and 4). Sodium (Na) is the dominant cation for both the springs and the sinkholes with median values of 1200 mg/l and 5000 mg/l, respectively, also showing a wide spread. Magnesium (Mg) is the least concentrated cation for both springs and sinkholes. Chloride (Cl) is by far the dominant anion in both the springs and sinkholes with median values of 2000 mg/l and 7000 mg/l respectively and forms approximately 56% and 78% of the anion content. Bicarbonate (HCO_3) has the lowest median concentration for anions in both the springs and the sinkholes. In general, ion content for springs is much lower than ion content for sinkholes. This trend might be due in part to evaporative processes in the sinkholes, with their greater surface area, being higher than in the springs.

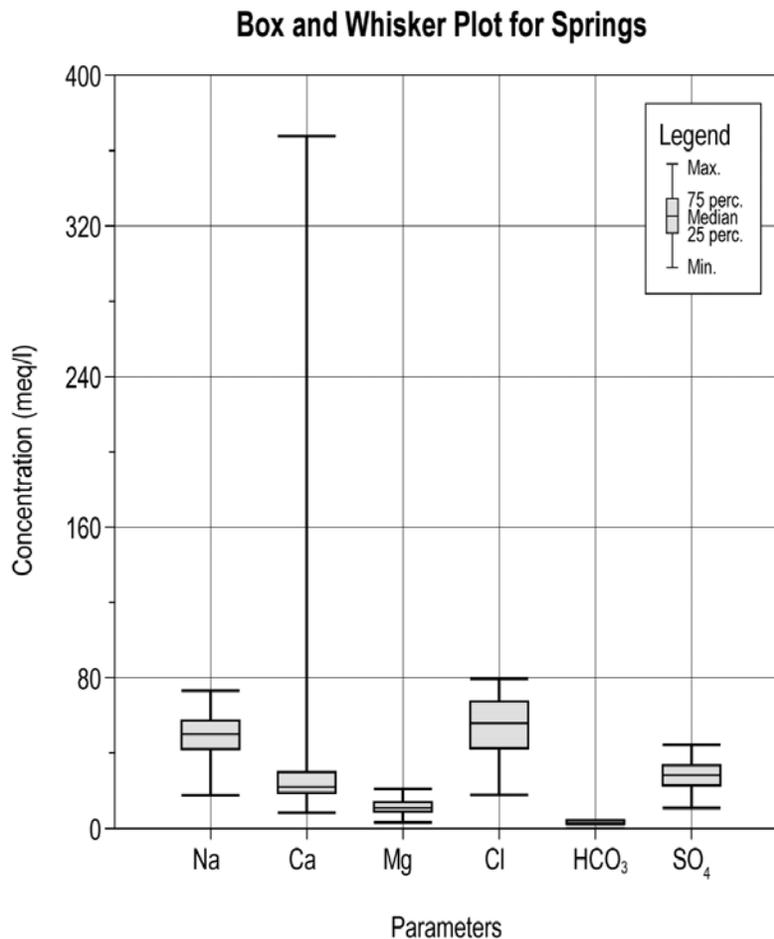


Figure 3: Box and whisker plot of major chemical constituents in springs in the study area.

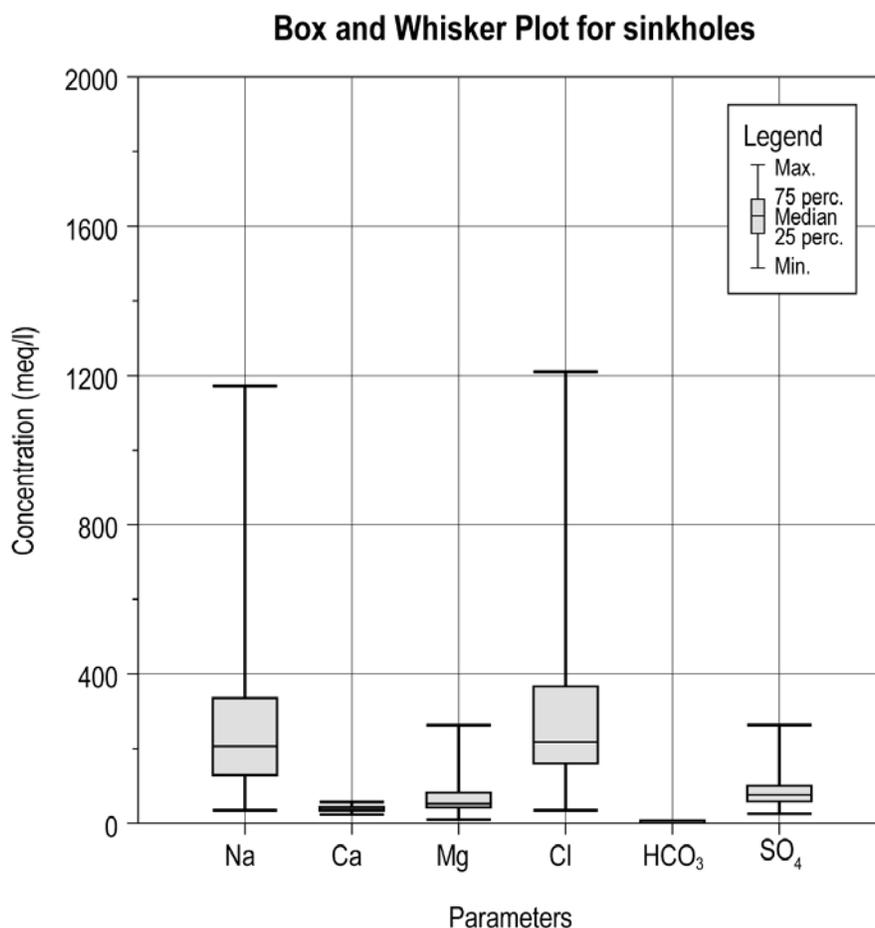


Figure 4: Box and whisker plot of major chemical constituents in sinkholes in the study area.

Stiff diagrams (Stiff, 1951) have been constructed for all the sinkhole and spring data and are displayed in Figures 5 and 6. The diagrams show average values from the springs and the sinkholes. Their purpose is to show simple patterns that can be used to indicate water sources. The average water chemistry of the springs has a K-shaped Stiff diagram that indicates relatively high Na, Ca, Cl, and SO₄ but low Mg and HCO₃ concentrations, probably due to short contact time of the spring water with the bedrock (dolomite) (Figure 5). The sinkhole Stiff diagram, by contrast, shows a funnel shape, clearly revealing a halite rich water source. The water samples are delineated as Na-Cl and Ca-Mg-SO₄ based on the classification of Back (1960) with relatively low HCO₃ concentrations (Figure 6). The “Mg-rich” water type that is associated with the sinkholes is not found in the springs. This observation reflects the fact that the springs have limited residence time with the Mg-rich rocks, hence relatively low concentrations.

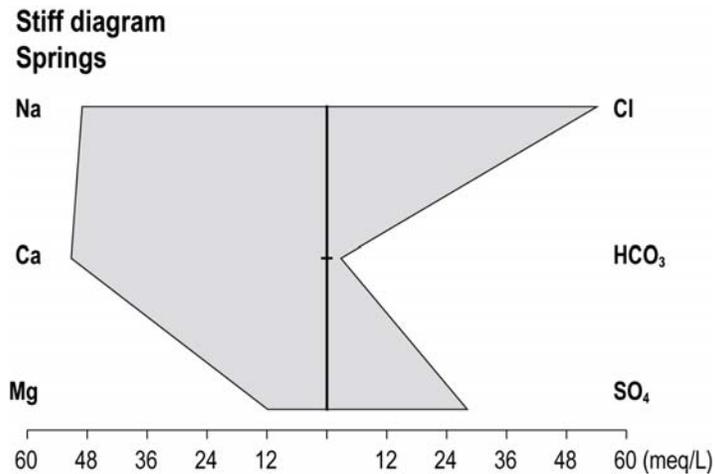


Figure 5: Stiff diagram of major chemical constituents in springs in the study area.

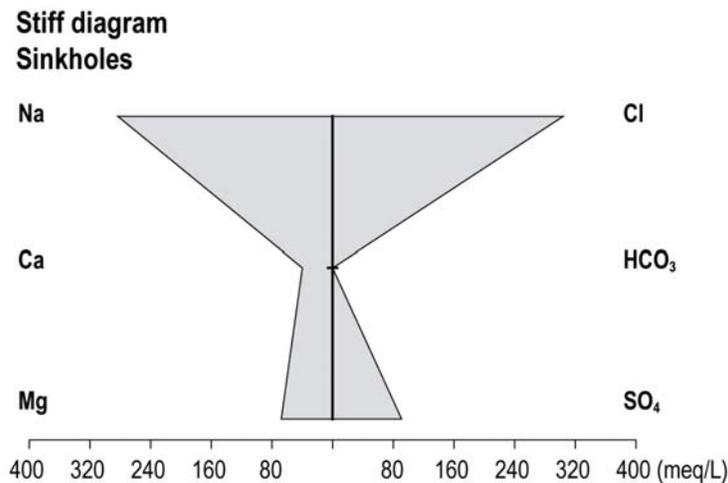


Figure 6: Stiff diagram of major chemical constituents in sinkholes in the study area.

Figures 7 and 8 show Piper Trilinear Plots of major ion concentrations of water samples from the springs and sinkholes in the study area. Two principal hydrochemical facies have been delineated for the springs. These are Na–Cl -type water (Gp 1) wherein the chemical properties of the water are dominated by NaCl with low concentrations of carbonic acids (HCO₃). This water type occupies the section designated as B (Figure 7). The second water type is Ca–SO₄ (Gp 2). In this water type, Ca is the cation that predominates while SO₄ is the main anion that dominates. It occupies the section designated as A (Figure. 7). The sinkholes also show two distinct water types: the Ca-Mg-SO₄ (section D, Gp 3) and Na-Cl (section C, Gp 4) water types. The water types from both the sinkholes and springs depict water-rock interactions involving the dissolution of gypsum and halite by the recharging groundwater. The rock types of the study area consist mainly of gypsum bedrock on the west side of the Pecos River floodplain where almost all the springs and sinkholes were sampled. The Na–Cl water type has very high conductivity, suggesting a deep-seated brine source.

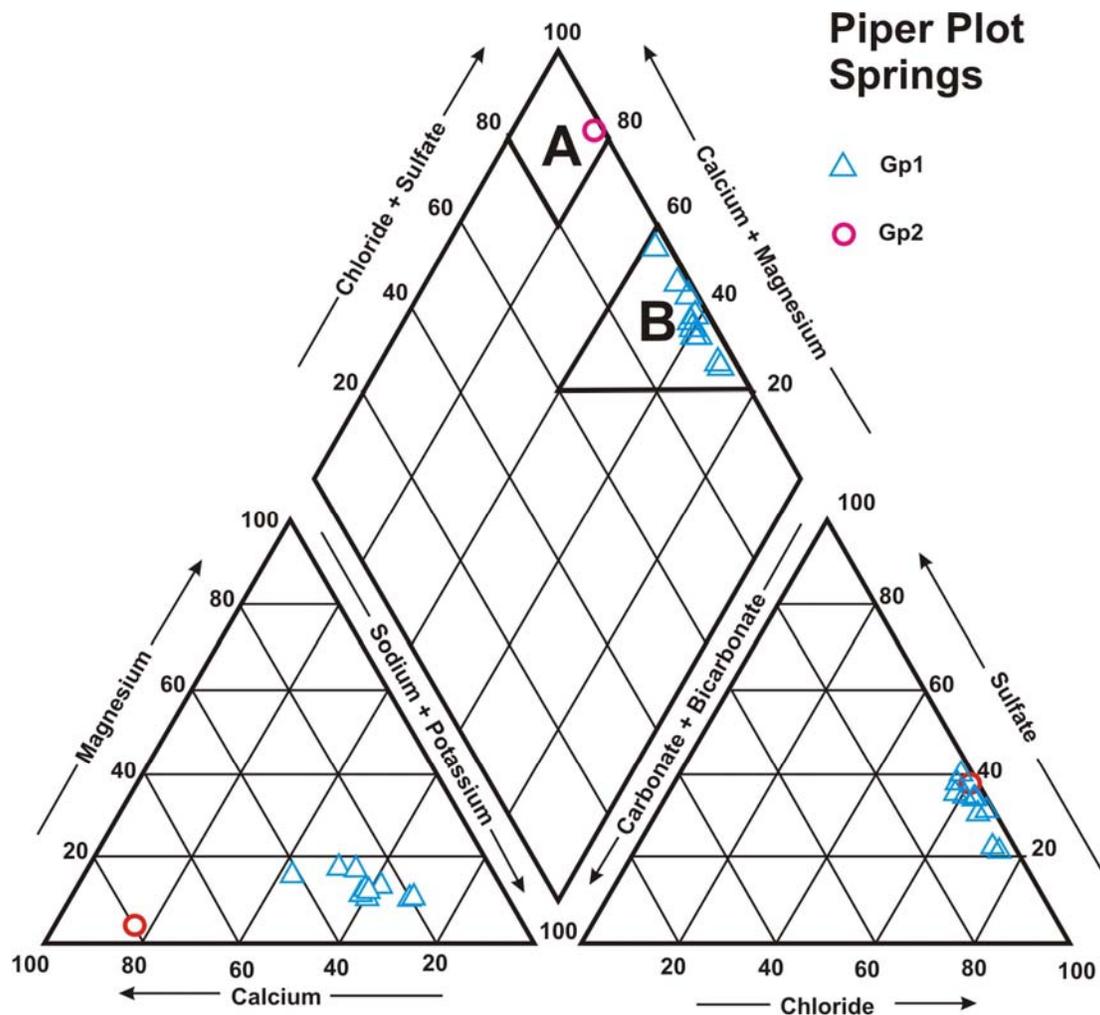


Figure 7: Piper plot of water samples from the springs. Gp1 = group 1, Gp2 = group 2. These groups were defined based on water chemistry of the springs.

The sinkholes and springs have similar water types; however, three of the sinkholes (SH 38, SH 7 and SH 3) contain Mg, which is nearly absent in all of the spring water samples. These results suggest that the sinkhole waters might be interacting to some extent with dolomite bedrock, which the springs are not interacting with. An alternate possibility is that the residence time of groundwater discharging from the springs is so short that there is not much time to dissolve the Mg-rich rocks.

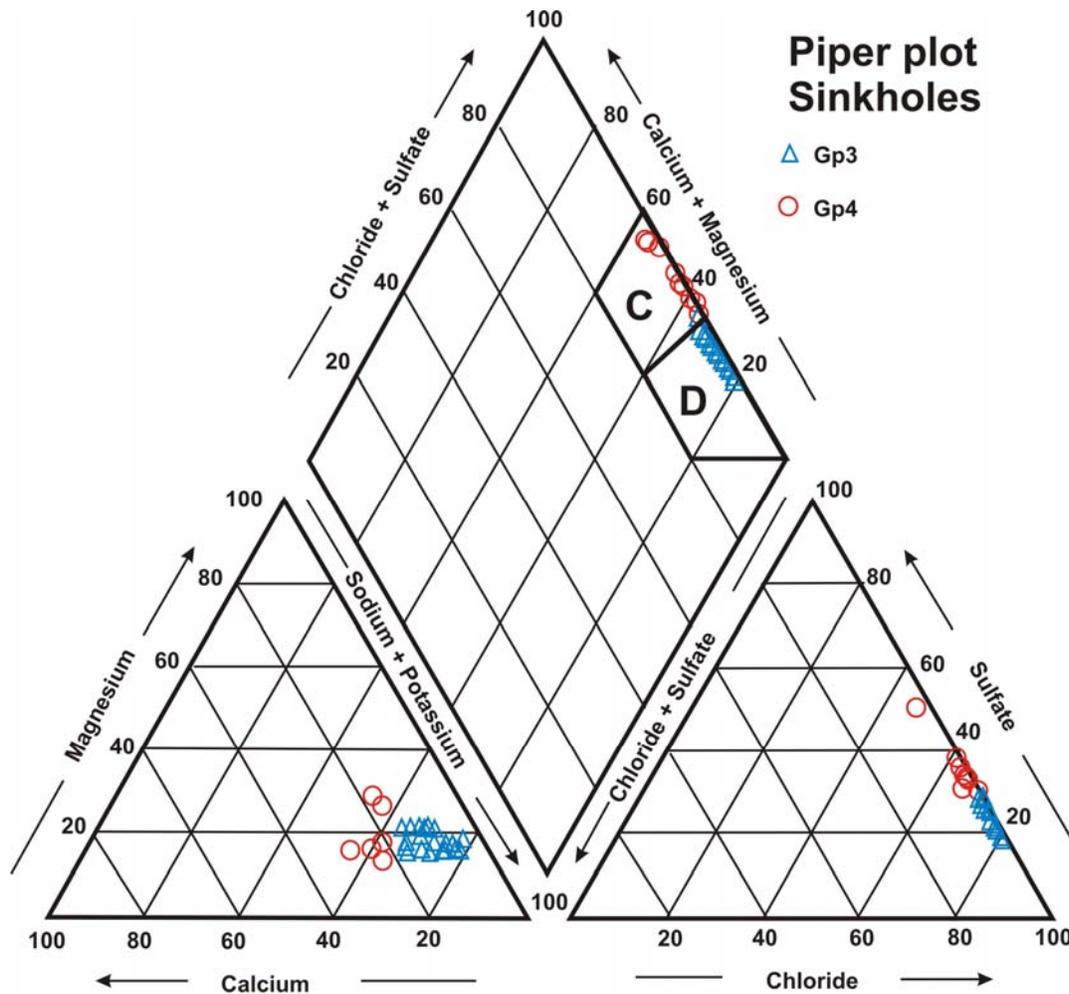


Figure 8: Piper plot of water samples from the sinkholes. GP3 = group 3, GP4 = group 4. These groups were defined based on water chemistry of the sinkholes.

Conductivity and total dissolved solids

Figures 3-8 illustrate that Cl, SO₄, Na and Ca make a large contribution to groundwater total dissolved solids (TDS) on the Refuge. The spatial distribution of conductivity and total dissolved solids (TDS) are illustrated by graduated circles in Figures 9 and 10. These figures show the conductivity and TDS of all the sampled sinkholes and springs. Conductivity is sensitive to variations in dissolved solids (mostly mineral salts). The degree to which the salts dissociate into ions, the amount of electrical charge on each ion, the mobility, and the temperature of the solution all have an influence on conductivity (UNESCO/WHO/UNEP, 1996). In other words, conductivity is a linear function of total dissolved solids and the mineral salt content of the groundwater (Hem, 1970; Freeze and Cherry, 1979). The conductivity and TDS distribution (Figures 9 and 10) show similar trends that may be caused by localized flow cells (restricted to particular areas). However, the conductivity and TDS values are generally low in the mid portion of the Refuge to the south and relatively high in the northeast portion of the Refuge. The high conductivity of the sinkhole waters to the north is probably caused by the gypsum and salt dissolution that formed the sinkholes and the associated release of Na, Ca, Mg, Cl and SO₄ into the water, hence the high conductivity and TDS in that area.

Conductivity Distribution

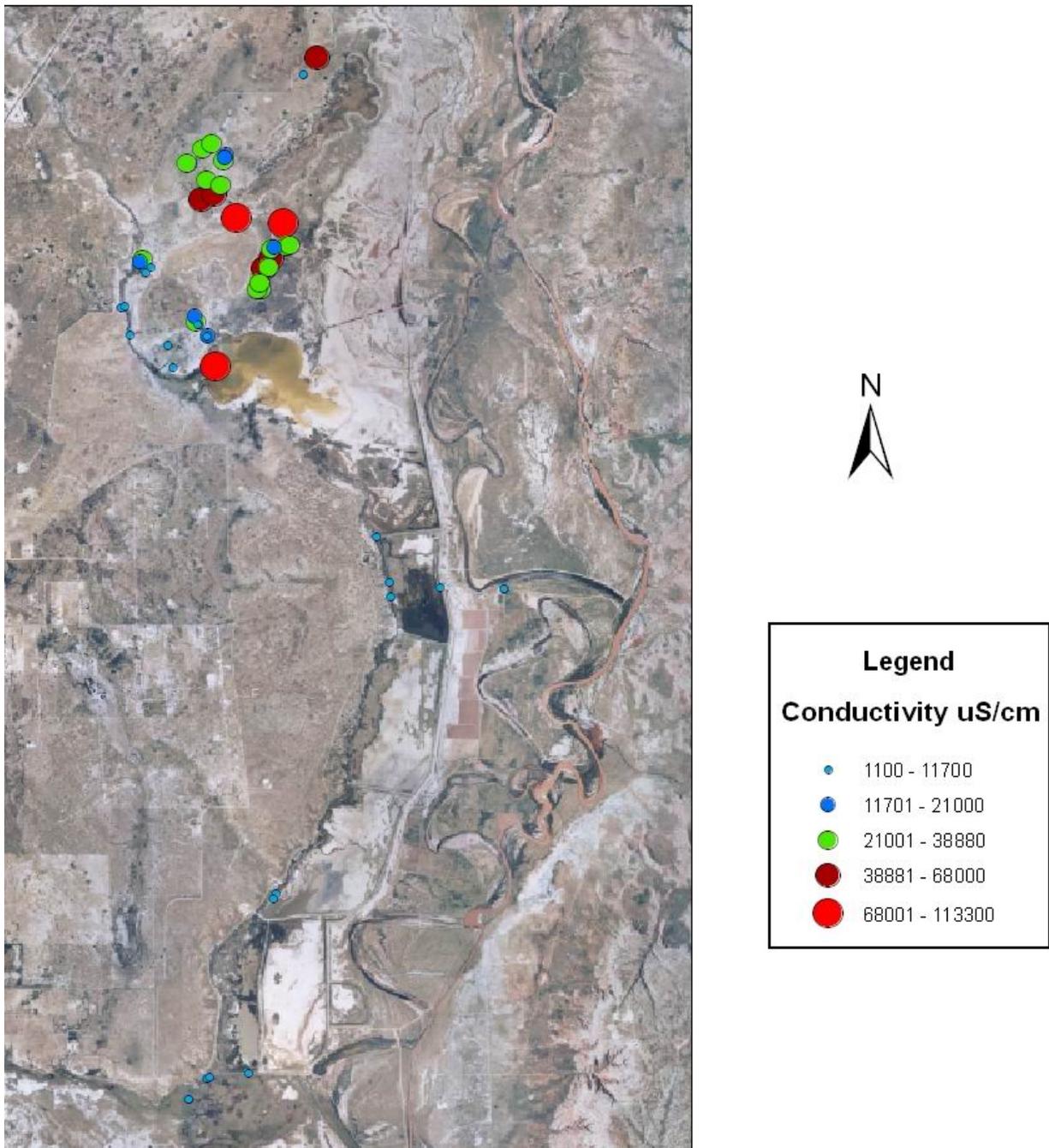


Figure 9: Distribution of conductivity in sinkholes and springs of BLNWR. Conductivity map is the same scale as sample location map (Figure 2).

Total Dissolved Solids Distribution

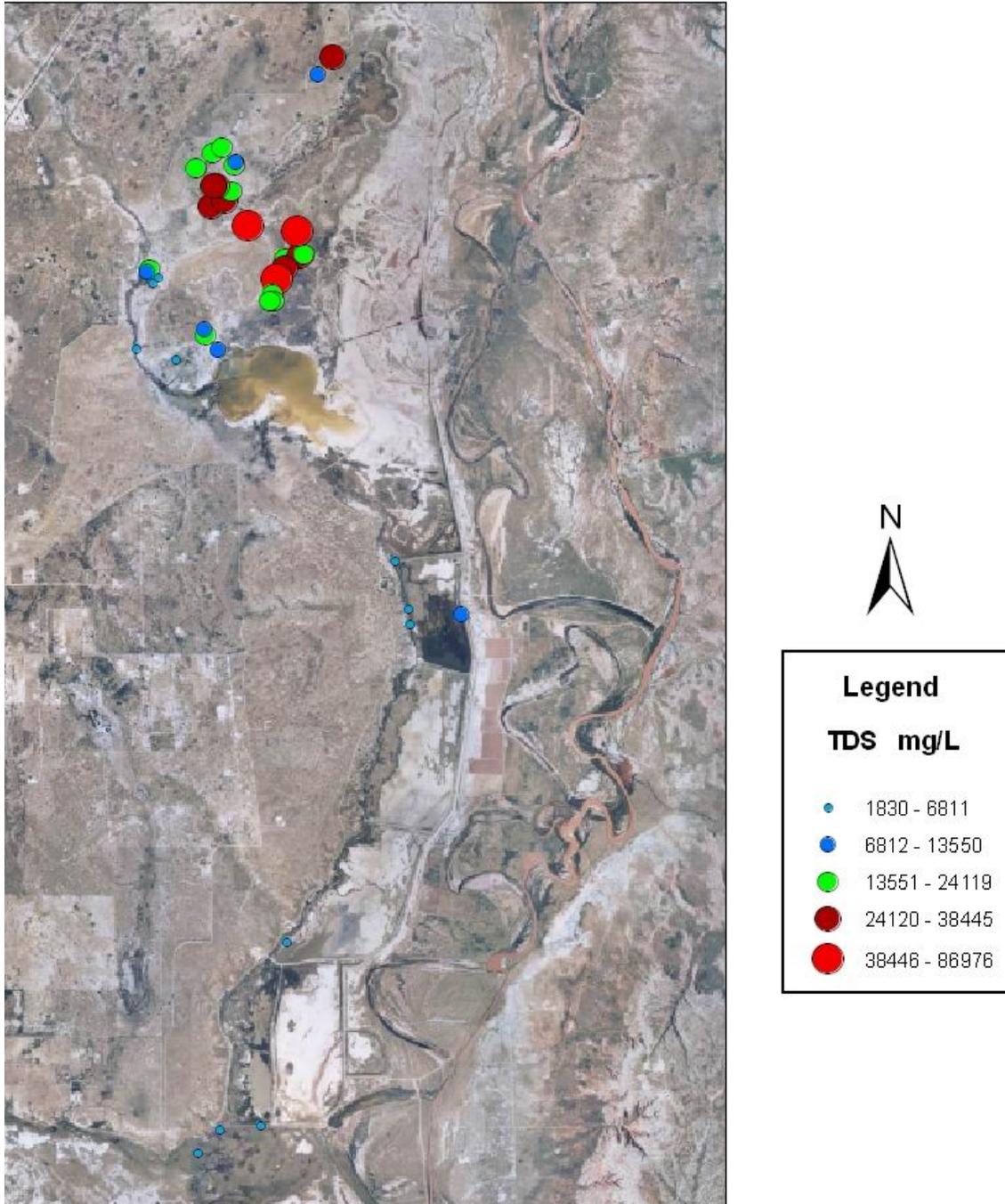


Figure 10: Distribution of total dissolved solids (TDS) in sinkholes and springs of BLNWR. TDS map is the same scale as sample location map (Figure 2).

pH Distribution

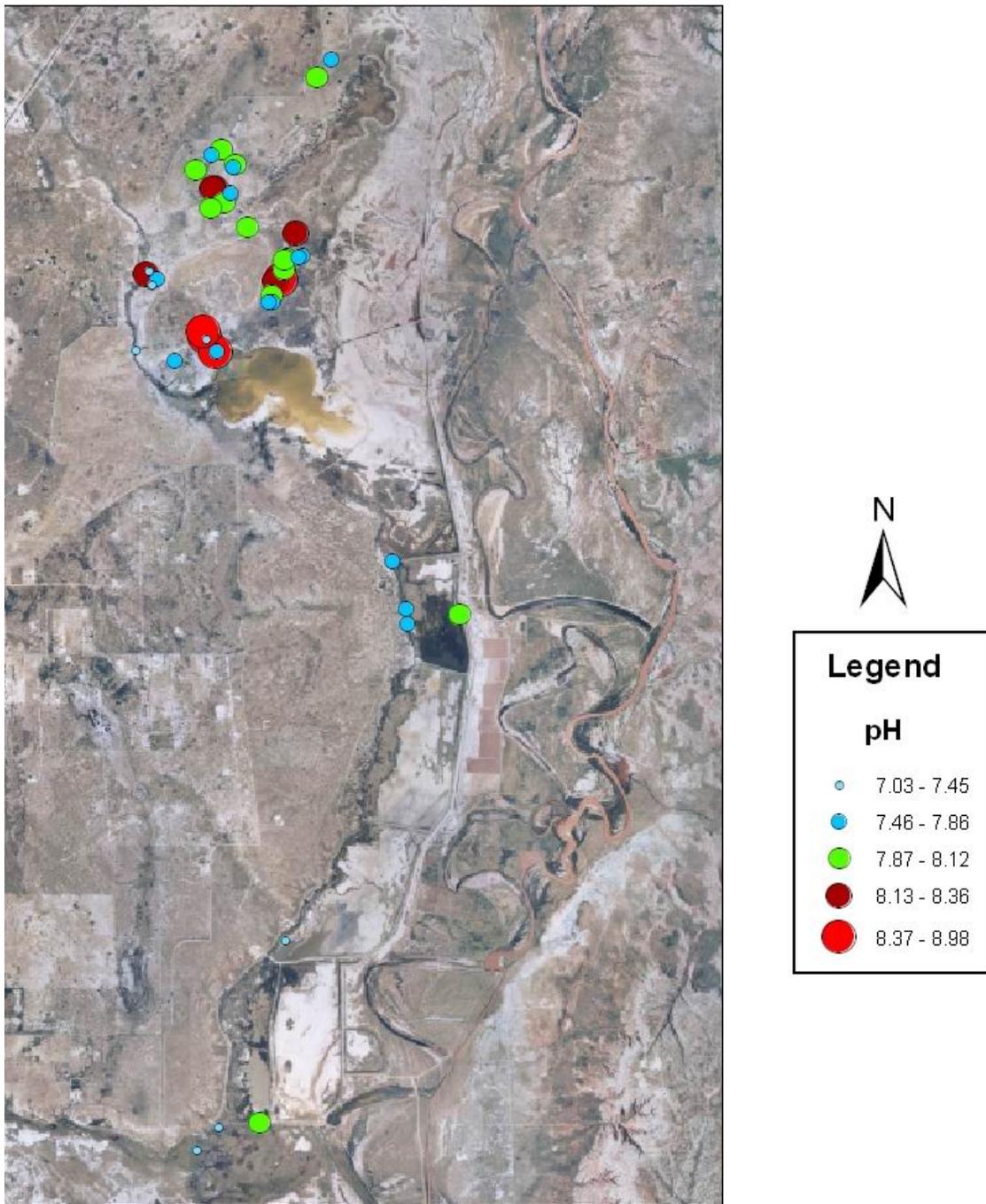


Figure 11: Distribution of pH in sinkholes and springs of BLNWR. pH map is the same scale as sample location map (Figure 2).

Bicarbonate Distribution

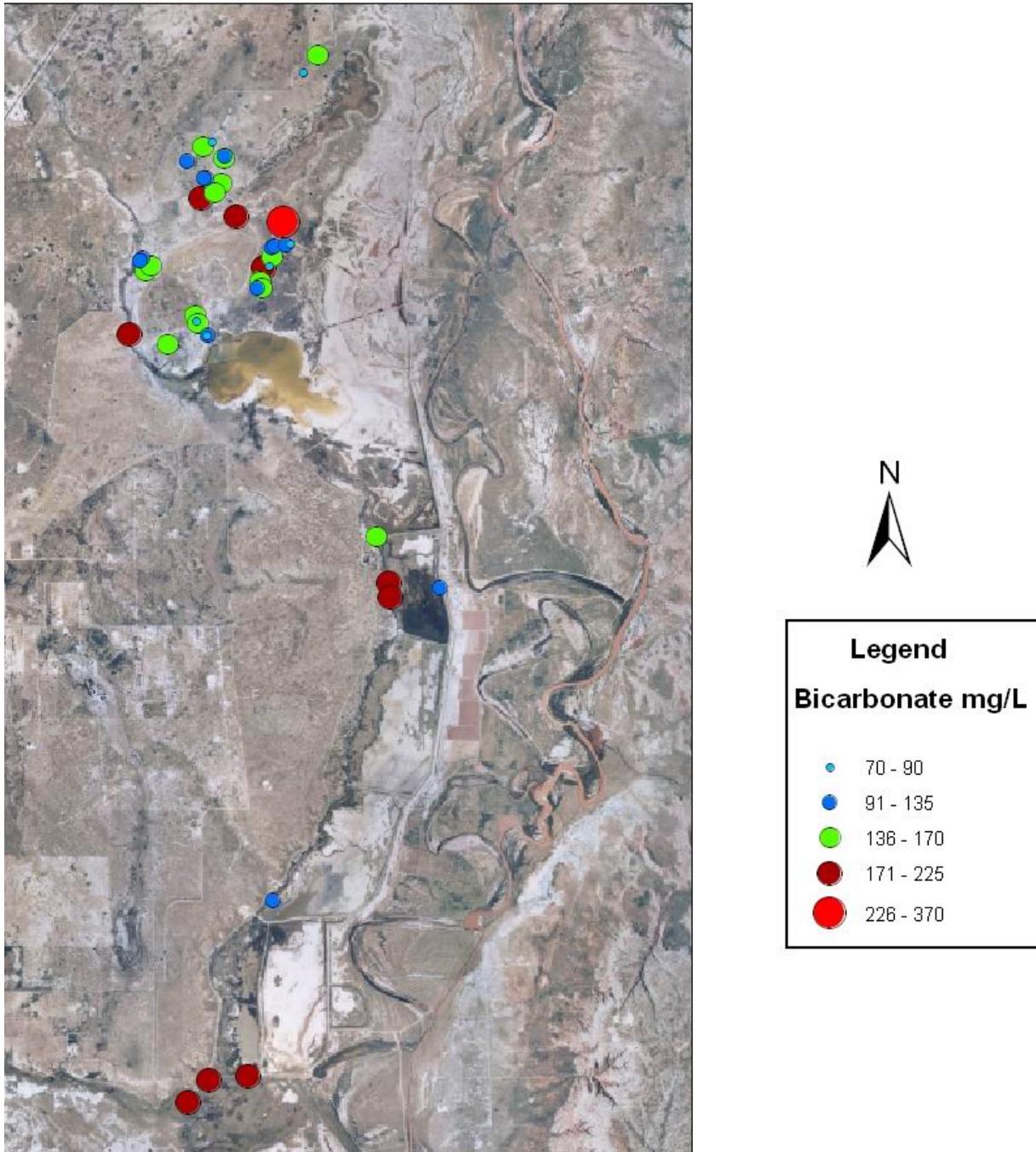


Figure 12: Bicarbonate distribution in sinkholes and springs of BLNWR. Bicarbonate map is the same scale as sample location map (Figure 2).

pH and Bicarbonate

Water is said to be either acidic or basic depending on the hydrogen ion concentration (pH) in the water. Hydrogen ions in water cause it to be acidic. The capability of water to neutralize acid, that is, to reduce the number of hydrogen ions in solution, is alkalinity. Carbonate and bicarbonate ions contribute to alkalinity. Earlier discussions of the ion content in the springs and sinkholes indicate relatively low carbonate and bicarbonate in the system compared to other anions in solution. Figures 11 and 12 show variations in pH and bicarbonate in the sinkholes and springs. There is relatively high pH in the north-central portion of BLNWR and relative low pH in the southern portion where most of the springs are located (Figure 11). The relatively high pH values are associated with the sinkholes, which also show relatively high alkalinity conditions (Figure 12). The alkaline conditions observed in the north-central portion of the refuge may be due to dissolution of limestone (CaCO_3) and dolomite (Ca, MgCO_3). These carbonate rocks consume the weak acid (HCO_3) in the system and control the low level of HCO_3 observed on the Stiff diagrams in Figures 5 and 6.

Surface Conditions Versus Depth

The chemical descriptions above are based on samples taken near the surface of sinkholes and springs. In some cases, major differences in solute concentration are noted when water is sampled at multiple depths. Some sinkholes, such as SH37, appear well-mixed, and retain a relatively uniform water column structure, with major ions, conductivity and pH reflecting parameters measured at the surface. However, water samples extracted from various depths in sinkhole SH21, for example, exhibit inconsistency with surface parameters and are noticeably stratified. Data collected from SH21 by NMSU researchers (W. Boeing and others) performing fish population surveys indicate that as one progresses further below the surface, the character of the water changes.

A geochemical survey of sinkholes conducted by UNM researchers (Premo and Crossey, 2008) suggests that while surface conditions are a good representation of total water chemistry for some sinkholes, not all may be characterized so simply. This stratification in the water column may be due to source water mixing, evaporative concentration, or varying supply of groundwater input, as well as biological effects.

Summary and Conclusions

During the course of this project, data were collected to learn about the spatial distribution of conductivity at BLNWR. Conductivity, TDS, pH and bicarbonate maps have been constructed from the water chemistry of springs and sinkholes at BLNWR. Piper plots and Stiff diagrams for the springs and sinkholes have been used to classify the water by hydrochemical facies and to indicate the relative proportions of different ions in the springs and sinkholes. Box and Whisker plots have also been constructed to show major chemical constituents in the two water bodies in the study area. These supplementary tools help explain the following trends found on the maps:

1. The springs have Ca-SO₄ and Na-Cl as the two principal hydrochemical facies in the area, while the sinkholes have Ca-Mg-SO₄ and NaCl-type waters. The principal water types for both the sinkholes and the springs depict water-rock interactions involving the dissolution of gypsum (CaSO₄) and halite (NaCl) by the recharging groundwater. The most significant difference between the two data sets is that the sinkholes are more concentrated in terms of ion chemistry than the springs. This phenomenon probably reflects in part greater evaporation in the sinkholes because of their larger surface area.

2. The average water chemistry of the springs indicates relatively high Na, Ca, Cl, and SO₄ but low Mg and HCO₃ concentrations, probably due to short contact time of the spring water with the bedrock (dolomite). The sinkholes however, show a halite rich water source. The “Mg-rich” water type that is associated with the sinkholes is not found in the springs. This observation reflects the fact that the springs have limited residence time with the “Mg-rich” rocks, hence relatively low concentrations.
3. Water in the sinkholes has a different chemical composition and higher TDS than water in the springs, and this difference is reflected in the spatial distribution of chemical species, pH and TDS (Figures 9 to 12). Conductivity and TDS values are generally low in the mid portion to the south where most of the springs are found and relatively high in the northeast part of the refuge.
4. pH values are relatively high in the north-central portion of the refuge and relative low in the southern portion where most of the springs are located. The higher pH values are associated with the sinkholes, which also show alkaline conditions. The alkaline conditions observed in the northern portion of the refuge may be due to dissolution of limestone and dolomite.
5. The strikingly different geochemistry of the springs and sinkholes may be the result of gypsum and salt dissolution processes that formed the sinkholes.
6. Chemical composition of the water in some sinkholes varies significantly with depth, reflecting varying degrees of source water mixing, evaporative concentration, volume of groundwater input, as well as biological processes.

Differences in water chemistry between the springs and sinkholes very likely influence aquatic species distribution. It would require a more geochemically and biologically-focused investigation to determine precise relationships between water chemistry and species distribution, but this report should lay the groundwork for very fruitful and productive future work by geochemists and wildlife biologists in delineating aquatic species and their location-specific relationships at Bitter Lake National Wildlife Refuge. Recognizing the complexity of these small lakes and springs is essential in understanding the geochemical story of the rocks, water, climate and biota contributing to observed conditions.

Future work

We suggest a more detailed geochemical study of individual sinkholes to better model the water rock interaction at BLNWR. This calls for monitoring seasonal changes in water chemistry for an extended period of time (years). Such a detailed study will aid in determining the mechanisms controlling groundwater chemistry.

Other geochemical tools such as stable isotopes (oxygen, deuterium, carbon and sulfur) are needed to better constrain the source of water causing the high conductivity in the sinkholes and springs at BLNWR.

Although the purpose of this study is to determine the spatial distribution of conductivity/dissolved solids and other chemical species, it is quite likely that the variable mineral content has some influence on species distribution. I suggest working with a biologist to more precisely determine those relationships.

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