

# NM WRRRI Student Water Research Grant Final Report

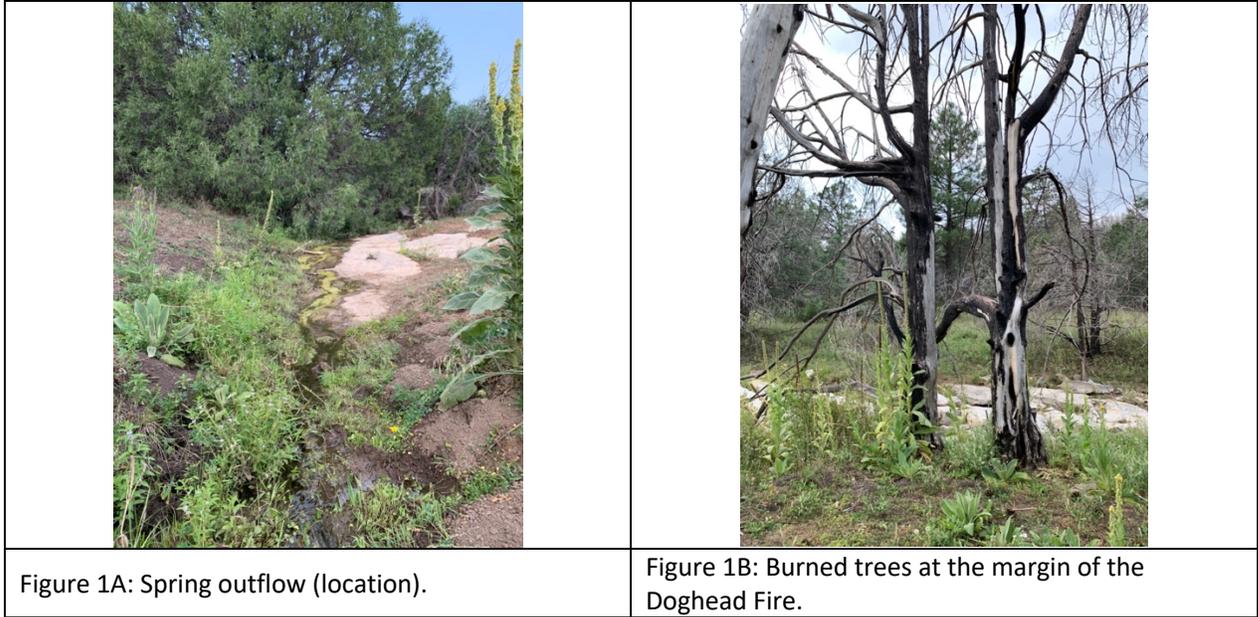
Date: 7/18/2022

1. **Student Researcher:** Naomi DeLay  
**Faculty Advisor:** Dr. Laura Crossey
2. **Project title:** Hydrogeochemical Analysis of Springs in the Cibola National Forest: Implications for Springs/Wetlands Sustainability & Geochemical Response to Forest Fire

### 3. **Problem**

Aridland springs are valuable hydrologic resources to ecologic communities of the southwestern United States. Springs and associated wetlands are vital ecosystems hosting diverse hotspot habitats (Stevens and Meretsky, 2008; Frus, 2016). These systems can be highly susceptible to the history of land use and forest fires. Historically, these springs have been used by livestock and wildlife. The water quality of these springs has a large influence on the ecosystems that depend on them (Stevens and Meretsky, 2008). New Mexico is a region with many examples of springs and wetlands threatened by pressures including increased groundwater use, impending climate change, and habitat loss due to land use change and wildfires. Cibola National Forest, situated in north-central New Mexico, includes many disparate land management units that are faced with several land challenges. In 2016, the Dog Head fire swept through much of the Cibola National Forest in the Manzano mountains (USDA, 2016), affecting local ecology and hydrology. The springs and surface waters in and adjacent to the burned area provides a focus for this research. The USFS has been documenting spring and wetland status by incorporating springs assessment protocols over the past five years (see Frus, 2016 and references therein). This work builds on recent regional springs assessments in the Sandia and Manzano mountains, (Frus, 2016). This study focuses on the geochemical characterization of these springs, and how the sustainability of these springs is being affected by wildfire and land management decisions.

Sustainability of spring systems is based on understanding the present conditions and impacts or threats to the flow system or groundwater. The sustainability is measured through seasonal monitoring and evaluating the water quality. Seasonal monitoring of the hydrology and hydrochemistry of Ojo del Rancho del Medio (OM) and Ojo del Rancho del Medio West (OMW), springs in the Mountainair District within the Manzano mountains, assist in quantitatively evaluating the water quality and understanding the flow paths, mixing scenarios, residence time, and recharge mechanisms of these two springs. The main objective of this portion of the overall study is to complete total solid chemistry and batch mobility experiments on ash, soil, sediments, and bedrock from the study area to determine and characterize the sources of mobile trace elements released into spring waters with particular focus on the mobility of ions from ash deposits of the Dog Head Fire (2016). The results of extraction experiments performed on these surface materials helps develop an understanding of how ash within the landscape affects the recharge or surface flow of these spring systems. Our main hypothesis is that the recent Dog Head Fire ash and material will have an impact on the water composition of the springs, and they will exhibit different trace element characteristics than other regional springs. See Figure 1 for photos of the field site.



**Purpose of Study & Research Goals**

The three specific goals of the study are to (i) use geochemical tools to characterize water quality and understand sustainability in selected springs of the Manzano Mountains (ii) characterize the hydrologic flow paths and spring-flow regions of the Manzano spring waters, and (iii) sample local surface materials and perform mobility experiments to identify sources of solutes and characterize trace elements mobilized in response to fire ash deposits.

The purpose of this study is focusing on the third research goal which is to identify sources of solutes and characterize trace elements mobilized in response to fire ash deposits to understand the effects of forest fire on water quality. End-members of possible ion sources will be determined through total chemistry analyses of the ash, soil, sediments, and bedrock within the study area. We can gain an understanding of the lithological and mineralogical sources within this watershed by analyzing samples of the bedrock, sediment, and soil and post-fire material from the Dog Head ash deposits for total chemistry (including the following elements Al, Ar, B, Be, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, V, Zn, etc.) (Blake et al., 2020; Blake et al., 2015). Certain metals like calcium, aluminum, manganese, magnesium, nickel, copper, zinc and iron can be mobilized into the waters from upgradient based on previous stream studies (Cerrato et al., 2016; Costa et al., 2014; Burton et al., 2016; Abraham et al., 2017; Pereira and Úbeda, 2010; Sherson et al, 2015; Murphy et al., 2015). The mobilization of solutes such as these can have adverse effects on water quality. Mobility experiments are used to understand the natural attenuation and mobilization of aqueous solutes through an ecosystem after saturation from storm events (Burrows and Peters, 2013). These experiments tell us about the total amount of aqueous ions that can release into the environment and identify the sources of significant reservoirs of mobile ions (Burrows and Peters, 2013). Additionally, we will compare the results of these experiments to the season water quality data (major and trace element chemistry) and the monitoring conducted on these selected springs as well as other springs within Cibola National Forest.

#### 4. Methodology:

This study is based on a multidisciplinary approach to characterizing the water quality through monitoring of springs by collection of hydrochemical and physico-chemical data and sampling, analysis of major and trace ion chemistry, and stable isotope analyses to quantitatively evaluate water quality and better understand the sustainability of these spring systems. During this study, seasonal monitoring started in the summer of 2019 and finished the fall of 2021. Water samples were collected quarterly for analyses of major ion chemistry and stable isotopic analysis of deuterium and oxygen. We deployed water quality field parameter sensors over limited timeframes (between August and October of 2020 and from March to September 2021). The above methods are currently funded under an agreement with the USFS to assess these spring systems. To determine whether the recent Dog Head Fire ash and material have had an impact on the water composition of these springs, we have and will be completing total/bulk chemistry analysis on the solids and conducting batch mobility experiments to characterize the water quality and the mobility of select ions. These methods of this study are the focus of this funding.

*Solid Sampling.* Surface materials were collected from the study area include samples of non-weathered sediment above gradient of the springs, exposed bedrock, and samples of ash along tributaries of the springs both in various fire severity zones and soil types (See Figure 2). A total of 11 solid material samples were collected from the summer to the fall of 2020: 1 composite bedrock, 1 composite sediment sample, 8 ash samples, and 1 soil sample. Ash was sampled from four soil units as determined by the USDA Soil Survey, including Witt loam, Wilcoxson stony loam, Turkeysprings stony loam, and Laporte-Rock outcrop complex. Ash samples from various soil burn severities ranging from low to high severity and were collected from *Pinus ponderosa* (ponderosa pine) and *juniperus scopulorum* (Rocky Mountain juniper).

*Bulk Chemistry Analysis.* To extract elements out of solid samples for bulk chemistry analysis, acid rock digestion was performed on samples. Before rock digestion, the solid samples were dried, crushed, and sieved to 100 mesh powder (Blake et al., 2020; Blake et al., 2015). During digestion,  $1 \pm 0.0005$  grams of solid samples was stepwise digested using aqua regia ( $\text{HNO}_3$  and  $\text{HCl}$ ) and 30% hydrogen peroxide (Blake and Peters, 2015; Blake et al., 2020). After rock digestion was completed, samples were filtered and diluted as a liquid and evaluated for total chemistry (including the following elements Al, Ar, B, Be, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, V, Zn, and other elements) using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) analyses (Blake et al., 2020; Blake et al., 2015). Additionally, trace element analysis was conducted using Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS). All laboratory analyses will be conducted in the Analytical Geochemistry Laboratory at UNM EPS. Currently, 8 selected ash samples have been prepped, total digested, and analyzed for ion analyses using ICP-OES. Soil, bedrock, and sediment samples have been prepped, digested, and are currently being analyzed. Additionally, ICP-MS analyses are being conducted on all solid samples as well.

*Batch Mobility Experiments and Analysis.* Due to the scope of this funding, 6 ash samples were selected to perform mobility experiments on. Composite samples of these ash samples were used in the batch experiments to evaluate the mobility of elements that reflect the environmental conditions of the study area. We compare the results of the total chemistry analyses and mobility experiments to determine the sources and availability of the mobile ions. The reagents for the mobility tests included (1) deionized water, (2) a dilute 10mM sodium bicarbonate, and (3) a 2mM acetic acid solution (Blake et al., 2020; Blake et al., 2015). The composite samples were subsampled in triplicate for each reagent. Each subsample was weighed to  $0.15 \pm 0.005$  grams and reagent added to a total volume of 50 mL of a specific reagent listed above (Blake et al., 2020;

Blake et al., 2015). The samples were placed on a rotator (shown in Figure 3 below) for time periods of approximately 1.5 hour, 5 hour, and 24 hours, and additional aliquots were sampled at each of these time periods (Blake et al., 2020; Blake et al., 2015). The quality of all chemical analyses were checked using triplicate samples and standard reference material were used during the total-sediment chemistry and mobility experiment analyses using the ICP-OES and ICP-MS. All aliquots collected during these mobility experiments from the 6 ash samples have been analyzed using ICP-OES and ICP-MS.



Figure 3. Batch mobility experiment procedure shown above. The image shows 50ml tubes on a rotator during the 5-hour time step of the experiment.

## 5. Results

The final results and conclusions of this study will be included in the second chapter of the complete thesis. The results from this study include the ICP-OES and ICP-MS results for the total/bulk chemistry of 8 ash samples and 162 mobility experiment samples. Results for the ICP-OES are the concentration of ions in mg/L adjusted for sample weight and reagent volume to assess the amount of each element released (in milligrams) per gram of sample. ICP-MS results are in  $\mu\text{g/L}$  and similarly adjusted by weight and volume. These corrections are completed after the analyses are completed.

The ICP-OES results for the total chemistry of the ashes indicate the highest concentration in Ca, Fe, K, Mg, Na, and Si. There was also high concentration for elements such as Al, Ba, Mn, Mo, Sb, Sr, and Ti. Elements such as Ag, As, B, Bi, Cd, Co, Cr, Cu, Li, Ni, Pb, Se, U, V, and Zn measured below detection for the ICP-OES.

The ICP-MS analyses for the mobility experiment samples were highest for elements such as Ba, Cu, Mn, Ni, Sr, Ti, and Zn. Additionally, there were also lower concentrations measured for As, Cd, Cr, Li, Pb, and Se. Elements such as Ce, Co, La, Mo, Sn, U, and V were all below detection using the ICP-MS. The highest concentration of potassium was measured from the mobility experiments for the second reagent, 10mM sodium bicarbonate acid solution. Other highest concentrations were observed from samples that were mixed with 2mM acetic acid solution, especially Ca and Si.

Trace element analyses of these mobility experiment samples indicate that Mn, Li, Zn, Cu, Ni, Ti, Ba, and Sr are the most highly mobile elements released from the ash. Additionally, elements such as Se, Pb, Cd, and Cr are released in lower concentrations. Reagent 2 and 3 (dilute 10mM sodium bicarbonate and 2mM acetic acid solutions, respectively) contain the largest concentration of solutes.

Figures 4 shows graphic representations of the results for selected elements. All extraction results, total elemental determinations and statistical analyses will be provided in an appendix in the final thesis, anticipated in December, 2022.

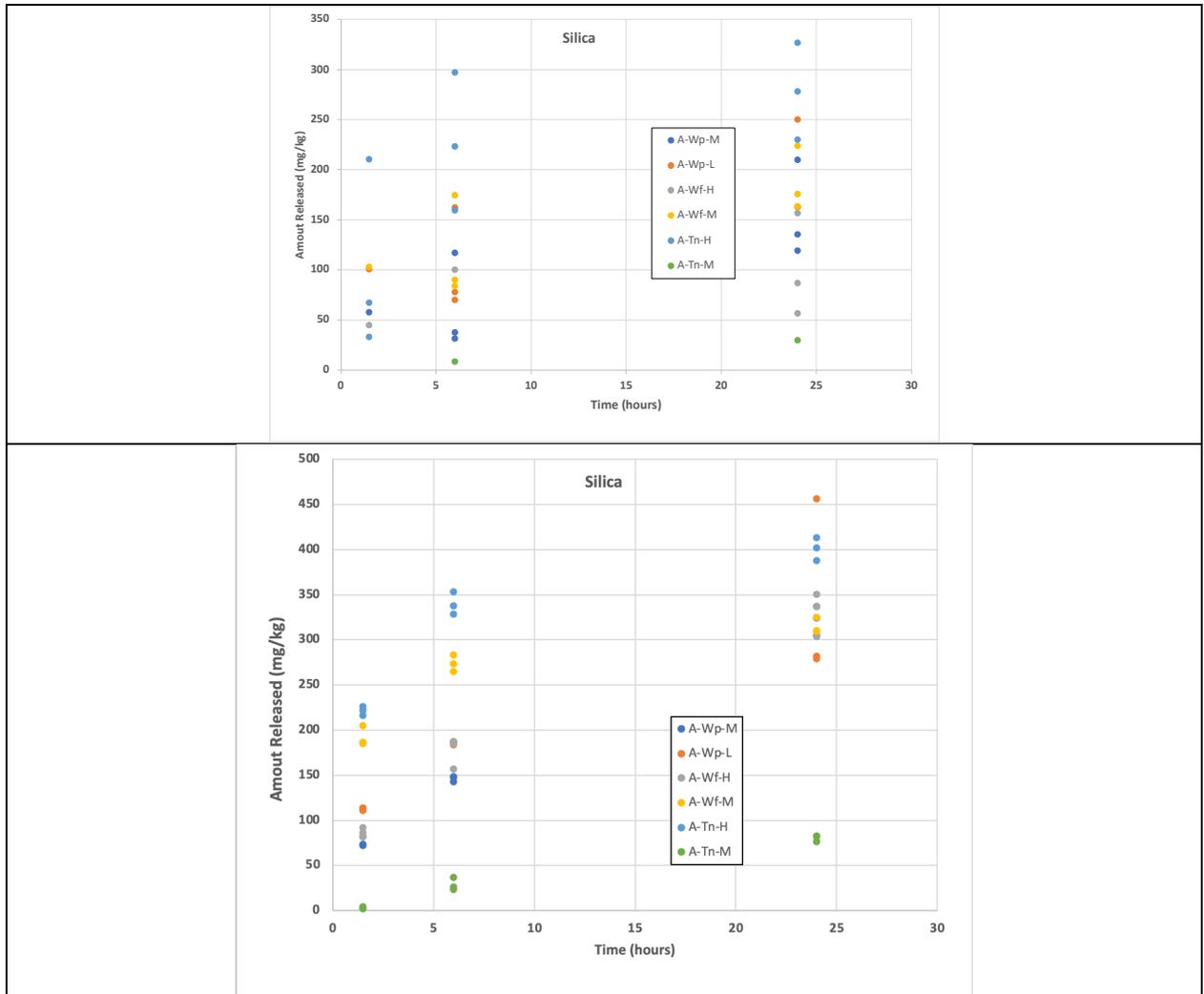


Figure 4: Mobility results for Si. Upper panel represents deionized water reagent. Second panel represents acetic acid reagent. Vertical axis represents the amount of the element released in mg/kg of ash. The x-axis represents the time elapsed during the mobility experiment in hours. Each series (color) represents a different ash sample, where H indicates ash from a high-severity burn, M=moderate, and L=low. Samples were run in duplicate, and in many cases triplicate to assess reproducibility. See text for discussion.

## Significance

The Dog Head fire is a recent disturbance which will be of significance when analyzing the quality of these natural waters. There will be some uncertainties studying this aspect of the study due to the lack of pre-fire water quality measurements. Therefore, by conducting these mobility experiments and characterizing the total/bulk chemistry of the local surface materials or solids we can better understand the water quality of springs in response to forest fires. Due to atmospheric warming, the frequency and severity of forest fires have increased. Based on previous work on streams and other water bodies, wildfires can change the structure of watersheds in influencing the quantity and quality of waters (Dahm, 2015; Sherson et al, 2015). The methods used in this study hope to provide methods to better understanding how springs and other water sources are affected by environmental events like forest fire. Conducting these mobility experiments will assist in determining how mobile ions might be extracted in these systems. These experiments serve as a representative a model for the interactions with real world reagents and local surface materials, particularly the Dog Head ash deposits. The main problem to address is to determine how the extraction of ions from these surface materials is affecting the recharge or surface flow of these spring systems. Total chemistry analyses provide information on the bulk chemistry of possible endmembers for sources of solutes to better understand the results of the mobility experiments and determine which sources have the biggest impact on the quality of these spring waters. Additionally, we can compare the ongoing analyses of the spring waters throughout this study with the water quality of other regional springs. In doing so, we will be addressing our main hypothesis.

By understanding the conditions and impacts to the flow and water quality of these springs, we can better understand the sustainability of these spring systems. These mountain recharge springs are important water resources for the local communities and wildlife in these areas. Livestock and wildlife have historically depended on these springs, so the quality of our springs affect food webs and the health of these ecosystems. This study will provide valuable baseline water quality information on these springs in an area with little historical data. Through understanding the threats to the preservation of these springs from livestock damage, reduced precipitation, and forest fire, we can better understand the sustainability of these springs to aid in management decisions in the future. This study will provide valuable data to inform the USFS on their land management decisions.

## **6. Benefits**

This grant provided invaluable funding for the purpose of examining the effects of forest fire on the water quality of airland springs in the Manzano Mountains. These springs are important components for the local hydrology and water quality of local communities that depend on these local recharge areas. Spring assessments and monitoring has been funded by the USFS for Cibola National Forest through cooperation with previous research with students. The USFS has been documenting spring and wetland status by incorporating springs assessment protocols over the past five years. This work builds on recent regional springs assessments in the Sandia and Manzano mountains. Because of the Dog Head Fire, understanding how these spring systems are affected by forest fire will be an important aspect of this study.

Research has not been conducted on the effects of forest fires on spring waters in the Cibola National Forest. Previous workers have completed research on other bodies of water such as streams and rivers. This research will provide invaluable research on spring waters that affect recharge to areas below these spring fed headwaters, especially due to this is a recent disturbance to the ecosystem. Not only does this research provide important baseline water quality for springs

in these regions, but it is also the first study using mobility experiments methods based on ash in the Cibola National Forest.

The significance of study is that it will provide valuable information on how spring waters are affected by forest fire. The methods used in this study might be applied in further research on the effects of environmental events like forest fire on water sources. Conducting these mobility experiments will assist in determining how mobile ions can be extracted out of a system by modeling the interactions with real world reagents and local surface materials, particularly the Dog Head ash deposits. By understanding the conditions and impacts to the flow and water quality of these springs, we can better understand the sustainability of these spring systems. Additionally, it will add additional information for land managers with the USFS interested in the water quality of springs in the Cibola National Forest.

**7. Budget:**

This funding has been used primarily toward the costs of analyses and supplies required to conduct lab analyses on total digested solid samples and analyze subsampled aliquots collected during mobility experiments. Supplies include the cost of sample preparation such as the cost of reagents and consumables. The costs associated with total/bulk chemical analysis, include sample preparation, acid digestion, and total/bulk solid chemistry ICP-OES and ICP-MS analysis. Mobility experiment costs include ICP-OES and ICP-MS analyses and material supplies required to conduct the experiments (centrifuge tubes, reagents, etc.). Representative ash samples have been prepped, undergone total digestion, and conducted analysis on the ICP-OES. Subsampled aliquots from these experiments have been analyzed for major ion chemistry through ICP-OES. The subsamples from these experiments have also been analyzed for trace elements using ICP-MS. The rest of the budget was allocated for ICP-MS costs and additional sample.

The bulk of this funding request has been directed toward the costs of major ion and trace element analyses using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) and Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS) analyses as described in the methods and above. ICP-OES analysis cost is \$15 per sample, and ICP-MS analysis costs range from \$25 to 40 per sample. All laboratory analyses were conducted in the Analytical Geochemistry Laboratory at UNM EPS at the standard fee schedule.

<b>Item Number</b>	<b>Budget Item</b>	<b>Amount charged to WRI</b>	<b>Total Amount Budgeted</b>	<b>Amount Requested from WRI</b>
1	Supplies: Sample Preparation, Materials & Consumables	45	210	100
2	Services: Laboratory ICP-OES Analyses	2805	4000	2500

3	Services: Laboratory ICP- MS Analyses	4460	6000	4900
4	Tritium Analyses	190	0	0
<b>Total:</b>		<b>7500</b>	<b>10210</b>	<b>7500</b>

## 8. Presentations

DeLay, N., Crossey, L. J., and Crowley, L., 2020, Hydrogeochemical Analysis of Springs in the Cibola National Forest: Implications for Springs/Wetlands Sustainability & Geochemical Response to Forest Fire: Proceedings of the 66<sup>th</sup> NM WRRRI Annual New Mexico Water Conference, Abstracts.

DeLay, N., Crossey, L. J., and Crowley, L., 2020, Hydrogeochemical Analysis of Springs in the Cibola National Forest: Implications for Springs/Wetlands Sustainability & Geochemical Response to Forest Fire: Proceedings of the 65<sup>th</sup> NM WRRRI Annual New Mexico Water Conference, Abstracts, p. 28.

DeLay, N., Crossey, L. J., and Crowley, L., 2020, Hydrogeochemical Analysis of Springs in the Cibola National Forest: Implications for Springs/Wetlands Sustainability & Geochemical Response to Forest Fire: Geological Society of America Abstracts with Programs, v.52, no. 6, doi: 10.1130/abs/2020am-356635.

## 9. Publications or reports in preparation:

- I completed a report for the USFS for the first chapter of my thesis on Cibola National Forest Spring Inventory covering the Hydrogeochemical and Biological Analysis of Spring Waters, Sandia and Manzano Mountains, New Mexico
- I intend on publishing this work (second chapter of thesis) with the journal Environmental Earth Sciences and my first chapter of my thesis in Applied Geochemistry

## 10. Acknowledgements:

Many thanks to my adviser, Dr. Laura Crossey, for her continued support and mentorship. Much of my thesis work is supported by the US Forest Service Co-operative agreement 10-CS-11030300-036 through the team work of my adviser and Livia Crowley, Forest Hydrologist/ Watershed Program Manager, with Cibola National Forest and Grasslands. I also thank Dr. Johanna Blake at the USGS Water Science Center in Albuquerque who provided assistance in the field, as well as discussion and guidance throughout this project. In addition, I would like to thank Dr. Abdulmehdi S. Ali and his staff at the Analytical Geochemistry Laboratory at UNM EPS for their help and guidance with the water analyses associated with this project. And lastly thanks to Laura Burkemper and Nicu-Viorel Atudorei for their work at the Center for Stable Isotopes at UNM for their assistance on water analyses on the other aspect of my thesis work.

### 11. Special recognition awards

2021 NMGS Robert Wellnitz Scholarship of \$1,000

2020 NMGS Beverly Wellnitz award of \$500

### 12. Degree completion and future career plans

Despite some delays from the COVID pandemic, it is my hope to complete my MS in Earth and Planetary Sciences at the University of New Mexico during the fall of 2022. My plan for my future career is to continue working in water quality within the community of Albuquerque. I am interested in working with agencies like the USGS, the USFS, and other private companies on water conservation, remediation, and reclamation with particular interest in projects that address mining legacy and post-fire effects on our water systems in New Mexico.

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