NM WRRI Student Water Research Grant Final Report

1. Student Researcher: William Weaver
   Faculty Advisor: Dr. Lambis Papelis

2. Project title: Pore-Scale Transport of Strontium and Chromate During Dynamic Water Content Changes in the Unsaturated Zone

3. Description of research problem and research objectives:

Dynamic water content changes in the unsaturated zone caused by natural and manmade processes, such as evaporation, rainfall, and irrigation, have an effect on contaminant mobility. In general, in the unsaturated zone, evaporation causes an increase in contaminant concentrations, potentially leading to sorption of contaminants on aquifer materials or precipitation of crystalline or disordered phases. On the other hand, an increase of water content may result in dissolution of precipitated phases and increased mobility of contaminants. For this work, strontium was selected as a surrogate for strontium-90, a cationic radioisotope and a by-product of nuclear reactions. Chromate (Cr^{VI}) was selected because of its known mobility in the environment, being a carcinogen, and a good surrogate for an anionic contaminant. The overall objectives of this study are:

- Determine the oxidation state of sorbed or precipitated on sand strontium and chromate using spectroscopic techniques, such as x-ray photoelectron spectroscopy (XPS).

- Develop a quantitative model for the transport of strontium and chromate through sand under dynamic water content conditions, as a function of strontium concentration, chromate concentration, pH, and ionic strength.

- Determine the degree of reversibility of the precipitation or sorption processes.

- Determine whether the duration of dry periods affects the reversibility of the precipitation or sorption processes.

4. Description of methodology employed.

The column experiments involve weighing quartz sand into a 6.9 cm^3 column. For each experiment, a breakthrough curve for bromide, a conservative tracer, was completed under saturated conditions. The quartz sand was exposed to a range of strontium concentrations, chromate concentrations, pH, and ionic strengths, using a syringe pump at flowrate of 0.5 mL/min. The dynamic water content was determined using an automated device for rapidly measuring the hysteretic capillary pressure—saturation relationship, followed by ambient air evaporation, and gravimetric water content measurement. Strontium concentrations and chromate concentrations were measured using inductively coupled plasma mass spectrometry (ICP-MS). The distribution of strontium and chromate on quartz sand grains, inside the column, will be determined using an extraction procedure and ICP-MS. Furthermore, reversibility (column) experiments include two types involving: (1) saturated and unsaturated phases and (2) only saturated phases:

- (1) This reversibility experiment was conducted by introducing the following, at a constant flowrate of 0.5 mL/min: a background ionic strength solution, then a solution at a specific pH value, strontium or chromate concentration, and ionic strength, followed by a draining phase, then an evaporation phase, and repetition of the above cycle one more time.

- (2) This planned reversibility experiment will be conducted in a similar way to the experiments described above, but without the draining and evaporation phases of the experiments, in other words, only under saturated conditions.

Flow interruption experiments were conducted to determine whether equilibrium conditions existed for a given flowrate. Batch sorption experiments were conducted to determine the conditions yielding optimum sorption. X-ray photoelectron spectroscopy (XPS) is planned to determine the oxidation state of strontium and chromate sorbed or precipitated on quartz sand.

5. Description of results; include findings, conclusions, and recommendations for further research.

Based on flow interruption experiments, it was determined that strontium sorption does not reach equilibrium, under the experimental conditions used; however, chromate sorption does reach equilibrium under similar experimental conditions. The reversibility experiments indicate that the sorption and/or precipitation of strontium are reversible; for example, Figures 1 through 8 display two different reversibility (column) experiments, with the following parameters: pH 5.0, strontium ion concentration 10^{-4} M, and ionic strengths 10^{-3} M and 10^{-1} M $NaNO_3$. Figures 1 and 5 show that the initial breakthrough is dependent on ionic strength: 4.5 pore volumes for 10^{-3} M $NaNO_3$ and 1.5 pore volumes for 10^{-1} M $NaNO_3$, respectively. Figures 3 and 7 show that the second breakthrough is also dependent on ionic strength: 5 pore volumes for 10^{-3} M $NaNO_3$ and 1.5 pore volumes for 10^{-1} M $NaNO_3$, respectively. Figures 2, 4, 6, and 8 show metal ion elution during reversibility (column) experiments; desorption or dissolution does not appear to be controlled by ionic strength.

Research already performed indicates that sodium in higher concentrations (10^{-1} M) can compete with strontium for sorption sites. However, at low sodium concentration (10^{-3} M) substantially more pore volumes were required to achieve breakthrough. The sorption experiment results indicate that, for both strontium and chromate, the greatest fractional sorption occurs at the lowest molar concentration and the lowest ionic strength. Furthermore, experiments conducted so far suggest an increase in sorption with increasing solid-solution ratio at 6.4×10^{-5} M strontium concentration and 10^{-1} M and 10^{-2} M ionic strengths. However, at 10^{-6} M strontium concentration and 10^{-1} M and 10^{-2} M ionic strengths experimental results indicate an increase in strontium sorption as the solid-solution ratio decreases.

In May 2017, experimental samples and reference standards were analyzed at the Stanford Synchrotron Radiation Lightsource (SSRL), a Directorate of the Stanford National Accelerator Laboratory, an Office of Science User Facility operated for the United States Department of Energy by Stanford University. Experimental samples were analyzed at SSRL, beamline 4-3, using x-ray absorption spectroscopy to determine the speciation of experimental samples exposed to chromium. Data reduction analyses of the x-ray absorption spectroscopy efforts are currently in process.

Figures

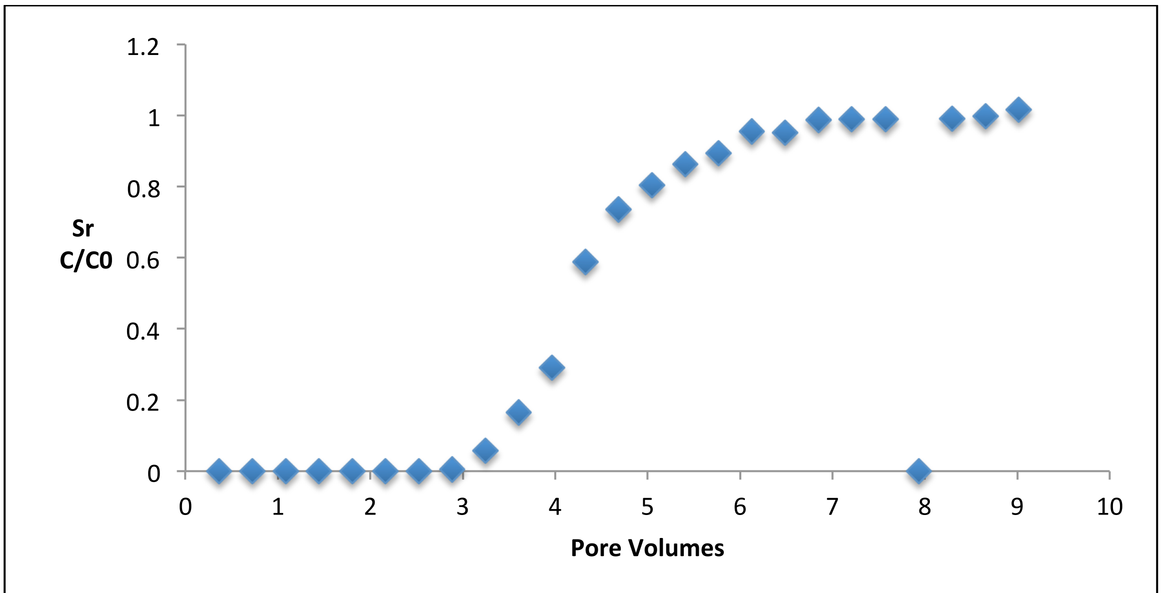

Figure 1. INITIAL Sorption 10^{-4} M Sr in 10^{-3} M $NaNO_3$, pH=5.0, Flowrate=0.5 mL/min.

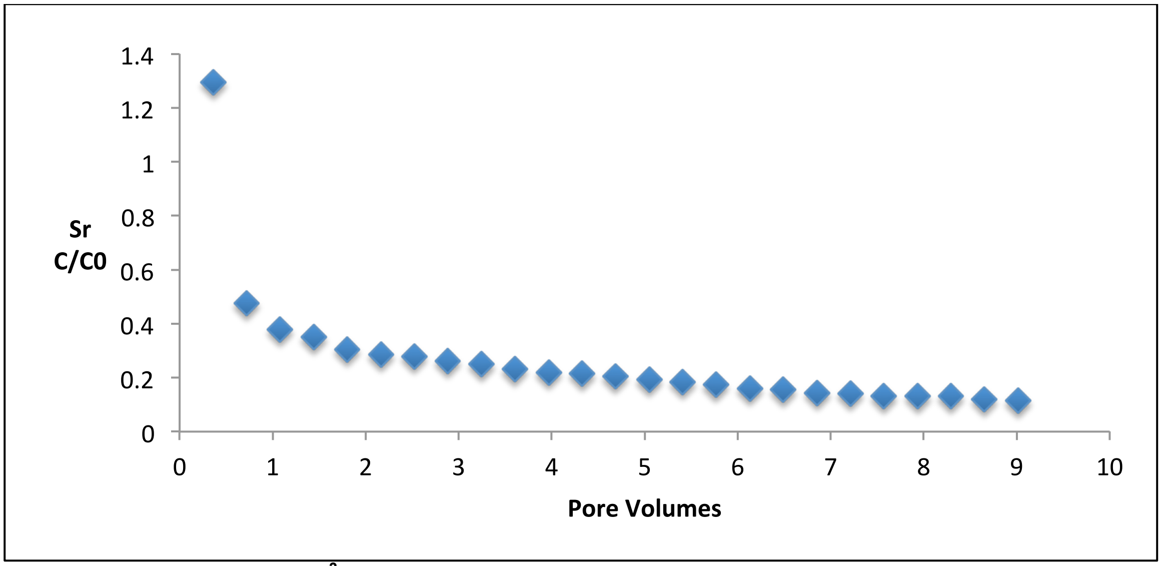

Figure 2. INITIAL Elution 10^{-3} M $NaNO_3$, pH 5.0, Flowrate=0.5 mL/min.

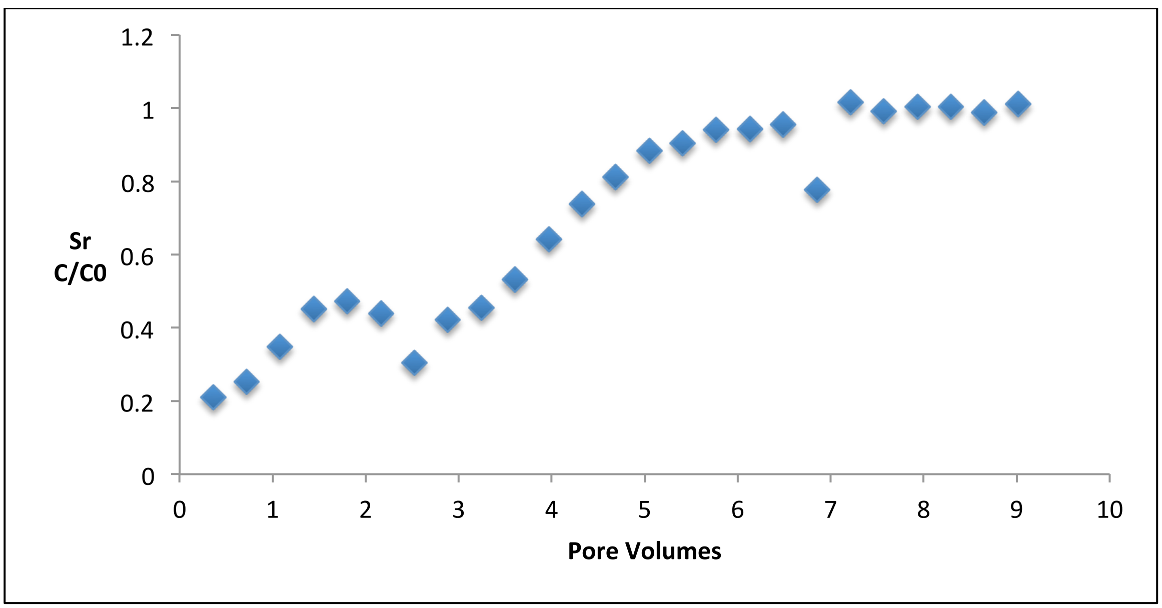

Figure 3. SECOND Sorption 10^{-4} M Sr in 10^{-3} M $NaNO_3$, pH=5.0, Flowrate=0.5 mL/min.

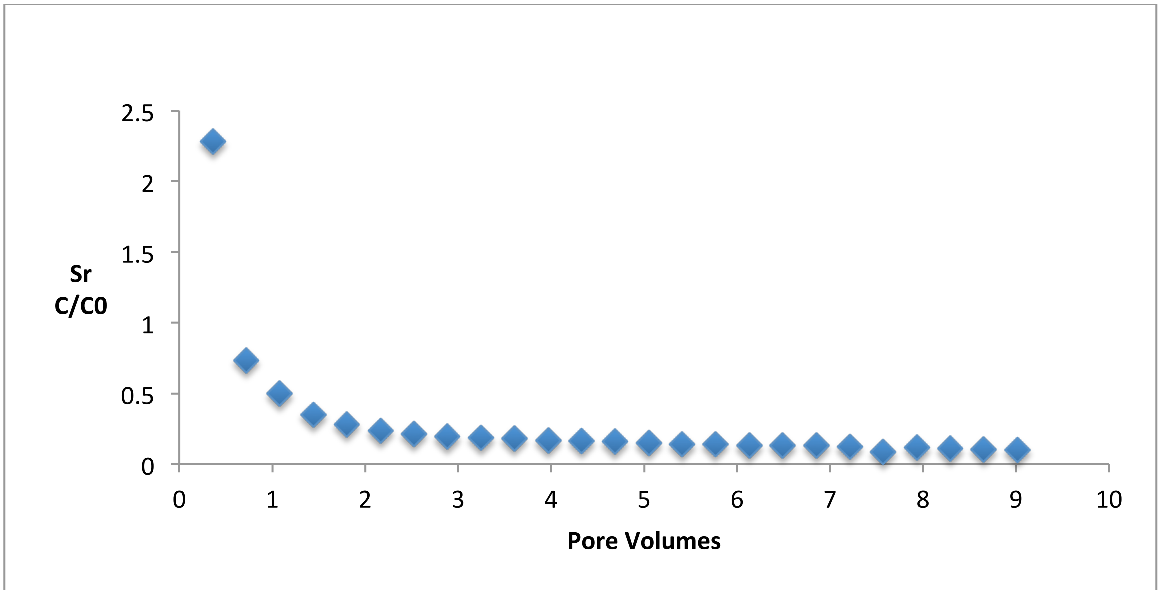

Figure 4. SECOND Elution 10^{-3} M $NaNO_3$, pH 5.0, Flowrate=0.5 mL/min.

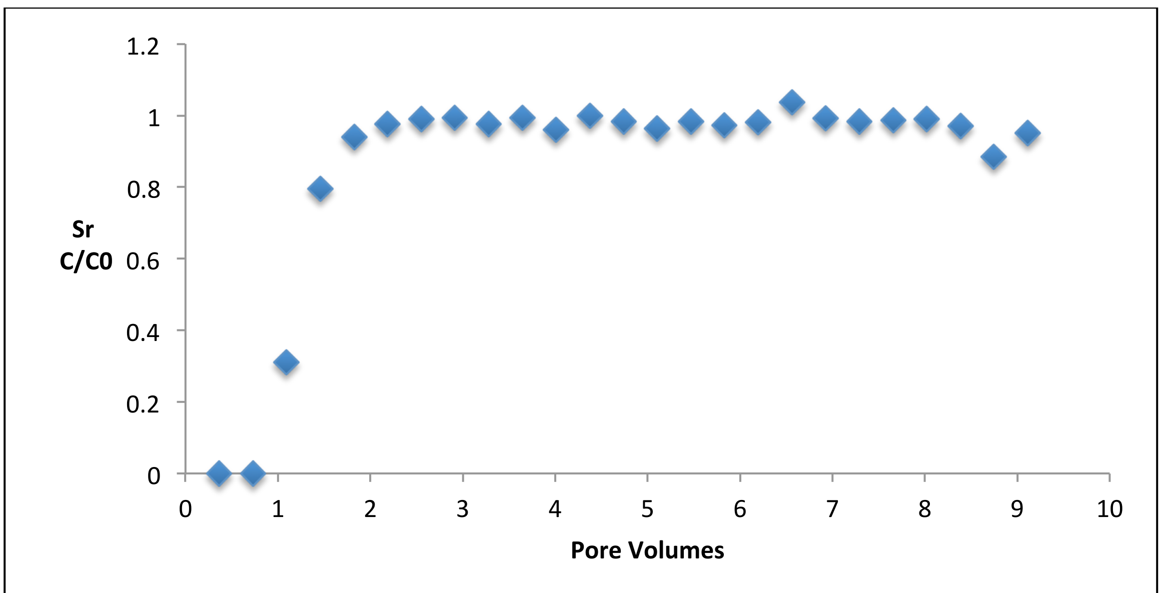

Figure 5. INITIAL Sorption 10^{-4} M Sr in 10^{-1} M $NaNO_3$, pH=5.0, Flowrate=0.5 mL/min.

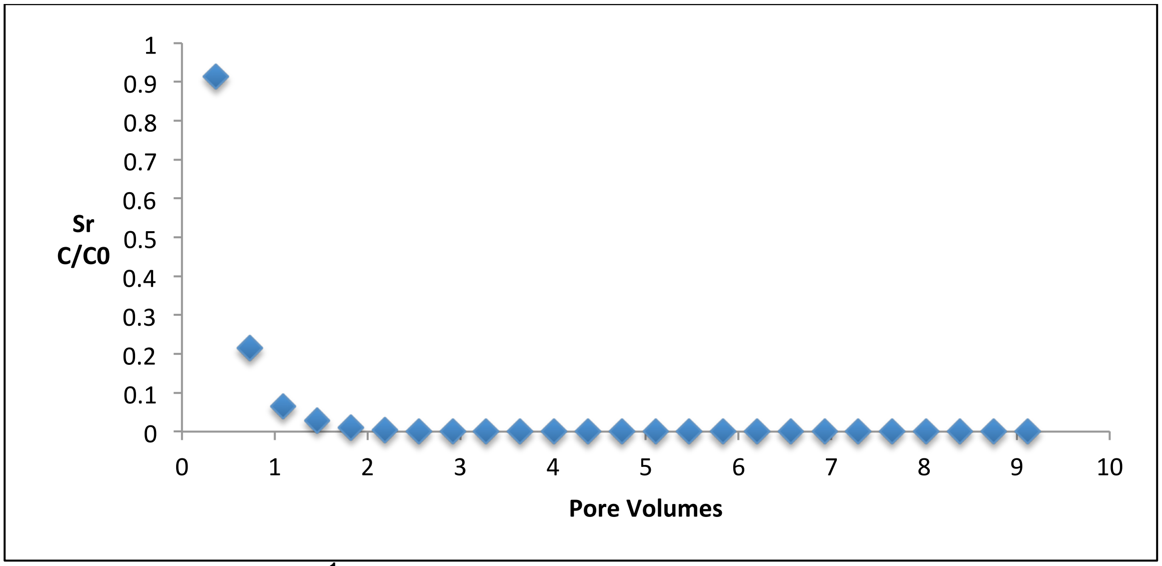

Figure 6. INITIAL Elution 10^{-1} M $NaNO_3$, pH 5.0, Flowrate=0.5 mL/min.

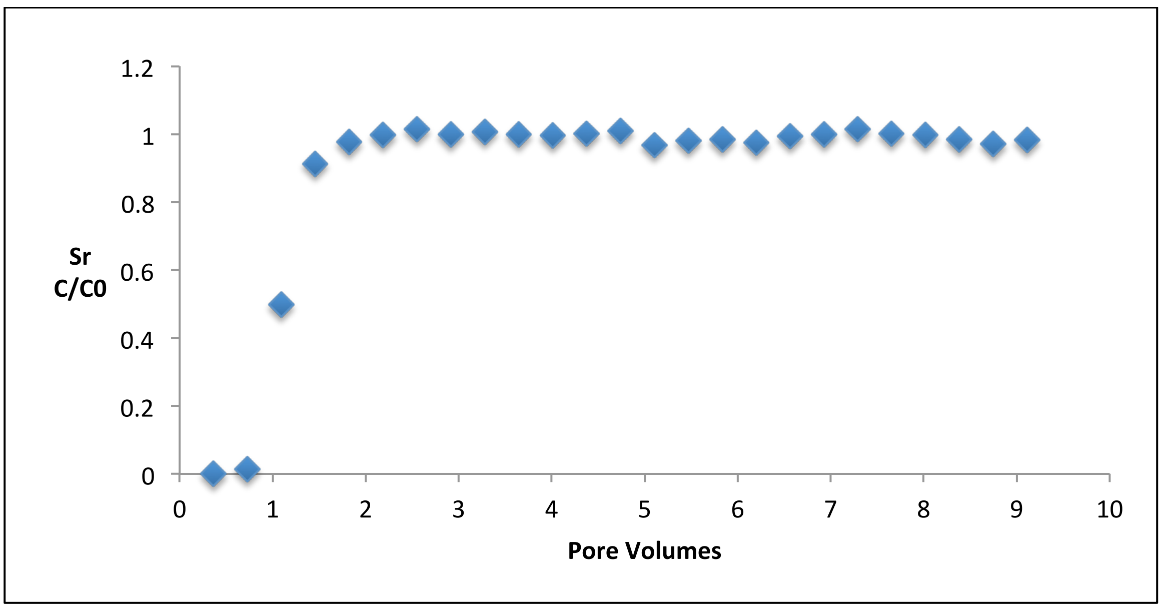

Figure 7. SECOND Sorption 10^{-4} M Sr in 10^{-1} M $NaNO_3$, pH=5.0, Flowrate=0.5 mL/min.

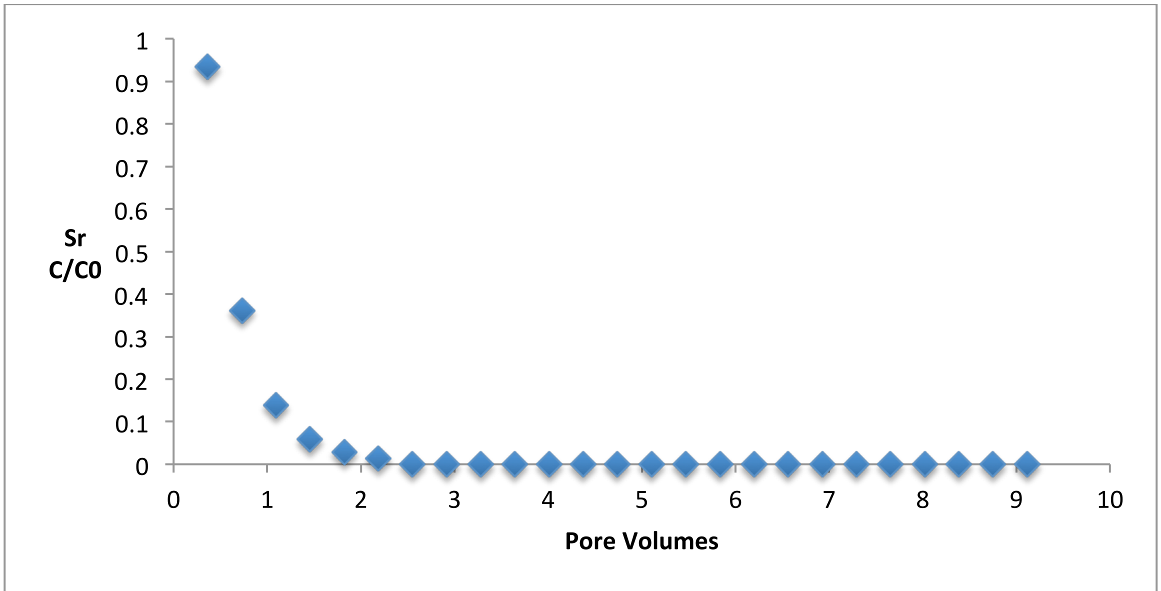

Figure 8. SECOND Elution 10^{-1} M $NaNO_3$, pH 5.0, Flowrate=0.5 mL/min.

6. Provide a paragraph on who will benefit from your research results. Include any water agency that could use your results.
   A water agency that could apply the results of this research is the New Mexico Environment Department for remediating contaminated sites.

7. Describe how you have spent your grant funds. Also provide your budget balance and how you will use any remaining funds. If you anticipate any funds remaining after June 1, 2017, please contact Carolina Mijares immediately. (575-646-7991; mijares@nmsu.edu)

   Approximately $5,975.00 has been spent by June 1, 2017.

8. List presentations you have made related to the project.

   American Geophysical Union Conference in San Francisco, California, December 2016.

9. List publications or reports, if any, that you are preparing. Remember to acknowledge the NM WRRI funding in any presentation or report that you prepare.

   The results from this research will be submitted for publication in peer-reviewed journals, such as *Chemosphere* and the *Journal of Contaminant Hydrology*.

10. List any other students or faculty members who have assisted you with your project.

    Not Applicable.

11. Provide special recognition awards or notable achievements as a result of the research including any publicity such as newspaper articles, or similar.

    Not Applicable.

12. Provide information on degree completion and future career plans. Funding for student grants comes from the New Mexico Legislature and legislators are interested in whether recipients of these grants go on to complete academic degrees and work in a water-related field in New Mexico or elsewhere.

    The student researcher, Mr. William Weaver, is a Ph.D. Candidate, majoring in Environmental Engineering. Mr. Weaver plans to continue his career in a water-related field working initially perhaps as a postdoctoral researcher and potentially as a faculty or member of a research organization.