2021 NM WRRI Student Water Research Grant
Final Report

1. **Student Researcher**: Rong He
Faculty Advisor: Dr. Meng Zhou

2. **Project title**: Determination of naturally occurring radioactive materials (NORM) in groundwater around the WIPP site

3. **Description of the research problem and research objectives**.

Groundwater may contain radioactive substances which can be dangerous to human health. The radioactivity in groundwater could be from naturally occurring radioactive materials that originate from the Earth's crust (**Figure. 1**). Aside from natural radionuclides, uncontrolled disposal of radioactive waste may also lead to an increase in radioactivity in the groundwater. The waste isolation pilot plant (WIPP) in Carlsbad, NM, is a deep geological repository for the permanent disposal of defense transuranic (TRU) wastes. The quality of water around the WIPP site is a significant concern. Once the radionuclides are present in the groundwater, they can be accumulated in the environment and pose a potential hazard to human health since radionuclides and their decay products can be absorbed by the human body through the food chain or water intake. People, especially those who live around the waste disposal sites, have concerns about the possible long-term effects of the radioactive substances on the environment and human health. The determination of radioactive contaminants and continuously monitoring the radioactivity level in the groundwater play an essential role in protecting the general population from being contaminated by potential radiation. The main challenges in determining the radioactivity in groundwater include radionuclide preconcentration and separation due to the complicated composition of groundwater.

The research objectives are:

a. To develop a rapid and accurate method for the sequential separation and determination of naturally occurring radioactive materials including polonium (Po), thorium (Th) and uranium (U) in groundwater.

b. To determine the radionuclide concentrations in shallow and deep groundwater and estimate the effective doses due to water intake.

c. To establish a baseline for radioactivity levels in water around the WIPP site and provide experimental data as references for future research and environmental monitoring.

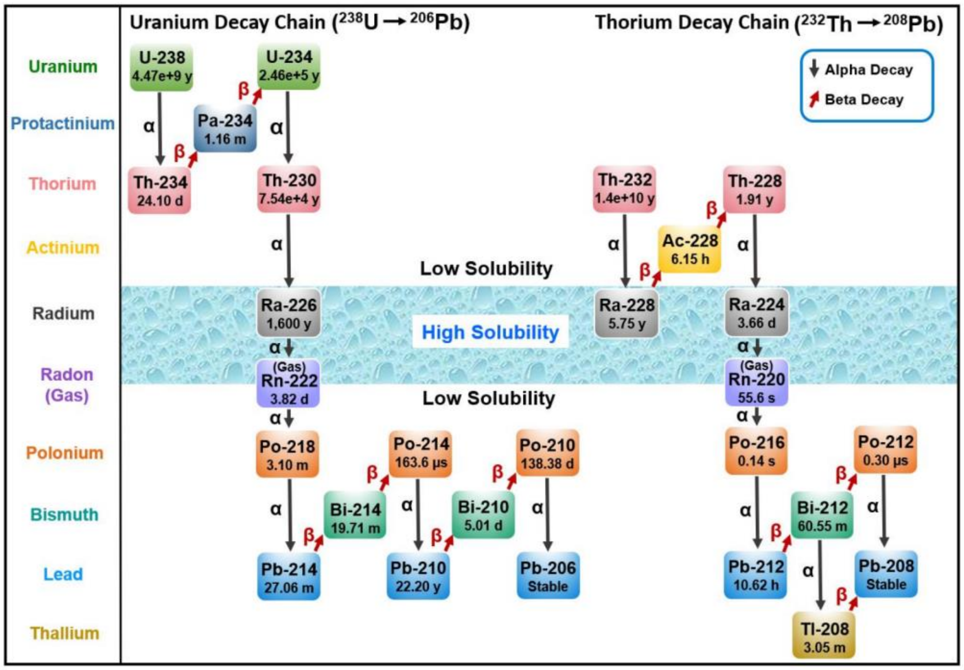

Figure 1. Natural U-238 and Th-232 decay chains. The decay information is from the NuDat 2.8 Database. y: years; d: days; h: hours; m: minutes; s: seconds.

4. **Description of methodology employed**.

Separation of Po, Th and U: Groundwater samples were collected from different locations in the vicinity of the WIPP site (Carlsbad, New Mexico). 200–250 mL of sample aliquot was taken for radioactivity analysis. The groundwater samples were put on a hot plate for digestion using 10 mL of concentrated HNO_3 and 5 mL of 30% H_2O_2 until the solution volume was reduced to ~150 mL. In the separation experiments, ^{209}Po and ^{229}Th, and ^{232}U were used as tracers, the separation of Po and Th was carried out using TEVA (TEtraValents Actinides) columns. UTEVA (Uranium and TEtraValents Actinides) columns were applied to separate U.

Radioactivity Determination of Po, Th and U: The final sample solutions were filtered by Resolve TM filters and micro-coprecipitated on stainless steel discs to prepare Alpha spectrometry sources for further Alpha counting. Po and Th alpha sources were prepared by CuS micro co-precipitation method and U alpha source was obtained using the NdF_3 Micro co-precipitation method. An alpha spectroscopy system (Oxford Oasis System, Oxford Instruments Inc.) equipped with 72 silicon surface barrier detectors (PIPS) connected to an Alpha Vision software system was used to obtain the alpha spectra and analyze the radioactivity of water samples. All the samples were counted for 24 hours.

Calculation of annual effective dose (AED): Annual effective dose (mSv y^{-1}) caused by ingestion of drinking water can be calculated by the following:

$$AED = D_f \, W_i \, A_c \qquad (1)$$

Where *AED* represents the annual effective dose of a given radionuclide; D_f is the effective dose conversion factor (mSv Bq^{-1}); W_i refers to the annual consumption rate of water (L $year^{-1}$); *Ac* is the activity concentration of radionuclides in drinking water (Bq L^{-1}).

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

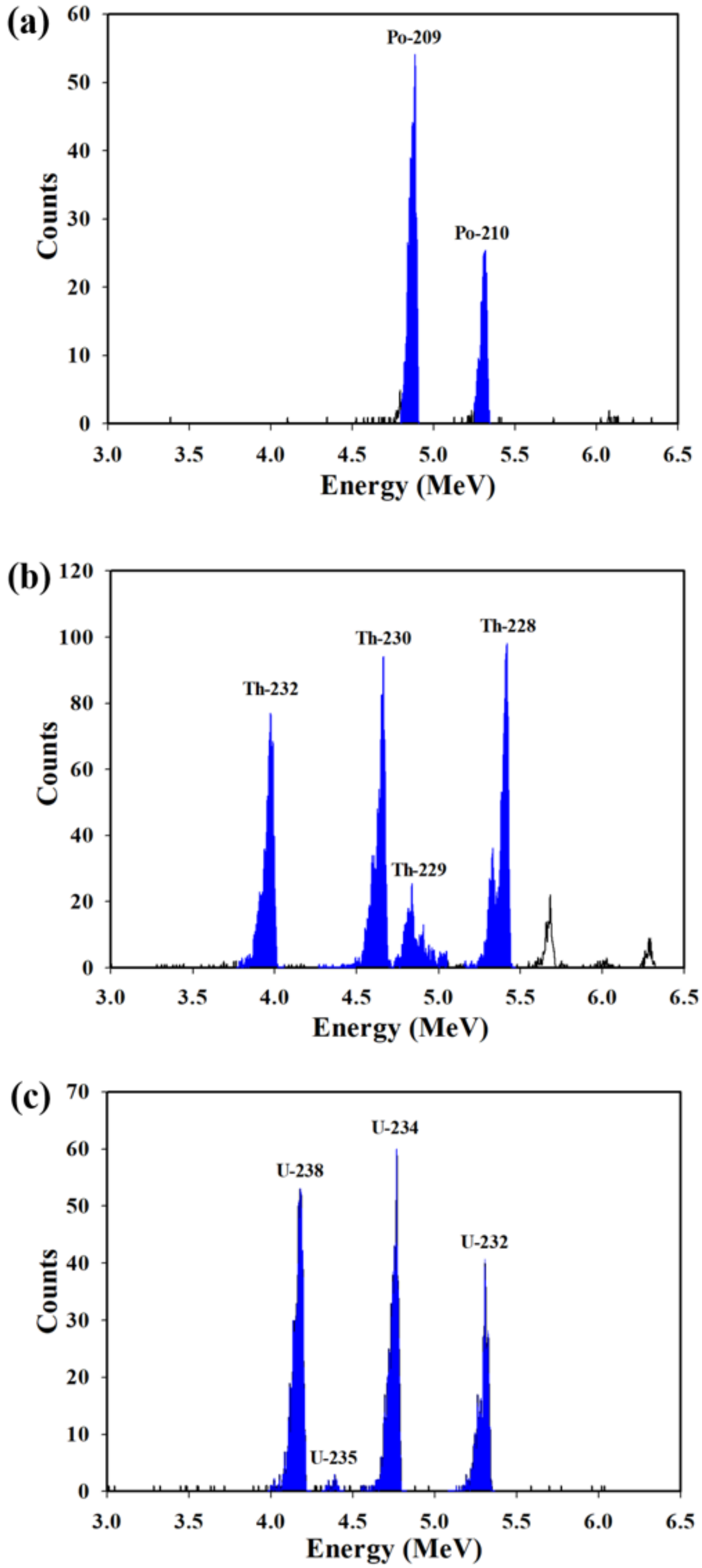

Figure. 2. Alpha spectra for Po, Th and U isotopes.

Table 1. Concentrations (Bq L^{-1}) of Po, Th, U isotopes in shallow and deep groundwater samples.

Sample ID	^{210}Po	^{228}Th	^{238}U	^{234}U
GW-1	0.11± 0.03	0.11 ± 0.01	0.22 ± 0.03	1.23 ± 0.16
GW-2	0.03 ± 0.01	0.06 ± 0.01	0.18 ± 0.03	1.13 ± 0.15
GW-3	0.18 ± 0.04	0.10 ± 0.01	0.02 ± 0.01	0.16 ± 0.03
GW-4	0.06 ± 0.02	0.09 ± 0.01	0.09 ± 0.02	0.50 ± 0.07
GW-5	0.03 ± 0.01	0.02 ± 0.01	0.05 ± 0.01	0.38 ± 0.05
GW-6	0.01 ± 0.01	0.01 ± 0.00	0.07 ± 0.01	0.52 ± 0.07
GW-7	0.01 ± 0.00	0.01 ± 0.00	0.11 ± 0.02	0.23 ± 0.03
GW-8	0.01 ± 0.01	0.09 ± 0.01	0.31 ± 0.04	0.97 ± 0.13
GW-9	0.01 ± 0.00	0.01 ± 0.00	0.06 ± 0.01	0.19 ± 0.03
GW-10	0.16 ± 0.04	0.03 ± 0.01	0.19 ± 0.03	0.68 ± 0.09
GW-11	0.04 ± 0.01	0.00 ± 0.00	0.22 ± 0.03	0.77 ± 0.11
GW-12	0.10 ± 0.03	0.08 ± 0.01	0.16 ± 0.02	0.58 ± 0.08
GW-13	0.01 ± 0.01	0.02 ± 0.00	0.05 ± 0.01	0.12 ± 0.02
GW-14	0.23 ± 0.03	0.02 ± 0.00	0.13 ± 0.02	0.48 ± 0.07
GW-15	0.03 ± 0.01	0.02 ± 0.00	0.16 ± 0.03	0.55 ± 0.08
GW-16	0.03 ± 0.01	0.01 ± 0.00	0.08 ± 0.01	0.31 ± 0.04
GW-17	0.04 ± 0.02	ND*	0.08 ± 0.01	0.31 ± 0.05
Mean-Deep	0.07 ± 0.02	0.07 ± 0.01	0.11 ± 0.02	0.65 ± 0.09
Mean-Shallow	0.06 ± 0.02	0.03 ± 0.00	0.14 ± 0.02	0.47 ± 0.07

*ND: Not detected.

Figure 2 shows the alpha spectra for Po, Th and U isotopes in groundwater samples and these peaks are separate, demonstrating that Po, Th and U were successfully separated by TEVA and UTEVA columns. Since the concentrations of ^{230}Th, ^{232}Th and ^{235}U are very low and some of them are not detected in the groundwater samples, we focused on the analysis of ^{210}Po, ^{228}Th, ^{234}U and ^{238}U in this work. Concentrations (Bq L^{-1}) of Po, Th and U isotopes in groundwater were summarized in **Table 1**. The radioactivity in deep groundwater is found to be higher than that in shallow groundwater. Compared to shallow groundwater, deep groundwater has been down there for a long time. Therefore, they have a higher possibility to interact with the solids or rocks and may dissolve more radionuclides in the aquifer. The measured radioactivity concentrations of Po, Th and U are in the range of the background concentrations of radionuclides in Carlsbad from 1999 to 2018. In addition, the activity concentrations of ^{210}Po, ^{228}Th, ^{234}U and ^{238}U are comparable to the radioactivity levels observed in groundwater in other areas, indicating that the radioactivity in groundwater is most likely from natural sources and the WIPP site did not increase the radioactivity in groundwater.

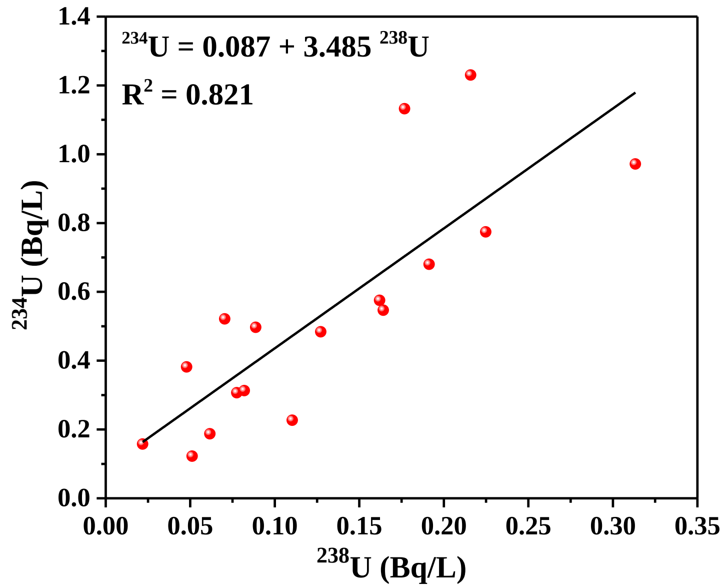

Figure 3. Correlation between ^{234}U and ^{238}U concentrations in groundwater.

The relationship between the concentrations of ^{234}U and ^{238}U in groundwater is investigated in this study. **Figure 3** presents the positive correlation between ^{234}U and ^{238}U found in groundwater, demonstrating that the enhancement of ^{234}U probably resulted from its parent ^{238}U or the dissolved uranium in water. ^{234}U and ^{238}U do not reach radioactive equilibrium in groundwater. ^{234}U recoil and crystal damage and leaching are the most likely mechanisms for the interaction of ^{234}U and ^{238}U, leading to the disequilibrium between ^{234}U and ^{238}U activity concentration in water.

Table 2. The annual effective doses in mSv per year (mSv y^{-1}) due to the ingestion of Po, Th, and U isotopes for deep and shallow groundwater.

Sample ID	^{210}Po	^{228}Th	^{238}U	^{234}U
GW-1	0.096	0.006	0.007	0.044
GW-2	0.026	0.003	0.006	0.040
GW-3	0.158	0.005	0.001	0.006
GW-4	0.053	0.005	0.003	0.018
GW-5	0.026	0.001	0.002	0.014
GW-6	0.009	0.001	0.002	0.019
GW-7	0.009	0.001	0.004	0.008
GW-8	0.009	0.005	0.010	0.035
GW-9	0.009	0.001	0.002	0.007
GW-10	0.140	0.002	0.006	0.024
GW-11	0.035	0.000	0.007	0.028
GW-12	0.088	0.004	0.005	0.021
GW-13	0.009	0.001	0.002	0.004
GW-14	0.201	0.001	0.004	0.017
GW-15	0.026	0.001	0.005	0.020
GW-16	0.026	0.001	0.003	0.011
GW-17	0.035	-	0.003	0.011
Mean-Deep	0.061	0.003	0.003	0.023
Mean-Shallow	0.053	0.002	0.005	0.017

Exposure doses are correlated with the activity concentrations of radionuclides in water as well as the dose coefficients of individual radionuclides, which can be used to express the radiological risk. The dose coefficients of ^{210}Po, ^{228}Th, ^{238}U and ^{234}U, based on the recommendations of the International Commission on Radiological Protection (ICRP), are 1.2×10^{-6}, 7.2×10^{-8}, 4.5×10^{-8} and 4.9×10^{-8}, respectively. The effective doses relating to ^{210}Po, ^{228}Th, ^{238}U and ^{234}U for the deep and shallow groundwater are listed in **Table 2.** The results show that ^{210}Po contributes to most of the effective doses in shallow and deep groundwater due to its high dose coefficient.

Our results indicate that (1) Po, Th and U can be separated by TEVA and UTEVA columns; (2) deep groundwater has higher radioactivity than shallow groundwater due to the longer residence time; (3) the radioactivity in groundwater is most likely from natural nuclides instead of the WIPP site; (4) ^{234}U has a higher activity concentration than other radionuclides in groundwater but ^{210}Po is the major contributor to groundwater effective doses due to its high dose coefficient.

The accumulation of radionuclides over time may lead to future radiological problems. Continuous monitoring of radioactivity in groundwater is significantly important. The results of this study provide valuable information for assessing the radioactivity levels in groundwater around the WIPP site and the potential effects of effective doses from radionuclides and the experimental data can be used as references for future research.

6. **Provide a paragraph on who will benefit from your research results. Include any water agency that could use your results**.

This work is expected to develop a rapid method to determine the radioactivity of groundwater samples. Firstly, it can help to monitor the source of radioactive contamination in groundwater. Secondly, the radioactivity data can be used to establish a baseline for radioactivity levels in groundwater around the WIPP site. Furthermore, if the water resources have any potential contamination with radionuclides, this determination method could provide accurate information about the identification and concentration of the individual radionuclides in a short time.

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 May 19, 2022, please contact Carolina Mijares immediately. (575-646-7991; mijares@nmsu.edu)**

The grant funds have been spent on necessary chemicals, lab supplies, and water analysis. The experiments were carried out at the Carlsbad Environmental Monitoring and Research Center (CEMRC). The student researcher spent funds on regular travel from Las Cruces to CEMRC, Carlsbad. The remaining balance of this grant is $485. We have a submitted manuscript (Under revision), which is supported by this grant. We plan to use the remaining funding to pay for the manuscript publication. Since the manuscript is still under revision, the hyperlink to the publication is not yet available.

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

Poster presentation at NM WRRI 66th Annual New Mexico Water Conference, October 2021

9. **List publications or reports, if any, that you are preparing. For all publications/reports and posters resulting from this award, please attribute the funding to NM WRRI and the New Mexico State Legislature by including the account number: NMWRRI-SG-2021.**

A manuscript has been submitted to a peer-reviewed journal and is under revision.

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

Steven Liaw (Master student, Department of Chemical & Materials Engineering, NMSU)
Dr. Meng Zhou (Faculty, Department of Chemical & Materials Engineering, NMSU)
Dr. Hongmei Luo (Faculty, Department of Chemical & Materials Engineering, NMSU)

11. **Provide special recognition awards or notable achievements as a result of the research including any publicity such as newspaper articles, or similar**.
An abstract was accepted to the NM WRRI 66th Annual New Mexico Water Conference.

12. **Degree completion and future career plans.**
I am a third-year Ph.D. student and expected to graduate in 2023 Fall. I would like to be a Postdoc in a research institution or college after graduation.