Determination of Chelating Agents in Non-regulated Water Sources on Navajo Lands

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Problem and Research Objectives

Following the approval of the Manhattan Project in 1942, the United States experienced an increased need for uranium. As a result, extensive uranium mining occurred from the mid to late 1900's on Navajo tribal lands in Northern Arizona, an area rich in natural uranium. Although mining activities have ceased and remediation has been attempted, previous open pit mining still affects those living in the area today; environmental uranium contamination persists in the region. Radiological and chemical properties of uranium in combination with a lack of access to regulated drinking water sources present a serious health concern for residents on the Navajo Reservation.

The potential health effects associated with the ingestion of uranium in drinking water are dependent on a number of variables, including solubility and speciation. The speciation and solubility of uranium in an aqueous environment can be altered by various factors, including pH, water hardness, and concentrations of potential ligands. Environmental mobility of uranium can also be heavily influenced by solubility and speciation. Speciation describes the overall chemical state of elements in solutions, solids, and gases. The distribution of chemical elements depends not only on their concentration, but also on the chemical behavior of complexes containing the element (Bernhard, 2005). Thus, a firm grasp on uranium speciation in aqueous environments is crucial in understanding both its solubility and mobility in the environment and also its bioavailability and potential toxicity (Fortin, 2007). In natural waters, uranium can occur in a variety of different species. A number of factors affecting uranium speciation and solubility in groundwater systems have been identified; these factors include content and leachability of uranium in sediments, proximity of water to the uranium source, degree of hydraulic isolation of the water from dilution by fresher water, climatic effects and seasonal variability, pH, concentrations of other species that can either form strong complexes with or precipitate insoluble uranium species, and presence of highly sorptive materials (Elless, 1997). Additional factors described by Bernhard include redox potential, ionic strength, solubility product, formation of colloids, presence of microorganisms, and types of interfaces present during the interaction of solved and sorbed complexes (Bernhard, 2005). Redox potential, pH, and concentrations of potential ligands have been determined to be key variables affecting uranium speciation and solubility in aqueous environments (Kumar et al., 2011).

The behavior of a metal, such as uranium, may be drastically altered as a result of variations in oxidation state and/or association with specific ligands (Reeder, 2006). In reducing environments, uranium in groundwater is typically present in the tetravalent state, as U(IV), which has a low solubility. U(IV) tends to precipitate as uraninite or UO_2 (s) and remain immobile in waters with low redox potentials (Markich, 2002). In oxidizing environments, however, uranium is more commonly present in the hexavalent state, which has a much higher solubility in comparison to U(IV) (Langmuir, 1997). The higher solubility of the hexavalent state is attributed to the tendency of the +6 cation to form uranyl di- and tri-carbonate anions (Osmond, 1976). The most common U(VI) species is the linear uranyl dioxocation, UO_2^{2+} (Van Horn, 2006). This cation forms stable, soluble complexes that are mobile and greatly affect uranium transport (Markich, 2002).

With respect to aqueous environments, the uranyl cation is one of the most important species. In natural waters, the uranyl cation is the predominant form of uranium; however, its speciation is very complex and highly dependent on various factors, including pH and water hardness (Antunes, 2007). Due to the capacity of the uranyl ion to form extremely stable complexes, it is highly soluble over a wide pH range. In natural waters, the uranyl species can complex with a number of different compounds, including sulfate, silicate, chloride, nitrate, and fluoride; most of the complexes that form possess very high

mobility in aqueous solution (Birke, 2009). However, most of these complexes are weak compared to the complexes that the uranyl cation forms with carbonate and phosphate anions (Markich, 2002).

Uranium, along with other elements in the actinide series, has a strong tendency to form complexes with oxygen-containing ligands; hydroxide, carbonate, and phosphate are ligands most commonly present in natural water sources (Sandino, 1992). In the majority of water sources, uranyl hydroxyl and carbonate species are the most predominant. The importance of these species, however, is highly determined by a number of other factors, including the total concentration of U(VI), redox potential, ligand concentration, and pH (Langmuir, 1978). The effect of pH on uranyl solubility and complexation is two-fold. Increasing pH results in increased complexation of the free uranyl cation by hydroxides and carbonates; increased complexation of heavy metals typically results in decreased bioavailability (Fortin, 2004). However, decreased pH, and thus an increase in protons competing with uranyl ions for binding sites of transport systems on the plasma membrane, has been shown to prevent uranium internalization (Fortin, 2007). The effects of pH counteract one another and make it difficult to interpret data related to the accumulation and toxicity related to the uranyl cation (Fortin, 2004).

At a higher groundwater pH (pH>5), carbonate will replace any weakly bound hydroxyl species, resulting in a higher concentration of uranyl carbonate complexes. Also, the solubility of any surrounding uranyl minerals in contact with the aqueous environment will increase when carbonate concentration is high, due to the preference of the uranyl cation to form uranyl carbonate complexes in aqueous solution. Unlike uranyl hydroxyl species, uranyl carbonate species do not adsorb strongly to mineral surfaces, and thus, the formation of uranyl carbonate complexes greatly enhances the mobility of uranium in the environment (Abdelouas, 2006). To summarize, the presence of carbonate species in the aqueous environment has two main effects (increasing uranium concentration in solution, and decreasing surface concentrations of uranium), both of which contribute to increased uranium mobility and bioavailability (Langmuir, 1997).

Cationic species present in aqueous solution can also affect uranium speciation. In relation to uranium speciation in ground and surface waters, calcium is one of the most important cations to consider. Under solution conditions in which carbonate complexes overcome all other complexes, calcium content is noted to be one of the primary speciation parameters; concentrations of carbonate complexes, such as $UO_2(CO_3)_3^{4-}(aq)$, $CaUO_2(CO_3)_3^{2-}(aq)$, and $Ca_2UO_2(CO_3)_3(aq)$, vary with calcium concentration when the system is at equilibrium (Prat, 2009). Equilibrium conditions are described by the equation $UO_2(CO_3)_3^{4-} + nCa^{2+} = Ca_nUO_2(CO_3)_3^{2n-4}$ (Prat, 2009). These calcium uranyl carbonate complexes are thought to be the predominant form of dissolved hexavalent uranium in numerous uranium containing groundwaters (Stewart, 2010).

Because of their large formation constants ($\log_{10}K° \sim 25 - 30$) (Prat, 2009), calcium uranyl carbonate complexes may play a significant role in the aqueous mobility of U(VI) species at alkaline pH values. Calcium cations may also affect the adsorption of hexavalent uranium through competition for sorption sites, alteration of the surface charge of minerals, and changing the aqueous speciation of U(VI), as described (Fox, 2006). An experimental study conducted by Zheng and colleagues clearly demonstrated the effect of the presence of calcium carbonate in soils on U(VI) sorption; decreased sorption was attributed to the presence and formation of calcium uranyl carbonate complexes, particularly the neutral $Ca_2UO_2(CO_3)_3$ specie (Zheng, 2003).

The overall objective of this work was to collect information that will lead to the determination of uranium speciation in unregulated wells in the southwestern region of the Navajo reservation. This information is needed to assess the bioavailability of uranium from a health standpoint as well as providing an understanding of the transport of uranium in the environment. Both of these concerns are highly dependent on the molecular nature of uranium species present, which is environment dependent. The approach for achieving this objective is to identify specific chelating agents present in the waters.

We had proposed to collect information on both the organic and inorganic chelating agents; however, the instrument that was to be used for the organic work (liquid chromatography/mass spectrometry) was not operational for these studies. Thus, we focused our efforts on the inorganic chelating agents.

Methodology

Water samples were collected from 18 unregulated water sources, located in the southwest region of the Navajo Reservation in Northern Arizona. Table 1 lists the name of the wells, their locations, and the time frame they were collected.

To characterize and quantify anionic species present in various well waters, various analytical techniques will be used. For the analyses of chloride and sulfate anions, ion chromatography (IC) will be utilized; this is a chromatographic technique based on charge interactions. Negatively charged components in the mobile phase interact with the positively charged surface of the stationary phase, allowing for the effective separation of uniquely charged analyte species. For the analysis of nitrate and phosphate anions, flow injection analysis colorimetry will be utilized. Lachat Instruments makes an instrument specifically for the analysis of nitrate and phosphate, which combines sample preparation and colorimetric analysis into one instrument. Bicarbonate concentrations of well water samples will be determined through the use of a simple acid/base titration, a method utilized by the U.S. EPA for the determination of alkalinity in natural water samples.

Table 1. GPS coordinates and sampling months of sampling locations for unregulated water sources in the southwestern region of the Navajo Reservation.

Well Number	Well Name	Latitude (degrees)	Longitude (degrees)	Month(s) sampled 2011/2012
5T-526	Hwy 99W	35.24	-110.98	July, Sept
5T-506	Hwy 99E	35.24	-110.97	July, Sept
5M-108	Leupp Windmill	35.30	-111.10	Feb, Sept
5T-518	Leupp Corral	35.31	-111.00	Feb
	El Paso	35.31	-111.08	July, Sept
5K-315		35.29	-111.15	July
	Phelps Well	35.35	-111.23	July, Sept
5T-529	Blackfalls Windmill	35.43	-111.11	Feb
5T-537		35.49	-111.16	Oct
5M-74	Box Springs	35.50	-111.24	Feb, Oct
	Tohatchi Springs	35.69	-111.10	Feb, Oct
	Badger Springs	35.64	-111.20	Feb, Oct
	Balokai	35.68	-111.28	Feb, Oct
3K-331	3K-331	35.77	-111.41	Aug, Oct
3T-539	6730 Windmill	35.84	-111.36	Feb, Aug, Oct
3T-527	Hwy 64	35.85	-111.45	Feb, Oct
	Tappen Springs	35.88	-111.45	Aug, Oct
	Cameron Trading Post	35. 87	-111.41	Aug, Oct

To quantify cationic species present in various well waters, a spectroscopic technique was employed. Flame atomic absorption spectroscopy (AAS) is an analytical technique, based on the absorption of light by a metal in the ground state, commonly used to quantify trace metals in solution. All of the instrumentation necessary to complete both the anion and cation analyses was available through the Merriam Powell Center for Environmental Research at Northern Arizona University. In the past, there has been collaboration between the Ingram laboratory and the Merriam Powell Center for the analyses of anionic content of previous well water samples from the Reservation; collaboration will again be essential for the completion of this work.

Following the completion of anion and cation analyses, Stiff diagrams were constructed. These plots are typically utilized by hydrogeologists and provide a visual representation of the ionic composition of a water sample. They can be useful in efficiently discovering similarities and differences in the water chemistry of natural water samples. In addition, charge balances were determined for filtered samples from each of the eighteen sample locations. Aqueous solutions are electrically neutral, implying that the total equivalents of anions should equal the total equivalents of cations in solution. Charge balances are an effective way to determine whether a significant error has occurred either in sample analysis or collection procedures; charge balance error can also indicate the presence of additional ions in solution that should be considered for analysis.

Elemental uranium concentrations were determined through the use of inductively coupled plasma mass spectrometry (ICP-MS). This technique employs the basic principle of elemental differentiation based on atomic mass, and is generally accepted as the most powerful multi-element analytical technique (Linge, 2009). Previous techniques utilized for the determination of uranium in environmental samples include alpha-spectroscopy, spectrophotometry, fluorescence spectrometry, laser-induced fluorescence, and neutron activation analysis; each of these techniques has limitations, however, including large sample volume, high cost, long analysis times, and high detection limits. Alternatively, analysis via ICP-MS requires small sample volumes, and allows for the detection of uranium at trace levels with relatively quick analysis times (Himri, 2000).

Based on the data obtained through the aforementioned analyses, uranium speciation is proposed (see Principal Findings and Significance). Because the mobility and bioavailability of uranium is dictated in part by the speciation, having an understanding of the dominant complexes present in the studied aqueous environments is essential to determining the potential health threat imposed by the consumption of water from unregulated sources located on Navajo tribal lands.

Principal Findings and Significance

Various aspects of the water chemistry of filtered water samples from 18 different unregulated sources on the Navajo Reservation were studied in this work. Concentrations of numerous analytes were determined, including both anions (bicarbonate, chloride, nitrate, sulfate, and phosphate), and cations (sodium, potassium, magnesium, and calcium). A wide array of analytical techniques was employed to obtain these data, including acid/base titration, ion chromatography, flow injection analysis, and flame atomic absorption spectroscopy. Results of the various analyses are summarized in Table 2

Stiff diagrams were constructed using AqQa software (Rockware; Golden, CO); average ion concentrations were utilized as the input for these plots. A number of select Stiff diagrams (Figures 1 to 6) are presented below to visually demonstrate the similarities and differences in water chemistry among the eighteen unregulated water sources analyzed

As is clearly demonstrated through Figures 1 to 6, there are some significant similarities and differences in the water chemistry of the unregulated water sources sampled. Tohatchi Springs (Figure 1) and Badger Springs (Figure 2) are both located in the remote Blackfalls region of the Navajo Reservation and are

within approximately 15 miles of one another.   They appear to have very similar water chemistry. Both wells contain a significant amount of both bicarbonate and sodium, but have a much lower concentration of calcium and magnesium. The high bicarbonate content of these locations is important to consider, as bicarbonate is one of the strongest complexing agents for uranium in aqueous environments and plays a large role in uranium speciation.   The low calcium content of these two wells is also an important result to consider; various groups have shown that calcium may decrease the potential toxicity of uranyl carbonate complexes by trapping the uranium in a nontoxic or nonbioavailable form (Carrière, 2004; Prat, 2009). Tohatchi Springs and Badger Springs also have chloride and sulfate concentrations similar to one another.

Table 2. Ionic Content and pH of Water Samples from Unregulated Sources on the Navajo Reservation.[a]

	Hwy 99W (5T-526)	Hwy 99E (5T-506)	Leupp Windmill (5M-108)	Leupp Corral (5T-518)	El Paso	5K-315	Phelps Well	Blackfalls Windmill (5T-529)	5T-537	Box Springs (5M-74)	Tohatchi Springs	Badger Springs	Balokai	3K-331	6730 Windmill (3T-539)	Hwy 64 (3T-527)	Tappen Springs	Cameron Trading Post	Trading Post Bathroom
pH	7.9	7.7	7.7	7.6	7.7	7.8	8	8	8.2	7.8	8.2	8.4	7.6	7.5	8.2	8.4	7.8	7.7	7.8
HCO_3^- (mg/L)	215	204	218	262	199	183	213	265	240	347	540	557	341	248	250	280	225	284	311
Cl^- (mg/L)	110	190	323	274	85	37	58	468	2330	24	154	93	132	1171	521	46	11	210	235
NO_3^- (mg/L)	0.2	0.18	0.28	0.25	0.26	0.22	0.19	0.13	0.03	2.5	1.28	1.04	0.05	0.25	0.02	1.28	4.11	0.06	0.08
SO_4^{2-} (mg/L)	270	276	297	223	220	262	277	245	288	195	151	136	364	293	226	177	107	263	326
PO_4^{3-} (mg/L)	BDL	0.01	0.01	0.01	BDL	BDL	BDL	BDL	0.02	0.01	0.07	0.01	BDL	BDL	0.01	BDL	0.03	0.08	0.09
Na^+ (mg/L)	67	113	200	181	50	29	44	312	1443	156	349	280	301	887	388	71	20	281	337
K^+ (mg/L)	3.5	4.8	3.1	3.2	2.8	3.4	3.8	3.6	5.5	3.8	2.1	1.2	1.8	6.6	5.1	6.1	4.2	2.9	3.2
Mg^{2+} (mg/L)	43	52	48	54	39	44	51	60	74	13	2	4	4	57	22	39	25	11	2
Ca^{2+} (mg/L)	93	79	90	94	76	83	71	100	74	32	5	7	27	78	49	40	48	21	4

[a]All measurements were taken at room temperature. Bicarbonate was determined via acid/base titration. Cl^- and SO_4^{2-} were determined via ion chromatography. NO_3^- and PO_4^{3-} were determined via flow injection analysis. For PO_4^{3-}, BDL indicates the concentration was below the detection limit of 0.01 mg/L. Na^+, K^+, Mg^{2+}, and Ca^{2+} were determined via flame atomic absorption spectroscopy.

The water chemistries of Tohatchi Springs and Badger Springs, although similar to one another, differ drastically from those of Leupp Corral (5T-518) (Figure 3) and El Paso (Figure 4); Leupp Corral (5T-518) and El Paso are also different from one another in terms of ionic content.   These wells are located east of Flagstaff, AZ in the Leupp region of the Navajo Reservation within roughly 10 miles of one another. With respect to anions, the water from Leupp Corral (5T-518) is dominated by chloride, whereas the water from El Paso is dominated by sulfate. The primary cations in the water from Leupp Corral (5T-518) are sodium and potassium; the primary cation in the water from El Paso is calcium. The utilization of Stiff diagrams allows for an efficient comparison of the water chemistry present at various sampling locations, thus simplifying comprehension of regional water chemistry variations that could potentially impact uranium speciation, mobility, and bioavailability.

Another interesting comparison can be observed in the Stiff diagrams for 5T-537 (Figure 5) and 3K-331 (Figure 6). As was seen when comparing the water chemistries of Tohatchi Springs and Badger Springs, there is an apparent similarity in the water chemistries of 5T-537 and 3K-331. Both of these wells appear to have high concentrations of chloride, sodium, and potassium, but lower concentrations of all other ions analyzed, including bicarbonate and calcium. The striking similarity between the water chemistries of these wells is interesting due to their geographical locations; 5T-537 is located towards the southernmost edge of the Blackfalls region of the Navajo Reservation, whereas 3K-331 is located further north, closer to the town of Cameron. The similarity in water chemistries seen for these two unregulated water sources, in spite of their relatively large distance from one another, suggests that these wells are both supplied by the same aquifer.
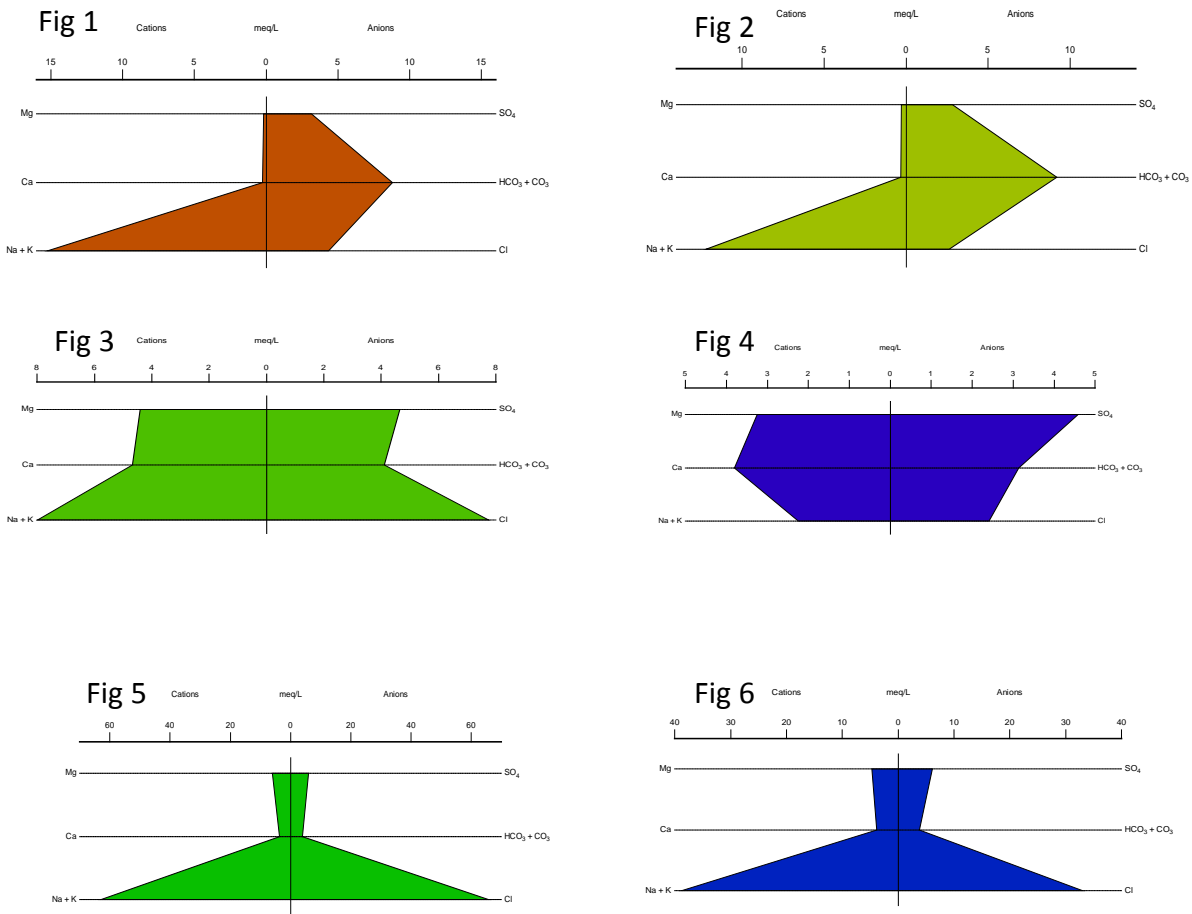
Figures 1 – 6: Stiff Diagrams of Tohatchi Spring (Fig 1), Badger Spring (Fig 2), Leupp corral (5T-518) (Fig 3), El Paso (Fig 4), 5T-537 .(Fig 5), and 3K-331 (Fig 6).

ICP-MS was utilized to determine the uranium content of water samples from each of the eighteen different unregulated sources. Filtered, acidified samples were utilized for these analyses. From an external calibration curve constructed prior to analyses, uranium concentrations were determined. Figure 7 shows the results of these analyses. For locations that were sampled on multiple days, an average analyte concentration is reported. Error bars are included; these represent the standard deviation of all measurements associated with the average analyte concentration.
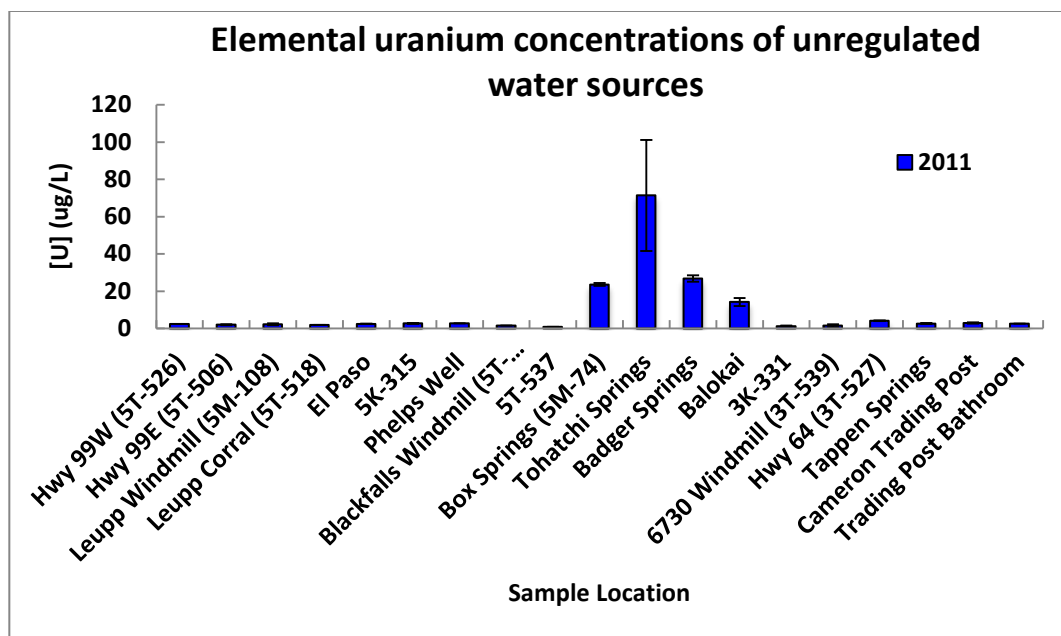
Figure 7. Uranium concentrations of acidic filtered water samples from unregulated water sources on the Navajo Reservation determined via inductively coupled plasma mass spectrometry.

As seen in Figure 7, most of the water sources sampled have relatively low uranium concentrations. There are four locations that were found to have uranium concentrations exceeding 10 μg/L; all other sample locations have uranium concentrations of approximately 5 μg/L or lower. One of the locations sampled has a uranium concentration that exceeds the U. S. EPA MCL of 30 μg/L; Tohatchi Springs was found to have a uranium concentration of approximately 70 μg/L. The large error bar associated with the uranium concentration of Tohatchi Springs can be attributed to the significant variation in concentration determined for samples collected at two different times during 2011. The concentration of uranium determined in February (100 μg/L) was higher than the concentration of uranium determined in October (45 μg/L). This seasonal variation could possibly be attributed to dilution of well water by runoff in months during which more precipitation was received.

The uranium concentrations in water samples from the Cameron region of the Navajo Reservation were much lower than expected. Considering that Cameron was a site of previous mining activity on the Reservation, uranium concentrations in this area were expected to be significantly higher than uranium concentrations in the Leupp area. One potential explanation for the surprisingly low concentrations seen in the Cameron region is contributions from runoff. Dilution of well water with runoff from seasonal precipitation could play a role in decreasing the uranium concentrations of these water sources.

Current results were compared with uranium concentration data previously collected in the Ingram laboratory, as well as data collected by the Army Corps of Engineers from 1994 to 2000. Figure 8 represents this comparison. Previous data was not available for all water sources. For locations that were sampled on multiple days within the same year, an average analyte concentration is reported. Error bars are included for 2011 data; these represent the standard deviation of all measurements associated with the average analyte concentration.
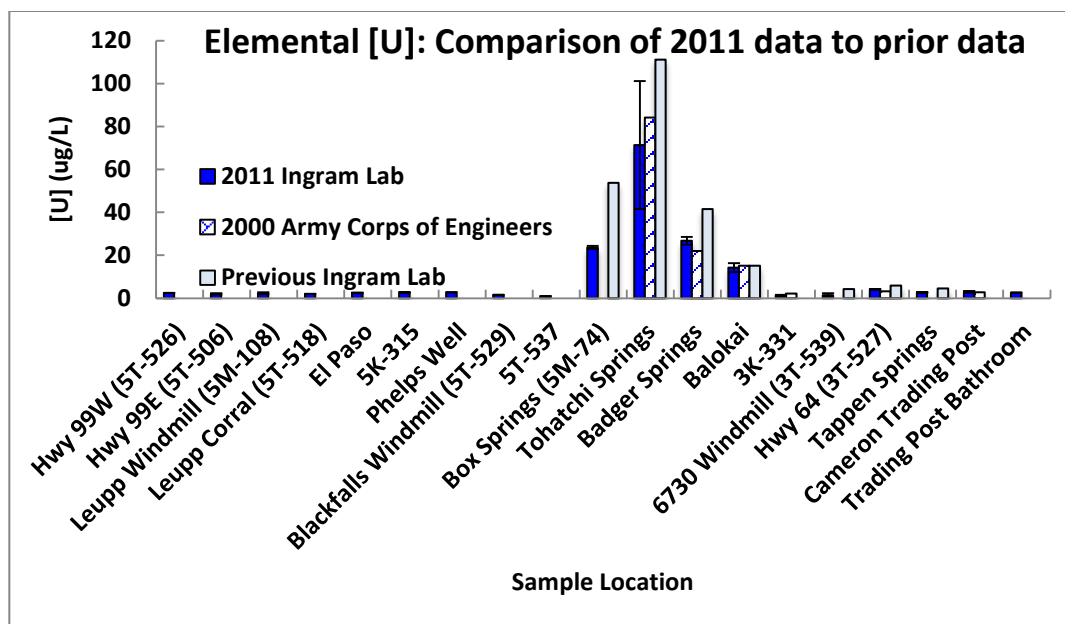
Figure 8. Comparison of uranium concentrations of water samples from unregulated sources on the Navajo Reservation (2011 data) with previously reported values from the Ingram laboratory and the Army Corps of Engineers.

As demonstrated in Figure 8, there is some discrepancy among the uranium concentrations determined in the Ingram laboratory, both in 2011 and previously, and the values reported by the Army Corps of Engineers. For example, the uranium concentration determined for water from Box Springs (5M-74) in 2011 was approximately half of the concentrations previously determined by the Ingram laboratory for that location. There is no data from the Army Corps of Engineers for this water source. The uranium concentration of water collected from Tohatchi Springs is different for all three data sets; the 2011 data from the Ingram laboratory resulted in an average concentration of approximately 70 μg/L, whereas previous Ingram laboratory data suggests a higher concentration of approximately 110 μg/L. The value of approximately 85 μg/L reported by the Army Corps of Engineers is between the two values from the Ingram laboratory. The large error associated with the 2011 result for Tohatchi Springs suggests that the true value is likely somewhere between 85 and 110 μg/L.

There are numerous factors that could explain the discrepancies in the data presented in Figure 8. As mentioned, the values reported prior to 2011 by the Ingram laboratory are averages determined for samples originating from multiple sample collections. It was not clearly indicated in the data whether the same student executed the collection and analyses or whether identical sample collection, preparation, and analysis procedures were utilized each time. Additionally, seasonal variations could have an effect on the previous values obtained in the Ingram laboratory. Data obtained from the Army Corps of Engineers also appears to be somewhat inconsistent with the 2011 results from the Ingram laboratory. This disagreement could be due to the fact that the Army Corps of Engineers reported the results of a single measurement as the determined uranium concentration. Additionally, the analytical method employed by the Army Corps of Engineers is not stated in the project atlas; this is another potential source of uncertainty between the concentrations determined by the Ingram laboratory and those reported by the Army Corps of Engineers.

The findings of this project were quite interesting and provided some important insight in regards to the potential health hazards associated with unregulated water sources on the Navajo Reservation in northern Arizona. Numerous aspects of the water chemistry in eighteen unregulated wells from the southwestern region of the Navajo Reservation were studied. Various factors, including pH and ionic content, can have

a significant impact on the speciation of heavy metals in aqueous environments. Two ionic species in particular, bicarbonate (HCO_3^-) and calcium (Ca^{2+}), play a crucial role in uranium speciation at alkaline pH values; as described, all of the water sources sampled in this work fall within a pH range of roughly 7.5 to 8.5. The complexation of uranium with bicarbonate is relevant in this pH range, and will most likely overcome complexation of uranium with other potential ligands, such as phosphate and hydroxyl ions and humic substances. Two sample locations in particular, Tohatchi Springs and Badger Springs, have much higher bicarbonate concentrations (~500 mg/L) than any of the other water sources sampled. Box Springs (5M-74) and Balokai have lower bicarbonate concentrations (~350 mg/L); however, the presence of bicarbonate at these two locations could still be relevant in the mobilization and solubility of uranium.

In wells containing significant amounts of bicarbonate, it is also important to consider the calcium cation; formation of calcium uranyl carbonate compounds has been proposed to decrease the toxicity and bioavailability of uranium (Carrière, 2004; Prat, 2009). Tohatchi Springs and Badger Springs do not have high calcium content (~5 mg/L), and it is thus unlikely that uranium at these sites will be trapped in a nontoxic form. Box Springs (5M-74) and Balokai have higher calcium content (~30 mg/L); uranium at these two locations likely has a higher potential to form nonbioavailable complexes with calcium and bicarbonate ions than does uranium at the previously mentioned locations.

Uranium concentrations were also determined for each of the eighteen different unregulated water sources sampled. Based on the results obtained in 2011, only one of the eighteen wells sampled has a uranium concentration above the U.S. EPA MCL of 30 μg/L; the water from Tohatchi Springs has an average uranium concentration of approximately 70 μg/L. However, after comparison to previous data from both the Ingram laboratory and the Army Corps of Engineers, it is possible that other wells, including Badger Springs and Box Springs (5M74), may also have uranium concentrations above the MCL.

The high uranium content of particularly Tohatchi Springs and Badger Springs, in combination with the previously determined high bicarbonate and low calcium concentrations, makes these wells a serious potential health threat to residents of the Navajo Reservation.   These wells are located within approximately 15 miles of one another in an extremely remote area of the Navajo Nation. Based on the comparison of Stiff diagrams constructed for each of these locations, it appears that the water chemistries of Tohatchi Springs and Badger Springs are very similar. This leads to the conclusion that uranium in these water sources, most likely present as hexavalent uranium in the form of a uranyl-hydroxyl or uranyl-carbonate complex, will have similar speciation. For many individuals, these wells in the remote Blackfalls region of the Navajo Reservation serve as the closest available water source; however, the water from these wells may indeed be unsafe for human consumption and not suitable as a drinking water source.

Future avenues for aqueous uranium research in the Ingram laboratory could include theoretical modeling and the utilization of different analytical techniques to gain a deeper understanding of the uranyl complexes that are in fact present in water sources on the Navajo Reservation. The 2009 publication from Odette Prat and colleagues focuses on modeling and characterizing uranyl carbonate complexes in drinking water from drilled wells in southern Finland. A computer simulation program, CHESS (chemical equilibrium speciation with surface), was used to predict the most probable uranium species present based on various aspects of the water chemistry of the wells. Following this simulation, time-resolved laser-induced fluorescence spectroscopy (TRLFS) was employed to experimentally determine whether the predicted complexes were in fact present in the well water. Theoretical modeling has been utilized for the purpose of simulating and predicting uranium speciation in various other works as well (Frelon, 2005; Sutton, 2004); TRLFS has also been employed by other groups to determine aqueous uranium speciation (Moulin, 1995). It would be interesting to follow a similar experimental approach to study the uranium complexes present in the unregulated wells on the Navajo Reservation.

Another direction for future work in the Ingram laboratory related to contaminated water sources on the Navajo Reservation includes qualitative and quantitative determination of other heavy metals in the previously studied water sources. These studies have already been initiated. ICP-MS was utilized to conduct survey scans on well water samples in an effort to identify trace metal contaminants other than uranium. The multi-element capabilities of ICP-MS make it an ideal technique for this type of analysis. Future work will involve quantitative studies of additional metal contaminants.

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