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Quantification of Elemental Contaminants in Unregulated Water across Western Navajo Nation

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Abstract: The geologic profile of the western United States lends itself to naturally elevated levels of arsenic and uranium in ground water and can be exacerbated by mining enterprises. The Navajo Nation, located in the American Southwest, is the largest contiguous Native American Nation and has over a 100-year legacy of hard rock mining. This study has two objectives; quantify the arsenic and uranium concentrations in water systems in the Arizona and Utah side of the Navajo Nation compared to the New Mexico side and to determine if there are other elements of concern. Between 2014 and 2017, 294 water samples were collected across the Arizona and Utah side of the Navajo Nation and analyzed for 21 elements. Of these, 14 elements had at least one instance of exceeding a national regulatory limit, and six of these (V, Ca, As, Mn, Li, and U) had the highest incidence of exceedances and were of concern to various communities on the Navajo Nation. Our findings are similar to other studies conducted in Arizona and on the Navajo Nation and demonstrate that there are other elements that may be a concern for public health beyond arsenic and uranium.

Keywords: Unregulated water; Navajo; arsenic; uranium; manganese

1. Introduction

The geology of the Four Corners region of the American Southwest is comprised of a sandstone and limestone bedrock with an iron-oxide and iron-sulfide mineralite matrix that contains an abundance of natural resources including coal, copper, uranium, and vanadium [1- 3]. For this reason, mining in the Four Corners region has been ongoing for the past 100 years and has left a legacy of widespread environmental contamination, affecting groundwater and soil near mine features. In addition to contamination from mining and ore refining, the iron-oxide and iron-sulfide mineralite matrix present an added hazard due to their association with heavy arsenic concentrations [4, 5]. Natural arsenic is bound loosely through ionic interactions with a variety of mineralites, including iron-oxides and iron-sulfides, which can be released into the surrounding environment. Mining practices expedite this process by bringing ores closer to the surface and increasing the surface area of these iron-arsenic species as well as concentrating waste through tailing piles and run-off [6, 7].

Rural and tribal communities are particularly vulnerable to environmental contamination, due to a lack of public infrastructure, insufficient medical facilities, and low socioeconomic status [8, 9]. Additionally, a higher density of large-scale mining and refining operations are found in these communities, which increases the risk of exposure and contamination to those living in these areas [10-12]. One example is the Navajo Nation, located within the Four Corners region of the American Southwest. From the 1940s through the 1980s, the Navajo Nation was the largest producer of uranium ore in the United States for use of nuclear munitions during the Cold War [13-15]. Uranium mining exposures have been directly linked to an increase in lung and other uranium related cancers in

miners and their families [14, 16, 17]. Though uranium mining ceased in the 1980s, the contamination left from these operations still represent a significant danger to the Navajo people [18]. Unregulated "Livestock Only" water sources found across the Navajo Nation are susceptible to contamination from previous mining operations, and their unregulated nature can result in exceedance of various United States Environmental Protection Agency (EPA) Maximum Contamination Levels (MCL) [19-22]. These unregulated water sources often represent the only source of water for human consumption and watering crops for families and communities across the Navajo Nation [12].

Both arsenic and uranium's health effects from ingestion of contaminated drinking water has been widely established. Arsenic is recognized as a known carcinogen and has been demonstrated to cause vascular damage like that seen in chronic heart disease. Additionally, studies have demonstrated that arsenic can play a significant role in the development of chronic diseases by acting as a potentiating agent in concert with other contaminants [23-26]. Uranium as a contaminant in drinking water has been demonstrated to accumulate in the kidneys causing progressive kidney damage, which can lead to renal compromise or compound kidney damage related to diabetes. Its link to cancer, especially with Navajo uranium miners, was primarily tied to inhalation of uranium dust and radioactivity [7, 27, 28].

Numerous papers have reported that both arsenic and uranium frequently exceed the EPA's MCLs in unregulated water sources on the Navajo Nation [29-32]. These studies further demonstrated that arsenic contamination is more widespread than that of uranium contamination. In one study by Hund and colleagues, showed that there is a strong association between arsenic and uranium and suggested the existence of a belt of contamination down the central portion the Navajo Nation [33]. Although a plethora of studies and information exists on arsenic and uranium contamination on the New Mexico side of the Navajo Nation, the same scale of information does not exist on the Arizona or Utah side. In these regions, studies have focused on specific areas of the Navajo Nation, while leaving the surrounding areas as an unknown. Furthermore, water quality studies on Navajo thus far have focused primarily on arsenic and uranium contamination. There has been recent interest in ascertaining the possible contamination of unregulated water systems on the Arizona and Utah side of the Navajo Nation from other common contaminants including copper, lead, manganese, and mercury following the possible reopening of uranium mines around the Grand Canyon and the subsequent transport of uranium through the Navajo Nation [34, 35]. This paper seeks to address two questions; the first is to determine if arsenic and uranium contamination is as widespread on the Arizona and Utah side of the Navajo Nation as demonstrated on the New Mexico side; and second to quantify the extent of other possible elemental contamination that may exist. The information presented in this paper will serve to provide information to regulatory agencies as well as affected communities on the quality of contamination of their water systems and will serve as baseline information for elements that, up to this point, have not been fully explored.

2. Materials and Methods

2.1. Study Area

The Navajo Nation is the largest contiguous Native American reservation in the continental United States. Located within the Four Corners region of the American Southwest its borders span 71,000 square kilometers across Arizona, New Mexico, and Utah. The Navajo Nation is recognized by the United States' government as a sovereign nation, though the United States retains plenary power, and is separated into 110 tribal Chapters governed through five management Agencies: Chinle (14 Chapters), Crownpoint/Eastern (31 Chapters), Ft. Defiance (27 Chapters), Shiprock (20 Chapters), Tuba City/Western (18 Chapters). The Navajo Nation has a varied topography from upland plains to mountainous regions, which produces different climates and can include warm, arid deserts with sparse flora; intermediate steppe with grasses and pinyon-juniper; and cold, sub-humid mountain climates with pines and oaks. The map in Figure 1 displays the borders of the Navajo Nation and outlines the study area. Samples included in this study are represented in yellow and previous sampling efforts by the Centers for Disease Control and Prevention (CDC), the United

States' Environmental Protection Agency (EPA), and Army Corps of Engineers are also provided [36]. The five major uranium regions are displayed in this map; larger and darker colored circles indicate larger uranium mines. The present study area was restricted to the Arizona and Utah Western, Chinle, Shiprock, and Fort Defiance Navajo Management Agencies.

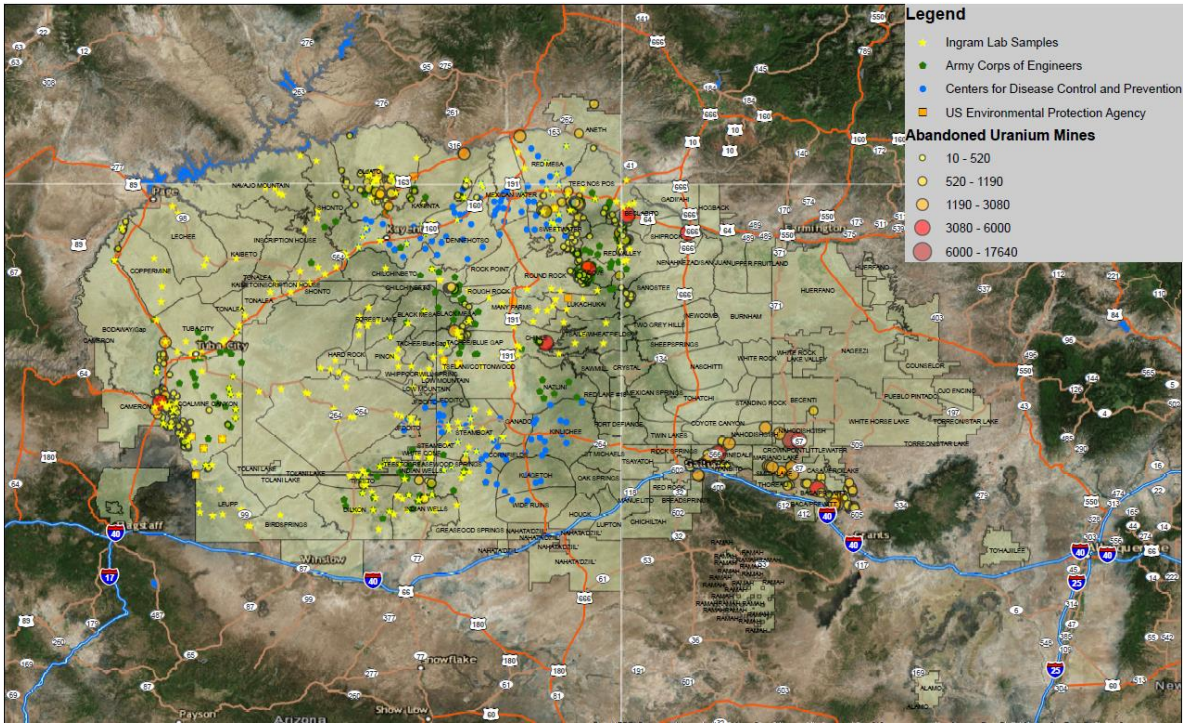


Figure 1. Map of the Navajo Nation. Sites of abandoned uranium mines are represented by circles, with larger and darker colored circles noting areas of larger scale mines. Samples collected for this study (n = 296) are represented in yellow and previous sampling efforts of government agencies are displayed in green (Army Corps of Engineers), blue (CDC), and orange (US EPA).

2.2. Sample Collection

Water samples (n=296) were collected from a variety of unregulated sources including windmills, troughs, springs, and tanks. Samples were identified from working with the Navajo Tribal Utility Authority (NTUA) branch offices, previous surveys conducted by the US Army Corps of Engineers (US EPA 2000a), along with community and chapter members. The unregulated nature of these water sources mean that they are not regularly monitored for bacterial or elemental contamination and are not upheld to the same Clean Drinking Water Act standards, despite often being an important, if not the only, source of water for communities. Their unregulated designation is due to these water sources falling outside of set active management areas as defined by the Arizona Department of Water Resources and the Navajo Nation Department of Water Resources or being given the designation of "livestock tanks" [37, 38].

Sampling was conducted during January – March and June - August of 2014, January – March of 2015, July 2016, and June and October 2017, with many sites being sampled numerous times for evaluation of seasonal fluctuation and verification of elemental concentrations. Upon arrival to each site, the GPS coordinates were recorded using WGS84 Map Datum, a site description including presence of flora and fauna and notable features, type of water source, and site pictures were collected. An identification code was assigned to each site based on previous labeled designations, if available, name given by community members, or readily identifiable features. Water sources were turned on and ran for one to two minutes prior to collection to ensure accurate representation; this delay in sample collection was not conducted if community members were present or if water levels were low. Samples for total elemental analysis were filtered through a 0.45-micron filter, preserved in nitric acid (HNO_3 – omnipure grade) to a pH below 2, and sent back to Northern Arizona

University (NAU) to be stored at 4°C until analysis [39]. Samples for total mercury analysis were acid preserved in hydrochloric acid (HCl) to a pH below 2, separated into two different collection populations, one had an aliquot of 5% (w/v) potassium permanganate ($KMnO_4$) in 0.1% HCl added in the field while the other set did not have the $KMnO_4$ added, and sent back to NAU to be stored at 4°C until analysis [40].

2.3. Sample Analysis and Instrumentation

Analysis was conducted by inductively coupled plasma mass spectrometry (ICP-MS) (table 1), inductively coupled plasma optical emission spectroscopy (ICP-OES) (table 2), flame atomic absorption (FAA), or cold vapor mercury atomic absorption (CVAA) for a variety of elements. All samples analyzed by ICP-MS and ICP-OES were diluted 1:10 with a dilution solution of 2% HNO_3 that contained an internal standard corresponding to the instrument and analysis method used. A Thermo Fisher Scientific X-Series 2 ICP-MS was used for all analyses with an ESI APEX HF dissolving nebulizer introduction system to produce higher sensitivity. Prior to each analysis, an auto-tune sequence and stage alignment were conducted followed by a manual tune for As or U signals to optimize detection and maintain stability throughout analysis. During element selection, both the most common and most stable masses were selected, and the resulting concentrations compared; lead had numerous masses selected to accurate quantitate its occurrence in the sample given the differing radiogenic origins [41, 42]. To overcome the isobaric interference from the $^{75}ArCl$ polyatomic species and produce accurate arsenic detection an internal correction equation was programed on the ICP-MS utilizing $^{77}ArCl$, ^{82}Se, ^{83}Kr signals [43]. To further limit isobaric interferences of polyatomic ions and optimize detection, analysis on the ICP-MS was separated into "light" and "heavy" elements for analysis. ICP-OES analysis was conducted with a Perkin-Elmer Optical Emission Spectrometer Optima 4300 DV with standard plasma settings and a 2-point background correction. To overcome spectral interferences from overlapping emission lines, analysis was split into two separate methods.

Table 1. Summary of ICP-MS Analysis.

ICP-MS Analysis			
Element	**Mass**	**Internal Standard**	**Light or Heavy**
Cr	52	Rh	Light
Ni	58, 60	Rh	Light
As	75	Ir	Heavy
Mo	95, 98	Rh	Light
Cd	111, 114	Ir	Heavy
Sn	118, 120	Ir	Heavy
Sb	121	Rh	Light
Pb	206, 207, 208	Ir	Heavy
U	238	Ir	Heavy

Table 2. Summary of ICP-OES Analysis.

ICP-OES Analysis			
Element	**Wavelength (nm)**	**Axial or Radial**	**Internal Standard**
Ba	455.403	Radial	Y
Be	313.042	Radial	Y
Cu	325.747	Radial	Y
Fe	259.933	Radial	Y
Mn	257.604	Radial	Y
V	292.399	Radial	Y
Zn	213.855	Axial	Y

A Perkin Elmer AAnalyst 200 Flame Atomic Absorption Spectrometer with standard operating settings was used to determine total calcium in collected samples. Samples were diluted either 1:10

or 1:100 with a 2% HNO_3 solution. In addition, an aliquot of both lanthanum nitrate and cesium chloride were added as matrix modifiers and ionic suppressants to a final concentration of 1,000 mg/L. Similar quality assurance and quality control methods from ICP-MS and ICP-OES analysis were applied to FAA analysis [44].

To evaluate total mercury in the samples, a Perkin-Elmer FIMS 100 Cold Vapor Mercury Analyzer with standard operating settings and procedures was used. Field samples were separated into those that had an aliquot of 5% (w/v) $KMnO_4$ in 1% HCl added in field and those that had not been added; 5% (w/v) $KMnO_4$ 1% HCl was added during sample preparation to those without $KMnO_4$. Prior to analysis hydroxylamine hydrochloride and an antifoaming agent were added to quench excess $KMnO_4$. To ensure quality assurance and quality control, a lab standard and a certified reference material were run alongside the samples [45].

2.4. Quality Assurance/Quality Control

To ensure accuracy of the analysis a National Institute of Standards and Technology Standard Reference Material 1640a (NIST 1640a), field and instrument blanks, and check standards were analyzed alongside the samples. Additionally, a subset of 121 samples were sent to two separate certified laboratories, the Arizona Laboratory for Emerging Contaminants at the University of Arizona in Tucson, Arizona and the University of New Mexico's Analytical Chemistry Laboratory in Albuquerque, New Mexico, to have 20 of the investigated elements analyzed to compare the analysis conducted at NAU.

3. Results

Water samples from unregulated sources on the Navajo Nation were sampled from 2013 through 2017 and were analyzed for 21 elements by ICP-MS, ICP-OES, FAA, and CVAA. The concentrations of each element were compared to US EPA MCLs [18, 46] and US national averages reported by Agency for Toxic Substances and Disease Registry [47], United States Geological Society [48], and Morr [49]. Table 3 displays the total number of samples for each element that had a reported value that exceeded, approached, was below the regulatory or national averages, or below detection by the method used. A sample was "approaching" a limit if its concentration was within 75% of the reported regulatory limit or national average, which has been suggested as a precautionary guideline to monitor water resources [50-55].

Of the elements analyzed, only 14 elements had samples that had at least one instance of exceeding either regulatory or national averages (Table 3). Of these 14 elements, six (V, Ca, As, Mn, Li, and U) were selected to contrast either because of many samples exceeding a guideline or based on possible detrimental health impacts [47].

Table 3. List of 21 elements analyzed by ICP-MS and number of samples categorized with respect to regulatory guidelines.

Element	Regulatory Guideline	Exceeding	Approaching	Below	Below Detect	Total Wells Sampled
V[α]	0.2 ug/L	97	1	19	4	121
Ca[∓]	21.8 mg/L	69	4	51	0	124
As[*]	10 ug/L	40	6	157	32	235
Mn[α]	50 ug/L	29	1	91	0	121
Li[α]	73 ug/L	28	10	83	0	121
U[*]	30 ug/L	21	10	179	21	231
Al[α]	50 – 200 ug/L	13	3	105	0	121
Mo[α]	80 ug/L	7	5	101	11	124
Sr[α]	4 mg/L	7	4	110	0	121
Fe[α]	300 ug/L	4	6	110	1	121
Ni[∓]	3-10 ug/L	3	16	100	5	124

Sn[₸]	1.1 – 2.2 ug/L	1	5	19	99	124
Be[*]	4 ug/L	1	0	42	78	121
Cd[*]	5 ug/L	1	0	9	114	124
Zn[α]	5 mg/L	0	1	120	0	121
Hg[*]	2 ug/L	0	0	124	0	124
Cu[α]	1.3 mg/L	0	0	121	0	121
Ba[*]	2 mg/L	0	0	121	0	121
Cr[*]	100 ug/L	0	0	105	19	124
Sb[*]	6 ug/L	0	0	106	18	124
Pb[*]	0 ug/L	0	0	78	46	124

*US EPA Primary MCL; ₸ Compared to US Average, [α]US EPA Secondary or Tertiary.

For arsenic and uranium analysis, 296 sites were visited but 61 sites were dry or otherwise unable to sample. Of the remaining 235 sites, these were sampled at least twice, the results from the analysis combined, and the averages reported (Table 4). The other 19 elements were conducted on a subset of 121 or 124 samples, which were also surveyed at least twice, and the averages of the analysis reported (Table 4). The median of the six selected elements demonstrate a right-skew, but comparison of the averages to the regulatory or national averages V, Ca, and Mn concentrations are above these limits, As and Li are approaching, and U is below. All the elements, except for Hg, had an outlier with a concentration value that exceeded the regulatory or national average. Evaluation of the location and identification of the samples that produced these numbers were collected from decommissioned water sources with open tops, so these values are likely the result of evaporation concentrating the contaminants in the water (Table 4).

Table 4. List of 21 elements analyzed by ICP-MS reporting the maximum, minimum, average, and median values from the set of samples listed in Table 1.

Element	Max (ug/L)	Min (ug/L)	Average (ug/L)	Median(ug/L)
V[α]	500.28	B.D.	28.20	2.73
Ca[₸]	431.16	0.35	44.66	25.62
As[*]	188.33	0.03	8.21	1.99
Mn[α]	14662.81	0.10	164.13	3.44
Li[α]	632.32	3.02	63.28	37.60
U[*]	490.65	0.04	14.05	3.05
Al[α]	64555.12	2.16	555.57	12.08
Mo[**]	1188.33	B.D.	27.23	2.89
Sr[α]	10349.91	18.90	1158.79	478.15
Fe[α]	604.52	0.02	61.47	23.13
Ni[₸]	559.64	0.02	6.42	1.09
Sn[₸]	2.51	0.01	0.53	0.40
Be[*]	60.30	B.D.	0.50	0.00
Cd[*]	11.10	0.01	0.30	0.05
Zn[α]	3886.65	3.38	196.91	48.06
Hg[*]	B.D.	B.D.	B.D.	B.D.
Cu[α]	26.01	0.02	2.80	1.21
Ba[*]	1203.07	7.91	177.22	93.70
Cr[*]	12.05	0.03	0.94	0.47
Sb[*]	2.79	0.03	0.33	0.27
Pb[*]	9.25	0.02	0.66	0.10

*US EPA Primary MCL; ** WHO Drinking Advisement; ₸ Compared to US Average, [α]US EPA Secondary or Tertiary Recommendation. B.D. Below Detect.

Vanadium had the most exceedances at 97 of 121 samples collected, whereas U had the lowest prevalence of exceeding values at 21 of 231 samples collected (Table 3). To ascertain if these six elements were associated with specific regions on the Navajo Reservation, the results were separated by the four agencies from which the samples were collected: Chinle, Fort Defiance, Shiprock, and Western Agency (Table 5). Fort Defiance and Western Agency had the highest exceedances for As, U, and V. Chinle and Western Agency had the highest exceedances for Ca, Li, and Mn.

Table 5. Distribution of As, U, V, Mn, Ca, and Li in relation to respective regulatory limits (US EPA MCLs and USGS averages) across the Chinle, Fort Defiance, Shiprock, and Western Agencies.

		Agency				
Element		**Chinle**	**Fort Defiance**	**Shiprock**	**Western**	**Totals**
Arsenic	Exceeding	3	23	3	11	40
	Approaching	0	4	0	2	6
	Below	31	29	10	89	159
	B.D.	11	2	2	15	30
	Totals	45	58	15	117	235
Uranium	Exceeding	3	7	1	7	18
	Approaching	3	3	0	5	11
	Below	32	44	14	93	183
	B.D.	6	2	0	11	19
	Totals	44	56	15	116	231
Vanadium	Exceeding	16	28	5	48	97
	Approaching	1	0	0	0	1
	Below	13	1	3	2	19
	B.D.	2	0	0	2	4
	Totals	32	29	8	52	121
Manganese	Exceeding	19	4	1	5	29
	Approaching	1	0	0	0	1
	Below	12	25	7	47	91
	B.D.	0	0	0	0	0
	Totals	32	29	8	52	121
Calcium	Exceeding	26	11	1	31	69
	Approaching	0	0	0	4	4
	Below	8	18	6	19	51
	B.D.	0	0	0	0	0
	Totals	34	29	7	54	124
Lithium	Exceeding	11	8	0	9	28
	Approaching	2	3	3	2	10
	Below	19	18	5	41	83
	B.D.	0	0	0	0	0
	Totals	32	29	8	52	121

4. Conclusions

A combination of a long history of hard rock mining, limited water infrastructure, and a natural geologic profile high in metal and metalloid species increases the potential for drinking water contamination on the Navajo Nation. An added factor for concern is that as much as 30% of those living on the Navajo Nation get their drinking water from unregulated sources [56]. The results presented in this study demonstrated that there is comparable level of arsenic in unregulated water resources to rural communities across the United States [5, 57]. Welch and colleagues found slightly less than half of 30,000 arsenic analyses of ground water in the United States were at 1 µg/L and about 10% exceeded 10 µg/L. However, arsenic concentrations exceeding 10 µg/L were more frequently

observed in the western United States than in the eastern half. Looking specifically at Arizona and the Navajo Nation, these results reveal comparable concentrations and incidences of regulatory infractions for elemental contaminants, especially arsenic [30, 58]. Jones and colleagues utilized public water databases to quantify arsenic concentrations across Arizona and found that rural areas and those associated with mining ventures had arsenic in water systems at similar concentrations to those represented in this study, but it lacked information about the Navajo Nation. Hoover and colleagues combined federal databases and sampling efforts by the University New Mexico to characterize the extent of elemental contamination in drinking water across the Navajo Nation. Like this study, they found elemental contamination existed across the Navajo Nation and was closely dependent on the agency where sampling was conducted. The variability of elemental contamination in water noted in this study and the Hoover study may be related to differing access to water across the Navajo Nation.

Beyond arsenic and uranium, the results demonstrate an elevation above US EPA MCLs and USGS average water content of four other metals (Ca, Li, Mn, V). These four metals have been investigated in only a few previous publications, the most significant being a spatial clustering analysis by Hoover (2018) that matched co-eluting contaminants in water sources across Navajo [44, 59, 60]. Elevations of calcium and vanadium in drinking water does not seem to have any significant detriment other than changes in aesthetic quality of the water, and these elevations seem reasonable given the geologic profile of the Navajo Nation. Some studies suggest lithium in drinking water is associated with decreased instances of some mental health conditions (depression, anxiety, and dementia); however, this is still hotly debated. Additionally, lithium exposure has been linked with the development of chronic kidney disease [60-64]. There is growing evidence that chronic exposure to manganese in drinking water may have similar neurotoxic effects as occupational exposure to manganese, resulting in intellectual impairment in children and visible brain deposition in mouse models [65-67]. Bouchard and colleagues in 2007 [68] conducted a pilot study investigating manganese exposure through tap water and the incidence of hyperactivity as a pathway for learning impairment in Canadian children. Their results demonstrated at concentrations like what was seen in the present study was correlated with more cases of hyperactive behavior and outbursts during classroom settings. They followed up this study in 2011 [69] with a cross-sectional study examining IQ scores in children and manganese exposure through water. Much like their earlier study, Bouchard and colleagues found that elevated levels of manganese in drinking water seemed to have a correlation with decreased IQ scores, and these findings have been repeated in other studies from other groups [70-72]. While the concentrations of manganese in the Canadian schoolchildren study conducted by Bouchard were slightly higher, an average of 200 ug/L, Bouchard makes the assertion that the children exposed to these concentrations were not relying on these water sources as their sole supply, and it is more important to look at a cumulative dose. Compared to this study, while the median manganese concentration is lower, the lack of available water in the areas sampled in this study may have a similar cumulative effect mentioned by Bouchard and is an avenue of study that warrants further investigation. Compared to arsenic and uranium in drinking water, both of which are recognized primary drinking water contaminants, elevated levels of calcium, lithium, manganese, and vanadium are based on secondary, tertiary drinking water standards and, in the case of manganese, these limits have been abolished. Despite this, these limits, as with primary standards, are a metric for which to compare the drinking water concentrations. Furthermore, arguments question if the current guidelines used to create enforceable regulatory limits on drinking water are insufficient, especially given research that opposes the previous dogma and support observable health consequences to exposed populations [50, 73].

This paper seeks to address two questions; the first is to determine if arsenic and uranium contamination is as widespread on the Arizona and Utah side of the Navajo Nation as demonstrated on the New Mexico side; and second to quantify the extent of other possible elemental contamination that may exist. The results reported here have demonstrated similarities in drinking water contaminants across the United States and in the American Southwest; they have additionally demonstrated the potential for other contaminants that may pose measureable health effects in those

exposed. A hydrogeochemical approach may expound upon the findings in this study, as well as others, especially elucidating the reason why certain regions of the Navajo Nation have a similar water contamination profiles despite differences in mining history and available infrastructure. This study contributes to the current understanding of water quality on the Navajo Nation and can help guide future policy decisions and the potential for health impacts from exposure to these contaminants.

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