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Spatial relationship between well water arsenic and uranium in Northern Plains Native lands

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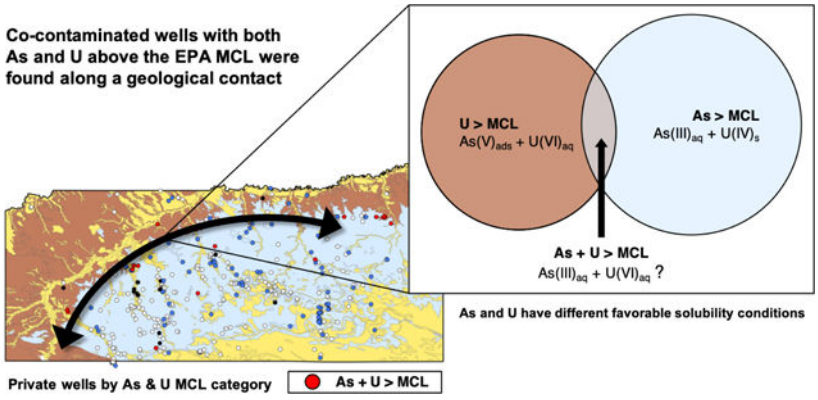
Abstract

Arsenic and uranium in unregulated private wells affect many rural populations across the US. The distribution of these contaminants in the private wells of most American Indian communities is poorly characterized, and seldom studied together. Here, we evaluate the association between drinking water arsenic and uranium levels in wells (n=441) from three tribal regions in North Dakota and South Dakota participating in the Strong Heart Water Study. Groundwater contamination was extensive; 29% and 7% of wells exceeded maximum contaminant levels for arsenic and uranium respectively. 81% of wells had both arsenic and uranium concentrations at one-tenth of their human-health benchmark (arsenic, 1 μg/L; uranium 3 μg/L). Well arsenic and uranium concentrations were uncorrelated (r_S=0.06); however, there appeared to be a spatial correlation of wells co-contaminated by arsenic and uranium associated with flow along a geologic contact. These findings indicate the importance of measuring multiple metals in well water, and to understand underlying hydrogeological conditions. The underlying mechanisms for the prevalence of arsenic and uranium across Northern Plains Tribal Lands in the US, and in particular the occurrence of both elevated arsenic and uranium in drinking water wells in this region, demands further study.

Graphical Abstract



Keywords

arsenic; uranium; well water; native lands

Introduction

Arsenic and uranium are naturally occurring trace elements present in groundwater[1, 2] across urban and rural areas of the United States.[3] As part of the Safe Drinking Water

Act Amendments of 1996,[4] the United States Environmental Protection Agency (US EPA) mandated protective standards for drinking water contaminants in public water supplies. The current maximum contaminant level (MCL) for arsenic is 10 μg/L and for uranium it is 30 μg/L.[5] Many rural populations, including American Indian communities, obtain their drinking water through private wells that, like most rural water supplies, are untested, or tested ad hoc for specific contaminants. There have been increasing efforts over the last two decades to install sizable rural water systems in North Dakota and South Dakota drawing in part from the Missouri river water. However, many communities and households still lack access to community water systems, relying instead upon potentially contaminated private wells.

Groundwater contamination appears to impact these communities.[6] For example, American Indian communities participating in the Strong Heart Study in the US Southwest and Northern Plains have higher urinary arsenic concentrations in study participants, compared to urban US populations.[3] In the Strong Heart Study, chronic arsenic exposure, primarily through drinking water, has been associated with cardiovascular disease,[7] some cancers (lung, pancreatic, and prostate),[8] diabetes,[9] chronic kidney disease,[10] and impaired lung function.[11] A study investigating patterns of multiple urinary metals identified a cluster of urinary arsenic, uranium, and tungsten as the most discriminant metal mixture when comparing a subset of the Strong Heart Study participants to a sample of an urban/sub-urban cohort (the Multi-Ethnic Study of Atherosclerosis (MESA)).[3] This metal cluster suggests groundwater as a possible common source of co-exposure among Strong Heart Study participants. Arsenic contamination is usually associated with anoxic groundwater, whereas uranium is most soluble in oxidizing conditions. In the Southwest, however, several studies have documented the presence of both elevated arsenic and uranium in groundwater.[12–14] This relationship stems from the concomitant enrichment of arsenic and uranium in rocks regionally, something exploited by regional mining, and solubility of both arsenic and uranium in local groundwaters.[13] These geological sources of metals and the industries that have exploited them can cause groundwater contamination. Although both uranium and arsenic contamination is abundant across the US Northern Plains, few studies have evaluated their combined occurrence, and thus whether arsenic and uranium represent a combined source of exposure regionally remains an open question.

The spatial distribution, organization, and coherence of contaminants measured using spatial statistics are useful because they directly relate to understanding the source of groundwater contamination and the processes that redistribute that contamination in the landscape.[15] These tools have been widely applied to understand groundwater arsenic, uranium contamination.[16–18] For example, we would expect similarity in water composition in nearby sources to indicate common contamination sources,[16] and concentrations to be correlated to the distance away from well-defined anthropogenic sources[19] or distributed natural sources of contamination.[17] Spatial statistics are also useful to extrapolate between datapoints in sparse datasets, something critical to estimate potential contaminant levels in understudied areas. For example, kriging methods turn a finite set of measurements into a continuous grid of concentrations.[18] Statistical methods are also useful to determine if this grid is or is not a faithful representation of the data presented. Among the most useful of these methods is the semivariogram, which determines the variance between samples as

a function of distance, to determine ideal sampling intervals and to understand potential limitations in kriging.[15, 20]

The main objective of this study was to measure well water arsenic and uranium concentrations in the Strong Heart Study (SHS) communities in North Dakota and South Dakota, and use statistical methods to better understand what is controlling their distribution across these areas. We used water samples collected through the Strong Heart Water Study (SHWS), a multilevel, participatory intervention to reduce arsenic exposure from private wells that was conducted in partnership with SHS American Indian communities in the Northern Plains.[21, 22] The SHWS implemented a community water testing program of private wells to identify households meeting the eligibility criteria for water arsenic treatment system installation and participation in the SHWS. We used spatial statistics and combined maps to visually represent known well water arsenic and uranium concentrations vs. predicted concentrations in the study areas. We hypothesized that well water arsenic and uranium would be positively associated across the SHWS communities, consistent with the findings in urine samples of the SHS participants.

Methods

Study Population

The SHWS is a randomized controlled trial for private well users aiming to reduce arsenic exposure in three SHS communities in North Dakota and South Dakota.[21] A water quality-monitoring program was implemented in February 2014, and is still ongoing, to identify eligible households for the intervention and to assess water quality parameters. As the point-of-use water arsenic treatment system is only installed in households with low uranium, both arsenic and uranium were measured prior to inclusion in the intervention. Unfiltered water samples from private wells used for drinking water were obtained at the tap in three Tribal Nations in North Dakota and South Dakota (N=452 unique wells), referred to as Regions 1, 2 and 3. The data is collected with the expectation of data sovereignty, that the SHWS participants and tribes would have a say in which data are collected, and that they would maintain ownership of the data and be directly involved in any and all future research involving that data. As such, the names of the communities and exact locations of well water samples are not included (other than that they are in SD and ND) to preserve the anonymity of the communities. The well sampling locations were determined by participant household location, and not uniformly nor randomly distributed. The average spacing between sampled wells is 15.5 km in Region 1, 23.7 km in Region 2, and 41.6 km in Region 3.

Water Arsenic and Uranium Concentrations

A detailed description of water collection and metal analysis has been published elsewhere.[22] Briefly, the SHWS collected water samples from kitchen faucets from 2014–2020, and analyzed them for arsenic and uranium using an EPA guided sampling plan.[23] GPS well locations of water sampling were collected from households. Using 20 mL scintillation vials, we collected a total of 723 water samples for metal analysis from a total of 452 unique wells. The number of wells sampled varied by year (29 wells in 2015, 64 wells in 2016, 211 wells in 2017, 115 wells in 2018, 31 wells in 2019, and 2 wells in

2020). Most wells were shallow and of unspecified depth and screen length. Of the 23 wells with known depths, the mean and median depths were 65 and 40 m. Although additional data about well water composition would be helpful to fully characterize the water, these data were not routinely measured in most samples, except for analysis performed on samples collected and analyzed in 2016. Cadmium and lead, as well as other parameters, were also analyzed in a subset (n=64), including alkalinity sulfate, silica, and pH and are reported in Powers et al (2018).[22] Of the 251 wells with duplicate samples, there was high agreement within wells (intraclass correlation coefficient (ICC): arsenic, 0.991 (95% confidence interval 0.988, 0.993); uranium, 0.999 (0.999, 0.999)). Average metal concentrations were calculated for wells with repeated measures. Water samples collected in 2014 (N=29 wells) were analyzed by inductively coupled plasma-mass spectrometry (ICPMS) in 2015 at the Johns Hopkins University Trace Metals Lab (Baltimore, Maryland). All other water samples were analyzed by ICPMS at Mid-Continent Testing Labs, Inc. (Rapid City, South Dakota) (N=423 wells). 53 wells did not have both metals measured and were therefore not included in this analysis. The limits of detection (LOD) varied depending on dilution factors, methods, and analytical facility. The LOD for arsenic were 0.1, 5.0, and 1.0 μg/L in 2015, 2016, and 2017–2020, respectively; and for uranium were 0.0015, 1.0, and 0.2 μg/L in 2015, 2016, and 2017–2020, respectively.[22] First, samples with arsenic concentrations below the LOD of 5 μg/L (N=58) were excluded from this analysis, as 5 μg/L is well within the range of meaningful arsenic exposure levels. We additionally excluded samples from wells missing geographical coordinate information (N=15). Then of the 441 wells with both arsenic and uranium measurements and geographical location, the total number of samples below the LOD was 114 for arsenic (30 below 1 μg/L) and 52 for uranium (30 below 0.2 μg/L and 22 below 1 μg/L). Concentration values for these samples were imputed as the $\mathrm{LOD}/\sqrt{2}$. Of the 441 wells, 58 were in Region 1, 10 in Region 2, and 373 in Region 3. Our main analysis focuses on Region 3; Region 1 and 2 are more exploratory due to the smaller sample sizes.

Statistical Analysis

We examined the relationship between arsenic and uranium concentrations using the Spearman's rank correlation coefficient. We categorized arsenic and uranium well concentrations relative to their MCL to visualize samples affected by neither, one, or both contaminants in each region. To understand the relative influence of neighboring wells on metal concentrations, we created semivariograms separately for each metal respective of geographical region. We then conducted a spatial kriging, a common method of estimating metal concentrations between measurements at known locations. We used inverse distance weighting (IDW) across the study area to create a smooth gradient of expected values of arsenic and uranium well water concentrations, respectively. Inverse distance weighting assigns values to unknown points using weighted averages of known points, with weighting based on the inverse distance to that point (points further away affect the average less). Our IDW interpolation model creates a smooth raster layer using a distance coefficient of 2. A 300-row grid of pixels that have individual values provided sufficient resolution. We transformed the raster grid produced from the interpolation into a vector layer, which permits different visualization techniques, to represent the estimated pattern by a gradient of color. Darkening of colors denotes an increased estimation of well water concentrations.

Finally, we evaluated the spatial relationship between arsenic and uranium well water concentrations and well location with respect to local geological units and their contacts using data obtained from USGS. All maps were created with QGIS (version 3.4.11). Spearman correlations, average spacing, and semivariograms were conducted using R (version 3.6.1) with packages stat, fossil, and gstat, respectively.

Results and Discussion

Metals Concentrations in Wells

Overall, 33% of wells had at least one of the two metals above their respective MCL. 29% of wells exceeded the US EPA MCL for arsenic, 7% of the wells exceeded the MCL for uranium, and 4% exceeded the MCL for both metals. Among wells with arsenic exceedances, 77% of wells had uranium present at one-tenth of its benchmark (1μg/L), a benchmark used in the US Geological Survey (USGS) study of domestic well water quality,[24] while 100% of uranium exceedances had arsenic present at one-tenth of its benchmark (3μg/L). Of the wells with both metals below MCLs, 81% had both metals present at one-tenth of their respective benchmarks. Across all regions, the median and interquartile range (IQR) well concentrations were 7.0 (4.7–11.2) μg/L for arsenic and 8.1 (4.2–16.0) μg/L for uranium. Region 1 had the highest median (IQR) arsenic concentration (9.0 [3.6–13.4] μg/L) and Region 3 had the highest median (IQR) uranium concentration (9.8 [5.8–17.3] μg/L). Region 2 had median concentrations <1 μg/L for both metals. Overall, water metal concentrations of arsenic and uranium showed no statistical correlation (Spearman correlation coefficient 0.06, p=0.2). In an analysis restricted to Region 3, the correlation remained weak and non-significant (Spearman correlation coefficient 0.08, p=0.1). Given the majority of data are in Region 3, our analysis focuses on this region. Descriptive statistics of well concentrations overall and for Region 3 are shown in Table 1 and in Supplementary Table 1 for Regions 2 and 3.

For descriptive purposes, we denoted wells with concentrations above the respective metal MCL as “high” and below the respective MCL as “low (Table 1, Supplementary Table 1). These categorizations are visualized in Figure 1A for Region 3 (Supplementary Figure 1 for Regions 1 and 2). Given that arsenic and uranium are derived from rocks, it is also useful to examine the spatial relationship of contamination to mapped geological features. Data plotted on a shallow geological map show the connection between contaminant levels and major geological units present within the aquifers (Figure 1B). Within Region 3, 68% of wells (N=255) had concentrations below the MCL for both metals (white color); 23% of wells (N=86) had arsenic concentrations above the MCL and uranium concentrations below the MCL (blue color); 4% of wells (N=16) had uranium concentrations above the MCL and arsenic concentrations below the MCL (black color); and 4% (N=16) had both metals above the MCL. In Region 1, 45% of wells had arsenic concentrations above the MCL, and no wells had uranium above the MCL (Supplementary Figure 1). In Region 2, most wells (9/10) were below the MCL for both arsenic and uranium (Supplementary Figure 1).

Spatial Correlation

Figure 2 shows semivariograms for arsenic and uranium well concentrations for Region 3. The semivariance of arsenic remains constant with increasing distance, indicating that well water concentrations were spatially uncorrelated at the scale of measurement. Uranium, however, shows some coherence (decreased variance) at distances <30 km. Semivariograms were not meaningful for Regions 1 and 2 due to small sample sizes (data not shown).

The constant semivariance of arsenic across all distances indicates that geological factors that affect arsenic levels are smaller in scale than the measured sampling intervals (an average distance of 41.6 km separated wells in this dataset). However, the decreased variance of uranium at distances <30 km indicates its concentration is controlled in part by geological conditions that vary on similar length scales. Higher levels of one metal were not correlated with higher levels of the other using individual water samples. However, there appeared to be a trend for wells with higher arsenic and high uranium levels arching from the Southwest corner towards the Northeast corner in Region 3 that coincides with the boundary of the Arikaree and White River formations, while elevated arsenic with low uranium levels were distributed throughout the Arikaree formation.

Spatial Interpolation

Spatial interpolation plots for Region 3 are shown in Figure 3. Wells are shown as yellow dots. Higher arsenic estimations were observed in the top section of Region 3 (darker blue colors) following a convex curve from the southwest corner to the northeast corner (Figure 3, Region 3). Higher uranium estimations, shown by the darker green colors, were present within the same space of the high arsenic estimation in Region 3. Visually, this trend is also seen in the wells with both metals above the respective MCLs (Figure 1, red color).

Co-Occurrence of Arsenic and Uranium in Wells

Water arsenic and uranium were detectable and often elevated across three regions in North Dakota and South Dakota for the Strong Heart Water Study. US EPA MCL exceedances were more common for arsenic (28%) than uranium (9%); 37% of all wells exceeded the MCL for one of the elements, and, surprisingly, 4% exceeded the MCL for both elements. This co-contamination of some water sources with both arsenic and uranium was limited to Region 3. This is unexpected as under reducing conditions where arsenic is usually mobilized as a result of iron reduction conditions,[25] but uranium is usually present as insoluble uranium(IV) oxide, uraninite.[26–28] Conditions favoring uranium solubilization are usually sufficiently oxidizing in that arsenic also oxidizes to arsenate, As(V), which adsorbs strongly to iron oxides, rendering it insoluble.[29, 30] Usually, the presence of mixed redox conditions is associated with perturbations in flow, ore deposits and mining.[12, 16, 31] It is possible that such occurrences within our study areas have geochemical similarities to mining sites in the Southwestern US, for example on the Navajo Nation, but geology in our study area differs considerably from those areas.[12, 32] High arsenic wells in Region 3 appear to be located primarily in aquifers found within felsic volcanic rocks (Figure 1: Ta, Arikaree Group) that contain reworked volcanic ash. Uranium is distributed regionally but highest in wells located in siltstone aquifers (Figure 1: Tw, White River Group) that contain sulfide minerals and presumably uraninite (UO_2), a reduced U(IV) mineral that

is susceptible to oxidative dissolution. It is possible that these wells sample heterogeneity within the aquifer where hydrogeological conditions and/or long well screens have mixed oxidized and reduced water, similar to that recently documented along the boundary of Minnesota and North Dakota and South Dakota.[33] Mixing would produce the spatial pattern for wells containing both uranium and arsenic contamination in areas where complex flow mixes groundwater along the boundary between those formations.

Evidence supporting the association of wells containing both arsenic and uranium above their respective MCLs includes the clear elevation of arsenic (and to some extent uranium) levels within the Arikaree formation within 5 km of the contact, and a higher prevalence of arsenic and uranium above their respective groundwater standards (Figure 4). In groundwater from <5 km from the contact, ~60% of the wells exceed arsenic drinking water standards, while 20% exceed uranium standards. Given these probabilities, we would expect 14% of wells would contain both elevated arsenic and uranium (assuming they are randomly distributed); however, 22% of wells in this zone contain both arsenic and uranium. In areas more distant from the contact, the observed frequency of exceedance matches those predicted by random distributions. Thus, these data indicate that arsenic and uranium groundwater contamination individually is more prevalent adjacent to the contact, and that they frequently co-occur in the same groundwater wells.

Swift Bird et al (2020) suggest an alternative hydrological explanation for the presence of dissolved arsenic and uranium in this region. Like our study, they identify groundwater in wells above the MCL for arsenic and uranium downgradient of the White River group and region within the Arikaree aquifer. They found increasing pH and alkalinity, along with Na^+ replacing Ca^+ as the dominant cation, across the region following groundwater flowing downgradient. They suggest that at a pH greater than 7.5, arsenic desorbs and the combination of Ca and carbonate enhance the formation of soluble $Ca_2(UO_2^{2+})(CO_3)_3$ complexes. Other evidence suggests that arsenic may also be desorbed under similar conditions.[34] It is likely that both hydrologic evolution of the groundwater, and redox disequilibrium affect uranium and arsenic levels in groundwater, though, given that they also report sufficiently high dissolved Fe (50 μg/L or greater, >1 mg/L in one group containing elevated arsenic and uranium) indicative at least partially reducing groundwater. Additionally, the increase in alkalinity above calcite saturation in many cases suggest it is not solely due to calcite dissolution, but to microbial respiration that produces alkalinity. That said, it is difficult to determine the role of each without detailed characterization of groundwater and aquifer redox state in our study, something we hope to do in follow up studies where a more comprehensive suite of groundwater analytes can be examined.

Native American communities in the Northern Plains are affected by both arsenic and uranium co-contamination. In a prior study, principal component analysis and cluster analysis revealed a consistent clustering of arsenic, uranium, and tungsten in urine samples among participants in the Strong Heart Study compared to participants from urban US populations in the Multi-Ethnic Study of Atherosclerosis (MESA) for which arsenic, uranium and tungsten did not cluster together.[3] In the Strong Heart Study, among the different metal clusters identified, arsenic-uranium-tungsten was the most prominent, and between the two populations (SHS vs MESA), drinking water is likely the major contributor

to potential exposure differences. Although few studies have specifically examined this combination of contaminants, wells containing multiple contaminants above MCLs are not rare and need to be considered more carefully in future research and mitigation efforts. Throughout the US, many private wells often exceed the MCL for at least one contaminant, yet private testing often only measures a single analyte. The US Geological Survey (USGS) study of domestic well water quality reported 23% of wells tested (n=1389) from 1991–2004 had at least one contaminant at concentrations greater than the MCL.[24] About 4% of wells had two or more contaminants above their human-health benchmark, consistent with our findings. Importantly, 73% of the USGS sampled wells contained mixtures of two or more contaminants at concentrations greater than one-tenth of their benchmarks.[24] Arsenic and uranium were among the most prevalent inorganic components of these well water mixtures, along with nitrate and radon, and less commonly, molybdenum and manganese. In our study, among wells with concentrations below their benchmarks, 80% of wells had both arsenic and uranium concentrations at one-tenth of their human-health benchmark.

Strengths & Limitations

This is the first study to use well water concentrations of arsenic and uranium to interpolate estimates and corroborates findings of well concentrations from another study of uranium and arsenic levels within these understudied regions. Arsenic and uranium water measurements are rare and imperative for this rural population, and include many data points across approximately 17,000 square miles in North Dakota and South Dakota. In the Strong Heart Study, the correlation of urinary arsenic and urinary uranium, which most recent data refers to samples collected in 2000–2003, had been hypothesized to both originate from water sources. The Strong Heart Study communities are located in parts of the United States with differing geologies. Though the urinary correlation may hold across the whole study, it may be driven by participants in the Southwestern US, and the correlation in the Northern Plains may be weaker. This is an area for future study. Further limitations include the short distance between wells with fairly different metal concentrations. This makes an IDW interpolation less reliable than measured values. However, it highlights an important health implication: it is necessary to measure arsenic levels in all wells because it is not possible to infer well arsenic concentrations of neighboring wells based on a well measurement. Additionally, this dataset is limited in relevant wellbore parameters that will be necessary for future work. With such complex geochemistry, further geospatial statistical analysis using additional analytes and data, including geological context, should be conducted to better predict areas of high co-contaminant exposure for the population.

The contamination that is documented is distributed throughout each study area. This widespread distribution, and its spatial incoherence except for a geological contact, suggests that the contamination is largely derived from natural (geogenic) sources. Other aqueous data and advanced tools like uranium isotopes would be useful in further differentiating between lithic (rock) sources (for example, those exploited in mining) from disseminated sedimentary sources. Because most wells are shallow, there is also potential for surficial contamination to influence groundwater composition. This surface contamination could be direct, from metal contamination transported from soils or surface water, or indirect in the form of organic contaminants or nitrate that can mobilize natural arsenic and uranium

contamination.[35–37] Future investigations should examine these potential source and their the spatial relationship to well water contamination, and how they interact with groundwater.

Given the new research being compiled about the health risks associated with consistent exposure to constant low levels of exposure, it will be important moving forward for repeated monitoring of private wells in regions affected by metals. Access to monitoring and effective water treatment is often inequitable, for example, water treatment that is ineffective for uranium (or nonexistent) leads to insufficient uranium removal and contamination of drinking water supplies in the Navajo Nation.[12, 38, 39] Regarding the health effects of uranium exposure, increasing evidence its toxicity, to the kidney which is well established, and to other organs and systems is growing;[40] similarly human studies, although still limited, support that uranium could increase the risk of cardiovascular disease and other metabolic factors.[38, 41–43] A review on uranium nephrotoxicity from 2010 suggested that chronic exposure to uranium predisposes individuals to renal impairment given further stressors.[44] A growing body of evidence shows that even at low levels of arsenic exposure, which includes levels below the current MCL, arsenic is associated with increased risk for several diseases as well as increased mortality.[7–11] Even as a recent study has shown evidence of some cardiovascular disease decline among those in the Strong Heart Study, chronic diseases remain a strong threat to American Indian health.[45] Currently, there is no evidence available on the joint health effects of arsenic and uranium, although there is evidence that both arsenic and uranium can disrupt similar pathways of DNA repair.[46]

Conclusions

The American Indian community at large deserves access to safe drinking water, and future research should be dedicated to this equitable goal. This study aims to add to the knowledge base of exposure characterization in high-risk communities, and is done so alongside mitigation efforts in the community. The fact that arsenic and uranium contamination appear to form due to heterogenous mixing, it is likely that wells containing both are unstable, and that the flow patterns that regulate water quality are not constant. Given this potential for change, it is important to regularly monitor private wells. EPA should continue to reevaluate current MCLs for toxics in water supplies and start to consider co-contaminants in human-health benchmarks, as there is potential for future research to reveal the current allowable levels remain still too high and continue to pose health risks.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Abbreviations

US EPA	United States Environmental Protection Agency
MCL	maximum contaminant level
MESA	Multi-Ethnic Study of Atherosclerosis
SHS	Strong Heart Study
SHWS	Strong Heart Water Study
ICC	intraclass correlation coefficient
LOD	limit of detection
IDW	inverse distance weighting
USGS	United States Geological Survey
IQR	interquartile range
As	arsenic
U	uranium

References

1. U.S. Geological Survey, Arsenic in ground-water resources in the United States. U.S. Geological Survey, Ed. 2000.
2. US Environmental Protection Agency, Environmental Radiation Data. Agency), U. E. U. S. E. P., Ed. 2006; Vol. Report128Oct-Dec2006.
3. Pang Y; Peng RD; Jones MR; Francesconi KA; Goessler W; Howard BV; Umans JG; Best LG; Guallar E; Post WS; Kaufman JD; Vaidya D; Navas-Acien A, Metal mixtures in urban and rural populations in the US: The Multi-Ethnic Study of Atherosclerosis and the Strong Heart Study. Environmental research2016, 147, 356–364. [PubMed: 26945432]
4. US Environmental Protection Agency, Understanding the Safe Drinking Water Act. EPA, U., Ed. 2016.
5. US Environmental Protection Agency Drinking Water Requirements for States and Public Water Systems.
6. Navas-Acien A; Umans JG; Howard BV; Goessler W; Francesconi KA; Crainiceanu CM; Silbergeld EK; Guallar E, Urine arsenic concentrations and species excretion patterns in American Indian communities over a 10-year period: the Strong Heart Study. Environ Health Perspect2009, 117 (9), 1428–33. [PubMed: 19750109]
7. Moon KA; Guallar E; Umans JG; Devereux RB; Best LG; Francesconi KA; Goessler W; Pollak J; Silbergeld EK; Howard BV; Navas-Acien A, Association Between Exposure to Low to Moderate Arsenic Levels and Incident Cardiovascular Disease: A Prospective Cohort Study. Annals of Internal Medicine2013, 159 (10), 649–659. [PubMed: 24061511]
8. García-Esquinas E; Pollán M; Umans JG; Francesconi KA; Goessler W; Guallar E; Howard B; Farley J; Best LG; Navas–Acien A, Arsenic Exposure and Cancer Mortality in a US-Based Prospective Cohort: The Strong Heart Study. Cancer Epidemiology Biomarkers & Prevention2013, 22 (11), 1944–1953.
9. Kuo C-C; Howard BV; Umans JG; Gribble MO; Best LG; Francesconi KA; Goessler W; Lee E; Guallar E; Navas-Acien A, Arsenic Exposure, Arsenic Metabolism, and Incident Diabetes in the Strong Heart Study. Diabetes Care2015, 38 (4), 620. [PubMed: 25583752]

10. Zheng LY; Umans JG; Tellez-Plaza M; Yeh F; Francesconi KA; Goessler W; Silbergeld EK; Guallar E; Howard BV; Weaver VM; Navas-Acien A, Urine Arsenic and Prevalent Albuminuria: Evidence From a Population-Based Study. American Journal of Kidney Diseases2013, 61 (3), 385–394. [PubMed: 23142528]
11. Powers M; Sanchez TR; Grau-Perez M; Yeh F; Francesconi KA; Goessler W; George CM; Heaney C; Best LG; Umans JG; Brown RH; Navas-Acien A, Low-moderate arsenic exposure and respiratory in American Indian communities in the Strong Heart Study. Environmental Health2019, 18 (1), 104. [PubMed: 31779614]
12. Hoover J; Gonzales M; Shuey C; Barney Y; Lewis J, Elevated Arsenic and Uranium Concentrations in Unregulated Water Sources on the Navajo Nation, USA. Exposure & health2017, 9 (2), 113–124. [PubMed: 28553666]
13. Lewis J; Hoover J; MacKenzie D, Mining and Environmental Health Disparities in Native American Communities. Current environmental health reports2017, 4 (2), 130–141. [PubMed: 28447316]
14. Credo J; Torkelson J; Rock T; Ingram JC, Quantification of Elemental Contaminants in Unregulated Water across Western Navajo Nation. Int J Environ Res Public Health2019, 16 (15).
15. Istok JD; Smyth JD; Flint AL, Multivariate Geostatistïcal Analysis of Ground-Water Contamination: A Case History. Groundwater1993, 31 (1), 63–74.
16. Hoover JH; Coker E; Barney Y; Shuey C; Lewis J, Spatial clustering of metal and metalloid mixtures in unregulated water sources on the Navajo Nation – Arizona, New Mexico, and Utah, USA. Science of The Total Environment2018, 633, 1667–1678.
17. Liesch T; Hinrichsen S; Goldscheider N, Uranium in groundwater--Fertilizers versus geogenic sources. Sci Total Environ2015, 536, 981–995. [PubMed: 26170113]
18. Chowdhury M; Alouani A; Hossain F, Comparison of ordinary kriging and artificial neural network for spatial mapping of arsenic contamination of groundwater. Stochastic Environmental Research and Risk Assessment2010, 24, 1–7.
19. Marchant BP; Tye AM; Rawlins BG, The assessment of point-source and diffuse soil metal pollution using robust geostatistical methods: a case study in Swansea (Wales, UK). European Journal of Soil Science2011, 62 (3), 346–358.
20. Cinti D; Poncia PP; Brusca L; Tassi F; Quattrocchi F; Vaselli O, Spatial distribution of arsenic, uranium and vanadium in the volcanic-sedimentary aquifers of the Vicano–Cimino Volcanic District (Central Italy). Journal of Geochemical Exploration2015, 152, 123–133.
21. Thomas ED; Gittelsohn J; Yracheta J; Powers M; O'Leary M; Harvey DE; Red Cloud R; Best LG; Black Bear A; Navas-Acien A; George CM, The Strong Heart Water Study: Informing and designing a multi-level intervention to reduce arsenic exposure among private well users in Great Plains Indian Nations. Science of The Total Environment2019, 650, 3120–3133.
22. Powers M; Yracheta J; Harvey D; MacDonald L; O'Leary M; Best LG; Susan J; Hasan K; Thomas E; Morgan C; Olmedo P; Chen R; Rule A; Schwab K; Navas-Acien A; George CM, Arsenic in Groundwater in Private Wells in Rural North Dakota and South Dakota: An Evaluation of a Rapid Field Arsenic Test. Author Manuscript: 2018.
23. EPA U, Quick Guide To Drinking Water Sample Collection. EPA, U., Ed. 2016.
24. DeSimone LAH, P. A; Gilliom RJ, The quality of our nation's waters—Quality of water from domestic wells in principal aquifers of the United States, 1991–2004—Overview of major findings. U.S. Geological Survey Circular, 2009; p 48.
25. Fendorf S; Michael HA; van Geen A, Spatial and temporal variations of groundwater arsenic in South and Southeast Asia. Science2010, 328 (5982), 1123–7. [PubMed: 20508123]
26. Gu B; Wu WM; Ginder-Vogel MA; Yan H; Fields MW; Zhou J; Fendorf S; Criddle CS; Jardine PM, Bioreduction of uranium in a contaminated soil column. Environ Sci Technol2005, 39 (13), 4841–7. [PubMed: 16053082]
27. Stewart BD; Amos RT; Nico PS; Fendorf S, Influence of Uranyl Speciation and Iron Oxides on Uranium Biogeochemical Redox Reactions. Geomicrobiology Journal2011, 28 (5–6), 444–456.
28. Wu W-M; Carley J; Gentry T; Ginder-Vogel MA; Fienen M; Mehlhorn T; Yan H; Caroll S; Pace MN; Nyman J; Luo J; Gentile ME; Fields MW; Hickey RF; Gu B; Watson D; Cirpka OA; Zhou J; Fendorf S; Kitanidis PK; Jardine PM; Criddle CS, Pilot-Scale in Situ Bioremedation of

Uranium in a Highly Contaminated Aquifer. 2. Reduction of U(VI) and Geochemical Control of U(VI) Bioavailability. Environmental Science & Technology2006, 40 (12), 3986–3995. [PubMed: 16830572]

29. Raven KP; Jain A; Loeppert RH, Arsenite and Arsenate Adsorption on Ferrihydrite: Kinetics, Equilibrium, and Adsorption Envelopes. Environmental Science & Technology1998, 32 (3), 344–349.
30. Dixit S; Hering JG, Comparison of Arsenic(V) and Arsenic(III) Sorption onto Iron Oxide Minerals: Implications for Arsenic Mobility. Environmental Science & Technology2003, 37 (18), 4182–4189. [PubMed: 14524451]
31. Ayotte JDG, J. M; Apodaca LE, Trace elements and radon in groudwater across the United States, 1992–2003. In U.S. Geological Survey Scientific Investigations Report 2011–5059, USGS, Ed. 2011; p 115.
32. Welch AH; Westjohn DB; Helsel DR; Wanty RB, Arsenic in Ground Water of the United States: Occurrence and Geochemistry. Groundwater2000, 38 (4), 589–604.
33. Erickson ML; Yager RM; Kauffman LJ; Wilson JT, Drinking water quality in the glacial aquifer system, northern USA. Science of Total Environment2019, 694.
34. Saalfield SL; Bostick BC, Synergistic effect of calcium and bicarbonate in enhancing arsenate release from ferrihydrite. Geochimica et Cosmochimica Acta2010, 74 (18), 5171–5186.
35. deLemos JL; Bostick BC; Renshaw CE; Sturup S; Feng X, Landfill-stimulated iron reduction and arsenic release at the Coakley Superfund Site (NH). Environ Sci Technol2006, 40 (1), 67–73. [PubMed: 16433334]
36. USGSNational Water Information System data available on the World Wide Web (USGS Water Data for the Nation). http://waterdata.usgs.gov/nwis/]. (accessedJan. 10, 2021).
37. USGS; Kenny JF; Barber NL; Hutson SS; Linsey KS; Lovelace JK; Maupin MA, Estimated use of water in the United States in 2005: U.S. Geological Survey Circular 1344. USGS, Ed. USGS: Denver, CO, 2009.
38. Corlin L; Rock T; Cordova J; Woodin M; Durant JL; Gute DM; Ingram J; Brugge D, Health Effects and Environmental Justice Concerns of Exposure to Uranium in Drinking Water. Current Environmental Health Reports2016, 3 (4), 434–442. [PubMed: 27815781]
39. Hoover JH; Erdei E; Begay D; Gonzales M; Jarrett JM; Cheng P-Y; Lewis J, Exposure to uranium and co-occurring metals among pregnant Navajo women. Environmental Research2020, 190, 109943. [PubMed: 32750552]
40. Medina S; Lauer FT; Castillo EF; Bolt AM; Ali A-MS; Liu KJ; Burchiel SW, Exposures to uranium and arsenic alter intraepithelial and innate immune cells in the small intestine of male and female mice. Toxicology and Applied Pharmacology2020, 403, 115155. [PubMed: 32710956]
41. Kurttio P; Auvinen A; Salonen L; Saha H; Pekkanen J; Mäkeläinen I; Väisänen Sari B; Penttilä Ilkka M; Komulainen H, Renal effects of uranium in drinking water. Environmental health perspectives2002, 110 (4), 337–342.
42. Kurttio P; Harmoinen A; Saha H; Salonen L; Karpas Z; Komulainen H; Auvinen A, Kidney Toxicity of Ingested Uranium From Drinking Water. American Journal of Kidney Diseases2006, 47 (6), 972–982. [PubMed: 16731292]
43. Hund L; Bedrick EJ; Miller C; Huerta G; Nez T; Ramone S; Shuey C; Cajero M; Lewis J, A Bayesian framework for estimating disease risk due to exposure to uranium mine and mill waste on the Navajo Nation. Journal of the Royal Statistical Society. Series A (Statistics in Society)2015, 178 (4), 1069–1091.
44. Vicente-Vicente L; Quiros Y; Pérez-Barriocanal F; López-Novoa JM; López-Hernández FJ; Morales AI, Nephrotoxicity of Uranium: Pathophysiological, Diagnostic and Therapeutic Perspectives. Toxicological Sciences2010, 118 (2), 324–347. [PubMed: 20554698]
45. Muller Clemma J; Noonan Carolyn J; MacLehose Richard F; Stoner Julie A; Lee Elisa T; Best Lyle G; Calhoun D; Jolly Stacey E; Devereux Richard B; Howard Barbara V, Trends in Cardiovascular Disease Morbidity and Mortality in American Indians Over 25 Years: The Strong Heart Study. Journal of the American Heart Association2019, 8 (21), e012289. [PubMed: 31648583]

46. Cooper KL; Dashner EJ; Tsosie R; Cho YM; Lewis J; Hudson LG, Inhibition of poly(ADP-ribose)polymerase-1 and DNA repair by uranium. Toxicology and Applied Pharmacology2016, 291, 13–20. [PubMed: 26627003]

- Drinking water of American Indian communities is poorly characterized
- 29% and 7% of wells exceeded maximum contaminant levels (MCL) for As and U
- Co-contaminated wells by As and U associated with flow along a geologic contact
- Approximately 60% of wells exceed As MCL, 20% U MCL, at <5 km from the contact

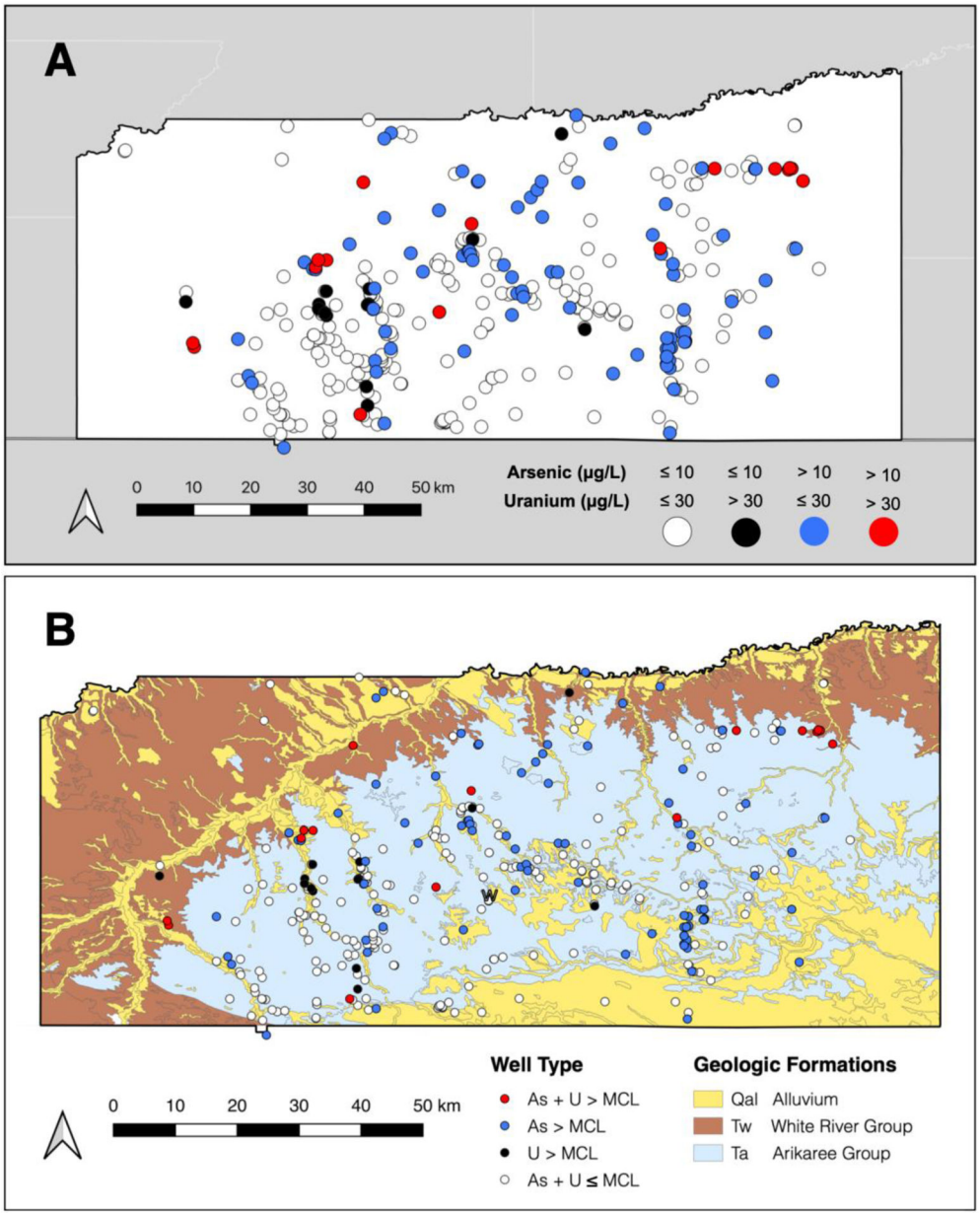

Figure 1.

(A) Maximum contaminant level (MCL) exceedance status of water arsenic and uranium concentrations in private wells in the Strong Heart Water Study, Region 3; (B) MCL) exceedance status of water arsenic and uranium concentrations in private wells in the Strong Heart Water Study, Region 3 overlaid on a shallow geological map.

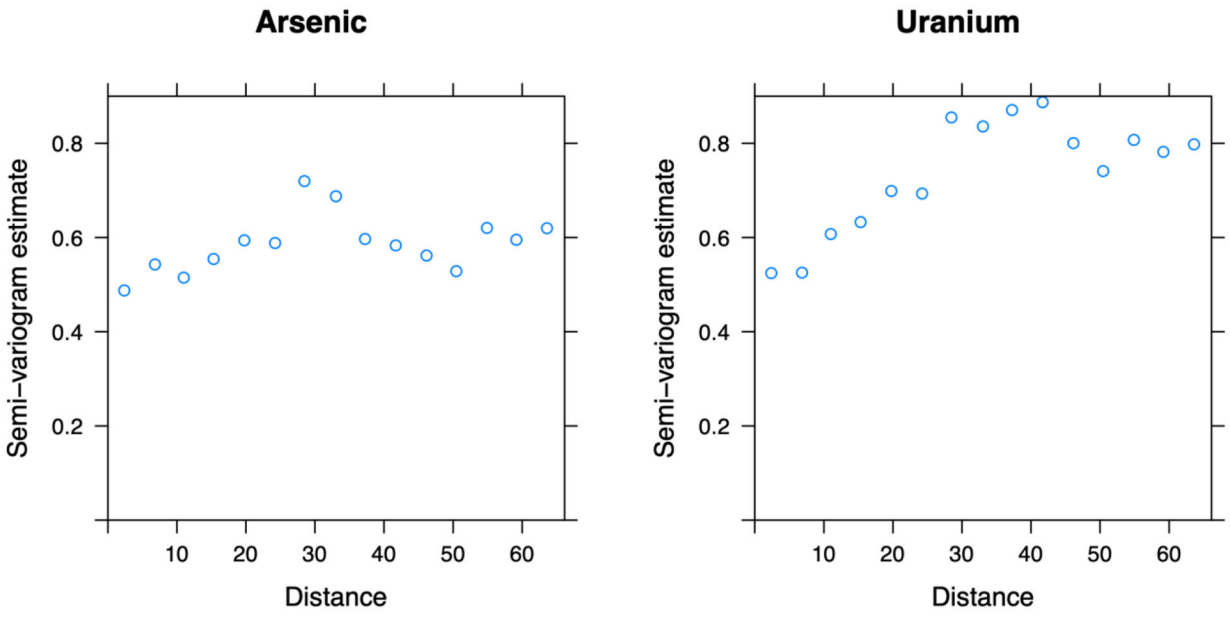

Figure 2.
Semivariograms of well water arsenic and uranium in the Strong Heart Water Study, Region 3

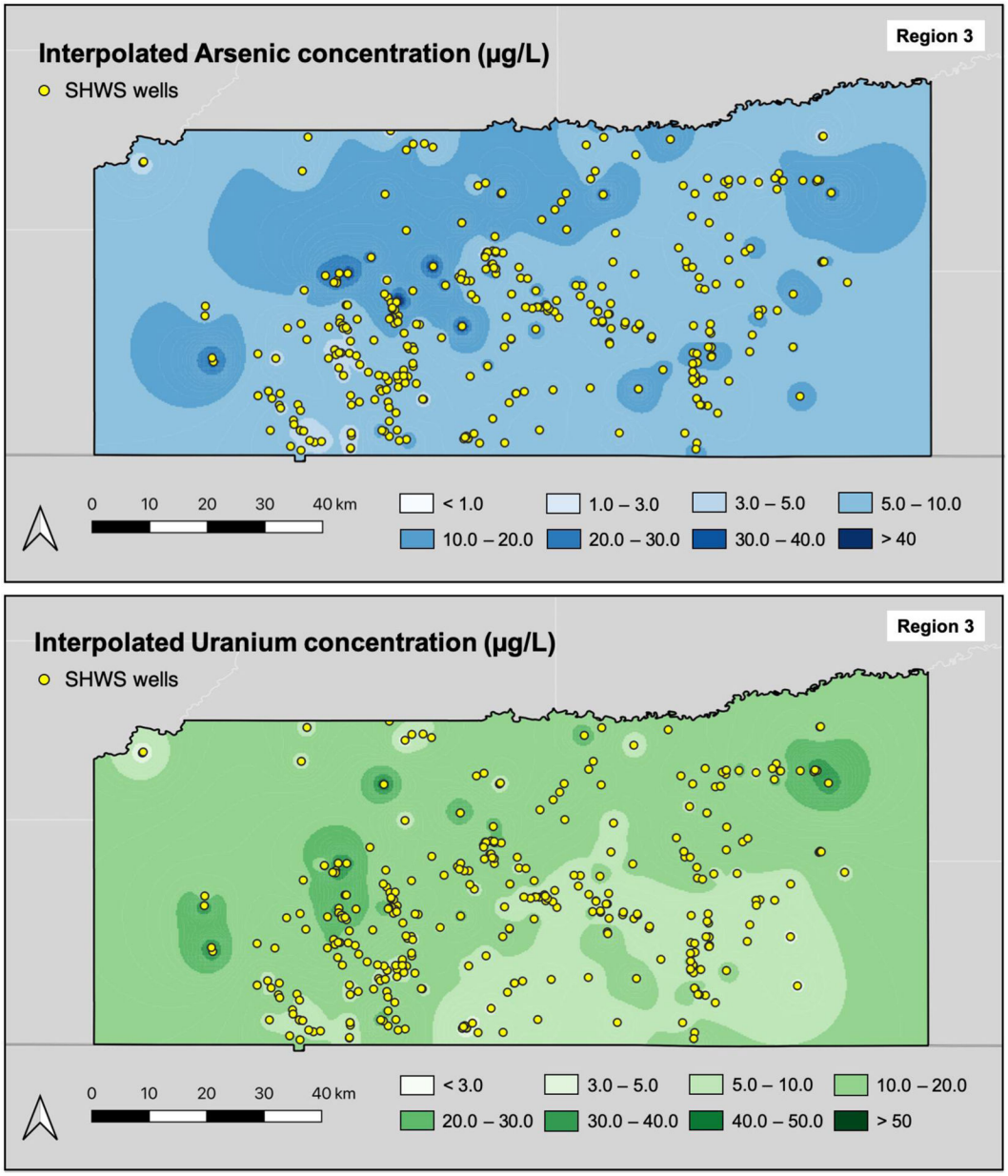

Figure 3.
Interpolated groundwater arsenic and uranium concentrations in the Strong Heart Water Study, Region 3

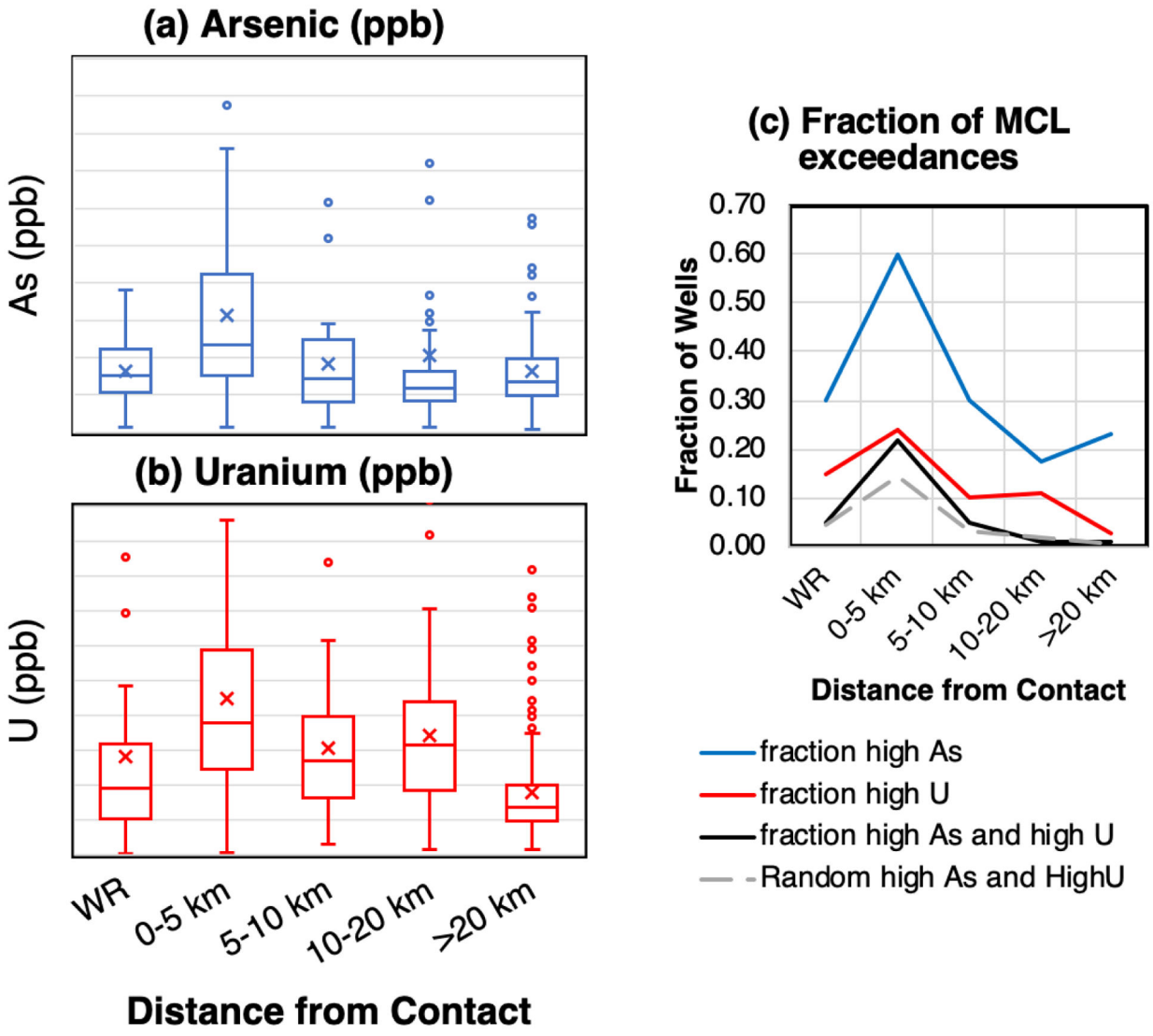

Figure 4.

The relationship between arsenic (a) and uranium (b) well water concentrations and the location of the well relative to the contact of the Arikaree and White River formations. Distance ranges are for wells in the White River formation (WR, NW of the contact), 0–5, 5–10, 10–20 and >20 km (SE of the contact, upgradient and largely in the Arikaree formation. Arsenic and uranium concentrations are higher within the Arikaree Formation near the White River formation, leading to higher levels of exceedances of arsenic and uranium MCLs (10 and 30 ppb respectively) (c). The predicted random distribution (gray in panel c) is determined by the product of arsenic and uranium probabilities. For most distances, the random and observed distributions are similar, but at the contact the observed probability of a well being contaminated with both arsenic and uranium is nearly double the ratio predicted based on random distribution.

Table 1.

Description of arsenic and uranium levels in Strong Heart Water Study wells, overall and for Region 3

	Region 3 ***N = 373***	**Overall** ***N = 441***
Arsenic concentration		
Median (IQR) (μg/L)	6.9 (4.9,11.0)	7.0 (4.7, 11.2)
Above MCL (10 μg/L), N (%)	102 (27)	129 (29)
Above 1/10th MCL (1 μg/L), N (%)	316 (97)	417 (95)
Uranium concentration		
Median (IQR) (μg/L)	9.8 (5.8, 17.3)	8.1 (4.2, 16.0)
Above MCL (30 μg/L), N (%)	32 (9)	33 (7)
Above 1/10th MCL (3 μg/L), N (%)	348 (93)	391 (87)
Well category, N (%) *		
Low As - Low U (white)	255 (68)	295 (67)
Low As - High U (black)	16 (4)	17 (4)
High As - Low U (blue)	86 (23)	113 (26)
High As - High U (red)	16 (4)	16 (4)

IQR, interquartile range; MCL; maximum contaminant level; As, arsenic; U, uranium.

*Well categories dichotomized by MCL. Color next to category indicates color used for Figures 2 and 3.