Large decadal-scale changes in uranium and bicarbonate in groundwater of the irrigated western U.S.

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Abstract

Samples collected about one decade apart from 1,105 wells from across the U.S. were compiled to assess whether uranium concentrations in the arid climate are linked to changing bicarbonate concentrations in the irrigated western U.S. Uranium concentrations in groundwater were high in the arid climate in the western U.S, where uranium sources are abundant. Sixty-four wells (6 percent) were above the U.S. EPA MCL of 30 µg/L; all but one are in the arid west. Concentrations were low to non-detectable in the humid climate. Large uranium and bicarbonate increases (differences are greater than the uncertainty in concentrations) occur in 109 wells between decade 1 and decade 2. Similarly, large uranium and bicarbonate decreases occur in 76 wells between the two decades. Significantly more wells are concordant (uranium and bicarbonate are both going the same direction) than discordant (uranium and bicarbonate are going opposite directions) ($p < 0.001$; Chi-square test). The largest percent difference in uranium concentrations occur in wells where uranium is increasing and bicarbonate is also increasing. These large differences occur mostly in the arid climate. Results are consistent with the hypothesis that changing uranium concentrations are linked to changes in bicarbonate in irrigated areas of the western U.S.

Keywords: uranium, bicarbonate, groundwater, irrigation

1. Introduction

Ingestion of uranium in drinking water is a human health concern due to its chemical toxicity and, to a lesser degree, radiological toxicity (Kurtio et al., 2002; World Health Organization, 2011a; World Health Organization 2011b). Natural uranium is found in groundwater around the world (Waseem et al., 2015) at concentrations above current drinking water standards of 30 µg/L (U.S. Environmental Protection Agency, 2000; World Health Organization 2011b) in countries such as Finland (Lahermo and Juntunen, 1991), Norway (Frengstad et al., 2000), Mongolia (Nriagu, et al., 2012), Switzerland (Stalder, et al., 2012), India (Kumar, et al., 2006), Pakistan (Ullah et al., 2013), and China (Wu, et al., 2014). Data for groundwater in the U.S. show that it is a relatively common contaminant in domestic wells, with 1.7% above the MCL (DeSimone et al., 2009). Natural uranium is contained largely in sedimentary rocks derived from granites and rhyolite, which are relatively enriched in uranium (Hobday, and Galloway, 1999). Anthropogenic sources of uranium include uranium mining, milling, and tailing disposal; combustion of coal and other fuels; and application of phosphate fertilizers from rocks containing uranium (e.g. Roessler, et al., 1979; Abdelouas, et al., 1999; Zielinski, et al., 2000; Davis, et al., 2004).

In the eastern San Joaquin Valley, California, uranium concentrations have increased over time and concentrations are high (Thiros, et al., 2014; Lindsey et al., 2016). Based on solid phase data and geochemical modeling, Jurgens et al. (2010) were able to determine the source of uranium and the mechanism of mobilization in this agriculturally-dominated area. The occurrence of uranium is dependent on uranium-bearing rocks and sedimentary materials, sufficiently oxidizing geochemical conditions, the presence of bicarbonate, and a change in chemistry (in this case, changes in bicarbonate). Uranium is sorbed on iron oxyhydroxide coatings on sediment grains, clay mineral edges, or to organic matter (Hsi and Langmuir, 1985; Waite et al., 1994; Porcelli and Swarzenski, 2003; Davis and Curtis, 2004; Catalano and Brown, 2005), derived from uranium-rich granitic rocks of the Sierra Nevada. In their study, they found that uranium was being leached by high-bicarbonate recharge, primarily from irrigated agriculture. Uranium and bicarbonate were highest in the young, shallow groundwater and decreased with depth. Increased irrigation and municipal pumping in the deeper part of the groundwater system has caused the high-uranium, high-bicarbonate water to move downward in the groundwater system, increasing the proportion of the aquifer with high concentrations of uranium.

The purpose of this paper is to test the hypothesis that bicarbonate is affecting uranium concentrations in groundwater using a dataset of decadal changes in uranium and bicarbonate across the U.S. Since it has been demonstrated that uranium is mobilized by downward movement of irrigation water (Jurgens et al., 2010), and given that large portions of the western U.S. are arid and are thus irrigated for crops and landscape watering, it may be expected that in the presence of uranium-bearing rocks and sediment and oxic conditions, changes in uranium in the arid west would also show corresponding changes in bicarbonate. This paper does not address the chemical mechanisms of mobilization of uranium. Rather, this work is an assessment of the changes in uranium and bicarbonate to evaluate whether the processes identified by Jurgens et al. (2010) were potentially occurring in other parts of the arid western U.S.

Since 1991, the U.S. Geological Survey (USGS) National Water Quality Assessment (NAWQA) project has been monitoring groundwater quality in primary aquifers of the U.S. using a common network design and sampling methods. Uranium and bicarbonate concentrations were available for wells with samples about a decade apart in 53 networks sampled between 1993 and 2014. The analysis presented here evaluates decadal changes in uranium at each well and corresponding bicarbonate concentrations at that well. This study is unique in that it is the first known national-scale assessment of changes in uranium concentrations across the U.S., which includes multiple aquifer systems across hydrogeologically diverse settings.

2. Methods

The wells selected for use in the analysis of changes in uranium concentrations were part of the data used by NAWQA to assess decadal-scale changes in a number of constituents (Lindsey et al., 2016). NAWQA monitoring networks were specifically designed to assess concentrations in areas with human activity. Network wells were located beneath urban, agricultural, or mixed land uses. Data from 1,105 wells were compiled (U.S. Geological Survey, 2014): most (856) of the wells were first sampled during 1993-2002 and then subsequently sampled during 2001-2012. Some wells (249) used in the analysis were first sampled in 2001-2005 and subsequently sampled during 2012-2014. The latter wells were used because there were no samples available during the 1993-2002 time period. Networks of wells that were included in the analysis had uranium and bicarbonate analyses in both decades, and had at least 10 pairs of samples.

Uranium concentrations were censored to a common reporting level of 1 $\mu\text{g/L}$. For example, a concentration of 0.9 was set to $<1 \mu\text{g/L}$. Although lower detection limits were available in later samples, censoring to a common reporting level avoided bias in the analysis of changes between decades. For use in the analysis, samples with a concentration of $<1 \mu\text{g/L}$ were assigned a value of 0.99 to make computations possible. This is an arbitrary value, but 0.99 was used because that is the same value used in the decadal network analysis done by Lindsey et al. (2016).

Additional data were collected to assist in interpretation of the changes in uranium and bicarbonate concentrations. The water quality data used includes field parameters, major ions, nitrate, phosphate, iron, manganese, molybdenum, and vanadium. The water quality parameters were used in assessing redox state and doing speciation calculations. Aeroradiometric data (Hill, et al., 2009) were used to estimate the average concentration of uranium in surficial rocks and sediment for a 15-km-radius buffer around each well, as an indicator of the availability of uranium.

The reduction/oxidation (redox) conditions of groundwater at the time of well sampling were evaluated using field measurements of dissolved oxygen, manganese, and iron using a defined redox classification (McMahon and Chapelle, 2008; Chapelle, et al., 2009). A redox workbook (Jurgens, et al., 2009) classified samples into oxic ($\text{O}_2 \geq 0.5 \text{ mg/L}$), suboxic, anoxic, and mixed classification groups. Samples classified by the workbook as oxic, suboxic (arid climate only), or NO_3 -reducing were assigned to an oxic category because uranium is not expected to be removed from solution under these redox conditions. Samples that were classified as Mn or Fe/ SO_4 -reducing (or suboxic in the humid climate) were assigned

to the anoxic redox category because uranium does not become reduced until about Mn-reducing conditions on the redox ladder. Samples that were classified in the workbook as mixed—i.e. display characteristics of both oxic and anoxic water—were assigned to the mixed redox category.

An aridity index (Zomer, et al., 2007; Zomer et al., 2008) was used to classify climate for individual wells. Wells were assigned to one of four groups—arid, semi-arid, dry sub-humid, and humid (Middleton and Thomas, 1997)—based on the aridity index value, then were further grouped into two categories: arid (arid and semi-arid) and humid (humid and dry sub-humid). In the presence of uranium-bearing aquifer materials, humid climates have plants (and bicarbonate) under natural conditions, so any uranium would have had an opportunity to be leached from the sediments and transported with the groundwater. Arid climates would not naturally have plants (bicarbonate) under natural conditions, so the sediments in the arid climate have not been leached. Irrigation may occur in both arid and humid environments; however, in the arid climate the irrigation causes a change in water chemistry that leads to uranium being mobilized into groundwater in oxic environments. An adequate national coverage of irrigated land was not available, so climate was used as a proxy to determine irrigated settings: arid settings are expected to require irrigation for crop or urban landscape demand, whereas the humid climate does not require additional irrigation water to meet plant demand. Although an accurate coverage of irrigation for each well would be ideal to demonstrate the link between bicarbonate concentrations and irrigated settings, the available coverages were evaluated and found to be incorrect at the scale of a single well. Maupin et al. (2014) corroborates the use of climate as a proxy for irrigation by showing the marked difference in irrigation water use in the western U.S. compared to the eastern U.S. Additionally, in an urban area in the arid west, Hevesi and Johnson (2016) demonstrated that urban irrigation was 56% of the total spatially distributed recharge, supporting the premise that urban area irrigation is also significant in the arid environment.

Speciation of dissolved uranium and saturation indices of uranium and carbonate minerals in groundwater were calculated using PHREEQC (Parkhurst and Appelo, 2013). Formation constants for uranium complexes in the PHREEQC thermodynamic database were updated (Grenthe et al., 1992) and other ternary complexes were added (Dong and Brooks, 2006). *pe* values were specified based on the redox classification for each sample (Table S1).

2.1 Distinguishing between large changes, small differences, concordance, and discordance in concentrations of uranium and bicarbonate

An analysis of replicate samples for uranium and bicarbonate concentrations was done to distinguish between changes that may be due to analytical uncertainty and changes that can be attributed to changes in groundwater conditions. For uranium, concentrations for 408 replicate pairs sampled between 1993 and 2014 were compared. For bicarbonate, concentrations for 151 replicate pairs also sampled between 1993 and 2014 were compared. Changes that are within the range of analytical uncertainty are defined here as small differences. Changes that are larger than analytical uncertainty are defined here as large differences, and are considered to be changes in concentration. Analysis of the replicate data indicates that a cutoff of 10% difference was used to identify samples with large changes in concentration for both uranium and bicarbonate. This value is midway between the 90th and 95th percentiles for both constituents, and hence provides a reasonable threshold between large and small differences in concentration.

Changes in chemistry between samples collected in decade 1 and decade 2 are considered concordant if uranium and bicarbonate concentrations have changed in the same direction (for example, both uranium and bicarbonate increase or both decrease). Decadal sample pairs are considered discordant if uranium and bicarbonate concentrations are changing in opposite directions. Concordance is consistent with the hypothesis of uranium complexation and mobilization by bicarbonate.

3. Results and Discussion

3.1 High concentrations of uranium are related to climate and uranium content in surficial rocks and sediment

Uranium concentrations in samples from across the U.S. ranged from below the detection limit of 1 $\mu\text{g/L}$ to as high as 1,240 $\mu\text{g/L}$ in a well sampled in 2002 in an urban area in the Carson Valley, NV. The Carson Valley is in the arid climate and the Carson River Basin area has documented high concentrations of uranium in groundwater related to irrigation processes (Thomas et al., 1993; Welch and Lico, 1998).

Uranium concentrations over the U.S. Environmental Protection Agency's (USEPA) Maximum Contaminant Level (MCL) of 30 $\mu\text{g/L}$ occur in 64 wells sampled in decade 2 (second decade of a pair of decadal samples)—all but one are in the arid climate (Fig. 1a). Within the extent of the areas sampled, clusters of concentrations over the MCL occur along the South Platte River in Colorado and Nebraska, the Rincon Valley in New Mexico, the Tucson Basin in Arizona, the Salt Lake Valley in Utah, the Reno metropolitan area and Carson Valley in Nevada, and the San Joaquin Valley in California. All of these locations are in irrigated settings that used to be dry. In the arid climate, uranium concentrations can be influenced by regional application of agricultural and urban irrigation for crops and landscapes because summer irrigation tends to increase the ions in recharge that can mobilize adsorbed uranium from

sediments (Thomas et al., 1993; Böhlke et al., 2007; Jurgens et al., 2010). Although evaporation could also influence uranium concentrations, it would likely not explain the widespread large increases in uranium overall. High concentrations of uranium have also been found in surface water in the Platte River drainage basin and that high concentrations in groundwater are influenced by irrigation with uranium-bearing surface water (Snow and Spalding, 1994; Böhlke et al., 2007), suggesting that processes related to mobilization of uranium in irrigated settings can be complex.

Uranium concentrations were lowest in the humid climate. Concentrations below the detection limit occur in the Gulf and Coastal Plain aquifers northward to the northeastern glacial deposits. Also many wells with concentrations below the detection limit are found in the humid climate in the Midwest, and in Oregon's Willamette Valley in the west. Differences in uranium concentrations between dry and humid climates were also noted by other researchers (Ayotte et al., 2011), where uranium occurred at greater concentrations in dry regions than humid regions across the U.S..

The only well in a humid climate to have a concentration over the MCL was a shallow monitoring well in an agricultural area in the surficial aquifer in Florida. The well had a concentration of 119 µg/L in decade 2. In southern Florida, agricultural soils have been shown to act as sources of dissolved uranium (Zielinski et al, 2000), and phosphate deposits of marine origin and ammoniated phosphate fertilizers were also shown to have significant concentrations of uranium in Central Florida (Roessler et al., 1979).

The occurrence of high concentrations of uranium in groundwater can be related, in part, to the occurrence of high concentrations of uranium in surficial rocks and sediment. There are large areas of the arid, western U.S. with high concentrations of uranium in surficial rocks and sediment (Fig. 1b), consistent with the pattern observed in groundwater. In contrast, in the humid climate, there are low concentrations of uranium in surficial rocks and sediment along the Gulf and Coastal Plain aquifers, in Florida, the upper Midwest, and the northeastern parts of Oregon and Washington, consistent with the lowest uranium concentrations in groundwater.

As also observed in the maps of uranium concentrations in groundwater, uranium concentrations in groundwater are significantly higher in wells in the arid climate than the humid climate (Figure 2). The median concentration in groundwater in the arid climate is 5.1 $\mu\text{g/L}$, compared to $<1 \mu\text{g/L}$ in the humid climate. Concentrations of uranium in surficial rocks and sediment are also significantly higher in the arid climate than the humid climate (Fig. 2). The median concentration is 2.2 ppm in the arid climate and 1.5 in the humid climate.

Given that the uranium content in surficial rocks and sediment in the arid climate is greater than the content in the humid climate, we need to account for those differences; therefore, the ratio between uranium concentrations in groundwater and concentrations in surficial rocks and sediment is computed (Fig. 2). The ratio is significantly higher in the arid climate than the humid climate; therefore, another process is causing higher concentrations in the arid climate besides just the source rocks alone or the ratio would have looked the same between the two climates.

3.2 Large changes in uranium and bicarbonate concentrations are generally concordant and uranium concentrations are increasing at a larger rate than decreasing

Large uranium and bicarbonate increases (differences are greater than the uncertainty in concentrations) occur in 109 wells between decade 1 and decade 2 (Fig. 3; Table S2). These large increases occurred throughout the western US, in a few wells in the Midwest and in the Northeast. Similarly, large uranium and bicarbonate decreases occur in 76 wells between decade 1 and decade 2. These large decreases occur in some of the same locations as the large increases. Significantly more wells are concordant (uranium and bicarbonate are both going the same direction) than discordant (uranium and bicarbonate are going opposite directions) ($p < 0.001$; Chi-square test). The concordance between large differences in uranium and bicarbonate concentrations is consistent with the hypothesis of changes in uranium concentrations being driven by changes in bicarbonate concentrations in groundwater.

There are many fewer discordant wells overall (Table S2), but these wells also tend to occur in the same regions as the concordant sites. Other processes unrelated to uranium and bicarbonate could be dominant at these wells, although uranium is still likely complexed with carbonate species. For example, several discordant samples occur in the Platte River drainage, and as noted earlier, high concentrations of uranium have also been found in surface water in the Platte River drainage basin and it is possible that high concentrations in groundwater are influenced by irrigation with uranium-bearing surface water (Snow and Spalding, 1994; Böhlke et al., 2007).

Concentrations of uranium or bicarbonate did not change (Figure 3), or concentrations changed by an amount that was smaller than the uncertainty in concentrations in a large proportion of the dataset (80%, 889 of 1,105 wells).

The difference in uranium concentrations between decade 1 and decade 2 versus uranium concentrations in decade 2 is shown in Figure 4. Large increases in bicarbonate are shown in red, concordant, large decreases in bicarbonate are shown in blue, and those wells with small or no differences in bicarbonate are shown in green. Wells within the range of uncertainty for uranium concentrations plot between the two lines at $\pm 10\%$ difference in uranium concentrations. Wells that appear to form an exponential curve

on the left side of the graph are wells where uranium was not detected in decade 1, but uranium was detected in decade 2.

Uranium increased by a much larger percentage than it decreased (Fig. 4). Generally, the largest percent difference in uranium concentrations are in wells where uranium and bicarbonate are increasing by a large amount. Concordant decreases in uranium concentration (blue dots below y-axis of zero) are much smaller in magnitude than the increases. These decreases in uranium occur in wells where bicarbonate concentrations are decreasing by a large amount, although the relative magnitude of the bicarbonate decreases is not shown. These results demonstrate an overall large percentage increase in uranium concentrations that are concordant with increases in bicarbonate between decade 1 and decade 2.

The percent difference in uranium concentration ranged from a decrease of -93% to an increase as large as 1,607 % in a well in an agricultural area in the surficial aquifer in Florida. This well was reduced and had a uranium concentration below the detection limit in decade 1; the well became oxic and had a concentration of 17 µg/L in decade 2, which is elevated, but still only about ½ the MCL. This well appears to be affected by changes in redox conditions, and as discussed earlier, agricultural areas in central and southern Florida have other mechanisms for elevated uranium concentrations which are unrelated to the hypothesis being tested in this paper.

Wells with small or no change in uranium concentrations plot within the bounds of uncertainty (0 to +/- 10% differences in uranium) (Figure 4). These wells generally have a corresponding small or no difference in bicarbonate, as indicated by the green dots that plot near the bounds of uncertainty for uranium.

3.3 Large changes in uranium and bicarbonate occur more frequently in the arid west

There are 109 wells with large concordant increases in uranium and bicarbonate, with 80% in the arid climate and 20% in the humid climate (Fig. 3, Table S2). However, only 40% of all the wells sampled are in the arid climate. Alternatively stated, 20% of the wells in the arid climate (87 of 443 wells) have large concordant increases in uranium and bicarbonate, whereas 3% of the wells in the humid climate (22 of 662 wells) do. Wells with large concordant increases in uranium and bicarbonate in the humid climate tend to occur in the Midwest, New England, and the Gulf Coastal Plain (Louisiana and Texas). The concordant large decreases in uranium and bicarbonate generally occur in the same places as the increases, with 79% (60 of 76 wells) in the arid climate and 21% (16 of 76 wells) in the humid climate.

Using the subset of 216 wells with large differences in uranium and bicarbonate concentrations, the difference in uranium between decade 1 and decade 2 is again plotted versus uranium concentration in decade 2, but this time the points are coded by whether the uranium and bicarbonate are concordant and by climate (Figure 5).

Concordant wells in the arid climate have the largest increases and the highest concentrations of uranium (Figure 5). Most of the wells in the humid climate are generally low in uranium concentration (<10 µg/L), with many of the wells with detections having concentrations of 1-2 µg/L. It is interesting to note that the proportion of concordant wells is relatively large (about 90%) in the arid climate. Similar to Table S2, this demonstrates the concordance between uranium and bicarbonate in most wells with large changes in uranium and bicarbonate.

Given the hypothesis that changes in uranium are caused by changes in bicarbonate in irrigated (arid) areas, and given the large number of wells with no detections of uranium in the humid climate, we expect

there to be a large number of wells with no differences in uranium concentrations in the humid climate. Indeed, all but 2 of 584 wells with no differences occurred where uranium was not detected in both decades. Further, 90% of the 582 wells where uranium was not detected in both decades were in the humid climate.

In contrast, 287 wells had small differences in uranium and bicarbonate concentrations; these wells mostly occurred in the arid climate (206 of 287 wells; 72%); only 81 wells occurred in the humid climate (28%). These results show the ubiquitous nature of uranium in groundwater in the arid climate, and, in contrast, the lack of detectable uranium concentrations in the humid climate.

3.4 Uranium concentrations are highest in shallow groundwater in the arid climate

Figure 6. (double column black and white image) Relation between uranium (A) and bicarbonate (B) concentrations in decade 2 and well depth for each climate. Shallow wells are those with screened interval ≤ 150 feet below land surface; deep wells are those with screened interval > 150 feet below land surface; overlapping wells are those with the top of screen ≤ 150 feet and bottom of screen > 150 feet below land surface. Letters A, B, C denote which groups are significantly different from each other. Differences between groups were tested using the Wilcoxon rank test.

In the arid climate, uranium concentrations are significantly higher in shallow wells than in deep wells, with intermediate concentrations at overlapping depths (Fig. 6a). Well depth can be used as a proxy for travel time (or age) in the aquifer. The shallow groundwater in the arid climate is most affected by recent recharge of irrigation water, which is high in bicarbonate in the arid climate (Fig. 6b). Therefore it is expected that uranium concentrations would be highest in the shallow groundwater and decrease with

depth because bicarbonate concentrations are highest in the shallow groundwater and the elevated bicarbonate would mobilize more available uranium, whereas the deeper groundwater would be lower in bicarbonate and thus uranium is lower. These results are consistent with that observed previously (Jurgens et al., 2008; Jurgens et al., 2010) where the highest uranium and bicarbonate concentrations were found in the shallowest wells with the youngest groundwater. Overall, uranium is increasing (58%) more than it is decreasing (42%) in this shallow, high uranium/high bicarbonate groundwater in the arid climate.

In the humid climate the processes are different, as uranium concentrations are highest in the overlapping depth category and lower in the shallow and deep wells (Fig. 6a). The overlapping wells are the most oxic (80%) compared to the shallow (54%) and deep (51%) wells, however, so higher concentrations would be expected because uranium would be the most mobile in oxic groundwater. Other evidence that suggests different processes in the humid climate is that bicarbonate concentrations increase with depth (Fig. 6b). Of the 101 wells in the deep category in the humid climate, 74 have bicarbonate concentrations above 200 mg/L. And of these 74 wells with elevated bicarbonate, 80% are represented by just two study areas (south-central Texas and the lower Illinois River basin). The wells in south-central Texas are in the Edwards aquifer (a carbonate aquifer) and elevated bicarbonate concentrations may be expected given adequate CO₂ in the system; however, low concentrations of uranium in the aquifer source rocks likely explains the lack of uranium concentrations above the detection limit; uranium concentrations in groundwater in the Edwards aquifer are generally below 1 µg/L (Cowart, 1980). In the lower Illinois River basin, nearly all wells have bicarbonate concentrations above 400 mg/L. Although other wells in the Lower Illinois River basin have elevated uranium values (maximum of 17 µg/L), the network described here is comprised of deep wells located in the Mahomet Buried Bedrock Valley, where reduced conditions likely inhibit mobilization of uranium in the groundwater (Morrow, 2001) and high bicarbonate concentrations are consistent with increasingly reduced conditions (see Figure S1).

Overall, these results are consistent with the hypothesis that shallow, high-bicarbonate irrigation water is mobilizing available uranium in the arid climate, whereas other processes such as redox and source predominate the control of uranium in groundwater in the humid climate.

3.5 Non-detections of uranium are more likely to occur in samples from the humid climate

Uranium was not detected in both decades in 79% of wells in the humid climate (525 of 662 wells), compared to 13% (57 of 443 wells) in the arid climate (Fig. S2). This could be due to differences in the availability of uranium and/or differences in redox conditions between the humid and arid climates. The

overall predominance of oxic conditions in the arid climate (84% of all arid wells are oxic) facilitates mobilization of uranium, causing there to be small but detectable differences in the arid climate compared to predominantly non-detectable differences in the humid climate (only 51% of wells are oxic in the humid climate).

It is notable that whereas we know that uranium is changing (even with some uncertainty in the direction) in the arid climate where there are small differences in concentration, we cannot determine the effects of small changes of uranium in the humid climate because we don't know the differences in concentration (because there are so many wells with no detection of uranium in the humid climate).

3.6 Uranium is primarily present as U(VI) complexed with CaCO_3

The PHREEQC speciation results are consistent with the species identified in Jurgens et al. (2010). In most wells (96%; Table S3), uranium is present in groundwater as U(VI), the oxic form of uranium. In terms of individual samples, not wells, (since PHREEQC calculations were done on samples from both decades), 98% of samples (1,021 of 1,042 samples) where uranium was detected in both decades were dominantly (>85%) U(VI). In 95% of the samples (995 of 1,042 samples), U(VI) comprised at least 99% of the species present.

Nearly all of the U(VI) samples are dominantly carbonate complexes (98%; Table S4), although a few samples are dominantly uranyl hydroxide species, predominantly $\text{UO}_2(\text{OH})_2$. Most of the dissolved U(VI) is in the form of ternary complexes of uranyl carbonate with calcium ($\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ or $\text{CaUO}_2(\text{CO}_3)_3^{-2}$), which are the same species observed in groundwater by Jurgens et al. (2010). CaCO_3 complexes are stable in oxic groundwater, thus keeping uranium in solution.

In a few samples (27 samples from 20 wells), uranium is present as U(IV), the reduced form of uranium, in one or both decades (Table S3); all of these wells are in the humid climate. Uranium in the U(IV) samples occurs primarily as $\text{UO}_2(\text{OH})_2$. Most concentrations of uranium are low in the U(IV) samples (<15 $\mu\text{g/L}$), although 1 site in the Biscayne aquifer had a uranium concentrations of 39 $\mu\text{g/L}$ in decade 1 under reduced conditions and a uranium concentration of 15 $\mu\text{g/L}$ in decade 2 under oxic conditions. Unlike the U(VI) samples, most of the U(IV) samples were supersaturated with respect to uraninite (UO_2).

The source of uranium (VI) in groundwater could have been mobilized by desorption processes as shown in the Central Valley (Jurgens et al., 2010) or by oxidation of U(IV) minerals (uraninite) with dissolved oxygen (Langmuir, 1978) or nitrate (Finneran et al., 2002; Nolan and Weber, 2015). If oxidation of U(IV) minerals by nitrate were the most significant mobilization process, then one would expect that this process would occur throughout the U.S., given that nitrogen fertilizer is applied and occurs at high concentrations in groundwater in the humid as well as the arid settings (Dubrovsky et al., 2010; Puckett et al., 2011) throughout the U.S. For example, in the humid climate in southern Georgia, where there is a moderate but present source of uranium in surficial rocks and sediment, 32 wells in a predominantly agricultural setting have concentrations of nitrate ranging from 3.5 to as high as 14 mg/L (as N), yet uranium is not detected. Therefore, there is more to understanding the occurrence of the high concentrations of uranium than the use of nitrogen fertilizer alone. Regardless of the source of the solid phase uranium, uranium remains mobile in groundwater because uranyl adsorption is limited by the formation of strong ternary complexes between divalent cations such as calcium, magnesium, strontium, and barium of calcium and inorganic carbon ($\text{H}_2\text{CO}_3(\text{aq})$, HCO_3^- , CO_3^{2-}) (Langmuir, 1978; Dong and Brooks, 2006).

3.7 Projected occurrence of high concentrations of uranium over the next 10 to 50 years

Uranium concentrations in the arid climate may continue to affect drinking-water quality in the future. Sixty-four of the 1,105 wells (6%) had concentrations of uranium above the MCL in decade 2. All but one of these wells are in the arid climate, and 80% are oxic. Uranium concentrations are a risk to drinking water sources, and wells in the arid climate are the most vulnerable if the rate of change in the last decade carries into the future.

Many of the wells with large percentage increases in uranium concentrations are already above the MCL. (Fig. 5). However, if the same conditions affecting the wells in the last decade are operating in the next decade, these wells could reach or exceed the MCL. Wells that could reach or exceed the MCL in the next decade are plotted on Fig. 5 in the envelope between the line labeled “10 years” and the line labeled as the USEPA MCL. Wells that could reach or exceed the MCL in the next 5 decades are in the area bounded by the two lines labeled “10 years” and “50 years.”

Ten of the 13 wells that could potentially reach or exceed the MCL in the next decade are in the arid climate. Nine of these 10 wells are classified as concordant with bicarbonate, indicating that bicarbonate could be the driver behind the significant increases in uranium concentrations. About half of the wells in

this dataset are shallow monitoring wells, however, which could have higher uranium concentrations than the typically deeper domestic and public-supply wells.

Wells that would reach or exceed the MCL within the 50-year timespan are mostly concordant wells in the arid climate as well. These data, combined with these hypothetical curves suggest the vulnerability of drinking water in the arid climate and the role of irrigation in driving bicarbonate and other constituents downward in the system, potentially causing concentrations of uranium to exceed drinking water limits in irrigated settings of the western U.S. Although these are hypothetical conditions, this potential increase in concentrations above the MCL is consistent with previous results (Jurgens et al., 2010), in which the number of public-supply wells in the study area with concentrations above the MCL increased from 6.8 to 9.2% of the total number of wells in just a short time period, from 1990-1998 to 1998-2006.

3.8 Conclusions

This is the first known national-scale assessment of changes in uranium concentrations across the U.S. This study has used a unique dataset of paired samples of uranium and bicarbonate analyses collected about a decade apart to assess changes in uranium and bicarbonate over the decade.

Many groundwater contamination problems are either anthropogenic or naturally occurring. The process of anthropogenically-induced contamination by naturally-occurring uranium is a unique combination of a natural source being mobilized by anthropogenic activity.

In the arid climate, irrigation of either agricultural or urban landscapes is needed to foster plant growth. This plant growth that takes place in arid climate is on land that has had sparse plant growth for thousands of years. The irrigation increases $p\text{CO}_2$ above the water table, resulting in an increase in bicarbonate at the water table. In the humid climate, more lush plant growth over a great length of time has resulted in long term leaching of bicarbonate through the root zone, resulting in minimal change in the recent decades.

Although this dataset does not contain the solid-phase data that would be needed to fully demonstrate the process discussed above, the dataset is consistent with the process of mobilization of uranium by bicarbonate in the arid climate by the resulting concordant changes in uranium and bicarbonate in the arid climate. In addition, this dataset demonstrates that uranium concentrations are increasing much more than they are decreasing, especially in the arid climate, and that should draw attention to this issue from a

human health perspective in that wells in the arid climate may be more vulnerable to exceedance of drinking-water standards in the future.

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