

Natural Uranium Contamination in Major U.S. Aquifers Linked to Nitrate

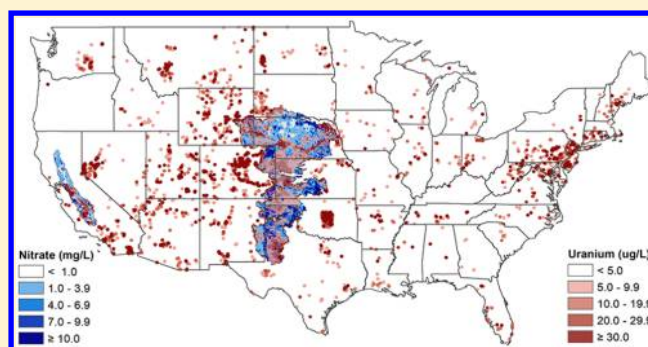
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Supporting Information

ABSTRACT: Groundwater geochemical data collected from two major U.S. aquifers, High Plains (HP) and Central Valley (CV), revealed naturally occurring groundwater uranium (U) exceeding the U.S. Environmental Protection Agency maximum contaminant level (MCL = 30 $\mu\text{g/L}$) across 22375 km^2 where 1.9 million people live. Analysis of geochemical parameters revealed a moderately strong correlation between U and nitrate, a common groundwater contaminant, as well as alkalinity and calcium [Spearman's rho (ρ) ≥ 0.30 ; $p < 0.001$]. Nitrate is recognized to alter U solubility by oxidative dissolution of reduced U(IV) minerals. Approximately 78% of areas where U concentrations were interpolated above the MCL were correlated to the presence of nitrate (Pearson's $r \geq 0.5$; $p < 0.05$). Shallow groundwater was determined to be the most susceptible to co-contamination (HP, $\rho = 0.46$; CV, $\rho = 0.52$). Together, these results indicate that nitrate, a primary contaminant, should be considered as a factor leading to secondary groundwater U contamination in addition to the recognized role of alkalinity and calcium.



INTRODUCTION

Uranium (U) contamination of groundwater has been primarily associated with anthropogenic activities such as mining, milling, nuclear testing, and disposal of spent nuclear fuel. However, groundwater U concentrations across the United States exceed the U.S. Environmental Protection Agency (EPA) MCL of 30 $\mu\text{g/L}$ (Figure S1) in many regions, including those without anthropogenic U activity, indicating a source of natural U contamination. This is significant because consumption of U-contaminated drinking water has been linked to nephrotoxicity² and osteotoxicity³ and, thus, poses a health risk.

The High Plains (HP) and Central Valley (CV) aquifers, two of the largest and most productive aquifers in the world,⁴ are among aquifers with high concentrations of dissolved U in groundwater (Figure S2). These two aquifers represent a common aquifer type, unconsolidated sand and gravel composed of silt, sands, poorly sorted clays, and gravel, deposited through weathering and alluvial processes (see the Supporting Information for details),¹ and provide drinking water to nearly 6 million people.⁵ In addition to being an important source of drinking water, these aquifers are also mined to irrigate 56700 km^2 of cropland accounting for 1/6 of all U.S. agricultural annual revenue.⁶ Drought has placed an increased reliance on groundwater,⁷ impacting not only quantity but also degradation of groundwater quality.⁸

Uranium is a ubiquitous ($\sim 2\text{--}4$ mg/kg of soil or sediment), naturally occurring radionuclide commonly deposited as a diagenetic secondary mineral in organic carbon-rich regions

subsequent to weathering of igneous parent materials.⁹ The majority of U exists in soils and sediments as insoluble reduced U(IV) minerals, e.g., uraninite, which may be associated with volcanic rocks, black shales, or granites,⁹ and as such is generally immobile or insoluble in suboxic groundwater. For decades, it has been recognized that exposing reduced U(IV) minerals to oxidizing groundwater leads to oxidative dissolution, producing aqueous or dissolved U(VI) species¹⁰ rendering U mobile. At pH $\sim 6\text{--}10$, U(VI) will strongly adsorb to sedimentary matrices.¹¹ However, mineral dissolution reactions will increase dissolved carbonate concentrations, favoring formation of soluble U(VI)–carbonate species, including U(VI)–Ca–CO₃ species, and adsorption becomes insignificant.¹² Thus, together, redox chemistry (oxidation state) and carbonate alkalinity are recognized as primary factors controlling U mobility.

Nitrate is a common groundwater contaminant (U.S. EPA MCL = 10 mg/L), primarily originating from surface-applied chemical and animal waste fertilizers.¹³ Nitrate also plays a role in U solubilization, leading to secondary U contamination. Biological nitrate reduction coupled to the oxidation of organic matter can generate alkalinity mobilizing U(VI). However, generation of alkalinity alone cannot account for U solubility if

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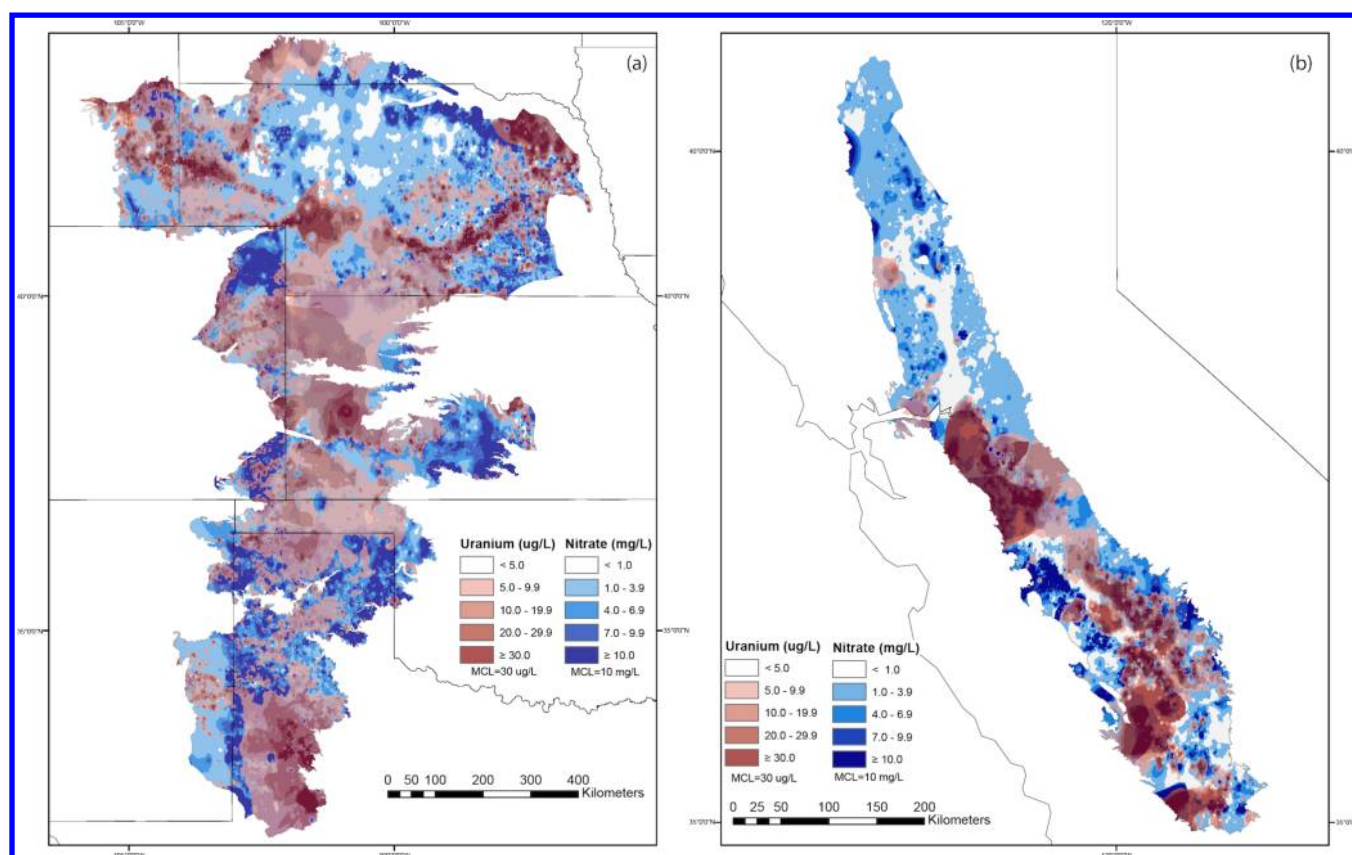


Figure 1. Interpolation of groundwater U and nitrate concentrations in the High Plains and Central Valley aquifers. Uranium concentrations (red color gradient) and nitrate (blue color gradient) in groundwater within the (a) High Plains and (b) Central Valley aquifers in the United States.

U originated as a U(IV) mineral. Nitrate can abiotically oxidize U(IV) minerals, yielding aqueous U(VI).^{14–16} Abiotic and biotic nitrate reduction reactions will also produce reactive intermediates such as nitrite and nitrous oxide that will abiotically oxidize U(IV) to U(VI) (Table S1).^{16,17} Nitrate-driven Fe(II) oxidation reactions can produce reactive Fe(III) oxides that will also oxidize U(IV) (Table S1).^{15,18} Reduced U(IV) minerals can also serve as a microbial energy source where U(IV) oxidation is coupled to nitrate reduction.¹⁴ Thus, nitrate, a primary groundwater contaminant, can be a factor leading to secondary U contamination.

Here we investigate the co-occurrence of nitrate and U as well as the correlation of additional geochemical parameters associated with U mobility within two major U.S. aquifers, the HP and CV aquifers, utilizing metadata assembled from federal, state, and local government agencies and academic institutions and data from the National Water Information System (NWIS). The results revealed widespread U and nitrate co-contamination of groundwater and implicate alkalinity and calcium as geochemical parameters that co-control U contamination.

■ MATERIALS AND METHODS

Groundwater Nitrate and Uranium Concentration Metadata. Assembly of the metadatabase originally included 450990 data points from 139320 sampling locations in nine states within the HP (Colorado, Kansas, Nebraska, New Mexico, Oklahoma, South Dakota, Texas, and Wyoming) and CV (California) aquifers before exclusion and truncation of location coordinates (Table S2). The metadatabase was

assembled from groundwater sample data with reported numerical latitude, longitude, collection date, nitrate concentration, and/or U concentration (analytical detection limit required) inside the boundaries of the HP and CV aquifers. In the event of a duplicate groundwater sample report (same sampling location on the same day with the same nitrate and/or U concentration), only one sample was included in the metadatabase. After data exclusion (see the Supporting Information for details), the metadatabase was reduced to 276511 groundwater samples from the HP and CV aquifers at 61964 sampling locations (Figure S3).

NWIS Groundwater Geochemical Data. In an effort to assess the statistical relationship between groundwater U and geochemical parameters demonstrated to influence U mobility, data collected from filtered groundwater samples were retrieved from the NWIS. A total of 1818 samples from the HP aquifer and 563 samples from the CV aquifer resulted in a data set that included U, pH, alkalinity, dissolved oxygen (DO), nitrate, iron, manganese, and calcium (see the Supporting Information for details). These parameters have been demonstrated to influence U mobility.^{11,12,15,19,20} In the absence of ligands, filtered groundwater samples collected for analysis of iron and manganese represent aqueous reduced species as solid-phase oxide minerals will not be measured in groundwater.²¹

Statistical Analyses. Spatial Interpolation. Spatial interpolation of metadata was used to estimate unknown values of groundwater U and nitrate concentrations in ArcGIS Desktop (release 10.1, Environmental Systems Research Institute, Redlands, CA). Nondetect (zero) values were converted to half the lower detection limit (LDL; 0.5 $\mu\text{g/L}$ for U and 0.05 mg/L for nitrate). From among four methods of interpolation

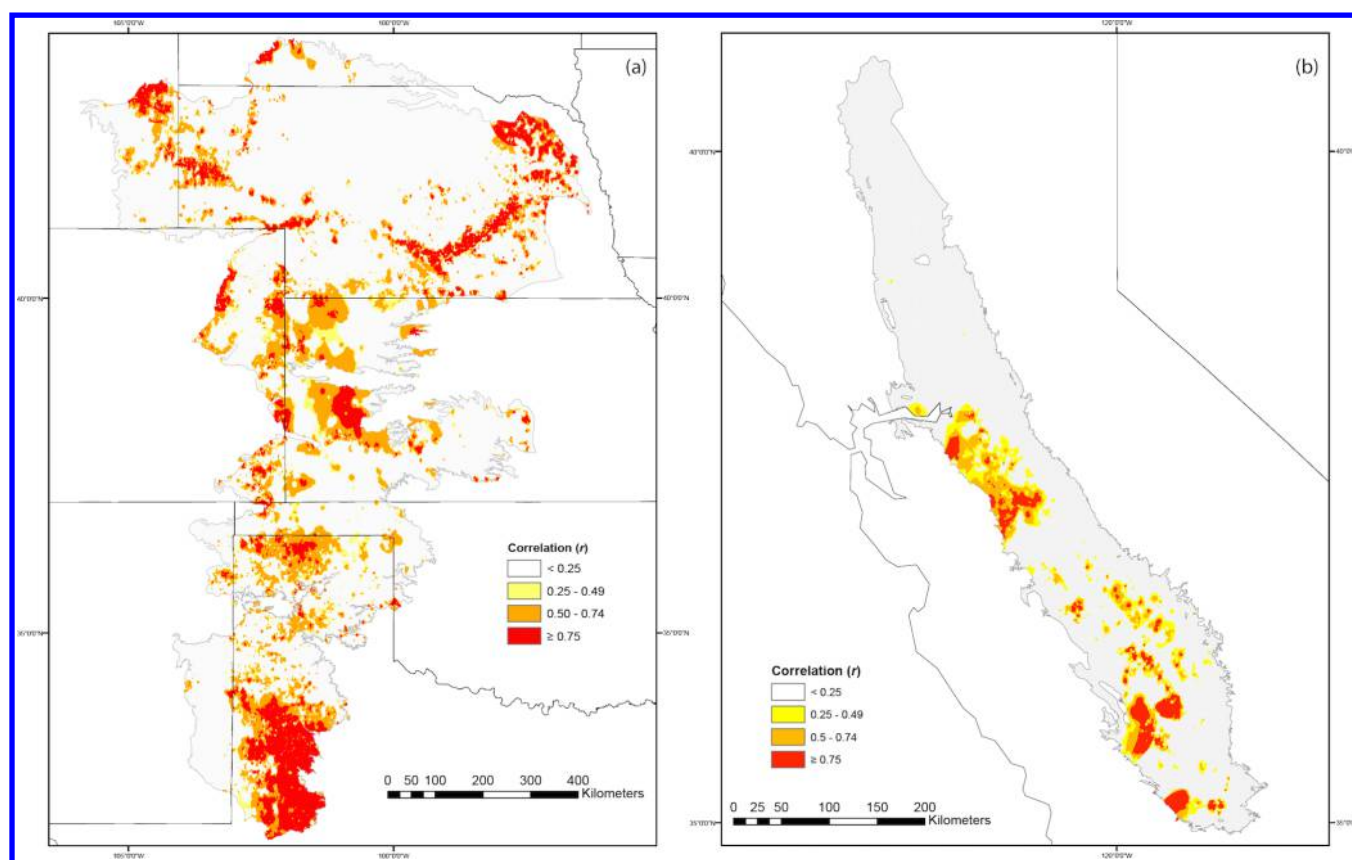


Figure 2. Spatial correlation grids indicating the statistical strength of association between groundwater U and nitrate concentrations demonstrating the relationship between the two contaminants in the (a) High Plains and (b) Central Valley aquifers in the United States.

(inverse distance weighting, ordinary kriging, local polynomial interpolation, and empirical bayesian kriging) conducted in ArcGIS,^{22,23} inverse distance weighting resulted in the smallest error as calculated by the root-mean-square error (Table S3; see the Supporting Information for details).

Spatial Correlation Analysis. A spatially referenced Pearson correlation coefficient (r_{xy}) was calculated from the interpolated nitrate and U concentrations to identify areas in which U was correlated to nitrate. Interpolated data were normalized for spatial grid creation.²² Estimated nitrate and U concentrations ($x_{\text{independent}}$ and $y_{\text{dependent}}$) within a $1 \text{ km} \times 1 \text{ km}$ (1 km^2) area were calculated by dividing the covariance (S_{xy}) of predicted concentrations by the product of standard deviations S_x and S_y (see the Supporting Information for details).²⁴ This method has been previously applied to the groundwater spatial distribution.²⁵ A nine-cell moving window was used to calculate the focal mean.²⁴ The analysis indicates linearity between nitrate and U concentrations in groundwater, with a Pearson correlation coefficient (r_{xy}) assigned to each grid cell. A perfect positive relationship is equal to 1. Strong correlation ranges from 0.75 to 1, moderate correlation from 0.5 to 0.74, weak correlation from 0.25 to 0.49, and no correlation from 0 to 0.24.

Descriptive Statistics and Correlation Analyses. Statistical analyses were performed on measured groundwater U and nitrate concentrations from the metadatabase. Nondetect (zero) values were treated as half the LDL (described above). Descriptive statistics (mean, median, maximum, and standard error) were calculated for nitrate and U data in Prism GraphPad version 5.00 (see the Supporting Information for details).

Spearman's rank-order correlation coefficients were calculated to determine the statistical relationship among U, geochemical parameters, and well depth (shallow well of <100 ft, 30.5 m) within the NWIS data set (see the Supporting Information for details).²⁶ The strength of correlation ranks, rho (ρ), is defined as follows: strong correlation from 0.75 to 1, moderate correlation from 0.25 to 0.75 and weak correlation from 0 to 0.24. A $p < 0.001$ was considered statistically significant.

RESULTS AND DISCUSSION

Groundwater U and nitrate concentrations exceeded the MCL in 10 and 21% of tested wells, respectively, in the HP and CV aquifer metadata (Table S4). In the HP aquifer, U concentrations of $\leq 2674 \mu\text{g/L}$ (89 times the MCL) and nitrate concentrations of $\leq 1894 \text{ mg/L}$ (189 times the MCL) were identified (Figure S4 and Table S5). Similarly, high groundwater U concentrations were identified in the CV aquifer with U concentrations of $\leq 5400 \mu\text{g/L}$ (180 times the MCL) and nitrate concentrations of $\leq 340 \text{ mg/L}$ (34 times the MCL) (Figure S5 and Table S5).

Spatial interpolation using inverse distance weighting estimated widespread groundwater U and nitrate concentrations in both the HP and CV aquifers in excess of the MCL across expansive areas [22375 km^2 for U and 99162 km^2 for nitrate (Figure 1 and Figure S6 and Table S6)]. One in nine communities (~ 1.9 million residents) above both aquifers is estimated within 1 km of groundwater U exceeding the MCL. There are regions in which no data are available (Figure S3), restricting the model to estimates between measured locations.

Table 1. Spearman's Rank-Order Correlation Analysis of Groundwater U Concentrations Relative to Geochemical Parameters in the High Plains and Central Valley Aquifers^a

	<i>n</i>	pH	alkalinity	dissolved oxygen	nitrate	iron	manganese	calcium
Central Valley								
ρ	563	-0.026	0.387	0.088	0.324	0.218	-0.130	0.444
<i>p</i> value		0.471	<0.001	0.015	<0.001	<0.001	<0.001	<0.001
High Plains								
ρ	1,818	-0.044	0.338	0.039	0.421	-0.082	0.091	0.491
<i>p</i> value		0.027	<0.001	0.050	<0.001	<0.001	<0.001	<0.001

^aAnalysis was conducted using the NWIS dataset. ρ denotes the correlation coefficient rho.

Spatial correlation analysis of interpolated groundwater U and nitrate concentrations revealed a strong correlation ($r \geq 0.75$) within various regions throughout the HP and CV aquifers (Figure 2). Within these regions, mean groundwater concentrations of both U (HP, 128.0 $\mu\text{g/L}$; CV, 71.0 $\mu\text{g/L}$) and nitrate (HP, 26.7 mg/L; CV, 18.3 mg/L) exceeded the MCL (Table S7). A strong correlation between groundwater U and nitrate concentrations is observed over 17494 km² in the HP aquifer, specifically regions in northern Texas and throughout the state of Nebraska and 1652 km² in the San Joaquin and Tulare Basins within the CV aquifer (Figure 2 and Table S7). The mean groundwater concentrations of both U (HP, 74.2.0 $\mu\text{g/L}$; CV, 33.0 $\mu\text{g/L}$) and nitrate (HP, 10.5 mg/L; CV, 10.8 mg/L) also exceeded the MCL in areas of moderate correlation (Table S7). Areas identified as having moderate and strong correlations ($0.50 \leq r$) account for 78% of U groundwater concentrations exceeding the MCL. In these areas, the mean nitrate concentration ranges from 10.5 to 18.3 mg/L and the median nitrate concentration ranges from 6 to 18 mg/L (Table S7). Regions also demonstrated no or negative correlation to weak correlation ($r \leq 0.25$) (Table S7), suggesting some regional/geochemical control of U solubility not accounted for by nitrate concentrations alone or a lack of data resulting in an under- or overestimation of U or nitrate concentrations.

Other geochemical constituents, pH, DO, alkalinity, calcium, iron, and manganese, also can control U mobility in groundwater.^{11,15,20,27} Spearman's rank-order correlation analysis of measured geochemical data within the NWIS database determined that calcium, alkalinity, and nitrate were moderately correlated with groundwater uranium concentrations (Table 1). Iron and manganese were weakly correlated with U concentrations. Dissolved oxygen and pH were not statistically correlated to groundwater U concentrations ($p > 0.001$). Nitrate is a better oxidant of U(IV) than DO;²⁸ thus, it is not surprising that DO was not correlated with U concentration. It is well recognized that microbial activity and water-rock interactions lead to increases in carbonate alkalinity and calcium in groundwater that then form aqueous complexes with U.¹¹ The U(VI)-Ca-CO₃ complexes are less likely to adsorb and are not as bioavailable to U-reducing bacteria for re-reduction and, thus, will remain mobile.^{19,29} Even if U(IV) is oxidized by nitrate, U mobility would be promoted and co-controlled by alkalinity and calcium.

In areas where groundwater U and nitrate concentrations were measured in the NWIS data set, Spearman's rank-order correlation analysis was significantly correlated to nitrate in both the HP ($\rho = 0.42$; $p < 0.001$) and CV ($\rho = 0.32$; $p < 0.001$) aquifers (Table 1 and Figure S7). Correlation analysis in shallow wells (<30.5 m, 100 ft) revealed an increased strength of correlation between groundwater U and nitrate concen-

trations in the HP ($\rho = 0.46$; $p < 0.001$) and CV ($\rho = 0.52$; $p < 0.001$) aquifers (Figure S8 and Table S8), indicating the susceptibility of shallow wells to both U and nitrate contamination. Uranium and nitrate concentrations in shallow wells were >8 times more likely to exceed the MCL relative to deeper wells (>30.5 m, >100 ft) for U (19 and 2%, respectively) and nitrate (17 and 2%, respectively). This result is consistent with prior reports of nitrate contamination in shallow wells not protected by confining layers resulting in infiltration rates exceeding microbial reduction rates.³⁰ Thus, an increased level of nitrate infiltration could play a role in stimulating U mobilization.

The correlation of U and nitrate in groundwater is not necessarily restricted to U.S. aquifers and likely occurs worldwide. Mobilization of naturally occurring U was identified in a shallow, fluvial aquifer in Germany, and both abiotic and biotic mechanisms including nitrate-mediated mobilization were suggested to control U solubility.³¹ However, the extent of this link remained unestablished. While anthropogenic U contamination occurs in western regions of the HP aquifer, only one of six wells identified to exceed the MCL was within 1 km of former or current mining/milling sites (Figure S2 and Table S9). Given that sampling locations in the metadata are ≥ 5 km from former legacy U milling/mining operation sites, the metadata are minimally impacted by direct anthropogenic U contamination.

Here we establish a link between groundwater U and nitrate contamination in the HP and CV aquifers. Our data indicate that nitrate concentrations near the MCL are correlated to groundwater U contamination. Thus, nitrate-mediated U solubilization presents a threat to the quality of groundwater resources already under pressure because of population growth and global environmental change.³² This has the potential to negatively impact the health of millions of residents in the United States and around the world utilizing U-contaminated drinking water. Additionally, irrigation accounts for an estimated 43% of global groundwater use.³³ Food crops irrigated with contaminated water have been demonstrated to accumulate U,^{34,35} thus leading to an additional route of U exposure through food crops. Given the ubiquitous nature of nitrate in aquifers and the strong correlation with U mobilization, increased testing of groundwater for U where nitrate is at or near the MCL should be conducted.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.estlett.5b00174.

Supporting methods; supporting figures (S1–S3 and S6) detailing well sampling locations and groundwater U and nitrate concentrations in the HP aquifer, additional

figures (S4, S5, S7, and S8) detailing groundwater data, relevant U redox reactions (Table S1), metadatabase sources and results from statistical analyses (Tables S2–S9), and supporting references (PDF)

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Notes

The authors declare no competing financial interest.

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