

**INVESTIGATING THE IMPACT OF NITRATE CONTAMINATION ON URANIUM
AND OTHER ELEMENTS OF EMERGING CONCERN IN WISCONSIN
GROUNDWATER**

**Amy Nitka
Paul McGinley**

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Amy L. Nitka
Water & Environmental Analysis Lab
University of Wisconsin-Stevens Point

Paul M. McGinley
Center for Watershed Science and Education
University of Wisconsin-Stevens Point

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Title: Investigating the impact of nitrate contamination on uranium and other elements of emerging concern in Wisconsin groundwater

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Investigators: Principle Investigators –
Amy L. Nitka, Outreach Specialist, Water & Environmental Analysis Lab
Paul M. McGinley, *title*, Center for Watershed Science and Education

Research Assistants –
Nicholas Salewski, Lab Assistant, Water & Environmental Analysis Lab
Andrew Wick, Lab Assistant, Water & Environmental Analysis Lab

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Background/Need: This project was designed to provide a rapid evaluation of uranium and other geochemical parameters in Wisconsin groundwater. This evaluation was intended to assist in formulating hypotheses about uranium chemistry in Wisconsin groundwater and identify if there is a need for more detailed work examining anthropogenic impacts to uranium in groundwater. The study was focused in an area with existing monitoring wells for which a history of nitrate concentrations over time was available.

Objectives: The objective of this study was to determine if groundwater uranium concentrations increase in response to anthropogenic changes to groundwater geochemistry. The project combined repeated sampling of groundwater from monitoring wells in areas with previously observed elevated and/or variable nitrate contamination and a vadose zone investigation exploring the distribution and mobility of uranium during groundwater geochemical evolution.

Methods: Twenty monitoring wells in Portage, Waupaca and Shawano Counties were sampled six times over one year. Groundwater samples were analyzed for uranium and nitrate, as well as other geochemical parameters including calcium, phosphorus, sulfate, iron, and elements of emerging concern, including vanadium (^{51}V), strontium (^{88}Sr), cobalt (^{59}Co), chromium (^{52}Cr), and molybdenum (^{98}Mo). Soil samples were collected from three sites with a bucket auger. Soil samples were dried and homogenized in paper bags. Soil pH was measured. Samples were digested according to EPA 3051A. Statistical comparisons developed correlation between chemical parameters in groundwater in each well.

Results and Discussion: The groundwater chemistry in the monitored wells was dominated by calcium, magnesium and bicarbonate. The groundwater chemistry in the monitored wells was dominated by calcium, magnesium and bicarbonate. Correlation tests show that some of the wells have very significant positive correlations between nitrate and calcium. In general, the strongest correlations are those with the largest range in nitrate concentrations. Only four wells (20%) had moderately strong correlations for nitrate and uranium. This suggests that the presence of nitrate is not influencing uranium concentrations in groundwater. Results from all samples ($n=118$) were evaluated. Unlike Nolan and Weber (2015) who determined Spearman's rho to be ≥ 0.30 ($p < 0.001$), results from this study yielded Spearman's rho of -0.71 ($p < 0.001$). The discrepancies in results may be due to various factors.

Soil samples from three profiles were extracted for uranium. The concentration of uranium is typically between 0.2 and 0.5 mg/kg. That is similar to the typical range reported for subsurface materials (Banning et al., 2013). A full profile in the agricultural soil showed an increase within a subsoil layer and an increase in uranium near the surface. The surficial concentration may reflect an addition of uranium through phosphorus fertilizers (Schnug and Lottermoser, 2013; Liesch et al., 2015; Banning and Rude, 2015). The very high concentration deep in the profile is consistent with the high iron and potassium in that sample.

The relationship between uranium and iron showed a much stronger correlation. That is consistent with the review by Davis et al. (2004) who found that soil uranium concentrations follow the iron concentrations. Similarly, Waite et al. (1994) showed strong adsorption of uranium by iron oxide between pH 5 and 8.5. The profiles in this study show how soil pH can vary in the region reflecting the presence or absence of carbonates and the addition of lime to agricultural soils, but that the range is within the range where strong uranyl adsorption is expected.

Conclusions/Implications/Recommendations: The results from the monitoring wells did not show a relationship between nitrate and uranium; however, repeated sampling did show important changes in geochemistry over the course of a year. Wells that had a greater range of nitrate concentrations over the course of sampling were generally correlated to changes in calcium and magnesium concentrations. This shows that higher levels of mineralization travels concurrently with nitrate in an aquifer.

Related Publications: Nitka, A., P. McGinley, N. Salewski, A. Wick. 2017. Uranium concentrations in central Wisconsin groundwater and their relationship to groundwater chemistry. American Water Resources Association–Wisconsin Section Annual Meeting (poster).

Key Works: uranium, nitrate, groundwater quality

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INTRODUCTION

The uranium concentration of groundwater should reflect the passage of groundwater recharge through the soil profile and aquifer and the transfer of uranium from the solid to the aqueous phase. Uranium has a solution chemistry with two oxidation states (VI and IV), a variety of possible precipitates, the ability to form complexes with carbonate and natural organic matter, and the potential to adsorb onto natural surfaces such as iron oxides. Concern about uranium contamination often emanates from visible anthropogenic sources, like mining and nuclear activities; however, in central and northern Wisconsin, the presence of uranium is more likely due to rock weathering. It is not clear what controls the uranium concentration in the shallow sand and gravel aquifer in central Wisconsin. In this water, the presence of nitrate and low iron concentrations suggest a sufficiently oxic environment that the dominant form of uranium would be the oxidized U(+VI) with solution chemistry related to the uranyl ion (UO_2^{2+}). The uranium concentrations are usually relatively low (e.g., less than ~ 5 $\mu\text{g/l}$) suggesting precipitation is unlikely to be controlling (Davis et al., 2004). The uranyl ion chemistry is likely to be controlled by the formation of solution complexes with carbonate and adsorption to iron oxides. Davis et al. (2004) summarized research on uranium in groundwater with a similar chemical composition and found that U(VI) transport would likely be controlled by adsorption onto iron oxides.

The objective of this study was to determine if groundwater uranium concentrations increase in response to anthropogenic changes to groundwater geochemistry. A recent study by Nolan and Weber (2015) suggested that higher concentrations of uranium in groundwater are correlated with higher nitrate concentrations. They postulated a combination of oxidative dissolution of U(IV) in minerals and enhanced complexation by carbonate ions resulting from the anthropogenic nitrogen addition to land. Several mechanisms for an oxidation dissolution of uranium has been proposed (Senko, 2005). Carbonate mineral dissolution linked to nitrate has also been shown (Aquilina et al., 2012). The extent to which these reactions combine to increase uranium mobility within Wisconsin aquifers is unknown. The project combined repeated sampling of groundwater from monitoring wells in areas with previously observed elevated and/or variable nitrate contamination and a vadose zone investigation exploring the distribution and mobility of uranium during groundwater geochemical evolution. This evaluation was intended to assist in formulating hypotheses about uranium chemistry in Wisconsin groundwater and identify if there is a need for more detailed work examining anthropogenic impacts to uranium in groundwater.

PROCEDURES AND METHODS

Groundwater Sample Collection

Twenty wells in Portage, Waupaca and Shawano Counties were selected for the study. These wells were selected from an initial evaluation of 37 wells. The wells were selected based on the results of nitrate and uranium analysis. All wells with nitrate-N concentrations above the drinking water standards of 10 mg/L or a uranium concentration greater than 3 $\mu\text{g/L}$ were selected for further sampling.

Prior to sampling, the wells were purged according to Wisconsin DNR groundwater sampling methods (Karklins, 1996). Samples for ICP-MS and ICP-OES analysis were collected in 60-mL HDPE bottles prepared with HNO_3 preservative. A separate 125-mL unpreserved sample was collected at the same time for alkalinity, nitrate and chloride analysis. Samples were stored at 4 degrees Celsius until the time of analysis. The intent of this sampling was to provide data for statistical evaluation of the geochemical influences on uranium contamination.

Vadose Zone Soil Collection and Extraction

Soil samples were collected from three sites with a bucket auger. Two of those sites were sampled from 1 to 2 meters by augering at the base of a soil pit. One of those was currently in deciduous trees such as maple and oak. Another of those was in pine. The third site has been an agricultural field for more than fifty years and is now in irrigated vegetable crops. That site was augered from the surface to three meters. Soil samples were dried and homogenized in paper bags. Soil pH was measured after mixing 10 g of soil with 50 ml of deionized water. Soils were digested according to EPA 3051A using a MARS 5 microwave digestion (CEM Corporation). The acid extractable soil chemical composition by microwave digestion of approximately 0.2 g soil with 10 ml nitric acid. The samples were heated to 180 degrees in the microwave for fifteen minutes. This method does not completely dissolve all the silicate material in the samples and left small rock fragments. We are using this as an aggressive treatment likely to assay all adsorbed ions and those in secondary minerals such as iron oxides.

Groundwater and Vadose Soil Extract Analysis

Samples were analyzed for uranium ^{238}U by inductively coupled plasma mass spectroscopy (ICP-MS) using EPA Method 200.8. (Instrument make and model?) This method was chosen because of the ability to measure the major mass isotope of uranium (^{238}U) with a high degree of sensitivity (USEPA, 1994). Elements of emerging concern, including vanadium (^{51}V), strontium (^{88}Sr), cobalt (^{59}Co), chromium (^{52}Cr), and molybdenum (^{98}Mo) were also analyzed by this method. Samples were analyzed for calcium, magnesium and phosphorus using a Varian Vista inductively coupled plasma – optical emission spectroscopy (ICP-OES). Nitrate and chloride were analyzed by a Lachat 8000 using flow injection analysis (FIA) (Lachat Method 10-107-04-1-A for nitrate; Lachat Method 10-117-07-1-B for chloride). Nitrate was measured as nitrate plus nitrite.

Statistical Analysis

The statistical comparison in this study used the correlation between chemical parameters in the groundwater from each well. This approach was predicated on the hypothesis that the geochemical changes attributable to land application of nitrogen would propagate through the aquifer at the same rate as the nitrate. For example, any mineral weathering products or consumption of alkalinity that would accompany nitrification would lead to a water chemistry change that would travel with the nitrate. The chemistry within each well was evaluated using a Spearman's correlation. We calculated the Spearman's rho and determined 95% confidence limits for the correlation using the statistical program R package cor.test (x64 3.4.1, R Core Team, 2017).

RESULTS AND DISCUSSION

Groundwater

The areas sampled in central and northern Wisconsin are typically in a sand and gravel aquifer, likely with simple groundwater flow lines (Kraft et al., 2008). Nitrate concentrations for the wells in the study ranged from below the detection limit of 0.1 mg/L to 48.5 mg/L. Concentrations within many wells also varied, often by more than 10 mg/L within a given well.

The groundwater chemistry in the monitored wells was dominated by calcium, magnesium and bicarbonate. Table 1 summarizes general chemistry results for the wells that is typical of this region where glacially deposited outwash and tills from Wisconsin-age glaciation form a surficial sand and gravel aquifer.

Previous studies of the region have shown how the groundwater flows horizontally and discharges to streams that drain the region (Kraft et al., 2008).

Table 1. Mean concentrations characterizing the chemistry in the study wells.

Well ID	Nitrate-N		Uranium		Alkalinity		Calcium		Iron	
	mean	sd	mean	sd	mean	sd	mean	sd	mean	sd
101	0.1	0.1	8.163	1.808	189	9	40.6	0.7	0.099	0.126
102	37.9	10.4	0.043	0.009	72	8	57.8	12.8	0.041	0.057
103	30.5	5.1	0.169	0.007	76	6	46.0	6.0	0.056	0.077
106	3.1	0.2	2.317	0.098	164	5	40.3	1.2	0.027	0.025
107	2.1	0.4	4.350	0.244	171	4	40.1	1.2	0.037	0.029
108	0.6	0.5	7.573	0.438	182	7	40.6	1.1	0.184	0.402
118	26.5	8.7	0.090	0.034	93	16	52.8	7.7	0.015	0.006
128	27.3	5.6	0.409	0.052	87	11	50.1	6.0	0.060	0.080
132	18.6	4.4	0.541	0.097	114	17	44.7	2.6	0.018	0.008
135	32.4	5.9	0.306	0.023	80	17	48.0	7.9	0.035	0.028
140	27.3	6.1	0.477	0.047	93	10	49.3	8.0	0.025	0.021
145	18.3	11.3	0.745	0.049	119	19	48.3	11.6	0.024	0.026
160	3.3	0.1	3.207	0.161	140	3	34.4	1.2	0.030	0.029
165	3.4	0.1	2.960	0.137	142	4	34.4	1.2	0.019	0.012
210	26.1	9.4	0.590	0.287	241	37	76.5	14.4	0.045	0.049
215	0.1	0.0	1.509	1.506	44	25	13.4	7.4	1.168	0.809
301	8.2	1.7	0.233	0.191	178	29	62.7	4.5	0.732	0.822
302	34.3	2.2	0.112	0.023	90	12	37.5	6.3	0.298	0.189
303	14.6	2.8	5.526	1.512	155	22	53.5	5.9	0.092	0.092
304	12.0	0.9	3.213	3.620	143	32	38.8	13.8	0.322	0.308

Well ID	Potassium		Magnesium		Phosphorus		pH		Sulfate	
	mean	sd	mean	sd	mean	sd	mean	sd	mean	sd
101	2.0	0.3	22.7	0.4	0.148	0.060	7.54	0.22	12.2	0.5
102	10.9	0.9	24.0	4.4	0.017	0.031	7.65	0.11	44.4	12.6
103	2.2	1.0	20.7	2.0	0.017	0.023	7.82	0.07	39.2	5.2
106	1.1	0.7	20.5	0.4	0.018	0.014	7.91	0.08	10.9	0.5
107	1.4	1.0	20.7	0.6	0.018	0.024	7.93	0.07	11.2	0.4
108	1.9	0.9	21.8	0.8	0.011	0.015	7.82	0.11	12.0	1.0
118	1.2	0.2	19.6	3.1	0.005	0.005	7.62	0.11	24.3	6.7
128	1.1	0.1	21.4	2.2	0.009	0.005	8.02	0.85	22.0	5.0
132	0.9	0.2	20.1	0.8	0.009	0.002	7.77	0.18	15.3	3.1
135	1.1	0.1	20.8	3.1	0.010	0.004	7.76	0.16	27.9	2.4
140	1.0	0.1	22.1	3.6	0.008	0.004	7.80	0.12	21.7	4.2
145	0.9	0.1	23.0	5.3	0.009	0.003	7.76	0.11	16.2	7.1
160	1.7	1.8	18.1	0.4	0.015	0.007	7.83	0.09	8.6	0.5
165	1.4	0.9	18.0	0.3	0.011	0.001	7.65	0.25	8.6	0.5
210	28.0	6.5	32.8	7.6	0.010	0.005	6.87	0.24	19.6	5.2
215	0.4	0.1	6.7	2.4	0.021	0.010	6.09	0.23	12.1	1.8
301	1.6	0.3	22.5	2.2	0.032	0.012	7.22	0.14	15.4	5.5
302	1.4	0.7	13.3	2.4	0.123	0.020	7.28	0.20	12.5	1.5
303	1.4	1.3	26.9	3.7	0.050	0.009	7.44	0.18	15.8	2.4
304	1.0	0.2	27.5	1.3	0.033	0.033	8.09	0.64	12.9	0.7

The range in groundwater chemical composition within a well showed large differences between wells. For example, Figures 1 and 2 show the range of nitrate concentrations and calcium concentrations, respectively, for each well. The nitrate concentration range between samplings was more than 15 mg N/l in some wells but less than 2 mg N/l in others. Similarly, the range in calcium concentrations between samplings varied between wells. If the concentration variation represents water that has taken a similar path to the well but has differences in chemistry because of the timing of fertilizer application, acidity generation from nitrification and other chemical additions relative to the timing of recharge, then we might expect there to be a correlation between these chemistry changes.

The correlation between nitrate and calcium concentrations in the wells is summarized in Table 2 and shown in Figure 6. The significance of the correlations shows that some of the wells have very significant positive correlations between nitrate and calcium. In general, the strongest correlations are those with the largest range in nitrate concentrations. Testing in those wells will likely have the greatest power to detect a correlation, as the variation between samples is large enough to overcome the inherent variations in groundwater chemistry from other sources. The positive correlations between calcium and nitrate in those wells with larger nitrate concentration ranges is consistent with the enhanced dissolution of carbonate minerals following acidity generation during nitrification (Gandois et al., 2011; Aqualina et al., 2012). The significant correlations show that the higher level of mineralization in the groundwater travels concurrently with the nitrate in the aquifer.

Correlations between nitrate concentration and calcium, sulfate, chloride, magnesium and phosphorus for wells with the greatest variation in nitrate are shown in Table 3. Similar to the calcium, the magnesium led to significant correlations with nitrate in many of the same wells. That is consistent with a dolomitic source of carbonate minerals in this region. The chloride concentration was also positively correlated to nitrate in several of the wells. Phosphorus did not show correlations with nitrate. That is consistent with their chemistry dominated by interactions in the soil that are not susceptible to dissolution through neutralizing acidity.

Analytical results for groundwater samples were evaluated. Boxplots for nitrate and uranium (Figures 1 and 3) indicate more of an inverse relationship. Graphs in Figure 5 also support this. Comparing boxplots for nitrate and calcium, there appears to be more of a direct relationship. Table 2 lists the mean, standard deviation, low, high and range nitrate-N (mg/L) concentrations for each well, as well as Spearman's rho for nitrate and uranium and nitrate and calcium. This table shows a weak or inverse correlation for nitrate and uranium in most wells. Only four wells (20%) had moderately strong correlations. This suggests that the presence of nitrate is not influencing uranium concentrations in groundwater. Results from all samples (n=118) were evaluated. Unlike Nolan and Weber (2015) who determined Spearman's rho to be ≥ 0.30 ($p < 0.001$), results from this study yielded Spearman's rho of -0.71 ($p < 0.001$). The discrepancies in results may be due to various factors. One, Nolan and Weber had a much greater sample size (n=2381) over a much greater area (22,375 km²). However, this study monitored the same wells six times over one year.

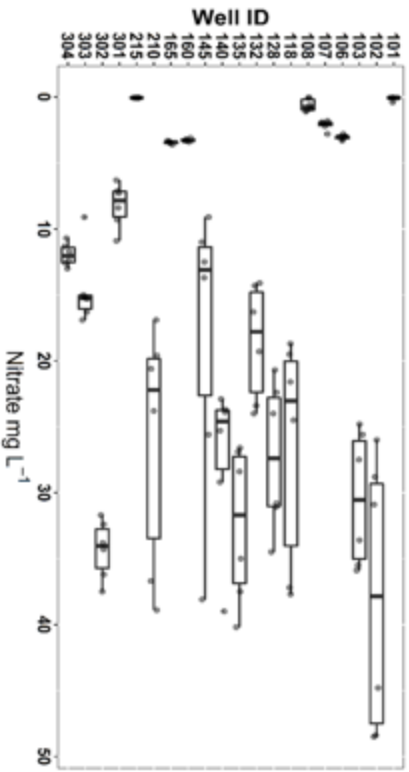


Figure 1. Boxplots for nitrate-N concentrations for wells in the study (wells 100 and 105, n=5; all other wells n=6).

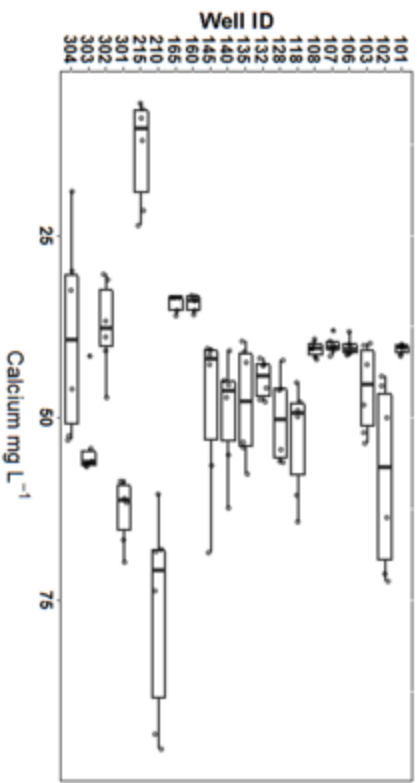


Figure 2. Boxplots for calcium concentrations for wells in the study (wells 100 and 105, n=5; all other wells n=6).

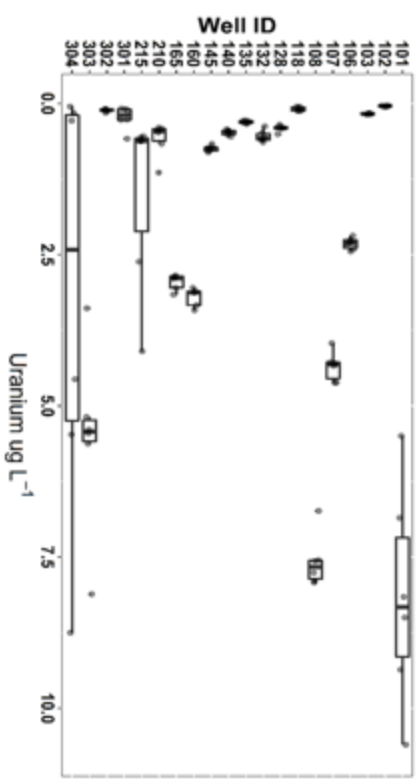


Figure 3. Boxplots for uranium concentrations for wells in the study (wells 160 and 165, n=5; all other wells n=6).

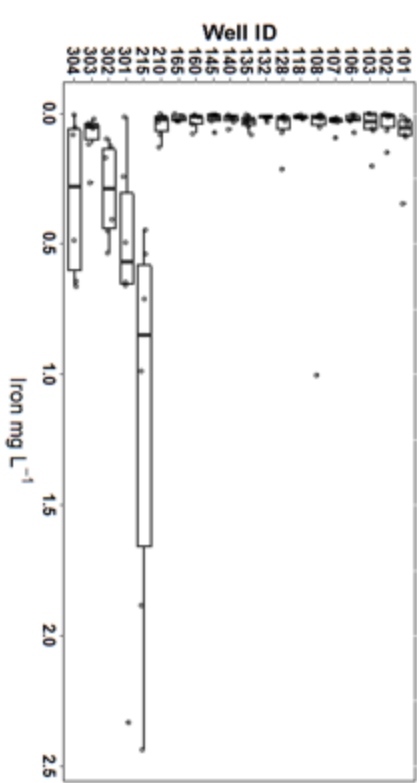


Figure 4. Boxplots for iron concentrations for wells in the study (wells 160 and 165, n=5; all other wells n=6).

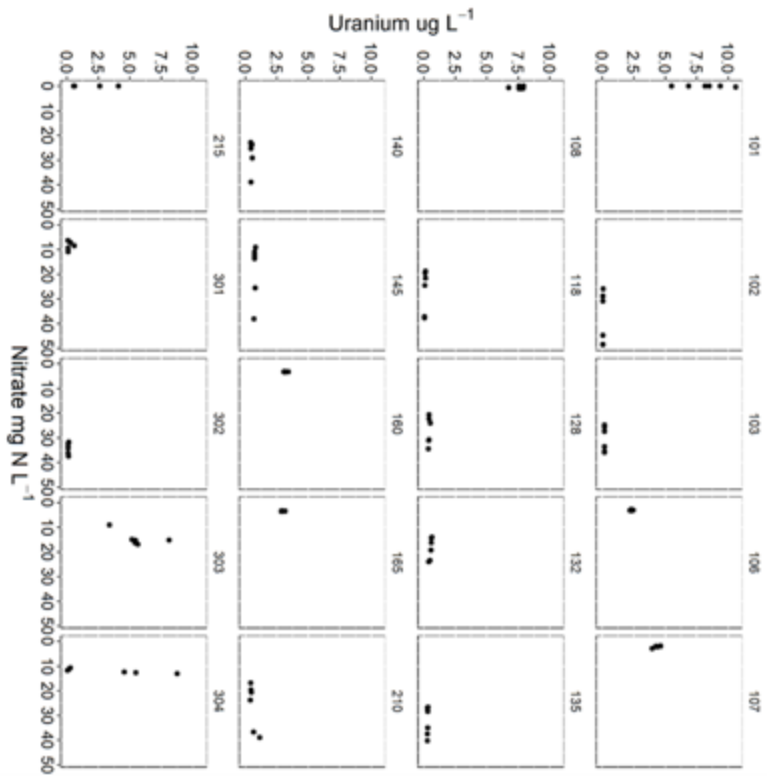


Figure 5. Graphs of nitrate-N (mg/L) vs. uranium ($\mu\text{g/L}$) for wells in the study (wells 100 and 165, $n=5$; all other wells $n=6$).

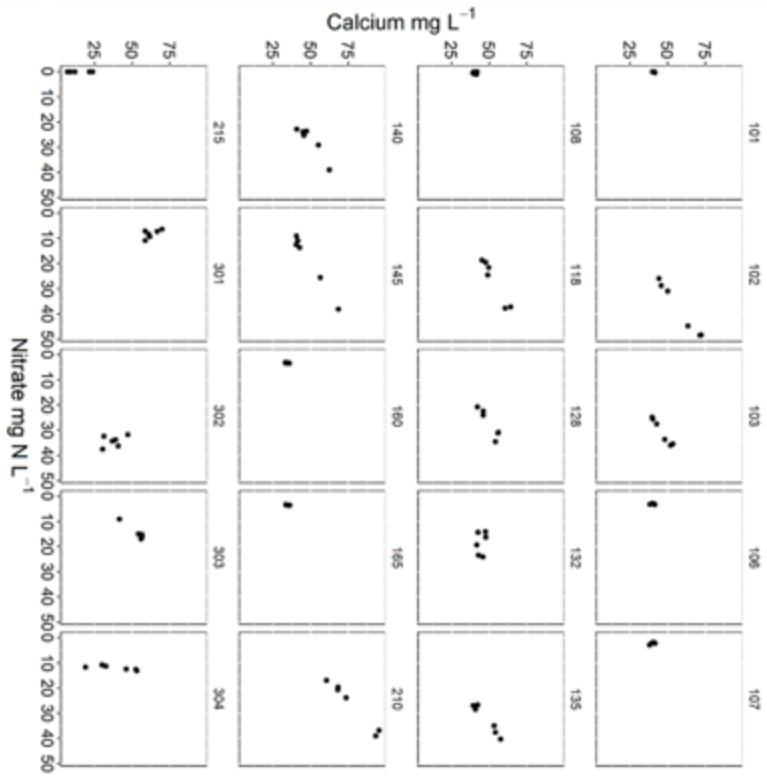


Figure 6. Graphs of nitrate-N (mg/L) vs. calcium (mg/L) for wells in the study (wells 100 and 165, $n=5$; all other wells $n=6$).

Table 2. The mean, standard deviation, low, high and range nitrate-N (mg/L) concentrations for each well, as well as Spearman's rho for nitrate and uranium and nitrate and calcium.

Nitrate-N											
Well ID	mean	sd	0%	100%	Max-Min	n	NA	U	p-value	Ca	p-value
101	0.1	0.1	0.1	0.4	0.4	6	0	0.65	0.16	0.65	0.16
102	37.9	10.4	26.0	48.5	22.5	6	0	-0.23	0.66	0.94	0.02
103	30.5	5.1	24.8	35.9	11.1	6	0	0.20	0.71	0.94	0.02
106	3.1	0.2	2.8	3.3	0.5	6	0	-0.15	0.77	0.33	0.52
107	2.1	0.4	1.8	2.8	1.0	6	0	-0.57	0.23	-0.32	0.54
108	0.6	0.5	0.1	1.1	1.1	6	0	-0.29	0.58	0.20	0.70
118	26.5	8.7	18.7	37.7	19.0	6	0	-0.94	0.02	0.89	0.03
128	27.3	5.6	20.7	34.5	13.8	6	0	-0.77	0.10	0.77	0.10
132	18.6	4.4	14.1	24.0	9.9	6	0	-1.00	0.00	-0.20	0.71
135	32.4	5.9	26.6	40.2	13.6	6	0	-0.35	0.50	0.83	0.06
140	27.3	6.1	22.9	39.0	16.1	6	0	0.20	0.71	0.83	0.06
145	18.3	11.3	9.1	38.1	29.0	6	0	-0.55	0.26	0.83	0.06
160	3.3	0.1	3.1	3.4	0.3	5	1	0.10	0.87	0.41	0.49
165	3.4	0.1	3.3	3.6	0.3	5	1	-0.10	0.87	0.76	0.13
210	26.1	9.4	16.9	38.9	22.0	6	0	0.66	0.18	0.89	0.03
215	0.1	0.0	0.1	0.1	0.0	6	0	NA	NA	NA	NA
301	8.2	1.7	6.3	10.9	4.6	6	0	0.14	0.80	-0.37	0.50
302	34.3	2.2	31.7	37.5	5.8	6	0	-0.09	0.92	-0.49	0.36
303	14.6	2.8	9.1	16.9	7.8	6	0	0.60	0.24	0.60	0.24
304	12.0	0.9	10.7	13.0	2.3	6	0	0.77	0.10	0.83	0.06

Table 3. A comparison of Spearman's correlations for uranium (U), calcium (Ca), sulfate, chloride (Cl), magnesium (Mg) and phosphorus (P) in wells with the greatest variation in nitrate-N concentrations.

Nitrate-N													
Well ID	Max-Min	U	p-value	Ca	p-value	Sulfate	p-value	Cl	p-value	Mg	p-value	P	p-value
102	22.5	-0.23	0.66	0.94	0.02	1.00	0.00	0.84	0.04	1.00	0.00	-0.88	0.02
103	11.1	0.2	0.71	0.94	0.02	0.83	0.06	0.60	0.24	0.94	0.02	-0.38	0.46
118	19.0	-0.94	0.02	0.89	0.03	1.00	0.00	1.00	0.00	0.94	0.02	-0.46	0.35
128	13.8	-0.77	0.10	0.77	0.10	0.94	0.02	0.77	0.10	0.89	0.03	0.32	0.53
135	13.6	-0.35	0.50	0.83	0.06	0.54	0.30	0.94	0.02	0.83	0.06	-0.41	0.42
140	16.1	0.2	0.71	0.83	0.06	0.77	0.10	0.55	0.26	0.60	0.24	-0.83	0.06
145	29.0	-0.55	0.26	0.83	0.06	1.00	0.00	0.94	0.02	0.94	0.02	-0.44	0.38
210	22.0	0.66	0.18	0.89	0.03	1.00	0.00	0.49	0.36	0.89	0.03	-0.03	0.96

Soil

Figure 7 shows the extractable uranium content of the subsoils of the three sampled profiles. The concentration of uranium is typically between 0.2 and 0.5 mg/kg. That is similar to the typical range reported for subsurface materials (Banning et al., 2013). A full profile in the agricultural soil is shown in Figure 8. That profile shows an increase within a subsoil layer and an increase in uranium near the surface. The surficial concentration may reflect an addition of uranium through phosphorus fertilizers (Schnug and Lottermoser, 2013; Liesch et al., 2015; Banning and Rude, 2015). The very high concentration deep in the profile is consistent with the high iron and potassium in that sample.

The soil uranium at different total calcium and iron concentrations is in Figure 10. Those relationships show a much stronger correlation between uranium and iron. That is consistent with the review by Davis et al. (2004) who found that soil uranium concentrations follow the iron concentrations. Similarly, Waite et al. (1994) showed strong adsorption of uranium by iron oxide between pH 5 and 8.5. Figure 9 shows the soil pH for the three soils. These profiles show how soil pH can vary in the region reflecting the presence or absence of carbonates and the addition of lime to agricultural soils, but that the range is within the range where strong uranyl adsorption is expected.

The chemical reactions of uranyl in soil are expected to follow surface and solution complexation and adsorption (e.g., Davis et al., 2004). Researchers have simplified this interaction by using a linear partition coefficient from the ratio of the adsorbed to the solution concentration (Curtis et al., 2009). If the uranium content is adsorbed by iron oxides, a simple distribution coefficient can be estimated assuming a solid phase uranium to iron concentration ratio of one to 20000 (Figure 10) or 0.05 μg uranium/g iron. Assuming a very approximate soil solution concentration of 5 $\mu\text{g}/\text{l}$, consistent with our groundwater concentrations, the uranium/iron distribution coefficient (solid/solution concentration ratio) would be 10 ml/g. Expressed on a whole soil basis, the distribution coefficient would be 0.1 ml/g. These distribution coefficients are in the general range reported for uranium/iron and uranium/soil reactions (Waite et al., 1994; Curtis et al., 2009). While they are very general estimates, they suggest that the acid extractable uranium concentrations are consistent with a soil profile control of potentially mobile uranium. In addition, the relatively low uranium to iron concentrations suggest a uranium density that is much lower than that in experimental studies of uranium sorption and we would expect higher affinity as the density of uranium decreases allowing stronger sites to dominate the sorption. These results must be considered preliminary as the retention could be reduced by higher calcium, high alkalinity and potentially high partial pressure of carbon dioxide (e.g., Fox et al., 2006; Davis et al., 2004). Further research will also be necessary to determine whether the relatively high iron to uranium ratio allows stronger site interactions to dominate the interaction or how the neutralization of acidity by alkalinity consumption in soils might actually lower pH and increase the amount of sorption onto iron oxides (Fox et al., 2006).

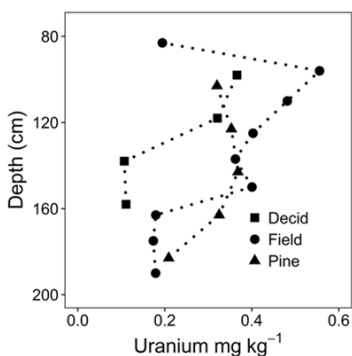


Figure 7. Variation in uranium concentration with depth in the three soils examined.

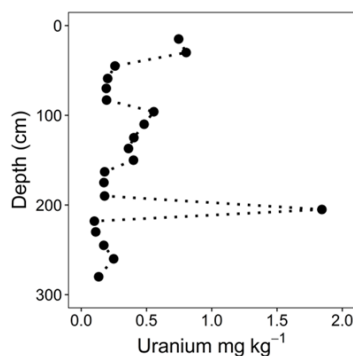


Figure 8. Vertical variation in uranium concentration across the upper three meters in an agricultural field.

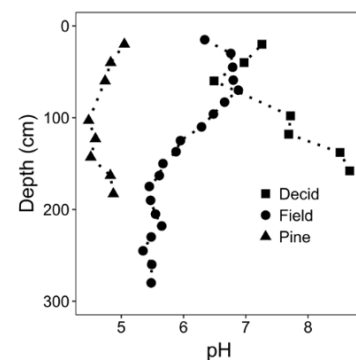


Figure 9. Soil pH with depth in the three soils collected in the study area.

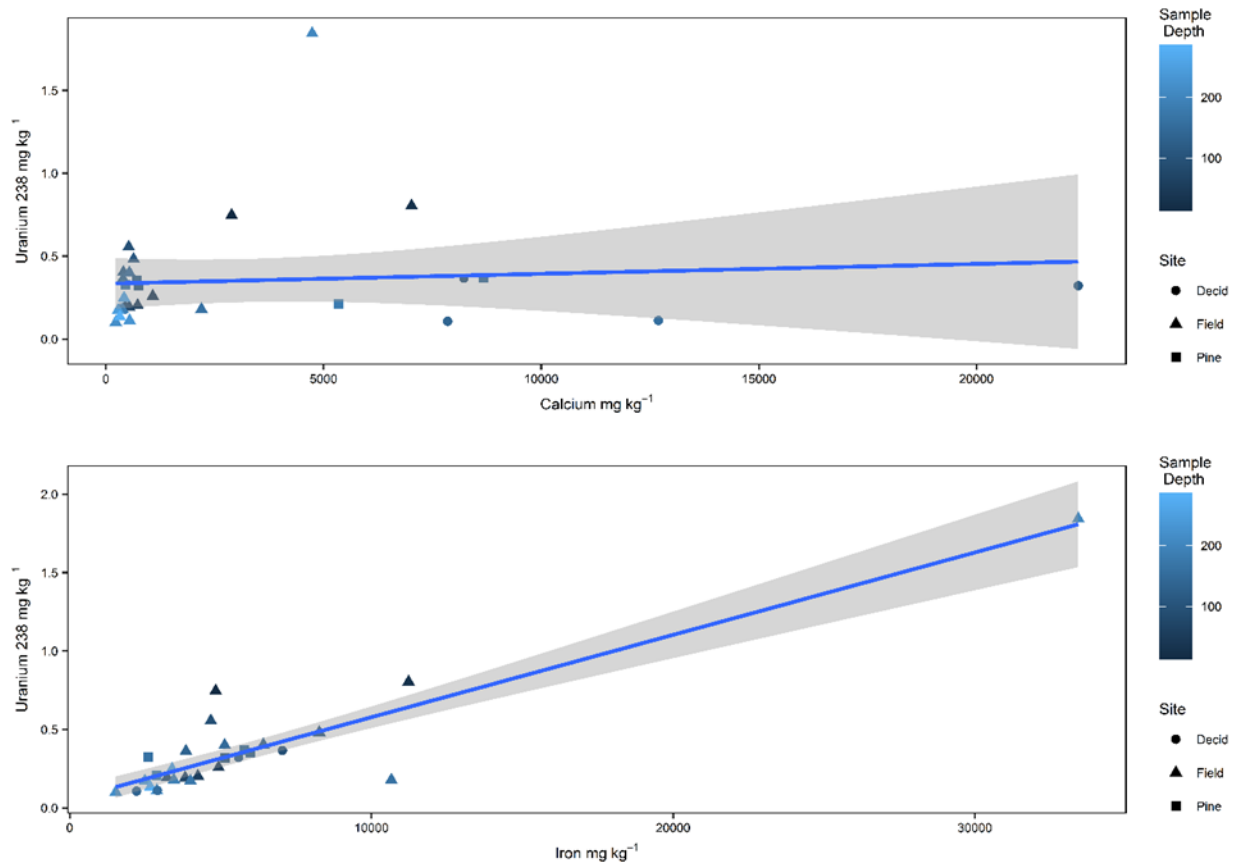


Figure 10. Relationship between soil uranium (²³⁸U) to calcium (above) and iron (below).

CONCLUSIONS AND RECOMMENDATIONS

The results from these monitoring wells did not show a relationship between nitrate and uranium. We examined wells with nitrate concentrations ranging from below detection limit to over 40 mg/L. Nitrate concentrations within some individual wells also varied over the course of sampling. The variation of nitrate in these wells did not have a strong correlations with changes in uranium concentrations.

The repeated sampling method did show other important changes in geochemistry over the course of a year. Specifically, we showed the relationship between nitrate and calcium. Wells that had a greater range of nitrate concentrations over the course of sampling were generally correlated to changes in calcium concentrations. Similar to calcium, magnesium also showed significant correlations with nitrate in many of the same wells. That is consistent with a dolomitic source of carbonate minerals in this region. This illustrates that higher levels of mineralization in groundwater travels with the nitrate in the aquifer.

This study provided two undergraduate students with training experiences in multiple areas. The students were responsible for water and soil sample collection, field and laboratory analyses, and sample preparation. They gained valuable experience in conducting and presenting analytical research.

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