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Uranium and Radon in Private Bedrock Well Water in Maine: Geospatial Analysis at Two Scales

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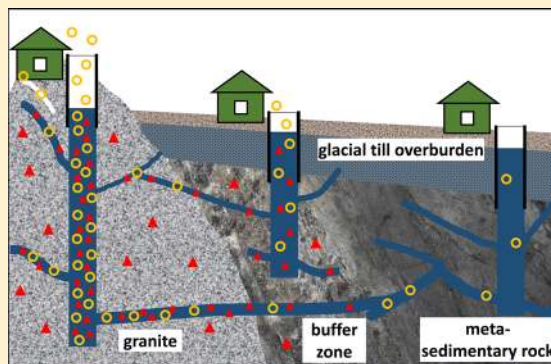
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Supporting Information

ABSTRACT: In greater Augusta of central Maine, 53 out of 1093 (4.8%) private bedrock well water samples from 1534 km² contained [U] >30 μg/L, the U.S. Environmental Protection Agency's (EPA) Maximum Contaminant Level (MCL) for drinking water; and 226 out of 786 (29%) samples from 1135 km² showed [Rn] >4,000 pCi/L (148 Bq/L), the U.S. EPA's Alternative MCL. Groundwater pH, calcite dissolution and redox condition are factors controlling the distribution of groundwater U but not Rn due to their divergent chemical and hydrological properties. Groundwater U is associated with incompatible elements (S, As, Mo, F, and Cs) in water samples within granitic intrusions. Elevated [U] and [Rn] are located within 5–10 km distance of granitic intrusions but do not show correlations with metamorphism at intermediate scales (10⁰–10¹ km). This spatial association is confirmed by a high-density sampling (*n* = 331, 5–40 samples per km²) at local scales (≤10⁻¹ km) and the statewide sampling (*n* = 5857, 1 sample per 16 km²) at regional scales (10²–10³ km). Wells located within 5 km of granitic intrusions are at risk of containing high levels of [U] and [Rn]. Approximately 48 800–63 900 and 324 000 people in Maine are estimated at risk of exposure to U (>30 μg/L) and Rn (>4000 pCi/L) in well water, respectively.



INTRODUCTION

Health effects of chronic exposure to uranium (U) in drinking water are emerging, including nephrotoxicity^{1,2} and possible toxicity on bones.³ Groundwater U concentrations ([U]) in excess of the U.S. Environmental Protection Agency (EPA) Maximum Contaminant Level (MCL) of 30 μg/L for drinking water have been reported worldwide including in the U.S.,⁴ Canada,¹ Finland,⁵ Korea,⁶ U.K.,⁷ Sweden,⁸ Bangladesh,⁹ Nigeria,¹⁰ India,¹¹ Switzerland,¹² and Mongolia.¹³ In the U.S., average groundwater [U] aggregated at county level were found to be higher in the west than in the east, except for Florida and the Appalachian Mountain states.^{14,15} An overall 105 fatal cancers in the U.S., assuming a 70.7-year lifetime exposure, was estimated from U in surface and ground waters used for drinking.¹⁶

The lung cancer risk of chronic exposure to radioactive radon (Rn) and its decay products through inhalation is well-known.¹⁷ In the U.S., the Appalachian Mountains, Rocky Mountains, Colorado Plateau, and northern glaciated states have the highest indoor air Rn levels.¹⁸ Health risks posed by Rn are thought to be insignificant from drinking water ingestion

and are mostly attributed to the transfer of Rn into air and the subsequent inhalation.^{17,19,20} Thus, factors including Rn concentrations in water ([Rn]), the amount of ingested water, the duration of exposure, house ventilation, and the water-to-air transfer factor all can affect health outcome.^{18,21} In the U.S., 4400–22 000 fatal cancers were estimated from Rn in domestic water using a 1:10 000 air–water transfer factor.¹⁶ The Appalachian Mountain states showed the highest county-average [Rn], maximum [Rn], and [Rn] exceedance percentages (% wells with [Rn] exceeding the U.S. EPA's Alternative MCL of 4000 pCi/L or 148 Bq/L for drinking water) in groundwater drawn from granitic or highly metamorphosed rock formations.^{14,16,22}

The U abundance in the upper crust of the Earth is 2.7 mg/kg,²³ with higher concentrations in granites (typically 2.2–6.1, up to 300 mg/kg), phosphates (50–300 mg/kg), and organic-

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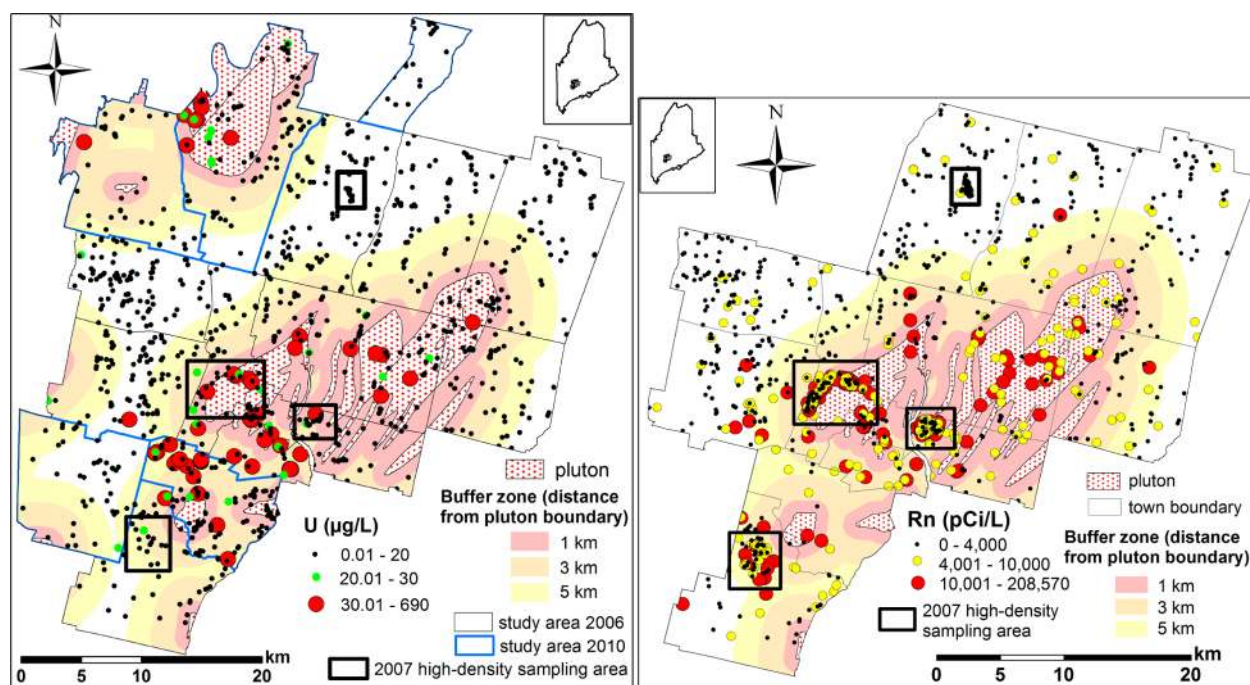


Figure 1. Uranium and radon concentrations in groundwater plotted with granitic plutons and distance zones in greater Augusta of central Maine (geology generalized from Osberg, et al., 1985). Both elevated U and Rn concentrations in well water are strongly associated with granitic plutons and adjacent areas.

rich sedimentary rocks, such as black shale (3–1250 mg/kg).^{15,24,25} The primary mineral uraninite (UO_2) is insoluble but can be oxidized to the more soluble UO_2^{2+} ion through water-rock interactions.²⁶ U can also occur as a major constituent of minerals such as coffinite ($\text{U}(\text{SiO}_4)_{1-x}(\text{OH})_{4x}$) and autunite ($\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 10\text{--}12\text{H}_2\text{O}$), which can be substantial localized sources of U in groundwaters in mineralized areas and granitic terrains.⁷ Complexation of UO_2^{2+} with carbonate, sulfate or phosphate in solutions can enhance U mobility.²⁷ High pH favors the formation of the carbonate complex and desorption of U(VI) from aquifer sediment containing metal oxides/oxyhydroxides and clay minerals,^{28–32} releasing U into groundwater. Low Eh favors reduction of U(VI) to insoluble U(IV), immobilizing U from water.^{7,33–35} On the other hand, the primary mechanisms that release ²²²Rn, the most abundant Rn isotope and a product of the ²³⁸U–²³⁴Th–²³⁴Pa–²³⁴U–²³⁰Th–²²⁶Ra decay series, into groundwater are dissolution, diffusion, and most importantly the direct ejection by alpha recoil to fluid-filled fractures (emanation).²⁷ The occurrence of Ra in groundwater depends largely on the concentration and distribution of U in the aquifer materials, the pH and redox conditions that influence their sorption on Fe- or Mn-oxyhydroxides and clay minerals, and the residence time of groundwater. Once released into groundwater, the mobility of Rn is decoupled from water chemistry because of its short half-life (3.82 day for ²²²Rn) and being a noble gas. Groundwater Rn distribution has been shown to depend on the primary source of U in bedrock at regional scales in New England, with influence from water flow patterns.³⁶ Theoretical models, including porosity, U content of the rock, emanating efficiency, and rock density, have been developed to estimate the flux of Rn from rock to groundwater.¹⁹

Although the linkage between groundwater U, Rn and bedrock geology, namely granites with higher concentrations of whole rock U, has been demonstrated at regional ($10^2\text{--}10^3$

km) to local ($\leq 10^{-1}$ km) scales, studies have not considered examining the correlation at multiple spatial scales within the same study area. Hydrogeochemical parameters in fractured bedrock aquifers likely to have influenced the concentrations and spatial patterns of U and Rn to different extents due to their divergent chemical properties are not well understood. In this study, high-density sampling (0.8 sample per km^2) of groundwater in the greater Augusta area of central Maine is conducted to determine the exceedance percentages and to delineate spatial distributions of U and Rn at intermediate spatial scales ($10^0\text{--}10^1$ km). Statistical and spatial analyses are used to establish the association between spatial distributions of groundwater U and Rn with bedrock geology and groundwater hydrogeochemistry. The correlations are then verified with groundwater collected in four clusters with a higher sampling density (5–40 samples per km^2) at local spatial scales, as well as the statewide data set at the regional scale (1 sample per 16 km^2). Mechanisms of U and Rn mobilization and transport in bedrock aquifers are then compared. Finally, an estimate of the population at risk of exposure to high U or Rn is provided for the greater Augusta area and also for the state of Maine.

■ MATERIALS AND METHODS

Bedrock in Maine. Bedrock in Maine consists of Precambrian to Devonian sedimentary or meta-sedimentary rocks, intruded by Ordovician to Carboniferous plutons (mostly granitic), which occupy $\sim 20\%$ of the land area.³⁷ These rocks underwent several regional metamorphic events from Precambrian to Carboniferous periods.³⁸

The study area encompasses 17 towns in the greater Augusta area of central Maine, spans the regional metamorphism gradient (Supporting Information (SI) Figure S1 and S2), and is composed of NE-SW striking nearly vertically dipping (80–89 degree) Silurian meta-sedimentary formations and Precambrian-Ordovician mafic to felsic volcanic rocks in the far eastern

part of the study area.^{39,40} These formations were intruded by Devonian plutons of biotite granodiorite, muscovite-biotite quartz monzonite, and granite⁴¹ in the center and northwestern corner of the study area (Figure 1). Quartz and carbonate veins are prevalent⁴² and demonstrate abundant flow of CO₂-rich and H₂O-rich hydrothermal fluids⁴³ prior to and after regional metamorphisms.

Sample Collection and Analysis. In 2006, 786 well water samples were collected from private bedrock wells from 13 towns in greater Augusta. In 2010, 307 well water samples were collected from 4 additional towns and the town of West Gardiner. The overall sampling density was approximately 0.8 sample per km². In 2007, 331 well water samples were collected from 4 clusters in towns of Manchester, Chelsea, Litchfield, and Sidney at a higher sampling density of 5–40 samples per km² (Figure 1). An aliquot of unfiltered groundwater samples was acidified to 1% nitric acid (Fisher Optima) for major and trace element analysis by high resolution ICP-MS (VG Axiom), including U (detection limit = 0.01 µg/L). Detailed sampling protocol and analytical methods have been described.^{39,40} Dissolved oxygen and pH were measured in the field using CHEMetrics DO test kits and a portable pH meter, respectively. An internal laboratory standard, LDEO artificial groundwater, with 2.9 µg/L of U was used for QA/QC.⁴⁴ An average value of 3.0 ± 0.5 µg/L (*n* = 52) was obtained for LDEO artificial groundwater for the samples analyzed. Well water [U] for the state of Maine (*n* = 5857, sampling density = 1 per 16 km²) were analyzed using an ICP-MS following the U.S. EPA method 200.8 by Maine Health and Environmental Testing Laboratory (SI).

In 2006 and 2007, well water samples for Rn analysis were also collected at the same time as the samples for U were collected, using airtight syringes (BD Luer-Lok no. 309604) from a funnel and 1 m section of hose connected to a water tap to provide nonaerated 10 mL samples. Each sample was injected into a 20 mL low-background scintillation vial (Kimble no. 74515–20, borosilicate glass, VWR International) containing 5 mL of mineral oil based scintillation cocktail (PerkinElmer no. 6NE9S79). Two vials were filled from each well and sent to the Environmental Radiation Laboratory at the University of Maine for liquid scintillation analysis with a detection limit of 10 pCi/L. The liquid scintillation analysis method developed by Pritchard and Gesell⁴⁵ is described by the Standard Method 7500-RN.^{46,47} Each pair of samples was counted using a liquid scintillation counter (PerkinElmer Packard Tri-Carb 1500) that was calibrated using a ²²⁶Ra in water standard obtained from U.S. EPA Environmental Monitoring Systems Laboratory, Las Vegas, Nevada.

Geographical and Statistical Analysis. Distance to pluton was calculated for each well outside of the plutons as the least distance to the boundary of the nearest granitic pluton using distance analysis in the Geographic Information System (GIS, ArcMap 9.3). Because the granitic plutons may be larger in size underground than the bedrock outcrops indicate, distance zones of 0–1, 1–3, and 3–5 km distance from pluton boundaries were generated (Figures 1 and 2). While well locations have been accurately located within a few meters using GPS units, the digital version of the 1:500 000-scale bedrock geologic map of Maine⁴⁸ to which we compare well data, has a positional accuracy of ~0.5–1 km, further justifying the application of distance zones.

The nonparametric Mann–Whitney *U* test⁴⁹ was used to compare the distribution of [U] or [Rn] between wells located

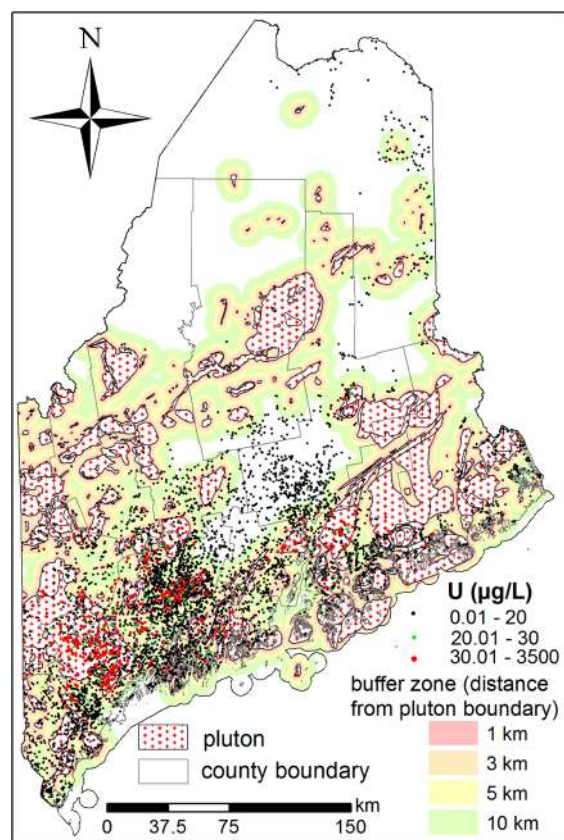


Figure 2. Uranium concentrations in groundwater plotted on plutons and distance zones in Maine (geology generalized from Osberg, et al., 1985; data from Maine Center for Disease Control & Prevention). Elevated U concentrations in well water are strongly associated with granitic plutons and adjacent areas.

within and outside plutons, and in each pair of metamorphic zones, bedrock units, or distance zones. The Kruskal–Wallis test by ranks⁵⁰ was used to compare the distribution of [U] or [Rn] without normality assumption among different metamorphic zones, bedrock units, or distance zones.

Spearman's rank correlation coefficient (ρ values) between groundwater [U] or [Rn] and other hydrogeochemical parameters was calculated because the data did not follow normal distributions. The tested significance (*p* values) was determined using two-tailed student's *t* test with *n* – 2 degrees of freedom.

All the statistical analyses were performed in R program.

Estimate of Population at Risk. The population at risk of exposure to elevated [U] in well water in 17 towns of greater Augusta and the state of Maine were estimated based on the interpolated exceedance percentages from indicator kriging³⁹ of 1093 and 5857 samples, respectively (SI). [U] exceedance percentages were interpolated for each census block in ArcGIS, which were then multiplied by the rural population in each block to obtain the estimate of population at risk (“interpolated”). Additionally, the observed [U] exceedance percentages in granitic plutons and surrounding distance zones of 0–1, 1–3, 3–5, and >5 km were applied to estimate the population at risk (“observed”) for comparison. Rural population data were extracted from the 2010 U.S. Census.⁵¹ An assumption is made that the majority of the rural population relies on private wells for water supply.

Table 1. Summary Statistics of Groundwater Uranium in Greater Augusta and Maine

distance to pluton	Greater Augusta ^a				State of Maine ^b			
	n	median	mean	%	n	median	mean	%
		($\mu\text{g/L}$)	($\mu\text{g/L}$)	>30 $\mu\text{g/L}$		($\mu\text{g/L}$)	($\mu\text{g/L}$)	>30 $\mu\text{g/L}$
within pluton	179	5.2	17.3	11.7%	1450	4.5	36.7	19.7%
0–1 km	176	2.1	11.9	6.3%	695	1.1	9.9	5.3%
1–3 km	213	1.2	9.3	6.6%	1036	0.6	4.1	2.8%
3–5 km	201	0.6	3.5	3.0%	934	0.5	5.6	3.3%
5–7 km	179	0.7	1.9	0.6%	634	0.3	3.4	1.9%
7–10 km	122	0.8	1.2	0.0%	451	0.5	2.3	1.6%
>10 km	26	0.9	1.2	0.0%	657	0.8	1.8	0.3%
outside pluton	917	1.0	5.8	3.5%	4407	0.6	4.7	2.7%
all samples	1096	1.1	7.7	4.8%	5857	0.9	12.6	6.9%

^aGreater Augusta data include 2006 and 2010 sampling. ^bState of Maine data are from the Maine Center for Disease Control & Prevention. The samples were analyzed using ICP-MS following the U.S. EPA method 200.8 in Maine Health and Environmental Testing Laboratory (HETL). The sample collection and analysis protocols are summarized in SI and reported in Nielsen et al., 2010.

The population at risk of exposure to elevated [Rn] in well water in 13 towns of greater Augusta were estimated using similar methods based on interpolated and observed [Rn] exceedance percentages of 786 samples, respectively. The observed [Rn] exceedance percentages in granitic plutons and surrounding distance zones in greater Augusta were applied to all other plutons to estimate the population at risk for the state of Maine.

RESULTS AND DISCUSSION

Groundwater U and Rn Concentrations. A combined data set at a sampling density of 0.8 per km² for well water [U] of samples collected in 2006 ($n = 786$) and 2010 ($n = 307$) reveals that the maximum [U] is 484 $\mu\text{g/L}$, found in a bedrock well in the town of Chelsea in the Silurian-age Waterville Formation, which consists of interbedded calcareous pelite and sandstone/limestone, but is <0.5 km from granite intrusions. Approximately 4.8%, or 53 out of 1093 wells have [U] above the MCL (Table 1). For the state of Maine ($n = 5857$, sampling density = 1 per 16 km²), the maximum [U] was 3500 $\mu\text{g/L}$, found in two wells in the towns of Durham and Naples, both drilled into the Sebago granite. The exceedance percentage of U is 6.9% (Table 1), and is higher for southern and coastal Maine (Figure 2). The exceedance percentage is 4% in the regional survey of groundwater from crystalline bedrock aquifers in New York and New England ($n = 117$, sampling density = 1 per 1600 km²),¹⁵ and is 1.7% ($n = 1725$, sampling density = 1 per 5000 km²) in a U.S. nationwide survey using domestic wells from 30 principal aquifers.⁵² Private wells ($n = 478$) from east-central Massachusetts displayed a [U] exceedance percentage of 3.5%.⁵³ Wells ($n = 25$) were revisited in 2013 to collect filtered (0.45 μm) water samples on site to compare with unfiltered samples. No significant difference in [U] between filtered and unfiltered samples was found (SI Figure S3), similar to a prior study.⁵⁴ Most of the 36 samples collected in 2006 and revisited in 2007 (SI Figure S4-A), and 25 samples collected during 2006–2010 and revisited in 2013 (SI Figure S4-B) did not show significant change in [U]. Significant [U] difference (>30% change and [U] > 5 $\mu\text{g/L}$) between two sampling events in four samples is accompanied by large changes in alkalinity, pH and/or redox conditions.

Concentrations of Rn were available only for 786 groundwater samples collected from 13 towns in 2006 (sampling density of 1 per 1.4 km²). The maximum [Rn] was 208 600

pCi/L in a well drilled into Devonian granite in the town of Manchester. The median [Rn] of 2390 pCi/L and the exceedance percentage of 29% (Table 2) are similar to those

Table 2. Summary Statistics of Groundwater Radon in Greater Augusta^a

distance to pluton	n	median (pCi/L)	mean (pCi/L)	% >4000 pCi/L	% >10 000 pCi/L
within pluton	115	7240	13 515	66%	33%
0–1 km	118	3693	7601	48%	14%
1–3 km	124	2258	4866	28%	6%
3–5 km	155	1715	2559	15%	3%
5–7 km	144	1773	2511	15%	3%
7–10 km	104	2042	2185	11%	0%
>10 km	26	2173	2317	8%	0%
outside pluton	671	2110	3796	22%	5%
all samples	786	2393	5220	29%	9%

^aGreater Augusta data are from 2006 sampling.

of 2120 pCi/L and 30% from the aforementioned regional survey of New York and New England crystalline bedrock aquifers, respectively.¹⁵ The exceedance percentage was 4.4% ($n = 1958$, sampling density = 1 per 4000 km²) based on the aforementioned U.S. nationwide survey.⁵² Eight out of 36 water samples from the same wells sampled in 2006 and revisited in 2007 (SI Figure S5) showed >50% [Rn] difference between two sampling events.

Association with Granitic Plutons. Wells with high [U] or [Rn] are located within the granitic plutons or their vicinity at local (SI Table S1) and intermediate (Figure 1) spatial scales in greater Augusta and the regional spatial scale in Maine (Figure 2). Median and mean values, and the exceedance percentages of [U] and [Rn] within the plutons are significantly higher than those from meta-sedimentary rocks outside the plutons (Tables 1 and 2). There is a significant difference between sample distributions in plutons and those in meta-sedimentary rocks for both U (Chi-square value = 44 307, $p < 0.0001$) and Rn (Chi-square value = 45 150, $p < 0.0001$) in greater Augusta as indicated by the Mann–Whitney U test.

Previously regional studies have found associations between elevated U in groundwater and two-mica granites with up to 29 mg/kg U.^{15,36,55} Rock units with high levels of U have been identified as the source of Rn.¹⁹ Our study is the first to demonstrate such an association between occurrence of

groundwater U and Rn and granitic plutons at an intermediate spatial scale. This association is to be expected because U is enriched in granitic intrusions due to the preferential fractionation during partial melting of the protolith.⁵⁶ Mobilization of U from granite to groundwater as U(VI) species is favored under oxic conditions, and when desorption from iron oxyhydroxide is favored under alkaline conditions.^{15,57} In greater Augusta, granitic bedrock aquifers have slightly higher alkalinity (1.5 mmol/L) and more oxic conditions (dissolved oxygen 4.0 mg/L) than meta-sedimentary aquifers (alkalinity 1.2 mmol/L and DO 1.5 mg/L) (Table 1 in Yang et al., 2012⁴⁰). Thus, aqueous chemistry may contribute to groundwater U differences as well. The difference in the U concentrations in the granites (up to 29 mg/kg) relative to those in the surrounding meta-sedimentary rocks of the region (2.1–4.6 mg/kg)⁵⁸ provides the key background upon which groundwater Rn distribution can be interpreted because bedrock U distribution has been suggested as the ultimate source and the most useful explanatory factor for groundwater [Rn].¹⁹

The distance zone analysis applied to the granitic pluton boundaries (Table 1) shows that high groundwater U is within 5 km of the mapped granitic pluton boundaries at both intermediate and regional spatial scales (Table 1 and SI Figure S8). These distance zones around granitic plutons at the land surface might reflect the influence of larger plutons in the subsurface, or pegmatite zones formed by the outward intrusion of fractionated U-rich melt into the adjacent meta-sedimentary rocks, or may be related to the positional inaccuracy of the geologic map that could be up to 1 km, or a combination of all these factors. This spatial association suggests that groundwater U occurrence is related to granitic intrusions.

Groundwater Rn also showed decreasing median and mean concentrations, and exceedance percentages from the mapped pluton boundaries to a distance up to 5 km (Table 2 and SI Figure S9).

Association with Metamorphic Grade. Endowment of U in rocks have been suggested to directly correlate with metamorphic grade,³⁶ because shearing during high grade metamorphism favors the release of U from minerals into foliation with iron oxides^{59,60} through fluids formed by rock dehydration and decarbonization.⁶¹ However, below the granulite facies,^{62,63} or a temperature of 700–900 °C,⁶⁴ the abundances of U in metamorphic rocks are not related to metamorphism. At intermediate scales in greater Augusta where the metamorphism temperatures ranged from 500 to 600 °C (high rank amphibolite facies) to 300 °C (low grade greenschist facies) (SI Figure S1), except for the slightly higher median groundwater [U] (3.2 µg/L) in the high rank amphibolites unit, the other metamorphosed units at lower ranks displayed comparable median [U] (0.4–1.3 µg/L, SI Tables S2 and S3-A) in groundwater. At the regional (state) scale there is also no systematic decrease of groundwater [U] with decreasing metamorphic grade (SI Tables S2 and S3-A). Although the well location is known with an accuracy within meters while the metamorphic zones are from a map of 1:2 000 000-scale, which can have errors of several km,³⁷ the results suggest that groundwater [U] in metamorphic rock formations is not related to the metamorphic grade below the granulite facies.

High groundwater [Rn] appeared more frequently in high grade metamorphic zones, including sillimanite and orthoclase grades (average [Rn] = 13 650 pCi/L), than in lower grade metamorphic zones (chlorite to staurolite grades, average [Rn]

= 1100 pCi/L) in 436 samples collected from areas with major granite bodies in southern and coastal Maine.²² However, in greater Augusta, metamorphosed units at lower ranks did not show significantly different distributions of groundwater [Rn] at intermediate spatial scales (SI Table S4). This finding suggests that groundwater [Rn] in meta-sedimentary rocks is not related to the metamorphic grade below the granulite facies.

Association with Hydrogeochemistry. The correlations between groundwater [U] and hydrogeochemical parameters are established by statistically significant Spearman's ρ value ($p < 0.05$), with higher values suggesting stronger correlations (SI Table S5). The hydrogeochemistry in major bedrock units and granitic plutons has been summarized elsewhere (Table 1 and Figures S1,2 in Yang et al., 2012⁴⁰). There are weak to moderate correlations between U and S, As, Mo, Cs, and F found within the granites and in the entire data set. However, such correlations cannot be interpreted to indicate a common sulfidic mineral source for these elements in fractured bedrock aquifers of greater Augusta. Because modern anoxic marine basins contain authigenic sulfides enriched in As, Mo, and U,^{65,66} such sulfidic mineral phases are expected to be more prevalent in the Silurian meta-sedimentary sequences deposited under reducing conditions in the past⁶⁷ but can now be oxidized to enter groundwater. If sulfides were a common source for As, Mo, and U, then we would expect simultaneous As, Mo, and U enrichment in groundwaters of meta-sedimentary rock units. This was not the case (Tables 1 and S1 in Yang et al., 2012⁴⁰). A more likely scenario, based on U correlations with incompatible elements such as Cs and F, is that hydrothermal activities possibly related to regional metamorphism, have mobilized these elements^{68,69} at high temperatures along fractures.⁴² Because F can be derived from the rapid degradation of fluorite during granite weathering that mobilizes U principally associated with hydrated Fe-oxide, Mn-oxide, and clay minerals,⁷⁰ the correlations observed thus reflect mobilization of these elements from secondary mineral phases along the fractures. This interpretation is consistent with the weak to moderate correlations between [U] with well depth, pH, [Ca] and alkalinity, suggesting that desorption from solid phase and complexation with carbonate in aqueous phase might be important for enhancing U mobility in both calcareous meta-sedimentary rock and granite aquifers. There are also weak to moderate negative correlations between [U] and dissolved oxygen (SI Table S5). At face value, this negative correlation "conflicts" with the enhanced dissolution of U from oxidation of uraninite (UO₂) in granite and associated pegmatite, a well-recognized mechanism.^{15,36,71} However, the studied aquifers are generally oxic to suboxic,⁵⁴ and a plausible and likely interpretation is that U from oxidation of uraninite accumulates along the groundwater flow path but oxygen is progressively lost to oxidation, resulting in a negative correlation between the two. Because the aquifers are oxic and alkaline, as indicated by the major water type of Ca-HCO₃ and the documented 5–50% calcite in metamorphosed sedimentary rocks in the region,⁵⁴ U dissolution and accumulation in groundwater is expected to continue with increasing residence time and TDS.^{15,71}

In contrast to U, Rn does not show correlations ($\rho > 0.2$) with the aforementioned geochemical parameters (SI Table S5). Hydrological and physical factors, including topography, overburden, porosity, groundwater flow rate, residence time, and water-rock ratio in fractured bedrock aquifers, may have greater impacts on Rn distribution in groundwater.^{19,27,36,72} Decay of uraninites could provide a constant source of Rn to

Table 3. Population at Risk of Uranium and Radon Exposure from Drinking Water in Greater Augusta of Central Maine and the State of Maine^a

town	total population	rural population	size of population at risk of [U] >30 $\mu\text{g/L}$ based on		size of population at risk of [Rn] >4000 pCi/L based on		size of population at risk of [Rn] >10,000 pCi/L based on	
			interpolation	observation	interpolation	observation	interpolation	observation
<u>Augusta</u>	19 136	5505	544	564	2700	3433	1105	1252
Belgrade	3189	3189	177	244	ND ^b	1374	ND	539
<u>Chelsea</u>	2721	2721	130	200	1470	1348	436	428
<u>China</u>	4328	4328	20	147	704	1275	53	386
Farmingdale	2956	1049	307	64	775	393	231	109
<u>Hallowell</u>	2381	963	103	91	553	576	347	202
<u>Litchfield</u>	3624	3624	109	81	1259	754	484	164
<u>Manchester</u>	2580	2580	253	152	934	1016	422	333
Monmouth	4104	4104	9	109	ND	713	ND	139
Mount Vernon	1640	1640	82	82	ND	408	ND	93
<u>Readfield</u>	2598	2598	0	0	225	333	1	39
<u>Sidney</u>	4208	4208	0	7	274	567	18	77
<u>Vassalboro</u>	4340	4340	8	96	923	959	112	243
Waterville	15 722	242	0	0	ND	31	ND	3
<u>West Gardiner</u>	3474	3378	433	195	2033	1,303	568	400
<u>Windsor</u>	2575	2575	19	140	876	977	168	309
<u>Winthrop</u>	6092	6092	58	25	1184	868	357	129
all 17 towns	85 668	53 136 (43 961)	2250	2,198	13 908	13 801	4302	4071
percentage			4.2%	4.1%	<u>31.6%</u>	<u>31.4%</u>	<u>9.8%</u>	<u>9.3%</u>
State of Maine	1 354 952	841 410	48 839	63 918	ND	324 044	ND	109 669
percentage			5.8%	7.6%	ND	38.5%	ND	13.0%

^aUnderscore: Rn data from underscored 13 towns only. Underlined population and percentage also only for 13 towns. ^bND: no data.

groundwater in granites. Additionally, Rn is influenced by sorbed U and ²²⁶Ra on secondary mineral formed during weathering in fractures;⁷³ variations in these radionuclide composition and distribution of this weathered layer may account for considerable variations in Rn concentrations of the groundwater in contact with the rocks. The weak correlations with U, S, As, Mo, and F found in the Manchester cluster located at the contact between granite intrusions and Silurian meta-sedimentary rocks (SI Table S5) suggest this Rn may have been influenced by U in secondary minerals derived from hydrothermal activities at the time of granite intrusion. Previous studies noted that groundwater [Rn] in Maine increased slightly with well depth up to 50–75 m and with decreasing [Na].²² Groundwater Rn in fractured bedrock aquifers in Rhode Island was correlated with F and alkalinity.⁷⁴ In North Carolina, groundwater Rn in fractured crystalline rock aquifers showed an inverse relationship with total dissolved ions and a direct relationship with dissolved oxygen probably due to the high efficiency for ²²⁶Ra adsorption onto Fe oxyhydroxide-coated fractures and the resulting increase of Rn emanation.⁷⁵ A study in Norway⁷⁶ found positive correlations between Rn and F in groundwater from crystalline bedrock aquifers in Precambrian granites ($n = 76$) and in the entire data set ($n = 1326$). Taken together, studies to date point to a secondary⁷⁷ and possibly hydrothermally derived U source for Rn in addition to primary U minerals in granites.

Decoupling of U and Rn in Granites. Although both groundwater [U] and [Rn] are elevated in the granitic plutons and their vicinities (Figure 1), they are not correlated for samples within the granite at intermediate spatial scales (SI Table S5). No correlation between [U] and [Rn] is observed for the granitic Chelsea cluster at the local scale. The correlation between U in rock or groundwater and Rn in groundwater has been noted at regional scales that include both

granite and meta-sedimentary aquifers.^{15,19,76,78} Our observation does not conflict with this observation because there is also a weak but positive correlation at intermediate scales between [U] and [Rn] (SI Table S5) if both types of rock aquifers are included. Thus, such correlations merely reflect the two end-member situations: high U in the granites and lack thereof in other rocks. With sufficient sampling density, the lack of correlation between U and Rn at local scales within granite is demonstrated for the first time. The ratios of [Rn] and [U] measured in the same water samples revealed that the [Rn] levels are several orders of magnitude higher than those expected from secular equilibrium from decay of U in water alone (SI Figure S6), suggesting that most Rn is derived from U in rocks. Further studies are necessary to investigate why groundwater U and Rn in fractured granitic bedrock aquifers is decoupled. The U retardation factor estimated based on $A(^{222}\text{Rn})/A(^{238}\text{U})$ ⁷⁹ varies widely from 5 to 700 000 in samples ($n = 115$) from granitic bedrock aquifers (SI Figure S6 and Table S5).

Population at Risk. About 4% of the rural population in 17 towns of greater Augusta are at risk of U exposure from drinking water above the U.S. EPA MCL of 30 $\mu\text{g/L}$ (Table 3), estimated by interpolation using indicator kriging (SI) or through calculation using observed exceedance percentages from within granitic plutons to surrounding distances up to 5 km. Despite the very high skewness (+9.6) of [U] in groundwater (SI), the two estimates are similar. About 48 840 people, or 5.8% of the rural population of 841 410 in the state of Maine, are at risk of U exposure estimated by interpolation. About 63 920 people, or 7.6% of the rural population, is estimated to be at risk through calculation using observed exceedance percentages. The latter estimation is higher, probably due to the high exceedance percentage of 20% within granitic plutons observed in the statewide data set.

About 32% of the rural population in 13 towns of greater Augusta, are at risk of exposure to >4,000 pCi/L Rn in drinking water, the U.S. EPA AMCL; and about 9.5% of the rural population are at risk of exposure to >10,000 pCi/L (370 Bq/L), the level at which the Maine Center for Disease Control & Prevention suggests homeowners treat the water for Rn (Table 3). About 2% (13/786) of households are estimated to have indoor air Rn levels exceeding the allowable limit of 4 pCi/L in 13 towns of greater Augusta when only considering the air Rn transferred from water and by applying an average 1:10 000 air–water transfer factor.¹⁶ This percentage increases to 5% for households with wells drilled into granites. In greater Augusta, Rn transferred from water alone contributes to a median 0.2 pCi/L of air Rn. In granitic intrusions, this contribution has a higher median value of 0.7 pCi/L (up to 21 pCi/L). An estimated population of 324 000, or 39% of the rural population in the state of Maine, are at risk of exposure to >4000 pCi/L Rn; and about 110 000 people, or 13% of the rural population, are at risk of exposure to >10 000 pCi/L Rn statewide, based on the observed exceedance percentages from within granitic plutons to surrounding distances up to 5 km in greater Augusta. Because U exceedance rates in other plutons of Maine are higher than those from greater Augusta, this estimate is likely a conservative estimate because the actual Rn exceedance rates in other plutons of Maine are likely to be higher.

Implications for Risk Assessment. The strong spatial association between the occurrence of elevated groundwater [U] or [Rn] and the granitic plutons in Maine suggests that other fractured bedrock aquifers in New England within or in the vicinity of granitic plutons are at risk of containing harmful levels of [U] and [Rn]. Given limited public health resources, we recommend that efforts related to promote well water testing for [U] and [Rn] target areas within a distance of 5–10 km from a mapped granitic boundary. Wells with elevated [U] are located mostly within ~5 km distance from granitic plutons with a few found up to 10 km distance at the intermediate to regional scales (Table 1 and SI Figure S8), and wells with elevated [Rn] are found mostly within 8 km distance with a few found up to 10 km (Table 2 and SI Figure S9). Extensive pegmatite dikes or pods enriched in incompatible elements, such as As⁸⁰ and possibly U, have been found adjacent to the syn-tectonic plutons typically within 5 km distance.

Although there are limitations to our study noted below, sampling density (≥ 1 per km²) is high enough to capture intermediate scale spatial patterns of groundwater [U], informing the aforementioned testing suggestion. The median concentrations and the probability of exceeding MCLs for U and Rn in four clusters in 2006 sampling (sampling density of 1–6 per km²) show the same order and ranking as those in 2007 sampling with a 5–6 times higher sampling density (SI Table S1). However, the spatial variance of groundwater U and Rn distribution as indicated by the interquartile range due to the lack of normal distribution of the data is very large at local scales, and generally increases with increasing median concentrations (SI Table S1). Even higher sampling density at about 100 wells per km² is desirable to ascertain the variance at local scales, although this is not currently feasible because there are simply not that many wells drilled in the study area. It is also likely that a high sampling density of 1 per km² can benefit characterizing regional scale groundwater U distributions because semivariograms (SI Figure S7) show a major range of 4–10 km for [U] and [Rn] for greater Augusta, but 28 km for U for the state of Maine. Considering similar

hydrogeochemical processes regulating U distribution in bedrock aquifers, it is possible that a higher sampling density at regional scale may result in comparable semivariograms.

Although groundwater [U] can differ by orders of magnitude among various rock types, there are insufficient data or understanding of geochemistry of U decay series products such as Ra at local and intermediate spatial scales to inform the geospatial analysis performed here. There is little doubt that better understanding of hydrogeochemical processes in fractured bedrock aquifers through characterization of glacial till overburden, well depth and yield, flow path, residence time, fracture characteristics and interconnectivity, alpha recoil emanation efficiency conditions in conjunction with groundwater chemistry will shed further light on groundwater U and Rn distribution in individual boreholes or at local scales.^{19,81} The role of weathering of U minerals in granites and the subsequent transport and distribution of its many decay products need further study to understand the decoupled U and Rn distribution within granites.

■ ASSOCIATED CONTENT

⑤ Supporting Information

To protect the privacy of the homeowners, U and Rn concentration data are not available for sharing with researchers in accordance of Institutional Review Board protocol. Distribution maps and summary statistics of groundwater U and Rn in greater Augusta and the state of Maine are available. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

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