

Matrix-Derived Radium Mobilization in Shallow Aquifers Near Unconventional Oil and Gas Operations

Allison Fenske, Jianfeng Su, Jennifer Baka, Brandon Forsythe, Lara Williams, Samuel W. Shaheen, Tao Wen, Susan L. Brantley, and Nathaniel R. Warner*



Cite This: <https://doi.org/10.1021/acs.est.6c05003>



Read Online

ACCESS |

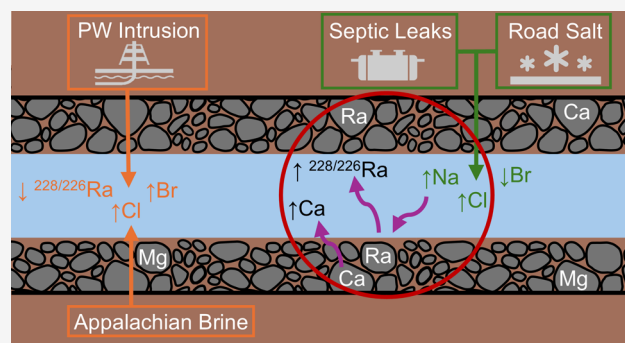
Metrics & More

Article Recommendations

Supporting Information

ABSTRACT: Previous studies in Pennsylvania identified localized “hotspots” of elevated salinity (Cl^- , Ba^{2+} , Sr^{2+}) in shallow groundwater thought to be associated with unconventional oil and gas (UOG) operations. Because produced water generated during UOG operations is both highly saline and enriched in radium, accidental releases could increase groundwater salinity and radium activity. Elevated salinity from other sources such as road salt or septic tanks could also release radium from aquifer solids through cation exchange. Therefore, we measured combined radium activity ($^{226+228}\text{Ra}$) in shallow groundwater ($n = 91$) and tested for associations with UOG wells, historical surface impoundments, or reported spills within 1, 3, or 5 km. All samples were below U.S. EPA maximum contaminant levels [0.185 Bq/L (5 pCi/L)] and consistent with regional background values. Radium activities were statistically greater within 3 km of spills and impoundments and correlated positively with the density of UOG wells within 3 km. Although radium correlated with Cl^- , Ba^{2+} , and Sr^{2+} , other geochemical indicators, Na/Cl , Cl/Br , and $^{228/226}\text{Ra}$, indicate that radium was likely not directly derived from UOG fluids. Only six samples were consistent with produced water mixing with shallow groundwater. Instead, most of the salinity was primarily attributed to shallow sources that released matrix-bound radium.

KEYWORDS: salinization, chloride, sodium, road salt, groundwater



INTRODUCTION

Unconventional oil and gas (UOG) operations have been linked to degradation of water quality in private drinking water in the Appalachian Basin at very low frequencies of contamination.^{1–6} Much of the degradation of water quality is linked with releases of “produced water” (PW), a mixture of formation brine and injection water, brought to the surface during drilling, fracturing, and oil or gas production.^{7–10} In the Appalachian Basin, PWs contain Na, Ca, and Cl at concentrations that are 5–10 times that of seawater.^{7,9,10} The high concentrations lead to large changes in shallow groundwater chemistry from small releases of PW. Despite infrequent issues of reported groundwater contamination in areas of UOG activities, investigations of large, publicly available data sets of water quality collected between 2008 and 2018 observed regional elevated concentrations of chloride (Cl^-)⁶ and metals barium (Ba) and strontium (Sr)¹¹ associated with proximity to or density of UOG wells.^{6,11} Likewise, increased concentrations of Cl, Ba,¹² and Sr in the surface water of the region were also linked to UOG operations.¹³ The slight increase in concentrations of these elements could originate from mismanagement or documented spills at the surface.^{6,11,14} In the Appalachian Basin, the brines also contain

elevated naturally occurring radioactivity, mainly in the form of radium.^{10,15}

Recently, studies have found links between proximity to UOG wells in production and an increase in cancer rates, asthma, and infant low birth weights.^{16–19} Radium is a known carcinogen and represents a potential exposure that could have contributed to the observations that show associations between proximity to UOG and negative health outcomes.^{20,21} Drinking water with elevated radium is associated with bone cancer, leukemia, and other negative health outcomes.^{20–24} Evaluating radium with respect to UOG operations can have important implications regarding human health.

Notably, there are few studies that examine if UOG operations increase radioactivity near UOG operations.^{25–27} There is a lack of radium data in the large data sets that were used for the analysis of Cl, Ba, and Sr noted above, primarily

Received: April 3, 2026

Revised: August 6, 2026

Accepted: August 7, 2026

because samples for radium were not collected in previous studies. Limited studies on oil and gas operations and impacts on radium in groundwater show the need for detailed examination of the geochemistry to elucidate the radium source and mechanisms of enrichment (if any).^{25,27} For example, radium activities in groundwater in Northeast Pennsylvania (NE PA) did not correlate with proximity to UOG wells.²⁶ Instead, radium activity was associated with deeper Appalachian Basin Brines (ABBs) that were naturally discharged to valley bottoms and diluted through mixing with meteoric water.²⁶ Indeed, elevated radium activity is often associated with elevated salinity²⁸ and could be released from the aquifer matrix because of shallow salt sources or from mixing with deeper saline groundwater. For example, in California, disposal of PW with elevated radium concentrations to unlined ponds did not directly lead to elevated radium in groundwater.²⁵ Instead, the radium of the PW precipitated in shallow ponds as radiobarite and did not leach into shallow groundwater.²⁵ However, where unlined ponds were used, the high-salinity PW (sodium and chloride) did leach into the shallow groundwater and changed the salinity, redox, and pH, which led to desorption of geogenic radium present in underlying sediments.^{25,29}

The PW from the Appalachian Basin contains elevated radium activities (median 91 Bq/L [2460 pCi/L];³⁰ medians of various formations ranged from 66.4–114.9 Bq/L [1794–3105 pCi/L]¹⁰). If PW is mismanaged or accidentally released at the surface (e.g., leaks, spills) during UOG operations, radium activities would likely become elevated in the nearby groundwater. Based on the evidence provided in Shaheen et al. (2022, 2024), we are the first to investigate radium in shallow groundwater from private water wells and springs in areas of Washington and Greene counties, Pennsylvania (PA).^{6,11} We hypothesize that radium activities are likely to be elevated closer to UOG wells, impoundments, and spills in areas of extensive UOG operations of Southwestern PA (SW PA) compared to other potential influences such as geology, land use, mining, and conventional oil and gas (COG) wells.^{6,31}

Our samples were collected at the same time and locations as the data published in Su et al. (2026) and Baka et al. (2026, in review).^{32,33} Spatial analyses by Su et al. (2026) characterized major and trace ions, dissolved gases, and volatile organic compounds and proximity to UOG wells, impoundments, and documented spills. Su et al. (2026) used nonparametric rank tests (Wilcoxon Mann–Whitney and Brunner–Munzel) with a false discovery rate (FDR) of 10%³² and found no evidence for widespread regional impacts on water quality from UOG.

MATERIALS AND METHODS

The study is located in SW PA in Washington and Greene counties. Both counties lie within the Appalachian Plateau Province, which is characterized by rolling uplands and steep valleys. Pennsylvanian- and Permian-age Conemaugh, Monongahela, and Dunkard Group sedimentary rocks of alternating layers of sandstone, shale, limestone, and coal seams are folded into low-amplitude anticlines and synclines.³⁴ These counties in SW PA have an extensive history of coal mining, conventional oil and gas operations, and, more recently, UOG that are often located near shallow drinking water wells.³⁵

Well and spring locations were identified through coordination with homeowners as part of a larger study to investigate potential impact from UOG activities.^{32,33} Homeowners in potentially impacted areas (nearby UOG wells, impoundment ponds, and spill locations) were identified and coordinated with to collect ground-

water samples. Impoundment ponds were previously used for PW storage during the initial UOG operations in the area but are no longer permitted. The PADEP SPUD Data report was used to identify impoundments reprimanded by the PADEP and matched to well pad names. The matching well pad location was used to determine distance to samples with ArcGIS.³³ UOG well locations were also extracted from the PADEP SPUD Data report and filtered to only include wells within the previously found CI hotspots in Shaheen et al. (2022).^{6,33} Spills of PW occurring within 3 years of sampling campaigns (2021–2024) in the region were identified using reports within the PA Oil and Gas Weekly Compliance Dashboard and locations within the PADEP Land Recycling Program listed under a major UOG company name (e.g., Range, CNX, EQT).³³ Distances from the water sample to the nearest UOG well within a CI hotspot and reported PW spill were determined using ArcGIS. Distances to all three “UOG activities” for each sample were provided by Su et al. (2026).

Homeowner identification in areas of interest involved utilizing county tax parcel data, PA Groundwater Information System (PAGWIS), mailed recruitment postcards, local community groups, Penn State Master Well Owner Network, Penn State Extension, cold calling homeowners in the region, and snowball sampling. Further information can be found in Baka et al. (2026, in review).³³ Baka et al. (2026, in review) include a demographic survey collected in tandem with water samples that is protected by Institutional Review Board (IRB) policies, including informed consent.³³

Water samples were collected in multiple field campaigns conducted from May to November 2024 (Figure 1). Only samples collected from private water wells ($n = 78$) and springs ($n = 13$) were included in this investigation of shallow groundwater.

Wells were purged to remove standing water from the well and associated piping. Continuously flowing springs were not purged. Water was collected prior to any holding tanks or treatment systems. Measurements of pH, temperature, dissolved oxygen (DO), and specific conductance were recorded at 5 min intervals using a YSI ProDSS meter. The ProDSS was calibrated daily. The probe was submerged in a 5-gallon bucket fitted with a valve to allow continuous water circulation until pH and temperature values varied by less than 5% over a 5 min period, after which samples were collected. Following parameter stabilization, 20 L of water was collected and passed through a column filled with 10 g of MnO-coated fibers at a flow rate of less than 1 L per minute to adsorb the radium onto the fibers.^{38–40}

Fibers were squeezed, sealed in plastic bags, and transported to the Tracing Salinity with Isotopes (SALTs) laboratory at Pennsylvania State University. Fibers were then compressed into 24 mL HDPE liquid scintillation vials. Once compressed, the vials were sealed with parafilm to prevent gas from escaping and were incubated for a minimum of 21 days. The incubation period allows for radium 226 to reach equilibrium with granddaughter products that have detectable radiation emissions during testing.

Radium isotopes 226 (²²⁶Ra) and 228 (²²⁸Ra) were measured utilizing a Canberra small anode germanium detector (SAGE). ²²⁶Ra was quantified by averaging keV peaks of 295 (Pb-214), 351 (Bi-214), and 609 (Pb-214). ²²⁸Ra was calculated with 911 (Actinium 228). Efficiency values per channel peak were calculated from fiber standards measured with the same geometry, materials, and incubation process. Major cations, anions, ⁸⁷Sr/⁸⁶Sr, and dissolved methane collected at the same time are reported in Su et al. (2026)³² and Baka et al. (2026, in review).³³

Analyses

Statistical analyses were conducted with RStudio (version 2025.09.01 + 401; packages provided in the Data Availability section). Normality was checked with the Shapiro–Wilk test for normality. Data that failed the normality test were transformed with natural log before retesting for normality and used in parametric statistical analysis. Analysis of variance (ANOVA), Tukey’s honestly significant difference (HSD), ordinary least squares (OLS), Pearson’s correlation (PC), and two-tailed *t*-tests were performed. Analytes that failed the normality test after natural log transformation were used in

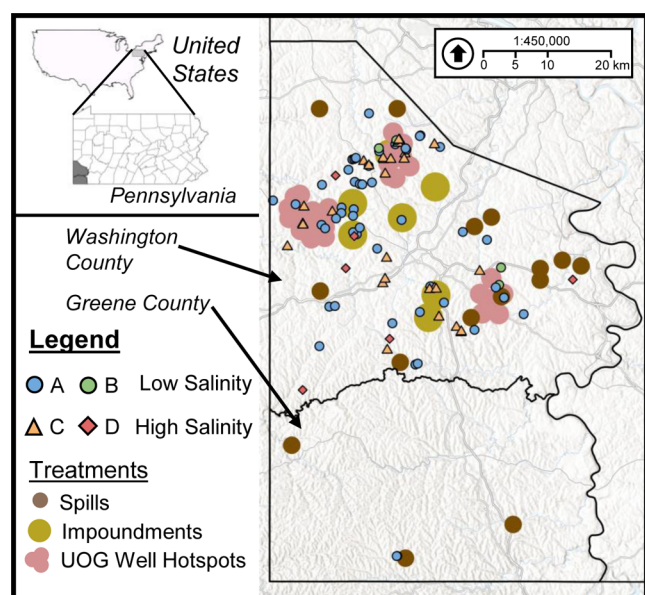


Figure 1. Spills (smaller circles without outlines, brown), impoundments (larger circles without outlines, yellow), and previously found Cl hotspots of UOG wells⁶ (amorphous clumped circles without outlines, red). The Cl hotspots represent areas with slightly elevated Cl concentrations near UOG wells that were identified using a large data set of “predrill” data and identified previously.⁶ Sample locations labeled by “type” (A, B, C, or D). “Types” based on the modified structure from Warner et al. (2012)²⁶ and Cravotta et al. (2022).³⁶ Samples with >30 mg/L Cl and >0.001 Br/Cl (mmol ratio) are type “D” and indicate Cl sourced from diluted brine (red diamond). Samples with >30 mg/L Cl and <0.001 Br/Cl (mmol ratio) are type “C” and indicate Cl sources from halite mixing (orange triangle). Samples with <30 mg/L are A or B and represent low salinity/background waters, dominated either by calcium bicarbonate (“A”) (blue circle) or sodium bicarbonate (“B”) (green circle). Washington and Greene counties are outlined in black and labeled.³⁷

nonparametric statistical analyses. Nonparametric analyses included Spearman’s rank correlation (SPC). PCA was also conducted.

We used two-tailed Student’s *t*-tests, OLS, and PC to evaluate if UOG activities may have led to regional (i.e., spatial) increases in radium activities in shallow groundwater. OLS and PC were used to evaluate if radium increased with decreased distance to UOG wells within Cl hotspots (hotspot UOG wells), impoundments, or spills. The *t*-tests specifically compared average values in areas “close” to a UOG activity compared to samples collected farther away. Potentially impacted samples were determined by distance to the nearest hotspot UOG well, nearest impoundment, and nearest spill. Distances were split by 1 km, 3 km, and 5 km thresholds and compared individually. When analyzing samples by the *X* km threshold, samples within *X* km of a UOG activity were categorized with that UOG activity. Samples outside of *X* km of all three UOG activities were labeled as controls. Radium activities, ²²⁸Ra, ²²⁶Ra, and ²²⁶⁺²²⁸Ra, were not normally distributed, but a natural log transformation passed the Shapiro–Wilk test for normality (²²⁶Ra *p* = 0.13, ²²⁸Ra *p* = 0.45, ²²⁶⁺²²⁸Ra *p* = 0.61). Therefore, to evaluate if there are differences in radium activities in areas near hotspot UOG wells, impoundments, and spills and areas farther away (control), we used parametric Student’s *t*-tests. Cl, Sr, and Ba were also evaluated by categories described above. Density of UOG wells at 1 km, 3 km, and 5 km (provided by Su et al. (2026)) was compared with radium activities via OLS and PC. OLS and PC were used to evaluate if radium increased with decreased continuous distance to hotspot UOG wells, impoundments, or spills. To further investigate geochemistry and identify the source of the observed radium, we evaluated ²²⁸Ra/²²⁶Ra ratios, Cl/Br mass ratios, and Na/Cl molar ratios and conducted PCA.

We additionally evaluated geology, land use, topography, well depth, and proximity to mining and COG wells as predictors of radium activity via ANOVA, Student’s *t*-tests, OLS, and PC. Geologic maps, land use, and mining operation locations were downloaded from Pennsylvania Spatial Data Access (PASDA), PennDOT Open Data, and ArcGIS Data and Maps for spatial analysis.^{37,41–45} Topographical information (TPI, Topographic Position and Index) for each sample was provided by Su et al. (2026) based on Weiss (2001).^{32,46} Data for PW composition were sourced from the United States Geological Survey (USGS) Produced Water Database (retrieved 10/7/24).⁴⁷ Data from Warner et al. (2012) and Szabo (2012) Supporting Information were also compiled and included for comparisons.^{26,48}

Radium activities were used to calculate benchmark quotient (BQ) values to represent health risk for the compounds in comparison to their respective MCLs.^{49,50} BQ is calculated by dividing the measured concentration of the contaminant by the maximum contaminant level (MCL).⁵⁰ A BQ value of >1 indicates a measured contaminant value that exceeds the maximum health risk guidance level for total radioactivity (0.1 mSv).⁴⁹

RESULTS AND DISCUSSION

Radium Activities Are Low and Consistent with Regional Background Levels

Radium in our samples was generally low, with no samples above the U.S. EPA maximum contaminant level (MCL) threshold of 0.185 Bq/L [5 pCi/L] (Supporting Information 1).⁵¹ Combined radium activities (²²⁶⁺²²⁸Ra) ranged from 0.019 to 0.050 Bq/L [0.5–1.36 pCi/L]. There are a limited number of studies that report radium activities in the groundwater of PA, but our values are similar (or lower) to other published values. For example, Warner et al. (2012) reported ²²⁶⁺²²⁸Ra from 0.005 to 0.191 Bq/L [0.13–5.17 pCi/L] in NE PA, another region with extensive UOG operations.²⁶ In a study with roughly 1000 radium values collected across 15 principal aquifers in the USA, Szabo et al. (2012) reported values of ²²⁶⁺²²⁸Ra from 0.018 to 0.756 Bq/L [0.49–20.43 pCi/L] (Supporting Information 2, Table S1).⁴⁸ Szabo et al. (2012) provided data based on aquifer type, including 58 samples for intermixed sandstone and limestone (²²⁶⁺²²⁸Ra: 0.021–0.068 Bq/L [0.58–1.826 pCi/L]). The majority of our samples were collected from intermixed sandstone and limestone aquifers, with our range in radium consistent with values published in Szabo et al. (2012).⁴⁸ Ratios of ²²⁸Ra/²²⁶Ra in our samples ranged from 0.24 to 3.23, near the range (1.83 to 6.45) reported by Szabo et al. (2012) for intermixed sandstone and limestone.

Radium Shows Limited Spatial or Distance Dependence with UOG Infrastructure

We did not observe any statistically significant differences between samples categorized as being near a UOG activity compared to controls at the 1 km or 5 km thresholds. However, we did observe statistically significant differences in categories at a distance of 3 km (Figure 2; Supporting Information 2, Tables S2–S5). ²²⁸Ra concentrations are 56% higher in samples within 3 km of historical impoundments (*p* = 0.03) and 47% higher in samples within 3 km of spills (*p* = 0.01) than those in samples outside of 3 km of all categories. ²²⁶⁺²²⁸Ra concentrations are 56% higher in samples within 3 km of impoundments (*p* = 0.03) and 44% higher in samples within 3 km of spills (*p* = 0.03) than in samples outside of 3 km of all categories.

There were few samples collected within 1 km of the UOG activities. Any samples (the vast majority) collected >1 km

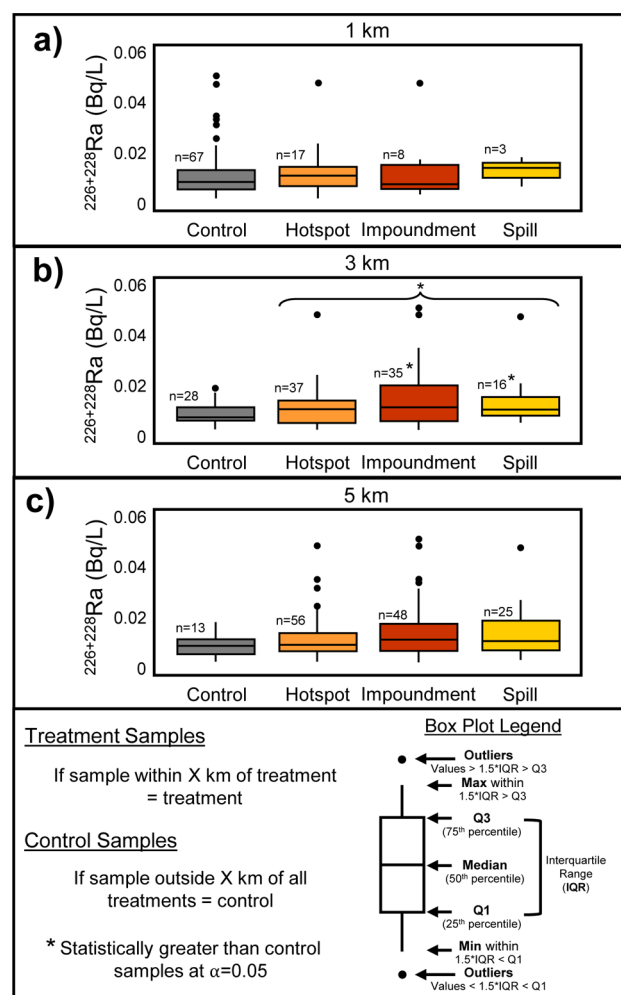


Figure 2. $^{226+228}\text{Ra}$ concentrations (Bq/L) by category. Categories were determined by examining distance to the nearest UOG well, historical impoundment, and spill. Distances were split by 1 km (a), 3 km (b), and 5 km (c). Samples collected within X km of a category were labeled with that category. Samples farther than X km away from all categories were labeled as controls.

were labeled “control” for the 1 km evaluation. The opposite was true with our sample designations at a 5 km distance, where few samples were farther than 5 km that could be considered controls (>5 km) and the majority of samples were <5 km away from UOG activities (e.g., hotspots, impoundments, and spills). When all UOG activity-designated samples were combined (i.e., samples within X km of the UOG well, impoundment, or spill) and compared to the controls, there was no statistical difference between UOG activities and control samples at 1 km and 5 km at $\alpha = 0.05$. We note that in each category (i.e., closer to UOG at 1, 3, and 5 km distances), mean combined radium activities, $^{226+228}\text{Ra}$, are greater than the mean of the control group. The statistical significance is only observed when the sizes of the control group and categories are most similar. When the continuous distance between the sample and UOG activity was analyzed with OLS and PC, none of the radium (^{226}Ra , ^{228}Ra , and $^{226+228}\text{Ra}$) activities yielded statistically significant p-values.

Again, only at 3 km did ^{226}Ra ($p = 0.01$), ^{228}Ra ($p = 0.02$), and $^{226+228}\text{Ra}$ ($p = 0.01$) activities positively, but weakly ($R^2 < 0.1$; $\text{cor} < 0.3$), correlate with density of UOG wells. The density of UOG wells at 1 km and 5 km did not yield a

statistically significant correlation. In West Virginia, Kozar et al. (2022) also found a relationship between ^{226}Ra and density of UOG wells, but at 0.5 km.²⁸

Geology, Land Use, and Topography Explain Some Variability in Radium Activities

There could be other possible explanations for differences in observed radium activity that should be considered.⁵² We explored the following potential explanations: (1) variations in bedrock geology,⁴¹ (2) topography (topographic position and index, TPI),⁴⁶ (3) well depth,³³ (4) land use,⁴³ (5) proximity to mining operations,^{31,44} and (6) COG.^{6,45} (Supporting Information 4, Figures S1–S3).

Geologic formations are known to have varying amounts of radium depending on rock type and source/parent U and Th material^{48,53} that can influence radium concentrations. There are formations in southeastern PA, for example, with known elevated U, Ra, and Rn activities. Indeed, previous studies show that 46% of groundwater samples collected within the Reading Prong and the Chickies Quartzite had radium activities above the EPA MCL of 0.185 Bq/L [5 pCi/L].^{51,54} Additionally, groundwater with elevated radium was observed in valley bottoms in NE PA and attributed to discharge of deeper brine to the shallow subsurface via natural flow paths.²⁶ To evaluate natural flow paths, we included TPI and well depth as potential influences on the radium activities. Finally, some fertilizers have relatively elevated concentrations of uranium and radium, which could raise radium activities in areas of extensive cultivation and fertilization.⁵⁵

Using ANOVA at $\alpha = 0.05$, we detected no statistical differences in radium concentrations based on land use, geology, or TPI to explain our variation in radium (Supporting Information 2, Tables S6–S11). Likewise, there is no evidence of well depth as a predictor of radium concentrations by OLS. The t -tests were also performed to compare the individual factor levels of land use/geology/TPI to all other levels. We found that samples within “urban built-up” land use have higher $^{226+228}\text{Ra}$ ($p = 0.04$) activities than all other land uses. Urban land areas have a greater density of impervious surfaces, including paved roads and footpaths, that are linked with increasing salinization of freshwater, mainly from salt applied during the winter.⁵⁶ Application of road salt has been associated with increased radium activity in shallow groundwater in other regions.⁵⁷ The road salt (NaCl) elevates Na, which then replaces radium that is absorbed to the aquifer matrix. Therefore, higher radium activity we observe in urban land-use areas could indicate road salt from impervious surfaces entering the aquifer and mobilizing radium from the aquifer matrix.⁵⁷

Via OLS and PC, radium activities did not yield statistically significant relationships ($\alpha = 0.05$) with distance to or density of mining operations at 1 km, 3 km, and 5 km. ^{226}Ra ($p = 0.01$), ^{228}Ra ($p = 0.05$), and $^{226+228}\text{Ra}$ ($p = 0.02$) positively correlate with density of COG wells at 1 km via PC; however, they yield very low R^2 values via OLS (^{226}Ra : $R^2 = 0.07$; ^{228}Ra : $R^2 = 0.05$; $^{226+228}\text{Ra}$: $R^2 = 0.06$).

We note that t -tests showed that wells have statistically higher concentrations of ^{226}Ra ($p = 0.01$), ^{228}Ra ($p = 0.05$), and $^{226+228}\text{Ra}$ ($p = 0.01$) than springs. A similar finding of the difference in water in wells and springs was indicated in Su et al. (2026). The authors noted higher nitrate, likely associated with agriculture, in the shallow springs, relative to the wells.

This provides further evidence that agriculture is not the likely source of elevated radium that we observe.

Radium Covaries with Salinity but Not with Produced Water Signatures

With limited evidence that geology, topography, or well depth influences radium activities and account for the differences observed near UOG operations, we explored the geochemistry of the water samples reported in Su et al. (2026) for potential explanations of the source of radium in groundwater. If the spatial variations we observe (i.e., elevated radium within 3 km of UOG operations) were the result of UOG operations, then we would expect other chemical indicators of UOG contamination to correlate with radium.

Previous studies in this region and other areas of UOG operations postulated that spills and leaks of surface-managed PW caused at least some of the elevated Cl, Sr, and Ba observed in groundwater^{6,11} and surface water.¹³ We compared our radium data to Cl, Sr, and Ba previously reported in Su et al. (2026). Cl, Ba, and Sr concentrations correlated with all ²²⁶Ra, ²²⁸Ra, and ²²⁶⁺²²⁸Ra activities (Supporting Information 2, Table S12). Along with Sr and Ba, radium is a divalent alkaline earth metal; therefore, coassociation of these metals that behave similarly is not uncommon, especially in high-salinity brines.⁵⁸ Ba, Sr, and Ra are often mobilized in aquifers with lower pH and higher chloride concentrations, thereby elevating concentrations of all three.⁴⁸ Ba and Sr are often used to infer radium activity in shallow groundwater.⁵⁹

Previous studies examining water quality in this region, Baka et al. (2026, in review) and Su et al. (2026), used nonparametric statistical approaches to evaluate UOG categories. Here, because Ra concentrations are normally distributed following natural log transformation, we used parametric approaches such as the Student's *t*-test on the natural log-transformed concentrations. Likewise, Cl and Sr are normally distributed following natural log transformation, so we applied parametric tests for Cl and Sr to our UOG operation categories to directly compare to radium results (Supporting Information 2, Tables S13–S15). We observe a statistically significant difference in Cl within categories. After ln transformation, Cl concentrations are 62% higher in samples within 1 km of a hotspot UOG well ($p = 0.004$) than samples outside of 1 km of all categories. Additionally, ln Sr concentrations are 40% higher in samples within 3 km of an impoundment ($p = 0.01$) than in samples outside of 3 km of impoundments. The ln Sr concentrations negatively correlate with distance to the nearest UOG well ($p = 0.03$) and nearest impoundment ($p = 0.03$), but ln Cl showed no statistical correlation with distance to categories with OLS or PC. Before applying the FDR correction, Su et al. (2026) also found elevated chloride in samples within Cl “hotspots” from Shaheen et al. (2022).³² Ba was not normally distributed following a natural log transformation. However, with a nonparametric correlation test (SPC), Ba positively correlates with ²²⁶Ra ($p = 0.00001$), ²²⁸Ra ($p = 0.0007$), and ²²⁶⁺²²⁸Ra ($p = 0.0001$).

Combined, the cooccurrence of Ba, Sr, Cl, and Ra in shallow groundwater could indicate that UOG operations impacted shallow groundwater and caused regional salinization.^{6,11} However, Su et al. (2026) examined Cl/Br ratios and found that the majority of higher salinity samples (Cl >30 mg/L) were consistent with animal waste, septic effluent, or halite contamination and not dilution of brine/PW.^{9,26,60} While some

groundwater samples ($n = 6$) have Cl/Br ratios consistent with brine dilution, they are spatially dispersed across categories (e.g., impoundments, spills, hotspot UOG wells, or controls) and both near and far from UOG operations. In contrast, the samples with elevated Cl >30 mg/L and Cl/Br ratios thought to be from road salt or septic are located more often in areas near UOG wells (Figure 1).

Release of NaCl from shallow sources such as road salt often results in Na/Cl (molar) ratios close to or slightly below 1 (e.g., ~0.9). The excess Na⁺ replaces other cations already sorbed to the aquifer matrix, which results in the release of monovalent/divalent cations (Ca²⁺, Mg²⁺, Li⁺, K⁺, Sr²⁺, Ba²⁺, and Ra²⁺) and median Na/Cl values slightly lower than 1.^{9,61} Lower salinity samples (Cl <30 mg/L) have a median Na/Cl (molar) ratio of 1.79. The higher salinity samples Na/Cl (Cl >30 mg/L) have a median Na/Cl ratio of 0.92. Halite-type and brine-type samples have median Na/Cl ratios of 0.78 ($n = 30$) and 4.96 ($n = 6$), respectively. The ABB is a Na–Ca–Cl-type brine with very high Ca and lower Na/Cl ratios.⁹ Combined Na/Cl and Cl/Br ratios indicate the most likely source of elevated salinity near UOG is shallow septic and/or road salt and not UOG operations.

Additionally, Na correlates positively with the density of primary roads (highways within the federal interstate highway system)⁴² at 3 km ($p = 0.02$) and 5 km ($p = 0.02$) (Supporting Information 2, Tables S16 and S17). Epuna et al. (2022) noted that road salt could account for 36–48% of the total chloride in PA groundwaters.⁶² In contrast, Su et al. (2026) find slight Na enrichment near spills (11% increase in Na concentrations per kilometer approaching spills) and state that limited enrichment of Na reflects residual impacts from surface or shallow subsurface rather than deep formation brines.³²

While radium covaries with salinity, the geochemical and halogen signatures indicate that this salinity is predominantly derived from shallower sources rather than UOG fluids, requiring an in situ mechanism to explain radium mobilization.

Radium Derived from the Aquifer Matrix and Mobilized by Cation Exchange

Radium isotope ratios can also help distinguish UOG and conventional oil and gas (COG) sources. Radium ratios of ^{228/226}Ra were shown to be distinct in UOG-produced water from the Marcellus Formation with ^{228/226}Ra ratios (<0.3) compared to ^{228/226}Ra ratios of produced water from COG (>1.6).^{15,47} If our elevated radium observed in groundwater near UOG wells were from the direct dilution of surface-spilled Marcellus PW, we would expect lower ^{228/226}Ra that looks isotopically similar to Marcellus UOG PW. Instead, the ^{228/226}Ra that we observe is most similar to values for sandstone aquifers (1.6)⁶⁴, the most common rock type in our study area (Figure 3). Median values of ^{228/226}Ra for all samples (^{228/226}Ra = 1.4) were not distinct compared to Cl >30 mg/L (^{228/226}Ra = 1.3). Reported ^{228/226}Ra in COG-produced water varies more widely but with a median of 1.2⁴⁸, similar to sandstone aquifers. Specifically, in our study area, two samples of COG PW from Washington County contained radium with ratios of ^{228/226}Ra of 1.8 and 1.95.⁶⁴

The median of ^{228/226}Ra (1.3) in elevated salinity samples is more consistent with COG (~1.2) and sandstone (~1.6) and not UOG (~0.3). Based on ^{228/226}Ra, the small set of samples ($n = 6$) that show evidence of brine dilution in shallow groundwater could be from UOG or COG operations because

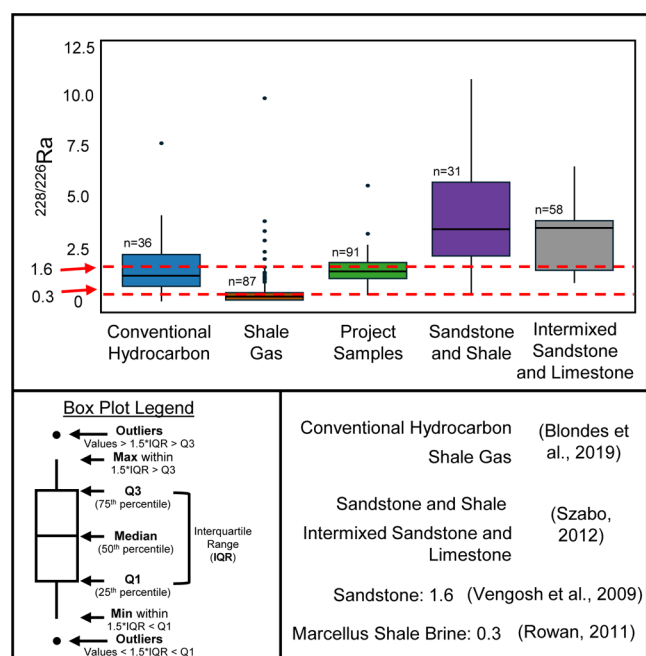


Figure 3. $^{228}/^{226}\text{Ra}$ ratios of the produced water collected from conventional hydrocarbon (blue) and shale gas (orange) wells in Pennsylvania from the USGS produced water database,⁴⁷ shallow groundwater samples collected in this project (green), and ranges in shallow groundwater reported in Szabo, et al.⁴⁸ The highest red dashed line at $y = 1.6$ represents the proposed $^{228}/^{226}\text{Ra}$ ratio of sandstone.⁶³ The lowest red dashed line at $y = 0.3$ represents the mean Marcellus shale brine.³⁰

their $^{228}/^{226}\text{Ra}$ is lower (~ 0.9). Some UOG-produced water samples do exhibit a greater ratio (Figure 3).

Alternatively, releases of PW at the surface from either impoundments or spills could change redox conditions in the groundwater and release geogenic radium from the aquifer.²⁵ McMahon et al. (2019) examined radium dynamics in areas of produced water storage and disposal.²⁵ Despite high-salinity water leaking from the ponds into shallow groundwater, the radium and barium did not leach out of the storage pond. Instead, the authors noted that radium in produced water likely precipitated with barium as low-solubility barite and stayed sequestered in the ponds. However, the saline water that leaked to the subsurface changed the pH, redox, and salinity of the underlying formation aquifer and released geogenic radium that was previously adsorbed to the aquifer matrix. The release occurred through a combination of redox release of radium associated with Fe and Mn and changes in pH²⁵ and cation exchange of Na^+ , Ca^{2+} , and Mg^{2+} with radium on exchange sites in the aquifer matrix.⁶¹

In the data presented here, ^{226}Ra , ^{228}Ra , and $^{226+228}\text{Ra}$ activities did not correlate with measured pH, Mn, or Fe at $\alpha = 0.05$ (Supporting Information 2, Table S18), indicating that changes in redox from the release of saline-produced water were not likely the cause of elevated radium observed. Iron and manganese were only present at concentrations above detection limits in 24 and 42 samples (respectively), which limited statistical analysis. However, low concentrations and infrequent detections of Fe and Mn in our samples likely preclude the determination of the relationship between redox controls on radium.

A PCA was conducted to include analytes representing potential halite mixing, brine mixing, and agricultural influence (Figure 4). Samples with NA values for PCA analytes were

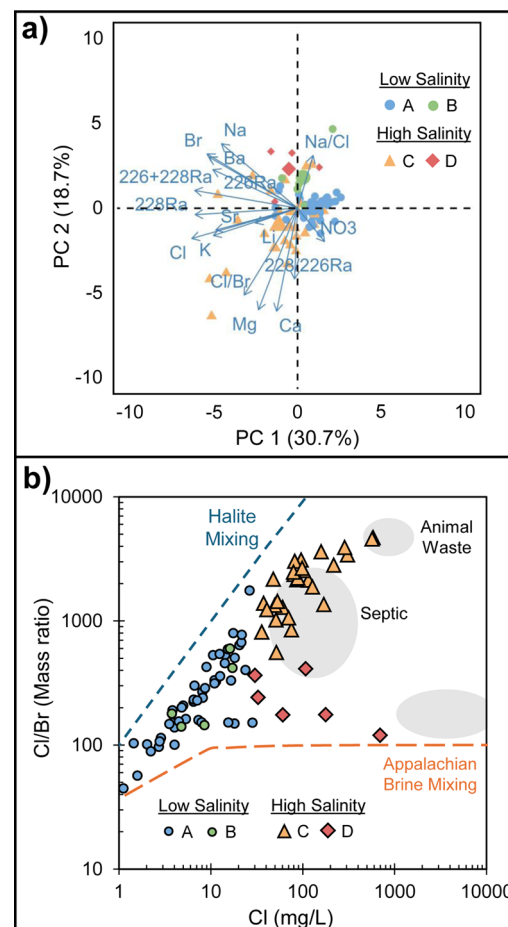


Figure 4. (a) Biplot of focused PCA, including Cl, Sr, Br, Ba, Na, K, Li, Mg, Ca, NO_3 , Cl/Br (mass ratio), Na/Cl (molar ratio), and radium data (pCi/L : ^{226}Ra , $^{226+228}\text{Ra}$, and $^{228}/^{226}\text{Ra}$). (b) Cl/Br (mass ratio) and Cl mixing plot, with shaded regions indicating possible salinity sources.⁶⁵ Samples for both plots are colored by “type”; those with >30 mg/L Cl and >0.001 Br/Cl (mmol ratio) are type “D” and indicate more likely a brine mix. Samples with >30 mg/L Cl and <0.001 Br/Cl (mmol ratio) are type “C” and indicate more likely shallow halite mixing. Samples with <30 mg/L are A or B and represent low salinity/background waters, dominated either by calcium bicarbonate (“A”) or sodium bicarbonate (“B”).

dropped; therefore, a total of 87 samples were included in PCA. Each sample was “typed” based on Cl concentrations and Br/Cl molar ratios, following a modified procedure used by Warner et al. (2012) and Cravotta et al. (2022).^{26,36} Samples with greater than 30 mg/L of Cl and a Br/Cl molar ratio >0.001 are type “D”. These are the samples most likely influenced by brine ($n = 6$). Samples with greater than 30 mg/L of Cl and a Br/Cl molar ratio <0.001 are type “C”, representing samples more likely influenced by halite ($n = 28$ in PCA and $n = 30$ in the entire data set). Samples with <30 mg/L of Cl are typed as “A” or “B”, representing low salinity/background groundwater, dominantly calcium bicarbonate (A) or sodium bicarbonate (B) waters. Na/Cl and NO_3 were plotted with type A/B samples, indicating agriculture is not influencing our radium activities. Cl/Br, Mg, Ca, and $^{228}/^{226}\text{Ra}$

plot together with type C samples, further supporting halite mixing in our samples. Br, Na, Ba, and ^{226}Ra plot together with both type C and type D samples.

On the basis of these analyses, there is limited evidence that the release of UOG brine, which contains elevated Br^- and Ra, led to an increase in regional radium activities. This implies that the effects of spills and/or leaking impoundments are localized and very limited spatially. The consistency of $^{228/226}\text{Ra}$ across salinity types and categories indicates a local source of the radium from the shallow aquifer itself.^{25,28} With no observable differences in Cl and Cl/Br ratios near spills/impoundments or Fe/Mn and redox condition changes, spills/leaking impoundments are likely not the source of the elevated radium.^{48,49}

Elevated Salinity Increases Radium-Associated Health Risks despite Low Absolute Activities^{49,50}

The MCL for radium is based on combined $^{226+228}\text{Ra}$ (0.185 Bq/L [5 pCi/L]),⁵¹ however, the half-lives of ^{226}Ra and ^{228}Ra vary significantly, at 1600 years and 5.8 years, respectively.⁶⁶ Therefore, there is a greater health risk from exposure to ^{228}Ra than from ^{226}Ra .⁴⁹ Indeed, the World Health Organization (WHO) notes a guidance level of 1 Bq/L for ^{226}Ra and 0.1 Bq/L for ^{228}Ra .⁶⁷ There has not been an MCL established for ^{224}Ra , and while not included in this study, Stackelberg (2018) notes ^{224}Ra closely correlates with ^{228}Ra .⁴⁹

Here, we consider the BQ values of our samples. Our low-salinity samples (A-B) have a median ^{226}Ra value of 0.003 Bq/L and a median ^{228}Ra value of 0.005 Bq/L, which results in BQ values of 0.003 for ^{226}Ra and 0.05 for ^{228}Ra . Samples with Cl >30 mg/L, likely sourced from road salt or other shallow sources, have a median value of 0.004 ^{226}Ra and 0.007 ^{228}Ra , resulting in BQ values of 0.004 for ^{226}Ra and 0.07 for ^{228}Ra . Compared to our low-salinity samples, the Cl >30 mg/L samples have 33% increased BQ for ^{226}Ra and 40% increased BQ for ^{228}Ra . Samples with Cl >30 mg/L but evidence of brine dilution ($n = 6$) have median values of 0.009 ^{226}Ra and 0.008 ^{228}Ra and BQ values of 0.009 for ^{226}Ra and 0.08 for ^{228}Ra . Again, compared to our low-salinity samples, the diluted brine samples have 200% increased BQ for ^{226}Ra and 60% increased BQ for ^{228}Ra . These results, while remaining below the MCL values from the EPA and WHO, demonstrate an increased health risk from ^{226}Ra and ^{228}Ra within samples with slightly elevated (>30 mg/L) Cl concentrations.

One sample included in Su et al. (2026), located near a documented spill site, contained multiple geochemical markers of influence by brine.³² This sample has a ^{226}Ra value of 0.023 Bq/L and a ^{228}Ra value of 0.024 Bq/L and, therefore, a BQ of 0.023 for ^{226}Ra and 0.24 for ^{228}Ra . This lone sample has a 667% increased health risk from ^{226}Ra and a 380% increased health risk from ^{228}Ra when compared with the median of our low-salinity samples.

IMPLICATIONS

This study assessed radium activities in groundwater within two counties, Washington and Greene, PA, with extensive historical hydrocarbon extraction and UOG operations. Radium activities in all of our samples are below regulatory levels. We found that $^{226+228}\text{Ra}$ concentrations are higher in groundwater samples collected within 3 km of impoundments and spills and a weak positive correlation between radium activities and density of UOG wells at 3 km. Using a combination of parametric and nonparametric statistical

analyses, we evaluated radium sources and determined that the primary source of radium is the geogenic shallow aquifer matrix and not dilution of UOG Marcellus-produced water. A PCA indicates that this increase in salinity is most likely from road salting, with evidence of salinity from brines for very few samples. These radium results are consistent with Su et al.'s (2026) major and trace geochemistry as well as previous studies in other regions.⁵⁷ While there is no way to differentiate whether the brine is naturally occurring or a result of UOG operations, our finding of the impact from road salting is not negligible. As roads will continue to be treated with salt during the winter, salinity will continue to increase in groundwater, releasing radium from aquifers. This elevation of salinity can contribute to an increased health risk of between 33 and 200% from ^{226}Ra and 40–60% from ^{228}Ra . Importantly, we did not observe radium concentrations above the MCL in any of the samples. These findings highlight the need to distinguish between fluid sources and geochemical mobilization processes when assessing the groundwater impacts in regions of hydrocarbon development. Finally, our assessment highlights the potential increased health risks of salinization of freshwater regardless of the salinity source.

ASSOCIATED CONTENT

Data Availability Statement

The R code for statistics and graphing (<https://github.com/allisonfenske-web/ES-T-Radium-Manuscript-No.-es-2026-05003s>) and the full code used for statistical analysis are provided.

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.est.6c05003>.

Measured, extracted, and provided data used in analyses, including three sheets labeled “Master_Datafile”, “Designation_Testing_Data”, and “USGS” (XLSX)

Tables summarizing statistical analyses and results, including statistical results for the project (XLSX)

Additional figures displaying context graphics and GIS layouts, including topographical context, land use map, and geology map with sample locations (PDF)

AUTHOR INFORMATION

Corresponding Author

Nathaniel R. Warner – Department of Civil and Environmental Engineering, Pennsylvania State University, University Park, Pennsylvania 16802, United States; orcid.org/0000-0002-6434-5118; Email: nrw6@psu.edu

Authors

Allison Fenske – Department of Civil and Environmental Engineering, Pennsylvania State University, University Park, Pennsylvania 16802, United States; Department of Civil and Environmental Engineering, Juniata College, Brumbaugh Academic Center, Huntingdon, Pennsylvania 16652, United States; orcid.org/0009-0004-2654-3502

Jianfeng Su – Department of Earth and Environmental Sciences, Syracuse University, Syracuse, New York 13244, United States

Jennifer Baka – Department of Geography, Pennsylvania State University, University Park, Pennsylvania 16802, United States; Earth and Environmental Systems Institute,

Pennsylvania State University, University Park, Pennsylvania 16802, United States

Brandon Forsythe – Department of Geosciences, Pennsylvania State University, University Park, Pennsylvania 16802, United States; orcid.org/0000-0001-9780-212X

Lara Williams – Department of Geosciences, Pennsylvania State University, University Park, Pennsylvania 16802, United States

Samuel W. Shaheen – Department of Earth & Environmental Sciences, University of Minnesota, Minneapolis, Minnesota 55455, United States; orcid.org/0000-0002-0111-7361

Tao Wen – Department of Earth and Environmental Sciences, Syracuse University, Syracuse, New York 13244, United States; orcid.org/0000-0002-6113-7532

Susan L. Brantley – Earth and Environmental Systems Institute, Pennsylvania State University, University Park, Pennsylvania 16802, United States; Department of Geosciences, Pennsylvania State University, University Park, Pennsylvania 16802, United States; orcid.org/0000-0002-9574-2693

Complete contact information is available at:
<https://pubs.acs.org/10.1021/acs.est.6c05003>

Author Contributions

Conceptualization: S.S., S.B., J.B., N.W., T.W.; data curation: A.F., L.W., B.F.; formal analysis: A.F., N.W.; funding acquisition: S.B., J.B., N.W., T.W.; investigation: A.F., N.W.; methodology: A.F., S.S., S.B., N.W., J.B.; project administration: S.B., J.B., N.W.; resources: N.W., J.B.; software: A.F.; supervision: N.W., J.B.; validation: A.F., N.W.; visualization: A.F.; writing—original draft: A.F., N.W.; writing—review and editing: A.F., J.S., J.B., B.F., L.W., S.S., T.W., S.B., N.W.

Funding

This work was supported by the Health Effects Institute (grant number 143815 to Jennifer Baka, Pennsylvania State University, with a subcontract to N.W.). Partial stipend support for A.F. was provided by NSF CBET CAREER 1942601 to PI Warner. Research described in this article was conducted under contract to the Health Effects Institute (HEI), an organization jointly funded by the United States Environmental Protection Agency (EPA) (Contract No. 68HERC19D0010) and certain oil and natural gas companies. Although the research was produced with partial funding by the EPA and industry, they have not been subject to their review, and therefore, the research does not necessarily reflect the views of the agency or the oil and natural gas industry, and no official endorsement by the agency or the industry should be inferred.

Notes

The authors declare no competing financial interest.

REFERENCES

- (1) Wen, T.; Niu, X.; Gonzales, M.; Zheng, G.; Li, Z.; Brantley, S. L. Big Groundwater Data Sets Reveal Possible Rare Contamination Amid Otherwise Improved Water Quality for Some Analytes in a Region of Marcellus Shale Development. *Environ. Sci. Technol.* **2018**, *52* (12), 7149–7159.
- (2) Clark, C. J.; Xiong, B.; Soriano, M. A.; Gutches, K.; Siegel, H. G.; Ryan, E. C.; Johnson, N. P.; Cassell, K.; Elliott, E. G.; Li, Y.; Cox, A. J.; Bugher, N.; Glist, L.; Brenneis, R. J.; Sorrentino, K. M.; Plano, J.; Ma, X.; Warren, J. L.; Plata, D. L.; Sifers, J. E.; Deziel, N. C. Assessing Unconventional Oil and Gas Exposure in the Appalachian Basin:

Comparison of Exposure Surrogates and Residential Drinking Water Measurements. *Environ. Sci. Technol.* **2022**, *56* (2), 1091–1103.

(3) Jackson, R. B.; Vengosh, A.; Darrah, T. H.; Warner, N. R.; Down, A.; Poreda, R. J.; Osborn, S. G.; Zhao, K.; Karr, J. D. Increased Stray Gas Abundance in a Subset of Drinking Water Wells near Marcellus Shale Gas Extraction. *Proc. Natl. Acad. Sci. U. S. A.* **2013**, *110* (28), 11250–11255.

(4) Osborn, S. G.; Vengosh, A.; Warner, N. R.; Jackson, R. B. Methane Contamination of Drinking Water Accompanying Gas-Well Drilling and Hydraulic Fracturing. *Proc. Natl. Acad. Sci. U. S. A.* **2011**, *108*, 8172–8176.

(5) Llewellyn, G. T.; Dorman, F.; Westland, J. L.; Yoxtheimer, D.; Grieve, P.; Sowers, T.; Humston-Fulmer, E.; Brantley, S. L. Evaluating a Groundwater Supply Contamination Incident Attributed to Marcellus Shale Gas Development. *Proc. Natl. Acad. Sci. U. S. A.* **2015**, *112* (20), 6325–6330.

(6) Shaheen, S. W.; Wen, T.; Herman, A.; Brantley, S. L. Geochemical Evidence of Potential Groundwater Contamination with Human Health Risks Where Hydraulic Fracturing Overlaps with Extensive Legacy Hydrocarbon Extraction. *Environ. Sci. Technol.* **2022**, *56* (14), 10010–10019.

(7) Neff, J.; Lee, K.; DeBlois, E. M.. In *Produced Water: Overview of Composition, Fates, and Effects*; Lee, K., Neff, J., Eds.; Springer: New York, NY, 2011. DOI: 10.1007/978-1-4614-0046-2.

(8) Capo, R. C.; Stewart, B. W.; Rowan, E. L.; Kolesar Kohl, C. A.; Wall, A. J.; Chapman, E. C.; Hammack, R. W.; Schroeder, K. T. The Strontium Isotopic Evolution of Marcellus Formation Produced Waters, Southwestern Pennsylvania. *Int. J. Coal Geol.* **2014**, *126*, 57–63.

(9) Dresel, P. E.; Rose, A. W. *Chemistry and Origin of Oil and Gas Well Brines in Western Pennsylvania*; Harrisburg, 2010. <https://catalog.libraries.psu.edu/catalog/12742742> (accessed 2025–12–29).

(10) Tasker, T. L.; Warner, N. R.; Burgos, W. D. Geochemical and Isotope Analysis of Produced Water from the Utica/Point Pleasant Shale, Appalachian Basin. *Environ. Sci.:Processes Impacts* **2020**, *22* (5), 1224–1232.

(11) Shaheen, S. W.; Wen, T.; Zheng, Z.; Xue, L.; Baka, J.; Brantley, S. L. Wastewaters Coproduced with Shale Gas Drive Slight Regional Salinization of Groundwater. *Environ. Sci. Technol.* **2024**, *58*, 17862.

(12) Niu, X.; Wendt, A.; Li, Z.; Agarwal, A.; Xue, L.; Gonzales, M.; Brantley, S. L. Detecting the Effects of Coal Mining, Acid Rain, and Natural Gas Extraction in Appalachian Basin Streams in Pennsylvania (USA) through Analysis of Barium and Sulfate Concentrations. *Environ. Geochem. Health* **2018**, *40* (2), 865–885.

(13) Bonetti, P.; Leuz, C.; Michelon, G. Large-Sample Evidence on the Impact of Unconventional Oil and Gas Development on Surface Waters. *Science* **2021**, *373*, 896–902.

(14) Patterson, L. A.; Konschnik, K. E.; Wiseman, H.; Fargione, J.; Maloney, K. O.; Kiesecker, J.; Nicot, J. P.; Baruch-Mordo, S.; Entekin, S.; Trainor, A.; Sifers, J. E. Unconventional Oil and Gas Spills: Risks, Mitigation Priorities, and State Reporting Requirements. *Environ. Sci. Technol.* **2017**, *51* (5), 2563–2573.

(15) Rowan, E. L.; Engle, M. A.; Kraemer, T. F.; Schroeder, K. T.; Hammack, R. W.; Doughten, M. W. Geochemical and Isotopic Evolution of Water Produced from Middle Devonian Marcellus Shale Gas Wells, Appalachian Basin, Pennsylvania. *AAPG Bull.* **2015**, *99* (2), 181–206.

(16) Jeanine Buchanich, F. M.; Fabisiak, J. P.; Sally Wenzel, H. E.; Youk, A. O.; Yuan, J.-M.; Maynard, D.; Andrew Mrkva, A.; Melanie Stangl, W.; Wu, F. *Final Report for Pennsylvania Department of Health, Bureau of Epidemiology Hydraulic Fracturing Epidemiology Research Studies: Birth Outcomes*; Pittsburgh, PA, 2023. https://paenv.pitt.edu/assets/Report_Birth_outcomes_Revised_2023_July.pdf (accessed 2026–04–02).

(17) Buchanich, J. M.; Bear, T. M.; Fabisiak, J. P.; Tersak, J.; Wenzel, S. E.; Youk, A. O.; Yuan, J.-M.; Foulds, A.; Allison Koller, R. C.; Michael Lann, P. F.; David Maynard, P.; Becky Meehan, A.; Andrew Mrkva, R.; Natalie Price, W. F.; Melanie Stangl, D.; Rachel Taber, A.; Renwei Wang, R.; Hoffman, C. *Final Report for Pennsylvania*

Department of Health, Bureau of Epidemiology Hydraulic Fracturing Epidemiology Research Studies: Childhood Cancer Case-Control Study: Pittsburgh, PA, 2023. https://paenv.pitt.edu/assets/Report_Cancer_outcomes_2023_August.pdf (accessed 2026–04–02).

(18) Glabicki, Q. Joint Pitt, State Studies Find Link between Proximity to Fracking and Increased Cancer Rates, Asthma Attacks, Low Birth Weight, 2023. <https://www.publicsource.org/fracking-proximity-cancer-asthma-southwestern-pa-pitt-wolf/>.

(19) Jeanine Buchanich, F. M.; Arena, V.; Emeritus, A.; Bear, T. M.; Fabisiak, J. P.; Wenzel, S. E.; Youk, A. O.; Yuan, J.-M.; Maynard, D.; Andrew Mrkva, A.; Melanie Stangl, W.; Wu, F. *Final Report for Pennsylvania Department of Health, Bureau of Epidemiology Hydraulic Fracturing Epidemiology Research Studies: Asthma Outcomes*: Pittsburgh, PA, 2023. https://paenv.pitt.edu/assets/Report_Asthma_outcomes_revised_2023_July.pdf (accessed 2026–04–02).

(20) Canu, I. G.; Laurent, O.; Pires, N.; Laurier, D.; Dublineau, I. Health Effects of Naturally Radioactive Water Ingestion: The Need for Enhanced Studies. *Environ. Health Perspect.* **2011**, *119* (12), 1676–1680.

(21) Fuortes, L.; McNutt, L. A.; Lynch, C. Leukemia Incidence and Radioactivity in Drinking Water in 59 Iowa Towns. *Am. J. Public Health* **1990**, *80*, 1261.

(22) Finkelstein, M. M.; Kreiger, N. Radium in Drinking Water and Risk of Bone Cancer in Ontario Youths: A Second Study and Combined Analysis. *Occup. Environ. Med.* **1996**, *53* (5), 305–311.

(23) Cohn, P.; Skinner, R.; Burger, S.; Fagliano, J.; Klotz, J. *Radium in Drinking Water and the Incidence of Osteosarcoma*, 2003.

(24) Finkelstein, M. M. Radium in Drinking Water and the Risk of Death from Bone Cancer among Ontario Youths. *CMAJ* **1994**, *151*, 565–571.

(25) McMahon, P. B.; Vengosh, A.; Davis, T. A.; Landon, M. K.; Tyne, R. L.; Wright, M. T.; Kulongoski, J. T.; Hunt, A. G.; Barry, P. H.; Kondash, A. J.; Wang, Z.; Ballentine, C. J. Occurrence and Sources of Radium in Groundwater Associated with Oil Fields in the Southern San Joaquin Valley, California. *Environ. Sci. Technol.* **2019**, *53*, 9398–9406.

(26) Warner, N. R.; Jackson, R. B.; Darrah, T. H.; Osborn, S. G.; Down, A.; Zhao, K.; White, A.; Vengosh, A. Geochemical Evidence for Possible Natural Migration of Marcellus Formation Brine to Shallow Aquifers in Pennsylvania. *Proc. Natl. Acad. Sci. U. S. A.* **2012**, *109* (30), 11961–11966.

(27) Kozar, M. D.; McAdoo, M. A.; Haase, K. B.; Reid, L. T. Groundwater Quality and Geochemistry of the Western Wet Gas Part of the Marcellus Shale Oil and Gas Play in West Virginia: Reston, Virginia, 2023. DOI: .

(28) Vengosh, A.; Coyte, R. M.; Podgorski, J.; Johnson, T. M. A Critical Review on the Occurrence and Distribution of the Uranium- and Thorium-Decay Nuclides and Their Effect on the Quality of Groundwater. *Sci. Total Environ.* **2022**, *808*, 151914.

(29) Zielinski, R. A.; Budahn, J. R. Mode of Occurrence and Environmental Mobility of Oil-Field Radioactive Material at US Geological Survey Research Site B, Osage-Skiatook Project, Northeastern Oklahoma. *Appl. Geochem.* **2007**, *22* (10), 2125–2137.

(30) Rowan, E. L.; Kirby, C. S.; Kraemer, T. F.; Engle, M. A. *Radium Content of Oil- and Gas-Field Produced waters in the Northern Appalachian Basin (USA): Summary and Discussion of Data*; U.S. Geological Survey, Scientific Report 2011–5135, 2011. <http://pubs.usgs.gov/sir/2011/5135/>.

(31) Cravotta, C. A. Dissolved Metals and Associated Constituents in Abandoned Coal-Mine Discharges, Pennsylvania, USA. Part 1: Constituent Quantities and Correlations. *Appl. Geochem.* **2008**, *23* (2), 166–202.

(32) Su, J.; Williams, L.; Fenske, A.; Shaheen, S. W.; Brantley, S. L.; Forsythe, B.; Warner, N. R.; Baka, J.; Wen, T. Targeted Sampling Reveals Localized Brine signals without Evidence of Regional Water Quality impacts from Unconventional Oil and Gas Development. *Environ. Sci.:Processes Impacts* **2026**, *28* (7), 1927–1940.

(33) Baka, J.; Brantley, S. L.; Wen, T.; Warner, N. R.; Pinto, C.; Bitzer, Z.; Forsythe, B.; Fenske, A.; Su, J.; Williams, L.; Mahugu, E. An

Analysis of Water Quality in the Oldest Hydrocarbon Basin in the USA; Health Effects Institute, In Revision.

(34) Berg, T. M.; Edmunds, W. E.; Geyer, A. R.; Glover, A. D.; Hoskins, D. M.; MacLachlan, D. B.; Root, S. I.; Sevon, W. D.; Socolow, A. A. *Geologic Map of Pennsylvania* (2nd Ed.); USGS National Geologic Map Database. https://ngmdb.usgs.gov/Prodesc/proddesc_34341.htm (accessed 2025–12–20).

(35) Jasechko, S.; Perrone, D. Hydraulic Fracturing near Domestic Groundwater Wells. *Proc. Natl. Acad. Sci. U. S. A.* **2017**, *114* (50), 13138–13143.

(36) Cravotta, C. A.; Senior, L. A.; Conlon, M. D. Factors Affecting Groundwater Quality Used for Domestic Supply in Marcellus Shale Region of North-Central and North-East Pennsylvania, USA. *Appl. Geochem.* **2022**, *137*, 105149.

(37) PennDOT, G. I. S. Pennsylvania County Boundaries; PennShare. <https://data-pennshare.opendata.arcgis.com/datasets/PennShare::pennsylvania-county-boundaries/about> (accessed 2025–12–20).

(38) Dulaiova, H.; Burnett, W. C. An Efficient Method for γ -Spectrometric Determination of Radium-226,228 via Manganese Fibers. *Limnol. Oceanogr.:Methods* **2004**, *2* (8), 256–261.

(39) Moore, W. S. Radium Isotope Measurements Using Germanium Detectors. *Nucl. Instrum. Methods Phys. Res.* **1984**, *223* (2–3), 407–411.

(40) Moore, W. S.; Reid, D. F. Extraction of Radium from Natural Waters Using Manganese-Impregnated Acrylic Fibers. *J. Geophys. Res.* **1973**, *78* (36), 8880–8886.

(41) USGS. State Geologic Maps, 2017. <http://pubs.usgs.gov/of/2005/1325/> (accessed 2025–02–17).

(42) Homeland Infrastructure Foundation Level Data HIFLD. Primary Roads; Pennsylvania Spatial Data Access. <https://www.pasda.psu.edu/uci/DataSummary.aspx?dataset=9190> (accessed 2026–01–29).

(43) Southwestern Pennsylvania Commission. Washington County Land Use/Land Cover 2010. *Pennsylvania Spatial Data Access (PASDA)*. <https://www.pasda.psu.edu/uci/DataSummary.aspx?dataset=1611> (accessed 2025–02–19).

(44) Pennsylvania Spatial Data Access. *Coal Mining Operations*; Pennsylvania Spatial Data Access (PASDA). <https://www.pasda.psu.edu/uci/DataSummary.aspx?dataset=271> (accessed 2025–02–18).

(45) Pennsylvania Spatial Data Access. *Oil Gas Locations—Conventional Unconventional*. <https://www.pasda.psu.edu/uci/DataSummary.aspx?dataset=1088> (accessed 2026–03–10).

(46) Weiss, A. Topographic Position and Landforms Analysis. *Poster presentation, ESRI User Conference 2001*, 64, 227–245.

(47) Blondes, M. S.; Gans, K. D.; Engle, M.; Kharaka, Y. K.; Reidy, M. E.; Saraswathula, V.; Thordsen, J. J.; Rowan, E. L.; Morrissey, E. A. U.S. Geological Survey National Produced Waters Geochemical Database v2.3 (Superseded by Ver. 3.0, December 2023); 2019. <https://www.usgs.gov/data/us-geological-survey-national-produced-waters-geochemical-database-v23-superseded-ver-30> (accessed 2024–10–7).

(48) Szabo, Z.; dePaul, V. T.; Fischer, J. M.; Kraemer, T. F.; Jacobsen, E. Occurrence and Geochemistry of Radium in Water from Principal Drinking-Water Aquifer Systems of the United States. *Appl. Geochem.* **2012**, *27* (3), 729–752.

(49) Stackelberg, P. E.; Szabo, Z.; Jurgens, B. C. Radium Mobility and the Age of Groundwater in Public-Drinking-Water Supplies from the Cambrian-Ordovician Aquifer System, North-Central USA. *Appl. Geochem.* **2018**, *89*, 34–48.

(50) Toccalino, P. L.; Norman, J. E.; Phillips, R. H.; Kauffman, L. J.; Stackelberg, P. E.; Nowell, L. H.; Krietzman, S. J.; Post, G. B. *Application of Health-based Screening Levels to Ground-Water Quality Data in a State-Scale Pilot Effort*; USGS, 2004.

(51) Environmental Protection Agency. National Primary Drinking Water Regulations. In *Ground Water and Drinking Water*. <https://www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations> (accessed 2026–02–23).

- (52) Soriano, M. A.; Deziel, N. C.; Saiers, J. E. Regional Scale Assessment of Shallow Groundwater Vulnerability to Contamination from Unconventional Hydrocarbon Extraction. *Environ. Sci. Technol.* **2022**, *56* (17), 12126–12136.
- (53) Szabo, Z.; Stackelberg, P. E.; Cravotta, C. A. Occurrence and Geochemistry of Lead-210 and Polonium-210 Radionuclides in Public-Drinking-Water Supplies from Principal Aquifers of the United States. *Environ. Sci. Technol.* **2020**, *54* (12), 7236–7249.
- (54) USGS. *Naturally Occurring Radionuclides in the Ground Water of Southeastern Pennsylvania*; 2000. <https://pubs.usgs.gov/fs/2000/0012/report.pdf> (accessed 2026–02–02).
- (55) Kadi, M. W.; Al-Eryani, D. A. Natural Radioactivity and Radon Exhalation in Phosphate Fertilizers. *Arabian J. Sci. Eng.* **2012**, *37* (1), 225–231.
- (56) Utz, R.; Bidlack, S.; Fisher, B.; Kaushal, S. Urbanization Drives Geographically Heterogeneous Freshwater Salinization in the Northeastern United States. *J. Environ. Qual.* **2022**, *51* (5), 952–965.
- (57) Lindsey, B. D.; Cravotta, C. A.; Szabo, Z.; Belitz, K.; Stackelberg, P. Relation between Road-Salt Application and Increasing Radium Concentrations in a Low-PH Aquifer, Southern New Jersey. *ACS ES&T Water* **2021**, *1* (12), 2541–2547.
- (58) Langmuir, D.; Melchior, D. The Geochemistry of Ca, Sr, Ba and Ra Sulfates in Some Deep Brines from the Palo Duro Basin, Texas. *Geochim. Cosmochim. Acta* **1985**, *49*, 2423–2432.
- (59) Ayotte, J. D.; Gronberg, J. A. M.; Apodaca, L. E. *Trace Elements and Radon in Groundwater Across the United States, 1992–2003*, 2011.
- (60) Naily, W.; Sudaryanto, W. N. Cl/Br Ratio to Determine Groundwater. IOP Conference Series: Earth and Environmental Science; *Global Colloquium on GeoSciences and Engineering*; IOP Publishing, 2018; Vol. 118, 012020.
- (61) Fan, W.; Hayes, K. F.; Ellis, B. R. Estimating Radium Activity in Shale Gas Produced Brine. *Environ. Sci. Technol.* **2018**, *52* (18), 10839–10847.
- (62) Epuna, F.; Shaheen, S. W.; Wen, T. Road Salting and Natural Brine Migration Revealed as Major Sources of Groundwater Contamination across Regions of Northern Appalachia with and without Unconventional Oil and Gas Development. *Water Res.* **2022**, *225*, 119128.
- (63) Vengosh, A.; Hirschfeld, D.; Vinson, D.; Dwyer, G.; Raanan, H.; Rimawi, O.; Al-Zoubi, A.; Akkawi, E.; Marie, A.; Haquin, G.; Zaarur, S.; Ganor, J. High Naturally Occurring Radioactivity in Fossil Groundwater from the Middle East. *Environ. Sci. Technol.* **2009**, *43* (6), 1769–1775.
- (64) Pennsylvania Department of Environmental Protection *Naturally Occurring Radioactive Material (NORM) Survey*, 1991.
- (65) Katz, B. G.; Eberts, S. M.; Kauffman, L. J. Using Cl/Br Ratios and Other Indicators to Assess Potential Impacts on Groundwater Quality from Septic Systems: A Review and Examples from Principal Aquifers in the United States. *J. Hydrol. (Amsterdam, Neth.)* **2011**, *397* (3–4), 151–166.
- (66) Molinari, J.; Snodgrass, W. J. The Chemistry and Radiochemistry of Radium and the Other Elements of the Uranium and Thorium Natural Decay Series. In *The Environmental Behavior of Radium*; IAEA, 1990.
- (67) World Health Organization *Guidelines for Drinking-Water Quality*, 4th ed.; World Health Organization: Geneva, 2022.