Wastewaters co-produced with shale gas drive slight regional salinization of groundwater

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Abstract

While unconventional oil and gas development (UOGD) is changing the world economy, processes that are used during UOGD such as high-volume hydraulic fracturing ("fracking") have been linked with water contamination. Water quality risks include leaks of gas and salty fluids (brines) that are co-produced at wellpads. Identifying the cause of contamination is difficult, however, because UOG wells are often co-located with other contaminant sources. We investigated the world's largest shale gas play with publicly accessible groundwater data (~29,000 analyses from the Marcellus Shale in Pennsylvania, U.S.A.) and discovered that concentrations of brine-associated species barium ([Ba]) and strontium ([Sr]) show small regional increases within 1km of UOGD. Higher concentrations in groundwaters are associated with greater proximity to and density of UOG wells. Concentration increases are even larger when considering the locations of i) spill-related violations and ii) some wastewater impoundments. These statistically significant relationships persist even after correcting for other natural and anthropogenic sources of salts. The most likely explanation is that UOGD slightly increases salt concentrations in regional groundwaters not because of fracking but because of the ubiquity of wastewater management issues. The high frequency of spills and leaks across shale gas basins suggests other plays could show similar effects.

Introduction

Unconventional oil and gas development (UOGD) has advanced United States (U.S.) energy independence but incited concerns surrounding its potential environmental and human health impacts. UOGD involves horizontal drilling and high-volume high-pressure hydraulic fracturing to extract hydrocarbons from unconventional formations such as shales and other

rocks with low permeability. UOGD in one of the world's largest shale gas plays, the Marcellus Shale, produces ~30x more gas and ~10x more wastewater per well compared to drilling in conventional reservoirs, accentuating the need for proper handling, recycling, and disposal of produced materials to avoid environmental impacts.[1,2] Analyses of publicly available data from regulatory agencies show that incidents such as well construction impairments or wastewater spills are reported at >2% of all UOG wells, creating potential for environmental degradation.[3–5] However, the extent to which issues such as compromised well integrity or improper waste handling translate to water quality impacts remains poorly understood.

Research into the impacts of UOGD on groundwater quality has extensively focused on methane, the primary constituent of natural gas and the most commonly cited contaminant during UOGD.[6–12] However, another commonly reported pollution incident during UOGD is the release of wastewater into soils or streams due to issues related to storage or transportation.[3,4,13] These wastewaters can contain a variety of contaminants. In the first weeks following hydraulic fracturing, waters that are co-produced with the gas (produced waters) are termed flowback waters. Flowback is comprised largely of fluids injected during the hydraulic fracturing of the well.[2] During the production lifetime of the well, in contrast, the produced water that returns with gas derives largely from so-called formation waters, i.e., waters in the shale formation itself that are geochemically identical to basin brines.[14,15] Typically, produced waters from UOGD are sodium (Na)-calcium (Ca)-chloride (Cl) brines with salinities up to 7x modern ocean water.[16] They also typically contain less common species such as barium, strontium, and bromide whose concentrations ([Ba], [Sr], [Br], respectively) can be used to fingerprint contamination related to produced waters.[16,17] For example, median [Ba] and [Sr] in produced waters from the Marcellus Shale (1125 and 1380 mg/L, respectively) are over 3 orders of magnitude greater than those

reported for shallow groundwater in the region.[18,19] The highly concentrated nature of many UOGD wastewaters creates the potential for their salts, metals, organic species, and naturally-occurring radioactive materials to degrade water resources.[20,21]

Scientists and the public are interested in both why contamination occurs and how frequently it occurs during UOGD. The former question generally requires time-, money-, and fieldwork-intensive case studies in locations generally only accessed by regulators.[8,11] Determining the frequency of incidents typically requires statistical analyses of large regulatory and geochemical datasets.[4,19] Such analyses applied to freshwater salinization during UOGD shows that regional salt concentrations may be increasing very slightly in streams near UOGD and that local increases in [Ba], [Sr] and [Cl] in streams impacted by UOGD wastewater leaks or spills can persist for years.[22–24] A recent nationwide analysis of stream chemistry reported a significant increase in brine salt (Ba, Sr, Cl) concentrations in watersheds with higher UOGD density (i.e., the number of UOG wells).[25] A regional analysis in southwestern Pennsylvania also documented a significant increase in [Ba], [Sr], and [Cl] in groundwaters that correlate with the proximity and density of UOGD.[26] This was attributed to localized incidents or "hotspots" where brines had escaped into groundwater.[26]

Despite these studies, the actual causes of regional UOGD impacts on water resources are difficult to identify because UOGD is broadly distributed across hydrocarbon basins and includes many processes ranging from drilling to "fracking" to waste disposal that could cause contamination. Additionally, water quality prior to UOGD is not well-characterized in many basins, and UOGD often overlaps with road salting and longstanding forms of hydrocarbon extraction such as conventional OGD or coal mining that have also been associated with groundwater impacts.[26–28] Many of the species most often associated with UOGD contamination,

such as methane and brine salts, are also naturally present in groundwater.[29,30] Nevertheless, determining the extent to which UOGD may impact water supplies is important because in most locations of UOGD, local populations rely on domestic wells for drinking water.[31,32] Furthermore, emerging studies link UOGD to negative effects on human health, and water supplies are one potential exposure pathway.[33–36]

In this study, we examined the concentrations of brine salt ions in groundwater to determine if they are impacted by specific processes during UOGD (e.g., well construction, wastewater management). Of the major shale plays identified worldwide, we are aware of only three states where the quantities and density of groundwater quality data readily available to the public in UOGD regions are suitable for regional-scale analyses (Texas, Colorado, Pennsylvania).[37] To investigate the potential for groundwater impact, we therefore chose the state with the largest publicly accessible water quality database, Pennsylvania.[38] PA is also a good testbed because of the size of the gas play as well as the observation that spill rates in PA are generally comparable to other major gas-producing states.[4,13] In addition, much of the information about such incidents is documented for PA.[4] As such, the availability of groundwater chemistry data for the Marcellus region of PA enables a large-scale investigation of the groundwater impacts of wellpad spills that may elucidate relevant processes in many other major shale plays where such an investigation is not feasible.[38] The two most heavily drilled parts of this region are northeastern and southwestern PA (NEPA and SWPA, respectively, Figure 1). NEPA is characterized by greater topographic relief but far more limited legacy hydrocarbon extraction (coal mining, conventional oil and gas) compared to SWPA.[26,39]

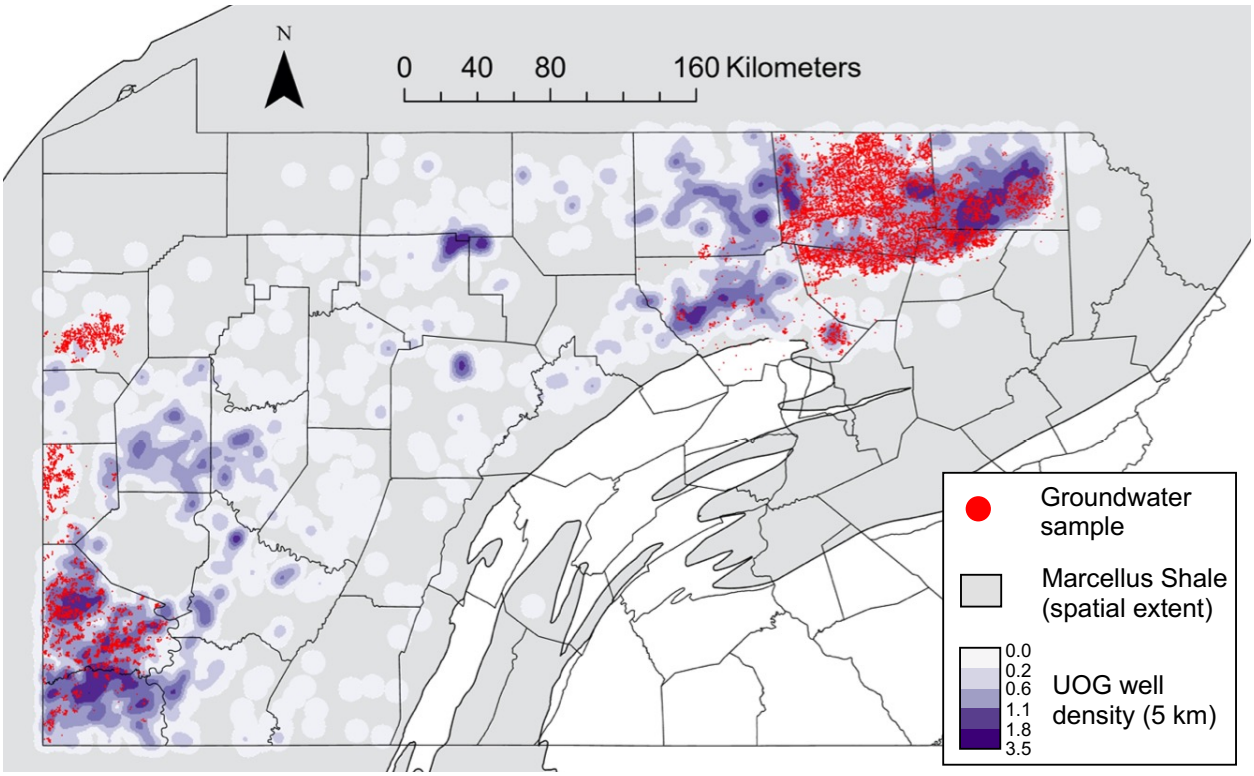

Figure 1: Locations of the 28,609 sampled groundwaters indicated on a map showing the average density of UOG wells within a 5km radius in Pennsylvania (calculated as the 5 km kernel density using 500m bins). For closeups of western PA and northeastern PA, see Figures S2 and S3. The locations of UOG wells, COG wells, and coal mining within our study area are shown in Figure S4.

Materials and Methods

Our dataset consists of 28,609 groundwater analyses from the Shale Network database, spanning the Marcellus Shale region of PA (Figure 1).[40] These samples were predominantly collected between April 2008 and April 2020 (for more about the dataset see Figure S1, Text S1). We examined relationships among groundwater chemistry and UOG wells, UOG impoundments, and locations of UOG-related violations documented by the state regulator, the Pennsylvania Department of Environmental Protection (PADEP). We analyzed 3 metrics to

understand relationships between groundwater samples and UOG activities: land usage (i.e., whether UOG activities were occurring within a specific radius of each sample), distance (i.e., the distance between the sample and nearest UOG activity), and density (i.e., the number of UOG activities within a specific radius of each sample). Each calculation only considered UOG activities which occurred before a respective water sample was collected (Text S2). We examined land usage and UOGD density within a buffer radius around sample sites of both 1km and 3km, but in the main text we emphasize the smaller radius because it is more conservative with respect to hydrologic transport distance. The SI summarizes the 3km results.

We focused intensively on two cationic species, barium (Ba) and strontium (Sr), both of which are widely analyzed and present at characteristically high concentrations in Appalachian Basin brines.[15] Ba is derived from rock dissolution but is found in generally low concentrations in uncontaminated surface and groundwaters in PA, and has previously been identified as an effective tracer for oil and gas development for the Marcellus[41] and nationwide.[25] While also derived from dissolution of the carbonate rocks that are common in hydrocarbon basins,[42] Sr is also an effective tracer for UOGD wastewater contamination.[22,23]

To exclude species that are greatly influenced by overlapping sources such as coal mining or road salting before selecting targeted groundwater species, we examined how median concentrations of Ba, Ca, Cl, Na, Sr, and sulfate (SO_4) varied across different hydrocarbon-related land uses. This comparison (Text S3, Table S1) suggests that Ba, Sr, and Cl are perhaps the best tracers for UOGD impacts. Of those three analytes, we emphasized Ba and Sr on the basis that both are widely analyzed (n = 25,878 and 17,649, respectively) and are generally detected above reporting limits (24,917 and 16,463, respectively) in our dataset, whereas Cl is

more frequently censored (21,584 / 27,599 above detection). As a check, we used specialized methods for highly censored data (Text S4) to validate our key conclusions using Cl (Text S5).

We assessed relationships between Ba and Sr and UOG wells both by comparing median concentrations in samples within the buffer radius to concentrations in samples outside the buffer, as well as with regression modeling comparing ion concentrations to the proximity and density of UOG wells. Additionally, we assessed relationships with violations documented by the PADEP for casing and cementing impairments, impoundment-related issues, and pollution incidents (e.g., spills or leaks). We classified relevant violations in the PADEP Oil and Gas Compliance database into these three categories after slightly modifying a published scheme (Table S2).[3,43] While casing or cementing problems are known to sometimes allow gas leakage into groundwater, leaks from faulty impoundments or spills could enter either surface or groundwaters. To investigate methods to account for the influence of background geologic and anthropogenic processes on our analyses, we also utilized a fixed effects regression model to de-trend the data for potentially confounding overlap with other sources of geogenic or anthropogenic salt. Finally, we included additional tests to account for the small portion of censored concentration data (Text S4). For full details on the methodology, see Text S2.

Results

Barium and strontium concentrations increase with proximity to UOG wells and spills

We first considered whether median concentrations of brine salts are elevated in samples near UOGD. For this comparison we use the Wilcoxon-Mann-Whitney (WMW) test, which is well-suited for non-parametric data. Throughout the paper we use statistical significance to refer to p-value < 0.05.

We observed significantly higher median [Ba] and [Sr] in samples located within 1km of a UOG well across PA (Figure 2). The differences in median [Ba] (11 µg/L) and [Sr] (32 µg/L) in samples within 1km compared to samples >1km from UOGD correspond to 12.2% higher median [Ba] and 10.5% higher median [Sr] (Table S3, Table S4). These comparisons remain statistically significant using the more stringent Brunner-Munzel statistical test (Table S3, Table S4).

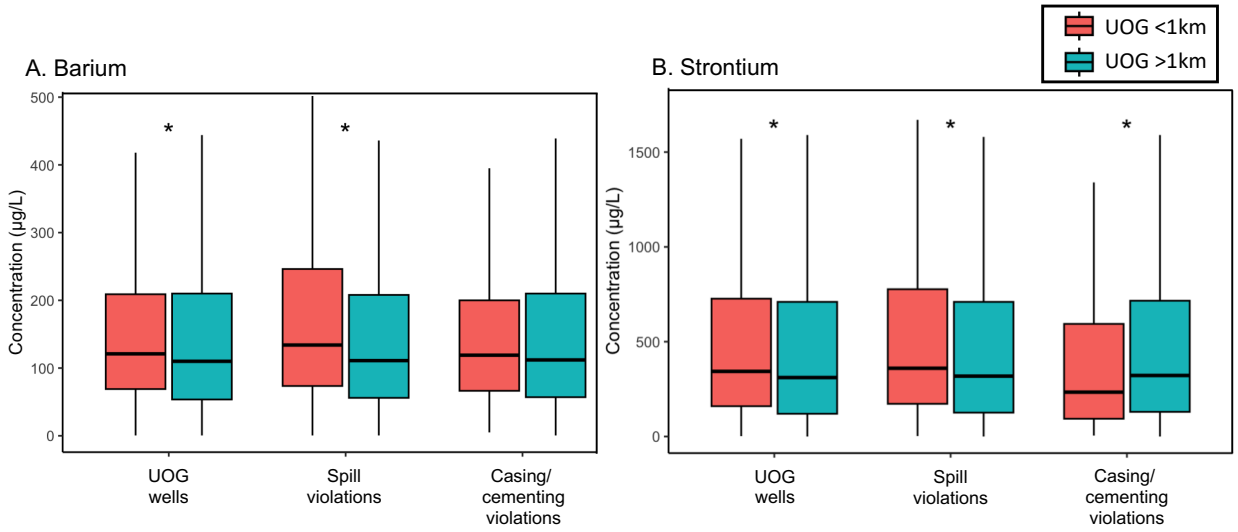

Figure 2: Box and whisker plots of (A) barium and (B) strontium concentrations for Pennsylvania samples <1km from locations of UOGD (red) and >1km from UOGD (aqua) for activities or violations as indicated. Asterisk (*) denotes a statistically significant difference in median concentrations. Outlier data (defined as > Q3 + 1.5 * IQR or < Q1 - 1.5 * IQR, where Q1 and Q3 are the first and third quartiles and IQR is the interquartile range) are not plotted due to the large right skew in the data. Data are only shown for parameters for which significant statewide differences were identified (see Figure S5 for the complete comparison). Calculations only include UOG wells spudded before water sample collection.

Next, we investigated whether these increases persist when considering specific UOG processes as documented by violations at UOG wellpads in the PADEP compliance database. Median [Ba] and [Sr] are significantly higher within 1km of a wellpad spill across the state (Table S3, Table S4). Furthermore, the magnitude of the increase within 1km of spills is larger than the increase within 1km of a UOG wellpad (Figure 2). Once again, these relationships remain statistically significant using the Brunner-Munzel test (Table S3, Table S4). In contrast, we observe no significant increase in median [Ba] or [Sr] within 1km of wellpads cited for violations related to impoundment or casing/cementing violations (Table S3, Table S4).

Brine salt concentrations increase with density of shale gas wells

Given observed increases in median [Ba] and [Sr] within 1km of UOG wellpads, we investigated whether these concentrations also show significant increases associated with higher density of UOG wells. We identified small but statistically significant relationships between [Ba] and [Sr] and the density of UOG wells within 1km (Figure 3A, Table S5). Regressions calculated using a radius of 3km rather than 1km typically revealed smaller regression coefficients (e.g., a smaller magnitude of impacts) but strengthened significance (i.e., smaller p-values), where the latter result is likely related to the larger number of samples within the 3km buffer (Table S5). Both [Ba] and [Sr] also significantly increase with proximity to the nearest UOG well (Table S5). In sum, these data are consistent with increasing [Ba] and [Sr] with UOGD.

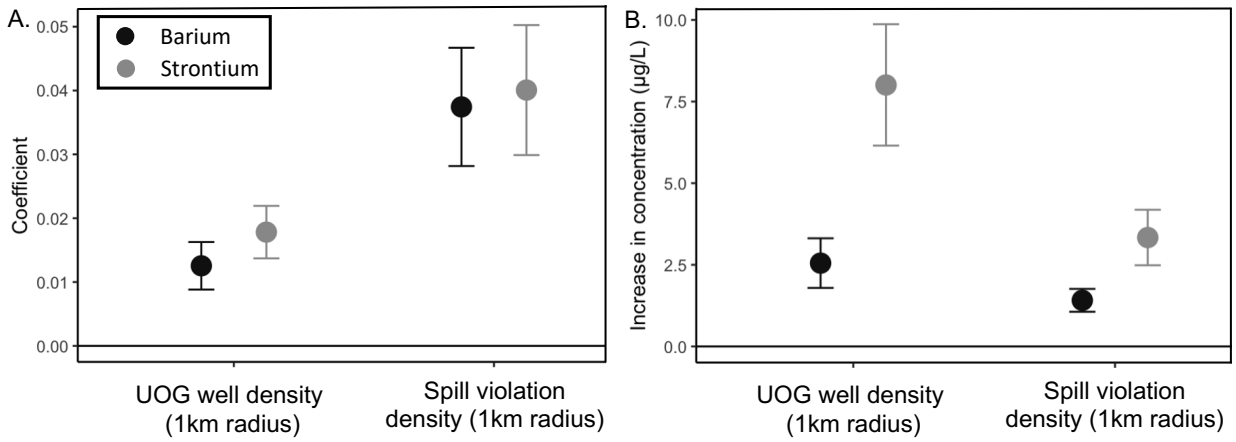

Figure 3: Regression coefficients calculated for the full statewide dataset for regressions analyzing the relationship between log[Barium] and log[Strontium] and UOG well density or UOG spill density within a 1km radius of water samples (A). The corresponding average increases in ion concentrations calculated using Equation 1 (based on mean concentrations and UOG well/spill density) are shown in (B). Error bars show standard error. All regressions yielded statistically significant ($p < 0.05$) correlations. Calculations only include UOG wells spudded before water sample collection.

Based on the regression coefficients calculated for relationships between logC and UOG density, the average µg/L increase in [Ba] or [Sr], ΔC_{avg}, for a given increase in UOG well density across the study area, #UOGD1km, is calculated as:

$$\Delta C_{avg} = C_{avg} * (e^{\beta * \#UOGD1km} - 1) \qquad \text{Equation 1}$$

where C_{avg} is the mean concentration of Ba or Sr across the region of interest (µg/L), #UOGD1km is the number of UOG wells within 1km (density), and β is the regression coefficient. Based on the calculated regression coefficients, mean [Ba] and [Sr] (283 µg/L and 623 µg/L, respectively), and mean #UOGD1km (0.72 UOG wells within 1km) for groundwater

samples in the full statewide dataset, the average concentration increase attributed to UOGD is 2.58 µg/L (Ba) and 8.04 µg/L (Sr) (Figure 3B). At the highest density of UOGD within 1km of a water sample in PA (n = 21 UOG wells), this corresponds to an 85.7 µg/L increase in Ba and a 282.4 µg/L increase in Sr. These estimates scale reasonably well with an estimated 2.2 - 2.6 µg/L increase in [Ba] and 6.1 - 8.2 µg/L increase in [Sr] per additional UOG well within 1km, calculated by estimating the Akritas-Theil-Sen slope (Text S6).

Potential sources of UOG wastewater releases

Across PA, [Ba] and [Sr] also increase with the number of pollution violations (i.e., spills) within 1km with p-values < 0.05 (Table S6, Table S7). Given both UOG well density and spill density are expressed as the number of UOG wells or spills, respectively, within 1km, we compared regression coefficients to understand the relative impacts of UOG wells and spills. One additional spill within 1km has a greater impact on concentration compared to one additional UOG well (Figure 3). Estimates of the Akritas-Theil-Sen slope are also consistent with 2-3x greater increases in [Ba] and [Sr] associated with an increasing number of spills within 1km compared to all UOG wells (Text S6). Consistent with the trends we observed in median concentrations, the other violations we considered were not associated with significant increases in [Ba] and [Sr] (Table S6, Table S7).

When [Ba] and [Sr] are evaluated relative to distance rather than density of UOGD metrics statewide, we identify significant relationships indicating increasing salt concentrations closer to UOGD for all metrics except [Sr] and impoundment violations (Table S6, Table S7).

Statistically significant relationships after de-trending overlapping sources

As discussed previously, UOGD overlaps with other sources of salt ions in groundwater and other features that could obscure contamination. These factors include legacy hydrocarbon extraction (e.g., conventional oil and gas brines and coal mining), structural features conducive to migration of natural basin brines (e.g., along faults or channelized by anticlinal folding), and road salting. When we implement a fixed effects regression to de-trend for these features (e.g., Bonetti et al.[25]), relationships between salt ions and UOGD density and distance are strengthened, with slightly higher coefficients and lower p-values (Table S8, Table S9, Figure S6).

Relationships between UOGD and brine salt ion concentrations in subregions of PA

To understand what causes statewide increases in salt ion concentrations in groundwater and to investigate why a few regressions do not yield significant correlations, we also examined whether confounding variables may affect statewide relationships by investigating two subregions of the state separately (NEPA and SWPA). The subregions are characterized by the highest density of UOGD but differ with respect to land use and geology (Text S1).

Consistent with the statewide data, median [Ba] and [Sr] are higher within 1km of UOG wells in both subregions (Table S3, Table S4). Additionally, median [Ba] and [Sr] are generally higher within 1km of spills (Table S3, Table S4). The only exception is [Sr] in SWPA (Table S4). Median [Ba] is also significantly higher within 1km of 2010 impoundments in SWPA (Table S3).

Investigating correlations within these subregions, we observed relationships that were statistically significant for both analytes in both SWPA and NEPA with respect to distance to the

nearest UOG well. In other words, both Ba and Sr increase in concentration closer to UOG wells in each subregion (Table S5). We also identify small, significant increases in both analytes with increased UOG well density in SWPA, just as we observed in the statewide analysis (Table S5). However, we did not observe this relationship with UOG well density in NEPA (Table S5).

Additionally, we observe significant increases in [Ba] and [Sr] in SWPA associated with a higher density of spills within 1km (Table S6). [Sr] in SWPA also increases with greater density of casing/cementing violations (Table S6, Table S7). In contrast, [Ba] and [Sr] are not significantly correlated with spill density within 1km in NEPA (Table S6, Table S7).

Most of the inconsistencies we observe between our statewide versus regional analyses disappear after implementing fixed effects for other salt sources. For example, when we include fixed effects, relationships among UOG well density and [Ba] and [Sr] are statistically significant in both SWPA and NEPA (Figure S6, Table S8, Table S9). Similarly, relationships between [Sr] and spill violation density are significant in both SWPA and NEPA when fixed effects are implemented (Table S9).

In summary, we observed statistically significant relationships statewide between [Ba] and [Sr] and UOG wells and spills across all methods of comparison (Table 1). These relationships were often statistically significant within subregions SWPA or NEPA as well, especially when fixed effects are included in regression analyses (Table 1).

Table 1: p-values for the relationship between barium or strontium, and UOGD variables across comparison of medians and regression analyses.

Species	UOG variable[1]	Comparison of medians (1km)[2]	Density (1km)	Distance	Density-with fixed effects	Distance-with fixed effects
Full PA dataset						
Barium	UOG wells	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**
	Spills	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**
Strontium	UOG wells	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**
	Spills	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**
NEPA						
Barium	UOG wells	**<0.001**	0.062	**<0.001**	**<0.001**	**<0.001**
	Spills	**<0.001**	0.198	**<0.001**	0.091	**<0.001**
Strontium	UOG wells	**<0.001**	0.893	**<0.001**	**<0.001**	**<0.001**
	Spills	**0.014**	0.114	**<0.001**	**<0.001**	**<0.001**
SWPA						
Barium	UOG wells	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**0.001**
	Spills	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**
Strontium	UOG wells	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**
	Spills	0.063	**0.012**	**<0.001**	**<0.001**	**<0.001**

1. Bolded values indicate statistically significant ($p<0.05$) correlations with the respective variable
2. p-value is displayed for a two-sided WMW test, see tables S2/S3 for one-sided and BM results

Discussion

Brine salts increase near UOGD probably because of wastewater mishandling

Statewide, we observed significantly higher median [Ba] and [Sr] within 1km of UOGD, as well as significant increases in [Ba] and [Sr] with a higher density of UOG wells. Such increases have been reported for surface waters nationwide[25] and for groundwaters in SWPA,[26] but our study is the first to indicate a statewide increase in groundwater brine salt ion concentrations associated with UOGD. The coefficients we calculate for increases in [Ba] and [Sr] in groundwater per UOG well are ~25-50 times larger than observed for PA surface water,[25] consistent with greater dilution of surface waters by meteoric water as compared to

groundwaters. Because many streams in PA are gaining streams, these observations also suggest that surface water trends are plausibly driven by groundwater contamination.

We also observed statewide that median [Ba] and [Sr] were higher within 1km of documented wellpad spills, and we identified significant increases in the concentrations of these ions correlated with higher spill density. The increases in concentration associated with spills were typically larger than the increases calculated for regressions versus proximity to or number of UOG wells alone. From this we infer that a subset of UOG wells that experienced spills may drive the regional correlations with UOG wells we identify. We emphasize spills as the likeliest pathway for salts to reach groundwater because we observed consistently significant relationships across multiple tests: comparison of medians, regressions with UOG density and distance, and fixed effects analysis. This observation suggests that surface impacts rather than downhole problems are responsible for groundwater salinization during UOGD.

To further test whether a surface source is the best explanation for the impacts we observe, we repeated our analyses considering only UOGD wellpads located at higher elevations than the respective water sample. We conducted this analysis because it is less likely that water samples could have been impacted by surface processes at a lower-elevation UOG wellpad due to the strong control of gravity on shallow groundwater flow in the Appalachian Basin[44,45]. When we consider only higher-elevation UOG wells, we observe that the effect of UOGD becomes even stronger: larger regression coefficients and increased significance for relationships between ion concentrations and UOG well density (Table S10). When only higher-elevation UOG wells are included in the calculation, we calculate 3.88 and 12.32 μg/L average increases in Ba and Sr based on the average density of higher elevation UOG wells, and 139 and 483 μg/L increases in Ba and Sr at the highest UOG well density. We similarly observe increased coefficients in

regressions analyzing only higher-elevation spills relative to those analyzing all spills (Table S11). As such, the strengthened relationship among UOGD and salt ion concentrations when only higher elevation wellpads are considered supports a surface source of contamination. The lack of significant positive relationships with casing/cementing violations further supports that surface sources of brine, rather than subsurface activities such as hydraulic fracturing, explain increased [Ba] and [Sr] nearby UOGD.

To further investigate the hypothesis that spills could explain increases in brine salt ions, we examined waste production data from UOG wells in proximity to water samples. Our working hypothesis was a greater volume of produced water may create more potential for mishandling and larger volumes of spillage when problems occur. Regressing log concentrations against log production volumes prior to water sample collection, we identify a significant increase in [Sr] associated with larger volumes of produced water at UOG wells within 1km of the respective water sample across PA and for [Ba] in SWPA (Text S7, Table S12).

While our data points to spills as a likely mechanism for increased salt ion concentrations in groundwaters, most wellpad spills are very small in volume.[4,13] For example, regulatory data indicate reported spills in PA are typically 100 L-10,000 L in volume.[13] A mass balance calculation informed by geological observations reveals that only produced water spills near the upper range of reported spill volumes (e.g., > ~1000 L) are likely to explain the average increase in [Ba] in groundwater we observe within 1km of UOG wells (Text S8). The salt contamination we observe is therefore most likely associated with the high-volume spills.

Although we wanted to assess local contamination on a spill-by-spill basis, spill volumes are not widely reported for violations cited by the PADEP: only 232 / 1338 spills catalogued up to 2014 include volume estimates.[4] If we nonetheless investigate those reported incidents and

define “large spills” as >250 gallons (~1000 L), we can calculate if large spills influenced [Ba] in the 102 or 1302 analyzed samples from nearby groundwater with respect to the two buffer distances, 1km or 3km respectively. We observed that the median [Ba] for samples within the buffer distance from large spills (137 µg/L for 1km or 131 µg/L for 3km) is ~23-24% higher than the median in samples over 1km or 3km from any reported spills (111 µg/L for 1km and 106 µg/L for 3km) (Table S13). Similar relationships were observed for the >500-gallon spills (Table S14) but the smaller number of documented >500-gallon spills (n = 63) yields statistical significance only for a buffer of 3km (where a larger number of samples, n = 902, are located within 3km of a >500 gallon spill vs. n = 77 samples within 1km).

The totality of these results leads us to attribute the slightly higher concentrations of brine salt ions in surface and ground waters near UOGD[25,26] to spills and leaks on wellpads. Consistent with this possibility, wastewater spills and leaks in some locations have resulted in well-documented increases in salt ion concentrations in nearby surface waters.[20,24,46] However, this is the first published study to document a regional impact of UOGD on water resources where evidence for the specific cause has also been identified.

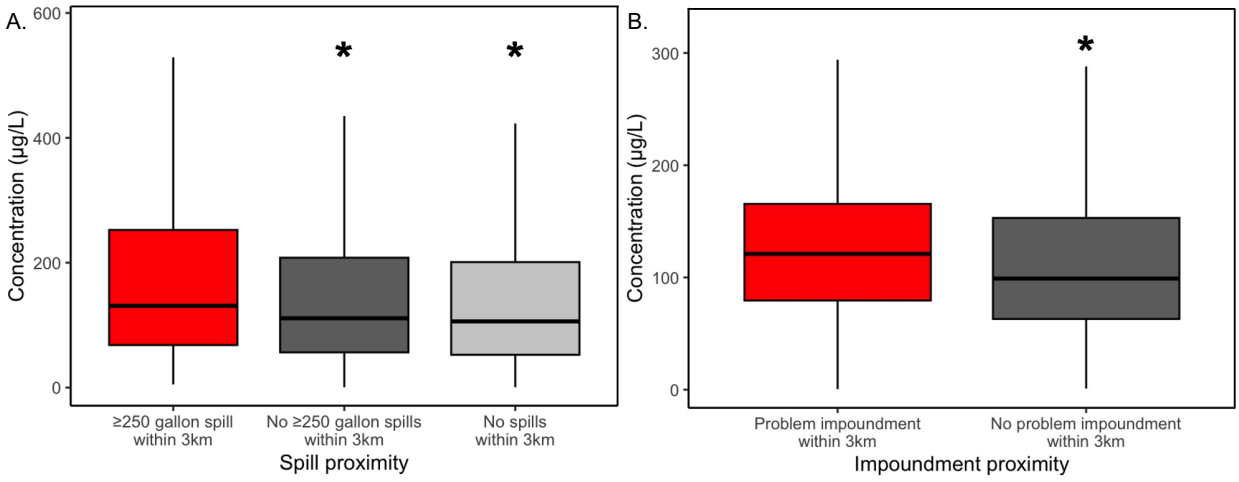

Figure 4: Box and whisker plots displaying barium concentrations for (A) samples within 3km of a large (≥250 gallon or 964L) spill vs. samples >3km from a large spill and samples >3km from any spill, and (B) SWPA samples within 3km of an impoundment that was mandated to close, upgrade, or store only freshwater by the PADEP as compared to SWPA samples >3km from these impoundments. In both A and B, a significant increase in median [Ba] was identified within 3km of the spills/impoundments, where an asterisk (*) denotes significant differences between sample groups relative to samples within 3km.

Wastewater impoundments may also release salt ions to groundwater

A second kind of spill or leakage may also have been important early in UOGD in PA, namely, leakage from impoundments of wastewaters. To investigate this, we considered correlations with the historical locations of wellpad impoundments (henceforth referred to as 2010 impoundments), which may have stored UOGD wastewaters (Text S1). Only these "2010 impoundments" were included because after 2016, temporary storage of wastewaters in wellpad impoundments was discontinued in PA.[47]

In particular, we observe the strongest evidence for impacts from these impoundments in SWPA, where [Ba] is significantly higher within 1km of 2010 impoundments and [Ba] increases with greater density and proximity of UOGD (Table S3, Table S6). This observation may also be supported by prior regulatory action surrounding problematic impoundments in SWPA. Specifically, because of observed or inferred infractions, 8 impoundments in SWPA were ordered by the PADEP in 2014 to i) be fully shut down, or ii) be upgraded with respect to liners and systems for leak detection, or iii) be limited to storage of only freshwater.[48] Additionally, the USEPA documented that Cl had likely leaked from one of these impoundments into downgradient groundwater at a location where significant health impacts were alleged.[49]

When we compare median [Ba] between SWPA samples within 1km of these 8 impoundments vs. samples >1km away, we find ~34% higher median [Ba] in samples within 1km of these impoundments (134 vs. 100 µg/L) (Table S15). We observe a similar increase when we compare median [Ba] across samples within 3km of an impoundment (123 µg/L) vs. samples >3km away (99 µg/L) (Figure 4B, Table S15). These differences are statistically significant within both 1km and 3km. Of further interest, one of these problematic impoundments is located within a previously identified subregion in SWPA where [Cl] increased with higher UOG well density.[26]

Regional differences in hydrogeology and land usage complicate identification of impact

We generally observed statistically significant relationships between [Ba] and [Sr] and UOGD density in SWPA but not in NEPA. This comparison of SWPA and NEPA is important not only because these subregions contain some of the highest density of UOGD in the world, but also because the data demonstrate how geology and land use combine to complicate the

detection of contamination during UOGD. In particular, SWPA and NEPA both support high density UOGD but differ with regard to the topographic relief (higher in NEPA) as well as the extent of prior hydrocarbon extraction (extensive legacy development in SWPA).[39]

The importance of topographic relief may explain why we observed increased significance in NEPA when we accounted for elevation or overlapping sources in our analyses. For example, when we investigated the association of salt ions with the density of UOG wells in NEPA, relationships were not statistically significant. However, when we considered only higher elevation UOG wells or implemented a fixed effects regression, increases in concentration associated with UOG density (Ba) and UOG distance (Ba and Sr) were of greater magnitude and statistically significant.

One explanation for these results is that strong topographic and geologic influence on brine salt occurrence in NEPA masks effects of UOGD in that region. In particular, where topographic relief is the highest (in NEPA), naturally elevated concentrations of species like Ba and Sr are generally observed in valley bottoms and other topographic lows.[30] This natural phenomenon has been attributed by some to upwelling of naturally occurring Appalachian basin brines from deeper than a few hundred meters depth into valleys.[30,50] An alternative explanation is that these natural brines were forced to migrate upward during tectonic orogeny in the deep geologic past, and although these brines are no longer migrating, the salts in the rock have not been completely flushed out yet.[39] Regardless of the explanation, natural brine migration may be or may have been particularly important in NEPA because of geologic features in that area such as anticlinal folding and faults.[19,29] While groundwater flow is still predominantly gravity-driven and brines can still occur at shallow depths in SWPA, topographic relief is smaller and the extent of surface faulting is more limited.[39,45] As a result, topographic forcing likely has a smaller

influence on groundwater chemistry in SWPA, with less differentiation between fresher (e.g., Ca-HCO_3 type) waters at high elevation and saltier (e.g., Na-Cl type) groundwaters at low elevations.[26,39] These hydrogeologic differences may serve to mask some of the impacts of brine spills on groundwater in NEPA compared to SWPA.

In addition to geogenic processes shaping groundwater chemistry, the long history of energy development in SWPA also complicates contaminant attribution. For example, our dataset shows significant increases in [Sr] and decreases in [Ba] associated with coal mining (Table S1). The increase in [Sr] nearby coal mining is not surprising because of the ubiquity of acidic mine drainage in the area and the likelihood that acids dissolve local carbonate bedrock, releasing Sr incorporated in the carbonate lattice during dissolution.[42] Lower [Ba] nearby coal mining may be explained by a) significantly higher median [SO_4] where coal mining is <1km from the water sample (likely reflecting sulfate produced via sulfide mineral oxidation, the driving force of acid mine drainage production) and b) the low solubility of Ba and SO_4 in co-solution.[51]

Despite such overlap, the significance of relationships between Ba and Sr and UOGD in SWPA persists after the implementation of fixed effects to control for overlapping anthropogenic sources of salts (Table S8, Table S9). In some cases, the impacts of UOGD on salt ion concentrations (particularly [Ba]) in groundwater appear strongest in SWPA, potentially implying that overlap with legacy hydrocarbon extraction may increase contamination during UOGD. However, our investigation also reveals that other attributes in SWPA (namely problematic impoundments) may explain why impacts sometimes appear greater. As such, we cannot conclude that overlap between UOGD and other forms of hydrocarbon extraction increases the frequency of contamination.

Environmental implications

Across the largest shale gas play with public access to high-density groundwater data in the world, UOGD is associated with slightly increased concentrations of brine salt ions in groundwater (this study) and surface waters (Bonetti et al.).[25] These regional impacts are best explained by a small subset of large spills or leaks that occurred at wellpads and impoundments. These incidents likely produce "hotspots" where concentrations of brine species increase nearby UOGD, explaining the regional effects.[26] The identified increases in [Ba] and [Sr] are low enough to not be associated with adverse health effects. For example, even at the highest UOGD density, our estimates suggest the average increases in [Ba] and [Sr] potentially attributable to UOGD should not exceed 15% of the United States Environmental Protection Agency (USEPA)'s recommended secondary maximum concentration levels for either species (2000 µg/L for [Ba], 4000 µg/L for [Sr]). To examine whether other species present in produced waters might have potential health effects even though they are not widely monitored or only reportable at very high concentrations in our data set, we investigated toxic trace elements (e.g., thallium, arsenic, cadmium) and radioactive species (radium). To do this, we examined the regional relationships among species concentrations in the USGS Produced Water database and [Ba] or [Sr]. Based on the median mass ratios of [X] to [Ba] or [Sr] (where X is one of the species measured in produced waters), other potentially hazardous species are also not likely to exceed USEPA limits at these levels (Table S16). As such, our estimates do not support widespread regional human health threats from groundwater salinization during UOGD. However, our work also shows that the regional concentrations are highly affected by localized contamination incidents. This is in-line with previous work that found increases in [Cl] per UOG well were over

10x greater in some geospatially-identified hotspots in SWPA than calculated regionwide.[26] Based on average produced water compositions in PA, mixing up to just 0.2% - 0.5% brine in more acutely-impacted water supplies could drive the concentrations of species including radium to exceed EPA limits.

Our study examined the largest shale gas play in the world where water quality data are publicly available. Given that spills and leaks are often associated with produced waters across major shale gas basins,[4,13] our study may help predict what is happening worldwide in similar plays where water data have not been released to the public. Small increases in salt concentrations in surface and groundwaters are likely to occur wherever large volumes of saline wastewaters are produced, and this occurs in every hydrocarbon basin (Text S9). The high production volumes and salinity of produced waters in other major shale gas plays[52] and similar frequencies of spills[4,13] supports the possibility of similar impacts across shale gas plays, and especially where very large spills have occurred.[13,24] As produced water volumes potentially exceed recycling and re-injection capabilities now and in the future,[53] our results also emphasize the need for stringent management of UOGD wastewaters to protect water resources.

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Supporting Information for **"Wastewaters co-produced with shale gas drive slight regional salinization of groundwater"**

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Table of Contents (10 supporting texts, 8 supporting figures, 31 supporting tables)

Supplementary Text

Text S1: Additional detail on datasets

Our primary dataset consists groundwater samples in the Shale Network database,[1] provided to Pennsylvania State University through an agreement with the regulator, the Pennsylvania Department of Environmental Protection (PADEP). This dataset comprises both previously published Shale Network data [2–4] as well as 2,542 previously unpublished analyses from NEPA and SWPA (now added to the Shale Network dataset). These samples were collected by certified environmental consultants (paid for by the gas companies) and analyzed by accredited commercial laboratories for release to the regulator. Each sample typically yields concentration data for ~40 analytes, including most major cations, anions, hydrocarbons (methane, ethane, propane), and BTEX (benzene, toluene, ethylbenzene, toluene), as summarized in Table S17. Additionally, a small subset of the dataset (n = 1,601 samples) derives from samples collected by the U.S. Geological Survey or PADEP between 1958 and 2000 from Lycoming and Mercer counties.[4,5] All data were cleaned and quality controlled through a previously outlined protocol.[3]

In additional to groundwater samples from the Shale Network database, we gathered additional spatial data from publicly available datasets for our analyses. The locations of unconventional wells and conventional wells were downloaded from the PADEP SPUD Data Report and coal mining areas from the PADEP Open Data Portal.[6,7] Violation data and waste production data for UOG wells were downloaded from the PADEP Oil and Gas Compliance Report and PADEP Oil and Gas Well Waste Report, respectively.[8,9] The locations of faults, synclines, and anticlines, as well as bedrock lithology, was downloaded from the USGS Pennsylvania Geologic Map database.[10] The locations of streams were obtained from the USGS NHDPlus HR Stream Order dataset for Pennsylvania, available from the Pennsylvania Spatial Data Access (PASDA) database.[11] The locations of highways (defined as primary/secondary roads) were downloaded from the U.S. Census Bureau TIGER/Line Shapefiles.[12] Finally, elevation data was downloaded using 3-meter DEM data from the PASDA database.[13]

In addition to regulatory data, we obtained the locations of UOG impoundments identified from 2010 satellite imagery by Skytruth.[14] The locations of these impoundments were identified from USDA aerial survey photography following outlined methods and QAQC protocols.[15] 2010 impoundments were selected because their construction predates a.) the collection of most samples in our dataset, and b.) updated regulations in 2016 that disallowed temporary storage of residual wastes at wellpads and strengthened permitting of centralized impoundments for wastewater storage.[16] As such, we considered these impoundments may be likeliest to show an impact in our dataset if wastewaters are escaping. We also considered locational and volume data for spills during UOGD in PA released as part of a prior analysis of regulatory data.[17] Finally, we compiled locational data for 8 impoundments in SWPA that were forced to shut down or modify their operations following an order from the PA DEP.[18] The exact

coordinates of these impoundments were not publicly released, thus we used coordinates from the closest identified or associated wellpads to extrapolate the locations of the impoundments (Table S18).

To calculate the Haversine distances between water samples in our dataset and UOG wells, conventional wells, and UOGD violations, we used the distm function in R 4.2.1. Our codes excluded any wells drilled or violations that occurred after the date the water sample was collected. The Haversine distances between water samples and other spatial features were calculated using the "Near" function in ArcGIS Pro. For spills in the Patterson et al. dataset, the exact date of the spill is unavailable, thus we excluded any spills that occurred after the year of sample collection in our calculations. For 2010 impoundments and the 8 impoundments in SWPA that were ordered by the PA DEP to shut down or modify their operations, we used 2010 and 2014 (the year of the DEP order) as the cut-off dates for the distance calculations.

To understand how relationships may geographically vary with different land use histories (which in turn depend upon geology), we classified samples in our dataset into three regions based on their somewhat unique geologies: northeastern PA (NEPA), southwestern PA (SWPA) and northwestern PA (NWPA). Samples were classified based on the county from which the sample was collected. We defined NEPA as Bradford County, Susquehanna County, Wyoming County, Sullivan County, Lycoming County, or Tioga County, defined SWPA as Greene County, Washington County, Beaver County, and NWPA as Mercer County. NEPA and SWPA have some of the highest densities of UOGD in the world, while NWPA (where the Marcellus Shale is much shallower) has only limited UOGD. Additionally, NEPA has higher topographic relief and a lower density of legacy hydrocarbon development (conventional oil and gas, coal mining); SWPA has lower relief and a higher density of oil/gas/coal development; and

NWPA has moderate relief, some of the shallowest oil and gas resources in the state, and hosts some of the oldest oil and gas wells in the world. Summary statistics for the calculated proximity of groundwater samples (both statewide and within these subregions) to UOG wells, UOG violations, and additional geologic and anthropogenic features considered are reported in Table S19-S21.

Text S2: Additional detail on analysis methods

Distributions of groundwater ion concentrations within the dataset are typically skewed rather than normal, with outlier values occurring at high concentrations, as is typically observed for groundwater ions.[19] In our comparison of different sample groupings, we therefore compare median rather than mean concentrations and utilize non-parametric comparisons such as the Wilcoxon–Mann–Whitney (WMW) rank sum test. For each analyte, 3.7% (Ba) to 6.7% (Sr) of samples are reported as non-detectable (ND), i.e., measured concentrations were below the reporting limit. To ensure our findings are robust, we compared medians after treating this censored data using different methods, detailed in Text S4. Results of median comparisons with a 1km buffer radius are described in the main text and Tables S3 and S4, results with a 3km buffer radius are presented in Tables S22 and S23.

To explore the quantitative relationship between UOGD activities and groundwater chemistry, we utilized regression modeling comparing ion concentrations to the proximity and density of UOGD. Given the skew in concentration distributions, we consider relationships between log concentrations (logC) and linear UOGD metrics. We confirmed based on an analysis of residuals and Q-Q plots that this log transformation is necessary for meaningful results. In the main text, we treat the concentrations of censored data as equal to the detection

limit. However, we also analyzed relationships using a Tobit regression, including a survival function to account for multiply left-censored data, and found it did not alter our conclusions (Text S4). Results of regression analyses using a 1km radius are discussed in the main text and presented in the Tables S5-S11, results using a 3km radius are presented in Table S24.

In our fixed effects modeling approach, we regressed the log concentrations of ions against the distance or density of UOG wells. A fixed effects model includes "dummy variables" to de-trend the data for potentially confounding overlap with other sources of geogenic or anthropogenic salt. As such, we assessed the relationship between groundwater ions and UOGD metrics using Equation S1 to de-trend for overlapping features:

$$\log C = \beta\ \mathrm{UOGD} + \mathrm{DV} + \varepsilon \qquad \text{Equation S1}$$

Here, C is the concentration of the ion of interest, β is the regression coefficient, UOGD is the UOGD-related metric of interest, DV represents fixed effect dummy variables included to de-trend the data for overlapping features, and ε is the standard error term. In particular, we used a fixed effects model to correct for proximity of water samples to coal mining, conventional oil and gas (COGD) wells, highways, anticlinal folds, geologic faults, and streams, as well as the primary bedrock lithology and seasonality. We selected these variables based on the potential for additional salt contamination in PA groundwater via coal mining, COGD, and road salting.[20,21] Faults are also well-established pathways for deep fluids and gases to migrate upwards into aquifers, especially in association with anticlines.[3,22] Finally, the proximity to streams allowed us to identify locations near valley bottoms or topographic lows, locations where natural brines, known to be present in the region at depths greater than several hundred meters, infiltrate into aquifers.[22,23]

To convert distance-based variables into binary variables appropriate for a fixed effects model, water samples were classified based on whether (or not) the sample is i) located within 1km of the feature of interest (coal mining, COG wells, highways, anticlines, faults), ii) located within 100m of a stream. In general, samples in our dataset had greater proximity to streams than other features considered (i.e., all samples in SWPA are <1km from a stream). Thus, we used a smaller radius to represent proximity to streams. To ensure a defensible selection of radii for these variables, we conducted sensitivity analyses. We confirmed that the value of the radius minimally affects the magnitude and significance of relationships with UOGD, provided that the radii is hydrologically plausible (Figure S7). Additionally, our model included categorical variables reflecting seasonality, i.e. whether the sample was collected during fall, winter, spring, or summer (to further control for road salting, as well as potential seasonal variability in species concentrations), and the primary bedrock lithology. In converting categorical variables into dummy variables, one was excluded as the base case to avoid multicollinearity effects. The fixed effect regression is represented using the following equation:

$$\log C = \beta 1\ \text{UOGD\#1km} + \text{COGD1km} + \text{CoalMining1km} + \text{anticline1km} + \text{fault1km} + \text{stream100m} + \text{highway1km} + \text{Lithology} + \text{Season} + \varepsilon \quad \text{Equation S2}$$

Dummy variables were added to detrend for conventional oil/gas wells (COGD1km), coal mines (CoalMining1km), anticlines (anticline1km), faults (fault1km) and highways (highway1km) within 1km and streams (a proxy for topographic lows) within 100 m (steam100m), as well as the primary bedrock lithology and the seasonality of the water sampling (Season).

Analyses in our main text were conducted in R (version 4.2.1). Comparisons of medians were conducted using the wilcox.test function in using the *stats* package (for Wilcoxon-Mann-Whitney rank sum tests) or the brunnermunzel.test function in the *brunnermunzel* package (for Brunner-Munzel tests). Regression analyses not utilizing a Tobit regression were conducted using the lm function in the *stats* package. Tobit regressions were run using the Surv function in the *survival* package.

Text S3: Comparison of median concentrations across hydrocarbon-related land uses

To understand how to detect contamination from produced waters, we first investigated how legacy hydrocarbon extraction such as coal mining and conventional OGD has impacted groundwaters and in turn may be interacting with UOGD. We considered Ba, Ca, Cl, Na, Sr, and sulfate (SO_4), all of which are widely analyzed in our dataset (25,878, 27,033, 27,599, 27,279, 17,649, and 27,315 analyses, respectively). All except SO_4 are present at high concentrations in UOG wastewaters.[24] While [SO_4] is not typically elevated in UOG produced waters, it is characteristically elevated in coal mine drainage,[25] which we wanted to ensure did not confound our analyses. Br is also well-established as an effective tracer for oil & gas wastewater, but it is both rarely analyzed and detected above reported limits in our dataset (527 / 4,745 total analyses above reporting limits), and thus we did not consider it suitable for our analyses. We conducted this analysis using samples from SWPA, where the overlap of these activities is especially frequent.

We compared median concentrations between i) samples with no current or prior hydrocarbon extraction within 1km and ii) samples with hydrocarbon extraction within 1km. Samples were grouped into 8 categories that included “control” (no UOGD, COGD, or coal

mining <1km from the sample at the time of collection), or the 7 permutations related to UOGD ± COGD ± coal mining based on presence or absence within 1km. For these tests, we compared concentrations of Ba, Ca, Cl, Na, Sr, and SO_4 between the control and the 7 hydrocarbon-related land uses using tests appropriate for non-parametric data, the Wilcoxon-Mann-Whitney and Brunner-Munzel tests (Table S1).

Median [Sr] was significantly higher compared to the control group in areas where UOGD or coal mining occurred within 1km (Table S1). The largest difference was observed where UOGD, COGD, and coal mining overlap. Median [Ba] is significantly higher where UOGD, UOGD+COGD, and UOGD+COGD+coal mining occur within 1km, although increases in median [Ba] are smaller where UOGD overlaps with coal mining (Table S1). In contrast to [Sr] and [Ba], the significance of differences between hydrocarbon and non-hydrocarbon land uses was inconsistent for [Na] and [Cl]. Median [Na] is higher with coal mining within 1km, but UOGD and COGD land uses are not associated with significantly higher [Na] unless they overlap with coal mining. Additionally, UOGD, UOGD + COGD, and UOGD + coal mining all showed significantly higher median [Cl] than the control group, but the increase in [Cl] for the UOGD + COGD + coal mining land use was not significant. Finally, [Ca] was significantly higher in all groups except COGD, whereas [SO_4] was higher with coal mining within 1km and lower in the UOGD and COGD groups.

Text S4: Treatment of censored data

While most measurements of Ba and Sr are above detection limits (96.3% and 93.3%, respectively), a small portion are censored (i.e., below detection/reporting limits). Further, because the samples in our data set were analyzed across multiple commercial laboratories,

reporting limits are not consistent across all censored samples (i.e., the data is multiply censored). In the main text, we treated censored data as equivalent to the detection limit. To ensure our findings were robust, we tested different treatments of censored data in our comparison of medians and regression analyses.

For our comparison of medians, we first treated censored data as equal to the reporting limit (as presented in the main text). To ensure our results were robust, we also calculated medians and explored whether differences across groupings were significant using different treatments of censored data. Specifically, we investigated a "minimum impact" scenario in which censored samples <1km from the feature of interest were set equal to 0 and censored samples >1km were set equal to the reporting limit and a "maximum impact" scenario in which samples <1km were set equal to reporting limits and samples >1km were set equal to 0. Across all scenarios, our results did not change from the values reported in Tables S3 and S4.

To examine how censored data may influence our regression analyses, we also considered correlations using a Tobit regression with a Gaussian survival function to account for our left-censored data (Tables S24-S26). Within a 1km radius, previously insignificant negative correlations between [Ba] and casing violation density statewide, as well as casing violation and 2010 impoundment density in NEPA, become statistically significant negative correlations. No significant positive correlation identified in the main text loses statistical significance. With a 3km radius, positive correlations in NEPA between [Sr] and UOG well density and [Ba] and casing violation density become statistically significant. However, positive correlations between [Ba] and a.) impoundment violation density statewide and in NEPA, b.) 2010 impoundment density in NEPA, and c.) spill density in NEPA, as well as [Sr] and impoundment violation density statewide, are no longer statistically significant. From the Tobit regression analysis, we

conclude that our primary conclusions from the regression analyses presented in the main text (spills are the primary driver of increasing salt ion concentrations) are unchanged by the handling of censored data.

In addition to censored data, 7 samples from Lycoming County report strontium concentrations of 0. When converting strontium concentration to log units, we uniformly added a small value (0.0001 mg/L) to all samples to address these samples. This addition did not alter any of our interpretations, and ensures these samples are not discarded.

Text S5: Relationships between chloride concentrations and UOGD metrics

We did not focus extensively on chloride (Cl) in our analyses, in part because it is more frequently censored than Ba and Sr in our dataset and in part because it can also be released to the environment through common sources beyond hydrocarbon extraction including road salting and sewage. However, we repeated a subset of analyses using [Cl] as a check that our interpretation of Ba and Sr sources reflects brine-derived rather than other geologic sources of Ba and Sr. Specifically, we investigated relationships between log[Cl] and UOG well density, UOG well distance, spill density, and spill distance for the full statewide, NEPA, and SWPA datasets (Table S28). We investigated these relationships using only a tobit regression (Text S4).

Our results were largely consistent with observations made for Ba and Sr. We observed statistically significant relationships between [Cl] and UOG well density, spill density, and spill distance statewide. We calculated larger coefficients and smaller p-values for relationships with spills compared to all UOG wells. We identified significant increases in [Cl] associated with UOG well density, UOG well distance, and spill density in SWPA, but no significant increases in

NEPA. This observation is largely consistent with previously identified strong topographic controls on [Cl] in Bradford County (NEPA) but not SWPA.[2]

Text S6: Estimating the Akritas-Theil-Sen slope

If we wish to calculate the increase in a species' concentration associated with an increase in UOGD density within a given radius, we must do so using methods appropriate for non-parametric data. For example, a linear regression is not appropriate for our highly skewed concentration data without log-transforming concentrations, at which point the slope is no longer directly interpretable as the increase in concentration relative to an increase in well density. One method capable of estimating this for data that is both censored and non-parametric is the Akritas-Theil-Sen (ATS) slope. Unfortunately, we found that widely available methods capable of calculating the ATS slope (alongside its associated intercept, p-value, and Kendall's tau) were not capable of handling the size of our full data set. These included the cenken function in the R package *NADA*, the ATS and ATSmini functions in the R package *NADA2*, and a custom-written python function. As such, we sought to instead estimate the ATS slope using an ensemble calculation with randomly selected subsets of the full dataset.

To attempt to validate this method, we calculated a "true" value for slope, intercept, p-value, and Kendall's tau for [Ba] vs. UOG well density within a randomly selected subset of 7,000 samples using the cenken function in R. Next, we attempted to replicate these values using calculated mean and median values from the ensemble output of 3 randomly selected, 2,400-sample subsets of the 7,000-sample dataset. We also tested using a 9 x 1,200-sample ensemble, with subsets selected by first generating 3, 2,400-sample subsets and subsampling each 2,400-sample subset to select 3, 1,200-sample subsets. The mean and median values using both

approaches replicated ATS slope, intercept, and Kendall's tau within one standard deviation of the true value, with the larger sample size ensemble (3 x 2,400-sample) performing slightly better (Table S29). However, p-values were a poor match, with estimated p-values exceeding the true value. From this, we surmise that an ensemble calculation can effectively estimate ATS slope, intercept, and Kendall's tau, but may overestimate p-values (i.e., understate statistical significance), particularly in smaller subsets.

Within our dataset, we calculated estimates for Kendall's tau, ATS slope, intercept, and p-value for [Ba], [Sr], and [Cl] vs. the density of UOG wells and spills within 1km (Table S30, Table S31). We did so using two separate ensemble calculations. First, we randomly selected 3, 6,000-sample subsets from each data set and ran the calculation for these 3 subsets. Next, we randomly selected 3, 9,000-sample subsets and then subsampled 3, 3,000-sample subsets from each 9,000-sample subset (for a 9 x 3,000-sample ensemble). Values for the slope, intercept, Kendall's tau, and p-value were typically within error across these two approaches (Table S30, Table S31).

Based on our ensemble calculations of ATS slope, we estimate a 2.2 – 2.6 μg/L increase in [Ba], 6.1 – 8.2 μg/L increase in [Sr], and 202 – 250 μg/L increase in [Cl] per additional UOG well within 1km (Table S30, Table S31). We estimate a 5.8 – 6.4 μg/L increase in [Ba], 12 – 23 μg/L increase in [Sr], and 120 – 289 μg/L increase in [Cl] per additional spill within 1km (although we note poor p-values for the [Cl] calculation).

Text S7: Correlations between brine salt species and waste production at nearby UOG wells

Using UOG well waste production data from the PA DEP, we investigated whether [Ba] and [Sr] increased in water samples with greater waste production at nearby UOG wells. For this

analysis, we calculated the cumulative waste production up to the year of sample collection at UOG wells within 1km of a water sample. Due to large skew in the surrounding production volumes across samples, we log-transformed waste production volumes before regressing against log[Ba] or log[Sr]. Because some samples have 0 waste produced within 1km prior to sample collection, we added a uniform value (0.0001 tons) to the waste production values for all samples in order to convert to log scale. Our results indicate significantly increased [Sr] statewide with greater waste production volumes within 1km, and significantly higher [Ba] and [Sr] in SWPA (Table S12). All other correlations were positive (i.e., concentrations increase with more waste produced within 1km) but not statistically significant.

Text S8: Determining spill volumes necessary for a slight increase in barium concentrations within 1km

To investigate whether the increases in brine salt concentrations we observe is consistent with potential effects of spills, we set up a back of the envelope calculation to test if spill volumes reported in regulatory data could plausibly produce the increases we observe. We used Ba as a test species, and used the average [Ba] (2,252 mg/L) in Pennsylvania shale gas produced waters in the U.S. Geological Survey Produced Waters database[26] as a representative concentration of Ba in spilled produced water.

Next, we calculated the volume of water contained within a theoretical parcel of groundwater within 1km of a wellpad. To do this, we calculated the volume of a cylinder with a radius of 1000m and a depth of 24m (assuming the well depth is 30m with a 6m vadose zone). Within this volume, we assumed a porosity of 10%, approximately within the range associated with sedimentary formations in Pennsylvania.

Based on this concentration of Ba and volume of groundwater, we calculated the increase in Ba following a 100L and 10,000L spill, the lower and upper bounds of typical spills in PA [27]. We calculate a 0.3 µg/L increase in Ba following a 100L spill and a 30 µg/L increase following a 10,000L spill. As such, the intermediate to upper end of spill volumes are consistent with the range of increases in Ba we calculated in our analyses.

In actuality, the transport of spilled wastewater from a wellpad to a drinking water source likely follows preferential pathways such as a fracture.[22,28] The even mixing across a relatively large area assumed in our model could thus an underestimate of the effects of a spill.

Text S9: Implications for groundwater impacts across shale gas basins and the future of wastewater management

While the increases in groundwater salt ion concentrations we document focused on one major shale gas basin, multiple lines of evidence suggest this phenomenon could occur across shale gas basins. For example, production volumes and total dissolved solids of produced waters from other major U.S. plays such as the Bakken and Eagle Ford are comparable to or greater than Marcellus Shale produced waters,[29] pointing to the possibility of similar groundwater impacts where incidents occur. Further, spills are common incidents across shale gas plays[17,27] and leakage from wellpad impoundments has been observed across the U.S.[30–32] Finally, increases in surface water salt ion concentrations with higher UOGD density in watersheds has been observed nationwide, and our results suggest these increases could be explained by localized increases in groundwater salt concentrations from spills.[33] However, the magnitude of impacts from wastewater mishandling is also a function of regional hydrogeology. In some areas such as the Bakken shale play in North Dakota and Montana, U.S., groundwater flow velocities

are likely slow enough to significantly limit the transport of salt ions from wellpads into more distant water supplies.[34]

While produced water is widely recycled for reuse in hydraulic fracturing fluids, future projections suggest produced water volumes will exceed water demand for hydraulic fracturing in major U.S. shale plays.[35] Other methods for handling produced water, such as reinjection via disposal wells or beneficial reuse, may be restricted by induced seismicity concerns and technological limitations.[29,36,37] As such, slowdowns in the rate at which new wells are hydraulically fractured could produce significant accumulations of produced water.

Text S10: Explanations for inverse relationships between groundwater species concentrations and UOGD

In some cases, we calculate significant decreases in species concentrations associated with UOGD. For example, median [Sr] is lower within 1km of casing violations across our data set, and median [Sr] is significantly lower within 1km of casing violations and 1km of 2010 impoundments in NEPA (Table S4). In our regression analyses, the only significant correlations we identified in NEPA were significant decreases in [Sr] associated with greater density of casing/cementing violations and 2010 impoundments (Table S7).

These negative correlations may reflect influences of background hydrologic processes. Specifically, UOG wellpads tend to be drilled near topographic highs in the Appalachian Basin (in part to avoid destruction of wetlands, which are more often found at topographic lows where water is more abundant, during wellpad construction). In contrast, brine salt species such as [Ba] and [Sr] tend to be naturally elevated in valley bottoms.[38] As such, if UOGD is not impacting groundwater chemistry, it may be expected that samples not located nearby UOGD (i.e., in

valley bottoms) may show higher [Ba] or [Sr]. We saw the strongest indication of this in NEPA, where these topographic effects are more pronounced.[38] Additionally, negative correlations were often associated with casing/cementing violations. While we consider this a less likely explanation, it is perhaps possible that contaminant leakage from poorly cased or cemented wellbores in the subsurface (as opposed to surface spills or leaks from impoundments) could travel further from the wellpad, leading to higher concentrations further from UOGD.

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Supporting Figures

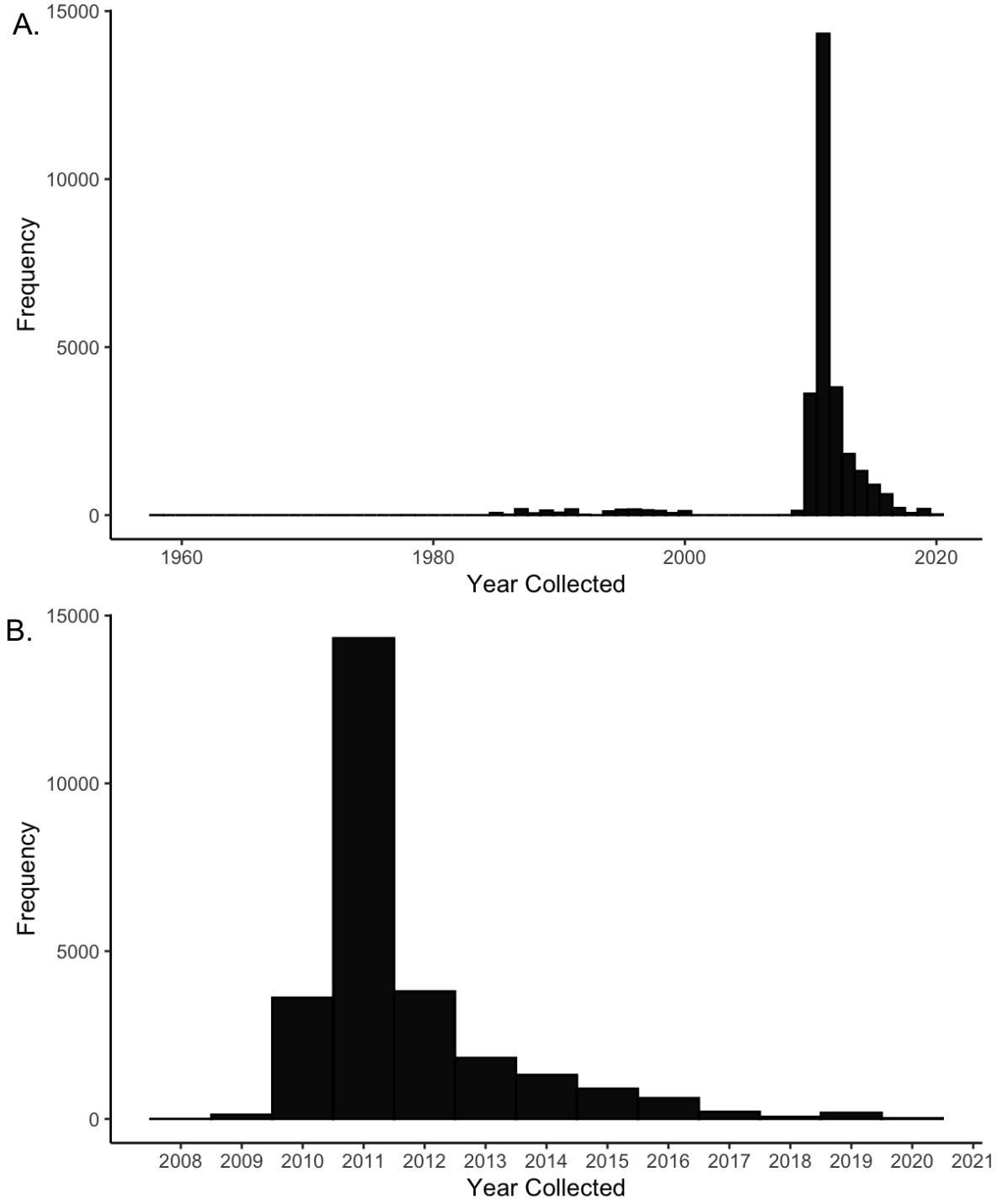

Figure S1: Histogram of groundwater sample collection years for A. the full dataset and B. just pre-drill samples

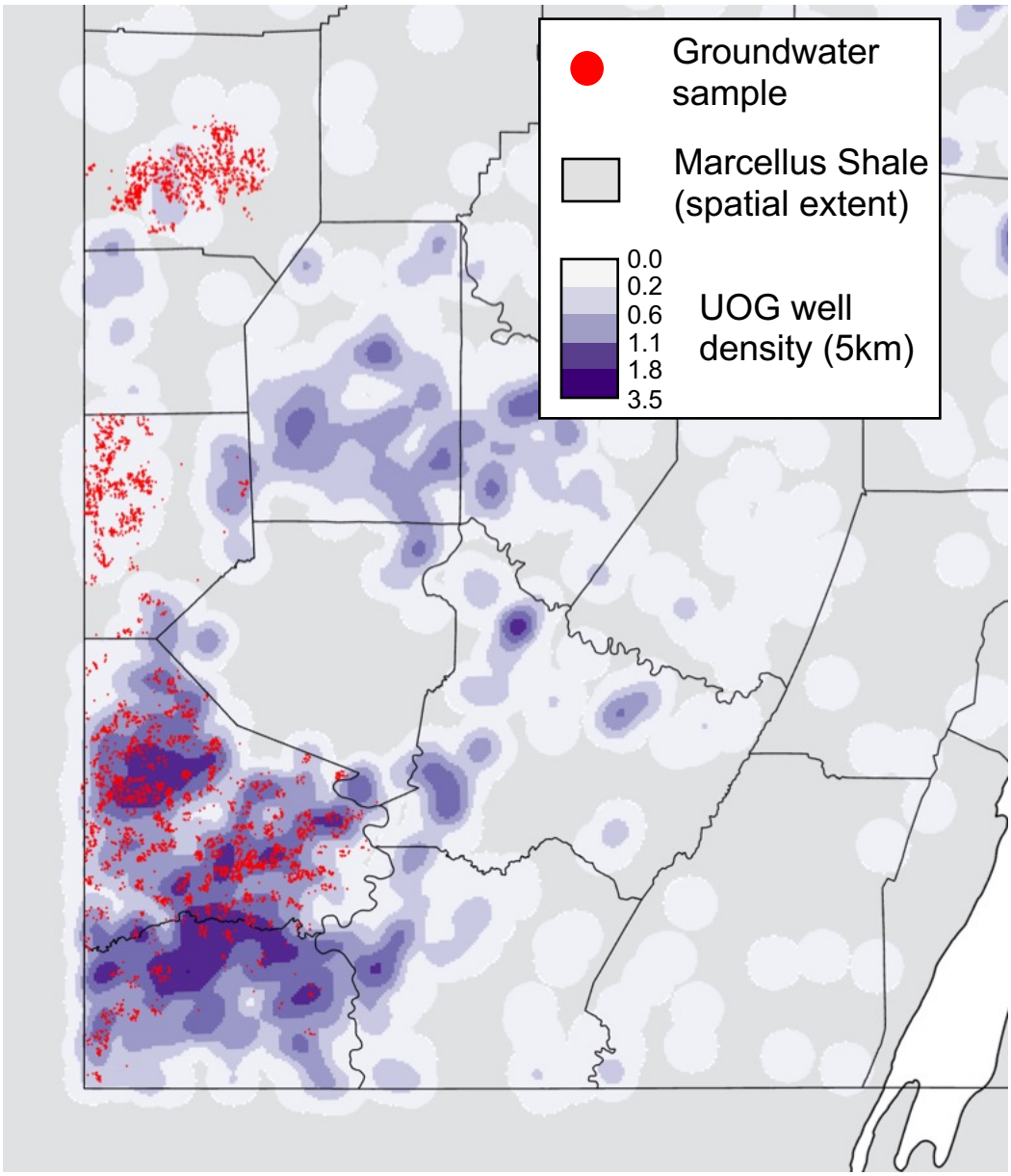

Figure S2: Inset on western PA from Figure 1

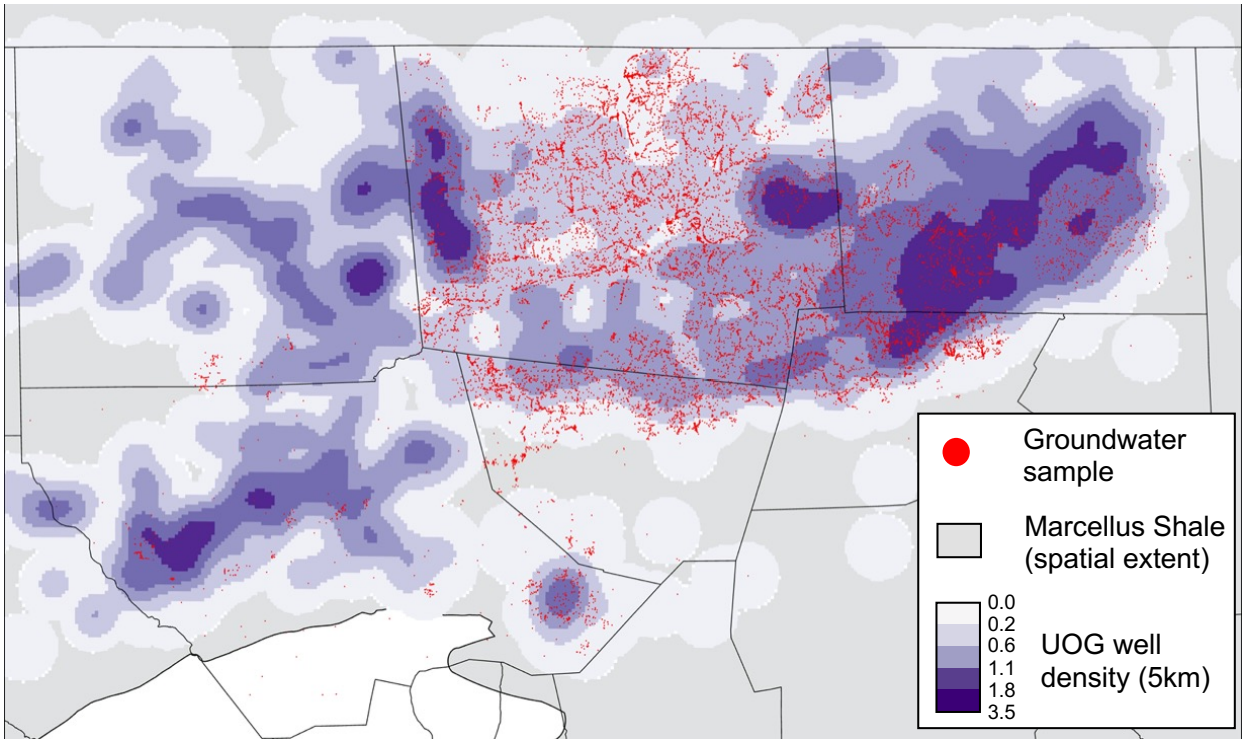

Figure S3: Inset on NEPA from Figure 1

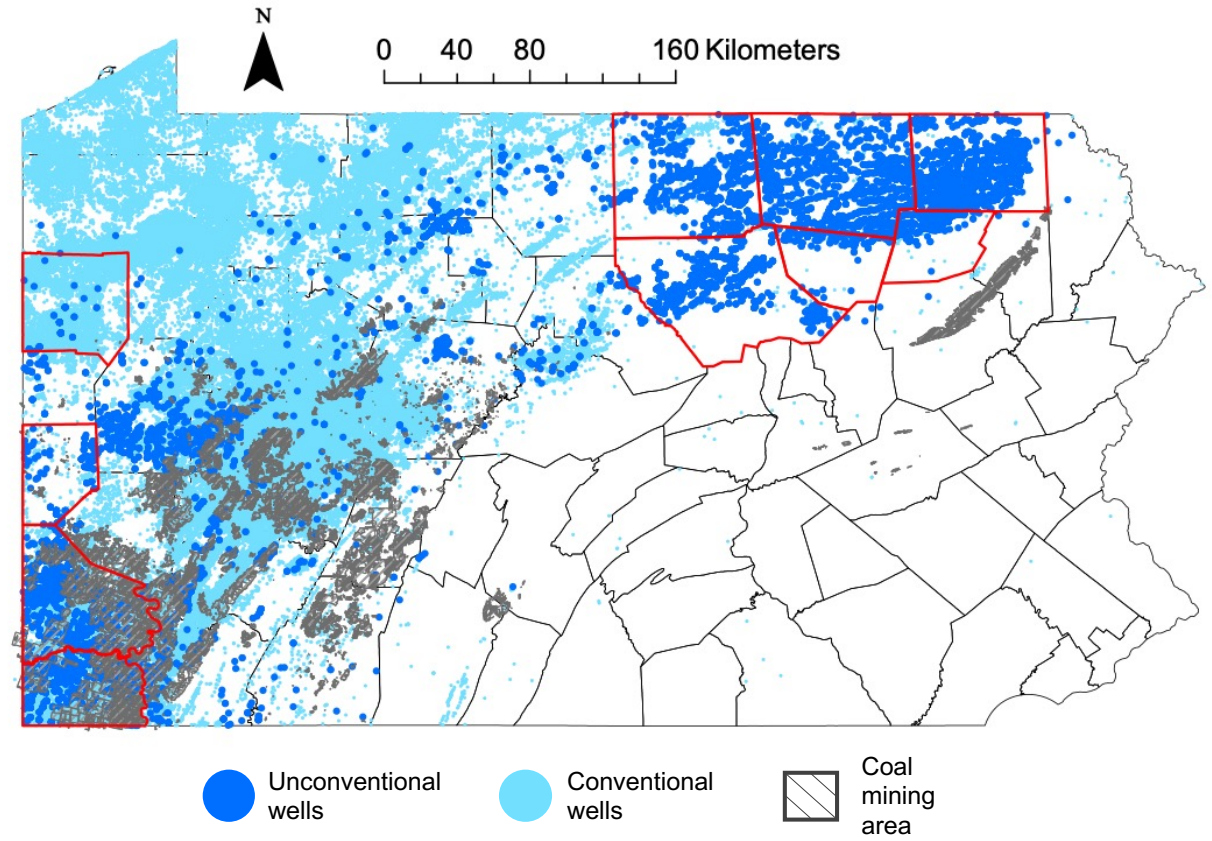

Figure S4: Map of UOG wells (dark blue), COG wells (light blue), and coal mining areas (gray) in PA. Counties included in the study are highlighted in red.

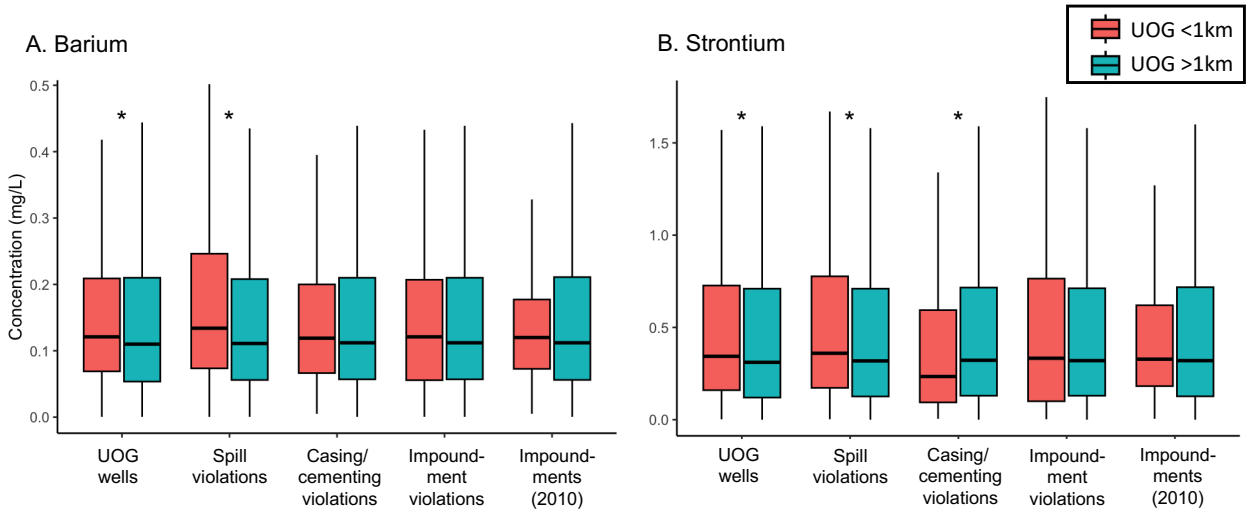

Figure S5: Comparison of median A. barium concentrations and B. strontium concentrations across all the UOG activities considered.

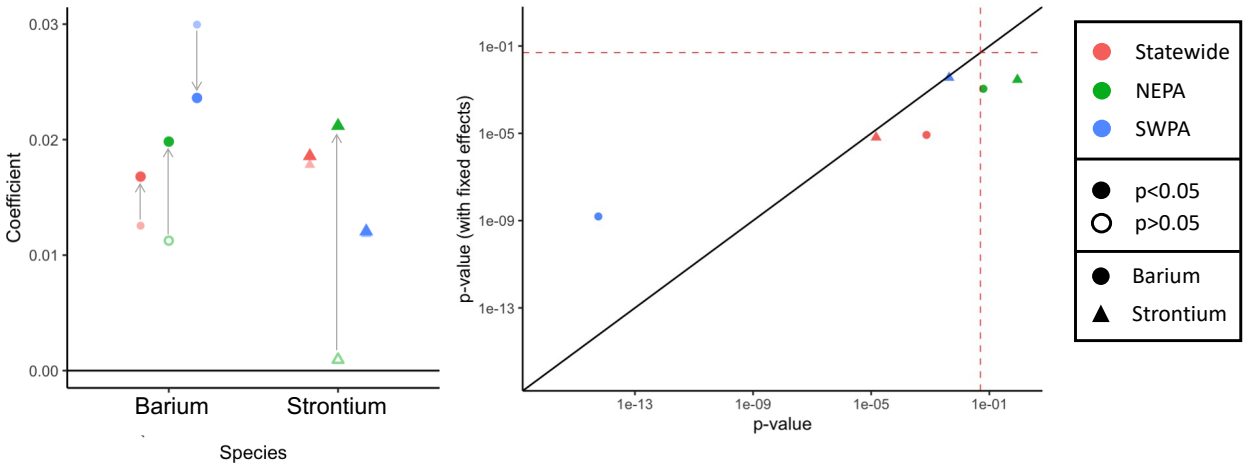

Figure S6: A. Regression coefficients for UOG well density within 1km vs. concentrations of barium and strontium, with and without fixed effects. Arrows depict the change in coefficient between linear regression and fixed effect regressions. B.) p-values with and without fixed effects included. Red lines indicate p = 0.05 for their respective axes, and the solid black line indicates a 1:1 ratio between models. Correlations are strengthened with fixed effects included in all cases except [Barium] in SWPA.

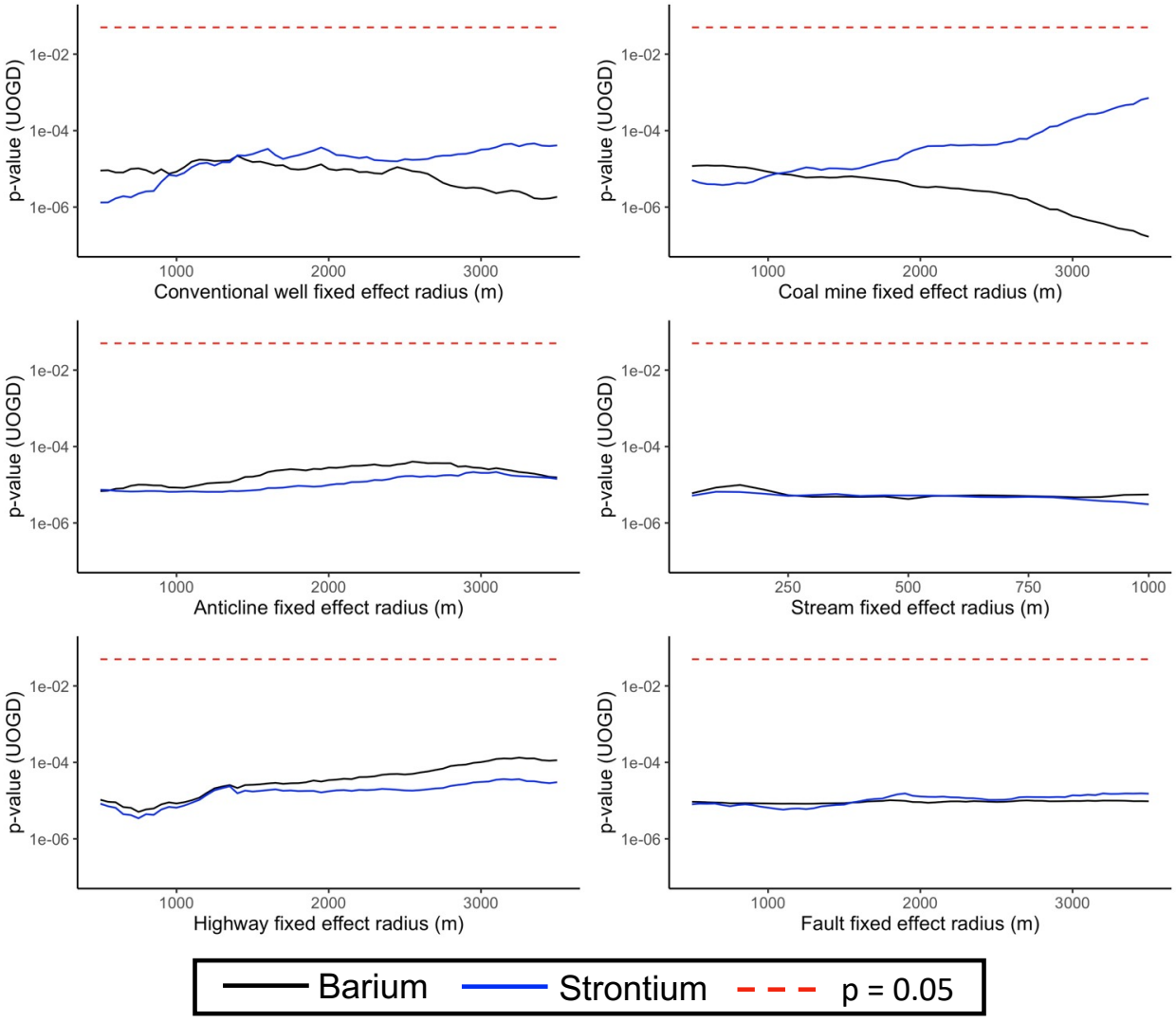

Figure S7: p-values calculated [Ba] and [Sr] vs. UOG well density (1km radius) using our fixed effects equation, varying the radius used to control for COG wells, coal mining, anticlines, streams, highways, and faults between 500m to 3500m (due to higher stream density, a smaller range of 50-1000m was tested). In all cases, the statistical significance of correlations between [Ba] and [Sr] and UOG well density persists regardless of the radius used. 500m was selected as a minimum radius due to small sample sizes for samples <500m from these features, whereas 3500m was selected as a maximum radius.

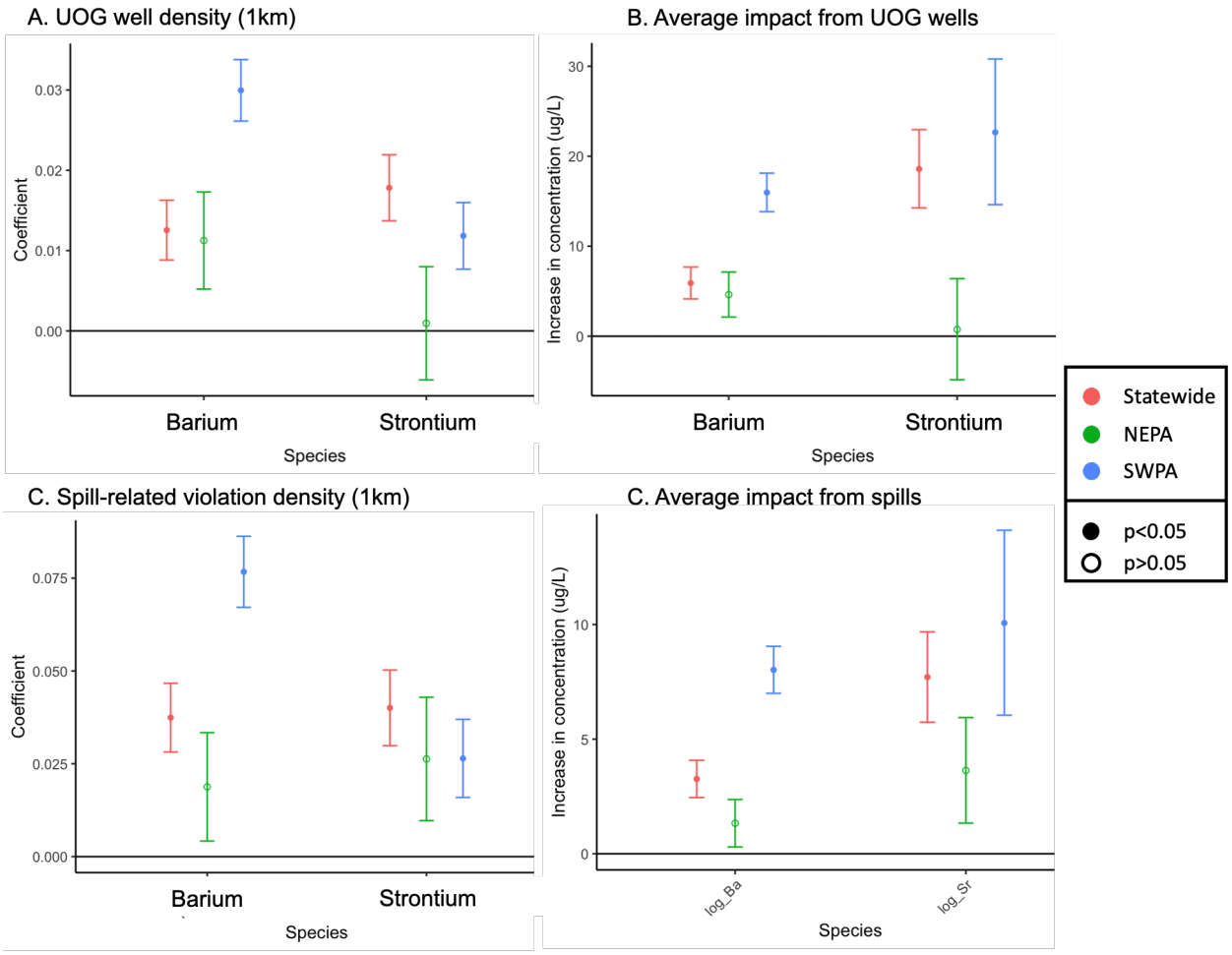

Figure S8: Correlation coefficients for regressions analyzing the relationship between log[barium] and log[strontium] and UOG well density within a 1km radius of water samples (A), as well as the average increase in species concentration calculated for using Equation 3 based on average concentrations and UOG density. Coefficients (C) and average increases (D) calculated for spill-related violation density within 1km are also shown. For each species, correlations and increases calculated for the full dataset ("Statewide"), as well as subregions NEPA and SWPA are shown. Error bars correspond to standard error. Solid circles correspond to statistically significant ($p < 0.05$) correlations, while hollow circles correspond to insignificant correlations.

Supporting Tables

Table S1: Comparison of median concentrations across different hydrocarbon land use classifications relative to samples without hydrocarbon extraction within 1km

Species	Land Use	p-value (WMW)[1]	p-value (BM)[2]	Median (mg/L)	Control group median (mg/L)	Confidence[4]
Barium	UOGD	1.4E-17	0.00E+00	0.124	0.1	***
	COGD	5.0E-01	5.05E-01	0.096		
	UOGD+COGD	9.4E-04	7.86E-04	0.112		***
	UOGD+COGD+CM	2.2E-02	1.51E-02	0.102		*
	UOGD+CM	1.8E-01	1.72E-01	0.098		
	COGD+CM	5.7E-02	5.05E-02	0.0915		
	CM	5.1E-01	5.06E-01	0.098		
Calcium	UOGD	1.6E-13	1.98E-13	75.3	60.33	***
	COGD	1.2E-01	1.11E-01	60.35		
	UOGD+COGD	6.9E-05	2.42E-05	77.3		***
	UOGD+COGD+CM	2.4E-11	6.67E-13	72.5		***
	UOGD+CM	1.1E-12	7.62E-14	73.5		***
	COGD+CM	8.8E-14	1.93E-14	74.7		***
	CM	2.3E-14	1.42E-14	71.9		***
Chloride	UOGD	3.9E-03	4.12E-03	11.7	10	***
	COGD	2.8E-01	2.61E-01	7.44		
	UOGD+COGD	2.2E-02	9.38E-03	12		**
	UOGD+COGD+CM	8.3E-02	6.02E-02	11		
	UOGD+CM	1.1E-07	4.63E-08	14		***
	COGD+CM	1.9E-04	1.31E-04	11.9		***
	CM	6.3E-01	6.26E-01	9.5		
Sodium	UOGD	2.7E-01	2.74E-01	9.16	11.6	
	COGD	1.0E-02	1.06E-02	8.987		*
	UOGD+COGD	8.8E-01	8.66E-01	11.3		
	UOGD+COGD+CM	4.8E-04	1.42E-04	13.869		***
	UOGD+CM	9.2E-04	5.87E-04	14.4		***
	COGD+CM	4.8E-05	2.75E-05	13.415		***
	CM	1.4E-02	1.41E-02	12.711		*
Strontium	UOGD	2.8E-05	1.73E-05	0.333	0.299	***
	COGD	1.5E-01	1.52E-01	0.264		
	UOGD+COGD	3.3E-06	2.08E-06	0.385		***
	UOGD+COGD+CM	2.2E-22	0.00E+00	0.495		***

	UOGD+CM	4.5E-13	1.84E-13	0.378		***
	COGD+CM	1.2E-17	0.00E+00	0.41		***
	CM	5.1E-24	0.00E+00	0.42		***
Sulfate	UOGD	1.8E-05	1.17E-05	32.8	34	***
	COGD	1.1E-12	4.57E-14	29		***
	UOGD+COGD	1.4E-01	1.36E-01	34		
	UOGD+COGD+CM	3.3E-08	3.89E-08	38.6		***
	UOGD+CM	6.9E-03	7.50E-03	37.8		**
	COGD+CM	2.1E-17	0.00E+00	41.8		***
	CM	8.8E-08	8.07E-08	38		***

1. Calculated using a two-sided Wilcoxon–Mann–Whitney test
2. Calculated using a two-sided Brunner-Munzel test
3. Significance corresponds to p-values calculated using the Brunner-Munzel test
4. * = 95% confidence, ** = 99% confidence, *** = 99.5% confidence

Table S2: Classification of violations into the three classes considered in this study, adapted from Brantley et al. (2014). Bolded violations represent violations newly added to the respective class for this study.

Violation Type	PADEP Violation Code
Casing/cementing violations	207B - Failure to case and cement to prevent migrations into fresh groundwater
	78.73A - Operator shall prevent gas and other fluids from lower formations from entering fresh groundwater.
	78.73B - Excessive casing seat pressure
	78.74 - Hazardous well venting
	78.81(b) - The operator failed to drill through fresh groundwater zones with diligence and as efficiently as practical to minimize drilling disturbance and commingling of groundwaters.
	78.81D1 - Failure to maintain control of anticipated gas storage reservoir pressures while drilling through reservoir or protective area
	78.81D2 - Failure to case and cement properly through storage reservoir or storage horizon
	78.83A - Diameter of bore hole not 1 inch greater than casing/casing collar diameter
	78.83COALCSG - Improper coal protective casing and cementing procedures
	78.83GRNDWTR - Improper casing to protect fresh groundwater
	78.84 - Insufficient casing strength, thickness, and installation equipment
	78.85 - Inadequate, insufficient, and/or improperly installed cement
	78.86 - Failure to report defective, insufficient, or improperly cemented casing w/in 24 hrs or submit plan to correct w/in 30 days
	79.12CW - Insufficient casing, BOP, cement or wait on cement to prevent waste from conservation well.
Impoundment violations	78.56(1) - Pit and tanks not constructed with sufficient capacity to contain pollutional substances.
	78.56(2) - Failure to maintain 2 ' of freeboard in an impoundment.
	78.56(3) - Impoundment not structurally sound, impermeable, 3rd party protected.
	78.56FRBRD - Failure to maintain 2' freeboard in an impoundment
	78.56LINER - Improperly lined pit
	78.56PITCNST - Impoundment not structurally sound, impermeable, 3rd party protected, greater than 20" of seasonal high ground water table
	78.57C2 - Failure to construct properly plug, frac, brine pits
	91.35IMPOUND - Adequate impoundment freeboard was not maintained.
Spill violations	208A - Failure to restore a water supply affected by pollution or diminution
	301CSL - Stream discharge of IW, includes drill cuttings, oil, brine and/or silt
	301UNPMTIW - Industrial waste was discharged without permit.
	307CSL - Discharge of industrial waste to waters of Commonwealth without a permit.
	401CAUSEPOLL - Polluting substance(s) allowed to discharge into Waters of the Commonwealth.
	401CLS - Discharge of pollultional material to waters of Commonwealth.
	401CSL - Discharge of pollultional material to waters of Commonwealth.
	402611 - Failure to meet effluent limits of permit
	691.401WPD - Failure to prevent sediment or other pollutant discharge into waters of the Commonwealth.
	691.402WPP - Site conditions present a potential for pollution to waters of the Commonwealth.
	78.51(A) - Failure to restore or replace an impacted water supply.
	78.51(H) - Failure to report receipt of notice from a landowner, water purveyor or affected person that a water supply has been affected by pollution or diminution, to the Department within 24 hours of receiving the notice.
	78.57(a) - Operator failed to collect the brine and other fluids produced during operation, service and plugging of the well in a tank, pit or a series of pits or tanks, or other device approved by the Department or Operator discharged brine or other fluids on or into the ground or into waters of the Commonwealth.
	78.57(A)* - Discharge of brine and other fluids on or into the ground or into the waters of the Commonwealth without a permit.
	78.54 - Failure to properly control or dispose of industrial or residual waste to prevent pollution of the waters of the Commonwealth.
	78.60B - Top hole water discharged improperly

	78.61A - Improper pit disposal of drill cuttings from above the casing seat
	78.62 - Improper encapsulation of waste
	78.64 - Inadequate containment of oil tank
	78.66A - Failure to report release of substance threatening or causing pollution
	78.66BRINE - Failure to report a reportable release of brine to DEP within 2 hours.
	78a66(b)1i - Operator or other responsible party failed to report a spill or release of a regulated substance causing or threatening pollution of the waters of this Commonwealth, in the manner required by 25 Pa. Code ¬ß 91.33 (relating to incidents causing or threatening pollution).
	91.33A - Failure to notify DEP of pollution incident. No phone call made forthwith
	91.33B - Failure to take measures to mitigate spill impact and/or clean up w/in 15 days
	91.33POLLINC - Pollution incident was not reported to DEP.
	91.34A - Failure to take all necessary measures to prevent spill. Inadequate diking, potential pollution
	91.34(B) - Failure to submit a report or plan, within the time specified in the Department notice, setting forth the nature of the activity and the nature of the preventative measures taken to prevent the substances from directly or indirectly reaching waters of this Commonwealth, through accident, carelessness, maliciousness, hazards of weather or from another cause.
	92A.3 - Discharge of pollutants from a point source into surface waters without NPDES permit.
	92.3 - Discharge of pollutants from a point source into surface waters without NPDES permit.
	CSL201BYPASS - Untreated or inadequately treated sewage was discharged
	CSL401 - Unauthorized, unpermitted discharge of polluting substances to waters of the Commonwealth resulting in pollution
	CSL401CAUSPL - Polluting substance(s) allowed to discharge into Waters of the Commonwealth
	CSL 402(b) - POTENTIAL POLLUTION - Conducting an activity regulated by a permit issued pursuant to Section 402 of The Clean Streams Law to prevent the potential of pollution to waters of the Commonwealth without a permit or contrary to a permit issued under that authority by the Department

Table S3: Comparison of median barium concentrations (in µg/L) across samples ≤1km and >1km from UOGD parameters

Species	Region	UOG parameter	Median (≤1km)	Median (>1km)	Difference	2-sided p-value (WMW)[1]	1-sided p-value (WMW)[2]	2-sided p-value (BM)[3]	1-sided p-value (BM)[4]	Confidence[5]
Barium	State-wide	Casing/ cementing violation	119	112	7	0.516	0.258	0.491	0.246	
		Impoundment (2010)	120	112	8	0.310	0.155	0.237	0.119	
		Impoundment violation	121	112	9	0.235	0.117	0.245	0.122	
		Spill violation	134	111	23	1.04E-12	5.20E-13	1.66E-13	8.31E-14	***
		UOG well	121	110	11	1.21E-13	6.03E-14	1.08E-14	5.40E-15	***
Barium	NEPA	Casing/ cementing violation	133	120	13	0.984	0.508	0.982	0.509	
		Impoundment (2010)	121.5	120	1.5	0.163	0.919	0.142	0.929	
		Impoundment violation	124.5	120	4.5	0.580	0.290	0.578	0.289	
		Spill violation	140	120	20	8.82E-04	4.41E-04	5.90E-04	2.95E-04	***
		UOG well	130	118	12	2.21E-07	1.11E-07	7.70E-08	3.85E-08	***
Barium	SWPA	Casing/ cementing violation	92.5	100	-7.5	0.809	0.595	0.693	0.653	
		Impoundment (2010)	120	99.8	20.2	2.65E-10	1.32E-10	1.79E-11	8.97E-12	***
		Impoundment violation	105	100	5	0.833	0.584	0.818	0.591	
		Spill violation	130	99.1	30.9	2.92E-21	1.46E-21	1.50E-20	7.49E-21	***
		UOG well	110	98	12	5.34E-16	2.67E-16	1.20E-16	6.01E-17	***

1. Calculated using a two-sided Wilcoxon–Mann–Whitney test
2. Calculated using a one-sided Wilcoxon–Mann–Whitney test, exploring the hypothesis that median concentrations are greater within 1km of UOGD
3. Calculated using a two-sided Brunner-Munzel test, which better accounts for small sample sizes and large ratios of variance
4. Calculated using a one-sided Brunner-Munzel test, exploring the hypothesis that median concentrations are greater within 1km of UOGD
5. For two-sided WMW tests: * = 95% confidence, ** = 99% confidence, *** = 99.5% confidence

Table S4: Comparison of median strontium concentrations (in µg/L) across samples ≤1km and >1km from UOGD parameters

Species	Region	UOG parameter	Median (≤1km)	Median (>1km)	Difference	2-sided p-value (WMW)[1]	1-sided p-value (WMW)[2]	2-sided p-value (BM)[3]	1-sided p-value (BM)[4]	Confidence[5]
Strontium	State-wide	Casing/ cementing violation	234	322	-88	9.81E-05	1.000	1.81E-04	1.00	***
		Impoundment (2010)	328	320	8	0.284	0.142	0.235	0.117	
		Impoundment violation	333	320	13	0.475	0.763	0.511	0.745	
		Spill violation	360	318.5	41.5	1.00E-05	5.00E-06	7.20E-06	3.60E-06	***
		UOG well	343.5	311	32.5	3.68E-08	1.84E-08	2.16E-08	1.08E-08	***
Strontium	NEPA	Casing/ cementing violation	190	280	-90	3.03E-03	0.998	2.20E-03	0.999	***
		Impoundment (2010)	196	280	-84	1.54E-05	1.000	1.64E-05	1.00	***
		Impoundment violation	297	276	21	0.689	0.344	0.696	0.348	
		Spill violation	353	272	81	4.02E-04	2.01E-04	4.37E-04	2.18E-04	***
		UOG well	295	270	25	0.0139	6.94E-03	0.0133	6.65E-03	*
Strontium	SWPA	Casing/ cementing violation	482	360	122	0.0928	0.046	0.0477	0.024	
		Impoundment (2010)	358	360	-2	0.377	0.188	0.364	0.182	
		Impoundment violation	458.5	359	99.5	0.0832	0.042	0.0815	0.041	
		Spill violation	373	359	14	0.127	0.063	0.126	0.063	
		UOG well	377	350	27	5.42E-06	2.71E-06	3.86E-06	1.93E-06	***

1. Calculated using a two-sided Wilcoxon–Mann–Whitney test
2. Calculated using a one-sided Wilcoxon–Mann–Whitney test, exploring the hypothesis that median concentrations are greater within 1km of UOGD
3. Calculated using a two-sided Brunner-Munzel test, which better accounts for small sample sizes and large ratios of variance
4. Calculated using a one-sided Brunner-Munzel test, exploring the hypothesis that median concentrations are greater within 1km of UOGD
5. For two-sided WMW tests: * = 95% confidence, ** = 99% confidence, *** = 99.5% confidence

Table S5: Regression results analyzing relationships between barium, strontium, and the density (within 1km) or distance of UOG wells

Region	Species	UOGD metric	Coefficient	Std. Error	p-value	Confidence[1]
Statewide	Barium	Density (1km)	1.26E-02	3.72E-03	7.46E-04	***
		Density (3km)	4.19E-03	7.05E-04	2.80E-09	***
		Distance	-6.79E-05	4.12E-06	8.35E-61	***
	Strontium	Density (1km)	1.78E-02	4.11E-03	1.47E-05	***
		Density (3km)	6.99E-03	8.06E-04	4.46E-18	***
		Distance	-4.71E-05	5.84E-06	7.15E-16	***
NEPA	Barium	Density (1km)	1.13E-02	6.04E-03	6.27E-02	
		Density (3km)	7.68E-03	1.09E-03	1.92E-12	***
		Distance	-9.42E-05	6.06E-06	3.30E-54	***
	Strontium	Density (1km)	9.46E-04	7.05E-03	8.93E-01	
		Density (3km)	2.49E-03	1.31E-03	5.86E-02	
		Distance	-7.89E-05	9.17E-06	8.44E-18	***
SWPA	Barium	Density (1km)	3.00E-02	3.83E-03	5.78E-15	***
		Density (3km)	5.32E-03	7.76E-04	7.77E-12	***
		Distance	-3.07E-05	4.55E-06	1.72E-11	***
	Strontium	Density (1km)	1.18E-02	4.15E-03	4.33E-03	***
		Density (3km)	6.46E-03	8.55E-04	4.62E-14	***
		Distance	-2.91E-05	6.22E-06	2.93E-06	***

1. * = 95%, ** = 99%, *** = 99.5%

Table S6: Regression results analyzing relationships between barium and UOGD metrics, including documented casing/cementing, impoundment, and spill-related violations and historical impoundment locations

Region	Species	UOGD metric[1]	Coefficient[2]	Std. Error	p-value	Confidence[3]
Statewide	Barium	Casing/ cementing violation density	-1.32E-02	1.22E-02	2.81E-01	
		Casing/ cementing violation distance	-1.38E-05	7.84E-07	2.49E-69	***
		Impoundment (2010) density	-1.83E-02	2.72E-02	5.00E-01	
		Impoundment (2010) distance	-1.80E-05	1.21E-06	3.96E-50	***
		Impoundment violation density	1.61E-02	1.39E-02	2.47E-01	
		Impoundment violation distance	-1.48E-05	9.75E-07	1.43E-51	***
		Spill violation density	3.74E-02	9.26E-03	5.33E-05	***
		Spill violation distance	-1.84E-05	1.07E-06	1.65E-66	***
NEPA	Barium	Casing/ cementing violation density	-1.95E-02	1.32E-02	1.42E-01	
		Casing/ cementing violation distance	-1.30E-05	1.24E-06	1.37E-25	***
		Impoundment (2010) density	-8.21E-02	4.98E-02	9.96E-02	
		Impoundment (2010) distance	-2.50E-05	1.72E-06	1.44E-47	***
		Impoundment violation density	9.82E-03	1.54E-02	5.23E-01	
		Impoundment violation distance	-2.33E-05	2.07E-06	2.08E-29	***
		Spill violation density	1.88E-02	1.46E-02	1.98E-01	
		Spill violation distance	-3.35E-05	2.36E-06	2.27E-45	***
SWPA	Barium	Casing/ cementing violation density	6.03E-05	8.17E-02	9.99E-01	
		Casing/ cementing violation distance	-1.10E-05	8.94E-07	2.87E-34	***
		Impoundment (2010) density	9.61E-02	2.57E-02	1.80E-04	***

Impoundment (2010) distance	-1.23E-05	1.39E-06	8.99E-19	***
Impoundment violation density	-2.51E-02	4.65E-02	5.89E-01	
Impoundment violation distance	-6.50E-06	9.90E-07	5.41E-11	***
Spill violation density	7.67E-02	9.57E-03	1.26E-15	***
Spill violation distance	-9.98E-06	9.68E-07	9.43E-25	***

1. Calculated for 1km density
2. Note that a positive coefficient for a density calculation indicates concentrations increase as UOG density increases (i.e., potentially indicative of a UOG impact), whereas a negative coefficient for a distance calculation indicates concentrations increase closer to UOGD (i.e., a positive coefficient is indicative of lower concentrations closer to UOGD).
3. * = 95%, ** = 99%, *** = 99.5%

Table S7: Regression results analyzing relationships between strontium and UOGD metrics, including documented casing/cementing, impoundment, and spill-related violations and historical impoundment locations

Region	Species	UOGD metric[1]	Coefficient	Std. Error	p-value	Confidence[2]
Statewide	Strontium	Casing/ cementing violation density	-5.47E-02	1.30E-02	2.54E-05	***
		Casing/ cementing violation distance	-8.00E-06	1.10E-06	4.79E-13	***
		Impoundment (2010) density	-3.80E-03	3.06E-02	9.01E-01	
		Impoundment (2010) distance	-2.25E-05	1.56E-06	1.17E-46	***
		Impoundment violation density	3.93E-03	1.53E-02	7.97E-01	
		Impoundment violation distance	-2.06E-06	1.21E-06	8.98E-02	
		Spill violation density	4.01E-02	1.02E-02	8.36E-05	***
		Spill violation distance	-9.23E-06	1.38E-06	2.27E-11	***
NEPA	Strontium	Casing/ cementing violation density	-4.42E-02	1.45E-02	2.23E-03	***
		Casing/ cementing violation distance	-2.84E-05	2.32E-06	4.13E-34	***
		Impoundment (2010) density	-3.11E-01	6.22E-02	5.67E-07	***
		Impoundment (2010) distance	-1.95E-05	2.50E-06	6.35E-15	***
		Impoundment violation density	2.17E-02	1.74E-02	2.12E-01	
		Impoundment violation distance	-2.89E-05	3.73E-06	1.03E-14	***
		Spill violation density	2.63E-02	1.66E-02	1.14E-01	
		Spill violation distance	-2.23E-05	3.38E-06	4.92E-11	***
SWPA	Strontium	Casing/ cementing violation density	1.90E-01	8.68E-02	2.90E-02	*
		Casing/ cementing violation distance	-1.60E-05	1.13E-06	4.68E-45	***
		Impoundment (2010) density	1.29E-02	2.80E-02	6.45E-01	

Impoundment (2010) distance	-2.00E-05	1.65E-06	9.22E-34	***
Impoundment violation density	6.49E-02	5.03E-02	1.97E-01	
Impoundment violation distance	-1.43E-05	1.15E-06	8.38E-35	***
Spill violation density	2.64E-02	1.05E-02	1.19E-02	*
Spill violation distance	-1.47E-05	1.21E-06	9.29E-34	***

1. Calculated for 1km density
2. * = 95%, ** = 99%, *** = 99.5%

Table S8: Fixed effects results analyzing relationships between barium and UOGD metrics, including documented casing/cementing, impoundment, and spill-related violations and historical impoundment locations

Region	Species	UOGD metric[1]	Coefficient	Std. Error	p-value	Confidence[2]
Statewide	Barium	UOG well density	1.68E-02	3.77E-03	8.42E-06	***
		UOG well distance	-6.50E-05	4.27E-06	3.50E-52	***
		Casing/ cementing violation density	-2.11E-03	1.23E-02	8.63E-01	
		Casing/ cementing violation distance	-1.29E-05	8.76E-07	4.25E-49	***
		Impoundment (2010) density	8.94E-03	2.73E-02	7.43E-01	
		Impoundment (2010) distance	-2.04E-05	1.32E-06	9.60E-54	***
		Impoundment violation density	1.86E-02	1.39E-02	1.83E-01	
		Impoundment violation distance	-1.51E-05	1.23E-06	1.63E-34	***
		Spill violation density	3.29E-02	9.32E-03	4.26E-04	***
		Spill violation distance	-1.90E-05	1.29E-06	7.15E-49	***
NEPA	Barium	UOG well density	1.98E-02	6.07E-03	1.10E-03	***
		UOG well distance	-1.01E-04	6.14E-06	7.06E-61	***
		Casing/ cementing violation density	-2.73E-03	1.33E-02	8.38E-01	
		Casing/ cementing violation distance	-1.44E-05	1.32E-06	9.08E-28	***
		Impoundment (2010) density	-3.10E-02	4.99E-02	5.34E-01	
		Impoundment (2010) distance	-2.72E-05	1.76E-06	8.09E-54	***
		Impoundment violation density	2.32E-02	1.55E-02	1.34E-01	
		Impoundment violation distance	-2.72E-05	2.12E-06	1.02E-37	***
		Spill violation density	2.49E-02	1.47E-02	9.07E-02	
		Spill violation distance	-3.67E-05	2.50E-06	1.78E-48	***
SWPA	Barium	UOG well density	2.36E-02	3.90E-03	1.55E-09	***

UOG well distance	-2.22E-05	4.89E-06	5.65E-06	***
Casing/ cementing violation density	2.18E-02	8.09E-02	7.87E-01	
Casing/ cementing violation distance	-1.23E-05	1.09E-06	4.01E-29	***
Impoundment (2010) density	6.09E-02	2.59E-02	1.88E-02	*
Impoundment (2010) distance	-1.16E-05	1.84E-06	2.95E-10	***
Impoundment violation density	-2.71E-02	4.62E-02	5.58E-01	
Impoundment violation distance	-5.48E-06	1.33E-06	4.00E-05	***
Spill violation density	5.72E-02	9.82E-03	6.02E-09	***
Spill violation distance	-1.03E-05	1.27E-06	3.78E-16	***

1. Calculated for 1km density
2. * = 95%, ** = 99%, *** = 99.5%

Table S9: Fixed effects results analyzing relationships between strontium and UOGD metrics, including documented casing/cementing, impoundment, and spill-related violations and historical impoundment locations

Region	Species	UOGD metric[1]	Coefficient	Std. Error	p-value	Confidence[2]
Statewide	Strontium	UOG well density	1.86E-02	4.12E-03	6.55E-06	***
		UOG well distance	-4.81E-05	6.00E-06	1.24E-15	***
		Casing/ cementing violation density	-2.12E-02	1.29E-02	1.00E-01	
		Casing/ cementing violation distance	-1.24E-05	1.27E-06	2.40E-22	***
		Impoundment (2010) density	-2.42E-02	3.03E-02	4.25E-01	
		Impoundment (2010) distance	-1.85E-05	1.70E-06	1.07E-27	***
		Impoundment violation density	4.31E-02	1.52E-02	4.47E-03	***
		Impoundment violation distance	-3.99E-06	1.53E-06	9.19E-03	**
		Spill violation density	5.50E-02	1.01E-02	6.03E-08	***
		Spill violation distance	-1.16E-05	1.63E-06	1.23E-12	***
NEPA	Strontium	UOG well density	2.12E-02	7.10E-03	2.85E-03	***
		UOG well distance	-7.22E-05	9.41E-06	1.84E-14	***
		Casing/ cementing violation density	-1.74E-02	1.45E-02	2.29E-01	
		Casing/ cementing violation distance	-2.90E-05	2.36E-06	1.80E-34	***
		Impoundment (2010) density	-2.02E-01	6.20E-02	1.12E-03	***
		Impoundment (2010) distance	-2.23E-05	2.54E-06	1.82E-18	***
		Impoundment violation density	4.68E-02	1.74E-02	7.20E-03	**
		Impoundment violation distance	-2.69E-05	3.81E-06	1.80E-12	***

		Spill violation density	4.86E-02	1.66E-02	3.50E-03	***
		Spill violation distance	-3.32E-05	3.66E-06	1.39E-19	***
SWPA	Strontium	UOG well density	1.21E-02	4.13E-03	3.55E-03	***
		UOG well distance	-1.67E-05	6.53E-06	1.05E-02	*
		Casing/ cementing violation density	1.75E-01	8.40E-02	3.75E-02	*
		Casing/ cementing violation distance	-1.27E-05	1.33E-06	1.99E-21	***
		Impoundment (2010) density	6.11E-03	2.77E-02	8.25E-01	
		Impoundment (2010) distance	-1.40E-05	2.02E-06	4.89E-12	***
		Impoundment violation density	1.10E-01	4.89E-02	2.49E-02	*
		Impoundment violation distance	-8.13E-06	1.46E-06	2.56E-08	***
		Spill violation density	4.56E-02	1.06E-02	1.67E-05	***
		Spill violation distance	-1.10E-05	1.48E-06	1.31E-13	***

1. Calculated for 1km density
2. * = 95%, ** = 99%, *** = 99.5%

Table S10: Regression results analyzing relationships between barium, strontium, and the density (within 1km) or distance of UOG wells, including only higher elevation UOG wells in the calculation

Region	Species	UOGD metric	Coefficient	Std. Error	p-value	Confidence[1]
Statewide	Barium	Density (1km)	1.90E-02	4.40E-03	1.53E-05	***
		Density (3km)	8.30E-03	8.99E-04	2.98E-20	***
		Distance	-3.39E-05	1.99E-06	1.50E-64	***
	Strontium	Density (1km)	2.73E-02	4.85E-03	1.79E-08	***
		Density (3km)	9.15E-03	1.02E-03	2.97E-19	***
		Distance	-3.77E-05	3.06E-06	8.85E-35	***
NEPA	Barium	Density (1km)	1.99E-02	7.43E-03	7.31E-03	**
		Density (3km)	1.46E-02	1.41E-03	3.91E-25	***
		Distance	-5.40E-05	2.90E-06	1.09E-76	***
	Strontium	Density (1km)	9.14E-03	8.70E-03	2.93E-01	
		Density (3km)	2.80E-03	1.69E-03	9.90E-02	
		Distance	-6.00E-05	4.73E-06	1.23E-36	***
SWPA	Barium	Density (1km)	3.65E-02	4.39E-03	1.10E-16	***
		Density (3km)	7.90E-03	9.67E-04	3.64E-16	***
		Distance	-7.60E-06	2.23E-06	6.38E-04	***
	Strontium	Density (1km)	1.82E-02	4.75E-03	1.26E-04	***
		Density (3km)	8.95E-03	1.06E-03	3.91E-17	***
		Distance	-1.77E-05	3.31E-06	8.34E-08	***

1. * = 95%, ** = 99%, *** = 99.5%

Table S11: Regression results analyzing relationships between barium, strontium, and the density (within 1km) or distance of reported spills, including only higher elevation wellpads in the calculation

Region	Species	UOGD metric	Coefficient	Std. Error	p-value	Confidence[1]
Statewide	Barium	Density (1km)	5.90E-02	1.07E-02	3.89E-08	***
		Density (3km)	2.53E-02	3.16E-03	1.25E-15	***
		Distance	-1.71E-05	8.20E-07	6.09E-96	***
	Strontium	Density (1km)	5.30E-02	1.17E-02	6.61E-06	***
		Density (3km)	2.29E-02	3.47E-03	4.25E-11	***
		Distance	-1.14E-05	1.10E-06	3.36E-25	***
NEPA	Barium	Density (1km)	3.79E-02	1.66E-02	2.29E-02	*
		Density (3km)	2.44E-02	4.49E-03	5.14E-08	***
		Distance	-2.45E-05	1.31E-06	2.66E-77	***
	Strontium	Density (1km)	4.94E-02	1.90E-02	9.47E-03	**
		Density (3km)	2.64E-02	5.13E-03	2.53E-07	***
		Distance	-2.00E-05	1.91E-06	1.31E-25	***
SWPA	Barium	Density (1km)	1.04E-01	1.12E-02	2.50E-20	***
		Density (3km)	3.62E-02	3.67E-03	9.63E-23	***
		Distance	-8.22E-06	8.59E-07	1.47E-21	***
	Strontium	Density (1km)	2.76E-02	1.22E-02	2.40E-02	*
		Density (3km)	1.06E-02	3.97E-03	7.63E-03	**
		Distance	-1.14E-05	1.09E-06	3.17E-25	***

1. * = 95%, ** = 99%, *** = 99.5%

Table S12: Correlation coefficients and p-values regressing Barium and Strontium concentrations against waste production volumes at UOG wells within 1km

	Barium		*Strontium*	
Region	Coefficient	p-value	Coefficient	p-value
Statewide	0.001918	0.12	0.009048	3.32E-11
NEPA	0.0007544	0.703	0.002999	0.181
SWPA	0.010758	4.70E-16	0.006071	2.62E-05

Table S13: Median [Ba] (mg/L) comparison between samples located nearby 250-gallon spills ("spill group") and samples >3km/1km from a spill

Spill group	Control group	Median [Ba] (spill group)	Median [Ba] (control)	Two-sided p-value[1]	One-sided p-value[2]	Confidence[3]
≥250 gallon spill within 1km	No spills within 1km	0.137	0.111	0.115	0.057	
≥250 gallon spill within 1km	No ≥250 gallon spills within 1km	0.137	0.112	0.135	0.068	
≥250 gallon spill within 3km	No spills within 3km	0.131	0.106	6.12E-13	3.06E-13	***
≥250 gallon spill within 3km	No ≥250 gallon spills within 3km	0.131	0.111	2.19E-8	1.10E-8	***

1. Calculated using a two-sided WMW test. Using the BM test, p-values are 0.148, 0.171, 5.88×10^{-13}, and 2.83×10^{-8}, respectively
2. Calculated with a one-sided WMW test evaluating the hypothesis that median concentrations are greater nearby spills. Using the BM test, p-values are 0.074, 0.086, 2.94×10^{-13}, and 1.41×10^{-8}, respectively
3. Based on results of the two-sided WMW test. * = 95%, ** = 99%, *** = 99.5%

Table S14: Median [Ba] (mg/L) comparison between samples located nearby 500-gallon spills ("spill group") and samples >3km/1km from a spill

Spill group	Control group	Median [Ba] (spill group)	Median [Ba] (control)	Two-sided p-value[1]	One-sided p-value[2]	Confidence[3]
≥500 gallon spill within 1km	No spills within 1km	0.140	0.111	0.271	0.108	
≥500 gallon spill within 1km	No ≥500 gallon spills within 1km	0.140	0.112	0.300	0.122	
≥500 gallon spill within 3km	No spills within 3km	0.122	0.106	5.15E-05	3.02E-05	***
≥500 gallon spill within 3km	No ≥500 gallon spills within 3km	0.122	0.112	0.014	0.007	***

1. Calculated using a two-sided WMW test. Using the BM test, p-values are 0.148, 0.171, 5.88×10^{-13}, and 2.83×10^{-8}, respectively
2. Calculated with a one-sided WMW test evaluating the hypothesis that median concentrations are greater nearby spills. Using the BM test, p-values are 0.074, 0.086, 2.94×10^{-13}, and 1.41×10^{-8}, respectively
3. Based on results of the two-sided WMW test. * = 95%, ** = 99%, *** = 99.5%

Table S15: Median [Ba] (mg/L) comparison between SWPA samples located nearby impoundments reprimanded by the PA DEP ("impoundment group") and SWPA samples >3km/1km from a reprimanded impoundment

Impoundment group	Control group	Median [Ba] (impoundment group)	Median [Ba] (control group)	Two-sided p-value[1]	One-sided p-value[2]	Confidence[3]
Impoundment within 1km	No impoundment within 1km	0.1345	0.100	8.89E-04	4.44E-04	***
Impoundment within 1km	No impoundment within 3km	0.1345	0.099	5.00E-04	2.50E-04	***
Impoundment within 3km	No impoundment within 1km	0.123	0.100	1.38E-07	3.42E-10	***
Impoundment within 3km	No impoundment within 3km	0.123	0.099	1.08E-08	1.04E-11	***

1. Calculated using a two-sided WMW test. Using the BM test, p-values are 1.13×10^{-3}, 6.09×10^{-4}, 5.85×10^{-11}, and 9.38×10^{-13}, respectively
2. Calculated using a one-sided WMW test evaluating the hypothesis that median concentrations are greater nearby spills. Using the BM test, p-values are 5.65×10^{-4}, 3.04×10^{-4}, 2.92×10^{-11}, and 4.69×10^{-13}, respectively
3. Based on results of the two-sided WMW test. * = 95%, ** = 99%, *** = 99.5%

Table S16: Median ratios of produced water species to [Ba] or [Sr] in PA shale gas produced waters

Species	Median [X] / [Ba]	Median [X] / [Sr]	EPA limit (mg/L)[2]	EPA limit type	[Ba] when [X] > limit (mg/L)	[Sr] when [X] > limit (mg/L)
Ag	1.92E-04	6.58E-05	0.1	SMCL	522	1519
Al	1.49E-03	5.14E-04	0.05	SMCL	34	97
As	4.24E-04	7.58E-05	0.01	MCL	24	132
Be	2.83E-04	5.27E-05	0.004	MCL	14	76
Cd	1.11E-04	4.19E-05	0.005	MCL	45	119
Cl	5.27E+01	4.19E+01	250	SMCL	5	6
Cr	1.45E-04	3.82E-05	0.1	MCL	692	2617
Cu	4.42E-04	1.89E-04	1	SMCL	2264	5286
F	1.08E-02	2.41E-03	2	SMCL	184	830
Fe (total)	5.53E-02	3.67E-02	0.3	SMCL	5	8
Hg	9.77E-07	2.10E-07	0.002	MCL	2046	9506
Mn	3.65E-03	2.96E-03	0.05	SMCL	14	17
Ni	4.40E-04	2.05E-04	0.1	MCL	227	488
Nitrite	2.65E-02	1.04E-02	1	MCL	38	96
Nitrate	1.31E-02	2.56E-03	10	MCL	763	3913
Pb	1.69E-04	6.11E-05	0.015	Action Level	89	246
Combined radium (Ra-226 + Ra-228)	6.92E-01	7.64E-01	5	MCL	7	7
Se	3.94E-04	6.58E-05	0.05	MCL	127	759
SO4	4.06E-01	6.79E-02	250	SMCL	616	3680
TDS	1.04E+02	8.13E+01	500	SMCL	5	6
Tl	5.00E-04	1.98E-04	0.002	MCL	4	10
Toluene	6.66E-08	1.74E-07	1	MCL	15022174	5757696
Xylene	1.59E-05	8.28E-03	10	MCL	629108	1208
Zn	6.03E-04	2.76E-04	5	SMCL	8288	18140

1. Calculated as the median ratio for shale gas produced waters from Pennsylvania in the USGS Produced Water database.[39]
2. Data for combined radium is in pCi/L

Table S17: Summary statistics of analytes with >500 reported measurements in the Shale Network database

Variable	Unit	Total Reported	Above Detection	Mean	Median
pH	mg/L	27877	27865	7.50	7.565
Methane	mg/L	27863	7272	0.9244	0.026
Total dissolved solids	mg/L	27759	27644	248.91	204
Magnesium (total)	mg/L	27720	26676	9.64	7.24
Specific conductance	µS/cm	27695	27685	466.14	366.7
Chloride	mg/L	27599	21584	29.15	7.49
Manganese (total)	mg/L	27443	14743	0.20	0.016
Iron (total)	mg/L	27414	17112	1.44	0.09
Sulfate (total)	mg/L	27315	25725	30.54	16.8
Sodium (total)	mg/L	27279	26793	33.20	12
Calcium (total)	mg/L	27033	26659	45.10	38.6
Barium (total)	mg/L	25878	24917	0.28	0.112
Total suspended solids	mg/L	25876	8624	22.19	2
Turbidity	NTU	25583	14467	16.39	1.04
Arsenic (total)	mg/L	24009	1624	0.01	0.01
Lead (total)	mg/L	23766	2991	0.011	0.005
Methylene blue active substances	mg/L	23721	2227	1.4176	0.05
Selenium (total)	mg/L	23188	173	0.02	0.01
Chromium (total)	mg/L	23127	601	0.05	0.005
Benzene	µg/L	22028	26	2.15	5.00E-04
Toluene	µg/L	22028	158	2.16	5.00E-04
Ethylbenzene	µg/L	21954	23	2.15	5.00E-04
Cadmium (total)	mg/L	21806	125	0.0059	0.001
Mercury (total)	mg/L	21738	77	0.0017	2.00E-04
Xylenes (total)	µg/L	21027	44	2.32	5.00E-04
Silver (total)	mg/L	20905	58	0.01	0.005
Temperature	°C	18492	18490	21.37	21.5
Ethane	mg/L	18210	436	0.46	0.026
Strontium (total)	mg/L	17649	16463	0.62	0.321
Alkalinity (bicarbonate)	mg/L	16554	16115	132.67	129
Sulfur	mg/L	15824	15158	8.37	4.35
Potassium (total)	mg/L	14800	13341	1.89	1.38
Propane	mg/L	14409	15	0.67	0.034
Alkalinity (total)	mg/L	14119	13860	155.11	141
Hardness (total)	mg/L	10138	10031	196.68	184
Ethane (dissolved)	mg/L	7999	95	0.02	0.026

Propane (dissolved)	mg/L	7999	2	0.03	0.034
Coliform (total)	Colonies/100mL	6103	4644	55.86	1
E. coli	Colonies/100mL	5632	4590	3.25	1
Bromide (total)	mg/L	4742	527	1.46	1
Lithium (total)	mg/L	4041	641	0.07	0.05
Coliform (fecal)	Colonies/100mL	3648	1884	208.32	2
Nitrogen (nitrate, NO3)	mg/L	3397	2089	1.32	1
Carbonate	mg/L	2370	104	10.23	10
Aluminum (total)	mg/L	1587	215	0.15	0.08
Oxygen (dissolved)	mg/L	1112	1112	6.87	5.61
Total organic carbon	mg/L	915	261	1.37	1
Sulfide (total)	mg/L	801	138	1.41	1
Alkalinity (carbonate)	mg/L	533	128	45.56	10

Table S18: Coordinates assigned to impoundments reprimanded by the PADEP in SWPA, based on coordinates of the nearest wellpad

Impoundment	Latitude	Longitude
Yeager	40.091528	-80.228111
Worstell	40.274217	-80.216301
Lowry	40.250996	-80.367778
Kearns	40.205607	-80.419141
Bednarski	40.206836	-80.367203
Day	40.122722	-80.215917
Carol Baker	40.230472	-80.277694
Carter	40.320314	-80.302272

Table S19: Summary statistics of sample proximity to anthropogenic and geologic features across the three subregions of the dataset

Region	Feature	Mean	Median	Min	Max
NEPA	UOG well density (1km)	0.54	0	0	19
	UOG well distance (m)	2204	1868	1	20899
	COG well density (1km)	0.02	0.00	0.00	3.00
	COG well distance (m)	7963	7465	54	23252
	Coal mining distance (m)	58905	60148	3678	107770
	Highway distance (m)	2067	1467	0	11482
	Anticline distance (m)	5772	4462	0	24395
SWPA	UOG well density (1km)	1.38	0.00	0.00	21.00
	UOG well distance (m)	2407	1711	72	26000
	COG well density (1km)	0.94	0.00	0.00	48.00
	COG well distance (m)	2359	1773	23	11822
	Coal mining distance (m)	1682	862	0	11241
	Highway distance (m)	1592	1222	0	9509
	Anticline distance (m)	7740	4510	1	35041
NWPA	UOG well density (1km)	0.03	0.00	0.00	11.00
	UOG well distance (m)	9789	6578	323	27112
	COG well density (1km)	3.97	3.00	0.00	14.00
	COG well distance (m)	752	480	0	4964
	Coal mining distance (m)	16944	17025	1116	31186
	Highway distance (m)	992	824	1	3122
	Anticline distance (m)	30572	31237	16708	42166

Table S20: The number of samples within 1km or 3km of UOGD features/violations

Region	Feature	# of samples (1km)	# of samples (3km)
Statewide	UOG well	6011	20738
	Spill violation	1320	7892
	Casing/cementing violation	306	2705
	Impoundment violation	621	4657
	2010 impoundment	1024	6361
NEPA (n = 19629)	UOG well	3887	15496
	Spill violation	802	5871
	Casing/cementing violation	282	2517
	Impoundment violation	558	4258
	2010 impoundment	364	3309
NWPA (n = 1840)	UOG well	33	44
	Spill violation	0	0
	Casing/cementing violation	0	0
	Impoundment violation	0	0
	2010 impoundment	0	0
SWPA (n = 7140)	UOG well	2091	5198
	Spill violation	518	2021
	Casing/cementing violation	24	188
	Impoundment violation	63	399
	2010 impoundment	660	3052

Table S21: Summary statistics for groundwater sample proximity to violations

Region	Feature	Mean	Median	Min	Max
Distance (m)					
NEPA	Spill distance	5612	4431	37	24644
	Casing violation distance	10140	7919	110	313547
	Impoundment violation distance	6643	5413	1	24456
	2010 impoundment distance	8286	6978	76	28971
NWPA	Spill distance	23228	21737	16648	32630
	Casing violation distance	44931	45442	38305	51989
	Impoundment violation distance	51209	52926	44279	56622
	2010 impoundment distance	50143	50416	42382	56329
SWPA	Spill distance	9785	5400	102	40984
	Casing violation distance	16718	12556	282	46157
	Impoundment violation distance	14003	11346	194	193691
	2010 impoundment distance	6781	3784	102	29708
Density (1km)					
NEPA	Spill density	0.09	0	0	14
	Casing violation density	0.06	0	0	15
	Impoundment violation density	0.07	0	0	15
	2010 impoundment density	0.02	0	0	5
NWPA	Spill density	0	0	0	0
	Casing violation density	0	0	0	0
	Impoundment violation density	0	0	0	0
	2010 impoundment density	0	0	0	0
SWPA	Spill density	0.28	0	0	10
	Casing violation density	0.01	0	0	3
	Impoundment violation density	0.02	0	0	4
	2010 impoundment density	0.12	0	0	5

Table S22: Comparison of median barium concentrations (in µg/L) across samples ≤3km and >3km from UOGD parameters

Species	Region	UOG parameter	Median (≤3km)	Median (>3km)	Difference	p-value (WMW)[1]	p-value (BM)[2]	Confidence[3]
Barium	State-wide	Casing/ cementing violation	136.5	110	26.5	3.89E-17	5.08E-17	***
		Impoundment (2010)	122	109	13	1.01E-18	2.86E-21	***
		Impoundment violation	125	110	15	2.28E-10	3.76E-10	***
		Spill violation	129	106	23	1.45E-45	3.64E-47	***
		UOG well	118	94	24	2.41E-47	2.54E-45	***
Barium	NEPA	Casing/ cementing violation	140	118	22	3.83E-09	1.15E-09	***
		Impoundment (2010)	142	115	27	1.45E-18	1.17E-20	***
		Impoundment violation	128	118	10	7.81E-05	6.05E-05	***
		Spill violation	140	113	27	6.05E-28	6.36E-29	***
		UOG well	126	98.65	27.35	2.28E-30	7.88E-29	***
Barium	SWPA	Casing/ cementing violation	112	100	12	0.125	0.0919	
		Impoundment (2010)	110	94	16	1.22E-23	2.10E-24	***
		Impoundment violation	106	100	6	0.818	0.812	
		Spill violation	113	96	17	3.11E-20	3.00E-21	***
		UOG well	104	89	15	1.87E-15	4.58E-14	***

1. Calculated using a two-sided Wilcoxon–Mann–Whitney test
2. Calculated using a two-sided Brunner-Munzel test, which better accounts for small sample sizes and large ratios of variance
3. * = 95%, ** = 99%, *** = 99.5%

Table S23: Comparison of median strontium concentrations (in µg/L) across samples ≤3km and >3km from UOGD parameters

Species	Region	UOG parameter	Median (≤3km)	Median (>3km)	Difference	p-value (WMW)[1]	p-value (BM)[2]	Confidence[3]
Strontium	State-wide	Casing/ cementing violation	302	323	-21	0.398	0.427	
		Impoundment (2010)	349	304	45	5.15E-20	1.58E-21	***
		Impoundment violation	333	320	13	0.188	0.212	
		Spill violation	344	308	36	1.62E-14	2.00E-14	***
		UOG well	330	282	48	1.30E-12	1.96E-12	***
Strontium	NEPA	Casing/ cementing violation	297.5	272.5	25	5.57E-03	5.72E-03	**
		Impoundment (2010)	307.5	270	37.5	2.84E-03	2.36E-03	***
		Impoundment violation	316	262.5	53.5	1.23E-08	1.46E-08	***
		Spill violation	327.5	254	73.5	1.57E-17	1.54E-17	***
		UOG well	291	212.5	78.5	2.45E-15	1.55E-14	***
Strontium	SWPA	Casing/ cementing violation	329	360	-31	0.424	0.402	
		Impoundment (2010)	364.5	353	11.5	1.18E-05	1.10E-05	***
		Impoundment violation	395	358	37	6.68E-03	3.01E-03	***
		Spill violation	361	358	3	2.39E-03	2.01E-03	***
		UOG well	365	335	30	3.89E-06	7.84E-06	***

1. Calculated using a two-sided Wilcoxon–Mann–Whitney test
2. Calculated using a two-sided Brunner-Munzel test, which better accounts for small sample sizes and large ratios of variance
3. * = 95%, ** = 99%, *** = 99.5%

Table S24: Regression results analyzing correlations between barium, strontium and UOD density, using a 3km radius

Region	Species	UOGD metric	Coefficient	Std. Error	p-values	Confidence[1]
Statewide	Barium	Casing/cementing violation	3.97E-03	2.38E-03	9.56E-02	
		Impoundments (2010)	-3.05E-03	5.35E-03	5.68E-01	
		Impoundment violations	1.34E-02	2.72E-03	8.90E-07	***
		Spill violations	1.21E-02	2.35E-03	2.57E-07	***
	Strontium	Casing/cementing violation	-7.28E-03	2.55E-03	4.37E-03	***
		Impoundments (2010)	2.85E-02	6.14E-03	3.48E-06	***
		Impoundment violations	7.30E-03	3.00E-03	1.48E-02	*
		Spill violations	1.61E-02	2.59E-03	4.98E-10	***
NEPA	Barium	Casing/cementing violation	1.11E-03	2.58E-03	6.68E-01	
		Impoundments (2010)	3.56E-02	9.91E-03	3.29E-04	***
		Impoundment violations	8.68E-03	2.98E-03	3.62E-03	***
		Spill violations	1.38E-02	3.45E-03	6.04E-05	***
	Strontium	Casing/cementing violation	-1.80E-03	2.85E-03	5.29E-01	
		Impoundments (2010)	-3.83E-02	1.23E-02	1.77E-03	***
		Impoundment violations	1.95E-02	3.41E-03	1.03E-08	***
		Spill violations	1.97E-02	3.95E-03	6.60E-07	***
SWPA	Barium	Casing/cementing violation	3.45E-02	2.38E-02	1.47E-01	
		Impoundments (2010)	7.44E-03	5.30E-03	1.60E-01	
		Impoundment violations	9.78E-03	1.73E-02	5.72E-01	
		Spill violations	1.82E-02	2.63E-03	5.53E-12	***
	Strontium	Casing/cementing violation	4.52E-02	2.53E-02	7.45E-02	
		Impoundments (2010)	1.65E-02	5.93E-03	5.45E-03	**
		Impoundment violations	1.03E-02	1.90E-02	5.89E-01	
		Spill violations	5.44E-03	2.85E-03	5.61E-02	

1. * = 95%, ** = 99%, *** = 99.5%

Table S25: Tobit regression results for [Ba] and [Sr] vs. UOG density (1km radius)

Region	Species	UOGD metric	Coefficient	Std. Error	p-value	Confidence[1]
Statewide	Barium	Casing/cementing violation	-2.87E-02	1.28E-02	2.43E-02	*
		Impoundments (2010)	-4.21E-02	2.82E-02	1.35E-01	
		Impoundment violations	1.69E-03	1.45E-02	9.07E-01	
		Spill violations	3.49E-02	9.56E-03	2.58E-04	***
		UOG wells	1.10E-02	3.84E-03	4.02E-03	***
NEPA	Barium	Casing/cementing violation	-3.56E-02	1.39E-02	1.02E-02	*
		Impoundments (2010)	-1.91E-01	5.33E-02	3.44E-04	***
		Impoundment violations	-5.50E-03	1.61E-02	7.32E-01	
		Spill violations	7.99E-03	1.53E-02	6.00E-01	
		UOG wells	4.40E-03	6.30E-03	4.84E-01	
SWPA	Barium	Casing/cementing violation	3.36E-03	8.32E-02	9.68E-01	
		Impoundments (2010)	1.00E-01	2.61E-02	1.24E-04	***
		Impoundment violations	-2.31E-02	4.73E-02	6.26E-01	
		Spill violations	7.78E-02	9.74E-03	1.36E-15	***
		UOG wells	3.07E-02	3.90E-03	3.56E-15	***
Statewide	Strontium	Casing/cementing violation	-6.09E-02	1.39E-02	1.22E-05	***
		Impoundments (2010)	1.22E-03	3.26E-02	9.70E-01	
		Impoundment violations	4.98E-04	1.63E-02	9.76E-01	
		Spill violations	4.51E-02	1.08E-02	3.15E-05	***
		UOG wells	2.20E-02	4.37E-03	4.96E-07	***
NEPA	Strontium	Casing/cementing violation	-4.95E-02	1.58E-02	1.76E-03	***
		Impoundments (2010)	-3.72E-01	6.90E-02	7.02E-08	***
		Impoundment violations	2.04E-02	1.90E-02	2.82E-01	
		Spill violations	3.10E-02	1.81E-02	8.73E-02	
		UOG wells	6.39E-03	7.67E-03	4.05E-01	
SWPA	Strontium	Casing/cementing violation	1.94E-01	8.86E-02	2.88E-02	*
		Impoundments (2010)	1.86E-02	2.86E-02	5.16E-01	
		Impoundment violations	6.83E-02	5.13E-02	1.84E-01	
		Spill violations	2.81E-02	1.07E-02	8.78E-03	**
		UOG wells	1.29E-02	4.24E-03	2.34E-03	***

1. * = 95%, ** = 99%, *** = 99.5%

Table S26: Tobit regression results for [Ba] and [Sr] vs. UOG density (3km radius)

Region	Species	UOGD metric	Coefficient	Std. Error	p-value	Confidence[1]
Statewide	Barium	Casing/cementing violation	-2.97E-03	2.50E-03	2.34E-01	
		Impoundments (2010)	-1.61E-02	5.55E-03	3.73E-03	***
		Impoundment violations	4.83E-03	2.86E-03	9.10E-02	
		Spill violations	7.21E-03	2.45E-03	3.29E-03	***
		UOG wells	3.66E-03	7.27E-04	4.69E-07	***
NEPA	Barium	Casing/cementing violation	-6.04E-03	2.71E-03	2.59E-02	*
		Impoundments (2010)	-1.07E-02	1.06E-02	3.13E-01	
		Impoundment violations	-1.96E-04	3.14E-03	9.50E-01	
		Spill violations	3.74E-03	3.66E-03	3.08E-01	
		UOG wells	6.02E-03	1.14E-03	1.17E-07	***
SWPA	Barium	Casing/cementing violation	3.58E-02	2.42E-02	1.40E-01	
		Impoundments (2010)	7.82E-03	5.40E-03	1.47E-01	
		Impoundment violations	9.14E-03	1.77E-02	6.05E-01	
		Spill violations	1.79E-02	2.68E-03	2.27E-11	***
		UOG wells	5.46E-03	7.90E-04	5.08E-12	***
Statewide	Strontium	Casing/cementing violation	-8.92E-03	2.74E-03	1.11E-03	***
		Impoundments (2010)	2.93E-02	6.55E-03	7.72E-06	***
		Impoundments violations	5.92E-03	3.20E-03	6.45E-02	
		Spill violations	1.67E-02	2.76E-03	1.50E-09	***
		UOG wells	7.94E-03	8.58E-04	2.14E-20	***
NEPA	Strontium	Casing/cementing violation	-2.79E-03	3.12E-03	3.72E-01	
		Impoundments (2010)	-5.06E-02	1.35E-02	1.75E-04	***
		Impoundment violations	2.00E-02	3.72E-03	7.84E-08	***
		Spill violations	2.02E-02	4.32E-03	2.74E-06	***
		UOG wells	3.99E-03	1.43E-03	5.34E-03	**
SWPA	Strontium	Casing/cementing violation	4.57E-02	2.59E-02	7.79E-02	
		Impoundments (2010)	1.58E-02	6.07E-03	9.34E-03	**
		Impoundment violations	2.65E-03	1.95E-02	8.92E-01	
		Spill violations	5.33E-03	2.91E-03	6.70E-02	
		UOG wells	6.49E-03	8.74E-04	1.13E-13	***

1. * = 95%, ** = 99%, *** = 99.5%

Table S27: Tobit regression results for [Ba] and [Sr] vs. UOG distance

Region	Species	UOGD metric	Coefficient	Std. Error	p-value	Confidence[1]
Statewide	Barium	Casing/cementing violation	-1.38E-05	8.24E-07	4.19E-63	***
		Impoundments (2010)	-1.70E-05	1.24E-06	2.90E-42	***
		Impoundment violations	-1.38E-05	1.00E-06	4.50E-43	***
		Spill violations	-1.79E-05	1.10E-06	1.24E-59	***
		UOG wells	-6.62E-05	4.24E-06	5.33E-55	***
NEPA	Barium	Casing/cementing violation	-1.29E-05	1.35E-06	9.44E-22	***
		Impoundments (2010)	-2.24E-05	1.78E-06	3.18E-36	***
		Impoundment violations	-2.06E-05	2.14E-06	7.36E-22	***
		Spill violations	-3.12E-05	2.45E-06	2.36E-37	***
		UOG wells	-9.14E-05	6.27E-06	4.23E-48	***
SWPA	Barium	Casing/cementing violation	-1.14E-05	9.11E-07	1.18E-35	***
		Impoundments (2010)	-1.27E-05	1.42E-06	3.06E-19	***
		Impoundment violations	-6.75E-06	1.01E-06	2.37E-11	***
		Spill violations	-1.03E-05	9.87E-07	2.36E-25	***
		UOG wells	-3.11E-05	4.64E-06	2.16E-11	***
Statewide	Strontium	Casing/cementing violation	-7.65E-06	1.18E-06	8.00E-11	***
		Impoundments (2010)	-2.46E-05	1.67E-06	2.36E-49	***
		Impoundment violations	-1.45E-06	1.29E-06	2.61E-01	
		Spill violations	-9.44E-06	1.47E-06	1.39E-10	***
		UOG wells	-5.12E-05	6.22E-06	2.01E-16	***
NEPA	Strontium	Casing/cementing violation	-2.93E-05	2.53E-06	6.39E-31	***
		Impoundments (2010)	-2.23E-05	2.74E-06	3.34E-16	***
		Impoundment violations	-3.20E-05	4.08E-06	4.94E-15	***
		Spill violations	-2.33E-05	3.69E-06	2.74E-10	***
		UOG wells	-8.86E-05	1.00E-05	9.81E-19	***
SWPA	Strontium	Casing/cementing violation	-1.66E-05	1.15E-06	9.78E-47	***
		Impoundments (2010)	-2.07E-05	1.68E-06	7.55E-35	***
		Impoundment violations	-1.47E-05	1.18E-06	1.64E-35	***
		Spill violations	-1.53E-05	1.24E-06	2.76E-35	***
		UOG wells	-3.04E-05	6.36E-06	1.74E-06	***

1. * = 95%, ** = 99%, *** = 99.5%

Table S28: Tobit regression results analyzing relationships between chloride and UOGD metrics (UOG wells and documented spill-related violations).

Region	UOGD metric	Coefficient	Std. Error	p-value	Confidence[1]
Statewide	UOG well density	2.69E-02	4.67E-03	8.37E-09	***
	UOG well distance	8.38E-06	4.49E-06	6.18E-02	
	Spill violation density	4.57E-02	1.18E-02	1.08E-04	***
	Spill violation distance	1.05E-05	1.36E-06	1.34E-14	***
NEPA	UOG well density	-3.13E-04	7.04E-03	9.65E-01	
	UOG well distance	-1.76E-05	7.24E-06	1.51E-02	*
	Spill violation density	-4.14E-04	1.72E-02	9.81E-01	
	Spill violation distance	-2.65E-06	2.79E-06	3.43E-01	
SWPA	UOG well density	1.94E-02	6.53E-03	2.95E-03	***
	UOG well distance	-2.21E-05	7.86E-06	4.95E-03	***
	Spill violation density	4.32E-02	1.65E-02	8.82E-03	**
	Spill violation distance	6.36E-07	1.72E-06	7.11E-01	

1. * = 95%, ** = 99%, *** = 99.5%

Table S29: Calculated ATS slope, intercept, Kendall's tau, and p-value for [Ba] vs. UOG well density (1km) within a 7,000-sample data selection, and corresponding mean and median values using ensemble calculations from subsets of the data.

	Slope	Intercept	Kendall's tau	p-value				
True value	0.0016	0.111	0.014	0.0252				
Mean								
Ensemble	Slope mean	Slope std. dev.	Intercept mean	Intercept std. dev.	Tau mean	Tau std. dev.	p-value mean	p-value std. dev.
9x1200	0.0011	0.0005	0.11	0.003	0.009	0.005	0.543	0.226
3x2400	0.0018	0.0004	0.111	0.002	0.015	0.004	0.13	0.145
Median								
Ensemble	Slope median	Slope std. dev.	Intercept median	Intercept std. dev.	Tau median	Tau std. dev.	p-value median	p-value std. dev.
9x1200	0.0011	0.0005	0.11	0.003	0.009	0.005	0.534	0.226
3x2400	0.0016	0.0004	0.112	0.002	0.014	0.004	0.2	0.145

Table S30: Ensemble estimates of Kendall's tau, p-value, Akritas-Theil-Sen slope, and intercept using mean outputs from ensemble calculations

Approach	Species	UOG parameter	Slope mean	Slope std. dev.	Intercept mean	Intercept std. dev.	Tau mean	Tau std. dev.	p-value mean	p-value std. dev.
9x3000 samples	Barium	Density	0.0026	0.0004	0.110	0.001	0.021	0.003	0.021	0.016
	Barium	Spill density	0.0058	0.0023	0.112	0.002	0.009	0.003	0.087	0.079
	Strontium	Density	0.0082	0.0021	0.305	0.007	0.026	0.007	0.023	0.037
	Strontium	Spill density	0.020	0.007	0.311	0.006	0.012	0.004	0.068	0.125
	Chloride	Density	0.231	0.060	7.22	0.14	0.017	0.004	0.082	0.113
	Chloride	Spill density	0.205	0.255	7.35	0.16	0.002	0.003	0.570	0.362
3x6000 samples	Barium	Density	0.0022	0.0004	0.109	0.001	0.018	0.003	0.010	0.013
	Barium	Spill density	0.0063	0.0006	0.110	0.001	0.009	0.001	0.004	0.004
	Strontium	Density	0.0072	0.0022	0.309	0.005	0.022	0.006	0.004	0.003
	Strontium	Spill density	0.013	0.003	0.305	0.002	0.009	0.002	0.031	0.029
	Chloride	Density	0.202	0.042	7.33	0.15	0.014	0.003	0.033	0.042
	Chloride	Spill density	0.281	0.278	7.44	0.18	0.004	0.003	0.386	0.508

Table S31: Ensemble estimates of Kendall's tau, p-value, Akritas-Theil-Sen slope, and intercept using median outputs from ensemble calculations

Approach	Species	UOG parameter	Slope median	Slope sd	Intercept median	Intercept sd	Tau median	Tau std. dev.	p-value median	p-value std. dev.
9x3000 samples	Barium	Density	0.0026	0.0004	0.110	0.001	0.021	0.003	0.018	0.016
	Barium	Spill density	0.0058	0.0023	0.112	0.002	0.009	0.003	0.062	0.079
	Strontium	Density	0.0080	0.0021	0.306	0.007	0.026	0.007	0.007	0.037
	Strontium	Spill density	0.023	0.007	0.312	0.006	0.014	0.004	0.008	0.125
	Chloride	Density	0.250	0.060	7.20	0.14	0.018	0.004	0.037	0.113
	Chloride	Spill density	0.120	0.255	7.32	0.16	0.002	0.003	0.719	0.362
3x6000 samples	Barium	Density	0.0023	0.0004	0.110	0.001	0.019	0.003	0.004	0.013
	Barium	Spill density	0.0064	0.0006	0.110	0.001	0.010	0.001	0.003	0.004
	Strontium	Density	0.0061	0.0022	0.310	0.005	0.019	0.006	0.005	0.003
	Strontium	Spill density	0.012	0.003	0.316	0.002	0.008	0.002	0.027	0.029
	Chloride	Density	0.216	0.042	7.34	0.15	0.015	0.003	0.011	0.042
	Chloride	Spill density	0.289	0.278	7.49	0.18	0.005	0.003	0.148	0.508