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

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Abstract

While unconventional oil and gas (UOG) development is changing the world economy, processes that are used during UOG development 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 (Marcellus Shale in Pennsylvania, U.S.A. with ~29,000 analyses) and discovered that concentrations of brine-associated barium ([Ba]) and strontium ([Sr]) show small regional increases within 1 km of UOG development. Higher concentrations in groundwaters are associated with greater proximity to and density of UOG wells. Concentration increases are even larger when considering associations with 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 UOG development slightly increases salt concentrations in regional groundwaters not because of fracking but because of the ubiquity of wastewater management issues. These results emphasize the need for stringent wastewater management practices across oil and gas operations.

Introduction

Unconventional oil and gas (UOG) development has advanced United States (U.S.) energy independence but incited concerns surrounding potential environmental and human health impacts. UOG development 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. UOG development 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.[1] While increased gas production from the Marcellus Shale has reduced emissions of CO_2 and some pollutants as power generation has shifted from coal to gas, the 570% increase in wastewater co-produced with natural gas accentuates the need for proper handling, recycling, and disposal of produced materials to avoid environmental impacts.[1–4] 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.[5–7] 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 UOG development on groundwater quality has extensively focused on methane, the primary constituent of natural gas and the most commonly cited contaminant during UOG development.[8–14] However, another commonly reported pollutant released during UOG development is wastewater, which can be spilled into soils or streams because of issues related to recovery, storage, or transportation.[5,6,15] 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.[16,17] Formation brines typically comprise 92-96% of the wastewater generated over a UOG well's production lifetime, and are generally sodium (Na)-

calcium (Ca)-chloride (Cl) brines with salinities up to 7x modern ocean water.[18,19] 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.[18,20] The highly concentrated nature of many UOG wastewaters creates the potential for their salts, metals, organic species, and naturally-occurring radioactive materials to degrade water resources.[21,22]

Many stakeholders including scientists, engineers, regulators, operators, and the public are interested in both why contamination occurs and how frequently it occurs during UOG development. The former question generally requires time-, money-, and fieldwork-intensive case studies in locations generally only accessed by landowners, regulators, or industry practitioners.[10,13] Determining the frequency of incidents typically requires statistical analyses of large regulatory and geochemical datasets.[6,23] Such analyses applied to the salinization of surface waters during UOG development shows that regional salt concentrations may be increasing very slightly in streams near UOG development and that local increases in [Ba], [Sr] and [Cl] in streams impacted by UOG development wastewater leaks or spills can persist for years.[24–26] A recent nationwide analysis of stream chemistry reported a significant increase in brine salt (Ba, Sr, Cl) concentrations in watersheds with higher UOG development density (i.e., the number of UOG wells).[27] 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 UOG development.[28] This regional increase was attributed to localized incidents or “hotspots” where brines had escaped into groundwater.[28]

Despite these studies, the actual causes of regional UOG impacts on water resources are difficult to identify because UOG development is broadly distributed across hydrocarbon basins and includes many processes that could cause contamination ranging from drilling to “fracking” to waste disposal. Additionally, water quality prior to UOG development is not well-characterized in many basins, and UOG development often overlaps with road salting and longstanding forms of hydrocarbon extraction such as conventional oil and gas (COG) development or coal mining that have also been associated with groundwater impacts.[28–30] Many of the species most often associated with UOG development contamination, such as methane and brine salts, are also naturally present in groundwater and can be released by COG development as well.[31–34] Nevertheless, determining the extent to which UOG development may impact water supplies is important because in most locations of such development, local populations rely on domestic wells for drinking water.[35,36] Emerging studies that link proximity to UOG development to negative effects on human health have led to research into whether water supplies are an exposure pathway.[37–40]

In this study, we examined the concentrations of brine salt ions in groundwater to determine if they are impacted by specific processes during UOG development (e.g., well construction, wastewater management). Of the major shale plays under development worldwide, we are aware of only three U.S. states where the quantities and density of groundwater quality data readily available to the public are suitable for regional-scale analyses (Texas, Colorado, Pennsylvania).[41] To investigate the potential for groundwater impact, we therefore chose the state with the largest publicly accessible water quality database, Pennsylvania.[42] We emphasize UOG wells instead of COG wells because publicly available data suggest that UOG wells are responsible for 97.4% of the wastewater produced by oil and gas wells since the implementation of UOG development in our study area (Text S1).

Pennsylvania (PA) is also a good test case 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.[6,15] In addition, much of the information about such incidents is publicly accessible for PA,[6] enabling a large-scale investigation of impacts on groundwater with an objective of elucidating relevant processes in many other major shale plays where such an investigation is not feasible.[42] The two most heavily drilled parts of this region are northeastern and southwestern PA (northeastern PA and southwestern PA, respectively, Figure 1). Northeastern PA is characterized by greater topographic relief but far more limited legacy hydrocarbon extraction (coal mining, conventional oil and gas) compared to southwestern PA.[28,43]

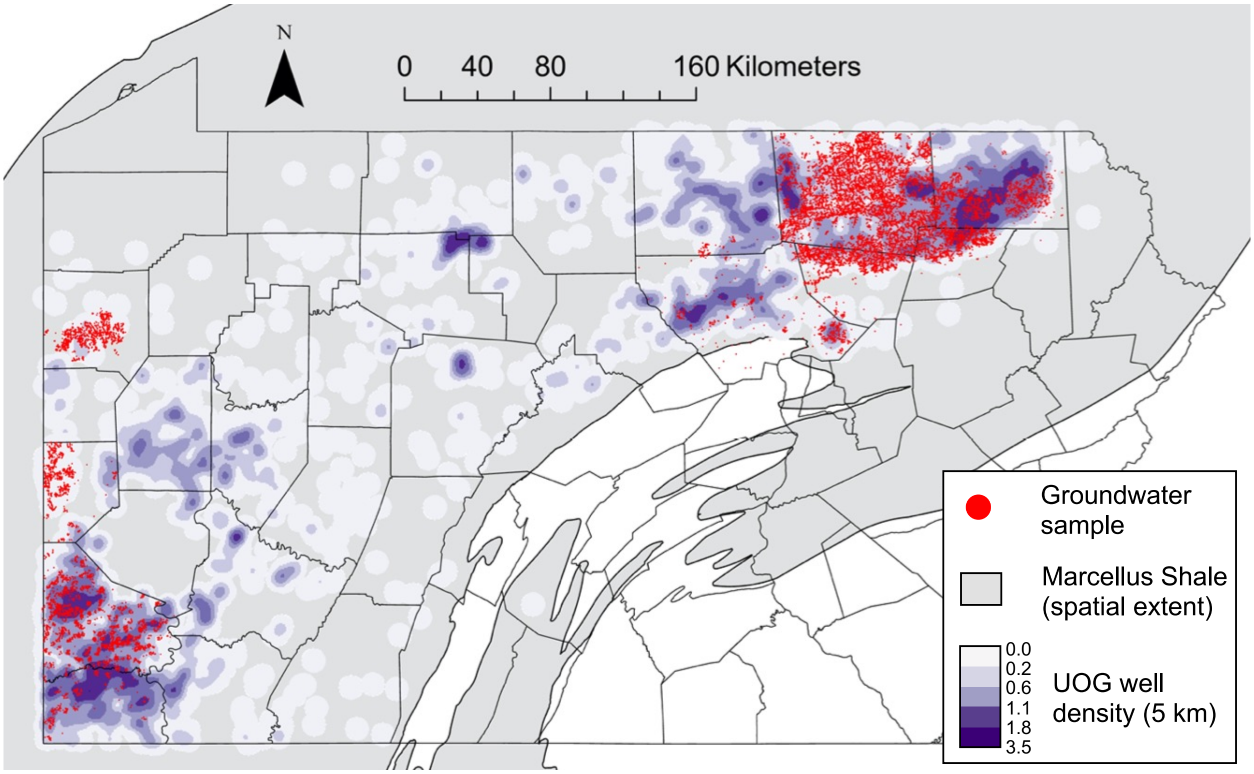

Figure 1: Locations of the 28,609 sampled groundwaters indicated on a map showing the average density of UOG wells within a 5 km radius in Pennsylvania (calculated as the 5 km kernel density using 500 m bins). For closeups of western PA and northeastern PA, see Figures S2 and S3 and for locations of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

Materials and Methods

Our dataset consists of 28,609 groundwater analyses from the Shale Network database (available at https://doi.org/10.26208/DT5Y-5B37 and https://doi.org/10.4211/his-data-shalenetwork), spanning the Marcellus Shale region of PA (Figure 1).[44] These samples were predominantly collected between April 2008 and April 2020, with the majority of samples collected pre-2014 (for more about the dataset see Figure S1, Text S2). We examined relationships among groundwater chemistry and the locations of UOG wells, UOG impoundments, and UOG-related violations documented by the state regulator, the Pennsylvania Department of Environmental Protection (PADEP). This is the most complete database of incidents during UOG development that we are aware of for the study area, although additional incidents not cited in violations could potentially occur. In addition to regulatory data, we obtained the locations of impoundments associated with UOG development identified from 2010 satellite imagery by Skytruth.[45] The locations of these impoundments were determined by Skytruth from USDA aerial survey photography following outlined methods and QAQC protocols.[46] Impoundments are often used to store fresh water for UOG wellpads in PA, but prior to 2016 the storage of UOG wastewaters in impoundments was less strictly regulated and led to putative issues with wastewater leakage.[5,47]

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 S3). We examined land usage and UOG development density within a buffer radius around sample sites of both 1 km and 3 km. We emphasize the smaller radius in the main text because 1 km is in best agreement with physics-based models analyzing the distance that groundwater may travel from UOG wellpads to domestic wells in the study area.[48] However, case studies have demonstrated fracture-mediated migration of UOG contaminants up to 3 km from a wellpad, and thus we conducted tests with a larger radius that are summarized in the SI.[5,10,13]

We focused intensively on two cationic species, barium (Ba) and strontium (Sr), both of which are widely analyzed and are present at characteristically high concentrations in Appalachian Basin brines.[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.[23,49] Ba is derived from rock dissolution but is found in generally low concentrations in uncontaminated surface and groundwaters in PA relative to oil and gas inputs.[50] While also derived from dissolution of the carbonate rocks that are common in hydrocarbon basins,[51] Sr can also serve as an identifier for UOG wastewater contamination.[24,25] While neither species can be considered truly conservative (i.e., they may adsorb or react as they migrate through an aquifer), both Ba and Sr have previously been identified as an effective tracer for wastewater leakage during oil and gas development in the Marcellus and nationwide.[27,50]

Before selecting Ba and Sr as foci, and to exclude species that are greatly influenced by overlapping sources such as coal mining or road salting, we examined how median concentrations of Ba, Ca, Cl, Na, Sr, and sulfate (SO_4) varied across different hydrocarbon-related land uses. This comparison suggests that Ba, Sr, and Cl are perhaps the best tracers for UOG impacts, and supports more widespread impacts of UOG vs. COG wells (Text S4, Table

S1). 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. In contrast, Cl is more abundant in road salt, which commonly impacts groundwater in PA, and Cl is more frequently censored in our dataset (i.e., present below reporting limits).[52,53] In particular, Cl is only reported to be above reporting limits in 21,584 out of 27,599 analyses. As a check, we used specialized methods for highly censored data (Text S5) to validate our key conclusions using Cl (Text S6).

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. Given the skew in concentration distributions, we consider medians as opposed to means and, in our regressions, relationships between log concentrations and linear UOG metrics (Text S3).

Additionally, we assessed relationships with three specific activities associated with UOG: problems surrounding the casing and cementing of wells, impoundment of wastes, and spills of wastes. To assess associations with specific activities, we analyzed 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).[5,54] While casing or cementing problems are known to sometimes allow gas leakage into groundwater, pollution incidents involving 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 better account for potentially confounding overlap with other sources of geogenic or anthropogenic salt. This regression includes binary, "dummy" variables reflecting a water sample's proximity to anthropogenic and geologic sources of salt ions, as well as the bedrock lithology and season of sample collection (Text S3). These variables subsequently group the samples based on shared land use characteristics, and the fixed effects models only use the variation within groups to estimate the effect of the predictors. This method allows a better analysis of within-group variation, which can help reduce omitted variable bias from confounding factors (see Text S3 for a full description). We included additional tests to account for the small portion of censored concentration data (Text S5). For full details on the methods, see Text S3.

Results

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

Throughout the paper we use statistical analyses to look for associations, and we define significance as referring to p-values < 0.05. We first considered whether median concentrations of brine salts are elevated in samples near UOG development. For this comparison we use the Wilcoxon-Mann-Whitney (WMW) test, as well as the more stringent Brunner-Munzel test, both of which are well-suited for non-parametric data.

We observed significantly higher median [Ba] and [Sr] in samples located within 1 km of a UOG well across PA (Figure 2). Median [Ba] and [Sr] in samples within 1 km of a UOG well are 11 μg/L and 32 μg/L higher, respectively, than samples farther than 1 km. UOG development within 1 km thus corresponds to 12.2% higher median [Ba] and 10.5% higher median [Sr]. These comparisons remain statistically significant using the Brunner-Munzel statistical test (Table S3, Table S4).

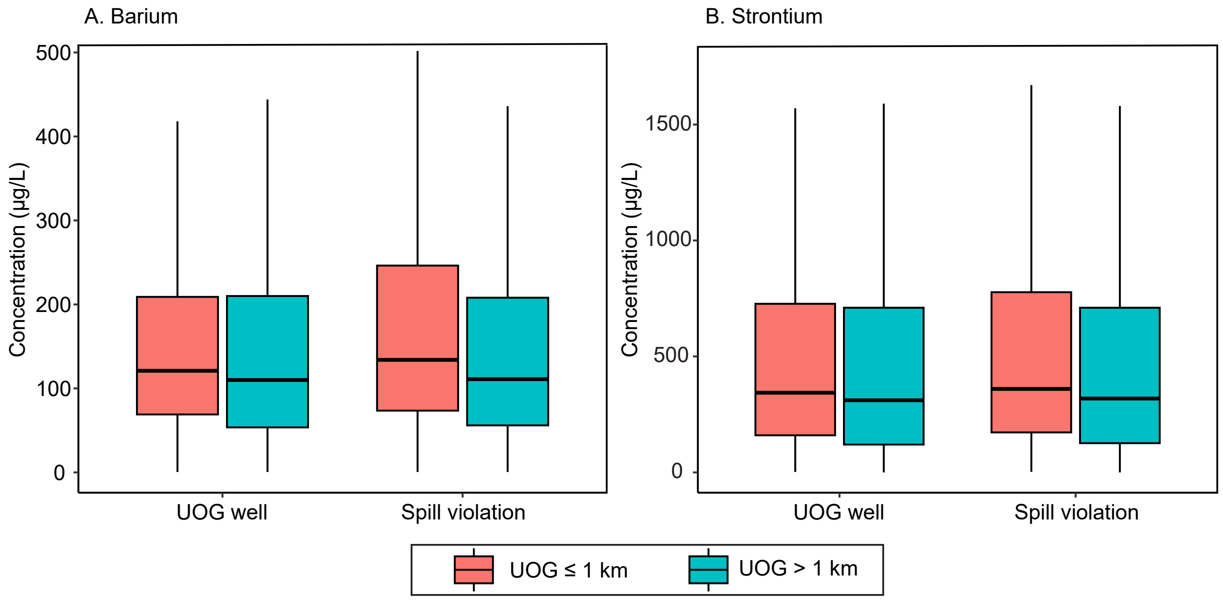

Figure 2: Box and whisker plots summarizing statewide (A) barium and (B) strontium concentrations for Pennsylvania samples ≤1 km from locations of UOG development (red) and >1 km from UOG development (aqua) for UOG wells and spill violations. The bounds of the boxes depict Q1 and Q3 concentrations, while the thick center line displays the median concentration. All comparisons shown found a statistically significant difference in median concentrations (see Figure S5 for the comparison of all UOG attributes considered). 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. 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 1 km of a pollution violation ("spill") across the state as compared to samples >1 km (Table S3, Table S4). Furthermore, the magnitude of the increase within 1 km of spills is larger than the increase within 1 km 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 1 km of wellpads cited for violations related to impoundment or casing/cementing violations (Table S3, Table S4).

Brine salt concentrations increase with density of UOG wells

Given observed statewide increases in median [Ba] and [Sr] within 1 km of UOG wellpads, we investigated whether [Ba] and [Sr] 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 1 km (Figure 3A, Table S5). Regressions calculated using a radius of 3 km rather than 1 km typically revealed smaller regression coefficients (e.g., a smaller magnitude of impacts) but strengthened significance, where the latter result is likely related to the larger number of samples within the 3 km 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 increases in groundwater [Ba] and [Sr] with UOG development.

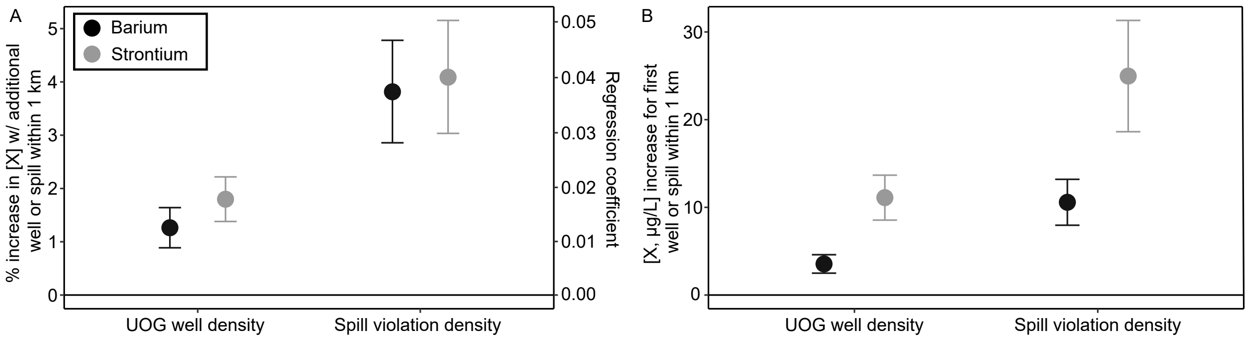

Figure 3: Percent increases in the concentration of barium and strontium associated with increasing UOG development density within 1km, and their associated regression coefficients (A). These values were calculated using Equation 1 for the full statewide dataset using regressions analyzing the relationship between log[Barium] and log[Strontium] and UOG well density or pollution violation ("spill") density within a 1 km radius of water samples. The corresponding average increase in ion concentrations for the first well spudded or spill within 1 km are shown in (B), calculated using Equation 2 with mean concentrations. Error bars show standard error. All regressions yielded statistically significant ($p < 0.05$) correlations. Calculations only include UOG wells spudded before water sample collection.

We next used our regressions to quantify the magnitude of increase in concentration (e.g., in µg/L) per additional UOG well within 1 km. In a log-linear model regression such as used here, the regression coefficient, β, calculated for relationships between log concentrations and UOG well density cannot be directly interpreted as the increase in concentration (e.g., in µg/L) per additional well. However, the percent increase in concentration for every additional well can be calculated as:

$$\% \text{ increase} = e^{\beta} - 1 \qquad \text{Equation 1}$$

where β is the calculated regression coefficient. Following equation 1, [Ba] increases by 1.27% and [Sr] by 1.80% for every additional UOG well within 1 km. We can corroborate these values by also assessing the increase in concentration for every additional well using an estimate of the Akritas-Theil-Sen slope (Text S7). Using this alternate regression calculation which can handle non-parametric, censored data, we estimate a 2.2 - 2.6 µg/L increase in [Ba] and 6.1 - 8.2 µg/L increase in [Sr] per additional UOG well within 1 km. These increases represent up to 2.3% and 2.5% of the median [Ba] and [Sr], respectively, and 0.92% and 1.32% of the mean [Ba] and [Sr] in our groundwater dataset.

From our regression coefficients, we can also estimate the average µg/L increase in [Ba] or [Sr] (ΔC_{avg}) from UOG well density (#UOG1km) across the entire study area as:

$$\Delta C_{avg} = C_{avg} * (e^{\beta * \#UOG1km} - 1) \qquad \text{Equation 2}$$

Here C_{avg} is the mean concentration of Ba or Sr across the region of interest (µg/L), #UOG1 km is the number of UOG wells within 1 km (density), and β is the regression coefficient. Based on the calculated regression coefficients and mean [Ba] and [Sr] (283 µg/L and 623 µg/L, respectively), we calculate that the first UOG well spudded within 1 km (#UOG1km = 1) increases [Ba] and [Sr] by 3.6 µg/L and 11.2 µg/L, respectively (Figure 3B). Using instead the mean #UOG1km (0.72 UOG wells within 1 km) for groundwater samples in the full statewide dataset, the average concentration increases attributed to UOG development are 2.58 µg/L (Ba) and 8.04 µg/L (Sr). At the highest density of UOG wells within 1 km 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].

Potential sources of UOG wastewater releases

Across PA, [Ba] and [Sr] also show a statistically significant increase with the number of pollution violations (i.e., spills) within 1 km (Table S6, Table S7). Given both UOG well density and spill density are expressed as the number of UOG wells or spills, respectively, within 1 km, we compared regression coefficients to understand the relative impacts of UOG wells versus spills. One additional spill within 1 km has a greater impact on concentration compared to one additional UOG well (Figure 3). For example, we calculate 3.8% and 4.1% increases in [Ba] and [Sr], respectively, for every additional spill within 1 km using Equation 1 and the coefficients from our regression analyses (Figure 3A, Table S6, Table S7). Following Equation 2, we calculate the average effect of the first spill within 1 km to be a 10.8 µg/L increase in [Ba] and a 25.5 µg/L increase in [Sr] (Figure 3B). 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 1 km compared to all UOG wells (Text S7). 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 UOG development metrics statewide, we identify significant relationships indicating increasing salt concentrations closer to UOG development for all metrics except [Sr] and impoundment violations (Table S6, Table S7).

Statistically significant relationships persist when accounting for overlapping sources

As discussed previously, UOG development 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 that better accounts for these features (Text S3), relationships between salt ions and UOG well density and distance remain statistically significant (Table S8, Table S9, Figure S6).

Relationships between UOG development 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 (northeastern PA and southwestern PA). The subregions are characterized by the highest density of UOG development but differ with respect to land use and geology (Text S2).

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

We also investigated correlations with respect to distance and density within these subregions. We observed relationships that were statistically significant for both analytes in both southwestern PA and northeastern PA 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 southwestern PA, just as we observed in the statewide analysis (Table S5). However, we did not observe this relationship with UOG well density in northeastern PA (Table S5).

Additionally, we observe significant increases in [Ba] and [Sr] in southwestern PA associated with a higher density of spills within 1 km (Table S6). [Sr] in southwestern PA 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 1 km in northeastern PA (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 southwestern PA and northeastern PA (Figure S6, Table S8, Table S9). Similarly, relationships between [Sr] and spill violation density are significant in both southwestern PA and northeastern PA 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 southwestern PA or northeastern PA as well, especially when fixed effects were included in regression analyses (Table 1).

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

Species	UOG variable[1]	Comparison of medians (1 km)[2]	Density (within 1 km)	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**
Northeastern PA						
Barium	UOG wells	**<0.001**	0.063	**<0.001**	**0.001**	**<0.001**
	Spills	**<0.001**	0.198	**<0.001**	0.088	**<0.001**
Strontium	UOG wells	**<0.001**	0.893	**<0.001**	**0.002**	**<0.001**
	Spills	**0.014**	0.114	**<0.001**	**0.004**	**<0.001**
Southwestern PA						
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**	**0.004**	**<0.001**	**0.004**	**0.025**
	Spills	0.127	**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 S3/S4 for one-sided and BM results

Discussion

Brine salts increases likely because of wastewater mishandling

Statewide, we observed significantly higher median [Ba] and [Sr] within 1 km of UOG wells, as well as significant increases in [Ba] and [Sr] with a higher density of UOG wells (Table 1). When we repeat these analyses to instead consider only COG wells or all oil and gas wells (UOG + COG), we do not identify such consistent relationships (Text S8). Similar increases associated with UOG development have been reported for surface waters nationwide[27] and for groundwaters in southwestern PA,[28] but our study is the first to indicate a statewide increase in groundwater brine salt ion concentrations associated with UOG development. 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,[27] consistent with greater dilution of surface waters by meteoric water as compared to groundwaters. The surface water trends are plausibly driven by groundwater contamination, especially considering that most streams in PA are gaining streams.[55]

We also observed statewide that median [Ba] and [Sr] were higher within 1 km of documented pollution violations, 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. In other words, the small regional increases may be explained by problematic, isolated sites. 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 (Table 1). In contrast, violations pertaining to subsurface well integrity (i.e., casing/cementing violations) were not associated with significant concentration increases across these tests. In the case of both spills and well integrity issues, we acknowledge that not all incidents that may merit a violation are necessarily reported or documented. However, this observation nonetheless suggests that surface impacts rather than downhole problems are primarily responsible for slight groundwater salinization during UOG development at the well depths reflected in our dataset.

To further test whether a surface source is the best explanation for the impacts we observe, we repeated our analyses considering only UOG 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.[48,56] When we consider only higher-elevation UOG wells, we observe that the effect of UOG development becomes even stronger, resulting in 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). The strengthened relationship among UOG development and salt ion concentrations when only higher elevation wellpads are considered further 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 UOG development.

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 identified a significant increase in [Sr] associated with larger volumes of produced water at UOG wells within 1 km of the respective water sample across PA and for [Ba] in southwestern PA (Text S9, Table S12).

While these associations point to spills as a likely mechanism for increased salt ion concentrations in groundwaters, most wellpad spills are very small in volume.[6,15] For example, regulatory data indicate reported spills in PA are typically 100 L-10,000 L in volume.[15] 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 1 km of UOG wells (Text S10). The salt contamination we document is therefore most likely associated with the small number of isolated 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.[6] 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, 1 km or 3 km respectively. We observed that the median [Ba] for samples within the buffer distance from large spills (137 µg/L for 1 km or 131 µg/L for 3 km) is ~23-24% higher than the median in samples over 1 km or 3 km from any reported spills (111 µg/L for 1 km and 106 µg/L for 3 km) (Figure 4A, 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 3 km (where a larger number of samples, n = 902, are located within 3 km of a >500 gallon spill vs. n = 77 samples within 1 km).

The totality of these results leads us to attribute the slightly higher concentrations of brine salt ions in surface and ground waters near UOG development[27,28] to isolated incidents of 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.[21,26,57] However, this is the first published study to document a regional impact of UOG development on water resources where evidence for the specific cause has also been identified.

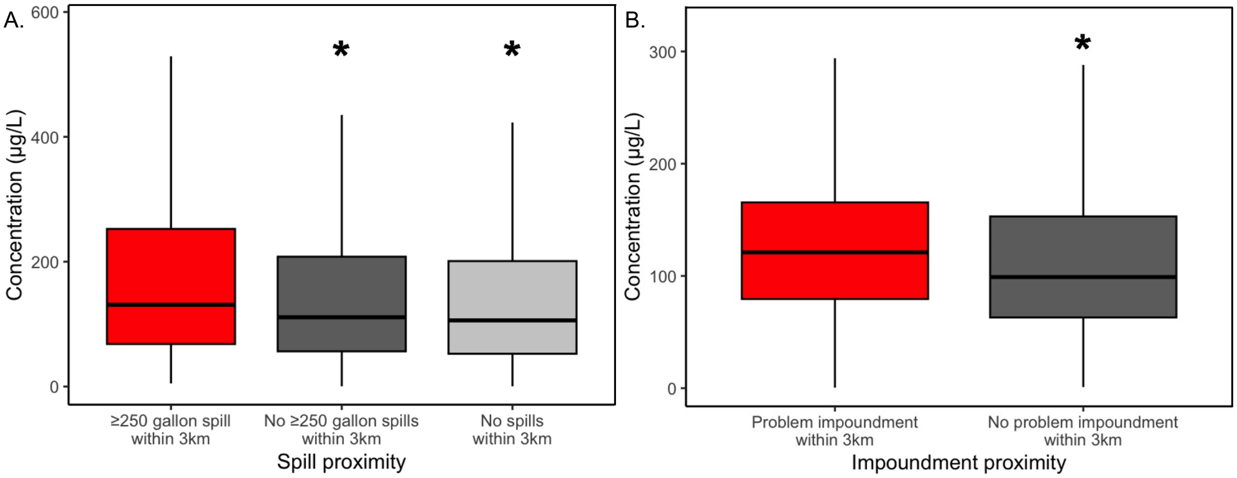

Figure 4: Box and whisker plots displaying barium concentrations for (A) samples within 3 km of a large (≥250 gallon or 964 L) spill vs. samples >3 km from a large spill and samples >3 km from any spill, and (B) southwestern PA samples within 3 km of an impoundment that was mandated to close, upgrade,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

Wastewater impoundments may also release salt ions to groundwater

A second kind of spill or leakage may also have been important early in UOG development in PA, namely, leakage of wastewaters from impoundments.[5] To investigate this, we considered correlations with the locations of wellpad impoundments identified using 2010 satellite imagery (henceforth referred to as historical impoundments), which may have stored UOG wastewaters (Text S2).[45] These "historical impoundments" are potentially important 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 southwestern PA: in that area, [Ba] is significantly higher within 1 km of historical impoundments and [Ba] increases with greater density and proximity of these impoundments (Table S3, Table S6). The problematic nature of some impoundments has previously resulted in regulatory action in southwestern PA. Specifically, because of observed or inferred infractions, eight impoundments in southwestern PA (out of an estimated 500-600 operating statewide yearly before 2016) were ordered by the PADEP in 2014 to be i) fully shut down, ii) upgraded with respect to liners and systems for leak detection, or iii) limited to storage of only freshwater.[45,58] The USEPA also documented likely leakage of Cl from one of the eight impoundments into downgradient groundwater at a location where significant health impacts were alleged.[59]

When we compare median [Ba] between southwestern PA samples within 1 km of the estimated locations of these eight impoundments vs. samples >1 km away (Text S2), we find ~34% higher median [Ba] in samples within 1 km of these impoundments (134 vs. 100 μg/L) (Table S15). We observe a similar increase when we compare median [Ba] for samples within 3 km of an impoundment (123 μg/L) vs. samples >3 km away (99 μg/L) (Figure 4B, Table S15). These differences are statistically significant within both 1 km and 3 km. In addition, one of these problematic impoundments is located within a previously identified subregion ("hotspot") in southwestern PA where [Cl] increased with higher UOG well density.[28]

Regional differences in hydrogeology and land usage complicate identification of impact

We generally observed statistically significant relationships between [Ba] and [Sr] and UOG development density in southwestern PA but not in northeastern PA. This comparison of southwestern PA and northeastern PA is important not only because these subregions contain some of the highest density of UOG development in the world, but also because the data demonstrate how geology and land use combine to complicate the detection of contamination during UOG development. In particular, southwestern PA and northeastern PA differ with regard to the topographic relief (higher in northeastern PA) as well as the extent of prior hydrocarbon extraction (extensive legacy development in southwestern PA).[43]

The importance of topographic relief may explain why we observed increased significance in northeastern PA 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 northeastern PA, 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 northeastern PA masks effects of UOG development in that region. In particular, where topographic relief is the highest (in northeastern PA), naturally elevated concentrations of species like Ba and Sr are generally observed in valley bottoms and other topographic lows.[32] This natural phenomenon has been attributed by some to natural upwelling of Appalachian Basin brines from deeper than a few hundred meters depth into valleys.[32,60] 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 yet been completely flushed out yet.[43] Regardless of the explanation, natural brine migration may be particularly important in northeastern PA because of geologic features in that area such as anticlinal folding and faults.[23,31] While groundwater flow is still predominantly gravity-driven and brines can still occur at shallow depths in southwestern PA, topographic relief is smaller and the extent of surface faulting is more limited.[43,56] As a result, topographic forcing likely has a smaller influence on groundwater chemistry in southwestern PA, 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.[28,43] These hydrogeologic differences may serve to mask some of the impacts of brine spills on groundwater in northeastern PA compared to southwestern PA, as the strong topographic forcing on brine salt occurrence in northeastern PA may obscure any increases in salt ion concentrations from UOG development.

In addition to geogenic processes shaping groundwater chemistry, the long history of energy development in southwestern PA also complicates contaminant attribution. For waters sampled in southwestern PA that were >1 km from UOG wells and coal mining but located <1 km from COG wells, we did not see significant differences in median [Ba] or [Sr] compared to samples >1 km from any hydrocarbon extraction (Table S1). From this we inferred the effects of these legacy COG wells on groundwater chemistry may be minor in southwestern PA. However, 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.[51] Lower [Ba] nearby coal mining may be explained by a) significantly higher median [SO_4] where coal mining is <1 km 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.[61]

Despite such overlap, the significance of relationships between Ba and Sr and UOG development in southwestern PA 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 UOG development on salt ion concentrations (particularly [Ba]) in groundwater appear strongest in southwestern PA, potentially implying that overlap with legacy hydrocarbon extraction may increase contamination during UOG development. However, our investigation also reveals that other attributes in southwestern PA (namely problematic impoundments) may explain why impacts sometimes appear greater in southwestern PA. As such, we cannot conclude that overlap between UOG development 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, UOG development is associated with slightly increased concentrations of brine salt ions in groundwater (this study) and surface waters (Bonetti et al.).[27] Our results also suggest 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 UOG development, explaining the regional effects.[28]

Our estimates suggest the average increases in [Ba] and [Sr] associated with UOG development should not exceed 15% of the USEPA's recommended levels for either Ba or Sr (2 mg/L and 4 mg/L, respectively). However, the occurrence of relatively elevated Ba and Sr in groundwaters near UOGD highlights the potential for the presence of more hazardous species in brines that are not widely monitored or only reportable at very high concentrations. These include toxic trace elements such as thallium, arsenic, and cadmium, and the species responsible for most of the radioactivity in the brines (radium). To investigate this, we calculated the statewide medians for species concentrations in the USGS Produced Water database, including trace metals, organics, and radioactive species. We then assumed that the statewide median mass ratios of [X] to [Ba] or [Sr] (where X is one of the species measured in produced waters) in the produced water could be used to estimate [X] as a function of our data for [Ba] and [Sr]. The increases we calculate statewide represent, on average, very small portions of brine mixing into water samples. For example, our calculated increases in [Ba] and [Sr] are always <150 μg/L (Ba) and <500 μg/L (Sr) even at the highest UOG well density, which would represent mixing of <0.04% brine based on median [Ba] and [Sr] reported for Marcellus produced waters. Based on these calculations, we estimate that other potentially hazardous species are also not likely to exceed USEPA limits when considered on a regional basis (Table S16).

However, these statewide estimates do not exclude the possibility of localized risks because the regional concentration effects we have documents are likely caused by localized contamination incidents. This is in-line with previous work that found increases in [Cl] calculated per UOG well in southwestern PA were over 10x greater in some geospatially-identified hotspots than calculated regionwide.[28] Mixing of just 0.2% - 0.5% brine in could drive the concentrations of species including radium to exceed EPA limits based on average produced water compositions in PA.

We show that brine contamination has likely affected groundwaters in the largest shale gas play in the world where water quality data are publicly available. The high production volumes and salinity of produced waters in other major shale gas plays[62] and relative ubiquity of spills[6,15] leads to the conclusion that similar impacts should be studied in other shale gas plays, and especially where very large spills have occurred (Text S11).[15,26] In some shale plays, produced water volumes exceed recycling and re-injection capabilities and this is projected to increase worldwide into the future.[63] Further, while UOG wells generate greater brine volumes than COG wells on a per-well basis, problems surrounding wastewater storage also occur and can contaminate groundwater during COG development. Our results emphasize the need for stringent management of oil and gas wastewaters to protect water resources.

Supporting Information:

Estimates of wastewater volumes produced from unconventional vs. conventional wells (Text S1), additional dataset details (Text S2), additional details on analysis methods (Text S3), comparison of medians across land uses (Text S4), treatment of censored data (Text S5), analyses with chloride (Text S6), estimates of Akritas-Theil-Sen slopes (Text S7), analyses for conventional and all oil and gas wells (Text S8), relationships with wastewater production volumes (Text S9), spill mixing calculation details (Text S10), implications across shale gas basins (Text S11), and potential explanations for inverse relationships (Text S12). Sample collection dates (Figure S1), insets of Figure 1 (Figures S2-3), map of oil and gas wells and coal mining locations in PA (Figure S4), full comparison of medians (Figure S5), regression coefficient and p-values with and without fixed effects (Figure S6), fixed effects sensitivity analyses (Figure S7). Comparison of median concentrations across land uses (Table S1), violation classification scheme (Table S2), comparison of median [Ba] and [Sr] (Tables S3-S4). Results for regression analyses considering UOG wells (Table S5), UOG violations (Tables S6-

S7), with fixed effects (Tables S8-S9), only higher-elevation wells/spills (Tables S10-S11), and waste production volumes (Table S12). Comparison of median [Ba] relative to locations of large spills and impoundments (Tables S13-S15), median ratios of additional species to [Ba] or [Sr] in PA produced waters (Table S16), summary statistics for species in the dataset (Table S17), coordinates estimated for impoundments (Table S18), summary statistics of sample proximity to relevant geologic and anthropogenic features (Table S19), number of samples nearby relevant features (Table S20), summary statistics for sample proximity to violations (Table S21), analyses using a 3 km radius (Tables S22-24), analyses using a tobit regression (Tables S25-S28), Akritas-Theil-Sen slope estimates (Tables S29-S31), and analyses considering conventional wells and all oil and gas wells (Tables S32-S34).

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