Geochemical evidence for possible natural migration of Marcellus Formation brine to shallow aquifers in Pennsylvania

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The debate surrounding the safety of shale gas development in the Appalachian Basin has generated increased awareness of drinking water quality in rural communities. Concerns include the potential for migration of stray gas, metal-rich formation brines, and hydraulic fracturing and/or flowback fluids to drinking water aquifers. A critical question common to these environmental risks is the hydraulic connectivity between the shale gas formations and the overlying shallow drinking water aquifers. We present geochemical evidence from northeastern Pennsylvania showing that pathways, unrelated to recent drilling activities, exist in some locations between deep underlying formations and shallow drinking water aquifers. Integration of chemical data (Br, Cl, Na, Ba, Sr, and Li) and isotopic ratios ($^{87}Sr/^{86}Sr$, $^2H/H$, $^{18}O/^{16}O$, and $^{228}Ra/^{226}Ra$) from this and previous studies in 426 shallow groundwater samples and 83 northern Appalachian brine samples suggest that mixing relationships between shallow ground water and a deep formation brine causes groundwater salinization in some locations. The strong geochemical fingerprint in the salinized (Cl > 20 mg/L) groundwater sampled from the Alluvium, Catskill, and Lock Haven aquifers suggests possible migration of Marcellus brine through naturally occurring pathways. The occurrences of saline water do not correlate with the location of shale-gas wells and are consistent with reported data before rapid shale-gas development in the region; however, the presence of these fluids suggests conductive pathways and specific geostructural and/or hydrodynamic regimes in northeastern Pennsylvania that are at increased risk for contamination of shallow drinking water resources, particularly by fugitive gases, because of natural hydraulic connections to deeper formations.

formation water | isotopes | Marcellus Shale | water chemistry

The extraction of natural gas resources from the Marcellus Shale in the Appalachian Basin of the northeastern United States (1, 2) has increased awareness of potential contamination in shallow aquifers routinely used for drinking water. The current debate surrounding the safety of shale gas extraction (3) has focused on stray gas migration to shallow groundwater (4) and the atmosphere (5) as well as the potential for contamination from toxic substances in hydraulic fracturing fluid and/or produced brines during drilling, transport, and disposal (6–9).

The potential for shallow groundwater contamination caused by natural gas drilling is often dismissed because of the large vertical separation between the shallow drinking water wells and shale gas formations and the relatively narrow zone (up to 300 m) of seismic activity reported during the deep hydraulic fracturing of shale gas wells (10, 11). Recent findings in northeastern Pennsylvania (NE PA) demonstrated that shallow water wells in close proximity to natural gas wells (i.e., <1 km) yielded, on average, higher concentrations of methane, ethane, and propane with thermogenic isotopic signature. By comparison, water wells farther away from natural gas development had lower combusti-

ble gas concentrations and an isotopic signature consistent with a mixture between thermogenic and biogenic components (4). In contrast, when inorganic water geochemistry from active drilling areas was compared to nonactive areas and historical background values, no statistically significant differences were observed (4). Increasing reports of changes in drinking water quality have nevertheless been blamed on the accelerated rate of shale gas development.

The study area in NE PA consists of six counties (Fig. 1) that lie within the Appalachian Plateaus physiographic province in the structurally and tectonically complex transition between the highly deformed Valley and Ridge Province and the less deformed Appalachian Plateau (12, 13). The geologic setting and shallow aquifer characteristics are described and mapped in greater detail in multiple sources (4, 14–19) and in *SI Methods*. The study area contains a surficial cover composed of a mix of unconsolidated glacial till, outwash, alluvium and deltaic sediments, and postglacial deposits (the Alluvium aquifer) that are thicker in the valleys (17–19) (Fig. S1). These sediments are underlain by Upper Devonian through Pennsylvanian age sedimentary sequences that are gently folded and dip shallowly (1–3°) to the east and south (Fig. S2). The gentle folding creates alternating exposure of synclines and anticlines at the surface that are offset surface expressions of deeper deformation (12, 20). The two major bedrock aquifers are the Upper Devonian Catskill and the underlying Lock Haven Formations (14, 15, 18, 19). The average depth of drinking water wells in the study area is between 60 and 90 m (Table S1). The underlying geological formations, including the Marcellus Shale (at a depth of 1,200–2,500 m below the surface) are presented in Fig. 2, Fig. S2 *A and B*, and *SI Methods*.

In this study, we analyze the geochemistry of 109 newly-collected water samples and 49 wells from our previous study (4) from the three principal aquifers, Alluvium (n = 11), Catskill (n = 102), and Lock Haven (n = 45), categorizing these waters into four types based on their salinity and chemical constituents (Figs. 1 and 2, and *S1 Text*). We combine these data with 268 previously-published data for wells in the Alluvium (n = 57), Catskill (n = 147), and Lock Haven (n = 64) aquifers (18, 19) for a total of 426 shallow groundwater samples. We analyzed major and trace element geochemistry and a broad spectrum of isotopic tracers ($\delta^{18}O$, δ^2H, $^{87}Sr/^{86}Sr$, $^{228}Ra/^{226}Ra$) in shallow
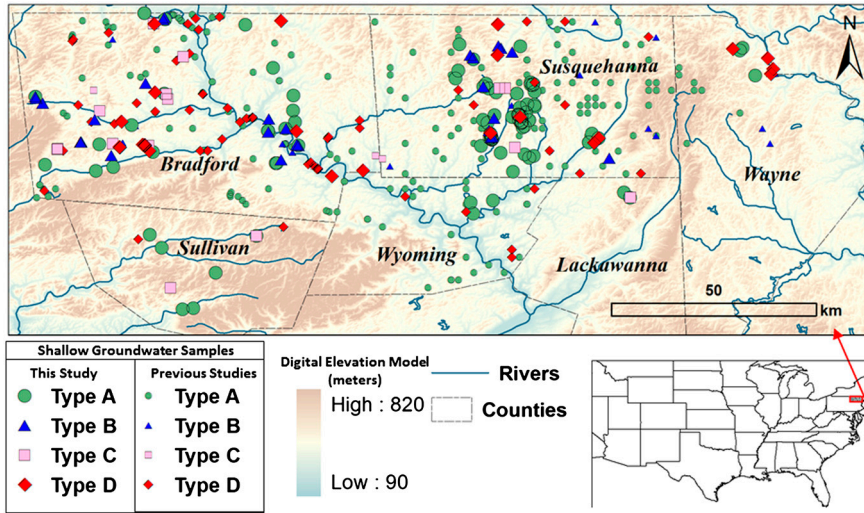
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Fig. 1. Digital elevation model (DEM) map of northeastern PA. Shaded brown areas indicate higher elevations and blue-green shaded areas indicate lower elevations (valleys). The distribution of shallow (<90 m) groundwater samples from this study and previous studies (18, 19) are labeled based on water type. Two low salinity (Cl < 20 mg/L) water types dominated by Ca-HCO$_3$ (type A = green circles) or Na-HCO$_3$ (type B = blue triangles) were the most common, and two higher salinity (Cl > 20 mg/L) water types were also observed: Br/Cl < 0.001 (type C = pink squares) and brine-type groundwater Br/Cl > 0.001 (type D = red diamonds). Type D groundwater samples appear associated with valleys (Table S1) and are sourced from conservative mixing between a brine and fresh meteoric water. The DEM data were obtained from NASA' Shuttle Radar Topography Mission http://srtm.usgs.gov/.

ground water and compared these to published (6, 21, 22) and new data of 83 samples from underlying Appalachian brines in deeper formations from the region (Table S2) to examine the possibility of fluid migration between the hydrocarbon producing Marcellus Formation and shallow aquifers in NE PA. We hypothesize that integration of these geochemical tracers could delineate possible mixing between the Appalachian brines and shallow groundwater.

Results and Discussion

The water chemistry data from the Alluvial, Catskill, and Lock Haven shallow aquifers (Table S1) reveal a wide range of solute concentrations from dilute groundwater with total dissolved solids (TDS) <500 mg/L and Cl < 20 mg/L to highly saline water (e.g., a salt spring with TDS of 7,800 mg/L and Cl approximately 4,000). Based on these characteristics, we divide the water samples into four types of ground water (Fig. 1). Two groundwater

types (A and B; n = 118 of 158 samples from this and our previous study (4) are characterized by low salinity and high Na/Cl and Br/Cl (all ratios reported as molar) ratios (Table S1). The two elevated salinity (Cl > 20 mg/L) water types (C and D) were divided based on their Br/Cl ratios. Type (C) (n = 13 of 158) has a distinctive low (<0.001) Br/Cl ratio (Fig. 3) and higher NO$_3^-$ concentrations that we attribute to salinization from domestic sources such as wastewater and/or road salt that have typically low Br/Cl ratios. The fourth subset of shallow groundwater (type D) (n = 27 of 158) was identified with a relatively high Br/Cl ratio (>0.001) and low Na/Cl ratio (Na/Cl < 5) with a statistically significant difference in water chemistry from types A–C (Table S3).

A geochemical analysis of published data collected in the 1980s (18, 19) revealed similar shallow salinized groundwater with a distinctive higher Cl (>20 mg/L) and low Na/Cl ratio. The saline groundwater mimics type D water with statistically indis-
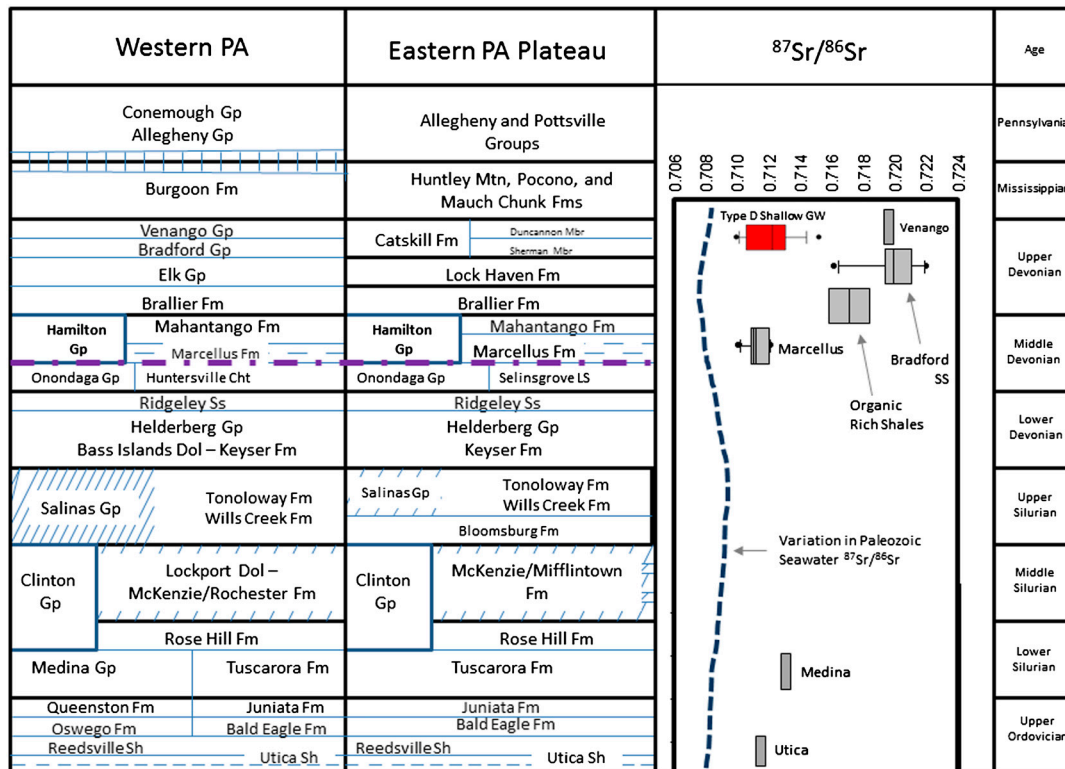

Fig. 2. Generalized stratigraphic section in the subsurface of western and eastern PA plateau adapted from (14, 15, 18, 19) and Sr isotope data of Appalachian brines and type D saline groundwater. Variations of $^{87}Sr/^{86}Sr$ ratios in Appalachian Brine and type-D groundwater samples show enrichment compared to the Paleozoic secular seawater curve (dashed grey line) (49). Note the overlap in values of type-D shallow ground water with $^{87}Sr/^{86}Sr$ values in Marcellus brines or older formations (21, 22, 24) but no overlap with the Upper Devonian brines in stratigraphically equivalent formations (Table S2) (21, 24).
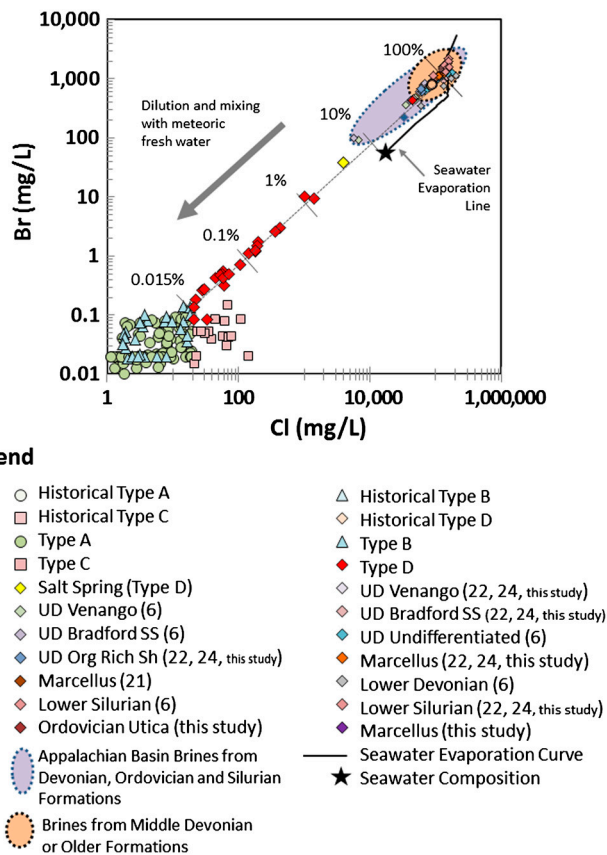
Legend

- ○ Historical Type A
- □ Historical Type C
- ● Type A
- □ Type C
- ◇ Salt Spring (Type D)
- ◇ UD Venango (6)
- ◇ UD Bradford SS (6)
- ◆ UD Org Rich Sh (22, 24, this study)
- ◆ Marcellus (21)
- ◇ Lower Silurian (6)
- ◆ Ordovician Utica (this study)
- ▨ Appalachian Basin Brines from Devonian, Ordovician and Silurian Formations
- ▨ Brines from Middle Devonian or Older Formations

- △ Historical Type B
- ◇ Historical Type D
- △ Type B
- ◆ Type D
- ◇ UD Venango (22, 24, this study)
- ◇ UD Bradford SS (22, 24, this study)
- ◆ UD Undifferentiated (6)
- ◆ Marcellus (22, 24, this study)
- ◇ Lower Devonian (6)
- ◇ Lower Silurian (22, 24, this study)
- ● Marcellus (this study)
- — Seawater Evaporation Curve
- ★ Seawater Composition

Fig. 3. Bromide vs. chloride concentrations (log-log scale) in shallow groundwater in NE PA and Appalachian brines from this and previous studies (18, 19). The linear relationship (type D: $r^2 = 0.99$, $p < 1 \times 10^{-5}$; sample types A–C: $r^2 = 0.14$) between the conservative elements Br and Cl demonstrates that the majority of the higher salinity samples of type D are derived from dilution of Appalachian brines that originated from evaporated seawater. Even with a large dilution of the original brine, the geochemical signature of type-D waters are still discernable in shallow groundwater from other high salinity (Cl > 20 mg/L) groundwater with low Br/Cl ratios (type C). Type C water likely originated from shallow sources such as septic systems or road deicing. Seawater evaporation line is from (25).

tinguishable (Table S3) concentrations of major cations and anions (Fig. 4 A and B); however, bromide concentrations were not available in the historical data set. Nonetheless, we designated historical samples with high Cl (>20 mg/L) and low Na/Cl ratio (Na/Cl < 5) as possible type D (n = 56 of 268). The remaining

historical samples with Cl concentrations (>20 mg/L) were designated as type C. All water types (A–D) were statistically indistinguishable from their respective historical types (A–D) (Table S3).

Type D saline waters are characterized by a Na-Ca-Cl composition with Na/Cl, Sr/Cl, Ba/Cl, Li/Cl, and Br/Cl ratios similar to brines found in deeper Appalachian formations (e.g., the Marcellus brine) (4, 6, 21, 22) (Table S2). This suggests mixing of shallow modern water with deep formation brines. Furthermore, the linear correlations observed for Br, Na, Sr, Li, and Ba with chloride (Fig. 3 and Fig. S3 A–F) demonstrate the relatively conservative and nonreactive behavior of these constituents and that the salinity in these shallow aquifers is most likely derived from mixing of deeper formation brines.

The stable isotopes ($\delta^{18}O = -8$ to $-11‰$; $\delta^2H = -53$ to $-74‰$) of all shallow groundwater types (A–D) are indistinguishable (p > 0.231) and fall along the local meteoric water line (LMWL) (23) (Fig. 5). The similarity of the stable isotopic compositions to the modern LMWL likely indicate dilution with modern (post-glacial) meteoric water. Shallow groundwater isotopic compositions do not show any positive $\delta^{18}O$ shifts towards the seawater evaporation isotopic signature (i.e., higher $\delta^{18}O$ relative to δ^2H) as observed in the Appalachian brines (Fig. 5 and Table S2). Because of the large difference in concentrations between the brines and fresh water, very small contributions of brine have a large and measureable effect on the geochemistry and isotopes of dissolved salts (Fig. 3) but limited effect on $\delta^{18}O$ and δ^2H. Mass-balance calculations indicate that only a brine fraction of higher than approximately 20% would change the $\delta^{18}O$ and δ^2H of salinized groundwater measurably. Oxygen and hydrogen isotopes are, therefore, not sensitive tracers for the mixing of the Appalachian brines and shallow groundwater because of the large percentage of the fresh water component in the mixing blend. For example, the salt spring at Salt Springs State Park with the highest salinity among shallow groundwater samples is calculated to contain <7% brine.

The discrete areas of type D water have lower average elevations and closer distances to valley centers but do not correlate with distance to the nearest shale gas wells (Fig. 1 and Fig. S1 and Table S1). The lack of geospatial association with shale-gas wells and the occurrence of this type of saline water prior to shale gas development in the study area (14, 15, 18, 19) (see distribution in Fig. 4 A and B) suggests that it is unlikely that hydraulic fracturing for shale gas caused this salinization and that it is instead a naturally occurring phenomenon that occurs over longer timescales.

Distinguishing the ultimate source of the salinized water in NE PA requires an evaluation of the geochemical signatures of underlying brines in the Appalachian Basin. The data presented
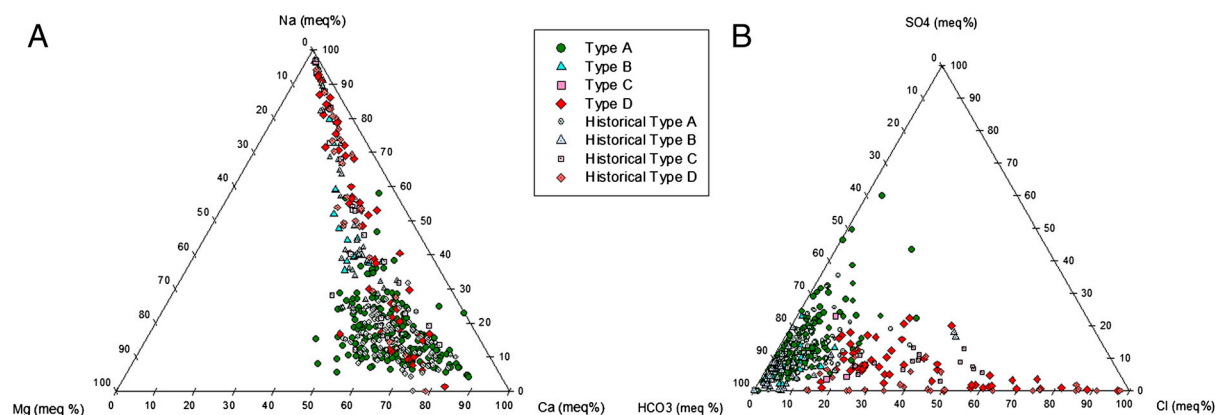

Fig. 4. Ternary diagrams that display the relative percent of the major cations (A) and anions (B) in shallow groundwater samples from this and previous studies (18, 19). The overlap indicates that Na-Ca-Cl type saline water was present prior to the recent shale-gas development in the region and could be from natural mixing.
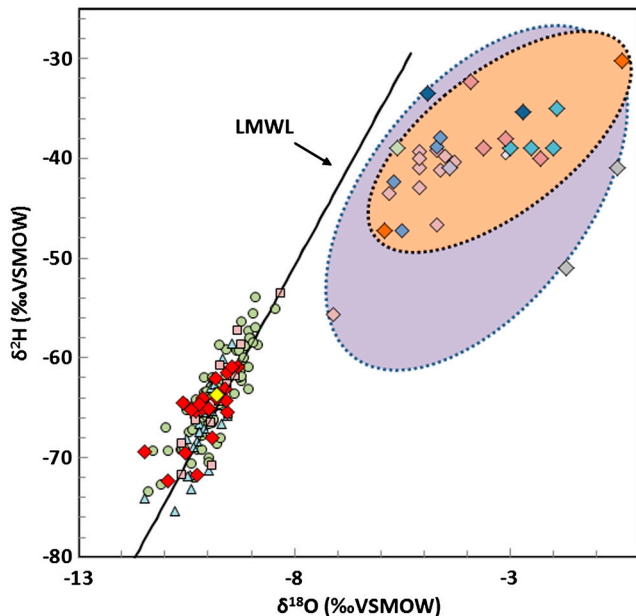
Fig. 5. δ^2H vs. δ^{18}O in shallow groundwater from this study and Appalachian brines. The water isotope composition of the shallow groundwater samples including the Salt Spring appear indistinguishable from each other and the local meteoric water line (LMWL) (23) and do not show any apparent trends toward the stable isotope ratios of the Appalachian brines (6, 22). The data indicate that dilution of the type-D waters likely occurred on modern (post-glacial) time scales. Symbol legend is provided in Fig. 3.

in this study (Figs. 2 and 3, and Fig. S3 *A–F* and Table S2) and previous studies (4, 6, 22, 24), suggest that the Appalachian brines evolved by evaporation from a common seawater origin but underwent varying stages of alteration. The first stage of evolution common to all of the brines is the evaporation of seawater beyond halite saturation resulting in brines with high Br/Cl and low Na/Cl ratios relative to seawater (6). The degree of evaporation that is computed based on the Br/Cl ratio in the Appalachian brines $(4–7 \cdot 10^{-3})$(Fig. 3) as compared to the evaporated sea water curve (25) is equivalent to 20–40-fold, though mixing between brines of different evaporation stages cannot be excluded. The brines then likely underwent dolomitization with carbonate rocks that enriched Ca and depleted Mg in the brine relative to the seawater evaporation curve (6) (Fig. S3 *B and C*) and sulfate reduction that removed all sulfate. In addition, the composition of each respective hypersaline Ca-Cl Appalachian brine (i.e., Salina and/or Marcellus) was differentially altered by interactions with the host aquifer rocks presumably under tectonically-induced thermal conditions (26) that resulted in resolvable variations in Sr/Ca, Ba/Sr, and ^{87}Sr/^{86}Sr ratios. The final stage of brine alteration that accounts for the observed brine compositions is dilution (6).

The net results of these processes generated large variations in brine salinity (TDS of 10–343 g/L), relatively homogeneous elevated Br/Cl ratios (range of $2.4 \cdot 10^{-3}$ to $7.6 \cdot 10^{-3}$) and enriched δ^{18}O (0‰ to −7‰) and δ^2H (−33‰ to −45‰) in all Appalachian brines. The remnant geochemical signatures (i.e., Sr/Ca, Ba/Sr, and ^{87}Sr/^{86}Sr) of formation specific brine-rock interactions provide the most suitable basis for differentiating the Appalachian brines. The Sr/Ca ratios (0.03–0.17) of the produced waters from Marcellus wells are significantly higher than brines evolved through calcite $(0.4–1.6 \cdot 10^{-3})$ or aragonite $(1.5–2.2 \cdot 10^{-2})$ dolomitization but are consistent with equilibrium with other minerals such as gypsum or celestite (27). Similarly, the Ba/Sr (0.01–1.78) ratios range up to values observed for typical upper continental crust (Ba/Sr = 1.3–1.7) (28).

New and compiled data presented in Table S2 show distinctive geochemical fingerprints (Sr/Ca, Ba/Sr, Sr/Cl, Ba/Cl, Li/Cl, and

^{87}Sr/^{86}Sr) among the Appalachian brines in the different formations. We, therefore, used these variables as independent tracers to differentiate possible brine sources for the shallow type D groundwater. Brines from the Marcellus Formation show systematically low (less radiogenic) ^{87}Sr/^{86}Sr (0.71000–0.71212; n = 50) and high Sr/Ca (0.03–0.17) ratios compared to the more radiogenic Upper Devonian brines (^{87}Sr/^{86}Sr ratio = 0.71580–0.72200; n = 12; Fig. 6) and low Sr/Ca (0.002–0.08)(Fig. S4). Because of the relatively high Sr concentration and diagnostic Sr/Ca, Ba/Sr, and ^{87}Sr/^{86}Sr ratios, this geochemical proxy has the potential to elucidate regional flow paths, salinity sources, and the specific source of the Appalachian brines (21, 24) (Fig. 6). The ^{87}Sr/^{86}Sr ratios (0.71030–0.71725 ± 0.000003 SE) of low-saline groundwater (type A and B) vary widely in the shallow aquifers, but the overwhelming majority are distinctly different from values of produced water brines from Upper Devonian (0.71580–0.72200) (24) (Table S2) and Middle Devonian Marcellus Formation (0.71000–0.71212) (21) (Fig. 6). Conversely, the type D shallow groundwater data show a linear correlation between Sr and Cl (i.e., conservative behavior of Sr) (Fig. S3D) and a decrease of ^{87}Sr/^{86}Sr from 0.71453–0.70960 with increasing Sr concentrations and salinity confirming that the resulting salinity is likely derived from mixing with Marcellus Formation brine (Fig. 6). Our data also display a strong association between ^{87}Sr/^{86}Sr and Sr/Ca ratios (Fig. S4), a relationship suggested as a sensitive indicator of Marcellus brines because of the unique combination of low ^{87}Sr/^{86}Sr ratios and high Sr/Ca ratios reported for brines from the Marcellus Formation (21).

The saline waters in the eastern portion of the study area follow the expected Sr-isotope mixing trend hypothesized from new and published data on produced water from the Marcellus Formation (Fig. 6). In contrast, the saline waters from the western portion of our study area show systematic mixing with an end
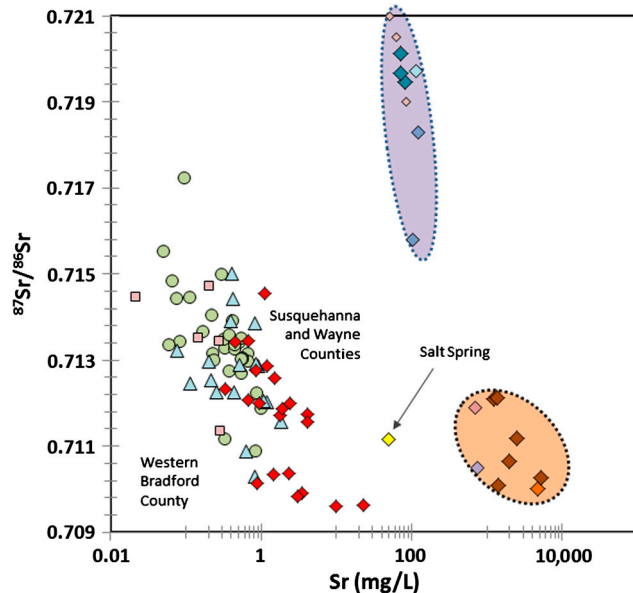

Fig. 6. ^{87}Sr/^{86}Sr vs. Sr concentrations (log scale) of Appalachian Brines (21, 24) and shallow groundwater samples in the study area. The shallow groundwater samples are divided in the figure based on water types. Increased concentrations of Sr in the shallow aquifers are likely derived from two component mixing: (*i*) A low salinity, radiogenic ^{87}Sr/^{86}Sr groundwater sourced from local aquifer reactions; and (*ii*) A high salinity, less radiogenic ^{87}Sr/^{86}Sr water consistent with Marcellus Formation brine. The Marcellus Formation ^{87}Sr/^{86}Sr appears lower in western Bradford than in Susquehanna and Wayne counties. Other brine sources such as the Upper Devonian formations have a more radiogenic ^{87}Sr/^{86}Sr ratio that does not appear to show any relationship to the salinized shallow groundwater. Symbol legend is provided in Fig. 3.

member of a slightly lower $^{87}Sr/^{86}Sr$ ratio (0.70960). This lower ratio could reflect provenance variations within the formation (e.g., lower siliclastic detrital component away from the Acadian clastic source) in the region (21). In sum, whereas the high Br/Cl ratio in type D saline groundwater reflects mixing with underlying Appalachian brines from a common evaporated seawater origin, the $^{87}Sr/^{86}Sr$ ratios indicate mixing with brines with lower $^{87}Sr/^{86}Sr$ fingerprints of approximately 0.7096–0.7110 that cannot be accounted for by Upper Devonian formations but are similar to the underlying Marcellus Formation brines.

Other features that characterize the produced waters from the Marcellus Formation are the high activities of naturally occurring nuclides of ^{226}Ra and ^{228}Ra and low $^{228}Ra/^{226}Ra$ ratios (7). ^{226}Ra and ^{228}Ra are the disintegration products of ^{238}U and ^{232}Th, respectively, and are generated in groundwater from alpha recoil, desorption from sediments, and dissolution of aquifer material (7, 29). In most of the shallow groundwater we sampled (Table S1), combined Ra activities were low (<5 pCi/L). In contrast, reported activities of Ra in Marcellus brines from the study area were high (1,500–3,100 pCi/L) (Fig. S5) with low $^{228}Ra/^{226}Ra$ ratios (0.12–0.73) (7). The highest Ra activities that we measured were in type D waters, and the range (0.4 to 28 pCi/L) is consistent with our calculated mixing range of approximately 0.01–7% based on chloride and bromide mass-balance calculations (Fig. 3), though some interaction such as adsorption with the aquifer rocks (29) is likely. In addition, the $^{228}Ra/^{226}Ra$ ratio in the salinized groundwater (mean = 0.56) is higher than that of the majority of the Marcellus produced waters from the study area (mean = 0.33) (7) (Table S2) indicating that the dissolved Ra in the shallow groundwater is likely derived from a combination of local water-rock interactions and conservative mixing.

Methane data from our previous studies (4, 30) can be examined based on the four water types (A–D) we found in this study. The highest average methane concentrations were observed in type D waters, followed by type B and A. In locations >1 km away from shale gas drilling sites only one sample, a type B water, out of total of 41 samples contained elevated methane concentrations (>10 mg/L). One newly sampled type D water from the spring at Salt Springs State Park (30) also had concentrations >10 mg/L. Within 1 km of a natural gas well, three type A, three type B, and five type D samples had methane concentrations >10 mg/L. In three type D groundwater samples that were located in the lowland valleys >1 km from shale gas drilling sites, methane concentrations were 2–4 mg/L for the two previously sampled shallow ground waters and 26 mg/L for the newly sampled salt spring. In contrast, type A groundwater >1 km away from drilling sites had methane concentrations <0.01 mg/L in all samples (n = 14). This could suggest that methane in type D water >1 km away from drilling sites could be derived from natural seepage (31) but at concentrations much lower than those observed near drilling (4).

Cross-formational pathways allowing deeper saline water to migrate into shallower, fresher aquifers have been documented in numerous study areas including western Texas (32, 33), Michigan Basin (34, 35), Jordan Rift Valley (36), Appalachian Basin (26), and Alberta, Canada (37). In the Michigan Basin, upward migration of saline fluid into the overlying glacial sediments (34, 35) was interpreted to reflect isostatic rebound following the retreat of glaciers, leading to fracture intensification and increased permeability (34). Alternatively, vertical migration of over-pressured hydrocarbons has been proposed for the Appalachian Basin in response to tectonic deformation and catagensis (i.e., natural gas induced fracturing) during the Alleghenian Orogeny (38–40). This deformation resulted in joints that cut across formations (J_2) in Middle and Upper Devonian formations (39). In addition, the lithostatic and isostatic rebound following glacial retreat significantly increased fracture intensification and

permeability in the Upper Devonian aquifers within our study area.

We hypothesize that regions with the combination of deep high hydrodynamic pressure and enhanced natural flow paths (i.e., fracture zones) (39, 41, 42) could induce steep hydraulic gradients and allow the flow of deeper fluids to zones of lower hydrodynamic pressure (43, 44). The higher frequency of the saline type D water occurrence in valleys (Table S1) is consistent with hydrogeological modeling of regional discharge to lower hydrodynamic pressure in the valleys with greater connectivity to the deep subsurface (43–45).

The possibility of drilling and hydraulic fracturing causing rapid flow of brine to shallow groundwater in lower hydrodynamic pressure zones is unlikely but still unknown. By contrast, the time scale for fugitive gas contamination of shallow aquifers can be decoupled from natural brine movement specifically when gas concentrations exceed solubility (approximately 30 cc/kg) and forms mobile free phase gases (i.e., bubbles). In western PA, on the Appalachian Plateau, contamination of shallow aquifers has been described as leakage of highly pressurized gas through the over-pressurized annulus of gas wells and into the overlying freshwater aquifers via fractures and faults (43, 44). The faults are often connected to local and regional discharge areas (i.e., valleys) where the methane contamination is observed (43). Buoyant flow of methane gas bubbles through these fractures is far more rapid than head-driven flow of dense brine, occurring on time scales of less than a year (46).

This study shows that some areas of elevated salinity with type D composition in NE PA were present prior to shale-gas development and most likely are unrelated to the most recent shale gas drilling; however, the coincidence of elevated salinity in shallow groundwater with a geochemical signature similar to produced water from the Marcellus Formation suggests that these areas could be at greater risk of contamination from shale gas development because of a preexisting network of cross-formational pathways that has enhanced hydraulic connectivity to deeper geological formations (43). Future research should focus on systematically monitoring these areas to test potential mechanisms of enhanced hydraulic connectivity to deeper formations, confirm the brine source, and determine the timescales for possible brine migration.

Methods

Drinking water wells were purged until pH, electrical conductance, and temperature were stabilized. Samples were collected prior to any treatment systems and filtered/preserved following USGS protocols (47). All major element and isotopic chemistry analyses were conducted at Duke University. Major anions were determined by ion chromatography, major cations by direct current plasma optical emission spectrometry, and trace metals by VG PlasmaQuad-3 inductively coupled plasma mass-spectrometry. Alkalinity was determined by titration with HCl to pH 4.5. Stable isotopes were determined by continuous flow isotope ratio mass spectrometry using a Thermo-Finnigan TCEA and Delta + XL mass spectrometer at the Duke Environmental Isotope Laboratory (DEVIL). Analytical precisions for $\delta^{18}O$ and δ^2H were estimated as ±0.1‰ and ±1.5‰, respectively. Radium isotope analyses (^{226}Ra and ^{228}Ra) were measured at the Laboratory for Environmental Analysis of RadioNuclides (LEARN) using a Durridge RAD7 radon-in-air monitor (^{226}Ra) and Canberra DSA2000BEGe gamma detector (^{228}Ra) following methods described in (29) and (48). Strontium isotopes were analyzed by a thermal ionization mass spectrometer on a ThermoFisher Triton. The mean $^{87}Sr/^{86}Sr$ of the Standard Reference Material-987 standard was 0.710266 ± 0.000005 (SD).

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