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 ($^{87}Sr/^{86}Sr$, $^{2}H/H$, $^{18}O/^{16}O$, 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 combustible 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 ($\delta^{18}O$, $\delta^{2}H$, $^{87}Sr/^{86}Sr$, $^{228}Ra/^{226}Ra$) in shallow

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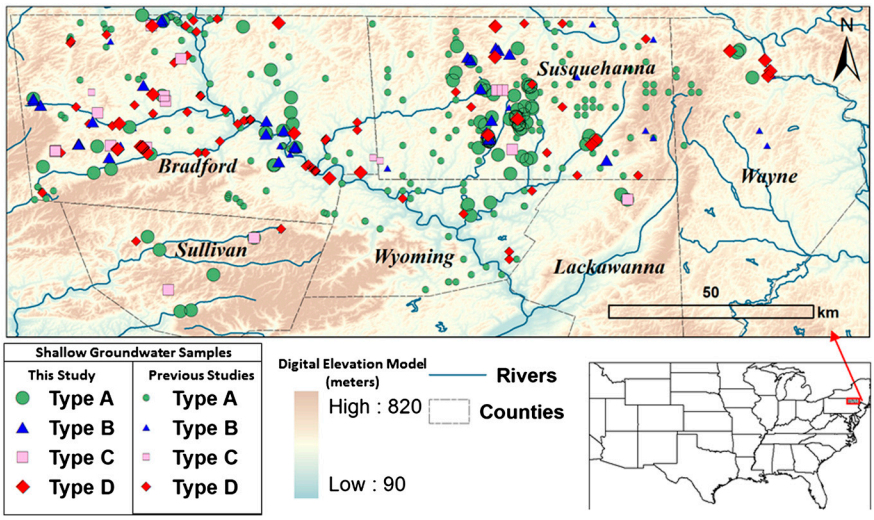

Fig. 1. Digital elevation model (DEM) map of northeastern PA. Shaded brown areas indicate higher elevations and blue-green shaded areas indicate lower elevations (valleys). The distribution of shallow (<90 m) groundwater samples from this study and previous studies (18, 19) are labeled based on water 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-

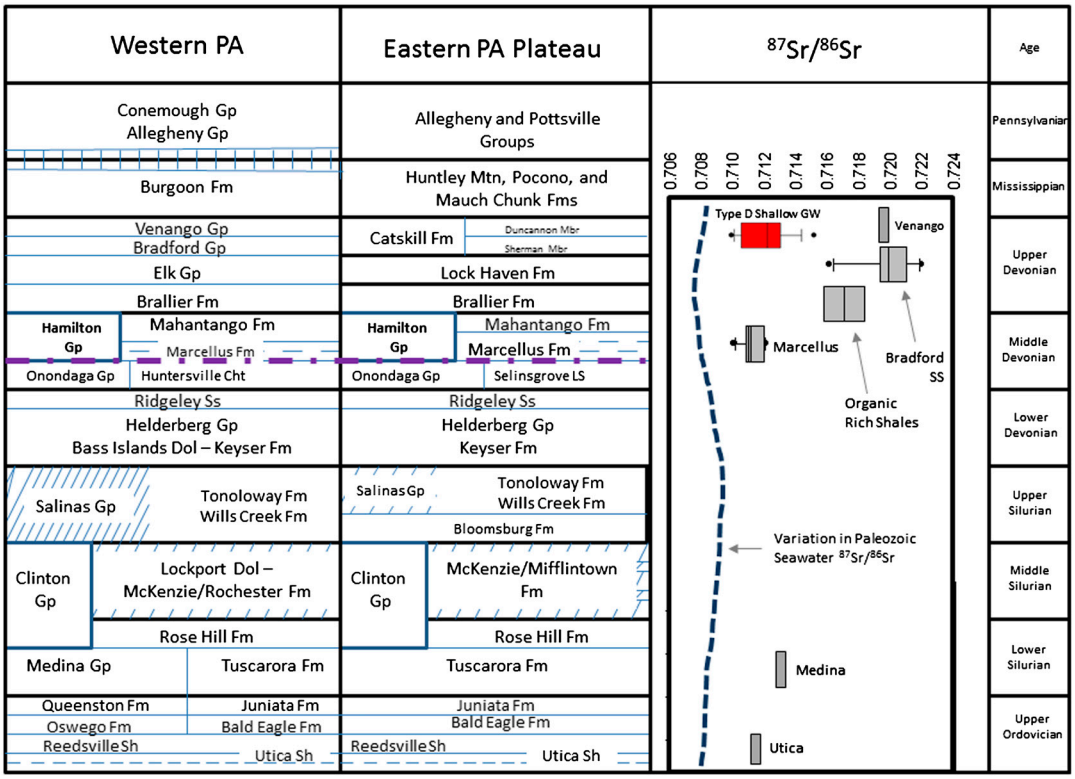

Fig. 2. Generalized stratigraphic section in the subsurface of western and eastern PA plateau adapted from (14, 15, 18, 19) and Sr isotope data of Appalachian brines and type D saline groundwater. Variations of $^{87}Sr/^{86}Sr$ ratios in Appalachian Brine and type-D groundwater samples show enrichment 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).

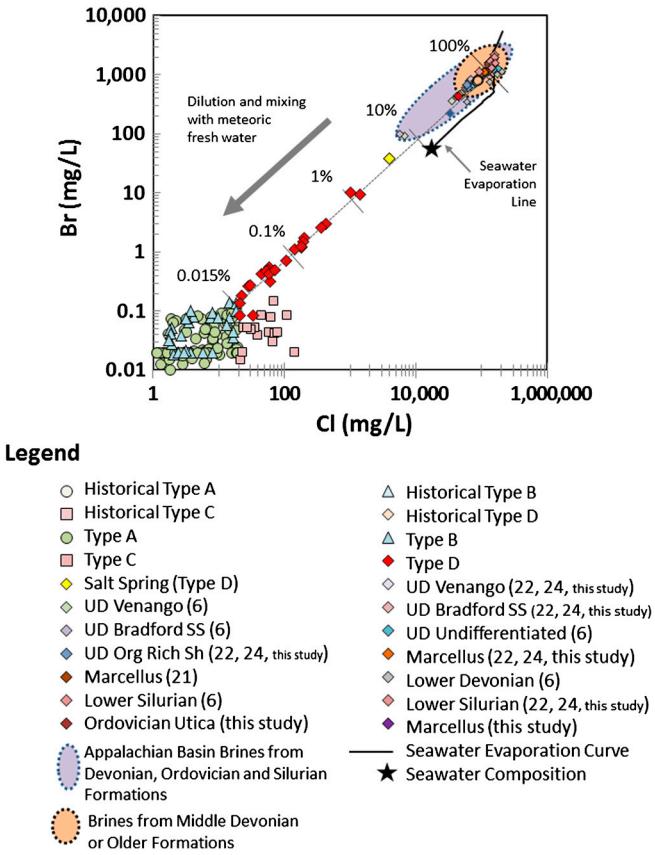

Fig. 3. Bromide vs. chloride concentrations (log-log scale) in shallow groundwater in NE PA and Appalachian brines from this and previous studies (18, 19). The linear relationship (type D: $r^2 = 0.99$, $p < 1 \times 10^{-5}$; sample types A–C: $r^2 = 0.14$) between the conservative elements Br and Cl 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

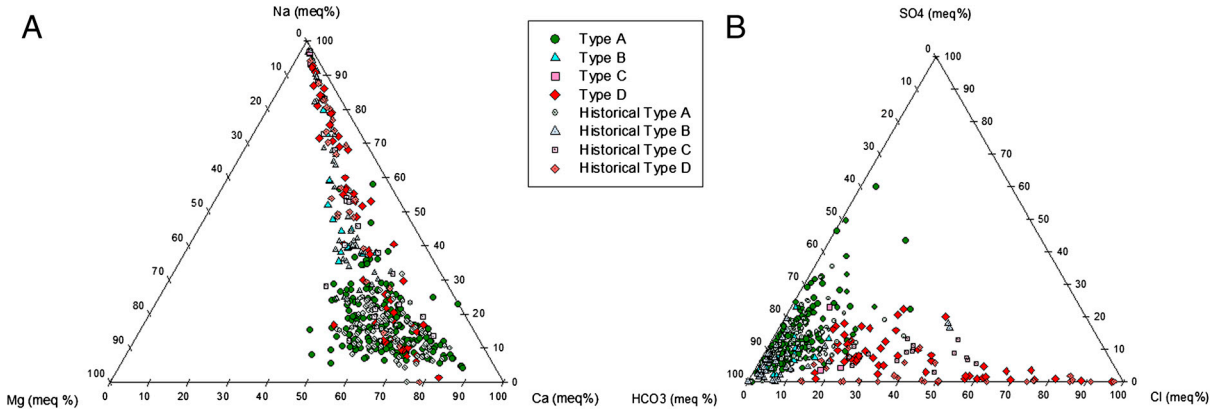

Fig. 4. Ternary diagrams that display the relative percent of the major cations (*A*) and anions (*B*) in shallow groundwater samples from this and previous studies (18, 19). The overlap indicates that Na-Ca-Cl type saline water was present prior to the recent shale-gas development in the region and could be from natural mixing.

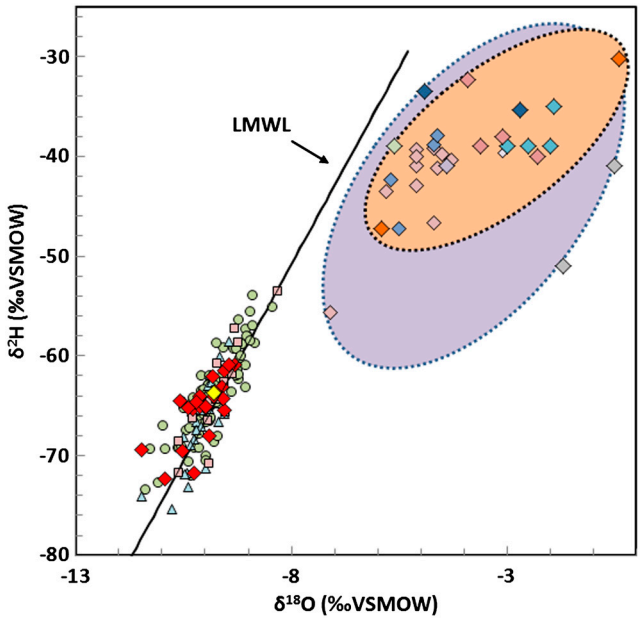

Fig. 5. δ^2H vs. δ^{18}O in shallow groundwater from this study and Appalachian brines. The water isotope composition of the shallow groundwater samples including the Salt Spring appear indistinguishable from each other and the local meteoric water line (LMWL) (23) and do not show any apparent trends 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. S3*D*) 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

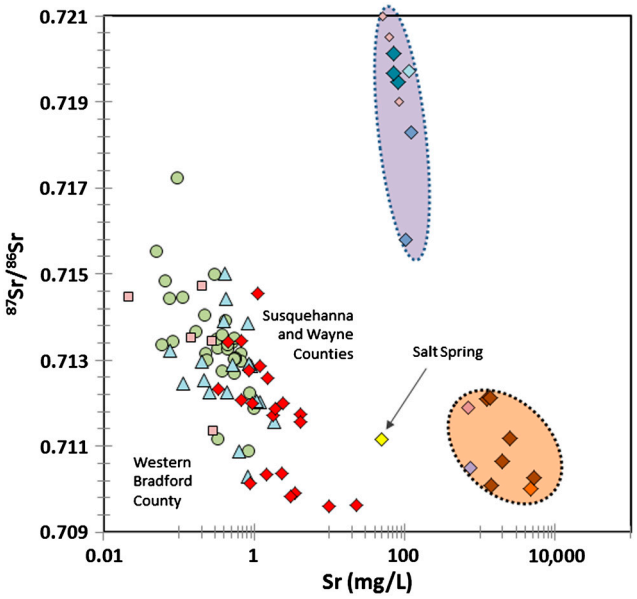

Fig. 6. ^{87}Sr/^{86}Sr vs. Sr concentrations (log scale) of Appalachian Brines (21, 24) and shallow groundwater samples in the study area. The shallow groundwater samples are divided in the figure based on water types. Increased concentrations of Sr in the shallow aquifers are likely derived from two 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 throughout the dataset, 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 $\delta^{2}H$ 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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1. Kerr RA (2010) Natural gas from shale bursts onto the scene. *Science* 328:1624–1626.
2. Kargbo DM, Wilhelm RG, Campbell DJ (2010) Natural gas plays in the Marcellus Shale: Challenges and potential opportunities. *Environ Sci Technol* 44:5679–5684.
3. Howarth RW, Ingraffea A, Engelder T (2011) Natural gas: Should fracking stop? *Nature* 477:271–275.
4. Osborn SG, Vengosh A, Warner NR, Jackson RB (2011) Methane contamination of drinking water accompanying gas-well drilling and hydraulic fracturing. *Proc Natl Acad Sci USA* 108:8172–8176.
5. Jiang M, et al. (2011) Life cycle greenhouse gas emissions of Marcellus shale gas. *Environ Res Lett* 6:034014.
6. Dresel P, Rose A (2010) Chemistry and origin of oil and gas well brines in Western Pennsylvania: Pennsylvania Geological Survey. *4th series Open-File Report OFOG 10-01.0* p 48 (Pennsylvania Department of Conservation and Natural Resources).
7. Rowan E, Engle M, Kirby C, Kraemer T (2011) Radium content of oil- and gas-field produced waters in the Northern Appalachian basin (USA)—Summary and discussion of data. *U.S. Geological Survey Scientific Investigations Report 2011–5135* p 31 (U.S. Geological Survey).
8. Gregory KB, Vidic RD, Dzombak DA (2011) Water management challenges associated with the production of shale gas by hydraulic fracturing. *Elements* 7:181–186.
9. Hayes T (2009) Sampling and analysis of water streams associated with the development of Marcellus shale gas. *Marcellus Shale Initiative Publications Database*.
10. Veil J (2011) White Paper on SPE Summit on Hydraulic Fracturing. *Society of Petroleum Engineers* (Society of Petroleum Engineers, Houston, TX).
11. Fisher K (2010) Data confirm safety of well fracturing. *Reporter*, http://www.fidelityepco.com/Documents/OilGasRept_072010.pdf.
12. Frey MG (1973) Influence of salina salt on structure in New York-Pennsylvania part of Appalachian plateau. *AAPG Bull* 57:1027–1037.
13. Faill R (1985) The Acadian orogeny and the Catskill Delta. *Geol S Am S* 201:15–38.
14. Lohman SW (1973) *Ground Water in North-Central Pennsylvania* (Department of Conservation and Natural Resources, Pennsylvania) p 219.
15. Lohman SW (1957) *Ground Water in Northeastern Pennsylvania* (Department of Conservation and Natural Resources, Pennsylvania) p 312.
16. Alexander S, Cakir R, Doden AG, Gold DP, Root SI (2005) Basementdepth and related geospatial database for Pennsylvania. *Pennsylvania Geological Survey* Open-File General Geology) Report 05-01.00.
17. Geyer A, Wilshusen JP (1982) Engineering characteristics of the rocks of Pennsylvania; environmental geology supplement to the state geologic map. *Pennsylvania Geological Survey* p 300.
18. Taylor L (1984) Groundwater Resources of the Upper Susquehanna River Basin, Pennsylvania: Water Resources Report 58. p 136 (Pennsylvania Department of Environmental Resources, Office of Parks and Forestry, Bureau of Topographic and Geologic Survey).
19. Williams J, Taylor L, Low D (1998) Hydrogeology and Groundwater Quality of the Glaciated Valleys of Bradford, Tioga, and Potter Counties, Pennsylvania: Water Resources Report 68. p 89 (Commonwealth of Pennsylvania Department of Conservation and Natural Resources).
20. Trapp H, Jr, Horn MA (1997) Ground Water Atlas of the United States: Delaware, Maryland, New Jersey, North Carolina, Pennsylvania, Virginia, West Virginia HA 730-L. (U.S. Geological Survey).
21. Chapman EC, et al. (2012) Geochemical and strontium isotope characterization of produced waters from Marcellus Shale natural gas extraction. *Environ Sci Technol* 46:3545–3553.
22. Osborn SG, McIntosh JC (2010) Chemical and isotopic tracers of the contribution of microbial gas in Devonian organic-rich shales and reservoir sandstones, northern Appalachian Basin. *Appl Geochem* 25:456–471.
23. Kendall C, Coplen T (2001) Distribution of oxygen-18 and deuterium in river waters across the United States. *Hydrol Process* 15:1363–1393.
24. Osborn SG, Mcintosh J, Hanor J, Biddulph D (2012) Iodine-129, $^{87}Sr/^{86}Sr$, and trace elemental geochemistry of northern Appalachian Basin brines: Evidence for basinal-scale fluid migration and clay mineral diagenesis. *Am J Sci*, in press.
25. McCaffrey M, Lazar B, Holland H (1987) The evaporation path of seawater and the coprecipitation of Br and K with halite. *J Sediment Petrol* 57:928–937.
26. Schedl A, McCabe C, Montanez I, Fullagar P, Valley J (1992) Alleghenian regional diagenesis: A response to the migration of modified metamorphic fluids derived from beneath the Blue Ridge-Piedmont thrust sheet. *J Geol* 100:339–352.
27. Sass E, Starinsky A (1979) Behaviour of strontium in subsurface calcium chloride brines: Southern Israel and Dead Sea rift valley. *Geochim Cosmochim Acta* 43:885–895.
28. Rudnick R, Gao S (2003) *The Composition of the Continental Crust, in the Crust* (Elsevier-Pergamon, Oxford).
29. Vinson DS, Vengosh A, Hirschfeld D, Dwyer GS (2009) Relationships between radium and radon occurrence and hydrochemistry in fresh groundwater from fractured crystalline rocks, North Carolina. *Chem Geol* 260:159–171.
30. Osborn SG, Vengosh A, Warner NR, Jackson RB (2011) Reply to Saba and Orzechowski and Schon: Methane contamination of drinking water accompanying gas-well drilling and hydraulic fracturing. *Proc Natl Acad Sci USA* 108:E665–E666.
31. Molofsky LJ, Connor JA, Farhat SK, Wylie AS, Jr, Wagner T (2011) Methane in Pennsylvania water wells unrelated to Marcellus shale fracturing. *Oil Gas J* 109:54–67.
32. Mehta S, Fryar AE, Banner JL (2000) Controls on the regional-scale salinization of the Ogallala aquifer, Southern High Plains, Texas, USA. *Appl Geochem* 15:849–864.
33. Hogan JF, et al. (2007) Geologic origins of salinization in a semi-arid river: The role of sedimentary basin brines. *Geology* 35:1063–1066.
34. Weaver TR, Frape SK, Cherry JA (1995) Recent cross-formational fluid flow and mixing in the shallow Michigan Basin. *Geol Soc Am Bull* 107:697–707.
35. Long DT, Wilson TP, Takacs MJ, Rezabek DH (1988) Stable-isotope geochemistry of saline near-surface ground water: East-central Michigan basin. *Geol Soc Am Bull* 100:1568–1577.
36. Farber E, et al. (2004) The origin and mechanisms of salinization of the lower Jordan river. *Geochim Cosmochim Acta* 68:1989–2006.
37. Tilley B, et al. (2011) Gas isotope reversals in fractured gas reservoirs of the western Canadian Foothills: Mature shale gases in disguise. *AAPG Bull* 95:1399–1422.
38. Lash GG, Engelder T (2009) Tracking the burial and tectonic history of Devonian shale of the Appalachian Basin by analysis of joint intersection style. *Geol Soc Am Bull* 121:265–277.
39. Engelder T, Lash GG, Uzcategui RS (2009) Joint sets that enhance production from Middle and Upper Devonian gas shales of the Appalachian Basin. *AAPG Bull* 93:857–889.
40. Lash G, Blood DR (2007) Origin of early overpressure in the Upper Devonian Catskill Delta Complex, western New York State. *Basin Res* 19:51–66.
41. Llewellyn G (2011) Structural and topographic assessment of shallow bedrock permeability variations throughout Susquehanna County PA: A focus area of Marcellus Shale Gas Development. *Abstr Programs Geol Soc Am* 43:567.
42. Jacobi RD (2002) Basement faults and seismicity in the Appalachian Basin of New York State. *Tectonophysics* 353:75–113.
43. Harrison SS (1983) Evaluating system for ground-water contamination hazards due to gas-well drilling on the glaciated Appalachian plateau. *Ground Water* 21:689–700.
44. Harrison SS (1985) Contamination of aquifers by overpressuring the annulus of oil and gas wells. *Ground Water* 23:317–324.
45. Tóth J (1970) A conceptual model of the groundwater regime and the hydrogeologic environment. *J Hydrol* 10:164–176.
46. Etiope G, Klusman RW (2002) Geologic emissions of methane to the atmosphere. *Chemosphere* 49:777–789.
47. USGS (2011) National Field Manual for the Collection of Water-Quality Data. (US Geological Survey, Washington, DC).
48. Kim G, Burnett WC, Dulaiova H, Swarzenski PW, Moore WS (2001) Measurement of ^{224}Ra and ^{226}Ra activities in natural waters using a radon-in-air monitor. *Environ Sci Technol* 35:4680–4683.
49. Denison RE, Kirkland DW, Evans R (1998) Using strontium isotopes to determine the age and origin of gypsum and anhydrite beds. *J Geol* 106:1–18.

Sample Number	Sample Type	pH	EC (µS/Cm)	TDS (mg/L)	Cl (mg/L)	Br (mg/L)	NO_3-N (mg/L)	SO_4 (mg/L)	Alkalinity as HCO3 (mg/L)	Ca (mg/L)	Mg (mg/L)	Sr (mg/L)	Na (mg/L)	Ba (mg/L)	Li (µg/L)	Ra-226 (pCi/L)	Ra-228 (pCi/L)	$^{87}Sr/^{86}Sr$	δ2H	δ18O	Rep. Well Depth (feet)	Water Type	Distance to nearest NG well (km)	Distance to Valley Center Line[1] (km)	Distance to Valley Center Line[2] (km)	Digital Elevation model (m)	Aquifer Type
1	GW	6.93	195	127	2	0.01	0.25	9.17	142	27	7	0.37	12	0.11	24	0.14	0.15	0.71327	*-65.0*	*-10.3*	200	A	5.33	0.87	0.85	402	Dck
2	GW	6.81	181	101	1	0.01	1.42	8.80	108	22	5	0.34	10	0.10	20	na	na	0.71342	*-62.4*	*-9.7*	175	A	4.86	1.08	1.39	455	Dck
3	GW	6.78	191	133	2	0.02	1.98	9.12	143	32	7	0.32	9	0.16	20	na	na	0.71329	*-69.3*	*-10.9*		A	5.15	0.72	0.67	405	Dck
4	GW	7.08	293	169	2	0.02	0.03	7.10	192	36	10	0.49	20	0.22	35	na	na	0.71343	*-64.2*	*-10.1*	200	A	5.17	0.51	0.52	387	Dck
5	GW	6.53	313	178	13	0.04	3.64	11.31	169	37	9	0.31	21	0.15	29	na	na	0.71349	*-62.9*	*-9.9*		A	2.74	0.06	0.06	335	Dck
6	GW	6.72	270	150	6	0.02	1.61	12.04	154	35	7	0.44	13	0.15	26	na	na	0.71328	*-63.7*	*-9.9*		A	3.19	0.52	0.52	374	Dck
7	GW	6.61	211	116	2	0.02	1.74	7.18	129	27	7	0.22	8	0.15	15	na	na	0.71317	*-63.7*	*-9.8*	400	A	4.90	0.86	0.86	431	Dck
8	GW	6.78	208	115	6	0.04	0.38	12.73	112	23	7	0.44	10	0.14	17	na	na	0.71339	*-63.8*	*-9.9*	150	A	4.39	0.06	0.06	337	Dck
9	GW	6.09	122	76	6	0.01	1.65	7.12	69	17	5	0.05	5	0.05	3	na	na	0.71554	*-67.4*	*-10.5*	117	A	3.65	3.07	2.12	536	Dck
10	GW	6.43	323	180	8	0.03	0.22	14.73	185	38	10	0.11	18	0.05	5	na	na	0.714461	*-62.4*	*-9.8*	250	A	1.72	1.68	0.08	470	Dck
11	GW	5.09	241	130	9	0.04	2.66	18.54	113	29	8	0.53	6	0.15	14	0.22	0.13	0.71354	*-66.2*	*-10.3*	274	A	1.72	1.30	0.39	484	Dck
12	GW	5.72	200	111	6	0.02	1.79	14.07	102	26	6	0.06	7	0.03	4	na	na	0.71485	*-66.4*	*-10.1*	250	A	1.48	1.36	0.36	476	Dck
13	GW	5.75	310	176	13	0.03	31.08	20.62	116	36	11	0.08	7	0.10	7	na	na		*-58.8*	*-9.2*	390	A	0.27	0.57	0.54	465	Dck
14	GW	6.05	262	142	17	0.02	3.64	10.57	119	35	8	0.38	9	0.18	16	na	na		*-61.9*	*-10.1*	270	A	2.48	1.72	0.55	463	Dck
15	GW	6.13	245	136	8	0.02	2.72	18.51	121	38	4	0.08	5	0.04	5	na	na	0.71345	*-59.1*	*-9.6*		A	0.23	3.02	0.87	512	Dck
16	GW	6.25	204	115	1	0.01	2.47	12.52	116	35	3	0.18	3	0.12	10	na	na		*-62.7*	*-9.9*	430	A	1.98	2.90	0.51	502	Dck
17	GW	5.82	288	177	12	0.06	1.06	12.89	187	37	9	0.64	12	0.10	17	0.08	0.05	0.71318	*-64.5*	*-10.6*		A	0.20	1.97	0.51	430	Dck
18	GW	6.49	253	142	7	0.02	3.52	9.85	143	33	7	0.64	12	0.22	26	0.21	na	0.71299	*-67.0*	*-11.0*		A	0.22	0.91	0.07	343	Dck
19	GW	5.87	161	89	3	0.01	1.94	12.67	84	19	7	0.07	4	0.05	6	na	na	0.71444	*-64.7*	*-10.3*	375	A	1.57	2.10	1.11	496	Dck
20	GW	5.59	59	88	1	0.01	1.82	6.53	134	11	1	0.06	1	0.02	1	na	na		*-69.3*	*-11.3*	300	A	2.72	2.00	0.56	484	Dck
21	GW	6.87	210	118	2	0.08	1.31	19.94	111	31	6	0.04	3	0.08	7	0.14	0.11		*-64.1*	*-10.3*	150	A	2.20	1.83	0.38	471	Dck
22	GW	7.92	218	130	4	0.08	3.50	10.73	138	28	6	0.31	10	0.10	13	na	na		*-73.4*	*-11.4*	375	A	0.16	1.43	0.33	387	Dck
23	GW	6.96	230	126	15	0.12	2.19	12.45	105	30	7	0.21	7	0.06	8	na	na		*-72.7*	*-11.1*		A	0.13	2.12	0.50	439	Dck
24	GW	8.33	246	132	4	0.08	1.33	9.84	152	29	6	0.55	8	0.28	39	0.24	0.21	0.71306	*-69.1*	*-10.6*	300	A	0.32	1.30	0.05	360	Dck
25	GW	8.12	249	132	5	0.08	2.21	9.38	149	31	6	0.55	4	0.23	33	na	na	0.71304	*-69.2*	*-10.6*		A	0.16	1.14	0.07	355	Dck
26	GW	8.40	859	148	8	0.08	4.48	10.60	143	33	7	0.57	14	0.06	24	0.14			*-67.2*	*-10.4*	250	A	0.29	1.02	0.07	351	Dck
27	GW	6.92	250	132	11	0.09	7.38	17.53	111	35	7	0.20	0	0.08	7	na	na		*-64.7*	*-9.8*	225	A	0.05	1.92	0.93	406	Dck
28	GW	8.23	253	147	8	0.08	3.78	9.30	145	34	7	0.54	14	0.06	28	na	na	0.71304	*-65.0*	*-9.9*	250	A	0.28	0.91	0.02	343	Dck
29	GW	6.64	194	104	15	0.08	2.53	10.91	75	30	4	0.09	4	0.06	7	na	na		*-58.7*	*-9.7*	400	A	1.39	0.70	0.70	341	Dck
30	GW	7.73	284	153	13	0.07		4.44	156	33	6	1.45	18	1.59	41	0.66	0.28		-64.8	-9.8	260	A	0.65	0.20	0.20	277	Alluvium
31	GW	7.45	336	160	4	0.04	1.06	0.10	195	41	11	0.09	7	0.05	13			0.71725	-64.0	-10.0	195	A	1.46	1.24	1.24	419	Dlh
32	GW	7.18	620	364	8	0.06	0.54	108.85	278	62	26	0.29	22	0.04	15	0.14	0.17	0.71501	-62	-9.9	57	A	0.55	2.23	0.32	394	Dlh
33	GW	6.80	271	151	7	0.05	0.06	21.67	140	31	8	0.96	14	0.18	16			0.71190	-70.6	-10.4	375	A	2.49	0.85	0.85	397	Dlh
34	GW	6.86	161	86	2	0.04	3.13	8.70	84	18	7	0.36	6	0.15	10	0.14	0.16	0.71275	-65.2	-10.5	305	A	2.16	0.87	0.87	518	Dck
35	GW	7.51	350	190	19	0.06	1.92	14.68	171	46	9	0.10	15	0.17	6	0.13			-61.9	-9.5		A	1.98	2.78	1.14	471	Dck
36	GW	6.17	113	61	3	0.05	7.13	12.00	39	14	3	0.03	3	0.05	2	0.13	0.18		-62.3	-9.7	270	A	0.87	1.71	0.50	452	Dck
37	GW	6.75	268	132	19	0.03	1.52	13.05	106	30	8	0.17	9	0.13	8	0.19	0.20	0.71368				A	3.55	1.31	0.05	462	Dck
38	GW	6.84	163	87	3	0.05	4.11	9.43	80	22	5	0.03	4	0.01	5	na	na	0.71629	-63.5	-9.7		A	3.40	1.67	1.23	465	Dck
39	GW	6.57	228	122	7	0.02	0.93	12.89	112	28	4	0.23	13	0.16	17	na	na	0.71302	-58.0	-9.0	275	A	3.40	1.67	1.23	465	Dck
40	GW	7.73	390	101	5	0.09	1.14	16.47		41	14	0.84	22	0.12	32	na	na	0.71224	-66.8	-10.1	200	A	0.11	1.19	0.58	297	Dlh
41	GW	6.07	236	114	5	0.02	0.01	18.27	97	26	8	0.81	9	0.10	18	na	na	0.71091	-63.4	-10.0	438	A	1.77	0.54	0.54	448	Dlh
42	GW	7.30	280	134	2	0.07	0.05	12.55	134	31	9	0.32	13	0.05	15	na	na	0.71119	-66.5	-9.9		A	1.25	0.15	0.15	291	Dlh
43	GW	7.38	554	303	8	0.04	0.01	49.23	302	70	14	0.21	14	0.04	3	na	na	0.71405	-59.2	-9.3	330	A	0.69	0.14	0.14	330	Dck
44	GW	7.41	247	133	15	0.05	3.36	10.08	114	35	5	0.37	9	0.15	7	na	na	0.71360	-65.8	-10.0	180	A	1.99	1.09	0.38	526	Dck
45	GW	6.82	117	57	10	0.02	2.25	9.54	34	11	2	0.06	5	0.03	0	0.08	0.16	0.71348	-63.1	-9.1	45-50	A	1.20	0.11	0.11	292	Dck
46	GW	6.69	87	66	3	0.02	1.39	9.76	59	19	1	0.09	3	0.03	3	na	na		-57.3	-9.1		A	2.44	0.10	0.10	317	Dck
47	GW	5.91	282	141	18	0.02	13.87	14.89	98	30	3	0.09	12	0.08	0	na	na		-56.9	-8.9	20	A	2.07	0.07	0.07	310	Dck
48	GW	6.51	215	121	4	0.02	12.24	8.89	108	34	4	0.34	5	0.19	6	na	na	0.71166	-58.7	-8.9	240	A	0.43	0.62	0.34	471	Dck
49	GW	7.83	301	161	3	0.08	0.05	4.02	193	32	9	0.41	17	0.26	22	0.40	0.24	0.71393	-69.0	-10.6	260	A	0.27	2.31	1.06	457	Dck
50	GW	7.28	306	165	3	0.02	0.00	14.25	168	39	13	1.69	11	0.25	19	na	na		-64.6	-9.9	100	A	0.54	1.43	0.88	414	Dlh
51	GW	7.57	319	183	3	0.02	0.02	16.21	194	45	16	0.28	7	0.12	9	na	na	0.71175	-72.0	-10.3	195	A	1.14	1.95	1.24	392	Dlh
52	GW	7.31	849	411	1	0.02	0.01	0.10	465	102	26	0.54	52	0.16	13	na	na	0.71271	-68.6	-9.8		A	1.06	0.38	0.38	322	Alluvium
53	GW	7.47	393	218	7	0.02	0.84	22.24	227	45	15	0.89	15	0.16	32	na	na	0.71225	-67.8	-10.1		A	0.63	1.20	0.40	371	Dlh
54	GW	6.27	82	41	1	0.02	0.13	8.15	37	8	3	0.03	2	0.04	17	na	na		-64.8	-9.7	200	A	0.78	0.31	0.31	452	Dck
55	GW	6.76	160	79	7	0.02	1.52	12.32	66	15	6	0.05	5	0.05	20	na	na		-62.9	-9.9	500	A	1.52	1.89	0.64	531	Dck
56	GW	7.49	260	143	15	0.02	1.35	14.63	130	29	9	0.08	10	0.11	15	na	na	0.71503	-63.5	-10.1	400	A	4.52	1.09	0.48	492	Dck
57	GW	6.43	119	60	6	0.02	0.24	10.50	48	12	4	0.07	4	0.07	12	na	na	0.71369	-64.3	-10.2		A	2.96	0.10	0.10	414	Dck

58	GW	6.67	116	55	1	0.02	0.13	6.15	59	12	4	0.03	3	0.05	11	na	na	0.71448	-69.2	-10.3		A	3.29	0.41	0.02	429	Dck
59	GW	8.08	214	116	1	0.02	0.74	11.42	132	29	3	0.07	6	0.02	9	na	na	0.71661	-66.3	-9.9	150	A	4.35	0.41	0.08	257	Dck
60	GW	7.4	277	148	9	0.05	1.43	15.95	145	42	3	0.07	6	0.05	12	na	na	0.71104	-62.5	-9.6		A	4.06	0.16	0.16	299	Dck
61	GW	7.87	273	146	3	0.02	0.33	12.25	161	35	6	0.48	10	0.08	26	na	na	0.71218	-64.5	-9.7		A	0.19	0.97	0.59	303	Dck
62	GW	na	na	146	9	0.02	1.00	7.50	149	44	5	0.12	5	0.16	5	na	na	0.71212	-58.0	-9.0		A	0.18	1.78	1.78	445	Dck
63	GW	7.33	295	149	18	0.02	1.36	17.25	125	38	4	0.07	9	0.05	10	na	na	0.71441	-61.3	-9.3	300	A	1.24	0.41	0.41	351	Dck
64	GW	7.56	237	124	6	0.02	0.01	12.06	129	30	4	0.17	9	0.03	14	na	na	0.71320	-63.6	-9.4	200	A	0.48	0.26	0.26	340	Dck
65	GW	7.71	320	173	2	0.02	0.01	10.21	205	38	11	0.28	11	0.31	16	na	na	0.71182	-64.6	-9.7	138	A	0.54	0.15	0.15	218	Alluvium
66	GW	7.86	324	173	4	0.02	0.01	13.33	197	36	11	0.37	13	0.22	18	0.65	0.36	0.71172	-70.5	-10.0	100	A	0.52	0.15	0.15	217	Alluvium
67	GW	7.65	461	262	2	0.07	0.02	20.33	294	51	15	1.34	28	0.10	29	na	na	0.71120	-69.2	-10.1	104	A	2.15	0.69	0.30	252	Dlh
68	GW	7.27	305	159	3	0.02	0.70	15.93	176	36	10	0.44	7	0.20	24	na	na	0.71117	-66.2	-9.9		A	1.14	0.88	0.73	359	Dlh
69	GW	6.88	250	124	9	0.02	0.80	12.75	117	31	4	0.28	8	0.30	17	na	na	0.71433	-68.0	-9.7		A	2.19	1.25	0.56	414	Dck
70	GW	6.94	315	160	16	0.09	2.55	14.72	143	43	5	0.21	10	0.14	14	na	na	0.71365	-62.3	-9.2	175	A	0.29	0.77	0.77	370	Dck
71	GW	8.65	127	92	1	0.02	0.22	10.11	98	22	5	0.06	6	0.02	2	na	na		-62.6	-9.8	200	A	1.56	0.67	0.34	469	Dck
72	GW	8.65	64	44	1	0.02	0.74	7.58	42	11	2	0.03	2	0.02	2	na	na		-58.4	-9.0	100	A	1.04	1.29	0.22	472	Dck
73	GW	7.58	241	132	1	0.02	0.22	9.80	145	36	4	0.60	8	0.10	14	na	na		-63.4	-10.0	300	A	1.24	0.57	0.28	366	Dck
74	GW	6.77	158	79	3	0.02	0.39	9.24	83	19	3	0.05	4	0.09	4	na	na		-62.0	-9.3		A	2.00	0.81	0.81	432	Dck
75	GW	7.78	237	123	3	0.02	0.24	11.99	134	26	6	0.53	9	0.11	20	na	na				500	A	2.46	0.44	0.44	430	Dck
76	GW	6.71	153	85	3	0.02	1.02	12.23	83	17	4	0.19	7	0.09	12	na	na		-60.9	-9.1		A	1.07	0.28	0.28	367	Dck
77	GW	6.53	145	73	2	0.02	0.58	11.85	74	15	4	0.19	4	0.05	9	na	na		-63.9	-10.0	154	A	2.34	0.06	0.06	346	Dck
78	GW	6.09	133	65	1	0.02	1.32	9.36	66	17	2	0.10	3	0.06	3	na	na		-55.1	-8.4	485	A	0.71	0.79	0.41	382	Dck
79	GW	7.75	261	152	3	0.02	0.57	9.65	171	34	5	0.90	15	0.34	15	na	na		-64.8	-10.2	280	A	0.90	1.63	1.03	395	Dck
80	GW	7.25	305	172	19	0.02	2.73	16.30	156	40	5	1.06	12	0.33	14	na	na				100	A	1.02	1.45	0.90	359	Dck
81	GW	7.69	278	150	2	0.02	0.21	10.15	173	31	5	0.60	16	0.15	25	na	na		-63.9	-9.9	300	A	0.78	1.49	0.58	450	Dck
82	GW	6.3	148	74	3	0.02	1.07	13.62	67	16	3	0.10	4	0.07	7	na	na		-60.2	-9.2		A	1.00	0.44	0.44	372	Dck
83	GW	6.29	229	117	5	0.02	1.43	14.52	116	25	5	0.20	8	0.11	16	na	na		-64.1	-9.8	180	A	0.89	0.60	0.60	383	Dck
84	Spring	5.91	114	63	2	0.01	1.37	9.40	58	16	3	0.06	3	0.05	4	na	na	0.71337	*-62.2*	*-9.7*		A	4.58	0.10	0.10	341	Dck
85	Spring	5.97	66	30	1	0.04	0.43	5.86	26	7	1	0.02	1	0.03	1	na	na		-55.5	-9.0		A	1.34	0.87	0.85	402	Dck
86	Spring	5.96	155	78	6	0.05	5.51	10.19	62	20	2	0.04	3	0.03	3	na	na		-53.9	-8.9		A	0.65	0.20	0.20	277	Alluvium
87	Spring	5.55	140	86	18	0.05	6.22	9.78	46	17	2	0.05	11	0.05	2	na	na		-56.4	-9.2		A	1.43	0.14	0.14	290	Alluvium
88	Spring	6.35	57	29	0	0.02	0.33	6.54	26	7	1	0.03	1	0.02	1	na	na		-60.0	-9.2		A	2.65	0.95	0.95	430	Dck
89	Spring	5.97	54	26	1	0.02	0.08	7.79	17	7	1	0.03	1	0.02	1	na	na		-61.8	-9.2		A	0.72	1.49	0.58	450	Dck
90	GW	8.85	492	291	15	0.08	0.06	5.84	304	8	2	0.12	112	0.06	173	0.35	0.25	0.71245			380	B	0.71	0.43	0.43	431	Dlh
91	GW	6.95	354	246	4	0.02	0.69	7.89	284	22	6	1.19	66	0.30	82	na	na	0.71202				B	0.71	0.43	0.43	431	Dlh
92	GW	8.30	450	269	15	0.14	0.02	1.60	300	4	1	0.08	101	0.04	348	0.09	0.10	0.71321			280	B	1.79	1.50	0.85	418	Dck
93	GW	6.58	315	177	17	0.04	7.57	16.71	143	34	7	0.20	24	0.18	50	0.14	0.16	0.71296	*-60.1*	*-9.6*		B	0.32	1.91	0.83	437	Dck
94	GW	9.32	529	297	8	0.08	0.03	3.11	335	2	0	0.15	119	0.07	380	0.21	0.18					B	0.22	1.30	0.29	376	Dck
95	GW	6.59	243	141	2	0.02	0.06	18.44	120	34	5	0.12	23	0.03	7	na	na		*-58.6*	*-9.5*		B	1.05	1.55	1.00	383	Dck
96	GW	6.45	473	285	18	0.14	1.31	9.98	290	8	2	0.43	103	0.06	149	0.28	0.21	0.71226	*-61.9*	*-9.9*	180	B	0.67	0.39	0.39	422	Dlh
97	GW	8.24	240	142	4	0.08	1.43	8.33	148	30	6	0.52	19	0.06	33	0.18	0.22	0.71289	*-74.0*	*-11.5*	250	B	0.21	1.27	0.04	357	Dck
98	GW	8.04	320	266	4	0.10	1.31	3.72	293	21	7	0.83	84	0.32	65	0.33	na	0.71030	*-65.4*	*-9.9*	280	B	0.84	1.92	0.41	402	Dlh
99	GW	7.23	176	89	2	0.05	0.03	2.94	106	12	4	0.25	15	0.10	615	0.23	0.18	0.71225	-66.6	-10.2	180	B	3.51	0.18	0.18	272	Dck
100	GW	8.08	456	303	17	0.04	0.01	12.88	320	26	6	1.09	83	0.26	66	na	na	0.71206	-67.1	-10.1	210	B	2.88	0.43	0.43	329	Dlh
101	GW	7.76	335	195	8	0.09	0.04	15.06	191	26	9	0.22	43	0.14	53	na	na		-65.6	-10.3	175	B	0.12	1.05	0.06	441	Dck
102	GW	8.89	308	166	2	0.05	0.32	5.80	188	7	2	0.24	57	0.45	84	0.37	0.34		-68.2	-10.5	700	B	2.46	0.44	0.44	508	Dck
103	GW	7.29	275	149	3	0.07	2.10	10.51	160	27	11	0.22	17	0.12	11	0.30	0.27	0.71253	-65.1	-10.3	160	B	2.61	0.11	0.11	448	Dck
104	GW	7.81	406	198	2	0.03	0.02	7.82	202	39	12	0.91	37	0.12	48	0.56	0.41	0.71286	-65.4	-10.1	200	B	0.11	1.19	0.58	297	Dlh
105	GW	9.07	520	307	13	0.06	0.00	9.85	319	13	5	0.85	109	0.32	208	0.10	0.10	0.71291	-66.6	-9.7	250	B	0.45	0.84	0.84	304	Dlh
106	GW	8.14	294	180	2	0.04	0.01	8.48	203	27	7	0.84	35	0.50	36	0.51	0.47	0.71385	-73.1	-10.4	30	B	2.10	0.44	0.22	399	Dck
107	GW	8.3	389	239	10	0.08	0.02	1.09	252	25	7	0.42	72	0.74	80	0.31	0.33	0.71443	-75.4	-10.8	125	B	0.56	1.96	0.67	430	Dck
108	GW	8.28	335	190	3	0.08	0.05	4.02	224	20	6	0.40	46	0.47	62	0.76	0.75	0.71391	-71.8	-10.4	127	B	0.27	2.31	1.06	457	Dck
109	GW	7.6	513	145	3	0.04	0.02	30.25		51	16	0.41	45	0.07	43	0.33	0.22	0.71500	-63.0	-9.9	180	B	1.37	3.85	0.85	382	Dlh
110	GW	7.94	348	202	18	0.10	0.05	8.45	188	37	8	1.82	36	0.26	46	na	na	0.71157	-71.9	-10.5	80	B	2.47	0.58	0.58	356	Dlh
111	GW	7.48	272	158	2	0.02	0.01	19.56	153	19	4	0.63	38	0.09	37	na	na	0.71089	-71.3	-10.0	140	B	1.89	0.95	0.14	305	Dlh
112	GW	7.44	515	298	3	0.02	0.10	23.79	326	46	16	2.13	47	0.45	66	na	na	0.71180	-68.4	-10.3	390	B	0.80	0.44	0.44	414	Dlh
113	GW	7.62	380	215	3	0.02	0.01	23.26	230	30	11	0.28	35	0.08	36	na	na	0.71401	-64.3	-9.9		B	1.02	1.27	0.03	388	Dlh
114	GW	7.38	372	211	1	0.02	0.01	39.18	206	36	13	0.17	22	0.03	8	na	na	0.71437	-67.5	-10.2	275	B	0.34	1.91	0.24	422	Dck
115	GW	7.9	252	136	8	0.02	0.28	13.20	135	25	9	0.39	14	0.18	28	na	na	0.71341	-68.9	-10.3		B	2.96	0.10	0.10	414	Dck
116	GW	8.07	351	198	6	0.02	0.01	8.16	219	27	7	1.94	41	0.66	76	na	na	0.71108	-65.8	-9.5	186	B	0.55	0.11	0.11	215	Alluvium
117	GW	7.68	463	263	2	0.03	0.01	22.32	293	50	14	0.65	31	0.09	30	na	na	0.71175	-62.6	-9.8	100	B	2.15	0.59	0.59	249	Dlh
118	GW	7.93	475	291	4	0.02	1.72	13.19	339	19	4	2.09	82	0.75	164	na	na		-64.9	-9.9		B	0.37	1.99	0.31	316	Dck
119	GW	6.01	298	159	40	0.04	4.67	13.99	89	35	8	0.27	13	0.20	10	na	na	0.71346	*-63.3*	*-9.8*	300	C	5.50	1.96	0.06	496	Dck

120	GW	6.69	439	238	59	0.04	5.20	19.47	134	68	6	0.10	14	0.07	6	na	na		*-60.7*	*-9.7*		C	0.35	2.96	0.89	508	Dck
121	GW	6.88	516	258	63	0.08	1.36	15.46	170	38	12	0.20	44	0.07	50	0.24	0.26	0.71473	-64.6	-9.9		C	0.53	0.04	0.04	274	Dlh
122	GW	6.35	274	139	36	0.05	0.81	14.36	82	29	7	0.16	12	0.08	3	0.12	0.17	0.71446	-62.6	-9.6	260	C	1.60	1.31	1.31	409	Dlh
123	GW	8.58	688	403	69	0.15	3.82	18.76	329	25	8	0.17	117	0.08	122	0.20	0.13	0.71443	-63.9	-9.8	265	C	1.55	0.88	0.88	424	Dck
124	GW	7.66	293	150	24	0.05	4.39	10.80	123	31	11	0.23	8	0.17	13	0.12	0.17		-66.1	-10.3	360	C	4.34	1.80	0.47	513	Dck
125	GW	6.06	386	198	73	0.04	6.35	9.65	78	28	6	0.28	36	0.14	7	na	na	0.71136	-61.7	-9.4	351	C	1.25	0.27	0.12	348	Dlh
126	GW	6.01	349	196	46	0.09	0.63	15.12	111	27	6	0.11	47	0.07	1	na	na	0.71325	-53.4	-8.3	305	C	0.31	0.04	0.04	307	Dlh
127	GW	7.02	296	157	31	0.05	5.29	12.98	121	35	3	0.12	11	0.06	5	na	na		-64.3	-9.8		C	1.92	1.16	0.32	521	Dck
128	GW	6.74	627	345	112	0.08	30.96	21.05	134	56	9	0.15	50	0.19	19	na	na	0.71353	-70.7	-9.9	40	C	1.11	0.44	0.20	408	Dlh
129	GW	6.95	473	251	79	0.04	13.01	18.65	110	48	6	0.10	31	0.11	15	na	na		-66.4	-10.0	65	C	1.02	0.59	0.19	410	Dlh
130	GW	6.31	280	143	23	0.02	0.70	15.06	114	31	5	0.12	13	0.05	8	na	na		-65.5	-9.5	375	C	1.30	1.52	0.80	424	Dck
131	Spring	5.98	175	87	27	0.05	3.95	9.56	35	13	6	0.02	10	0.01	140	na	na	0.71446	-58.6	-9.3		C	1.60	1.31	1.31	409	Dlh
132	GW	8.04	418	220	59	0.56	0.02	2.48	153	27	9	0.68	47	2.12	144	na	na	0.71346	*-65.3*	*-10.3*	150	D	4.25	0.18	0.11	343	Dck
133	GW	6.27	290	175	21	0.09	2.27	11.47	171	41	8	0.45	7	0.09	13	na	na	0.71343	*-64.5*	*-10.6*	340	D	0.39	3.15	0.74	522	Dck
134	GW	6.94	800	327	197	1.75	0.03	0.31	31	21	6	0.94	84	1.44	514	0.47	0.28	0.71201	*-69.4*	*-11.5*	220	D	3.37	0.05	0.05	270	Dck
135	GW	7.11	497	301	29	0.26	1.30	0.58	293	28	6	2.35	90	0.06	64	0.49	0.31	0.71037	*-64.0*	*-10.1*	250	D	0.16	0.64	0.64	386	Dlh
136	GW	6.62	604	335	57	0.50	1.32	0.01	299	18	3	1.45	107	0.78	95	na	na	0.71034	*-65.2*	*-10.0*	200	D	0.21	0.69	0.69	388	Dlh
137	GW	7.06	524	312	30	0.28	1.30	1.28	319	36	9	1.13	77	0.55	64	0.95	0.52	0.71453	*-62.1*	*-9.8*	240	D	0.51	0.16	0.16	280	Dlh
138	GW	8.53	417	245	22	0.18	11.86	11.02	208	36	8	1.51	52	0.06	83	0.46	na	0.71258	*-72.3*	*-10.9*	200	D	0.63	1.57	0.62	290	Dck
139	GW	6.99	275	146	21	0.13	1.78	13.91	116	35	8	0.28	9	0.06	8	0.19	0.19		*-65.1*	*-10.1*	475	D	0.13	1.80	0.56	442	Dck
140	GW	8.38	324	204	45	0.42	0.02	0.69	185	22	7	0.68	37	0.69	16	0.32	0.22		-64.6	-10.2	300	D	3.64	0.04	0.03	265	Dck
141	GW	9.34	525	316	54	0.48	0.01	0.60	272	4	1	0.34	122	0.19	678	na	na	0.71232	-65.2	-10.4	220	D	2.71	0.43	0.15	278	Dck
142	GW	7.46	469	228	60	0.32	0.01	12.49	148	48	8	0.95	26	0.43	67	1.18	0.29		-61.5	-9.5		D	0.26	0.07	0.07	278	Alluvium
143	GW	7.65	441	243	59	0.43	0.01	4.19	161	23	3	0.43	73	0.40	216	na	na		-60.9	-9.3		D	1.43	0.14	0.14	290	Alluvium
144	GW	7.30	474	241	33	0.09	0.02	10.21	236	59	11	0.88	11	1.18	24	na	na	0.71015	-64.1	-9.8	303	D	0.50	0.05	0.05	302	Dlh
145	GW	7.56	1088	558	183	1.19	0.02	2.69	365	85	18	3.50	85	2.42	237	1.26	0.47	0.70991	-60.9	-9.4	305	D	0.47	0.06	0.06	308	Dlh
146	GW	7.80	628	330	71	0.50	0.01	0.10	232	41	14	3.00	87	1.25	127	na	na	0.70983	-63.1	-9.6	307	D	0.82	0.02	0.02	304	Dlh
147	GW	7.23	4700	2385	1412	9.51	7.23	0.10	399	254	47	23.11	437	13.97	1701	3.54	1.63	0.70962	-63.6	-9.8	293	D	1.51	0.08	0.08	293	Dlh
148	GW	7.72	1080	547	191	1.51	0.01	1.69	319	33	9	2.40	152	3.35	212	2.03	0.77	0.71198	-65.0	-10.0	75	D	0.15	0.61	0.12	292	Dlh
149	GW	8.37	1180	570	292	2.26	0.02	0.00	179	22	4	2.74	160	1.50	302	na	na	0.71183	-68.5	-10.6	212	D	3.22	0.12	0.12	337	Dck
150	GW	8.2	3568	2058	1003	9.99	5.40	30.82	266	105	20	1.80	752	1.82	853	1.54	1.10	0.71173	-71.8	-10.3		D	0.67	2.11	0.14	321	Dlh
151	GW	8.13	808	644	143	1.13	0.11	0.11	276	42	9	4.10	310	2.12	488	na	na	0.71175	-69.6	-10.5	90	D	0.73	1.16	0.09	272	Dlh
152	GW	7.84	1951	919	425	3.00	0.02	1.59	252	66	12	9.79	278	5.24	692	na	na	0.70960	-65.5	-9.6	37	D	0.40	0.01	0.01	298	Dlh
153	GW	8.52	1452	789	368	2.55	0.01	2.37	199	26	5	1.92	285	1.50	42	na	na	0.71187	-68.0	-9.9	250	D	1.13	0.12	0.12	219	Dlh
154	GW	7.64	695	355	108	0.73	0.01	18.16	187	48	11	1.18	76	0.55	233	na	na	0.71287	-64.3	-9.6		D	3.88	0.28	0.28	232	Alluvium
155	GW	8.15	688	391	178	1.25	0.01	0.08	175	52	9	0.86	64	0.35	38	na	na	0.71277			130	D	0.24	0.07	0.07	278	Alluvium
156	Salt Spring	7.59	11950	6418	4014	37.9	1.69	0.65	169	370	61	48.5	1800	84.4	4345	18.42	9.27	0.71115	-63.7	-9.8	800	D	2.21	0.31	0.31	426	Dck
157	GW	7.85	1791	1151	623	5.10	0.01	5.30	163	58	11	4.10	364	6.22	663	na	na	0.71155	-65.2	-10.3	100	D	1.60	0.01	0.01	358	Dlh
158	GW	8.08	2050	328	141	1.08	0.01	0.10		40	9	3.01	134	2.99	142	na	na		-71.6	-10.6	125	D	0.78	1.15	0.02	271	Dlh

Table S1. Analytical results for shallow groundwater samples collected during this and previous studies (4, 30). Blank spaces= no reported data. na = no available data. Alluvium = Alluvium Aquifer, Dck = Upper Devonian Catskill Formation, Dlh = Upper Devonian Lock Haven Formation. [1] Distance calculated with respect to the national stream network. [2] Distance determined manually in reference to the digital elevation model (DEM) layer valley centers.

Formation	Source Ref	Sample Name	Age	Cl ppm	Br ppm	SO4 ppm	Ca ppm	Mg ppm	Sr ppm	Na ppm	Ba ppm	Ra-226 pCi/L	Ra-228 pCi/L	$^{87}Sr/^{86}Sr$	$\delta^{2}H$ ‰	$\delta^{18}O$ ‰	TDS ppm
Berea Ss.	22,24	M1	L. Miss.	32,579	228	88	4,520	972	221	11,381				0.710800	-33.5	-4.9	
Berea Ss.	22,24	M4	L. Miss.	87,881	894	412	15,320	3,281	609	30,457					-35.4	-2.7	
Berea Ss.	this study [1]	M1	L. Miss.	32,579	228	88	4,548	1,092	173	12,279	12			0.710886			
Berea Ss.	this study [1]	M4	L. Miss.	87,881	894	412	16,078	3,293	476	32,101	8			0.711479			
Organic-rich Sh.	22,24	D6	U. Dev.	60,903	602	194	9,560	1,604	123	25,327				0.718300	-42.4	-5.7	
Organic-rich Sh.	22,24	D7	U. Dev.	80,542	783	127	12,360	2,066	180	30,503					-38.9	-4.7	
Organic-rich Sh.	22,24	D14	U. Dev.	60,655	675	184	10,000	1,920	104	23,289				0.715800	-37.9	-4.6	
Organic-rich Sh.	22,24	D17	U. Dev.	60,655	675	184	10,000	1,920	104	23,289					-47.2	-5.5	
Venango Grp. Ss.	22,24	D24	U. Dev.	70,581	642	483	10,920	1,798	171	27,457							
Venango Grp. Ss.	22,24	D33	U. Dev.	99,792	918	564	18,720	2,333	128	34,510					-39.7	-3.1	
Bradford Grp. Ss.	22,24	D10	U. Dev.	61,399	653	-	8,640	1,823	85	23,198				0.719000	-39.3	-5.1	
Bradford Grp. Ss.	22,24	D27	U. Dev.	62,108	631	119	11,160	1,458	84	24,411					-41.2	-4.6	
Bradford Grp. Ss.	22,24	D29	U. Dev.	131,697	944	62	24,760	2,430	2,317	44,586					-43.5	-5.8	
Bradford Grp. Ss.	22,24	D30	U. Dev.	148,784	1,037	-	30,760	2,965	3,601	57,548					-39.2	-4.7	
Bradford Grp. Ss.	22,24	D31	U. Dev.	81,003	692	706	12,680	1,823	74	29,770					-40.9	-5.1	
Bradford Grp. Ss.	22,24	D32	U. Dev.	83,095	734	314	12,760	1,944	77	32,701					-46.7	-4.7	
Bradford Grp. Ss.	22,24	D34	U. Dev.	91,213	804	110	15,800	2,138	325	30,114					-39.8	-4.5	
Bradford Grp. Ss.	22,24	D37	U. Dev.	45,376	463	1,182	8,440	1,191	47	19,305					-55.6	-7.1	
Bradford Grp. Ss.	22,24	D38	U. Dev.	96,424	984	657	16,080	2,430	126	34,739					-40.4	-4.3	
Bradford Grp. Ss.	22,24	D39	U. Dev.	72,070	723	286	10,880	1,774	62	29,060				0.720500	-42.9	-5.1	
Bradford Grp. Ss.	22,24	D40	U. Dev.	72,566	730	249	10,960	1,677	52	27,343				0.721000	-40.0	-5.1	
Upper Devonian	6	ED-82-01	U. Dev.	122,000	1,170	4	18,000	2,520	691	56,700	171				-39.0	-2.5	
Upper Devonian	6	ED-82-02	U. Dev.	123,000	1,180	1	18,800	2,500	1,490	58,300	843						
Upper Devonian	6	ED-82-03	U. Dev.	123,000	1,100		19,000	2,520	1,470	58,500	815						
Upper Devonian	6	ED-82-04	U. Dev.	111,000	1,070	8	17,100	2,410	1,290	52,100	1020						
Upper Devonian	6	ED-82-05	U. Dev.	151,000	1,340	2	24,700	2,880	2,340	63,500	1840						
Upper Devonian	6	ED-82-06	U. Dev.	155,000	1,350	11	25,100	2,850	2,420	63,700	2010	1900					
Upper Devonian	6	ED-82-07	U. Dev.	181,000	1,250	18	34,400	3,140	6,080	71,900	698						
Upper Devonian	6	ED-82-08	U. Dev.	70,600	622	5	11,000	1,650	404	30,600	174						
Upper Devonian	6	ED-82-09	U. Dev.	151,000	1,210	140	24,500	2,970	1,420	61,900	7	200			-35.0	-1.9	
Upper Devonian	6	ED-82-10	U. Dev.	105,000	983	50	14,900	2,150	578	47,400	623				-39.0	-3.0	
Upper Devonian	6	ED-82-11	U. Dev.	123,000	1,190	1	17,700	2,600	936	58,900	668				-39.0	-2.0	
Venango Second	6	ED-82-13	U. Dev.	57,400	586	270	8,150	1,570	129	25,000	2						
Venango First and Third	6	ED-82-15	U. Dev.	35,400	365	8	3,930	910	124	15,200	355						
Venango Second and Third	6	ED-82-23	U. Dev.	50,000	472	17	6,490	1,400	137	21,800	52				-39.0	-5.6	
Red Valley	6	ED-82-12	U. Dev.	6,780	94	2	1,580	195	22	3,400	17						
Glade	6	ED-82-14	U. Dev.	80,500	800	570	12,700	2,110	117	35,000	1						
Glade	6	ED-82-16	U. Dev.	63,200	792	390	11,800	2,050	152	30,000	3						
Glade	6	ED-82-17	U. Dev.	55,800	609	350	8,680	1,510	141	24,000	ND						
Glade	6	ED-82-18	U. Dev.	67,800	835	850	12,600	2,180	151	31,000	ND				-41.0	-4.4	
Cooper	6	ED-82-19	U. Dev.	5,760	99	4	920	100	5	3,000	7						
Kane	6	ED-82-20	U. Dev.	44,000	436	14	5,780	1,150	191	19,800	ND						
Cooper	6	ED-82-21	U. Dev.	41,200	437	310	6,110	1,040	39	17,400	ND						
Upper Devonian SS	this study	PAGB-3a	U. Dev.	87,000	780	93	13,677	1,740	160	37,054	69						
Upper Devonian SS	this study	PAGB-4a	U. Dev.	90,000	826	36	14,786	1,777	216	36,350	165						
Organic-rich Sh.	this study [1]	D6	U. Dev.	60,903	602	194	9,419	1,692	107	27,883	10			0.718347			
Organic-rich Sh.	this study [1]	D14	U. Dev.	60,655	675	184	10,375	2,050	96	25,402	13			0.715800			
Bradford Grp. Ss.	this study [1]	D27	U. Dev.	62,108	631	119	10,693	1,535	82	26,187	22			0.719459			
Bradford Grp. Ss.	this study [1]	D31	U. Dev.	81,003	692	706	12,639	1,912	72	31,107	7			0.719670			
Bradford Grp. Ss.	this study [1]	D32	U. Dev.	83,095	734	314	13,098	2,004	72	32,771	8			0.720131			
Venango Grp. Ss.	this study [1]	D33	U. Dev.	99,792	918	564	18,243	2,504	115	39,383	8			0.719725			
Bradford Grp. Ss.	this study [1]	D34	U. Dev.	91,213	804	110	14,707	2,083	266	35,642	13			0.716113			
Bradford Grp. Ss.	this study [1]	D37	U. Dev.	45,376	463	1,182	7,937	1,308	47	20,517	7			0.722000			
Bradford Grp. Ss.	this study [1]	D40	U. Dev.	72,566	730	249	10,770	1,718	61	28,950	10			0.721026			
Marcellus Sh.	21	BR-A1	M. Dev.	77,000			6,120	538	1,970	30,400	5490			0.710653			
Marcellus Sh.	21	BR-A2	M. Dev.	159,000			20,800	1,750	5,230	49,400	12000			0.710270			

Marcellus Sh.	21	BR-A3	M. Dev.	68,000			11,300	1,110	3,340	41,900	7820			0.710742			
Marcellus Sh.	21	BR-A4	M. Dev.	77,000			7,930	840	2,870	34,000	6470			0.710757			
Marcellus Sh.	21	BR-A5	M. Dev.	73,000			7,050	726	2,600	27,600	5860			0.710733			
Marcellus Sh.	21	WE-A1.5	M. Dev.				349		46		70			0.711992			
Marcellus Sh.	21	WE-A2	M. Dev.	10,300			624	43	88	2,792	179			0.712013			
Marcellus Sh.	21	WE-A4	M. Dev.	29,000			2,278	217	381	11,747	740			0.712036			
Marcellus Sh.	21	WE-A5	M. Dev.	32,200			2,880	254	450	14,216	888			0.712027			
Marcellus Sh.	21	WE-A7	M. Dev.	42,000			3,938	381	651	18,288	1405			0.712044			
Marcellus Sh.	21	WE-A12	M. Dev.	47,900			5,603	518	934	23,928	2193			0.712013			
Marcellus Sh.	21	WE-A15	M. Dev.	53,500			6,292	629	1,127	24,820	2687			0.712019			
Marcellus Sh.	21	WE-A29	M. Dev.	76,600			6,236	671	1,215	26,297	2987			0.712091			
Marcellus Sh.	21	WE-B3	M. Dev.	19,000			1,239	694	214	9,901	333			0.712076			
Marcellus Sh.	21	WE-B5	M. Dev.	30,600			2,782	376	533	16,704	1058			0.712108			
Marcellus Sh.	21	WE-B7	M. Dev.	40,700			3,900	490	738	18,288	1490			0.712088			
Marcellus Sh.	21	WE-B9	M. Dev.	46,800			4,627	559	900	18,510	1892			0.712108			
Marcellus Sh.	21	WE-B13	M. Dev.	71,100			5,749	211	1,063	22,437	2306			0.712117			
Marcellus Sh.	21	WE-B18	M. Dev.				6,278		1,380		2700			0.712113			
Marcellus Sh.	21	WA-A11	M. Dev.	88,500			12,278	1,267	1,393	32,500	151			0.711129			
Marcellus Sh.	21	WA-A13	M. Dev.	102,100			14,028	1,478	1,694	35,070	194			0.710988			
Marcellus Sh.	21	WA-A15	M. Dev.	107,300			15,269	1,632	1,832	37,100	253						
Marcellus Sh.	21	WA-A17	M. Dev.	102,600			15,875	1,671	1,872	38,530	296			0.711056			
Marcellus Sh.	21	WA-A20	M. Dev.	115,300			16,509	1,820	1,888	40,350	328			0.711088			
Marcellus Sh.	21	WA-A25	M. Dev.	116,100			17,612	1,896	2,045	46,260	349			0.711021			
Marcellus Sh.	21	WA-A30	M. Dev.				18,080	1,992	2,151	47,881	379			0.711076			
Marcellus Sh.	21	WA-B1-8	M. Dev.	59,600			8,682	880	1,192	20,310	176			0.710880			
Marcellus Sh.	21	WA-B1-4	M. Dev.	65,300			8,796	890	1,205	20,440	191			0.710905			
Marcellus Sh.	21	WA-B2-9	M. Dev.	59,400			8,779	859	1,277	20,510	389			0.710969			
Marcellus Sh.	21	WA-B2-6	M. Dev.	58,700			8,818	866	1,296	20,910	339			0.710954			
Marcellus Sh.	21	WA-B3-10	M. Dev.	36,700			5,674	570	795	12,890	11			0.710737			
Marcellus Sh.	21	WA-B3-5	M. Dev.	36,800			5,733	589	803	12,940	10			0.710722			
Marcellus Sh.	21	GR-AF	M. Dev.	41,900			4,377	567	1,389	20,923	393			0.710084			
Marcellus Sh.	21	GR-A1	M. Dev.	63,700			6,532	776	1,397	26,020	1108			0.710988			
Marcellus Sh.	21	GR-A2	M. Dev.	65,000			7,903	828	1,823	30,100	1560			0.710976			
Marcellus Sh.	21	GR-A3	M. Dev.	67,300			7,372	866	1,721	26,840	1487			0.710957			
Marcellus Sh.	21	GR-A4	M. Dev.	70,200			8,874	755	2,009	30,910	1756			0.710961			
Marcellus Sh.	21	GR-A5	M. Dev.	71,200			7,952	762	1,868	28,270	1638			0.710975			
Marcellus Sh.	21	GR-A7	M. Dev.	81,900			8,786	841	2,415	32,800	962			0.710148			
Marcellus Sh.	21	GR-A15	M. Dev.	86,500			9,634	953	2,275	32,380	2273			0.711160			
Marcellus Sh.	21	GR-A20	M. Dev.	87,700			10,390	976	2,484	34,520	2525			0.711173			
Marcellus Sh.	22,24	D60	M. Dev.	132,087	1,213	-	22,840	3,038	4,788	41,335				0.710000	-47.2	-5.9	
Marcellus Sh.	22,24	D61	M. Dev.	105,854	1,081	-	21,160	2,187	1,975	37,785					-30.2	-0.4	
Marcellus Sh.	22,24	D62	M. Dev.	112,377	1,142	-	22,720	2,819	1,844	37,304							
Marcellus Sh.	this study	PAGB-1a	M. Dev.	88,000	815	5	13,215	1,342	2,305	34,371	2655						
Marcellus Sh.	this study[2]	PAGB-2a	M. Dev.	94,000	819	3	13,625	1,333	2,421	36,019	3100						
Marcellus Sh.	this study [1]	D61	M. Dev.	105,854	1,081	-	21,741	2,183	1,624	36,222	240			0.711432			
Marcellus Sh.	this study [1]	D62	M. Dev.	112,377	1,142	-	22,334	2,261	1,532	38,407	268			0.711605			
Marcellus Sh.	7	127	M. Dev.									2,653	318				122,527
Marcellus Sh.	7	128	M. Dev.									3,082	935				250,112
Marcellus Sh.	7	129	M. Dev.									1,958	572				134,880
Marcellus Sh.	7	130	M. Dev.									1,486	472				222,681
Marcellus Sh.	7	131	M. Dev.									1,756	377				117,259
Marcellus Sh.	7	3	M. Dev.									50	37				333,000
Marcellus Sh.	this study[2]	4-0	M. Dev.	46,000	451	55	6,522	660	1,229	21,300	472	1277		0.710115			
Marcellus Sh.	this study[2]	4-1	M. Dev.	59,000	583	18	7,898	972	1,047	26,224	899	2780					
Marcellus Sh.	this study[2]	4-2	M. Dev.	59,000	581	30	8,390	1,023	1,198	27,246	1104	4044		0.711016			
Marcellus Sh.	this study[2]	4-3	M. Dev.	56,000	543	26	7,956	965	1,170	25,175	1073	4835		0.710998			
Marcellus Sh.	this study[2]	4-4	M. Dev.	54,000	531	37	8,186	983	1,236	25,993	1135	4988		0.710995			
Marcellus Sh.	this study[2]	4-5	M. Dev.	62,000	608	27	8,310	1,009	1,256	26,703	1199	4769		0.710997			

Marcellus Sh.	this study[2]	4-7	M. Dev.	75,000	733	34	10,308	1,134	1,732	32,622	771	3548	0.710185		
Marcellus Sh.	this study[2]	4-15	M. Dev.	68,000	668	29	10,884	1,235	1,611	31,628	1746	5863	0.711197		
Marcellus Sh.	this study[2]	4-20	M. Dev.	66,000	655	32	9,138	1,178	1,321	24,735	1388	5383	0.711220		
Ridgeley	6	ED-82-37	L. Dev.	58,900	349	2	8,930	797	4,400	24,400	1510			-41.0	-0.5
Ridgeley	6	ED-82-38	L. Dev.	133,000	763		17,600	1,580	8,930	61,300	3890			-51.0	-1.7
Ridgeley	6	ED-82-39	L. Dev.	174,000	1,010	1	23,800	2,050	13,100	79,900	4370	5000			
Ridgeley	6	ED-82-40	L. Dev.	207,000	1,130		28,400	2,390	12,800	83,300	3680			-42.0	2.0
Medina Ss.	6	ED-82-22	L Sil.	93,000	943	400	16,600	2,050	477	37,600	ND				
Medina Ss.	6	ED-82-27	L Sil.	159,000	2,240	280	41,600	4,150	1,610	42,400		500			
Medina Ss.	6	ED-82-28	L Sil.	151,000	1,860	360	26,900	2,750	1,030	59,900	4				
Medina Ss.	6	ED-82-29	L Sil.	187,000		270	36,300	3,790	1,430	78,900	4			-38.0	-3.1
Medina Ss.	6	ED-82-30	L Sil.	130,000	1,490	260	22,000	2,160	893	51,100	3			-39.0	-3.6
Medina Ss.	6	ED-82-31	L Sil.	159,000	1,990	300	30,100	3,120	1,160	65,300	4				
Tuscarora	6	ED-82-36	L Sil.	152,000	1,540	3	25,500	1,370	3,810	70,700	919	5300		-40.0	-2.3
Medina Ss.	22,24	S70	L Sil.	159,383	1,609	262	27,800	2,989	747	60,639					
Medina Ss.	22,24	S73	L Sil.	141,623	1,311	164	25,040	3,353	705	54,571			0.711900	-32.3	-3.9
Medina Ss.	this study [1]	S73	L Sil.	141,623	1,311	164	22,201	2,836	520	45,253	7		0.711954		
Utica	this study	RW-1	Ord.	43,866	440	363	3,717	516	747	19,113	578	157	0.710505		

Table S2. Analytical results for produced water and flowback samples collected during this and previous studies (4, 6, 7, 21, 22, 24). [1] Results from analysis of cation and strontium isotope samples analyzed at Duke University. Data presented for anions of these samples are originally reported in (22, 24). [2] Split samples of GR samples published in (21). If blank, no value reported/recorded. Ss.=sandstones; Sh.=shales; L. Miss.=Lower Mississippian; U. Dev.=Upper Devonian; M. Dev.=Middle Devonian; Sil.=Silurian; Ord. = Ordovician, ppm = part per million, pCi/L = pico Curie per liter.

Historical and 2010-2011 Groundwater Comparison				
Constituent	Type A p-value	Type B p-value	Type C p-value	Type D p-value
Ca	0.06	0.78	0.97	0.79
Cl	0.96	0.93	0.15	0.18
Na	0.11	0.68	0.55	0.38
Ba	0.89	0.68	N/A	0.12
Sr	0.38	0.66	N/A	0.89

Table S3. Statistical comparison of major element chemistry in water types A-D in shallow groundwater samples collected during this and previous (18, 19) studies. p-values > 0.05 for all values indicate that there is statistical similarity in major element chemistry between the historical data set collected in the 1980's and the 2010-2011 groundwater when divided by water type. N/A -Not analyzed because of limited reported values in the historical data for Type C water.

Descriptive Statistics for Each Water Type									
						95% Confidence Interval for Mean			
		N	Mean	Std. Deviation	Std. Error	Lower Bound	Upper Bound	Minimum	Maximum
pH	A	88	6.92	.77	.08	6.76	7.08	5.09	8.65
	B	29	7.89	.73	.13	7.61	8.16	6.45	9.32
	C	13	6.71	.75	.21	6.26	7.17	5.98	8.58
	D	27	7.72	.66	.13	7.46	7.98	6.27	9.34
	Total	157	7.22	.86	.07	7.08	7.35	5.09	9.34
Cl (mg/L)	A	89	6.25	5.30	.56	5.14	7.37	.49	19.35
	B	29	6.49	5.91	1.10	4.24	8.74	1.64	18.22
	C	13	52.35	26.38	7.32	36.41	68.29	22.79	111.73
	D	26	224.06	328.85	64.49	91.23	356.88	20.75	4014.00
	Total	157	46.18	154.55	12.33	21.82	70.55	.49	4014.00
Br (mg/L)	A	89	.04	.02	.00	.03	.04	.01	.12
	B	29	.07	.04	.01	.05	.08	.02	.14
	C	13	.06	.03	.01	.04	.08	.02	.15
	D	27	3.08	7.41	1.43	.15	6.01	.09	37.89
	Total	158	.56	3.23	.26	.06	1.07	.01	37.89
Ca(mg/L)	A	89	30.02	14.00	1.48	27.07	32.97	6.56	102.34
	B	29	23.65	11.94	2.22	19.11	28.20	2.38	51.06
	C	13	35.63	14.54	4.03	26.85	44.42	12.96	68.47
	D	27	60.78	77.17	14.85	30.25	91.31	4.24	370.47
	Total	158	34.57	35.91	2.86	28.93	40.21	2.38	370.47
Mg(mg/L)	A	89	6.64	4.50	.48	5.69	7.59	.95	26.37
	B	29	6.45	3.86	.72	4.98	7.92	.31	15.84
	C	13	7.19	2.45	.68	5.71	8.67	3.29	11.76
	D	27	12.15	12.98	2.50	7.02	17.28	1.33	61.23
	Total	158	7.59	6.83	.54	6.52	8.66	.31	61.23
Sr(mg/L)	A	89	.32	.33	.04	.25	.39	.02	1.69
	B	29	.56	.50	.09	.37	.74	.08	2.13
	C	13	.16	.07	.02	.11	.20	.02	.28
	D	27	4.52	9.87	1.90	.62	8.43	.28	48.52
	Total	158	1.07	4.33	.34	.39	1.75	.02	48.52
Na(mg/L)	A	89	9.31	7.20	.76	7.80	10.83	.00	52.24
	B	29	55.07	31.31	5.81	43.16	66.98	15.45	118.84
	C	13	31.42	30.14	8.36	13.21	49.64	7.86	117.29
	D	27	212.10	357.35	68.77	70.74	353.46	7.20	1800.16
	Total	158	54.18	163.99	13.05	28.41	79.95	.00	1800.16
Ba (mg/L)	A	89	.127	.175	.019	.090	.164	.014	1.592
	B	29	.195	.180	.033	.127	.264	.032	.745
	C	13	.100	.059	.016	.064	.136	.006	.199
	D	27	5.028	16.123	3.103	-1.350	11.406	.064	84.439
	Total	158	.975	6.818	.542	-.096	2.046	.006	84.439

Descriptive Statistics for Each Water Type									
						95% Confidence Interval for Mean			
		N	Mean	Std. Deviation	Std. Error	Lower Bound	Upper Bound	Minimum	Maximum
Br/Cl (molar)	A	89	4.3E-03	4.1E-03	4.4E-04	3.5E-03	5.2E-03	4.7E-04	2.0E-02
	B	29	7.9E-03	6.5E-03	1.2E-03	5.5E-03	1.0E-02	9.4E-04	2.3E-02
	C	13	5.8E-04	2.7E-04	7.4E-05	4.2E-04	7.4E-04	2.4E-04	9.6E-04
	D	27	3.4E-03	7.6E-04	1.5E-04	3.1E-03	3.7E-03	1.1E-03	4.4E-03
	Total	158	4.5E-03	4.6E-03	3.6E-04	3.8E-03	5.2E-03	2.4E-04	2.3E-02
Sr/Ca	A	89	4.61E-03	4.11E-03	4.36E-04	3.74E-03	5.47E-03	5.58E-04	2.02E-02
	B	29	1.20E-02	8.38E-03	1.56E-03	8.85E-03	1.52E-02	1.65E-03	3.08E-02
	C	13	2.19E-03	1.21E-03	3.36E-04	1.46E-03	2.92E-03	6.88E-04	4.63E-03
	D	27	2.62E-02	1.81E-02	3.49E-03	1.91E-02	3.34E-02	3.64E-03	6.74E-02
	Total	158	9.47E-03	1.20E-02	9.54E-04	7.58E-03	1.14E-02	5.58E-04	6.74E-02
$^{87}Sr/^{86}Sr$	A	53	.71332	.00138	.00019	.71294	.71370	.71091	.71725
	B	25	.71283	.00107	.00021	.71239	.71327	.71030	.71500
	C	8	.71371	.00110	.00039	.71279	.71463	.71136	.71473
	D	22	.71162	.00138	.00029	.71101	.71223	.70960	.71453
	Total	108	.71289	.00145	.00014	.71261	.71317	.70960	.71725
$^{228}Ra/^{226}Ra$	A	13	.967	.467	.129	.685	1.249	.422	2.160
	B	15	.920	.164	.042	.829	1.011	.683	1.212
	C	4	1.113	.329	.165	.589	1.636	.666	1.368
	D	11	.556	.201	.061	.421	.691	.247	.978
	Total	43	.859	.352	.054	.751	.967	.247	2.160
Distance to nearest Natural Gas Well (km)	A	89	1.73	1.42	.15	1.43	2.03	.05	5.33
	B	24	1.21	1.00	.20	.79	1.64	.11	3.51
	C	13	1.72	1.52	.42	.80	2.64	.31	5.50
	D	27	1.33	1.31	.25	.82	1.85	.13	4.25
	Total	153	1.58	1.36	.11	1.36	1.79	.05	5.50
Distance to Valley[1](km)	A	89	1.03	.75	.08	.87	1.18	.06	3.07
	B	24	1.11	.86	.17	.75	1.48	.11	3.85
	C	13	1.10	.85	.24	.59	1.61	.04	2.96
	D	27	.56	.79	.15	.25	.87	.01	3.15
	Total	153	.96	.80	.06	.84	1.09	.01	3.85
Distance to Valley[2](km)	A	89	.52	.41	.04	.43	.61	.02	2.12
	B	24	.47	.31	.06	.34	.60	.03	1.06
	C	13	.51	.47	.13	.22	.80	.04	1.31
	D	27	.20	.23	.04	.11	.29	.01	.74
	Total	153	.46	.39	.03	.39	.52	.01	2.12
DEM (m)	A	89	397	74	8	382	413	217	536
	B	24	391	58	12	366	416	272	508
	C	13	419	78	22	372	466	274	521
	D	27	316	67	13	290	343	219	522
	Total	153	384	77	6	372	396	217	536

Multiple Comparisons - Dunnett T3							
Dependent Variable	(I) Type	(J) Type	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
						Lower Bound	Upper Bound
pH	A	B	-.968*	.158	.000	-1.399	-.537
		C	0.209	.224	.917	-.457	.876
		D	-.797*	.152	.000	-1.212	-.382
	B	A	.968*	.158	.000	.537	1.399
		C	1.177*	.249	.001	.464	1.890
		D	0.171	.186	.927	-.335	.676
	C	A	-0.209	.224	.917	-.876	.457
		B	-1.177*	.249	.001	-1.890	-.464
		D	-1.007*	.245	.003	-1.712	-.301
	D	A	.797*	.152	.000	.382	1.212
		B	-0.171	.186	.927	-.676	.335
		C	1.007*	.245	.003	.301	1.712
Cl (mg/L)	A	B	-0.237	1.233	1.000	-3.627	3.152
		C	-46.0968346*	7.339	.000	-68.764	-23.430
		D	-217.805	64.495	.014	-401.061	-34.549
	B	A	0.237	1.233	1.000	-3.152	3.627
		C	-45.8594774*	7.399	.000	-68.593	-23.126
		D	-217.568	64.502	.014	-400.837	-34.298
	C	A	46.0968346*	7.339	.000	23.430	68.764
		B	45.8594774*	7.399	.000	23.126	68.593
		D	-171.708	64.906	.077	-355.778	12.361
	D	A	217.8051472*	64.495	.014	34.549	401.061
		B	217.5677900*	64.502	.014	34.298	400.837
		C	171.708	64.906	.077	-12.361	355.778
Br (mg/L)	A	B	-.0318427*	.007	.000	-.051	-.012
		C	-0.026	.009	.084	-.054	.003
		D	-3.045	1.427	.218	-7.088	.997
	B	A	.0318427*	.007	.000	.012	.051
		C	0.006	.011	.994	-.026	.038
		D	-3.013	1.427	.228	-7.056	1.029
	C	A	0.026	.009	.084	-.003	.054
		B	-0.006	.011	.994	-.038	.026
		D	-3.019	1.427	.226	-7.062	1.023
	D	A	3.045	1.427	.218	-.997	7.088
		B	3.013	1.427	.228	-1.029	7.056
		C	3.019	1.427	.226	-1.023	7.062

Multiple Comparisons - Dunnett T3							
Dependent Variable	(I) Type	(J) Type	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
Ca(mg/L)	A	B	6.364	2.668	.115	-.902	13.630
		C	-5.612	4.297	.721	-18.428	7.205
		D	-30.762	14.925	.249	-72.980	11.457
	B	A	-6.364	2.668	.115	-13.630	.902
		C	-11.976	4.601	.094	-25.336	1.384
		D	-37.125	15.015	.110	-79.527	5.276
	C	A	5.612	4.297	.721	-7.205	18.428
		B	11.976	4.601	.094	-1.384	25.336
		D	-25.150	15.388	.493	-68.347	18.048
	D	A	30.762	14.925	.249	-11.457	72.980
		B	37.125	15.015	.110	-5.276	79.527
		C	25.150	15.388	.493	-18.048	68.347
Mg(mg/L)	A	B	0.189	.862	1.000	-2.159	2.537
		C	-0.548	.830	.984	-2.900	1.805
		D	-5.511	2.542	.203	-12.677	1.654
	B	A	-0.189	.862	1.000	-2.537	2.159
		C	-0.737	.988	.972	-3.483	2.009
		D	-5.700	2.598	.190	-12.983	1.583
	C	A	0.548	.830	.984	-1.805	2.900
		B	0.737	.988	.972	-2.009	3.483
		D	-4.963	2.588	.317	-12.228	2.301
	D	A	5.511	2.542	.203	-1.654	12.677
		B	5.700	2.598	.190	-1.583	12.983
		C	4.963	2.588	.317	-2.301	12.228
Sr(mg/L)	A	B	-0.236	.098	.121	-.509	.037
		C	.1646630*	.041	.001	.055	.274
		D	-4.202	1.900	.189	-9.584	1.180
	B	A	0.236	.098	.121	-.037	.509
		C	.4003334*	.094	.001	.137	.664
		D	-3.966	1.902	.239	-9.352	1.420
	C	A	-.1646630*	.041	.001	-.274	-.055
		B	-.4003334*	.094	.001	-.664	-.137
		D	-4.366	1.900	.159	-9.748	1.015
	D	A	4.202	1.900	.189	-1.180	9.584
		B	3.966	1.902	.239	-1.420	9.352
		C	4.366	1.900	.159	-1.015	9.748

Multiple Comparisons - Dunnett T3							
Dependent Variable	(I) Type	(J) Type	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
Na(mg/L)	A	B	-45.7581696*	5.865	.000	-62.246	-29.270
		C	-22.112	8.394	.111	-48.017	3.793
		D	-202.785	68.776	.038	-397.618	-7.951
	B	A	45.7581696*	5.865	.000	29.270	62.246
		C	23.647	10.183	.154	-5.380	52.674
		D	-157.027	69.017	.166	-352.341	38.288
	C	A	22.112	8.394	.111	-3.793	48.017
		B	-23.647	10.183	.154	-52.674	5.380
		D	-180.673	69.278	.082	-376.515	15.169
	D	A	202.7848115*	68.776	.038	7.951	397.618
		B	157.027	69.017	.166	-38.288	352.341
		C	180.673	69.278	.082	-15.169	376.515
Ba (mg/L)	A	B	-0.068	.038	.388	-.173	.037
		C	0.027	.025	.855	-.041	.095
		D	-4.901	3.103	.532	-13.691	3.889
	B	A	0.068	.038	.388	-.037	.173
		C	0.095	.037	.084	-.008	.198
		D	-4.833	3.103	.547	-13.624	3.958
	C	A	-0.027	.025	.855	-.095	.041
		B	-0.095	.037	.084	-.198	.008
		D	-4.928	3.103	.526	-13.718	3.862
	D	A	4.901	3.103	.532	-3.889	13.691
		B	4.833	3.103	.547	-3.958	13.624
		C	4.928	3.103	.526	-3.862	13.718
Br/Cl (molar)	A	B	-.0036013*	.001	.045	-.007	.000
		C	.0037570*	.000	.000	.003	.005
		D	0.001	.000	.193	.000	.002
	B	A	.0036013*	.001	.045	.000	.007
		C	.0073583*	.001	.000	.004	.011
		D	.0045809*	.001	.004	.001	.008
	C	A	-.0037570*	.000	.000	-.005	-.003
		B	-.0073583*	.001	.000	-.011	-.004
		D	-.0027774*	.000	.000	-.003	-.002
	D	A	-0.001	.000	.193	-.002	.000
		B	-.0045809*	.001	.004	-.008	-.001
		C	.0027774*	.000	.000	.002	.003

Multiple Comparisons - Dunnett T3							
Dependent Variable	(I) Type	(J) Type	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
Sr/Ca	A	B	-.0074262*	.002	.000	-.012	-.003
		C	.0024202*	.001	.000	.001	.004
		D	-.0216215*	.004	.000	-.032	-.012
	B	A	.0074262*	.002	.000	.003	.012
		C	.0098464*	.002	.000	.005	.014
		D	-.0141953*	.004	.004	-.025	-.004
	C	A	-.0024202*	.001	.000	-.004	-.001
		B	-.0098464*	.002	.000	-.014	-.005
		D	-.0240417*	.004	.000	-.034	-.014
	D	A	.0216215*	.004	.000	.012	.032
		B	.0141953*	.004	.004	.004	.025
		C	.0240417*	.004	.000	.014	.034
$^{87}Sr/^{86}Sr$	A	B	0.000	.000	.432	.000	.001
		C	0.000	.000	.926	-.002	.001
		D	.001700109*	.000	.000	.001	.003
	B	A	0.000	.000	.432	-.001	.000
		C	-0.001	.000	.328	-.002	.001
		D	.001211504*	.000	.011	.000	.002
	C	A	0.000	.000	.926	-.001	.002
		B	0.001	.000	.328	-.001	.002
		D	.002088614*	.000	.004	.001	.004
	D	A	-.001700109*	.000	.000	-.003	-.001
		B	-.001211504*	.000	.011	-.002	.000
		C	-.002088614*	.000	.004	-.004	-.001
$^{228}Ra/^{226}Ra$	A	B	0.047	.136	.999	-.362	.456
		C	-0.146	.209	.973	-.871	.580
		D	0.411	.143	.058	-.011	.833
	B	A	-0.047	.136	.999	-.456	.362
		C	-0.193	.170	.811	-1.008	.622
		D	.3639082*	.074	.001	.149	.579
	C	A	0.146	.209	.973	-.580	.871
		B	0.193	.170	.811	-.622	1.008
		D	0.557	.175	.139	-.226	1.339
	D	A	-0.411	.143	.058	-.833	.011
		B	-.3639082*	.074	.001	-.579	-.149
		C	-0.557	.175	.139	-1.339	.226

Multiple Comparisons - Dunnett T3							
Dependent Variable	(I) Type	(J) Type	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
Distance to nearest Natural Gas Well (km)	A	B	0.514	.254	.249	-.179	1.208
		C	0.006	.448	1.000	-1.333	1.345
		D	0.395	.293	.693	-.409	1.199
	B	A	-0.514	.254	.249	-1.208	.179
		C	-0.509	.469	.850	-1.884	.867
		D	-0.120	.324	.999	-1.007	.767
	C	A	-0.006	.448	1.000	-1.345	1.333
		B	0.509	.469	.850	-.867	1.884
		D	0.389	.491	.961	-1.029	1.807
	D	A	-0.395	.293	.693	-1.199	.409
		B	0.120	.324	.999	-.767	1.007
		C	-0.389	.491	.961	-1.807	1.029
Distance to Valley Center[1](km)	A	B	-0.086	.192	.998	-.622	.449
		C	-0.072	.248	1.000	-.815	.672
		D	0.468	.171	.052	-.002	.939
	B	A	0.086	.192	.998	-.449	.622
		C	0.014	.293	1.000	-.818	.847
		D	0.555	.231	.115	-.079	1.188
	C	A	0.072	.248	1.000	-.672	.815
		B	-0.014	.293	1.000	-.847	.818
		D	0.540	.280	.318	-.262	1.342
	D	A	-0.468	.171	.052	-.939	.002
		B	-0.555	.231	.115	-1.188	.079
		C	-0.540	.280	.318	-1.342	.262
Distance to Valley[2](km)	A	B	0.051	.077	.985	-.161	.263
		C	0.012	.138	1.000	-.403	.426
		D	.3187538*	.062	.000	.151	.486
	B	A	-0.051	.077	.985	-.263	.161
		C	-0.039	.146	1.000	-.467	.388
		D	.2676800*	.077	.008	.054	.481
	C	A	-0.012	.138	1.000	-.426	.403
		B	0.039	.146	1.000	-.388	.467
		D	0.307	.138	.211	-.108	.722
	D	A	-.3187538*	.062	.000	-.486	-.151
		B	-.2676800*	.077	.008	-.481	-.054
		C	-0.307	.138	.211	-.722	.108

Multiple Comparisons - Dunnett T3							
Dependent Variable	(I) Type	(J) Type	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
DEM (m)	A	B	6.204	14.226	.998	-32.840	45.249
		C	-22.130	22.902	.903	-90.478	46.218
		D	80.7953782*	15.129	.000	39.330	122.261
	B	A	-6.204	14.226	.998	-45.249	32.840
		C	-28.334	24.568	.814	-99.710	43.041
		D	74.5913087*	17.550	.001	26.577	122.605
	C	A	22.130	22.902	.903	-46.218	90.478
		B	28.334	24.568	.814	-43.041	99.710
		D	102.9254139*	25.102	.003	30.524	175.327
	D	A	-80.7953782*	15.129	.000	-122.261	-39.330
		B	-74.5913087*	17.550	.001	-122.605	-26.577
		C	-102.925	25.102	.003	-175.327	-30.524

Table S4. Statistical results and comparison between water types for shallow groundwater results. p-values < 0.05 indicate a statistically significant difference between the water types. Note that type-D water is statistically different in nearly every category.

Supporting Information

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SI Text

SI Methods. For strontium isotope measurements, water samples were prepared by total desiccation of sample aliquot containing approximately 2–4 μg of Sr. The dried sample was then digested in 3 N ultrapure HNO_3 and extracted using Teflon microcolumns containing Eichrom Sr resin. The extracted Sr was then dried again before digestion with TaCl solution and loaded onto Re filaments for a final dry down. Distance to natural gas wells was calculated using data collected from (1).

Statistical summaries of elemental concentrations and isotopic composition including mean and median are shown for each water type (i.e., A, B, C, D) in Table S4. Before each statistical comparison, the normality was verified using a one-sample Kolmogorov-Smirnov test. Parameters that did not achieve normality were transformed using log transformation and verified for normality. In order to simultaneously test whether several means are equal [e.g., whether type D (Cl), Br/Cl, and $^{87}Sr/^{86}Sr$ are significantly different than the types A–C and the variance observed in the suite of samples], we performed a post-hoc, one-way ANOVA for each of the water types (Table S4).

Geological setting. In the northern Appalachian Basin, sedimentary deposition is relatively continuous throughout the Paleozoic Era, though several unconformities erase sequence records regionally (e.g., The Tri-States unconformity removes Lower Devonian strata in western New York, whereas complete sequences are found in central New York and northeastern PA) (2). The sedimentary column represents periods of deposition, burial, lithification, uplift, and subsequent erosion that form relatively simple sets of horizontal strata (approximately 1–3 degree dip to the south and east) derived from various depositional environments (ranging from proposed deep-to midbasin black shale to terrestrial red beds) within the Plateau region (northeastern and western PA and most of NY) (2–5). The monocline, including the entire Appalachian sedimentary sequence, is bound on the north by the Precambrian Canadian Shield and Adirondack uplift (N-NE), on the west by the Algonquin and Findlay arches, and on the south and east by the Appalachian fold belt (i.e., Valley and Ridge Province) (6, 7). Bedrock thickness ranges within the basin from approximately 920 meters along the southern shore of Lake Ontario in the north (northern NY) to approximately 7,600 meters along the Appalachian structural front in the south. Erosion has beveled the monocline flat allowing for elongate, east-west trending outcrop belts of strata across the majority of the Appalachian Plateau physiographic province. The stratigraphic names and continuity of specific stratigraphic sequences change regionally. As a result, we present a simplified stratigraphic reconstruction in Fig. 2 showing the stratigraphy from western and eastern PA (2–5, 8, 9). The study area constitutes a transition from the Valley and Ridge to the Plateau province and includes sequential low amplitude anticline/syncline structures, numerous thrust faults, lineaments, joints, and natural fractures (10–15) (Fig. S1).

The Appalachian Basin sedimentary sequence is underlain by Precambrian crystalline basement rocks of the (Grenville province) Canadian Shield (2). The Appalachian Basin consists primarily of sedimentary sequences of Ordovician to Pennsylvanian age that are derived from the Taconic (approximately 450 Ma), Acadian (approximately 410–380 Ma), and Alleghanian (approximately 330–250 Ma) orogenic events (7, 16). Exposed at its northern extent near Lake Ontario is the Upper Ordovician-Lower Silurian contact (Cherokee unconformity). Younger deposits (Upper Silurian, Devonian, and Mississippian) occur in successive outcrop belts to the south towards the Appalachian structural front (2, 4, 5), whereas erosion has removed any post-Pennsylvanian deposition within western-central New York and the majority of our study area within northeastern PA (exceptions noted in Fig. S1).

The Middle Ordovician Trenton/Black River Group consists of interbedded limestones and shales overlain by the calcareous and organic-rich Utica Shale derived primarily by sediment offloading from the Taconic orogeny approximately 420 Ma (2, 17, 18). The lower most Silurian age strata is fine-grained Tuscarora Formation sandstones that are overlain by the middle Silurian Clinton Group with locally interbedded limestone, dolostone, sandstone, and shale (Fig. 2). The Upper Silurian is characterized by the transition from the Silurian Lockport Dolomite/McKenzie argillaceous limestone to the Bloomsburg red sandstone and evaporitic Salina Group in the plateau region of the Appalachian Basin (2, 19, 20). The Salina Group consists of interbedded shales, dolomites, and primarily salt deposits that act as the decollement to younger stratigraphic units (21, 22). As a result, structural folds and faults above the decollement (i.e., Devonian and younger stratigraphic units) bear no resemblance in deformation style to those present beneath the Salina Group (21–24). The transition from Upper Silurian to Lower Devonian is comprised of the Helderberg Group (layered dolomites and limestones often lost in western NY) and Tri-States Group consisting of the Oriskany Sandstone and Onondaga and Selinsgrove Limestones, that lie directly beneath the Hamilton Group (4, 9, 25). The Hamilton Group is an eastward to southeastward thickening wedge of marine sediments that includes the Marcellus Formation.

The Marcellus Formation is an organic-rich, hydrocarbon producing, siliciclastic-rich black shale present beneath much of Pennsylvania, New York, and the northeastern US. The Marcellus Formation constitutes the stratigraphically lowest subgroup of the Middle Devonian Hamilton Group (3, 4, 9, 25) and was deposited in the foreland basin of the Acadian Orogeny (approximately 385–375 Ma). The Marcellus Formation includes two distinct calcareous and iron-rich black shale members; i.e., the Union Springs (lower) and Mount Marion/Oatka Creek (upper) interrupted by the Cherry Valley limestone (3, 4, 9, 15, 25). By comparison to the Valley and Ridge province or the region in close proximity to the Appalachian Structural Front, the plateau portion of the Marcellus Formation is significantly less deformed (e.g., 23, 26, 27).

Like the Marcellus, the upper part of the Devonian sequence is deposited from material sourced from the Acadian orogeny. Above the Marcellus, the Hamilton Group consists of the Mahantango grey shale, locally interbedded by limestones, and the Tulley limestone. The Upper Devonian consists of thick synorogenic sequences of grey shales (i.e., the Brallier Formation), beneath the Lock Haven Formation sandstone and Catskill Formation clastic deltaic red sandstones deposited in foreland basin of the Acadian Orogeny. The latter two sequences, the Lock Haven and Catskill Formations, constitute the two primary aquifer lithologies in northeastern PA along with the overlying glacial and sedimentary alluvium, which is thicker in valleys than the uplands. Deformation of Devonian lithologies (i.e., the Hamilton Group including the Marcellus Formation) and the Upper Devonian (Lock Haven and Catskill aquifers) began during the onset of the Alleghanian orogeny in the latest Carboniferous Age (330–250 Ma). In the plateau physiographic province, deformation is accommodated by a combination of layer parallel shortening,

folding that leads to the gentle anticline/syncline sequences, and low angle thrust faulting structures observable in northeastern PA (15, 22, 28–35). The initiation of deformation during the Alleghanian orogeny also likely led to the onset of catagenesis for the Marcellus Formation and the joint sets observed in the Upper Devonian sedimentary rocks (28). The majority of stratigraphic sequences above the Catskill Formation are eroded in our study area and, therefore, are only briefly discussed. More complete reviews of Carboniferous Age deposition (Mississippian and Pennsylvanian) are available elsewhere (e.g., 23, 26, 27).

1. Pennsylvania Spatial Data Access (2012) Online mapping, data access wizard, oil and gas locations. (Pennsylvania Department of Environmental Protection Harrisburg, PA) http://www.pasda.psu.edu/uci/SearchResults.aspx?searchType=mapservice&condition=OR&entry=PASDA.
2. Brett CE, Goodman WM, LoDuca ST, Lehmann DF (1996) Upper Ordovician and Silurian strata in western New York: Sequences, cycles and basin dynamics. *New York State Geological Association Field Trip Guide, 1996*, ed Brett CE (University of Rochester, Rochester, NY), pp. 71–120.
3. Brett CE, Baird GC, Bartholomew AJ, DeSantis MK, Straeten CAV (2011) Sequence stratigraphy and a revised sea-level curve for the Middle Devonian of eastern North America. *Palaeogeogr Palaeoclimatol Palaeoecol* 304:21–53.
4. Straeten CAV, Brett CE, Sageman BB (2011) Mudrock sequence stratigraphy: A multiproxy (sedimentological, paleobiological and geochemical) approach, Devonian Appalachian Basin. *Palaeogeogr Palaeoclimatol Palaeoecol* 304:54–73.
5. Lash GG, Engelder T (2011) Thickness trends and sequence stratigraphy of the Middle Devonian Marcellus Formation, Appalachian Basin: implications for Acadian foreland basin evolution. *AAPG Bulletin* 95:61–103.
6. Milici RC, de Witt W, eds. (1988) The Appalachian Basin. *The Geology of North America* (Geological Society of America, Boulder, CO), Vol D-2, pp 427–469.
7. Jenden PD, Drazan DJ, Kaplan IR (1993) Mixing of thermogenic natural gases in northern Appalachian Basin. *AAPG Bulletin* 77:980–998.
8. Brett C, Baird G, eds (1996) *Middle Devonian sedimentary cycles and sequences in the northern Appalachian Basin*. (Geological Society of America Boulder, Colorado), Vol 306.
9. Straeten CAV, Griffing DH, Brett CE (1994) *The lower part of the Middle Devonian Marcellus "shale", central to western New York State: Stratigraphy and depositional history.* (New York State Geological Association, Albany, NY).
10. Trenton-Black River Research Consortium (2006) *A Geologic Play Book for Trenton-Black River Appalachian Basin Exploration* (USDOE Final Report) Award No DE-FC26-03NT41865, p 543.
11. Alexander S, Cakir R, Doden AG, Gold DP, Root SI (2005) *Basement Depth and Related Geospatial Database for Pennsylvania*. (USGS Open-File General Geology) Report OFGG 05-01.
12. Pohn H (2000) *Lateral Ramps in the Folded Appalachians and in Overthrust Beltsworldwide—A Fundamental Element of Thrust-belt Architecture*. USGS Bulletin 2163.
13. Jacobi RD (2002) Basement faults and seismicity in the Appalachian Basin of New York State. *Tectonophysics* 353:75–113.
14. Engelder T, Lash GG, Uzcategui RS (2009) Joint sets that enhance production from Middle and Upper Devonian gas shales of the Appalachian Basin. *AAPG Bulletin* 93:857–889.
15. Lash GG, Engelder T (2009) Tracking the burial and tectonic history of Devonian shale of the Appalachian Basin by analysis of joint intersection style. *Geol Soc Am Bull* 121:265–277.
16. Rast N, ed (1989) *The Evolution of the Appalachian Chain* (Geological Society of America, Boulder, CO), Vol A, pp 347–358.
17. Lehmann D, Brett CE, Cole R, Baird G (1995) Distal sedimentation in a peripheral foreland basin-Ordovician black shales and associated flysch of the western taconic foreland, New York State and Ontario. *Geol Soc Am Bull* 107:708–724.
18. Lavoie D (1994) Diachronous tectonic collapse of the Ordovician continental-margin, eastern Canada—Comparison between the Quebec reentrant and St. Lawrence promontory. *Can J Earth Sci* 31:1309–1319.
19. Ryder TT (1998) *Characteristics of Discrete and Basin-Centered Parts of the Lower Silurian Regional Oil and Gas Accumulation, Appalachian Basin: Preliminary results from data set of 25 Oil and Gas Fields*. (USGS Open-File General Geology) Report 98-216.
20. Ryder RT, et al. (1996) *Possible Continuous-type (unconventional) Gas Accumulation in the Lower Silurian "Clinton" Sands, Medina Group, and Tuscarora Sandstone in the Appalachian basin: A Progress Report of 1995 Activities*. (USGS Open-File General Geology) Report 96–42.
21. Frey MG (1973) Influence of Salina salt on structure in New York-Pennsylvania part of the Appalachian Plateau. *AAPG Bulletin* 57:1027–1037.
22. Scanlin MA, Engelder T (2003) The basement versus the no-basement hypotheses for folding within the Appalachian plateau detachment sheet. *Am J Sci* 303:519–563.
23. Faill R, Nickelsen R, eds (1999) *Appalachian Mountains Section of the Valley and Ridge Province* (Pennsylvania Geological Survey, Harrisburg, PA).
24. Faill R (1985) The Acadian Orogeny and the Catskill Delta. *Spec Pap Geol Soc Am* 201:15–38.
25. Baird G, Staeten CV (1999) The first great Devonian flooding episodes in Western New York: Reexamination of Union Springs, Oatka Creek, and Skaneateles formation successionss (Latest Eifelian-Lower Givetian) in the Buffalo-Seneca lake Region: Field Trip Guidebook. (New York State Geological Association 71st meeting).
26. Faill RT (1997) A geologic history of the north-central Appalachians .1. Orogenesis from the mesoproterozoic through the taconic orogeny. *Am J Sci* 297:551–619.
27. Faill RT (1997) A geologic history of the north-central Appalachians .2. The Appalachian basin from the Silurian through the Carboniferous. *Am J Sci* 297:729–761.
28. Engelder T, Whitaker A (2006) Early jointing in coal and black shale: Evidence for an Appalachian-wide stress field as a prelude to the Alleghanian orogeny. *Geology* 34:581–584.
29. Lash G, Loewy S, Engelder T (2004) Preferential jointing of Upper Devonian black shale, Appalachian Plateau, USA: Evidence supporting hydrocarbon generation as a joint-driving mechanims. *Geol Soc Lond S P* 231:129–151.
30. Davis DM, Engelder T (1985) The role of salt in fold-and-thrust belts. *Tectonophysics* 119:67–88.
31. Engelder T, Geiser P (1980) On the use Of regional joint sets as trajectories of paleostress fields during the development of the Appalachian plateau, New York. *J Geophys Res* 85:6319–6341.
32. Engelder T (1979) Mechanisms for strain within the Upper Devonian clastic sequence of the Appalachian Plateau, western New York. *Am J Sci* 279:527–542.
33. Engelder T, Engelder R (1977) Fossil distortion and decollement tectonics of Appalachian plateau. *Geol* 5:457–460.
34. Evans MA (1995) Fluid inclusions in veins from the middle Devonian Shales—A record of deformation conditions and fluid evolution in the Appalachian plateau. *Geol Soc Am Bull* 107:327–339.
35. Gray MB, Mitra G (1999) Ramifications of 4D progressive deformation in contractional mountain belts. *J Struct Geol* 21:1151–1160.

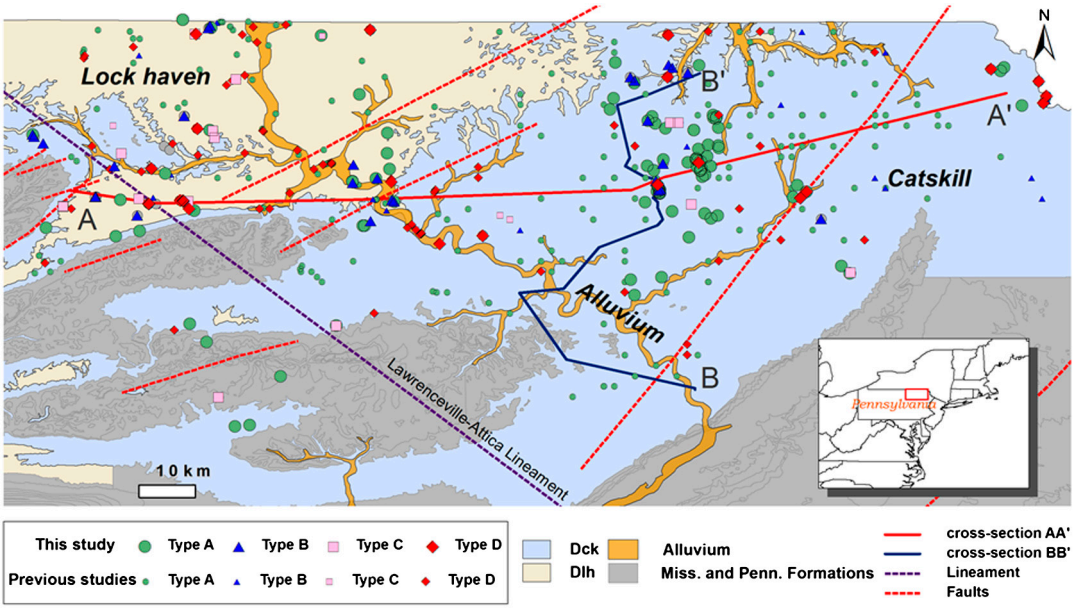

Fig. S1. Geologic map of the study area with the three major aquifers [Alluvium, Catskill (Dck), and Lock Haven (Dhl)] and samples collected during this study. Other formations of Mississippian and Pennsylvanian are shown in gray. Cross section lines are approximated based on (1) and (2).

1 Osborn SG, Vengosh A, Warner NR, Jackson RB (2011) Methane contamination of drinking water accompanying gas-well drilling and hydraulic fracturing. *Proc Natl Acad Sci USA* 108:8172–8176.

2 Molofsky LJ, Connor JA, Farhat SK, Wylie AS, Jr, Wagner T (2011) Methane in Pennsylvania water wells unrelated to Marcellus shale fracturing. *Oil Gas J* 109:54–67.

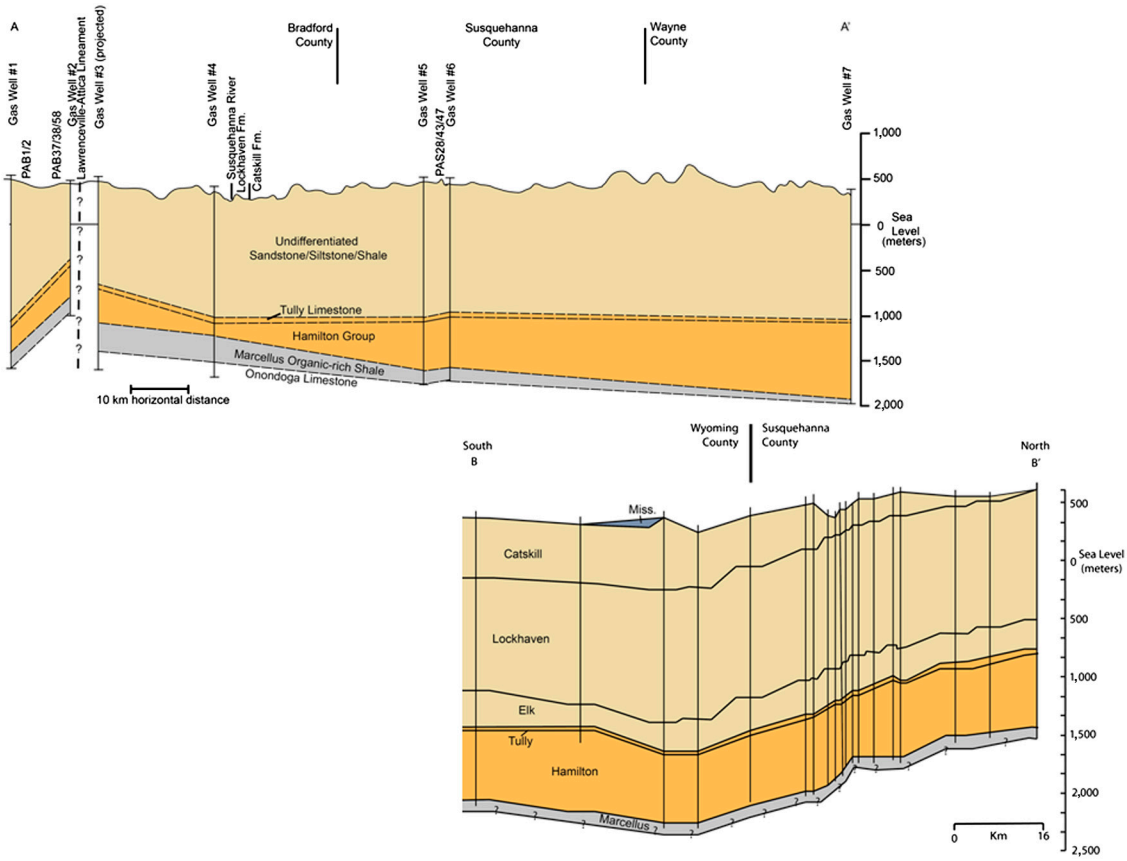

Fig. S2. *A* and *B*. Generalized cross sections adapted from (1) and (2) that display the relative vertical separation between the shallow aquifers (Alluvium, Catskill, and Lock Haven) and underlying formations. Note that the alluvium aquifer is not depicted nor was it included in the source for the well logs (Geological Sample Co., Farmington, NM); however, it is present and is thicker in valleys than uplands. The vertical separation between the water wells and the Marcellus Formation ranges between 800–2,000 m with the minimum found at the apex of the anticlinal hinge displayed in S2*B*. Note that these low amplitude anticline-syncline features are common in this region of the Appalachian plateau.

1 Osborn SG, Vengosh A, Warner NR, Jackson RB (2011) Methane contamination of drinking water accompanying gas-well drilling and hydraulic fracturing. *Proc Natl Acad Sci USA* 108:8172–8176.

2 Molofsky LJ, Connor JA, Farhat SK, Wylie AS, Jr, Wagner T (2011) Methane in Pennsylvania water wells unrelated to Marcellus shale fracturing. *Oil Gas J* 109:54–67.

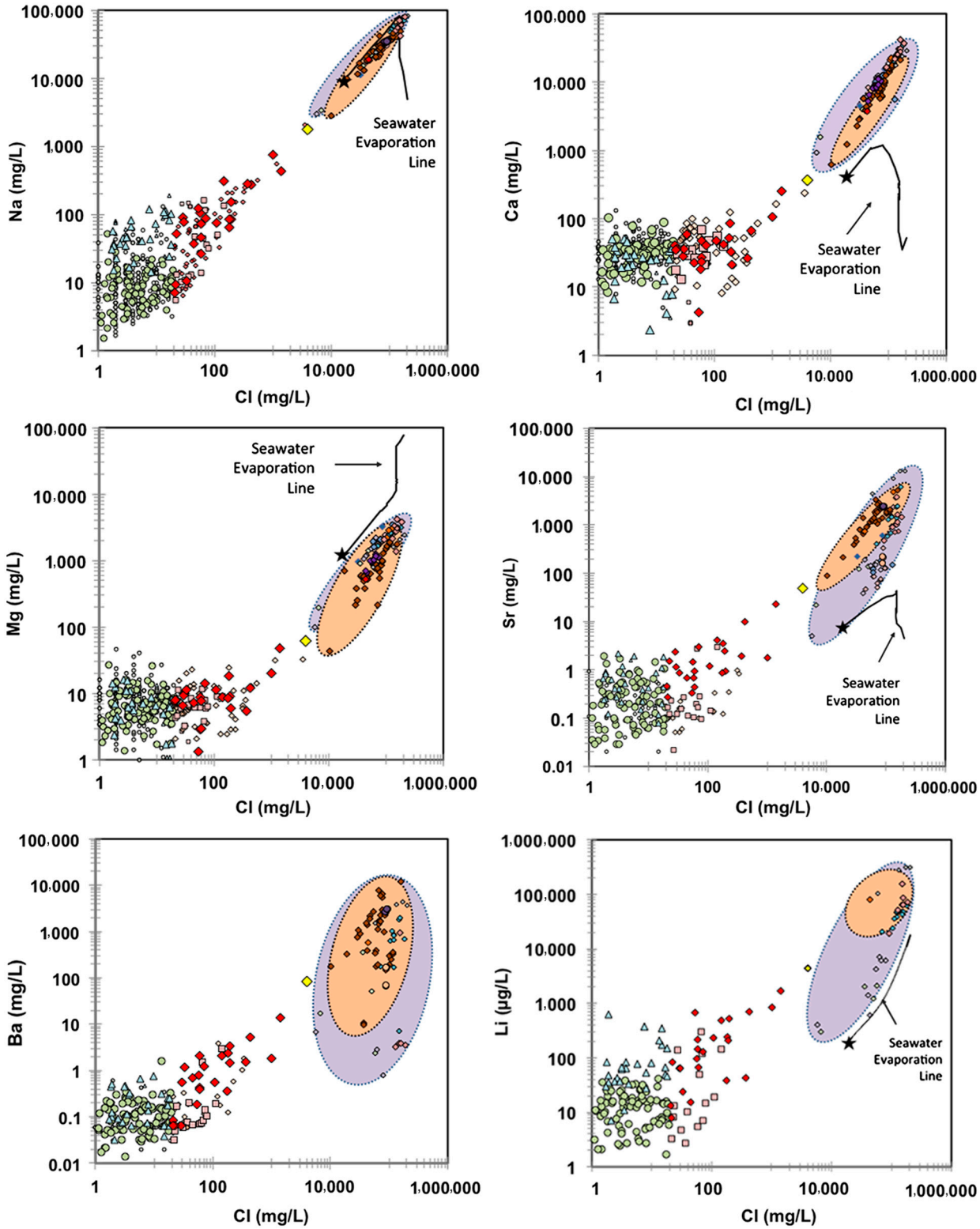

Fig. S3. Na, Ca, Mg, Sr, Ba, and Li versus Cl concentrations (log-log scale) in investigated shallow groundwater in NE PA and deep Appalachian basin brines from this and previous studies (1, 2). The linear relationship between the different elements and the conservative Cl demonstrates that the majority of the higher salinity samples of type D are derived from conservative dilution (mixing) of Appalachian brine in NE PA. Type D regression results (r^2, p-value) between Cl and Ca (0.89, $2.17 \cdot 10^{-12}$), Mg (0.83, $2.4 \cdot 10^{-10}$), Sr (0.92, $4.8 \cdot 10^{-14}$), Na (0.94, $1.33 \cdot 10^{-15}$), Ba (0.92, 3.23×10^{-14}), and Li (0.96, $3.7 \cdot 10^{-17}$). See Fig. 3 legend for symbol description. Seawater evaporation line is adapted from (3).

1 Taylor L (1984) *Groundwater Resources of the Upper Susquehanna River Basin* (Water Resources Report 58, Pennsylvania) (Pennsylvania Department of Environmental Resources-Office of Parks and Forestry—Bureau of Topographic and Geologic Survey) , p 136.
2 Williams J, Taylor L, Low D (1998) *Hydrogeology and Groundwater Quality of the Glaciated Valleys of Bradford, Tioga, and Potter Counties* (Water Resources Report 68, Pennsylvania) (Commonwealth of Pennsylvania Department of Conservation and Natural Resources), p 89.
3 McCaffrey M, Lazar B, Holland H (1987) The evaporation path of seawater and the coprecipitation of Br and K with halite. *J Sediment Petrol* 57:928–937.

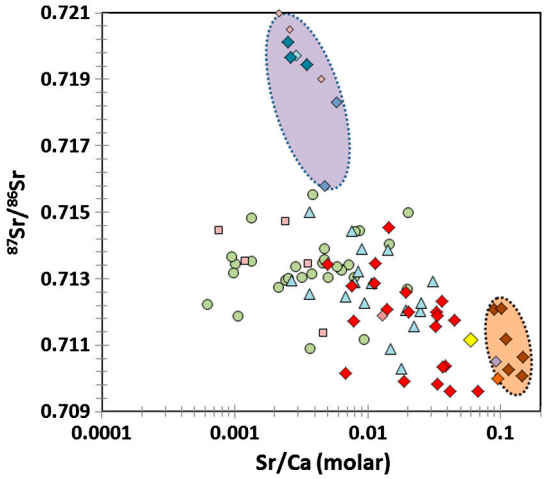

Fig. S4. $^{87}Sr/^{86}Sr$ vs. Sr/Ca ratios in shallow ground water samples in NE PA and Appalachian brines. The distinctive high Sr/Ca and low $^{87}Sr/^{86}Sr$ fingerprints of the Marcellus Formation brine (1) appear to control the Sr/Ca and $^{87}Sr/^{86}Sr$ variations of the saline groundwater of type D. These values are distinct from the compositions of other Appalachian Brines collected from Upper Devonian formations (Venango, Bradford sandstone, and organic-rich shales). See Fig. 3 for symbol description.

1 Chapman EC, et al. (2012) Geochemical and strontium isotope characterization of produced waters from Marcellus Shale natural gas extraction. *Environ Sci Technol* 46:3545–3553.

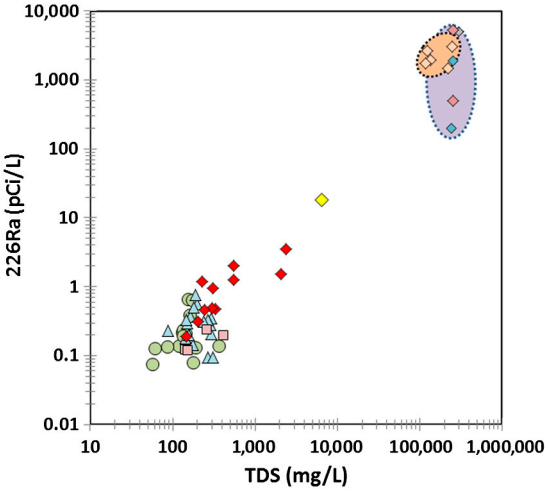

Fig. S5. ^{226}Ra activities (pCi/L) vs. total dissolved salts (TDS) in shallow groundwater and Marcellus brines (1–4) from NE PA. The increase of ^{226}Ra with salinity appears consistent with conservative mixing (Type D: $r^2 = 0.93$, $p = 3.39 \times 10^{-7}$) with Marcellus Formation brine from the study area. The activities of Ra in most of the shallow aquifer samples are rarely above the EPA guideline (5 pCi/L). See Fig. 3 legend for symbol description.

1 Rowan E, Engle M, Kirby C, Kraemer T (2011) Radium content of oil-and gas-field produced waters in the northern Appalachian Basin (USA)—Summary and discussion of data (USGS Scientific Investigations) Report 2011–5135, p 31.
2 Osborn SG, McIntosh JC (2010) Chemical and isotopic tracers of the contribution of microbial gas in Devonian organic-rich shales and reservoir sandstones, northern Appalachian Basin. *Appl Geochem* 25:456–471.
3 Osborn SG, Vengosh A, Warner NR, Jackson RB (2011) Reply to Saba and Orzechowski and Schon: methane contamination of drinking water accompanying gas-well drilling and hydraulic fracturing. *Proc Natl Acad Sci USA* 108:E665–E666.
4 Dresel P, Rose A (2010) Chemistry and origin of oil and gas well brines in western Pennsylvania: Pennsylvania Geological Survey (USGS Open-File General Geology, Pennsylvania Department of Conservation and Natural Resources) Report OFOG 10-01, p 48.

Other Supporting Information Files

Table S1 (PDF)
Table S2 (PDF)
Table S3 (PDF)
Table S4 (PDF)