Environmental Science & Technology

Critical Review

pubs.acs.org/est

A Critical Review of the Risks to Water Resources from Unconventional Shale Gas Development and Hydraulic Fracturing in the United States

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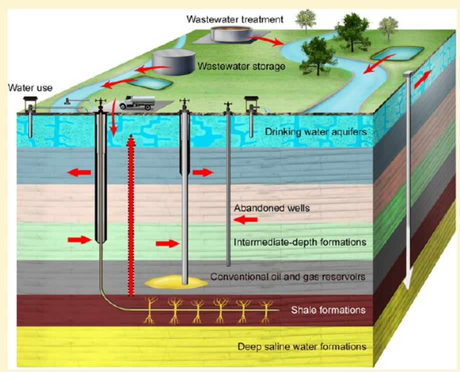
ABSTRACT: The rapid rise of shale gas development through horizontal drilling and high volume hydraulic fracturing has expanded the extraction of hydrocarbon resources in the U.S. The rise of shale gas development has triggered an intense public debate regarding the potential environmental and human health effects from hydraulic fracturing. This paper provides a critical review of the potential risks that shale gas operations pose to water resources, with an emphasis on case studies mostly from the U.S. Four potential risks for water resources are identified: (1) the contamination of shallow aquifers with fugitive hydrocarbon gases (i.e., stray gas contamination), which can also potentially lead to the salinization of shallow groundwater through leaking natural gas wells and subsurface flow; (2) the contamination of surface water and shallow groundwater from spills, leaks, and/or the disposal of inadequately treated shale gas wastewater; (3) the accumulation of toxic and radioactive elements in soil or stream sediments near disposal or spill sites; and (4) the overextraction of water resources for high-volume hydraulic fracturing that could induce water shortages or conflicts with other water users, particularly in water-scarce areas. Analysis of published data (through January 2014) reveals evidence for stray gas contamination, surface water impacts in areas of intensive shale gas development, and the accumulation of radium isotopes in some disposal and spill sites. The direct contamination of shallow groundwater from hydraulic fracturing fluids and deep formation waters by hydraulic fracturing itself, however, remains controversial.



1. INTRODUCTION

Production from unconventiognal natural gas reservoirs has substantially expanded through the advent of horizontal drilling and high-volume hydraulic fracturing (Figure 1). These technological advances have opened vast new energy sources, such as low-permeability organic-rich shale formations and "tight-sand" reservoirs, altering the domestic energy landscape in the United States.[1−3] The total production of natural gas has increased by more than 30% during the past decade. In 2012, unconventional shale gas and tight sand productions were respectively accounting for 34% and 24% of the total natural gas production in the U.S. (0.68 trillion m^3).[4]

The increase in energy production has been broadly distributed across the United States (Figure 2) and densely distributed within specific shale plays (Figure 3). Unconventional hydrocarbon extraction from organic-rich shale formations is now active in more than 15 plays in the U.S. In PA alone, 7234 shale gas wells were drilled into the Marcellus Formation[5] in addition to the 34 376 actively producing conventional oil and gas wells in that state (2012 data; Figure 3).[6] At the end of 2012, the Marcellus Shale (29%), Haynesville Shale (23%), and Barnett Shale (17%) dominated production of natural gas (primarily methane, ethane, and propane) from shales in the U.S., with the remaining 31% of total shale gas production contributed by more than a dozen basins (Figure 1). Oil and hydrocarbon condensates are also targeted in numerous basins, including the Barnett, Eagle Ford, Utica-Point Pleasant, and Bakken. [4]

Future energy forecasts suggest that U.S. unconventional natural gas production from shale formations will double by

Special Issue: Understanding the Risks of Unconventional Shale Gas Development

Received: November 18, 2013
Revised: February 9, 2014
Accepted: February 18, 2014
Published: March 7, 2014

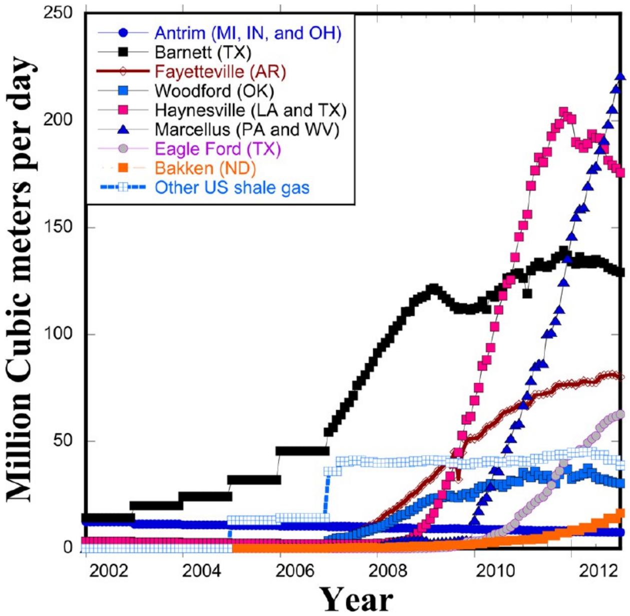


Figure 1. Evolution of the volume of natural gas production from different unconventional shale plays in the U.S. Data from the U.S. Energy Information Administration.[4]

2035 and generate ∼50% of the total domestic natural gas production.[4] Similarly, U.S. domestic oil production from unconventional shale formations is projected to increase by as much as 15% over the next several decades.[7] Unconventional extraction (horizontal drilling and high volume hydraulic fracturing) for shale gas has already expanded to Canada[8] and will soon be launched on a global scale, with significant reservoirs in South America, northern and southern Africa, Europe, China,[9,10] and Australia.[11,12] The current global estimate of natural gas reserves in unconventional shale is approximately 716 trillion m^3 (2.53×10^{13} Mcf).[11,12]

Despite the large resource potentials and economic benefits, the rapid expansion of shale gas development in the U.S. has triggered an intense public debate over the possible environmental and human health implications of the unconventional energy development. Some primary concerns include air pollution, greenhouse gas emissions, radiation, and groundwater and surface water contamination.[1,3,13−36] These concerns have been heightened because the 2005 Energy Policy Act exempts hydraulic fracturing operations from the Safe Drinking Water Act (SDWA). The only exception to the exemption is the injection of diesel fuel. Additionally, because environmental oversight for most oil and gas operations is conducted by state rather federal agencies, the regulation, monitoring, and enforcement of various environmental contamination issues

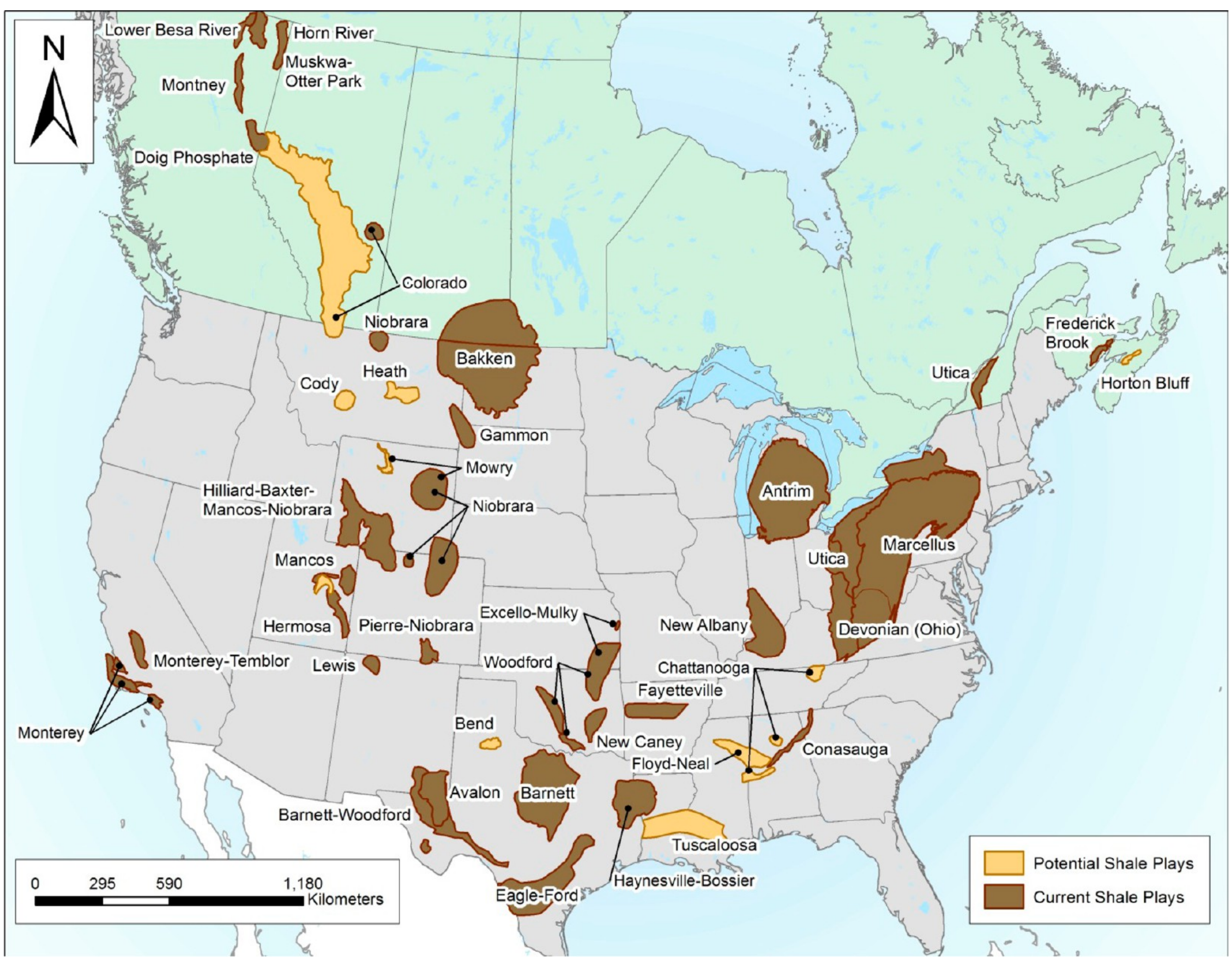


Figure 2. Map of unconventional shale plays in the U.S. and Canada, based on data from the U.S. Energy Information Administration.[4]

dx.doi.org/10.1021/es405118y | *Environ. Sci. Technol.* 2014, 48, 8334−8348

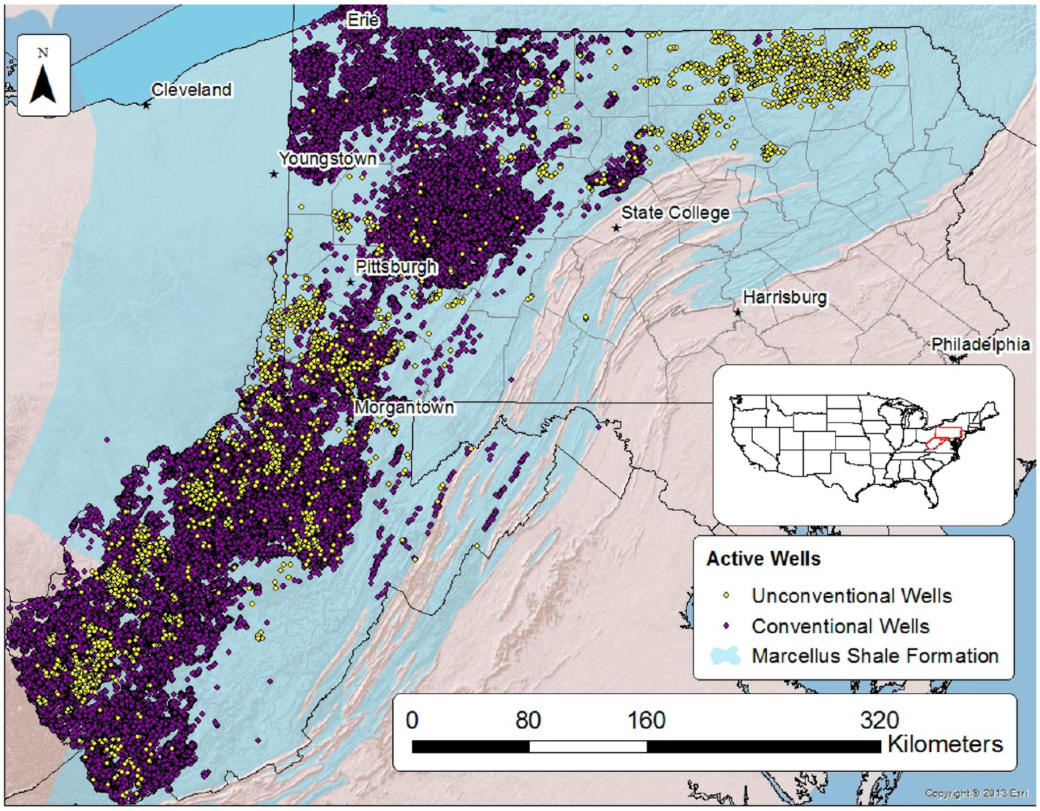


Figure 3. Map of active unconventional (yellow) and conventional (purple) oil and gas wells in Pennsylvania and West Virginia. Note areas of coexisting conventional and unconventional development (e.g., southwestern PA and WV) relative to areas of exclusively unconventional development (e.g., northeastern PA). Well locations were obtained from the West Virginia Geological Survey (http://www.wvgs.wvnet.edu/) and the Pennsylvania Department of Environmental Protection's oil and gas reporting Web site (https://www.paoilandgasreporting.state.pa.us/publicreports/Modules/Welcome/Welcome.aspx). The background topographic map, Marcellus Formation outline, and state boundaries were downloaded from http://www.pasda.psu.edu/ and the Carnegie Museum of Natural History.[148]

related to unconventional shale gas development are highly variable throughout the U.S.[37−39]

This paper provides an overview and synopsis of recent investigations (updated to January 2014) into one set of possible environmental impacts from unconventional shale gas development: the potential risks to water resources. We identify four potential modes of water resource degradation that are illustrated schematically in Figure 4 and include (1) shallow aquifers contaminated by fugitive natural gas (i.e., stray gas contamination) from leaking shale gas and conventional oil and gas wells, potentially followed by water contamination from hydraulic fracturing fluids and/or formation waters from the deep formations; (2) surface water contamination from spills, leaks, and the disposal of inadequately treated wastewater or hydraulic fracturing fluids; (3) accumulation of toxic and radioactive elements in soil and the sediments of rivers and lakes exposed to wastewater or fluids used in hydraulic fracturing; and (4) the overuse of water resources, which can compete with other water uses such as agriculture in water-limited environments.

2. GROUNDWATER CONTAMINATION

2.1. Stray Gas Contamination. Elevated levels of methane and other aliphatic hydrocarbons such as ethane and propane in shallow drinking water wells pose a potential flammability or explosion hazard to homes with private domestic wells. The saturation level of methane in near-surface groundwater is about ∼28 mg/L (∼40 cc/L) and thus the U.S. Department of the Interior recommends monitoring if water contains more than 10 mg/L (∼14 cc/L) of methane and immediate action if concentrations rise above 28 mg/L. Several states have defined a lower threshold (e.g., 7 mg/L in PA), from which household utilization of methane-rich groundwater is not recommended.

Stray gas migration in shallow aquifers can potentially occur by the release of gas-phase hydrocarbons through leaking casings or along the well annulus, from abandoned oil and gas wells, or potentially along existing or incipient faults or fractures[40] with target or adjacent stratigraphic formations following hydraulic fracturing and drilling (Figure 4).[27] The latter mechanism poses a long-term risk to shallow groundwater aquifers. Microseismic data suggest that the deformation and fractures developed following hydraulic fracturing typically extend less than 600 m above well perforations, suggesting that fracture propagation is insufficient to reach drinking-water aquifers in most situations.[41] This assertion is supported by noble gas data from northeastern PA,[42] yet stray gas migration through fractures and faults is considered a potential mechanism for groundwater contamination.[40]

Across the northeastern Appalachian Basin in PA, the majority of shallow groundwater had detectable, naturally occurring methane with thermogenic stable-isotope fingerprints (e.g., $\delta^{13}C-CH_4$ and $\delta^{2}H-CH_4$).[27−29,42,43] These findings imply that the high methane in shallow aquifers from this region is predominantly thermogenic in origin.[28,29,42,43] In northeastern PA, however, a subset of shallow drinking water wells consistently showed elevated methane, ethane, and

dx.doi.org/10.1021/es405118y | Environ. Sci. Technol. 2014, 48, 8334−8348

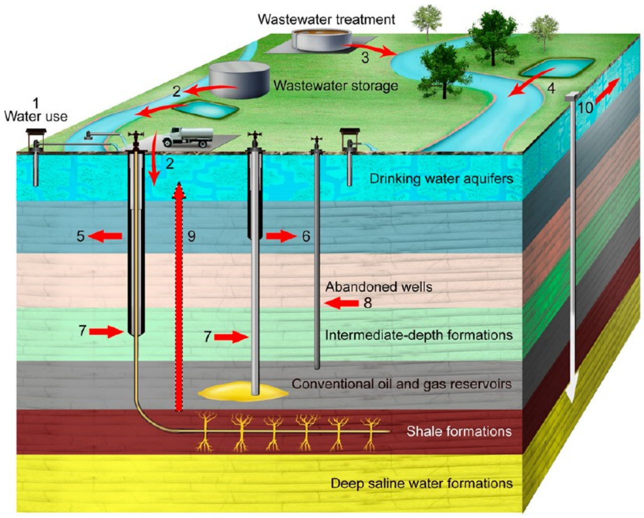


Figure 4. Schematic illustration (not to scale) of possible modes of water impacts associated with shale gas development reviewed in this paper: (1) overuse of water that could lead to depletion and water-quality degradation particularly in water-scarce areas; (2) surface water and shallow groundwater contamination from spills and leaks of wastewater storage and open pits near drilling; (3) disposal of inadequately treated wastewater to local streams and accumulation of contaminant residues in disposal sites; (4) leaks of storage ponds that are used for deep-well injection; (5) shallow aquifer contamination by stray gas that originated from the target shale gas formation through leaking well casing. The stray gas contamination can potentially be followed by salt and chemical contamination from hydraulic fracturing fluids and/or formational waters; (6) shallow aquifer contamination by stray gas through leaking of conventional oil and gas wells casing; (7) shallow aquifer contamination by stray gas that originated from intermediate geological formations through annulus leaking of either shale gas or conventional oil and gas wells; (8) shallow aquifer contamination through abandoned oil and gas wells; (9) flow of gas and saline water directly from deep formation waters to shallow aquifers; and (10) shallow aquifer contamination through leaking of injection wells.

propane concentrations (i.e., relatively low hydrocarbon ratios (C_1/C_2)) and relatively enriched thermogenic carbon isotope fingerprints in groundwater exclusively <1 km from shale gas drilling sites. A subset of samples with evidence for stray gas contamination display isotopic reversals ($\Delta^{13}C = \delta^{13}CH_4-\delta^{13}C_2H_6 > 0$) and proportions of methane, ethane and propane that were consistent with Marcellus production gases from the region, while some other wells had natural gas compositions consistent with production gases in conventional wells from the overlying Upper Devonian formations.[27,29] New evaluations of the helium content[29] and noble gas geochemistry[42] in these samples further supports a distinction between naturally occurring "background" hydrocarbon gases and groundwater with stray gas contamination in wells located near (<1 km) shale gas drilling sites. "Background" gases typically had lower proportions of ethane and propane and elevated helium concentrations that reflect the history of natural gas migration from the Marcellus source rock to the Upper Devonian reservoir rocks throughout geological time.[29,42] Thus, the combination of gas geochemical fingerprinting suggests that stray gas groundwater contamination, where it occurs, is sourced from the target shale formations (i.e., the Marcellus Formation) in some cases, and from intermediate layers (e.g., Upper Devonian Formations) in others.

In cases where the composition of stray gas is consistent with the target shale formation, it is likely that the occurrence of fugitive gas in shallow aquifers is caused by leaky, failing, or improperly installed casings in the natural gas wells. In other cases, hydrocarbon and noble gas data also indicated that fugitive gas from intermediate formations apparently flowed up through the outside of the well annulus and then leaked into the overlying shallow aquifers.[27,29,42] In these cases, the isotopic signatures and hydrocarbon ratios matched the gases in intermediate formations rather than Marcellus shale production gases. In sum, the combined evidence of hydrocarbon stable isotopes, molecular hydrocarbon ratios, and helium geochemistry indicate that stray gas contamination occurs in a subset of wells <1km from drilling in northeastern PA.

In contrast to these reports, other investigators[22,43,44] have suggested that higher methane concentrations in shallow groundwater were natural and could be explained by topographic factors associated with groundwater discharge zones. Geochemical data do suggest that some natural gas migrated to shallow aquifers in northeastern PA through geologic time. However, these characteristics occur in areas with higher hydraulic connectivity between the deep and shallow formations.[34,42] A recent analysis showed that topography was indeed a statistically significant factor in some cases but did not explain the variations in methane and ethane concentrations with respect to distance to gas wells.[29]

Additional evidence for stray gas contamination because of poor well construction is provided by the isotopic composition of surface casing vent flow (SCV). Integrating the $\delta^{13}C$ data of methane (C1), ethane (C2), and propane (C3)[45−47] showed that stray gas contamination associated with conventional oil wells in Alberta, Canada reflected methane sourced from intermediate formations leaking into shallow aquifers and not from the production formations such as the Lower Cretaceous Mannville Group.[48] Jackson et al. (2013)[49] listed several other case studies that demonstrate evidence for stray gas contamination. While such studies have shown evidence for methane, ethane, and propane contamination associated with conventional oil production[48,50] and coal bed methane,[45] Muehlenbachs (2013)[51] also showed direct evidence for SCV leakage from intermediate zones in newly completed and hydraulically stimulated horizontal shale gas wells in the Montney and Horn River areas of northeastern British Columbia, Canada.[51] Methane leaking from the annulus of conventional oil and gas wells was also demonstrated in PA.[52,53] Combined, these studies suggest that stray gas contamination can result from either natural gas leaking up through the well annulus, typically from shallower (intermediate) formations, or through poorly constructed or failing well casings from the shale target formations.

The migration of natural gas to the surface through the production casing and/or well annulus is "a common occurrence in the petroleum industry"[51] and can affect a large fraction of conventional wells. Among the 15 000 production oil wells tested from the Gulf of Mexico, 43% have reported cement damage after setting that leads to sustained casing pressure (SCP). These effects increased with time; whereas 30% reported damage during the first 5 years after drilling, the percentage increased to 50% after 20 years.[54] Likewise, the BP Deepwater Horizon oil spill was partly attributed to the fact that "cement at the well bottom had failed to seal off hydrocarbons".[55] In PA the overall reports of cementing, casing, and well construction violations total 3% of all shale gas wells.[22] However a closer look at the distribution of violations shows large variations in percentage with time (before and after 2009), space, and type of wells.[5,56] In particular, the percentage of well violations was much higher in northeastern and central counties in PA (10−50%).[5] Consequently, reports of stray gas contamination in areas of unconventional shale gas development in the northeastern Appalachian Basin (U.S.) and Montney and Horn River Basins (Canada) may be associated with leaking of oil and gas wells.

In contrast to the results from the Marcellus, Montney, and Horn River Basins, the Fayetteville Shale in north-central Arkansas showed no evidence of methane contamination in groundwater. Studies in this area showed low methane concentrations with a mostly biogenic isotopic fingerprint.[36,57] The authors hypothesized the potential for stray gas contamination likely depends on both well integrity and local geology, including the extent of local fracture systems that provide flow paths for potential gas migration.[36]

In addition to groundwater, surface waters could serve as an indicator of regional migration from unconventional shale gas development. To date, streams in areas of shale gas drilling have not shown systematic evidence of methane contamination. A new methodology for stream-gas sampling as a reconnaissance tool for evaluating natural and anthropogenic methane leakage from natural gas reservoirs into surface waters was recently demonstrated using inorganic and gas geochemical tracers and could be applied more widely in areas of oil and gas development.[59]

2.2. Groundwater Contamination with Salts or Other Dissolved Constituents. The presence of fugitive gas in shallow drinking water wells could potentially lead to salinization and other changes of water quality in three possible ways. First, the leaking of natural gas can be associated with the flow of hydraulic fracturing fluids and saline formation waters to overlying shallow aquifers. Given the buoyancy of gas, the flow rate of denser saline water would be substantially slower than the flow of natural gas, and would depend on both the pressure gradients and hydraulic connectivity between the overpressurized annulus or leaking sites on the wells and the overlying aquifers.[53]

An EPA study[60] near the town of Pavillion, Wyoming found water contamination in two shallow monitoring wells. Although this initial study was questioned for adequate sampling protocols,[22] a follow up study by the U.S. Geological Survey confirmed elevated levels of specific conductance (1500 mS/cm), pH (10−11), methane (25−27 mg/L), ethane, and propane.[61] However, the mechanisms that caused the apparent contamination of the shallow groundwater in this area are still under investigation (i.e., contamination from surface ponds or subsurface leaking cement from shale gas wells).

The ability to trace and identify contamination from shale gas exploration is limited because of the relatively short time frame since the beginning of large-scale shale gas exploration in early-2000s compared to typical groundwater flow rates (i.e., decades). However, an evaluation of water contamination associated with conventional oil and gas exploration provides a much longer time frame for evaluating possible groundwater contamination. Possible evidence of long-term (2000−2007) increases in the salinity of groundwater associated with conventional oil and gas drilling was reported from Garfield County, CO. There, a rise of chloride concentrations in drinking water wells was associated with an increase of methane with a thermogenic isotopic fingerprint, both of which were associated with an increase in the number of conventional oil and gas wells.[62] The fraction of drinking water wells that had chloride concentrations >250 mg/L (EPA threshold for drinking water) in groundwater from Garfield County doubled between 2002 (4%) and 2005 (8%), with chloride up to 3000 mg/L in drinking water wells.[62] The parallel rise in salinity and methane with a thermogenic isotope signature in Garfield County could reflect either migration from leaking oil and gas wells or contamination from unlined surface impoundments.[62] Overall, the geochemical composition of the salinized groundwater in such scenarios would mimic the composition of either the formation water in the production formations[34] or the fluids in the shallower or intermediate units (that typically have a different water chemistry). While there might be evidence for water contamination in some areas of conventional oil and gas exploration, groundwater sites in areas affected by stray gas contamination near shale gas sites in northeastern PA have not to our knowledge shown signs of salinization induced directly by leaking natural gas wells.[27,29,34] Unlike other areas in PA, northeastern PA was developed recently and almost exclusively for shale gas (Figure 3), with few legacy wells reported in the area. Thus, any water contamination in this area attributable to natural gas extraction would be related to current shale gas operations rather than to older legacy wells. Therefore conclusions regarding contamination from saline water and hydraulic fracturing fluids flow are restricted in both space and time and further studies are needed to address this question.

A second mode of groundwater contamination that could evolve from stray gas contamination is oxidation of fugitive methane via bacterial sulfate reduction.[50] Evidence for dissimilatory bacterial sulfate reduction of fugitive methane near conventional oil wells in Alberta, Canada, includes sulfide generation and ^{13}C-depleted bicarbonate, with lower residual sulfate concentrations relative to the regional groundwater.[50] Bacterial sulfate reduction reactions due to the presence of fugitive methane could trigger other processes such as reductive dissolution of oxides in the aquifer that would mobilize redox-sensitive elements such as manganese, iron, and arsenic from the aquifer matrix and further reduce groundwater quality. Low levels of arsenic and other contaminants, recorded in some drinking water aquifers in TX, were suggested to be linked to contamination from the underlying Barnett Shale,[63] although evidence for a direct link to the Barnett remains uncertain.

A third hypothetical mode of shallow groundwater contamination associated with the presence of stray gas contamination is the formation of toxic trihalomethanes (THMs), typically co-occurring with high concentrations of halogens in the saline waters. THMs are compounds with halogen atoms (e.g., Cl, Br, or I) substituted for hydrogens in the methane molecule. The formation of THMs were previously recorded in untreated groundwater in the U.S., unrelated to shale gas activities, but associated with agricultural contamination of shallow aquifers.[64,65] Numerous studies have demonstrated that the presence of halogens together with organic matter in source waters can trigger the formation of THMs, specifically in chlorinated drinking water (see references in Section 2.1). However, no data has to our knowledge been reported for the presence of THMs in groundwater associated with stray gas contamination from shale gas wells.

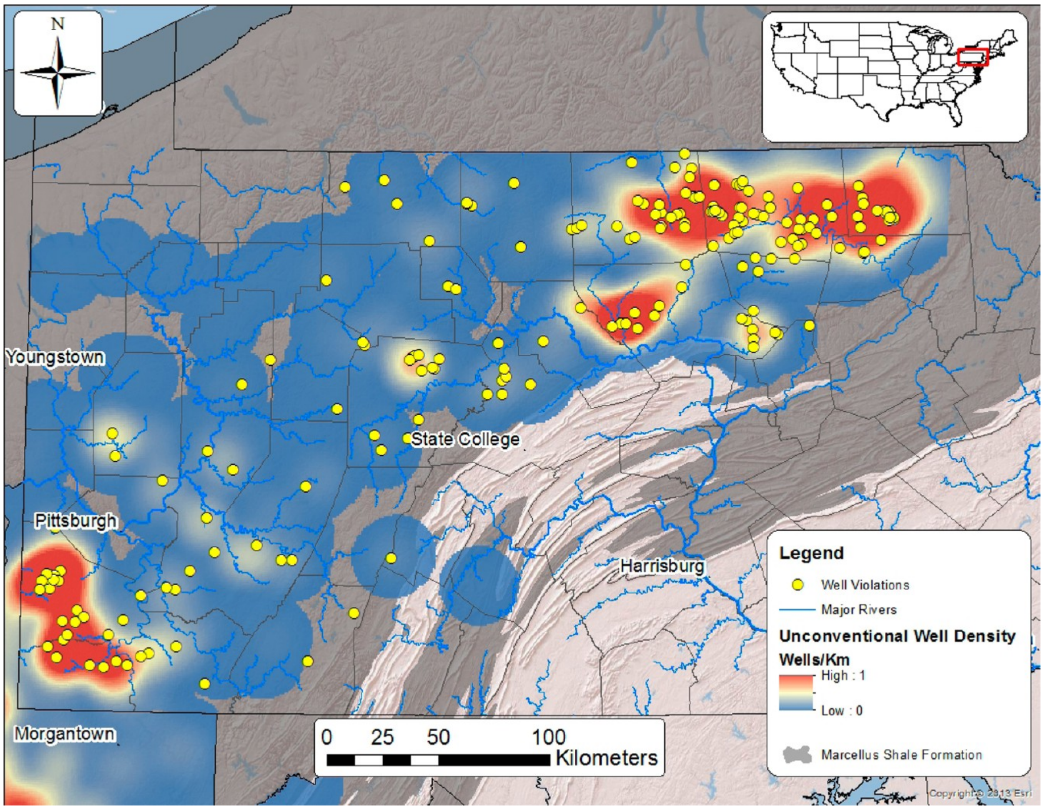


Figure 5. Map of Pennsylvania with density of unconventional well drilling and occurrence of reported environmental violations. Warm colors (red) represent areas of higher density of unconventional well drilling while cooler colors (blue) are areas of lower drilling density. Unconventional wells with reported violations of a release to the environment are shown by yellow dots. Violations include discharge of industrial waste to streams, drill cuttings, oil, brine and/or silt, discharged without a permit, and polluting substances discharged to waterways. Data on violations was obtained from http://www.fractracker.org/downloads/. Unconventional well density was derived from unconventional well data points obtained from the Pennsylvania Department of Environmental Protection's oil and gas reporting Web site (https://www.paoilandgasreporting.state.pa.us/publicreports/Modules/Welcome/Welcome.aspx). Background maps, the Marcellus Formation, and state boundaries were downloaded from http://www.pasda.psu.edu/ and the Carnegie Museum of Natural History[148]

In addition to the effects of poor oil and gas-well integrity, shallow aquifers could potentially be contaminated by the migration of deep hypersaline water or hydraulic fracturing fluids through conductive faults or fractures.[15,34] The potential upward flow of fluids from the impermeable shale formations is highly debated; one model has suggested that the advective preferential flow through fractures could allow the transport of contaminants from the fractured shale to overlying aquifers in a relatively short time of six years or less.[15] Other studies have disputed this model,[66−68] suggesting that the upward flow rate of brines would typically be fairly low because of the low permeability of rocks overlying the shale formations, low upward hydraulic gradients, and the high density of fluids.[41,69,70] The hydraulic conductivity along a fault zone seems to have an important effect on the potential for upward migration of hydraulic fracturing fluid or underlying brines.[40]

Evidence for cross-formational fluid flow of deep saline groundwater into overlying shallow aquifers, independent of oil and gas operations, was demonstrated in the Devonian oil-bearing formations in southwestern Ontario, Canada,[71] east-central Michigan Basin,[72] Ogallala Aquifer, Southern High Plains, Texas,[73,74] and shallow aquifers overlying the Marcellus Shale in northeastern PA.[34] The latter case appears to be an example of a naturally occurring process in which deep-seated Middle Devonian Marcellus-like saline waters (deterimined by Br/Cl and $^{87}Sr/^{86}Sr$ ratios) migrated upward to shallow Upper Devonian aquifers in northeastern PA. In this area of PA, which had little oil and gas drilling prior to recent shale gas development (Figure 3), the presence of elevated salts was recorded in a subset of domestic wells during the 1980s.[34] These findings indicate that the salinization phenomenon is not related to recent unconventional drilling in shales.[34] The presence of naturally occurring saline groundwater in areas of shale gas development in the Appalachian Basin poses challenges for quantifying contamination from active shale gas development, including the ability to distinguish naturally occurring groundwater salinization from anthropogenic sources of groundwater pollution.

3. SURFACE WATER CONTAMINATION

Few studies have analyzed the major chemical constituents in injected hydraulic fracturing fluids (although considerable information is available on the Web site www.fracfocus.org). Based on the available information, hydraulic fracturing fluids include water (either fresh water or reused hydraulic fracturing water), proppants (sand, metabasalt, or synthetic chemicals added to "prop" incipient fractures open), acids (e.g., hydrochloric acid), additives to adjust fracturing fluid viscosity (guar gum, borate compounds), viscosity reducers (ammonium persulfate), corrosion inhibitors (isopropanol, acetaldehyde), iron precipitation control (citric acid), biocides (glutaralde-hyde), oxygen scavengers (ammonium bisulfite), scale inhibitors (e.g., acrylic and carboxylic polymers), and friction reducers (surfactants, ethylene glycol, polyacrylamide).[22,49,75−77] Based on different hazardous components of hydraulic fracturing fluid additives used in wells from the Marcellus Shale, it was suggested that sodium hydroxide, 4,4-dimethyl, oxazolidine, and hydrochloric acid would be good indicators to monitor water contamination upon a leak or a spill of hydraulic fracturing fluids.[78]

More information is available on the inorganic chemistry of the "flowback" fluids (fluids that return to the surface after the hydraulic fracturing process is complete) and produced waters (fluids that are extracted together with the natural gas during production). Flowback water is a mixture of the injected hydraulic fracturing fluids and the natural fluids within the formation (e.g., brine). In some cases the injected fluid contains recycled flowback water from one or more different drill sites. About 10−40% of the volume of the injected fracturing fluids returns to the surface after hydraulic fracturing, and the flow rates of flowback water slow with time to levels of 2−8 m^3/day during the production stage of a shale gas well.[75] The typical salinity of flowback water increases with time after hydraulic fracturing due to an increasing proportion of the formation water mixing with injection fluids.[79] Produced waters are typically composed of naturally occurring hypersaline formation water, and can also contain oil, bitumen, and hydrocarbon condensates with high concentrations of total dissolved organic carbon (up to 5500 mg/L), in addition to the added organic chemicals that were reported in flowback waters (e.g., solvents, biocides, scale inhibitors).[34,35,49,75,79,80−86] In most flowback and produced waters, the concentrations of toxic elements such as barium, strontium, and radioactive radium are positively correlated with the salinity.[34,49,79,81,82] Some flowback and produced waters, such as those found in the Marcellus shale, are also enriched in arsenic and selenium[87] that are associated with the high metal contents in shale rock.[88] The correlation of toxic and radioactive elements with salinity suggests that many of the potential water quality issues associated with wastewaters from unconventional shale gas development may be attributable to the geochemistry of the brines within the shale formations. The total dissolved salts (TDS) content of produced water ranges from below seawater (25 000 mg/L) to 7 times more saline than seawater, depending on the shale formation. For example, the Fayetteville (25 000 mg/L), Barnett (60 000 mg/L), Woodford (110 000−120 000 mg/L), Haynesville (110 000−120 000 mg/L), and Marcellus (up to 180 000 mg/L) shale formations vary by nearly an order of magnitude in TDS values.[83] The salinity, strontium, and barium contents vary geographically within formations as shown for the Marcellus shale.[79,82] The volume and the salinity of flowback waters also vary spatially among shale gas wells. [75]

In some cases the flowback and produced waters are stored in ponds near the drilling sites. The salinity variations of the wastewater generate chemical stratification within the ponds that is also associated with anoxic conditions of the bottom waters in the ponds.[89,90] The high salinity and temperature of the flowback water and the anoxic conditions control the microbial community in these storage ponds by increasing the proportion of halotolerant and anaerobic bacteria species.[76,77,89−91]

Given that produced waters have much higher salinities than surface waters (typically TDS ≪ 1000 mg/L), even small inputs can impact freshwater quality. We consider three potential modes of impacts on surface water: (1) surface leaks and spills of flowback and produced water associated with shale gas operations (e.g., overflow or breaching of surface pits, insufficient pit lining, onsite spills); (2) direct, unauthorized, or illegal disposal of untreated wastewater from shale gas operations; and (3) inadequate treatment and discharge of shale gas wastewater (e.g., treatment at plants not sufficiently designed to remove halogens, radionuclides, or heavy metals).

The first mode of impact from spills and leakage typically occurs near drilling locations. Figure 5 presents the locations of sites where violations related to spills and leaks associated with shale gas operations have been reported in PA (data on violations was obtained from http://www.fractracker.org/downloads/). The occurrence and frequency of the spills and leaks appear to coincide with the density of shale gas drilling,[92] as demonstrated by the co-occurrence of Marcellus unconventional well density in northeastern and western PA (Figure 5). An analysis shows that the number of reported violations increases in areas closer to higher (>0.5 well per km^2) shale gas drilling density, and the frequency of violations per shale gas well doubles in areas of higher drilling density (Supporting Information Figure S1). One of the unique features of the unconventional energy production of low permeable shale and tight sand formations is the rapid decrease of the natural gas production, up to 85% during the first three years of operation.[93,94] In order to overcome this decline in production, unconventional wells are drilled at high rates, and over 20 000 wells have been constructed since the mid 2000s through the U.S. The rapid growth and intensity of unconventional drilling could lead to a higher probability of surface spills or leaks and potential stray gas contamination of adjacent drinking water wells.

Spills or leaks of hydraulic fracturing and flowback fluids can pollute soil, surface water, and shallow groundwater with organics, salts, metals, and other constituents. A survey of surface spills from storage and production facilities at active well sites in Weld County, Colorado that produces both methane gas and crude oil, showed elevated levels of benzene, toluene, ethylbenzene, and xylene (BTEX) components in affected groundwater. Following remediation of the spills, a significant reduction (84%) was observed in BTEX levels in the affected wells.[95] As mentioned earlier, an EPA study[60] in Pavillion, Wyoming found increased concentrations of benzene, xylenes, gasoline range organics, diesel range organics, hydrocarbons, and high pH in two shallow monitoring wells.[60] The U.S. Geological Survey conducted a follow up study and found similar elevated levels of specific conductance (1500 mS/cm), pH (10−11), methane (25−27 mg/L), ethane and propane, yet low levels of organic compounds.[61] The shallow groundwater contamination was linked in part to surface pits used for the storage/disposal of drilling wastes and produced and flowback waters.[60] Similarly, leaks, spills, and releases of hypersaline flowback and produced waters are expected to impact the inorganic quality of surface water because these brines contain highly elevated concentrations of salts (Cl, Br), alkaline earth elements (e.g., Ba, Sr), metalloids (e.g., Se, As), and radionuclides (e.g., Ra).

A second mode of contamination would be disposal of untreated wastewater from shale gas operations. A joint U.S. Geological Survey and U.S. Fish and Wildlife Service study showed that the unauthorized disposal of hydraulic fracturing fluids to Acorn Fork Creek in southeastern Kentucky in May and June 2007 likely caused the widespread death or distress of aquatic species.[96] Likewise, an experimental release of hydraulic fracturing fluids in a forest in WV has shown severe damage and mortality to ground vegetation over a very short time (10 days). Over a longer time (two years), about half of the trees were dead and sodium and chloride increased by 50 fold in the soil.[97]

A third mode of surface water contamination can occur through improper handling and disposal of hydraulic fracturing fluids and associated wastewater. These types of environmental releases may occur through the disposal of inadequately treated wastewater. In the U.S., wastewater from unconventional energy production is managed in various ways; wastewater is sometimes recycled for subsequent hydraulic fracturing operations, injected into deep injection wells, or treated. The treatment options include publicly owned treatment works (POTWs), municipal wastewater treatment plants (WWTP), or commercially operated industrial wastewater treatment plants. In addition to these wastewater management techniques, some states allow operators to spread the fluids onto roads for dust suppression or deicing.[23,35,39,98−102]

The disposal of inadequately treated wastewater from shale gas operations may contaminate surface waters at the disposal sites.[23,35,99] Effluent discharge from treatment sites in PA were characterized by high levels of salinity (TDS up to 120 000 mg/L), toxic metals (e.g., strontium, barium), radioactive elements (radium isotopes), and organic constituents such as benzene and toluene.[23] For example, chlorine concentrations were elevated 6000-fold above stream background levels at the point of wastewater effluent discharge into surface water at a treatment facility, while bromide was enriched by up to 12 000-fold.[35] In spite of significant dilution, bromide levels in downstream streamwater (∼2 km) were still elevated (16-fold) above background stream levels.[35]

Such bromide enrichment in waterways has important implications for downstream municipal water treatment plants, given the potential formation of carcinogenic THMs in chlorinated drinking water.[103−111] As the volume of wastewater treatment from unconventional energy development has expanded, bromide concentrations downstream from wastewater disposal sites along the Monongahela River in PA,[112] and THM concentrations, especially of brominated species, increased in municipal drinking water in Pittsburgh, PA.[113] Both sources of contamination were linked directly to the disposal and ineffective removal of bromide from wastewater from shale gas development.[112−114] In spite of a 2011 ban on the disposal of shale gas wastewater to streams in PA, evidence for the Marcellus wastewater disposal based on isotopic ratios[35] and elevated Br levels collected from the Clarion River after May 2011 was suggested[113] to reflect either illegal dumping or incomplete implementation of the ban where a portion of unconventional wastewater is still being transferred to brine treatment facilities. [113]

In several disposal sites examined in PA, the wastewater effluent had Marcellus-like geochemical fingerprints such as high TDS, low SO_4/Cl ratio[99] and distinctive Br/Cl, $^{228}Ra/^{226}Ra$, and $^{87}Sr/^{86}Sr$ ratios.[35] These geochemical parameters suggest that at least some of the stream contamination in western Pennsylvania was related to wastewater disposal from shale gas operations, in addition to the legacy disposal of wastewater from conventional oil and gas activities on longer (decades) time scales. The potential formation of THMs in bromide-rich water is not restricted to shale gas operations, and could also result from disposal of wastewaters from conventional oil and gas or coalbed methane operations. Overall, more data is needed to evaluate the impact of wastewater management in the Marcellus and other unconventional shale gas basins, especially in areas where surface water discharge for dust and ice control is still common.

The increasing volume and the potential environmental impacts associated with wastewater treatment have increased the demand for deep well injection sites, catalyzed the development of new suitable treatment processes, and led to the reuse and recycling of a larger fraction of the wastewater. In many states (e.g., Texas), deep injection is the most commonly applied wastewater management practice, although reuse and recycling is becoming increasingly common during the last several years.[102] However, each of these wastewater management methods has environmental risks. For example, the injection of high volumes of wastewater into deep disposal wells may induce seismicity and earthquakes,[115−122,123] and groundwater near injection wells may become contaminated by cement failure or issues of injection well integrity.[124] In addition, many of the injection wells are associated with storage ponds that could also pose environmental risks upon leakage from improper lining and management.

4. THE ENVIRONMENTAL LEGACY OF CHEMICAL RESIDUES IN AREAS OF DISPOSAL AND LEAKS

Over time, metals, salts, and organics may build up in sediments, scales, and soil near wastewater disposal and/or spill sites. Each respective compound has a fixed solubility and reactivity (e.g., adsorption), the latter commonly described by the distribution coefficient (K_d) that varies as a function of pH, Eh, temperature, and the occurrence of other components in the water. As a result, the physicochemical conditions of surface waters and the distribution coefficients of each compound will determine how it interacts with particulate matter (e.g., colloidal particles) or river sediments. Ultimately, these properties will determine the long-term environmental fate of such reactive contaminants; reactive constituents would be adsorbed onto soil, stream, or pond sediments and potentially pose long-term environmental and health risks.

Marcellus wastewaters contain elevated levels of naturally occurring radionuclides (NORM) in the form of radium isotopes.[34,35,81,85] The elevated radium levels in Marcellus brines is due to the mobilization of radium from uranium-rich source rocks into the liquid phase under high salinity and reducing conditions.[85] Disposal of the NORM-rich Marcellus waste fluids to freshwater streams or ponds would cause radium adsorption onto the stream sediments in disposal and/or spill sites because radium adsorption is inversely correlated with salinity.[125−128] Disposal of treated wastewater originating from both conventional and unconventional oil and gas production in western Pennsylvania has caused radium accumulation on stream sediments downstream of a disposal site from a brine treatment facility.[35] The radium accumulated in the stream sediments had $^{228}Ra/^{226}Ra$ ratios identical to those of the Marcellus brines, thus linking this accumulation directly to the disposal of unconventional shale gas wastewater. The level of radioactivity found in sediments at one brine-treatment discharge site exceeded the management regulations in the U.S. for a licensed radioactive waste disposal facility.[35] Elevated NORM levels were also found in soils near roads associated with road spreading of conventional oil and gas brines for deicing[129] and on pond bottom sediments associated with a spill from hydraulic fracturing activities.[58] High NORM levels were recorded also in soil and sludge from reserve pits used in unconventional natural gas mining.[130] In addition to the high γ

Table 1. Water Use and Wastewater Production Per Shale Gas Well in Different Shale Gas Basins in the U.S. Based on Previous Reports and on Data Compiled in This Study[a]

basin	water use per well (m^3)	wastewater per well (m^3)	source
Horn River Basin (British Columbia, Canada)	50 000		Johnson and Johnson (2012)[136]
Marcellus Shale, PA (<2010)	7700−38 000		Kargbo et al. (2010)[1]
Marcellus Shale, PA (2008−2011)	11 500−19 000	5200	Lutz et al. (2013) [101]
Marcellus Shale, PA (2012)		3500	this study
Woodford Shale, OK	16 000		Murray (2013)[135]
Barnett Shale, TX	10 600		Nicot and Scanlon (2012)[134]
Haynesville Shale, TX	21 500		Nicot and Scanlon (2012)[134]
Eagle Ford, TX	16 100		Nicot and Scanlon (2012)[134]
Niobrara, CO (2012)	13 000	4000	this study

[a]Calculations for water use and wastewater volume per well for Marcellus Shale in PA were made for 2012 data retrieved from PA Department of Environmental Protection's oil and gas reporting website (https://www.paoilandgasreporting.state.pa.us/publicreports/Modules/Welcome/Welcome.aspx) and for the Niobrara Shale in CO were taken from the Colorado Oil and Gas Conservation Commission (http://cogcc.state.co.us/).

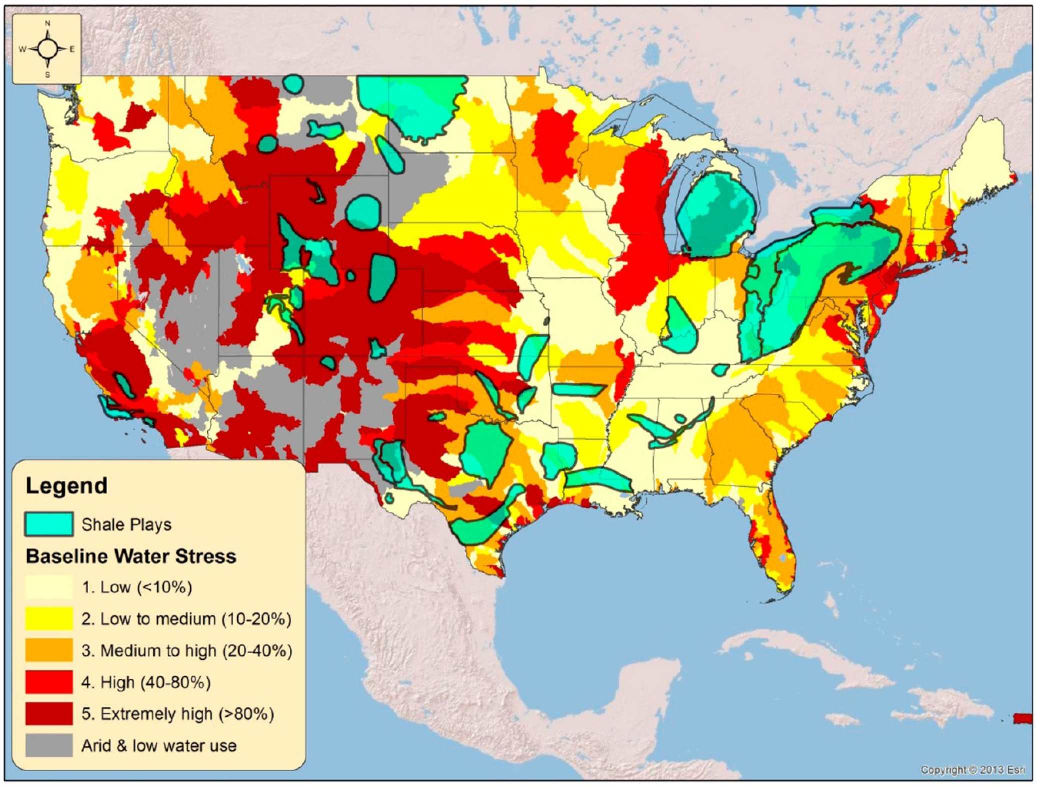


Figure 6. Map of the baseline water stress conditions[139] in relation to shale play locations across the U.S. Note that many of the western shale plays are associated with high to severe baseline water stress, which reflects the ratio between water withdrawals and availability.[139]

radiation associated with radionuclides from the ^{226}Ra decay series (^{214}Pb, ^{214}Bi, ^{210}Pb) and ^{232}Th- decay series (^{228}Ra, ^{228}Th, ^{208}Tl), elevated beta radiation was observed, up to 50 000 Bq/kg.[130]

These results highlight the risks associated with the disposal or spill of NORM-rich flowback and produced waters; even if the disposal is within regulations, the high volumes of wastewater can lead to a buildup of radium, and radiation can pose substantial environmental and health risks. Likewise, radium-bearing barite is a common constituent of scale and sludge deposits that are associated with conventional oil and gas exploration.[130−133] Elevated radium levels were recorded in soil and pipe-scale near oil production sites in the U.S., with ^{226}Ra activity up to ∼490 000 Bq/kg.[131] We expect that solid wastes from drilling and soil near shale gas drilling sites as well as solids from brine treatment facilities[132] will sometimes have similar high levels of radioactivity. We conclude that reactive residuals in brines, such as metals and radioactive elements, can accumulate in river and lake sediments and could pose long-term environmental and health effects by slowly releasing toxic elements and radiation in the impacted areas.

5. WATER SCARCITY AND SHALE GAS DEVELOPMENT

Evaluations of the water footprint for shale gas development have been based on the amount of water used for drilling and hydraulic fracturing. Reports of the water consumption for shale gas development from the Marcellus,[101] Barnett, Haynesville, Eagle Ford,[134] Woodford Shale,[135] and Horn River in British Columbia[8,49,136] showed that water use varies

dx.doi.org/10.1021/es405118y | Environ. Sci. Technol. 2014, 48, 8334−8348

from 8000 to 100 000 m^3 (2−13 million gallons) per unconventional well (Table 1).

Total water use for shale gas development overall is relatively low compared to other water withdrawal sources, such as cooling water for thermoelectric-power generation, which consists ~40% of total freshwater withdrawals in the U.S.[137,134,135] Based on two independent reports,[6,138] the total number of shale gas wells in the U.S. was about 20 000 in 2012. That number of wells accounts for an overall (cumulative) water footprint (based on an average of 15 000 m^3 used per well) of $\sim 300 \times 10^6$ m^3. A different study has suggested a similar volume of water use of $\sim 250 \times 10^6$ m^3.[139] Assuming that 10% of the water used for thermoelectric-power generation is lost through evaporation[137] ($\sim 27.8 \times 10^9$ m^3 out of 278×10^9 m^3 per year), the total water volume that has been consumed during the past decade for hydraulic fracturing ($\sim 300 \times 10^6$ m^3) was only ~1% of that annual water loss from cooling thermoelectric-power generation.

However, in geographic areas with drier climates and/or higher aquifer consumption, such as Texas, Colorado, and California, groundwater exploitation for hydraulic fracturing can lead to local water shortages[134] and subsequent degradation of water quality. Even in wet areas, variations in the stream flows can induce water shortage upon water extraction for hydraulic fracturing.[140] In small to moderate streams in the Susquehanna River Basin of northern Appalachian Basin, water withdrawals for hydraulic fracturing can exceed the natural flows, particularly during low-flow periods.[37] Likewise, water use for hydraulic fracturing in southern Alberta, Canada has become limited because the river waters is already allocated for other users, and in other locations in British Columbia, the variability in stream discharge is a limiting factor for withdrawals for shale gas exploration.[8] In addition to detailed water balance evaluations in several basins,[134,135] nearly half of the shale gas wells in the U.S. were developed in basins with high water scarcity, particularly in Texas and Colorado.[139] The overlap of the shale plays with water basins where water withdrawal exceeds 40% of the annual replenishment[139] is illustrated in Figure 6 and consistent with the exceptional 2013 drought conditions in western U.S. (SI Figure S2). Alternative water sources, such as brackish to saline groundwater,[8] treated domestic wastewater, and/or acid mine drainage in the Appalachian Basin[141−143] should be considered as potential alternatives for drilling and hydraulic fracturing in these areas. Likewise, the increased reuse of shale gas wastewater for hydraulic fracturing could mitigate the water gap.[75]Overall the expected rise in unconventional wells will increase the water use and possibly the water footprint in the U.S.

6. POSSIBLE SOLUTIONS

Given the different risks to water resources that are associated with shale gas development in the U.S., we consider several plausible solutions that could mitigate some of the identified problems. Previous studies have identified stray gas contamination particularly in drinking water wells located less than 1 km from drilling sites.[27,29] Enforcing a safe zone of 1 km between new installed shale gas sites and already existing drinking water wells could reduce the risk of stray gas contamination in drinking water wells in these areas. Second, the debate whether the occurrence of natural gas in drinking water is naturally occurring or related directly to contamination through leaking from shale gas wells could be addressed by mandatory baseline monitoring that would include modern geochemical techniques such as major and trace elements, $\delta^{18}O$ and δ^2H in water and $\delta^{13}C$ in DIC, methane concentration, and stable isotopes of methane ($\delta^{13}C-CH_4$, δ^2H-CH_4) for adequate characterization of the chemical and isotopic composition of regional aquifers in areas of shale gas development. The baseline data, followed by data generation from continuous monitoring and production gas chemistry should become accessible to the scientific community and will be used to evaluate cases where water contamination may occur. Third, transparency and data sharing, including full disclosure of all hydraulic fracturing chemicals, are critical for establishing an open and scientific discussion that could alleviate potential legal and social conflicts.

With respect to wastewater management, enforcing zero discharge policy for untreated wastewater and establishing adequate treatment technologies could prevent surface water contamination. Currently two types of wastewater treatment are used; thermal evaporation/distillation and brine treatment through lime and Na_2SO_4 addition.[100,144]While thermal evaporation/distillation removes all dissolved salts in the wastewater, brine treatment with lime and Na_2SO_4 addition only removes metals such as barium and NORM but does not remove halogens (chloride and bromide)[23,35] In order to reduce the potential formation of THM compounds in downstream drinking water facilities, additional remediation technologies, such as complete desalination,[145] should be introduced for removal of the dissolved salts to levels acceptable for healthy stream ecology (e.g., TDS <500 mg/L). Likewise, reduction of the radioactivity from wastewater and safe disposal of NORM-rich solid wastes and/or solid residues from treatment of wastewater is critical in preventing contamination and accumulation of residual radioactive materials.[35] Since disposal of wastewater through deep-well injection is not always possible and large volume of injection could induce seismicity in some areas, developing remediation technologies for adequate treatment and safe disposal of wastewater is critical for protecting waterways.

Finally, the possible limitation of fresh water resources for shale gas development could be mitigated by either using alternative water resources that would substitute for fresh water or using other types of liquids (e.g., gel) for hydraulic fracturing. The beneficial use of marginal waters (i.e., water with low quality that cannot be used for the domestic or agricultural sectors) is that in many cases such water is discharged and can harm the environment; using these water sources for hydraulic fracturing could therefore have multiple advantages. For example, the use of acid mine drainage (AMD) for hydraulic fracturing could mitigate the current AMD discharge and contamination of numerous waterways in eastern U.Sly. Experimental blending of AMD and Marcellus flowback waters has shown that the blending causes the formation of Sr-Barite salts that in turn capture some of the contaminants in both fluids (e.g., sulfate and iron in AMD, barium, strontium, and radium in flowback waters).[143] In the Horn River Basin of British Columbia, Canada, saline groundwater with TDS of up to 30 000 mg/L is treated to remove H_2S and other gases and used for hydraulic fracturing.[8] The current upper limit for salinity (for adjusting to friction reducers) in hydraulic fracturing fluids is about 25 000 mg/L, although a salt-tolerant and water-based friction reducer has been developed to enable recycling of even higher saline wastewater for hydraulic fracturing.[146] Consequently, utilization of saline, mineralized, and other types of marginal waters should be considered for hydraulic fracturing and drilling, particularly in areas highly water scarcity. Recycling shale gas wastewater with marginal waters can generate both a new water source for hydraulic fracturing and mitigate the environmental effects associated with the wastewater disposal. Likewise, oil and gas produced waters can be beneficially used upon adequate treatment and management[147]

7. CONCLUSIONS

Our survey of the literature has identified four plausible risks to water resources associated with shale gas development and hydraulic fracturing, as illustrated in Figure 4. The first risk is contamination of shallow aquifers in areas adjacent to shale gas development through stray gas leaking from improperly constructed or failing gas wells. Over a longer-time scale, the quality of groundwater in aquifers where stray gas contamination has been identified could potentially be impacted by both leaking of saline water and hydraulic fracturing fluids from shale gas wells and by secondary processes induced by the high content of methane in the groundwater (i.e., sulfate reduction). Thus, evidence of stray gas contamination could be indicative of future water quality degradation, similar to that observed in some conventional oil and gas fields. The second risk is contamination of water resources in areas of shale gas development and/or waste management by spills, leaks, or disposal of hydraulic fracturing fluids and inadequately treated wastewaters. The third risk is accumulation of metals and radioactive elements on stream, river and lake sediments in wastewater disposal or spill sites, posing an additional long-term impact by slowly releasing toxic elements and radiation to the environment in the impacted areas. The fourth risk is the water footprint through withdrawals of valuable fresh water from dry areas and overexploitation of limited or diminished water resources for shale gas development.

Much of the debate on the possibility of water contamination is related to the availability of baseline water chemistry data in aquifers before shale gas development. Yet full baseline data is often unavailable, given the lack of systematic and component-specific monitoring of private wells and surface water systems across the U.S. Developing novel geochemical and isotopic tracers that would confirm or refute evidence for contamination can help fill this data gap. The study of water contamination is often based on the characterization of water quality in a regional aquifer and/or surface water away from contamination sites, rather than monitoring water quality changes through time. Retrospective studies of water contamination associated with shale gas development should therefore include a comprehensive investigation of the hydrology, hydrogeology, water chemistry, and isotopic tracers for delineating the sources and mechanisms of water contamination in questioned areas.

Finally, more studies are needed across a broader geographic area, particularly because many shale gas developments occur in areas that have been historically exploited for conventional oil and gas (e.g., PA, WV, CO, TX, and in the future also CA). Most of the scientific publications thus far have addressed water issues in the Appalachian Basin, whereas information for many other basins is limited or not available. Future research should include studies from other basins in order to overcome these gaps and determine the overall risks to water resources from shale-gas development. Importantly, many of the risks identified in the literature thus far appear possible to mitigate with increased engineering controls during well construction and alternative water-management or water-disposal options to alleviate the impact of shale-gas development on water resources.

ASSOCIATED CONTENT

Supporting Information

Supplement figures on the association of water spill violations to shale gas well density and water scarcity are presented in Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

Notes. The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The Nicholas School of Environment at Duke University, the National Science Foundation (EAR-1249255), and the Park Foundation supported some parts of the research described in this study.

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