Impact of Shale Gas Development on Regional Water Quality

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Background: Natural gas has recently emerged as a relatively clean energy source that offers the opportunity for a number of regions around the world to reduce their reliance on energy imports. It can also serve as a transition fuel that will allow for the shift from coal to renewable energy resources while helping to reduce the emissions of CO_2, criteria pollutants, and mercury by the power sector. Horizontal drilling and hydraulic fracturing make the extraction of tightly bound natural gas from shale formations economically feasible. These technologies are not free from environmental risks, however, especially those related to regional water quality, such as gas migration, contaminant transport through induced and natural fractures, wastewater discharge, and accidental spills. The focus of this Review is on the current understanding of these environmental issues.

Advances: The most common problem with well construction is a faulty seal that is emplaced to prevent gas migration into shallow groundwater. The incidence rate of seal problems in unconventional gas wells is relatively low (1 to 3%), but there is a substantial controversy whether the methane detected in private groundwater wells in the area where drilling for unconventional gas is ongoing was caused by well drilling or natural processes. It is difficult to resolve this issue because many areas have long had sources of methane unrelated to hydraulic fracturing, and pre-drilling baseline data are often unavailable.

Water management for unconventional shale gas extraction is one of the key issues that will dominate environmental debate surrounding the gas industry. Reuse of produced water for hydraulic fracturing is currently addressing the concerns regarding the vast quantities of contaminants that are brought to the surface. As these well fields mature and the opportunities for wastewater reuse diminish, the need to find alternative management strategies for this wastewater will likely intensify.

Outlook: Improved understanding of the fate and transport of contaminants of concern and increased long-term monitoring and data dissemination will help effectively manage water-quality risks associated with unconventional gas industry today and in the future. Confidentiality requirements dictated by legal investigations combined with the expedited rate of development and the limited funding for research are major impediments to peer-reviewed research into environmental impacts. Now is the time to work on these environmental issues to avoid an adverse environmental legacy similar to that from abandoned coal mine discharges in Pennsylvania.

Drilling multiple horizontal wells from a single well pad allows access to as much as 1 square mile of shale that is located more than a mile below. [Image courtesy of Range Resources Appalachia]

ARTICLE OUTLINE

BACKGROUND READING

General overview that includes geology of major shale plays, description of the extraction process, relevant regulations, and environmental considerations: www.netl.doe.gov/technologies/oil-gas/publications/EPreports/Shale_Gas_Primer_2009.pdf

Detailed information about individual shale gas wells, including chemical additives used in each hydraulic fracturing treatment: http://fracfocus.org

Findings of the U.S. Environmental Protection Agency study on the potential impact of hydraulic fracturing on drinking water resources: www.epa.gov/hfstudy

Comprehensive information from the British Geological Survey about shale gas (including articles and videos): www.bgs.ac.uk/shalegas

Site developed in collaboration with the Geological Society of America promoting the rational debate about energy future: www.switchenergyproject.com

Latest news and findings about shale gas. www.shale-gas-information-platform.org

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Impact of Shale Gas Development on Regional Water Quality

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Unconventional natural gas resources offer an opportunity to access a relatively clean fossil fuel that could potentially lead to energy independence for some countries. Horizontal drilling and hydraulic fracturing make the extraction of tightly bound natural gas from shale formations economically feasible. These technologies are not free from environmental risks, however, especially those related to regional water quality, such as gas migration, contaminant transport through induced and natural fractures, wastewater discharge, and accidental spills. We review the current understanding of environmental issues associated with unconventional gas extraction. Improved understanding of the fate and transport of contaminants of concern and increased long-term monitoring and data dissemination will help manage these water-quality risks today and in the future.

Natural gas has recently emerged as an energy source that offers the opportunity for a number of regions around the world to reduce their reliance on energy imports or strive toward energy independence (1, 2). It may also be a potential transition fuel that will allow for the shift from coal to renewable energy resources while helping to reduce the emissions of CO_2, criteria pollutants, and mercury by the power sector (3). The driving force behind this shift is that it has become economically feasible to extract unconventional sources of gas that were previously considered inaccessible. Conventional gas is typically extracted from porous sandstone and carbonate formations, where it has generally been trapped under impermeable caprocks after migration from its original source rock. In contrast, unconventional gas is usually recovered from low-permeability reservoirs or the source rocks themselves, including coal seams, tight sand formations, and fine-grained, organic-rich shales. Unconventional gas formations are characterized by low permeabilities that limit the recovery of the gas and require additional techniques to achieve economical flow rates (2).

The archetypical example of rapidly increasing shale gas development is the Marcellus Shale in the eastern United States (Fig. 1). Intensive gas extraction began there in 2005, and it is one of the top five unconventional gas reservoirs in the United States. With a regional extent of 95,000 square miles, the Marcellus is one of the world's largest known shale-gas deposits. It extends from upstate New York, as far south as Virginia, and as far west as Ohio, underlying 70% of the state of Pennsylvania and much of West Virginia. The formation consists of black and dark gray shales, siltstones, and limestones (4). On the basis of a geological study of natural fractures in the formation, Engelder (5) estimated a 50% probability that the Marcellus will ultimately yield 489 trillion cubic feet of natural gas.

Concerns that have been voiced (6) in connection with hydraulic fracturing and the development of unconventional gas resources in the United States include land and habitat fragmentation as well as impacts to air quality, water quantity and quality, and socioeconomic issues (3, 5, 7). Although shale gas development is increasing across several regions of the United States and the world (such as the United Kingdom, Poland, Ukraine, Australia, and Brazil), this review focuses on the potential issues surrounding water quality in the Appalachian region and specifically the Marcellus Shale, where the majority of published studies have been conducted. Our Review focuses on chemical aspects of water quality rather than issues surrounding enhanced sediment inputs into waterways, which have been discussed elsewhere (4, 7, 8).

Cause of the Shale Gas Development Surge

Recent technological developments in horizontal drilling and hydraulic fracturing have enabled enhanced recovery of unconventional gas in the United States, increasing the contribution of shale gas to total gas production from negligible levels in 1990 to 30% in 2011 (1). Although the first true horizontal oil well was drilled in 1929, this technique only became a standard industry practice in the 1980s (9). Whereas a vertical well allows access to tens or hundreds of meters across a flat-lying formation, a horizontal well can be drilled to conform to the formation and can therefore extract gas from thousands of meters of shale. Horizontal wells reduce surface disturbance by limiting the number of drilling pads and by enabling gas extraction from areas where vertical wells are not feasible. However, horizontal drilling alone would not have enabled exploitation of the unconventional gas resources because the reservoir permeability is not sufficient to achieve economical gas production by natural flow. Hydraulic fracturing—"hydrofracking," or "fracking"—was developed in the 1940s to fracture and increase permeability of target formations and has since been improved to match the characteristics of specific types of reservoirs, including shales.

Hydraulic fracturing fluids consist of water that is mixed with proppants and chemicals before injection into the well under high pressure (480 to 850 bar) in order to open the existing fractures or initiate new fractures. The proppant (commonly sand) represents generally ~9% of the total weight of the fracturing fluid (10) and is required to keep the fractures open once the pumping has stopped. The number, type, and concentration of chemicals added are governed by the geological characteristics of each site and the chemical characteristics of the water used. The fracturing fluid typically used in the Marcellus Shale is called slickwater, which means that it does not contain viscosity modifiers that are often added to hydrofracture other shales so as to facilitate better proppant transport and placement.

Chemical additives in the fluids used for hydraulic fracturing in the Marcellus Shale include friction reducers, scale inhibitors, and biocides (Table 1 and Box 1). Eight U.S. states currently require that all chemicals that are not considered proprietary must be published online (11), whereas many companies are voluntarily disclosing this information in other states. However, many of the chemicals added for fracturing are not currently regulated by the U.S. Safe Drinking Water Act, raising public concerns about water supply contamination. From 2005 to 2009, about 750 chemicals and other components were used in hydraulic fracturing, ranging from harmless components, including coffee grounds or walnut hulls, to 29 components that may be hazardous if introduced into the water supply (6). An inorganic acid such as hydrochloric acid is often used to clean the wellbore area after perforation and to dissolve soluble minerals in the surrounding formation. Organic polymers or petroleum distillates are added to reduce friction between the fluid and the wellbore, lowering the pumping costs. Antiscalants are added to the fracturing fluid so as to limit the precipitation of salts and metals in the formation and inside the well. Besides scaling, bacterial growth is a major concern for the productivity of a gas well (quantity and quality of produced gas). Glutaraldehyde is the most common antibacterial agent added, but other disinfectants [such as 2,2-dibromo-3-nitrilopropionamide (DBNPA) or chlorine dioxide] are often considered. Surfactants (alcohols such as methanol or isopropanol) may also be added to reduce the fluid surface tension to aid fluid recovery.

Methane Migration

As inventoried in 2000, more than 40 million U.S. citizens drink water from private wells (12). In some areas, methane—the main component of natural gas—seeps into these private wells from either natural or anthropogenic sources. Given its low solubility (26 mg/L at 1 atm, 20°C), methane

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that enters wells as a solute is not considered a health hazard with respect to ingestion and is therefore not regulated in the United States. When present, however, methane can be oxidized by bacteria, resulting in oxygen depletion. Low oxygen concentrations can result in the increased solubility of elements such as arsenic or iron. In addition, anaerobic bacteria that proliferate under such conditions may reduce sulfate to sulfide, creating water- and air-quality issues. When methane degasses, it can also create turbidity and, in extreme cases, explode (13, 14). Therefore, the U.S. Department of the Interior recommends a warning if water contains 10 mg/L of CH_4 and immediate action if concentrations reach 28 mg/L (15). Methane concentrations above 10 mg/L indicate that accumulation of gas could result in an explosion (16).

The most common problem with well construction is a faulty seal in the annular space around casings that is emplaced to prevent gas leakage from a well into aquifers (13). The incidence rate of casing and cement problems in unconventional gas wells in Pennsylvania has been reported previously as ~1 to 2% (17). Our count in Pennsylvania from 2008 to March 2013 for well construction problems [such as casing or cementing incidents (18)] cited by the Pennsylvania Department of Environmental Protection (DEP) revealed 219 notices of violation out of 6466 wells (3.4%) (19). Of these, 16 wells in northern Pennsylvania were given notices with respect to the regulation that the "operator shall prevent gas and other fluids from lower formations from entering fresh groundwater" (violation code 78.73A). Most of the time, gas leakage is minor and can be remedied. However, in one case attributed to Marcellus drilling and leaky well casings, stray gas that accumulated in a private water well exploded near the northeastern Pennsylvania town of Dimock. A study of 60 groundwater wells in that area, including across the border in upstate New York (20), showed that both the average and maximum methane concentrations were higher when sampled from wells within 1 km of active Marcellus gas wells as compared with those farther away. Much discussion has since ensued as to whether the methane detected in these wells was caused by drilling or natural processes (21–24) because the area has long had sources of both thermogenic and biogenic methane unrelated to hydraulic fracturing, and no predrilling baseline data are available. The averages reported in that study for sites both near and far from drilling are not dissimilar from values for groundwater from areas of Pennsylvania and West Virginia sampled by the U.S. Geological Survey (USGS) before the recent Marcellus Shale development began, or samples in New York state where high-volume hydrofracturing is currently banned (Fig. 2).

The reason gas is found so often in water wells in some areas is because methane not only forms at depth naturally, owing to high-temperature maturation of organic matter, but also at shallow depths through bacterial processes (25, 26). Both these thermogenic and biogenic gas types can migrate through faults upward from deep formations or laterally from environments such as swamps (swamp gas) or glacial till (drift gas) (14, 27). In addition, gas can derive from anthropogenic sources such as gas storage fields, coal mines, landfills, gas pipelines, and abandoned gas wells (28). In fact, ~350,000 oil and gas wells have been drilled in Pennsylvania, and the locations of ~100,000 of these are unknown (29). Thus, it is not surprising that gas problems have occurred in Pennsylvania long before the Marcellus development (30). Pennsylvania is not the only state facing this problem because about ~60,000 documented orphaned wells and potentially more than 90,000 undocumented orphaned wells in the United States have not been adequately plugged and could act as vertical conduits for gas (31).

As natural gas moves in the subsurface, it can be partially oxidized, mixed with other gases, or diluted along flow paths. To determine its provenance, a "multiple lines of evidence approach" must be pursued (24). For example, researchers measure the presence of other hydrocarbons as well as the isotopic signatures of H, O, and C in the water or gas (16, 27, 31). Thermogenic gas in general has more ethane and a higher $^{13}C/^{12}C$ ratio than that of biogenic gas. Stable isotopes in thermogenic gas may sometimes even yield clues about which shale was the source of the gas (24, 32). In northeastern Pennsylvania, researchers argue whether the isotopic signatures of the methane in drinking-water wells indicate the gas derived from the Marcellus or from shallower formations (20, 24).

Although determining the origin of gas in water wells may lead to solutions for this problem, the source does not affect liability because gas companies are responsible if it can be shown that any gas—not just methane—has moved into a water well because of shale-gas development activity. For example, drilling can open surficial fractures that allow preexisting native gas to leak into water wells (13). This means that pre- and post-drilling gas concentration data are needed to determine culpability. Only one published study compares pre- and post-drilling water chemistry in the Marcellus Shale drilling area. In that study, a

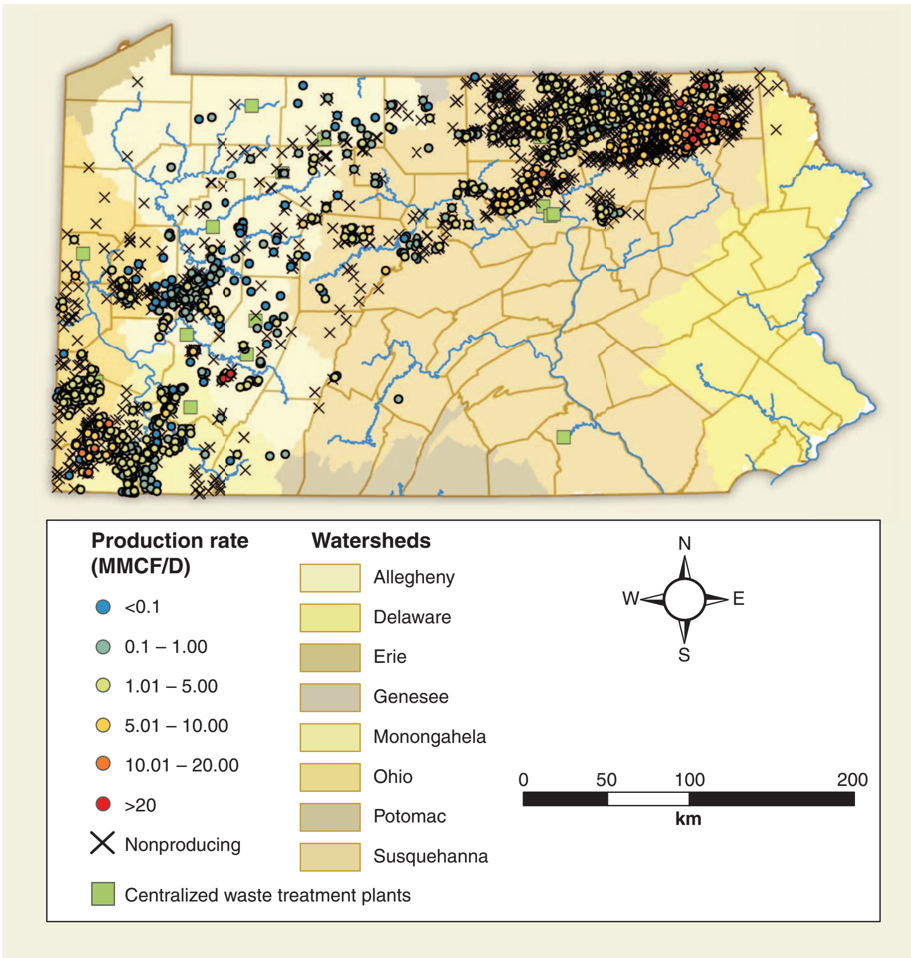

Fig. 1. Marcellus Shale wells in Pennsylvania. Rapid development of Marcellus Shale since 2005 resulted in more than 12,000 well permits, with more than 6000 wells drilled and ~3500 producing gas through December 2012 (average daily production ranged from <0.1 to >20 million cubic feet/day (MMCF/D). Current locations of centralized wastewater treatment facilities (CWTs) are distributed to facilitate treatment and reuse of flowback and produced water for hydraulic fracturing.

sample of 48 water wells in Pennsylvania investigated between 2010 and 2011 within 2500 feet of Marcellus wells showed no statistical differences in dissolved CH_4 concentrations before or shortly after drilling (*33*). In addition, no statistical differences related to distance from drilling were observed. However, that study reported that the concentration of dissolved methane increased in one well after drilling was completed nearby, which is possibly consistent with an average rate of casing problems of ~3%.

The rate of detection of methane in water wells in northeast Pennsylvania [80 to 85% (*20*, *24*)] is higher than in the wider region that includes southwestern Pennsylvania [24% (*33*)], where pre- and post-drilling concentrations were statistically identical. This could be a result of the small sample sizes of the two studies or because the hydrogeological regime in the northeast is more prone to gas migration (*34*). Such geological differences also may explain why regions of the Marcellus Shale have been characterized by controversy in regard to methane migration as noted above, whereas other shale gas areas such as the Fayetteville in Arkansas have not reported major issues with respect to methane (*35*). Reliable models that incorporate geological characteristics are needed to allow prediction of dissolved methane in groundwater. It is also critical to distinguish natural and anthropogenic causes of migration, geological factors that exacerbate such migration, and the likelihood of ancillary problems of water quality related to the depletion of oxygen. Answering some of these questions will require tracking temporal variations in gas and isotopic concentrations in groundwater wells near and far from drilling by using multiple lines of evidence (*16*, *24*). Research should also focus on determining flow paths in areas where high sampling density can be attained.

Table 1. Common chemical additives for hydraulic fracturing.

Additive type	Example compounds	Purpose
Acid	Hydrochloric acid	Clean out the wellbore, dissolve minerals, and initiate cracks in rock
Friction reducer	Polyacrylamide, petroleum distillate	Minimize friction between the fluid and the pipe
Corrosion inhibitor	Isopropanol, acetaldehyde	Prevent corrosion of pipe by diluted acid
Iron control	Citric acid, thioglycolic acid	Prevent precipitation of metal oxides
Biocide	Glutaraldehyde, 2,2-dibromo-3-nitrilopropionamide (DBNPA)	Bacterial control
Gelling agent	Guar/xanthan gum or hydroxyethyl cellulose	Thicken water to suspend the sand
Crosslinker	Borate salts	Maximize fluid viscosity at high temperatures
Breaker	Ammonium persulfate, magnesium peroxide	Promote breakdown of gel polymers
Oxygen scavenger	Ammonium bisulfite	Remove oxygen from fluid to reduce pipe corrosion
pH adjustment	Potassium or sodium hydroxide or carbonate	Maintain effectiveness of other compounds (such as crosslinker)
Proppant	Silica quartz sand	Keep fractures open
Scale inhibitor	Ethylene glycol	Reduce deposition on pipes
Surfactant	Ethanol, isopropyl alcohol, 2-butoxyethanol	Decrease surface tension to allow water recovery

Box 1. Glossary of Terms

Casing: steel pipe that is inserted into a recently drilled section of a borehole to stabilize the hole, prevent contamination of groundwater, and isolate different subsurface zones.

Cementing: placing a cement mixture between the casing and a borehole to stabilize the casing and seal off the formation.

Class II disposal wells: underground injection wells for disposal of fluids associated with oil and gas production.

Flowback water: water that returns to the surface after the hydraulic fracturing process is completed and the pressure is released and before the well is placed in production; flowback water return occurs for several weeks.

Produced water: water that returns to the surface with the gas after the well is placed in production; production water return occurs during the life of a well.

Proppant: granular material, such as silica sand, ceramic media, or bauxite, that keeps the fractures open so that gas can flow to the wellbore.

Slickwater fracturing: fracturing with fluid that contains mostly water along with friction reducers, proppants, and other additives; used for predominantly gas-bearing formations at shallower depths.

Source rock: organic-rich sedimentary rocks, such as shale, containing natural gas or oil.

Stray gas: gas contained in the geologic formation outside the wellbore that is accidentally mobilized by drilling and/or hydraulic fracturing.

How Protective Is the "Well Armor"?

The protective armor shielding the freshwater zones and the surrounding environment from the contaminants inside the well consist of several layers of casing (hollow steel pipe) and cement (Fig. 3). When the integrity of the wellbore is compromised, gas migration or stray gas can become an issue (*14*). Gas migration out of a well refers to movement of annular gas either through or around the cement sheath. Stray gas, on the other hand, commonly refers to gas outside of the wellbore. One of the primary causes of gas migration or stray gas is related to the upper portion of the wellbore when it is drilled into a rock formation that contains preexisting high-pressure gas. This high-pressure gas can have deleterious effects on the integrity of the outer cement annulus, such as the creation of microchannels (*36*). Temperature surveys can be performed shortly after the cementing job is completed in order to ensure that cement is present behind the casing. Acoustic logging tools are also available to evaluate the integrity of the cement annulus in conjunction with pressure testing.

It is well known that to effectively stabilize wellbores with cement in areas with zones of overpressurized gas, proper cement design and proper mud removal are essential (*37*, *38*). If the hydrostatic pressure of the cement column is not higher than the gas-bearing formation pressure, gas can invade the cement before it sets. Conversely, if this pressure is too high, then the formation can fracture, and a loss of cement slurry can occur. Even when the density is correct, the gas from the formation can invade the cement as it transitions from a slurry to a hardened state (*39*). The slurry must be designed to minimize this transition time and the loss of fluid from the slurry to the formation. Also, if drilling mud is not properly cleaned from the hole before cementing, mud channels may allow gas migration through the central portion of the annulus or along the cement-formation interface. Even if the well is properly cleaned and the cement is placed properly, shrinkage of the cement during hydration or as a result of drying throughout the life of the well can result in crack development within the annulus (*40*, *41*).

Although the primary mechanisms contributing to gas migration and stray gas are understood, it is difficult to predict the risk at individual sites because of varying geological conditions and drilling practices. To successfully protect fresh water and the surrounding environment from the contaminants inside the well, the site-specific risk factors contributing to gas migration and stray gas must be better understood, and improvements in the diagnostics of cement and casing integrity are needed for both new and existing wells. Finding solutions to these problems will provide environmental agencies the knowledge needed to develop sound regulations related to the distances around gas wells that can be affected. It will also provide operators the ability to prevent gas migration and stray gas in a more efficient and economical manner.

The Source and Fate of Fracturing Fluid

The drilling and hydraulic fracturing of a single horizontal well in the Marcellus Shale may require 2 million to 7 million gallons of water (*42*). In contrast, only about 1 million gallons are needed for vertical wells because of the smaller formation contact volume. Although the projected water consumption for gas extraction in the Marcellus Shale region is 18.7 million gallons per day in 2013 (*39*), this constitutes just 0.2% of total annual water withdrawals in Pennsylvania. Water withdrawals in other areas are similarly low, but temporary problems can be experienced at the local level during drought periods (*3*). Furthermore, water quantity issues are prevalent in the drier shale-gas plays of the southwest and western United States (*43*). It is likely that water needs will change from these initial projections as the industry continues to improve and implement water reuse. Nevertheless, the understanding of flow variability—especially during drought conditions or in regions with already stressed water supplies—is necessary to develop best management practices for water withdrawal (*44*). It is also necessary to develop specific policies regarding when and where water withdrawals will be permitted in each region (*45*).

After hydraulic fracturing, the pressure barriers such as frac plugs are removed, the wellhead valve is opened, and "flowback water" is collected at the wellhead. Once the well begins to produce gas, this water is referred to as "produced water" and is recovered throughout the life of the well. Flowback and produced waters are a mixture of injected fluids and water that was originally present in the target or surrounding formations (formation water) (*42*, *46*–*50*). The fraction of the volume of injected water that is recovered as flowback water from horizontal wells in Pennsylvania ranges from 9 to 53% (*9*, *41*), with an average of 10%. It has been observed that the recovery can be even lower than 10% if the well is shut-in for a period of time (*51*). The well is shut-in—or maintained closed between fracturing and gas production—so as to allow the gas to move from the shale matrix into the new fractures. Two of the key unanswered questions is what happens to the fracturing fluid that is not recovered during the flowback period, and whether this fluid could eventually contaminate drinking water aquifers (*23*, *33*, *34*, *52*–*54*). The analyses of Marcellus Shale well logs indicate that the low-permeability shale contains very little free water (*55*, *56*), and much of the hydraulic fracturing fluid may imbibe (absorb) into the shale.

Fracturing fluid could migrate along abandoned and improperly plugged oil and gas wells, through an inadequately sealed annulus between the wellbore and casing or through natural or induced fractures outside the target formation. Indeed, out-of-formation fractures have been documented to extend as much as ~460 m above the top of some hydraulically fractured shales (*57*), but still ~1.6 km or more below freshwater aquifers. Nonetheless, on the basis of the study of 233 drinking-water wells across the shale-gas region of rural Pennsylvania, Boyer *et al*. (*33*) reported no major influences from gas well drilling or hydrofracturing on nearby water wells. Compared with the pre-drilling data reported in that study, only one well showed changes in water quality (salt concentration). These changes were noticed within days after a well was hydrofractured less than ~460 m away, but none of the analytes exceeded the standards of the U.S. Safe Drinking Water Act, and nearly all the parameters approached pre-drilling concentrations within 10 months.

In the case of methane contamination in groundwater near Dimock, Pennsylvania, contamination

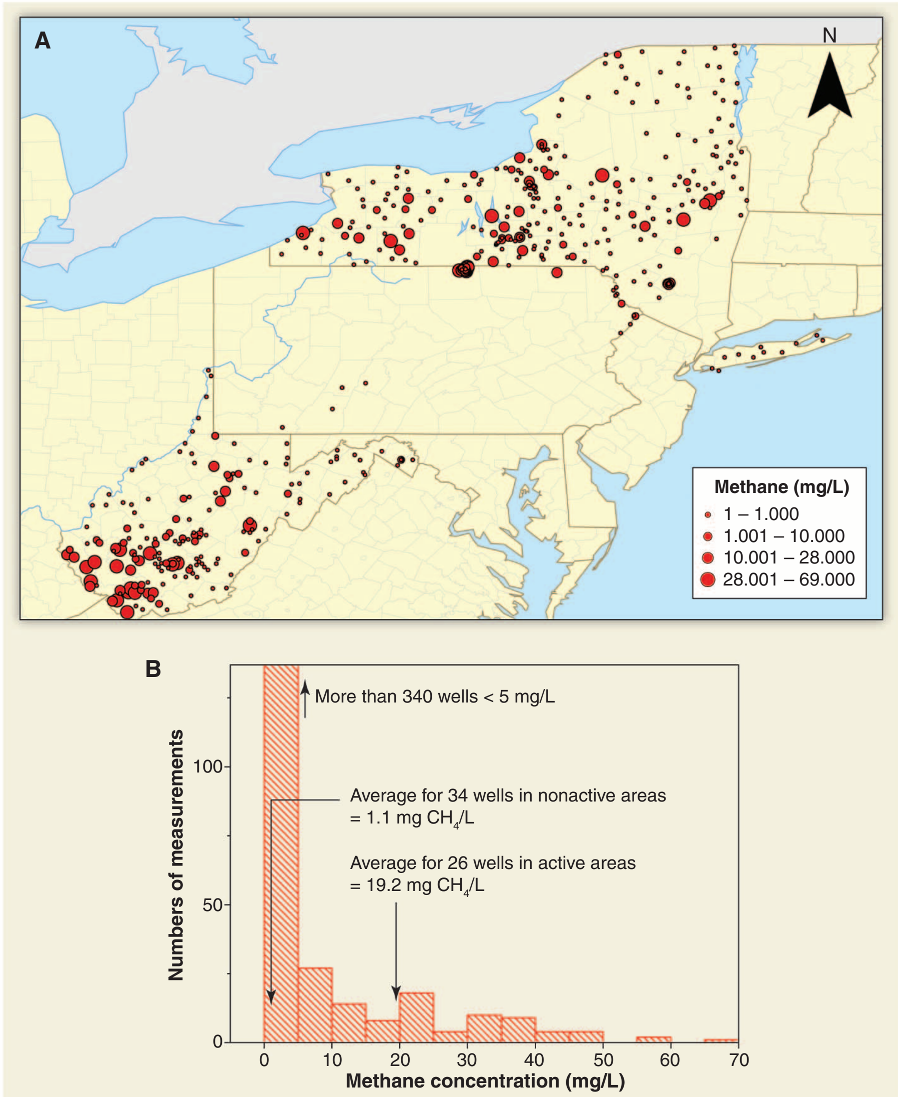

Fig. 2. Methane concentrations in groundwater and springs. (**A**) Published values for groundwater or spring samples include 239 sites in New York from 1999 to 2011 (*84*), 40 sites in Pennsylvania in 2005 (*27*), and 170 sites in West Virginia from 1997 to 2005 (*85*). Maxima varied from 68.5 mg/L in West Virginia, to 44.8 mg/L in Tioga County, Pennsylvania, where an underground gas storage field was leaking, to a value approaching 45 mg/L in New York. (**B**) Values shown with down arrows are averages for a set of wells in southeastern New York and northeastern Pennsylvania located <1 km (26 wells) and >1 km (34 wells) from active gas drilling (*20*).

by saline flowback brines or fracturing fluids was not observed (*20*). One early U.S. Environmental Protection Agency (EPA) report (*54*) suggested that a vertically fractured well in Jackson County, West Virginia, may have contaminated a local water well with gel from fracturing fluid. This vertical well was fractured at a depth of just ~1220 m, and four old natural gas wells nearby may have served as conduits for upward contaminant transport. A recent EPA study (*53*) implicated gas production wells in the contamination of deep groundwater resources near Pavillion, Wyoming. However, resampling of the monitoring wells by the USGS showed that the flowrate was too small to lend confidence to water-quality interpretations of one well, leaving data from only one other well to interpret with respect to contamination, and regulators are still studying the data (*58*). The Pavillion gas field consists of 169 production wells into a sandstone (not shale) formation and is unusual in that fracturing was completed as shallow as 372 m below ground. In addition, surface casings of gas wells are as shallow as 110 m below ground, whereas the domestic and stock wells in the area are screened as deep as 244 m below ground. The risk for direct contaminant transport from gas wells to drinking-water wells increases dramatically with a decrease in vertical distance between the gas well and the aquifer.

A recent study applied a groundwater transport model to estimate the risk of groundwater contamination with hydraulic fracturing fluid by using pressure changes reported for gas wells (*52*). The study concluded that changes induced by hydraulic fracturing could allow advective transport of fracturing fluid to groundwater aquifers in <10 years. The model includes numerous simplifications that compromise its conclusions (*59*). For example, the model is based on the assumption of hydraulic conductivity that reflects water-filled voids in the geological formations, and yet many of the shale and overburden formations are not water-saturated (*60*). Hence, the actual hydraulic conductivity in the field could be orders of magnitude lower than that assumed in the study (*59*). Furthermore, although deep joint sets or fractures exist (*14*), the assumption of preexisting1500-m long vertical fractures is hypothetical and not based on geologic exploration. Hence, there is a need to establish realistic flow models that take into account heterogeneity in formations above the Marcellus Shale and realistic hydraulic conductivities and fracturing conditions.

Last, it has long been known (*14*, *34*, *47*, *48*, *61*, *62*) that groundwater is salinized where deeper ancient salt formations are present within sedimentary basins, including basins with shale gas. Where these brines are present at relatively shallow depths, such as in much of the northeastern and southwestern United States and Michigan, brines sometimes seep to the surface naturally and are unrelated to hydraulic fracturing. An important research thrust should focus on understanding these natural brine transport pathways to determine whether they could represent potential risk for contamination of aquifers because of hydraulic fracturing.

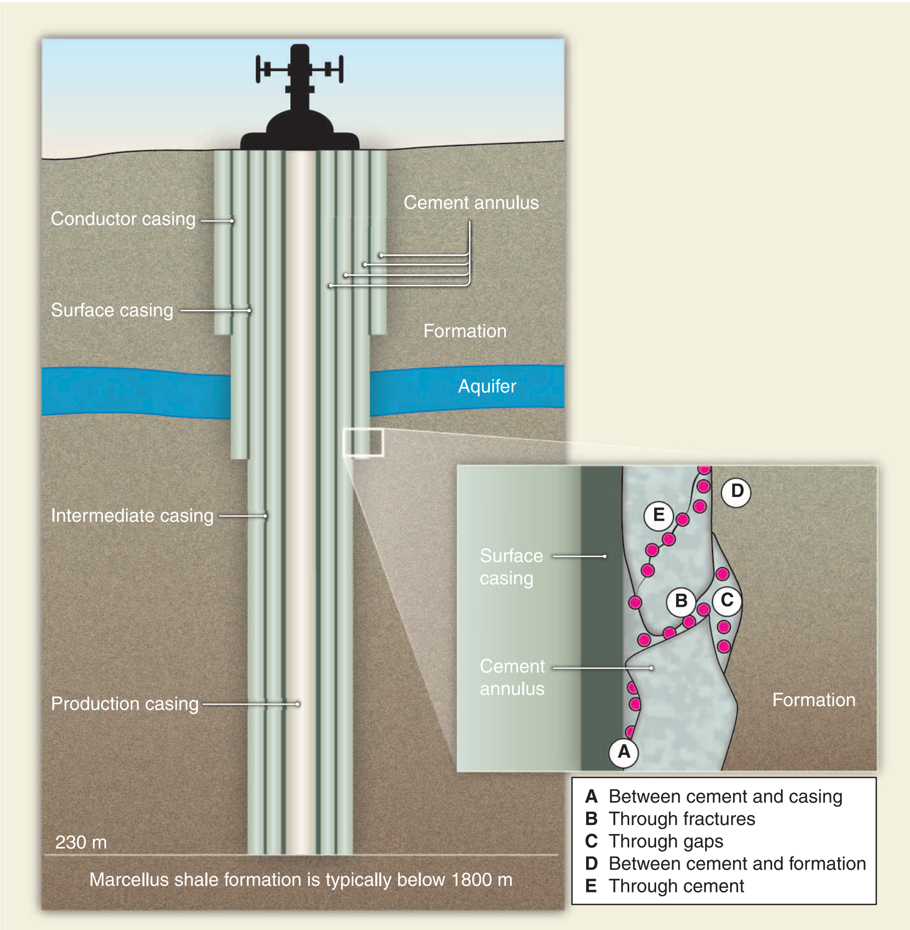

Fig. 3. Typical Marcellus well construction. (i) The conductor casing string forms the outermost barrier closest to the surface to keep the upper portion of the well from collapsing and it typically extends less than 12 m (40 ft) from the surface; (ii) the surface casing and the cement sheath surrounding it that extend to a minimum of 15 m below the lowest freshwater zone is the first layer of defense in protecting aquifers; (iii) the annulus between the intermediate casing and the surface casing is filled with cement or a brine solution; and (iv) the production string extends down to the production zone (900 to 2800 m), and cement is also placed in the annulus between the intermediate and production casing. Potential flaws in the cement annulus (Inset, "A" to "E") represent key pathways for gas migration from upper gas-bearing formations or from the target formation.

Appropriate Wastewater Management Options

The flowback and produced water from the Marcellus Shale is the second saltiest (*63*) and most radiogenic (*50*) of all sedimentary basins in the United States where large volume hydraulic fracturing is used. The average amount of natural gas-related wastewater in Pennsylvania during 2008 to 2011 was 26 million barrels per year (a fourfold increase compared with pre-Marcellus period) (*64*). Compared with conventional shallow wells, Marcellus Shale wells generate one third of the wastewater per unit volume of gas produced (*65*). However, the wastewater associated with Marcellus development in 2010 and 2011 accounted for 68 and 79%, respectfully, of the total oil and gas wastewater requiring management in Pennsylvania. Flowback/produced water is typically impounded at the surface for subsequent disposal, treatment, or reuse. Because of the large water volume, high concentration of dissolved solids, and complex physical-chemical composition of this wastewater, which includes organic and radioactive components, the public is becoming increasingly concerned about management of this water and the potential for human health and environmental impacts associated with the release of untreated or inadequately treated wastewater to the environment (*66*). In addition, spills from surface impoundments (*14*) and trucks or infiltration to groundwater though failed liners are potential pathways for surface and groundwater contamination by this wastewater.

Treatment technologies and management strategies for this wastewater are constrained by regulations, economics of implementation, technology performance, geologic setting, and final disposal alternatives (*67*). The majority of wastewater from oil and gas production in the United States is disposed of effectively by deep underground injection (*68*). However, the state of Pennsylvania has only five operating Class II disposal wells. Although underground injection disposal wells will likely increase in number in Pennsylvania, shale gas development is currently occurring in many areas where Class II disposal wells will not be readily available. Moreover, permissions for and construction of new disposal wells is complex, time-consuming, and costly. Disposal of Pennsylvania brines in Ohio and West Virginia is ongoing but limited by high transportation costs.

The lack of disposal well capacity in Pennsylvania is compounded by rare induced low-magnitude seismic events at disposal wells in other locations (69–71). It is likely that the disposal of wastewater by deep-well injection will not be a sustainable solution across much of Pennsylvania. Nonetheless, between 1982 and 1984, Texas reported at most ~100 cases of confirmed contamination of groundwater from oilfield injection wells, saltwater pits, and abandoned wells, even though at that time the state hosted more than 50,000 injection wells associated with oil and gas (72). Most problems were associated with small, independent operators. The ubiquity of wells and relative lack of problems with respect to brine disposal in Texas is one likely explanation why public pushback against hydraulic fracturing is more limited in Texas as compared with the northeastern United States.

Another reason for public pushback in the northeast may be that in the early stages of Marcellus Shale development, particularly in 2008 to 2009, flowback/produced water was discharged and diluted into publicly owned treatment works (POTWs, or municipal wastewater treatment plants) under permit. This practice was the major pathway for water contamination because these POTWs are not designed to treat total dissolved solids (TDS), and the majority of TDS passed directly into the receiving waterways (6, 73), resulting in increased salt loading in Pennsylvania rivers, especially during low flow (74). In response, the Pennsylvania DEP introduced discharge limits to eliminate disposal of Marcellus Shale wastewater to POTWs (75). In early 2010, there were 17 centralized waste treatment plants (CWTs) in Pennsylvania that were exempted from the TDS discharge limits. However, according to Pennsylvania DEP records none of these CWTs reported to be currently receiving Marcellus wastewater, although they may receive produced water from conventional gas wells. Nevertheless, the TDS load to surface waters from flowback/produced water increased from ~230,000 kg/day in 2006 to 350,000 kg/day in 2011 (64).

It is difficult to determine whether shale gas extraction in the Appalachian region since 2006 has affected water quality regionally, because baseline conditions are often unknown or have already been affected by other activities, such as coal mining. Although high concentrations of Na, Ca, and Cl will be the most likely ions detected if flowback or produced waters leaked into waterways, these salts can also originate from many other sources (76). In contrast, Sr, Ba, and Br are highly specific signatures of flowback and produced waters (34, 47). Ba is of particular interest in Pennsylvania waters in that it can be high in sulfate-poor flowback/produced waters but low in sulfate-containing coal-mine drainage. Likewise, the ratio of $^{87}Sr/^{86}Sr$ may be an isotopic fingerprint of Marcellus Shale waters (34, 77).

Targeting some of these "fingerprint" contaminants, the Pennsylvania DEP began a new monitoring program in 2011. Samples are collected from pristine watersheds as well as from streams near CWT discharges and shale-gas drilling. The Shale Network is collating these measurements with high-quality data from citizen scientists, the USGS, the EPA, and other entities in order to assess potential water quality impacts in the northeast (78, 79). Before 2003, mean concentrations in Pennsylvania surface waters in counties with unconventional shale-gas development were 27 ± 32, 550 ± 620, and 72 ± 81 μg/L for Ba, Sr, and Br ($\pm 1\sigma$), respectively (Fig. 4). Most values more than 3σ above the mean concentrations since 2003 represent samples from areas of known brine effluents from CWTs. A concern has been raised over bromide levels in the Allegheny River watershed that may derive from active CWTs because of health effects associated with disinfection by-products formed as a result of bromide in drinking water sources (64, 80). Given the current regulatory climate and the fact that the majority of dissolved solids passes through these CWTs, it is expected that these treatment facilities will likely not play a major role in Marcellus Shale wastewater management.

The dominant wastewater management practice in the Marcellus Shale region nowadays is wastewater reuse for hydraulic fracturing [a review of Pennsylvania DEP data for the first 6 months of 2012 indicates 90% reuse rate (81)]. Wastewater is impounded at the surface and used directly, or after dilution or pretreatment. Reuse of wastewater minimizes the volume that must be treated and disposed, thus reducing environmental control costs and risks and enhancing the economic feasibility of shale-gas extraction (67). Currently, operators in the Marcellus region do not fully agree about the quality of wastewater that must be attained for reuse. Major concerns include possible precipitation of $BaSO_4$ and, to a lesser extent, $SrSO_4$ and $CaCO_3$ in the shale formation and the wellbore and the compatibility of wastewater with chemicals that are added to the fracturing fluid (such as friction reducers and viscosity modifiers). Hence, a better understanding of chemical compatibility issues would greatly improve the ability to reuse wastewater and minimize disposal volumes. In addition, radioactive radium that is commonly present in flowback/produced water will likely be incorporated in the solids that form in the wastewater treatment process and could yield a low-concentration radioactive waste that must be handled appropriately and has potential on-site human health implications.

The wastewater reuse program represents a somewhat temporary solution to wastewater management problems in any shale play. This program works only as long as there is net water consumption in a given well field. As the well field matures and the rate of hydraulic fracturing diminishes, the field becomes a net water producer because the volume of produced water will exceed the amount of water needed for hydraulic fracturing operations (82, 83). It is not yet clear how long it will take to reach that point in the Marcellus region, but it is clear that there is a need to develop additional technical solutions (such as effective and economical approaches for separation and use of dissolved salts from produced water and treatment for naturally occurring radioactive material) that would allow continued development of this important natural resource in an environmentally responsible manner. Considering very high salinity of many produced waters from shale gas development, this is truly a formidable challenge. Research focused on better understanding of where the salt comes from and how hydrofracturing might be designed to minimize salt return to the land surface would be highly beneficial.

Conclusions

Since the advent of hydraulic fracturing, more than 1 million hydraulic fracturing treatments have been conducted, with perhaps only one documented case of direct groundwater pollution resulting from injection of hydraulic fracturing chemicals used for shale gas extraction (54). Impacts from casing leakage, well blowouts, and spills of contaminated fluids are more prevalent but have generally been quickly mitigated (17). However, confidentiality requirements dictated by legal investigations, combined with the expedited rate of development and the limited funding for research, are substantial impediments to peer-reviewed research into environmental impacts. Furthermore, gas wells are often spaced closely within small areas and could result in cumulative impacts (5) that develop so slowly that they are hard to measure.

The public and government officials are continuing to raise questions and focus their attention on the issue of the exact composition of the hydrofracturing fluid used in shale formations. In 2010, the U.S. House of Representatives directed the EPA to conduct a study of hydraulic fracturing and its impact on drinking-water resources. This study will add important information to account for the fate of hydraulic fracturing fluid injected into the gas-bearing formation. It is well known that a large portion (as much as 90%) of injected fluid is not recovered during the flowback period, and it is important to document potential transport pathways and ultimate disposition of the injected fluid. The development of predictive methods to accurately account for the entire fluid volume based on detailed geophysical and geochemical characteristics of the formation would allow for the better design of gas wells and hydraulic fracturing technology, which would undoubtedly help alleviate public concerns. Research is also needed to optimize water management strategies for effective gas extraction. In addition, the impact of abandoned oil and gas wells on both fluid and gas migration is a concern that has not yet been adequately addressed.

Gas migration received considerable attention in recent years, especially in certain parts of the Appalachian basin (such as northeast Pennsylvania).

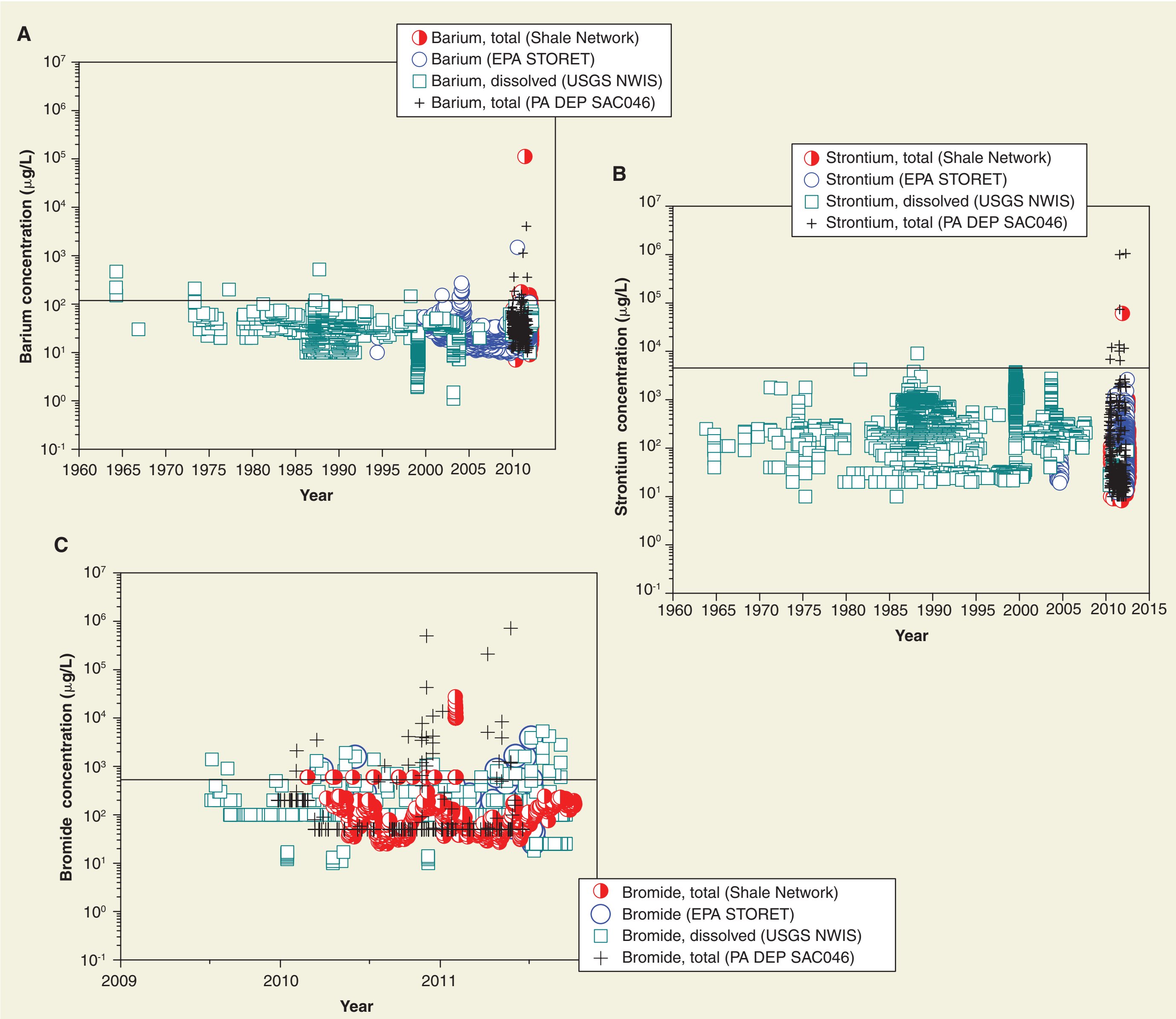

Fig. 4. Concentrations of three ions in surface waters of Pennsylvania in counties with unconventional shale-gas wells: (A) barium, (B) strontium, and (C) bromide. Data reported by EPA (STORET data), USGS (NWIS data), Susquehanna River Basin Commission, Appalachian Geological Consulting and ALLARM [from Shale Network database (*78*, *79*)], and from the Pennsylvania DEP (SAC046) include all rivers, streams, ponds, groundwater drains, lysimeter waters, and mine-associated pit, seep, and discharge waters accessed by using HydroDesktop (www.cuahsi.org) in the relevant counties (data before 2009 for bromide are not shown). Lines indicate 3σ above the mean of data from 1960 to 2003 for the longest duration dataset (USGS). Most values above the lines since 2003 represent targeted sampling in areas of known brine effluents from conventional oil and gas wells (such as Blacklick Creek receiving brine effluent from a CWT). The highest plotted Ba concentration was measured in Salt Springs in northern Pennsylvania. Three of the four samples with highest Sr and Br are from Blacklick Creek; next highest is from Salt Springs. Original values reported beneath the detection limit are plotted at that limit (10 to 100 μg Sr/L; 10 μg Ba/L; and 10 to 200 μg/L Br). The EPA maximum contaminant level (MCL) for Ba is 2000 μg/L. EPA reports no MCL for Sr or Br. Lifetime and 1-day health advisory levels for Sr are 4000 and 25000 μg/L, respectively, and a level under consideration for Br is 6000 μg/L.

It has been known for a long time that methane migrates from the subsurface (such as coal seams, glacial till, and black shales), and the ability to ignite methane in groundwater from private wells was reported long before the recent development of the Marcellus Shale (*14*). However, in the absence of reliable baseline information, it is easy to blame any such incidents on gas extraction activities. It is therefore critical to establish baseline conditions before drilling and to use multiple lines of evidence to better understand gas migration. It is also important to improve drilling and cementing practices, especially through gas-bearing formations, in order to eliminate this potential pathway for methane migration.

Water management for unconventional shale gas extraction is one of the key issues that will dominate environmental debate surrounding the gas industry. Reuse of flowback and produced water for hydraulic fracturing is currently addressing the concerns regarding the vast salt quantities that are brought to the surface (each Marcellus well generates as much as 200 tons of salt during the flowback period). However, there is a need for comprehensive risk assessment and regulatory oversight for spills and other accidental discharges of wastewater to the environment. As these well fields mature and the opportunities for wastewater reuse diminish, the need to find alternative management strategies for this wastewater will likely intensify. Now is the time to work on these issues in order to avoid an adverse environmental legacy similar to that from abandoned coal mine discharges in Pennsylvania.

References and Notes

1. U.S. Energy Information Administration, "Annual Energy Outlook 2013, Early Release" (U.S. Department of Energy, 2013); available at www.eia.gov/forecasts/aeo/erindex.cfm.
2. S. Holditch, K. Perry, J. Lee, "Unconventional Gas Reservoirs—Tight Gas, Coal Seams, and Shales, Working Document of the National Petroleum Council on Global Oil and Gas Study" (National Petroleum Council, 2007).
3. MIT, "The future of natural gas," http://mitei.mit.edu/publications/reports-studies/future-natural-gas. (Massachusetts Institute of Technology, 2011).
4. S. M. Olmstead, L. A. Muehlenbachs, J.-S. Shih, Z. Chu, A. J. Krupnick, *Proc. Natl. Acad. Sci. U.S.A.*, published online 11 March 2013. doi: 10.1073/pnas.1213871110
5. T. Engelder, *Fort Worth Basin Oil Gas Mag.* **20**, 18 (2009).
6. U.S. House of Representatives Committee of Energy and Commerce Minority Staff, "Chemicals used in Hydraulic Fracturing" (prepared for H. A. Waxman, E. J. Markey, D. DeGette, 2011).
7. S. Entrekin, M. Evans-White, B. Johnson, E. Hagenbuch, Rapid expansion of natural gas development poses a threat to surface waters. *Front. Ecol. Environ.* **9**, 503 (2011). doi: 10.1890/110053
8. P. J. Drohan, M. Brittingham, *Soil Sci. Soc. Am. J.* **76**, 1696 (20120).
9. Energy Information Administration, *Drilling Sideways–A Review of Horizontal Well Technology and Its Domestic Application, DOE/EIA-TR-0565* (U.S. Department of Energy, Washington, DC, 1993).
10. NYS DEC, "Draft Supplemental Generic Environmental Impact Statement on the Oil, Gas and Solution Mining Regulatory Program, Well Permit Issuance for Horizontal Drilling And High-Volume Hydraulic Fracturing to Develop the Marcellus Shale and Other Low-Permeability Gas Reservoirs" (New York State Department of Environmental Conservation, 2009).
11. www.FracFocus.org.
12. S. Hutson *et al.*, *Geol. Surv. Circ.* **1268**, 1 (2004).
13. A. W. Gorody, Factors affecting the variability of stray gas concentration and composition in groundwater. *Environ. Geosci.* **19**, 17 (2012). doi: 10.1306/eg.12081111013
14. S. S. Harrison, Evaluating system for ground-water contamination hazards due to gas-well drilling on the glaciated Appalachian plateau. *Ground Water* **21**, 689 (1983). doi: 10.1111/j.1745-6584.1983.tb01940.x
15. K. K. Eltschlager, J. W. Hawkins, W. C. Ehler, F. J. Baldassare, "Technical measures for the investigation and mitigation of fugitive methane hazards in areas of coal mining" (U.S. Dept. of the Interior, Office of Surface Mining Reclamation and Enforcement, Pittsburgh, PA, 2001).
16. K. M. Révész, K. J. Breen, F. J. Baldassare, R. C. Burruss, Carbon and hydrogen isotopic evidence for the origin of combustible gases in water-supply wells in north-central Pennsylvania. *Appl. Geochem.* **25**, 1845 (2010). doi: 10.1016/j.apgeochem.2010.09.011
17. T. Considine, R. Watson, N. Considine, J. Martin, "Environmental Impacts during Marcellus Shale Gas Drilling: Causes, Impacts, and Remedies, Report 2012-1" (Shale Resources and Society Institute, State University of New York, Buffalo, 2012).
18. Total count included violations 78.73A, 78.81D1 and D2, 78.83A and B, 78.83GRNDWTR, 78.83COALCSG, 78.84, 78.85, 78.86, and 207B. Wells with multiple violations were counted only once.
19. PA DEP Office of Oil and Gas, "Oil and Gas Compliance Report, www.portal.state.pa.us/portal/server.pt/community/oil_and_gas_compliance_report/20299" (Pennsylvania Department of Oil and Gas, 2013).
20. S. G. Osborn, A. Vengosh, N. R. Warner, R. B. Jackson, Methane contamination of drinking water accompanying gas-well drilling and hydraulic fracturing. *Proc. Natl. Acad. Sci. U.S.A.* **108**, 8172 (2011). doi: 10.1073/pnas.1100682108; pmid: 21555547
21. R. B. Jackson, S. G. Osborn, N. R. Warner, A. Vengosh, "Responses to frequently asked questions and comments about the shale-gas paper by Osborn *et al.*, June 15, 2011" (www.nicholas.duke.edu/cgc/FrackFAQ6_15_11.pdf, 2012).
22. S. C. Schon, Hydraulic fracturing not responsible for methane migration. *Proc. Natl. Acad. Sci. U.S.A.* **108**, E664 (2011).
23. R. J. Davies, Methane contamination of drinking water caused by hydraulic fracturing remains unproven. *Proc. Natl. Acad. Sci. U.S.A.* **108**, E871 (2011).
24. L. J. Molofsky, J. A. Connor, S. K. Farhat, A. S. Wylie Jr., T. Wagner, *Oil Gas Dev.* **109**, 54 (2011).
25. C. D. Laughrey, F. J. Baldassare, *Am. Assoc. Pet. Geol. Bull.* **82**, 317 (1998).
26. M. J. Whiticar, Carbon and hydrogen isotope systematics of bacterial formation and oxidation of methane. *Chem. Geol.* **161**, 291 (1999). doi: 10.1016/S0009-2541(99)00092-3
27. G. Etiope, A. Drobniak, A. Schimmelmann, *Marine and Petroleum Geology*, http://dx.doi.org/10/1016/j.marpetgeo.2013.02.009 (2013).
28. K. J. Breen, K. Revesz, F. J. Baldassare, S. D. McAuley, "Natural gases in ground water near Tioga Junction, Tioga County, North-central Pennsylvania–Occurrence and use of isotopes to determine origins, 2005" (U.S. Geological Survey, Scientific Investigations Report Series 2007-5085, 2007).
29. PA DEP, "Oil and Gas Well Drilling and Production in Pennsylvania" (Pennsylvania Department of Environmental Protection, PA DEP Fact Sheet, 2011).
30. W. R. Gough, B. A. Waite, in *Water Resources in Pennsylvania: Availability, Quality, and Management*, S. K. Majumdar, E. W. Miller, R. R. Parizek, Eds. (Pennsylvania Academy of Science, 1990), pp. 384–398.
31. IOGC, "Protecting our Country's Resources: The States' Case, Orphaned Well Plugging Initiative" (Interstate Oil and Gas Compact Commission, National Energy Technology Laboratory, 2008).
32. S. G. Osborn, J. C. McIntosh, 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 (2010). doi: 10.1016/j.apgeochem.2010.01.001
33. E. W. Boyer, B. R. Swistock, J. Clark, M. Madden, D. E. Rizzo, "The impact of Marcellus gas drilling on rural drinking water supplies" (The Center for Rural Pennsylvania, Pennsylvania General Assembly, www.rural.palegislature.us/documents/reports/Marcellus_and_drinking_water_2011_rev.pdf, 2012).
34. N. R. Warner *et al.*, Geochemical evidence for possible natural migration of Marcellus Formation brine to shallow aquifers in Pennsylvania. *Proc. Natl. Acad. Sci. U.S.A.* **109**, 11961 (2012). doi: 10.1073/pnas.1121181109; pmid: 22778445
35. T. M. Kresse *et al.*, *U.S.G.S. Scientific Investigations Report 2012-5273* (2012).
36. G. Bol, H. Grant, S. Keller, F. Marcassa, J. de Rozieres, *Oilfield Rev.* **3**, 35 (1991).
37. A. Bonnett, D. Pafitis, *Oilfield Rev.* **8**, 36 (1996).
38. V. Gonzalo, B. Aiskely, C. Alicia, in *SPE Latin American and Caribbean Petroleum Engineering Conference, Society of Petroleum Engineers International* (Rio de Janeiro, Brazil, 2005).
39. M. J. Rogers, R. L. Dillenbeck, R. N. Eid, *Society of Petroleum Engineers*, 90829 (2004).
40. M. B. Dusseault, M. N. Gray, *Society of Petroleum Engineers*, 64733 (2000).
41. J. M. Tinsley, E. C. Miller, D. L. Sutton, *Society of Petroleum Engineers*, 8257 (1979).
42. T. D. Hayes, "Marcellus Shale water chemistry" (Appalachian Shale Water Conservation and Management Committee, 2009).
43. J.-P. Nicot, B. R. Scanlon, Water use for Shale-gas production in Texas, U.S. *Environ. Sci. Technol.* **46**, 3580 (2012). doi: 10.1021/es204602t; pmid: 22385152
44. D. Soeder, W. M. Kappell, "Water resources and natural gas production from the Marcellus Shale" (U.S. Geological Survey Fact Sheet 2009-3032, Reston, VA, 2009).
45. B. G. Rahm, S. J. Riha, Toward strategic management of shale gas development: Regional, collective impacts on water resources. *Environ. Sci. Policy* **17**, 12 (2012). doi: 10.1016/j.envsci.2011.12.004
46. E. Barbot, N. S. Vidic, K. B. Gregory, R. D. Vidic, Spatial and Temporal Correlation of Water Quality Parameters of Produced Waters from Devonian-Age Shale following Hydraulic Fracturing. *Environ. Sci. Technol.* **47**, 2562 (2013). doi: 10.1021/es304638h; pmid: 23425120
47. L. O. Haluszczak, A. W. Rose, L. R. Kump, Geochemical evaluation of flowback brine from Marcellus gas wells in Pennsylvania, USA. *Appl. Geochem.* **28**, 55 (2013). doi: 10.1016/j.apgeochem.2012.10.002
48. P. E. Dresel, A. W. Rose, Pennsylvania Geological Survey, 4th series Open File Report OFOG 10-01.0, www.dcnr.state.pa.us/topogeo/pub/openfile/ofog10_01.aspx (2010), p. 48.
49. M. E. Blauch, R. R. Myers, T. R. Moore, B. A. Lipinski, N. A. Houston, paper presented at the SPE Eastern Regional Meeting, Society of Petroleum Engineers SPE 125740, Charleston, WV, 2009.
50. E. L. Rowan, M. A. Engle, C. S. Kirby, T. F. Kraemer, "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 Investigation Report 2011-5135, 2011).
51. M. E. Mantell, in *EPA Hydraulic Fracturing Study Technical Workshop 4. Water Resources Management, Chesapeake Energy* (Oklahoma City, OK, 2011).
52. T. Myers, Potential contaminant pathways from hydraulically fractured shale to aquifers. *Ground Water* **50**, 872 (2012). doi: 10.1111/j.1745-6584.2012.00933.x; pmid: 22509908
53. D. C. DiGiulio, R. T. Wilkin, C. Miller, G. Oberly, "DRAFT: Investigation of Ground Water Contamination near Pavillion, Wyoming" (U.S. Environmental Prodection Agency Office of Research and Development, 2011).
54. U.S. Environmental Protection Agency, "Report to Congress: Management of wastes from the exploration, development, and production of crude oil, natural gas, and geothermal energy" (U.S. Environmental Protection Agency, Washington, DC, 1987).
55. T. Engelder, in *GSA Annual Meeting and Exposition* (Charlotte, NC, 2012); available at https://gsa.confex.com/gsa/2012AM/webprogram/Paper207549.html.
56. T. Engelder, Capillary tension and imbibition sequester frack fluid in Marcellus gas shale.. *Proc. Natl. Acad. Sci. U.S.A.* **109**, E3625 (2012). doi: 10.1073/pnas.1216133110
57. K. Fisher, N. Warpinski, *SPE Prod. Oper.* **27**, 8 (2012).
58. P. R. Wright, P. B. McMahon, D. K. Mueller, M. L. Clark, "Groundwater-Quality and Quality-Control Data for Two Monitoring Wells near Pavillion, Wyoming, April and May 2012" (U.S.G.S. Data Series 718, http://pubs.usgs.gov/ds/718/DS718_508.pdf, 2012).
59. J. E. Saiers, E. Barth, Potential contaminant pathways from hydraulically fractured shale aquifers. *Ground Water* **50**, 826, discussion 828 (2012). doi: 10.1111/j.1745-6584.2012.00990.x; pmid: 23003107
60. K. R. Bruner, R. A. Smosna, "Comparative study of the Mississippian Barnett Shale, Fort Worth Basin, and Devonian Marcellus Shale, Appalachian Basin, DOE/NETL-2011/1478" (Department of Energy, National Energy Technology Laboratory, 2011).
61. C. W. Poth, *Pennsylvania Geol. Surv. Bull.* **M47**, 1 (1962).
62. J. A. Williams, *U.S. Geological Survey Scientific Investigations Report 2010-5224* (2010).
63. US DOE, "Cost-Effective Recovery of Low-TDS Frac Flowback Water for Re-use" (U.S. Department of Energy, www.netl.doe.gov, 2011).
64. J. M. Wilson, J. M. VanBriesen, *Environ. Pract.* **14**, 288 (2012). doi: 10.1017/S1466046612000427
65. B. D. Lutz, A. N. Lewis, M. W. Doyle, Generation, transport, and disposal of wastewater associated with Marcellus Shale gas development. *Water Resour. Res.* **49**, 647 (2013). doi: 10.1002/wrcr.20096
66. D. M. Kargbo, R. G. Wilhelm, D. J. Campbell, Natural gas plays in the Marcellus Shale: challenges and potential opportunities. *Environ. Sci. Technol.* **44**, 5679 (2010). doi: 10.1021/es903811p; pmid: 20518558
67. K. B. Gregory, R. D. Vidic, D. A. Dzombak, Water Management Challenges Associated with the Production of Shale Gas by Hydraulic Fracturing. *Elements* **7**, 181 (2011). doi: 10.2113/gselements.7.3.181

68. C. E. Clark, J. A. Veil, "Produced Water Volumes and Management Practices in the United States, ANL/EVS/R-09/1" (Environmental Science Division, Argonne National Laboratory, 2009).
69. C. J. de Pater, S. Baisch, "Geomechanical study of Bowland Shale seismicity, Synthesis Report" (Cuadrilla Resources, Ltd., 2011).
70. Reuters, "Ohio earthquake was not a natural event, expert says," *Reuters*, 2012.
71. National Academy of Sciences, *Induced Seismicity Potential in Energy Technologies* (National Academies Press, Washington, DC, 2012).
72. Texas Department of Agriculture, "Agricultural Land and Water Contamination from Injection Wells, Disposal Pits, and Abandoned Wells Used in Oil and Gas Production" (TX Department of Agriculture, Department of Natural Resources, 1985).
73. K. J. Ferrar *et al*., *Environmental Science & Technology*, dx.doi.org/10.1021/es301411q (2013).
74. D. J. Rozell, S. J. Reaven, Water pollution risk associated with natural gas extraction from the Marcellus Shale. *Risk Anal.* **32**, 1382 (2012). doi: 10.1111/j.1539-6924.2011.01757.x; pmid: 22211399
75. PA DEP, "Wastewater Treatment Requirements, 25 PA Code 95" (Pennsylvania Department of Environmental Protection, 2010).
76. J. R. Mullaney, D. L. Lorenz, A. D. Arntson, "Chloride in Groundwater and Surface Water in Areas Underlain by the Glacial Aquifer System, Northern United States" (U.S. Department of the Interior, U.S. Geological Survey, Scientific Investigations Report 2009-5086, 2009).
77. E. C. Chapman *et al*., Geochemical and strontium isotope characterization of produced waters from Marcellus Shale natural gas extraction. *Environ. Sci. Technol.* **46**, 3545 (2012). doi: 10.1021/es204005g; pmid: 22360406
78. S. L. Brantley, C. Wilderman, J. Abad, Workshop discusses database for Marcellus water issues. *Eos Trans. AGU* **93**, 328 (2012). doi: 10.1029/2012EO340006
79. Shale Network database is accessible through HydroDesktop (www.cuahsi.org).
80. S. States *et al*., paper presented at the AWWA-WQTC, Phoenix, AZ, November 13 to 17, 2011.
81. K. O. Maloney, D. A. Yoxtheimer, Production and Disposal of Waste Materials from Gas and Oil Extraction from the Marcellus Shale Play in Pennsylvania. *Environ. Pract.* **14**, 278 (2012). doi: 10.1017/S146604661200035X
82. C. Kuijvenhoven *et al*., paper presented at the Shale Gas Water Management Conference, Dallas, TX, November 30 to December 1, 2011.
83. R. D. Vidic, T. D. Hayes, S. Hughes, in *Shale Gas Water Management Marcellus Initiative* (Pittsburgh, PA, 2011).
84. W. M. Kappell, E. A. Nystrom, Dissolved methane in New York groundwater, 1999–2011. U.S. Geological Survey Open-File Report 2012-1162 (2012); available at http://pubs.usgs.gov/of/2012/1162.
85. J. S. White, M. V. Mathes, "Dissolved-gas concentrations in ground water in West Virginia" (U.S. Geological Survey Data Series 156, 2006).

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Science

Impact of Shale Gas Development on Regional Water Quality

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Fracturing Hydrology?

Hydraulic fracturing, widely known as "fracking," is a relatively inexpensive way to tap into what were previously inaccessible natural gas resources. **Vidic *et al.*** (p. 826) review the current status of shale gas development and discuss the possible threats to water resources. In one of the hotbeds of fracking activity, the Marcellus Shale in the eastern United States, there is little evidence that additives have directly entered groundwater supplies, but the risk remains. Ensuring access to monitoring data is an important first step toward addressing any public and environmental health concerns.