

Groundwater Protection and Unconventional Gas Extraction: The Critical Need for Field-Based Hydrogeological Research

by R.E. Jackson¹, A.W. Gorody², B. Mayer³, J.W. Roy⁴, M.C. Ryan³, and D.R. Van Stempvoort⁴

Abstract

Unconventional natural gas extraction from tight sandstones, shales, and some coal-beds is typically accomplished by horizontal drilling and hydraulic fracturing that is necessary for economic development of these new hydrocarbon resources. Concerns have been raised regarding the potential for contamination of shallow groundwater by stray gases, formation waters, and fracturing chemicals associated with unconventional gas exploration. A lack of sound scientific hydrogeological field observations and a scarcity of published peer-reviewed articles on the effects of both conventional and unconventional oil and gas activities on shallow groundwater make it difficult to address these issues. Here, we discuss several case studies related to both conventional and unconventional oil and gas activities illustrating how under some circumstances stray or fugitive gas from deep gas-rich formations has migrated from the subsurface into shallow aquifers and how it has affected groundwater quality. Examples include impacts of uncemented well annuli in areas of historic drilling operations, effects related to poor cement bonding in both new and old hydrocarbon wells, and ineffective cementing practices. We also summarize studies describing how structural features influence the role of natural and induced fractures as contaminant fluid migration pathways. On the basis of these studies, we identify two areas where field-focused research is urgently needed to fill current science gaps related to unconventional gas extraction: (1) baseline geochemical mapping (with time series sampling from a sufficient network of groundwater monitoring wells) and (2) field testing of potential mechanisms and pathways by which hydrocarbon gases, reservoir fluids, and fracturing chemicals might potentially invade and contaminate useable groundwater.

Introduction

Increased natural gas extraction from low-permeability rocks (rather than traditional permeable reservoirs) has transformed the outlook for electricity

¹Corresponding author: Geofirma Engineering Ltd., 11 Venus Crescent, Heidelberg, Waterloo Region, Ontario, Canada; rjackson@geofirma.ca

²Universal Geoscience Consulting, Inc., 1214 West Alabama Street, Houston, TX; awgorody@gmail.com

³Department of Geoscience, University of Calgary, Calgary, Alberta, Canada; bmayer@ucalgary.ca; cryan@ucalgary.ca

⁴National Water Research Institute, Environment Canada, Burlington, Ontario, Canada; jim.roy@ec.gc.ca; dale.vanstempvoort@ec.gc.ca

Received December 2012, accepted April 2013.

© 2013, National Ground Water Association.

doi: 10.1111/gwat.12074

generation, building heating, industry, and transportation in North America over a mere 10 years (MIT 2011). The economic development of unconventional gas reservoirs has been spurred by recent advances in both directional drilling and reservoir stimulation by hydraulic fracturing. Deep and long horizontal wells (up to 3 km or 9000 ft in horizontal length) combined with multi-stage hydraulic fracturing can now effectively exploit geographically extensive (Figure 1), often relatively thin (tens of meters) formations that contain unconventional hydrocarbon resources, resulting in an increased supply of natural gas and a commensurate increase in gas use in North America; between 1989 and 2009, 88% of the 306 GW of electrical generation capacity constructed in the United States was gas-fired. Gas-fired energy now provides about one quarter of U.S. energy uses (MIT 2011),

approximately 90% of which comes from U.S. gas-field production and approximately 10% from Canadian fields (U.S. Energy Information Administration 2012).

Unconventional gas resource developments have occurred both in frontier areas and areas with historic conventional oil and gas development (Figure 1). While conventional gas extraction activities are typically focused in well-defined, spatially restricted areas above oil and gas reservoirs, unconventional gas fields are developed on the premise that the gas-bearing formations are widely distributed in the subsurface. Unconventional gas wells are thus typically drilled in densely spaced and equidistant surface patterns that cover far larger subsurface areas than conventional plays. Although recent advances in directional drilling technology permit over 20 horizontal wells to be drilled from a single well pad, large numbers of well pads can still create extensive regional footprints.

The rapid expansion of the unconventional gas industry has been accompanied by public concern regarding protection of environmental and human health particularly over possible pollution of shallow groundwater¹ by migration of natural gas, formation water, and/or fracturing fluids from deep formations induced by hydraulic fracturing. In some jurisdictions—New York State, France, and Québec (Canada) for example—explicit or de-facto moratoria on hydraulic fracturing exist until uncertainties surrounding the process have been resolved. Indeed many articles in newspapers, journals, and the electronic news media regarding pollution of groundwater by the hydraulic fracturing industry (e.g., Zoback et al. 2010; Molofsky et al. 2011; Osborn et al. 2011; Myers 2012; Schnoor 2012; Warner et al. 2012) convey widely differing views regarding risks of groundwater contamination by the development of unconventional gas plays. Unfortunately, little peer-reviewed scientific information is available on the hydrogeological conditions—shallow groundwater quality in particular—associated with unconventional gas production or, for that matter, with conventional oil and gas production. There is a distinct possibility such moratoria will continue until more objective scientific information is available.

As an example of widely differing views, a recent national review in the UK concluded that while it may be possible to propagate a fracture to the ground surface from deep unconventional reservoirs (i.e., more than 2000 m or more than 6000 ft) by hydraulic fracturing, it is generally not practically feasible to do so because the pressures required to increase the fracturing over the full depth are not tractable in hydraulic stimulation (UK Royal Society/Royal Academy of Engineering 2012). In contrast,

an article in this Journal (Myers 2012) suggested that under some conditions there could be surface discharge of fracturing fluids along naturally occurring fractures in less than 10 years after hydraulic fracturing of unconventional gas wells.

Widely differing views, such as those expressed above (the UK's Royal Society/Royal Academy of Engineering [2012] vs. Myers [2012]) clearly indicate the need for a more comprehensive and conclusive knowledge base. This is best approached with more extensive field and laboratory-based research, which is needed to support the development of groundwater models with well-defined hydrogeological settings, calibrated parameter values, and appropriate initial and final boundary conditions. This Issue Paper identifies issues and related hydrogeological research needs and approaches that will help protect groundwater quality during the development of unconventional gas resources. As such, we outline a new challenge in contaminant hydrogeology. Addressing this challenge will require an improved cooperation and communication between hydrogeological researchers and industry, ideally through collaborative research.

To support our case, we briefly describe the nature of unconventional gas production activities as they relate to identifying contaminants of concern. We discuss the potential contaminant migration pathways to shallow groundwater and the behavior of these contaminants in shallow groundwater and factors affecting aquifer vulnerability. We stress that many of these problems are also common to conventional hydrocarbon production activities and are not solely related to unconventional gas production. Finally we address the field-based hydrogeological research needs necessary to help protect groundwater quality during the development of unconventional gas resources and briefly describe how such research might be conducted.

Stimulation and Extraction of Unconventional Gas

The recovery of economic volumes of unconventional natural gas from low permeability and regionally extensive formations requires stimulation through hydraulic fracturing—that is, “fracing” or “fracking”—of the host rock. Hydraulic fracturing has been conducted in vertical boreholes since the 1940s for enhanced conventional production of oil and gas.

The increasingly long horizontal wells (most laterals are more than 1 km or more than 3000 ft) with an increasing number of fracturing stages (Tutuncu et al. 2012) used in unconventional gas production require substantially higher hydraulic fracturing-fluid injection volumes, however. For example, water-based hydraulic fracturing of the Horn River Basin (British Columbia, Canada) requires approximately 50,000 m³ of fluid (10–20 million gallons) and approximately 2000 metric tons of proppant per horizontal well with 20 fracs per well (Johnson and Johnson 2012). Similarly, 7700 to 38,000 m³ of fluid (2–10 million gallons) is used to fracture each horizontal deep well in the

¹We use the term “shallow groundwater” throughout this article as a short-hand to indicate potable or otherwise useable water with a total dissolved solids (TDS) content of less than 1,000 mg/L that is—or may in future—be used as a groundwater supply for homes, farms, industries or municipalities. Thus the term “groundwater protection” refers to the protection of this groundwater, while “saline groundwater” and “saline aquifers” indicate waters with higher TDS, typically more than 4,000 mg/L, which are not suitable for human or livestock consumption.

Shale Gas Overview

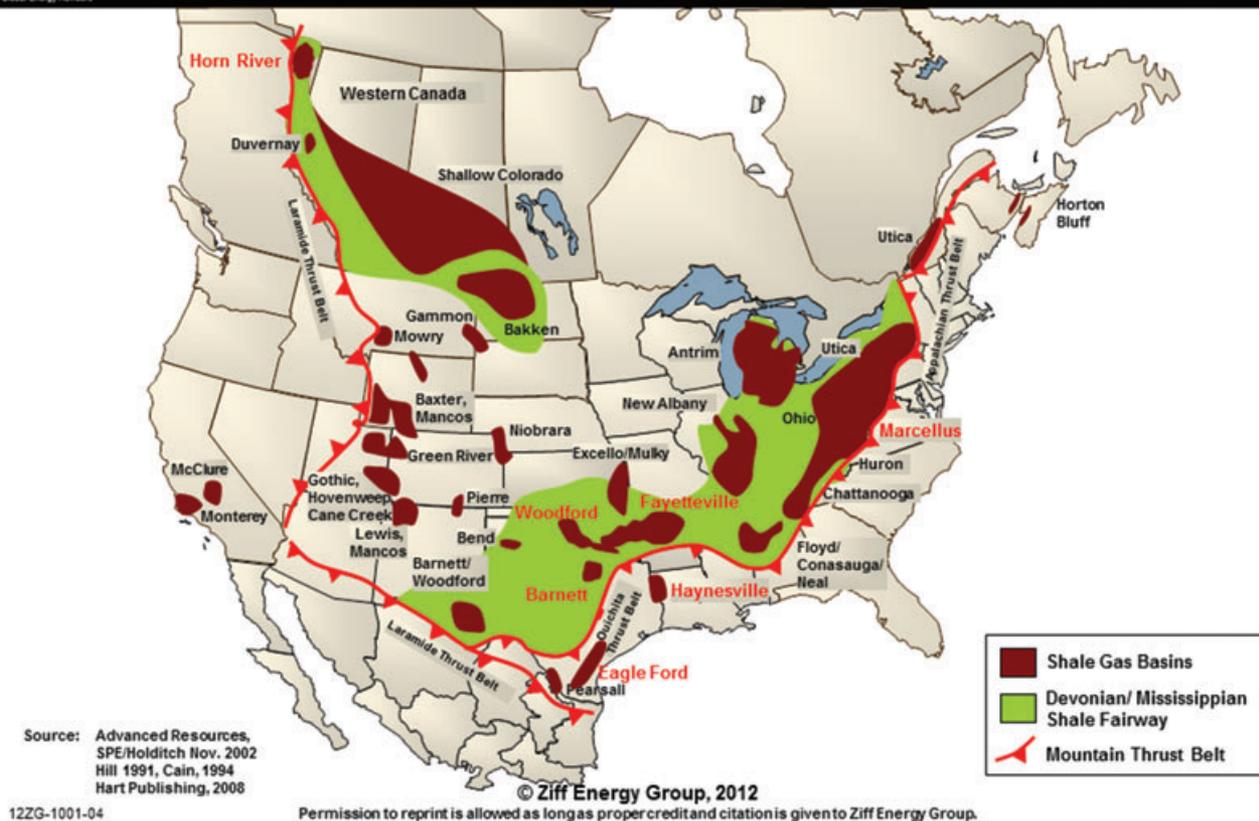


Figure 1. Distribution of shale gas plays in North America. Note that other unconventional formations (e.g., tight-gas, sandstones, and coal formations) are not shown. (Courtesy of Ziff Energy Group, Calgary, 2012.)

Marcellus Shale in the northeastern United States (Kargbo et al. 2010). Because water used in hydraulic fracturing can imbibe into the host rock's matrix and reduce gas relative permeability (and hence gas production), nonaqueous based fracturing fluids (Table 1; e.g., Lestz et al. 2007) provide an alternative approach that also assists with water supply and gas recovery issues.

Hydraulic fracturing is conducted sequentially in "stages" or perforated sections of the horizontal production casing (Figure 2), and involves the injection of fluids (gases, liquids, foams), with a mix of additives (discussed below), at elevated hydraulic pressures around each "stage" to produce and propagate fractures. The fractures increase the bulk formation permeability through shear failure (see Zoback et al. 2012), allowing hydrocarbon gases to flow into the production well. The hydraulic fracturing liquids are designed to conduct proppants (e.g., sand and other noncrushable substances; Table 1) that enter the new fractures formed in shales and tight sandstones, preventing them from reclosing.

Hydraulic fracturing-induced fractures predominantly develop in the plane perpendicular to the orientation of the least principal stress, which in deep shale gas reservoirs (more than 2 km or more than 6000 ft) is usually one of

the two horizontal stresses (Zoback 2010). In some cases "preferential opening of the natural fracture systems" is more dominant than opening of new hydraulic fractures (King 2010). While "pre-existing fractures and faults have some influence on fracture propagation, the overall trajectory of fracture propagation is controlled by the orientation of the least principal stress" (Zoback 2010).

While most shale gas plays in North America are deeper than one kilometer, a few shallower plays are exploited to a limited extent (e.g., the eastern extent of the Colorado Group in Alberta (~300 m depth) and the Antrim Shale in Michigan [180 to 670 m]). Many coal-bed gas formations are also present at shallower depths (less than 600 m), where vertical wells that are typically fracked with nitrogen (NEB 2009) and horizontal fracturing orientation predominate. Empirical data suggest that horizontal fracturing predominates in stimulation conducted shallower than 450 m depth, while vertical fracture orientations predominate below 600 m depth (Warpinski 2011), because of the principal stress orientations. This is because at these shallow depths within the overburden the direction of least principal stress is vertical due to erosional unloading that has occurred in sedimentary basins (for discussion see Goodman, 1989

Table 1
Composition of Fluids Potentially Present in Fracking Fluids

Component and Purpose	Chemical
Carrier or “make-up” fluid	Water, N ₂ , CO ₂ , LPG, foams, emulsions
Proppants—designed to keep fractures open after fracking fluid pressure decreases	Sand, resin-coated sand, sintered bauxite, alumina, ceramics, and silicon carbide
Clean up damage from initial drilling, initiate fracturing	HCl, other acids
Additives to adjust frack fluid viscosity, and form gels—designed to keep proppants suspended in frack fluid so it will enter and “prop open” new fractures	Viscosity adjusters: Guar gum, cellulose-based derivatives. Gel formation: Cross-linking agents (borate compounds or metal complexes)
Viscosity “breakers” (reducers) designed to decrease viscosity after frack fluid has reached its target zone	Ammonium persulfate, sodium peroxydisulfate
Stabilizers to delay the action of breakers, biocides, fluid-loss additives, friction reducers	Latex polymers or copolymers of acrylamides, and acid corrosion inhibitors, e.g., alcohols
Acid corrosion or scale inhibitors	Isopropanol, methanol, formic acid, acetaldehyde
Friction reducers for low-viscosity “slickwater” fracking where proppants penetrate more deeply into fractures	Surfactants, polyacrylamide, ethylene glycol
Biocides to inhibit sulfate reducers	Aldehydes, amides
Surfactants to improve relative gas permeability	Isopropanol
Clay stabilizer to prevent clay flocculation	KCl (for clays)
Other	Glycols, amines, defoamers

Sources: Lyons and Plisga 2004; Kaufman et al. 2008, MIT 2011; US EPA 2011; van Stempvoort and Roy, 2011, and Schlumberger (www.slb.com), and OpenFrac.com.

and Zoback 2010). Data from tiltmeters and microseismic imaging also indicate that mixed vertically and horizontally oriented fractures are often generated when stimulating reservoirs at depths below 450 m and above 2 km.

Fracture growth monitoring by microseismic and microdeformation techniques suggests that induced vertical fracture heights do not exceed “tens to hundreds of feet” (Fisher and Warpinski 2012). The evidence available is largely related to remotely measured or modeled fracture propagation. For instance, the empirical analyses of microseismic data from several thousand fracturing operations in four U.S. shale gas plays by Davies et al. (2012) indicated a maximum fracture height of approximately 590 m and a probability estimate of approximately 1% that a stimulated hydraulic fracture would extend vertically more than 500 m. From this, the authors (Davies et al. 2012) derived a general minimum separation distance of 600 m between target shale and overlying freshwater aquifers but they also suggested that minimum separation distances be investigated for each new geologic area.

However, a Society of Exploration Geophysicists research committee has reported that “downhole microseismic monitoring has limited spatial coverage creating a bias at the event locations and an incomplete view of the stimulated reservoir volume” (Tutuncu et al. 2012). Reducing this bias would require one or more shallow (30 to 60 m deep) boreholes drilled exclusively for seismic monitoring (which, notably, could be used for subsequent groundwater monitoring). A related technique, near surface microseismic data acquisition, has also recently been adopted for hydraulic fracturing monitoring (Duncan and

Table 2
Composition of Inorganic Ions in Flow-back Fluids from Three U.S. Shale Plays

Analytes (mg/L)	Formation		
	Fayetteville	Marcellus	Barnett
Na	5363	24,445	12,453
Mg	77	263	253
Ca	256	2921	2242
Sr	21	347	357
Ba	0.8	679	42
Mn	0.5	3.9	44
Fe	28	26	33
SO ₄	149	9.1	60
HCO ₃	1281	261	289
Cl	8042	43,578	23,798
TDS	15,219	72,533	39,570
Sp Gravity	1.01	1.05	1.03
Depth (m)	300–2000	1200–2600	2000–2600

Source: Aqua-Pure Ventures, Calgary, Alberta, http://www.fountainquail.com/news/presentations/assets/IOGCC_Shale_Gas_Water_Mngt.pdf.

Eisner 2010) to improve the estimation of the reservoir volumes that are stimulated by hydraulic fracturing, identify subsurface faults, and monitor posthydraulic fracturing microseismic activity after the hydraulic fracturing pumps are turned off (Wessels et al. 2011).

“Flow-back fluids” are extracted from the gas well after hydraulic fracturing to improve relative gas permeability and enhance gas production. These fluids (Table 2) initially tend to be comprised mainly of the

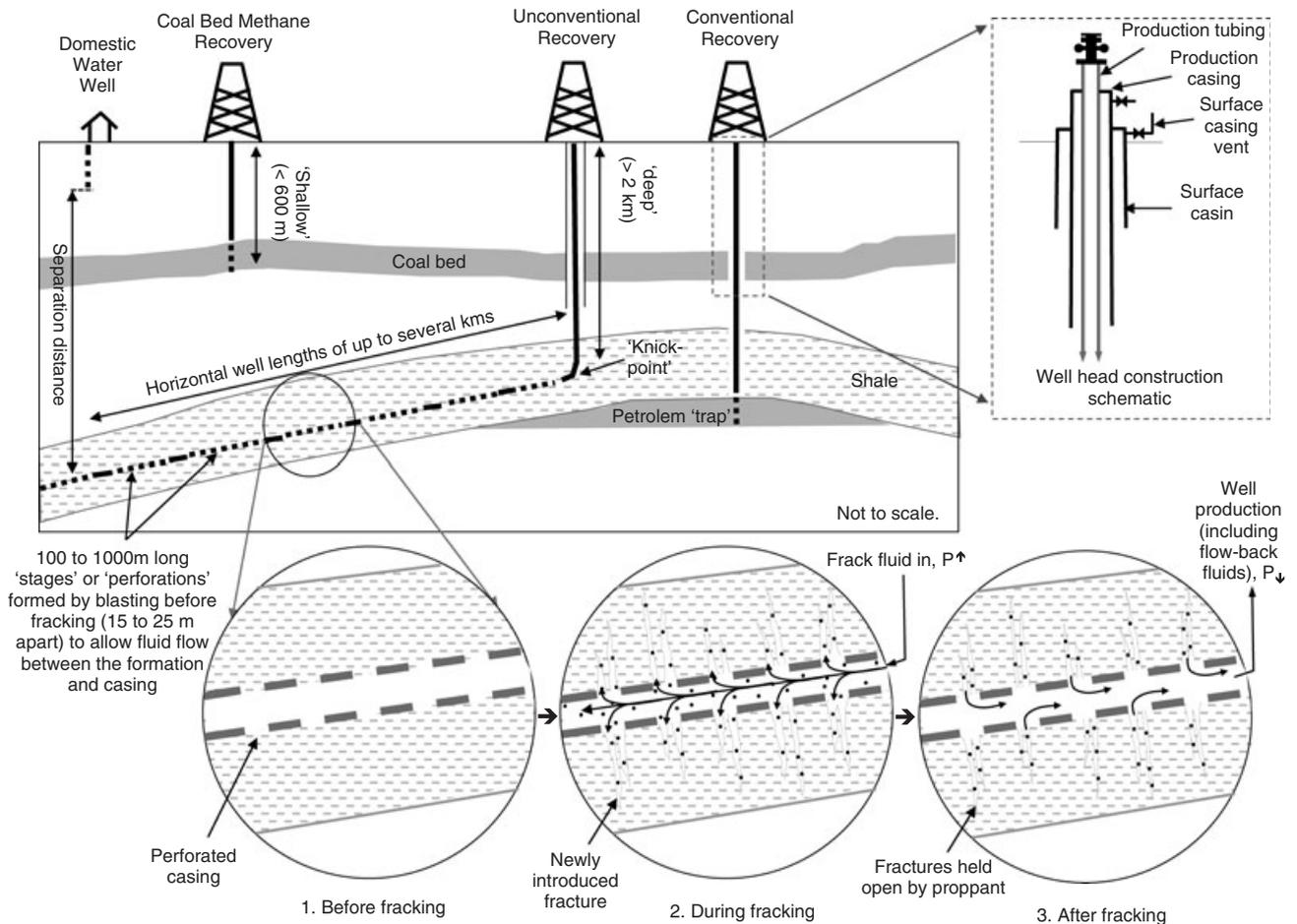


Figure 2. Schematic illustrating (i) the nature of conventional, coal-bed methane, and “unconventional” resource recovery, (ii) the hydraulic fracturing process; and (iii) the nature of surface and production casing (and associated borehole annulus cementing).

injected fracturing fluids, but with continued production an increasing contribution may come from formation waters if the formation contains “movable fluids,” that is, they exhibit higher than irreducible water saturation. Injected fluids can react with the host formation and leach both salts and radionuclides that change flow-back water quality.

These flow-back fluids usually require on-site storage followed by recycling, reinjection, or deep-well disposal into a saline aquifer. The potential for groundwater contamination by flow-back fluids is therefore quite varied. For example, flow-back fluids may contaminate shallow groundwater due to releases from lagoons during extreme precipitation events or failure of the impoundments. Consequently, regulatory agencies have increasingly required on-site storage containers (and lagoons) to be covered to prevent such releases (e.g., ERCB 2011).

Contaminants of Concern

Groundwater can be affected during unconventional gas production by substances associated with natural gas itself, that is, principally methane (US NIOSH 1983). The primary problem with methane in shallow aquifers is that

it poses both an explosion and asphyxiation (confined spaces) hazard either during well water extraction or by escaping and accumulating in basements, well pits, etc. The American Conference of Governmental Industrial Hygienists’ (ACGIH) methane exposure limit in air is 1000 ppm (time-weighted average). Many jurisdictions require reporting for “trigger levels” of dissolved methane in well water (e.g., 28 mg/L is a “recommended action level” from the U.S. Department of the Interior Office of Surface Mining Reclamation and Enforcement; US DOI 2001).

Within shales, we may expect roughly equal gas-phase and water-phase porosities, that is, saturations (Curtis 2002). However, methane dissolved in formation waters will have a solubility controlled by the temperature, hydraulic pressure, and salinity of the formation (Duan et al. 1992) that is likely far greater than the solubility of methane in groundwater at ground-surface temperatures and atmospheric pressure ($\sim 30\text{ mg CH}_4/\text{L}$). By fracturing the gas reservoir, an operator removes some formation water to increase the relative gas permeability and recovers the gas as it desorbs, depressurizes (decreasing the bubbling pressure), enters the fractures and is extracted (see Figure 2). If this gas is not captured,

it is available to migrate as the buoyant free gas phase up the annulus of poorly cemented wells.

Free gas exsolving or bubbling through water in water wells may also lead to deterioration of water quality including well water discoloration and turbidity due to microbubbles or particulate suspension (Harrison 1983; Bair et al. 2010; Gorody 2012). Microbiologically-mediated oxidation of free and dissolved hydrocarbons (e.g., methane) can be accompanied by iron and sulfate reductions leading to Fe(II) and/or Mn(II) sulfide mineral precipitation, and the attendant odor of reduced gases such as H₂S (Rauch 1983; Kelly et al. 1985; Gorody 2012). Free gases in groundwater around well screens can also cause a decrease in hydraulic conductivity with an associated decrease in water well yield (Yager and Fountain 2001; Gorody 2012). “Stray gas” or “fugitive gas” is one of the main concerns around unconventional gas recovery. Chemical and isotopic analyses (see Box 1) are used to differentiate between “thermogenic” gases produced from the target reservoirs, mixed gases from intermediate formations, and “biogenic” gases most frequently found in shallower geologic formations and aquifers.

Box 1

Geochemistry of Natural Gas

Natural gas forms in the subsurface by the transformation of organic matter to methane (CH₄ or C₁) and potentially other low molecular weight, volatile hydrocarbons such as ethane (C₂H₆ or C₂) and propane (C₃H₈, or C₃). This can occur through anaerobic microbial reactions such as methanogenesis resulting in “biogenic” or “bacterial” gas mainly composed of CH₄, or by abiotic processes at elevated temperatures and pressures, resulting in “abiogenic”, “thermocatalytic”, or “thermogenic” natural gas. The latter often contains not only methane (C₁) and ethane (C₂), but also higher alkanes such as propane (C₃), butane (C₄), and pentane (C₅).

Over the course of the last 30 years the natural formation of biogenic and thermogenic methane has been documented to occur in a wide array of anaerobic environments (e.g., Barker and Fritz 1981; Schoell 1988; Whiticar 1999). Biogenic methane is commonly associated with organic-rich marine and lacustrine sediments, peat, and coal deposits and is generated in low-temperature and -pressure environments. For some shallow aquifers in Alberta (Taylor et al. 2000) and Texas (Grossman et al. 1989) it has been suggested that not only methane but also ethane is generated by biogenesis. In other shallow aquifers in Ontario (Aravena et al. 1995), Illinois (Coleman et al. 1988) and

Iowa (Simpkins and Parking 1993) only biogenic methane has been found. The absence of propane, butane, and pentane in biogenic natural gas results typically in wetness parameters (the ratio of C₁/C₂-C₅) > 1000. Thermogenic methane is created under high temperatures (>120 °C) and pressures (50–80 MPa) found at depth (>2500 m) within sedimentary basins (Hunt 1979; Barker 1990). Due to often appreciable amounts of ethane, propane, butane, and pentane in thermogenic gas its wetness parameter is typically much lower than 1000. Coal-bed gas systems can contain thermogenic, migrated thermogenic, biogenic, or mixed (thermogenic and biogenic) gas. Mixed gas may be produced through a variety of mechanisms including the incursion of Pleistocene meltwaters into sedimentary basins containing organic-rich shales (Martini et al. 2003).

Natural gas formed through these different processes and in different formations can be distinguished by a suite of geochemical and isotopic analyses. These include the concentrations of methane (C₁), ethane (C₂), propane (C₃), butane (C₄), and pentane (C₅), the stable carbon and hydrogen isotope ratios contained within these normal alkanes, as well as ¹⁴C, which allows discrimination between recent biogenic and fossil thermogenic hydrocarbons. The upper figure presents a cross-plot of δ¹³C and δ²H values of biogenic and thermogenic methane for selected shallow aquifers and resource plays in North America. δ¹³C values predominantly < -55‰ in shallow groundwaters of Alberta and selected groundwater wells from Pennsylvania suggest that the methane is of biogenic origin (Cheung et al. 2010; Osborn and McIntosh 2010). In contrast, thermogenic and mixed gas from various resource plays is typically characterized by δ¹³C values > -60‰ and sometimes higher δ²H values (Jenden et al. 1993; Desrocher 1997; Laughrey and Baldassare 1998; Martini et al. 2003; Hill et al. 2007; Cheung et al. 2010; Osborn and McIntosh 2010; Rodriguez and Philip 2010; Tilley et al. 2011; Tilley and Muehlenbachs 2013) compared to those found for biogenic methane. This graph is typically known as a Schoell (1988) diagram. The lower figure shows a Bernard diagram where biogenic gas is typically distinguished by δ¹³C values < -55‰ and wetness parameters more than 1000 (Cheung et al. 2010; Osborn and McIntosh 2010) from thermogenic gases that are often characterized by δ¹³C values of methane > -60‰ and wetness parameters less than 1000 (Jenden et al. 1993; Desrocher 1997; Laughrey and Baldassare

1998; Martini et al. 2003; Hill et al. 2007; Cheung et al. 2010; Osborn and McIntosh 2010; Rodriguez and Philip 2010; Tilley et al. 2011).

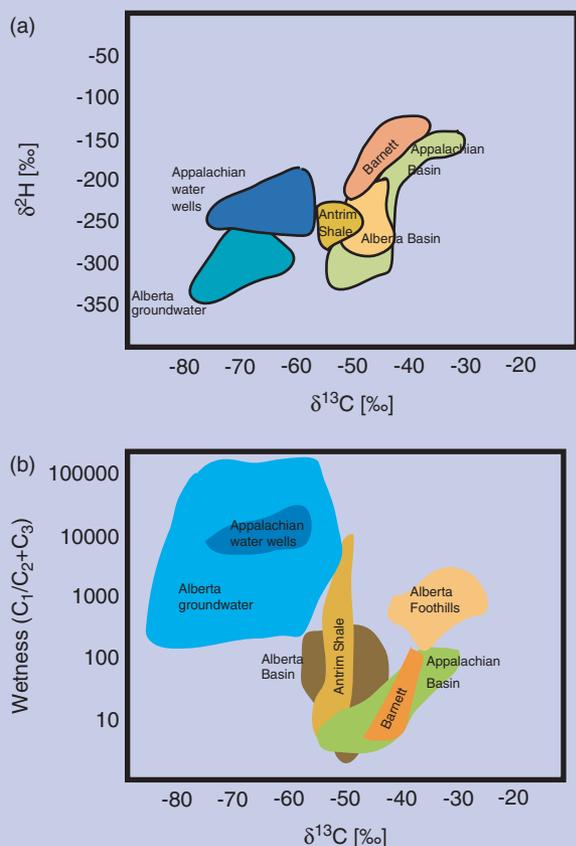


Figure for Box 1. Schoell (upper) and Bernard (lower) diagrams displaying the $\delta^{13}\text{C}$ values of methane vs. $\delta^2\text{H}_{\text{CH}_4}$ values (Schoell) and gas wetness (Bernard) in shallow groundwater of Alberta (Cheung et al. 2010, unpublished data) and Pennsylvania (Osborn and McIntosh 2010), and various natural gas plays in Northern America (Jenden et al. 1993; Desrocher 1997; Laughrey and Baldassare 1998; Martini et al. 2003; Hill et al. 2007; Cheung et al. 2010; Osborn and McIntosh 2010; Rodriguez and Philip 2010; Tilley et al. 2011).

There is much public concern that specific chemicals present in fracturing fluids may pollute shallow groundwater in the vicinity of unconventional gas sites. Fracturing fluids may be based on, or made up with, a number of fluids (water, hydrocarbon, emulsions, foams, or gases, e.g., N_2 or CO_2), and may contain a wide range of chemical additives (Table 1 and Van Stempvoort and Roy 2011). Access to information about the chemical composition of hydraulic fracturing fluids and additives is emerging as appropriate information databases are published (e.g., <http://fracfocus.org/>).

Shallow groundwater might also become contaminated by natural liquids from the producing formation, including saline formation waters and gas condensates (Box 2). Formation waters are usually Na-Cl saline fluids or brines with elevated total dissolved solids and can contain naturally occurring heavy metals (e.g., barium) and radionuclides (e.g., ^{226}Ra from decay of natural ^{238}U in the shales). Because of the deleterious effects of saline formation waters or brines on activated sludge processes in municipal treatment plants, the disposal of brines is increasingly directed to injection wells or to recycling facilities where they exist (e.g., Pennsylvania and Texas). Condensates can also have elevated salinity, sodium, metals, naturally occurring radionuclides, and organic compounds (Hitchon et al. 1971; Orem et al. 2007; Kargbo et al. 2010).

Box 2

Defining 'Groundwater Gas' Terms—An Interdisciplinary Challenge States in which “gases” can exist:

- True “gas” state, also known as “free” gas or bubbles.
- *Sorbed* gas—coal-bed gases (i.e., mostly methane) that don’t flow into wells unless the formation pressure is lowered by pumping.
- *Dissolved* gas—gas molecules that are dissolved in water. Dissolved gas concentrations are discussed below.
- *Nonaqueous phase liquid (NAPL)*—many hydrocarbons can occur as an oily liquid. This can also be called “liquid natural gas” or “condensate”.
- Gas *condensate*—hydrocarbons, usually coproduced with (or “condensed from”) natural gas, which are near-liquid at ambient conditions. Typically C_2 to C_{20} compounds.

Terminology

Gasoline or **petrol** is comprised mainly of fractionally distilled petroleum that is liquid under ambient conditions.

Gasoline Range Organic’ (GRO) compounds include four volatile petroleum compounds often known by their acronym “**BTEX**”: benzene, toluene, ethylbenzenes, and xylene. They are commonly used as indicator parameters for gasoline or petrol spills.

Natural Gas is dominantly methane, but can have minor concentrations of CO_2 , H_2S , and C_2 - C_5 hydrocarbons.

Shale Gas (also known as **Unconventional Gas** and **Tight Gas**) is natural gas produced from relatively impermeable formations.

Methane in natural gas can be:

- biogenic—formed by microbial processes (e.g., CO₂ reduction in relatively shallow, low temperature environments)
- thermogenic—formed by “cracking” of organic matter in deeper formations at higher temperature (more than 120 °C). Also called “thermo-catalytic” gas.

Liquefied petroleum gas—gas mixtures that occur in the liquid and/or nonaqueous phase under ambient conditions (e.g., propane and butane).

Wet or associated gas is natural gas with liquid hydrocarbon or condensate phases present.

Dry or nonassociated gas is more than 95% methane (or C₁).

C₁-C_n gases—one of two nomenclature approaches, where the subscript indicates the number of carbons in a chain (aliphatic) or ring (aromatic) structure (for example methane is C₁; ethane, also known as ethylene are C₂, etc.).

“**Wetness**” is often used to characterize natural gas—often estimated as $(C_1/\sum C_{2+3})$ where biogenic gas typically more than 1000 and thermogenic less than 1000. Thermogenic gas often is rich in C₂₊₃ hydrocarbons, whereas biogenic gas is not.

Gas as biogeochemical parameter:

- “**biogeochemical**” gases (formed of carbon, hydrogen, oxygen, nitrogen, and sulfur; e.g., O₂, CO₂, CH₄, N₂, H₂, H₂S, etc.)—gases are produced or consumed in major biogeochemical processes. Almost all of these gases are redox sensitive or redox determining.
- “**permanent**” or “**fixed**” gases have two possible definitions:
 - do not form a liquid phase under near-surface temperatures and pressures—also known as “incondensable” gases;
 - are those gases within the atmosphere with relatively constant (i.e., “permanent”) concentrations (e.g., O₂, N₂, and Ar);
- **inert** gases can be defined as monoatomic gases with low chemical reactivity (e.g., He, Ne, Ar, Kr, Xe, and Rn),

Describing gas “concentration” in the subsurface:

- **Total dissolved gas pressure (TDGP or P_{TGD})**—sum of the partial pressures of all dissolved gases, measured *in situ* or by

using advanced gas sampling and analytical techniques. P_{TGD} can be measured in absolute or gauge (absolute minus atmospheric pressure). At the groundwater table, absolute P_{TGD} is equal to atmospheric pressure and gauge P_{TGD} is equal to zero. Because dissolved gas solubility increases with water pressure (Manning et al. 2003), estimation of true dissolved gas concentrations requires the measurement of *in situ* total dissolved gas pressure (P_{TDG}; Manning et al. 2003) together with gas composition unless advanced sampling and laboratory techniques (Beyerle et al. 2000; Gardner and Solomon 2009) are used. True or *in situ* dissolved gas concentration can be estimated as the product of the lab-estimated dissolved gas concentration (really equivalent to a gas composition since it is measured at the atmospheric pressure in the lab; P_{LAB}) multiplied by the ratio of P_{TDG}:P_{LAB} (McLeish et al. 2007). Dissolved groundwater gas concentrations are at their maximum at a depth in the subsurface (or a given hydraulic pressure) when P_{TDG} is at its “bubbling pressure” (equal to absolute pressure, or the sum of atmospheric and hydraulic pressures; Manning et al. 2003; Roy and Ryan 2010). At this point, the groundwater is saturated with respect to dissolved gases, and increased gas production can result in a phase change to free gas state, or bubble exsolution. Since stray gas migration often involves free gas transport, the P_{TDG} can be compared to the bubbling pressure to determine the likelihood that free gas would be present in a formation. Although the build up, and possibly “pulsed migration”, of free gases (Gorody 2012) can cause significant changes in the mass of gases within a formation, the P_{TDG} may stay at or near the bubbling pressure. In this case, changes with time or space in dissolved gas and isotopic composition may be more diagnostic than changes in P_{TDG}.

- **Gas composition** is the relative concentrations of different gases as a percentage of all gases. Gas compositions can be expressed as equivalent volumetric ratios (i.e., ppmv) or volume percentages in the gas phase. When they are at STP (Standard Temperature & Pressure), gas compositions can be equal to gas concentrations if they are expressed as volume ratios (e.g., the atmosphere is 78.1% N₂, or 780,900 ppmv).
- **Dissolved gas concentration** is
 - the mass of a gas per unit volume of water (or unit mass of water for brines).

Common dissolved gas units are (1) mg/L or mmol/L; (2) $\text{cm}^3_{\text{STP}}/\text{L}$ or ppmv, or (3) equivalent partial pressure of gas phase (atm or mm Hg). If units like ppmv are used, care needs to be taken to ensure both the units of the gas solute and matrix (i.e., mass or volume; gas or liquid state of matrix) are clearly stated;

- limited by formation of free gas or mass transfer with free gas at the “bubbling pressure”;
- a function of Henry’s Law (temperature and salinity dependent) and the *in situ* partial pressure of the gas of interest;
- Although *dissolved gas concentrations* are often estimated by “headspace extraction” (Kampbell and Vandegrift 1998), this technique is only valid if the P_{TDG} is close to water equilibrated with the atmosphere (i.e., absolute P_{TDG} equal to atmospheric pressure).
- **Bubbling pressure** is reached when P_{TDG} is equal to the hydrostatic pressure. If P_{TDG} increases past this pressure, mass transfer into the free gas phase should occur—i.e., exsolution, field effervescence, bubbling.
- **gas solubility** is the maximum concentration of a gas that can exist in water at specific salinity, temperature, and (hydrostatic) pressure in combination with the other gases in the same water.

Gas “Saturation” can have multiple meanings:

1. The relative proportion of gas phase to total porosity (also known as gas porosity) within subsurface pore space. The presence of a free gas phase implies that there is a measureable gas saturation, S_g , in the pore volume (PV) such that the PV is “saturated” with gas (S_g), water (S_w) and perhaps oil (S_o) in which $PV = S_g + S_w + S_o$.
2. Critical gas saturation (in coal-bed methane) is the gas saturation (or gas porosity) upon which coal yields gas when pumped. Gas saturation can be increased by decreasing the formation pressure (and hence decreasing the critical bubbling pressure).
3. *Dissolved gas* saturation occurs when the P_{TDG} is equal to the *bubbling pressure*.

Stray or fugitive gas: Terms usually applied to natural gas (or perhaps carbon dioxide) that has escaped from a well or gas-handling facility near the oil or gas well and has been detected in a

location where it is unwanted. In the context of this article, it is natural gas that has migrated into shallow groundwater from a geological source most likely through a poorly or incompletely cemented well.

The State of the Science

Over the past few years numerous editorials, reports, and issue papers have been written about environmental issues related to shale gas development, all of which address groundwater issues to varying extents (e.g., Kargbo et al. 2010; Zoback et al. 2010; Schnoor 2012; ALL Consulting 2012; Groat and Grimshaw 2012; Rozell and Reaven 2012; Tutuncu et al. 2012; UK Royal Society/Royal Academy of Engineering 2012). Many of these contributions are “white papers,” focusing mainly on delineating the potential environmental issues, probable causes, and possible solutions (largely associated with more rigorous regulation and improved industry practices).

Here we address the state of hydrogeologic science, that is, what is known and what is not known, with reference to a series of case histories or grouped study work (Table 3). We argue that a better understanding of the hydrogeologic conditions, gas-migration processes and potential leakage pathways is required—that is, critical science gaps remain—to minimize the potential environmental effects of groundwater contamination by development of unconventional gas plays. The wide range of probabilities used in a recent risk analysis of potential groundwater pollution by hydraulic fracturing (Rozell and Reaven 2012) reflects the lack of field data used in their probability bounds analysis. Many of these probability ranges were based on newspaper articles or were the authors’ “estimates,” which clearly demonstrates the critical science gaps that confront hydrogeologists and regulatory officials as well as risk estimators.

Contaminant Pathways to Shallow Groundwater

Fugitive Gas Leakage from Active Production Wells

Many of the current, well-publicized controversies surrounding unconventional gas development in particular relate likely to the accidental releases of “stray” or “fugitive” gases into shallow aquifers via the annuli of imperfectly cemented gas wells. The source(s) of these stray gases are rarely clear (Bair et al. 2010; Gorody 2012). Although they could include the production zone, the shallower overlying formations in the “intermediate zone” between producing formations and shallow groundwater appear to be a more common source.

In an extensive study comparing the chemical and isotopic compositions of gases from surface casing vent flows (SCVF) and production zones accessed by almost 300 conventional oil and gas wells in Alberta (Canada), the majority of the SCVF samples (~75%) were sourced from formations above the production

Table 3
Case Histories of Gas Migration to Shallow Aquifers and What They Reveal About the Sources, Migration, and Fate of Fugitive Gas

Location	Source of Gas	Outcome	References
Animas River Valley, Colorado and New Mexico	Primarily leaking conventional gas wells and uncemented annuli of conventional gas wells in coal-bed formations. Less important were seeps into buried valley aquifers from gas-bearing sandstone.	Gas well annuli were more important than natural fractures as the primary source of fugitive gas contaminating shallow water wells in the Animas River Valley. Tectonic history important in reducing significance of natural fractures.	Chafin (1994)
Lloydminster, Alberta	Oil well venting natural gas along annulus of well	Contamination of groundwater sampled from monitoring wells in sand and gravel aquifer; isotope geochemistry used to document bacterial sulfate reduction associated with fugitive methane	Van Stempvoort et al. (2005)
Hutchinson, Kansas	Gas release from gas storage caverns apparently due to casing failure and a damaged annular well seal penetrating the storage caverns	Gas migration over 11 km apparently in fractures through a few relatively tight dolostone layers within shale; gas emergence to the surface via abandoned solution mining wells	Allison (2001), Watney et al. (2003)
Bainbridge Township, Ohio	Gas release due to poorly completed primary cement job allowed gas to migrate up surface casing annulus into sandstone aquifer	Gas penetration of the sandstone aquifer which contained numerous water wells. Structural features within sandstone acted as a gas trap resulting in long-term gas release to the water wells.	Bair et al. (2010)
Southern Alberta	Shallow coal-bed methane development with beds approximately 400 m depth	Demonstrated the importance of full geochemical and isotopic analysis to establish baseline shallow groundwater quality and to identify any natural gas that might migrate from producing formations	Cheung et al. (2010)
Southern Alberta	Widespread SCVF and contamination of shallow wells from deeper gas reservoirs	$\delta^{13}\text{C}$ for CH_4 and C_2H_6 and use of mixing curves was able to resolve the origin of methane occurrences in certain water wells. Complete identification of sources requires gas isotope analysis of each potential source formation.	Tilley and Muehlenbachs (2011)
Several U.S. gas fields	Commercial gas wells extracting from a variety of gas reservoirs are associated with shallow groundwater contamination	Surface casing head & produced gases may be different, thus source gases should be sampled repetitively and while drilling, (i.e., mud gas samples). Free and dissolved $\text{CH}_4:\text{C}_2\text{H}_6$ ratios provide the best baseline sampling and analysis criteria to differentiate thermogenic and biogenic fugitive gas sources. Sampling and analysis from a single gas well should be conducted multiple times.	Gorody (2012)

zones, while the remainder of the SCVF samples were often isotopically similar to gases from the production formation (Muehlenbachs 2012; Tilley and Muehlenbachs 2013). Similar measurements recently conducted at newly completed and hydraulically stimulated horizontal shale gas wells in the Montney and Horn River areas of northeastern British Columbia also revealed in some cases SCVF from intermediate zones and in other cases from the production formation (Muehlenbachs 2012; Tilley and Muehlenbachs 2013).

The potential for stray gas migration into shallow aquifers depends on various parameters including reservoir pressures, well completion details, etc., but is often thought to be related to inadequate construction, completion or maintenance of production wells (Chafin 1994). Indeed, unintended natural gas migration along production wellbores for conventional gas has been a “*chronic problem for the oil and gas industry . . . as a result of poor primary cement jobs, particularly in gas wells*” (Stein et al. 2003). Between 7% and 19% of more than 1000 wells drilled from 2005 to 2007 in western Canada had gas migration along the casing annulus, and 9% to 28% of them had gas leakage through surface casing vents (Bexte et al. 2008). Similarly, a 1995 study determined that 15% of primary cement completions in the United States had failed (Dusterhoft et al. 2002).

Uncemented well annuli can become primary migration pathways for stray or fugitive gas migration into shallow aquifers. For example, uncemented well annuli were identified as the principal source of stray gases migrating along vertical wells in the San Juan basin of New Mexico and Colorado (Chafin 1994). Other causes of stray gas migration include casing corrosion (particularly prevalent prior to the advent of cathodic protection) and accidental rupture. Historically, regulators have not required casing cement across formations above the principal production target zone.

The problem of leaky hydrocarbon wells is not confined to a few areas of western Canada and the southwestern states of the United States. A report by Louisiana State University (Bourgoyne et al. 1998) indicated that there were 11,500 strings of casing in over 8000 offshore wells in the Gulf of Mexico that exhibit gas migration in the annular space between casing and rock or within inner casings. The pressure gauges on all casing strings should measure zero pressure after any hydrocarbon well comes to steady state flowing conditions and once the gauge has been opened and the pressure bled off through its needle valve. If continual bleeding off is required, the effect is known as sustained casing pressure (SCP). Brufatto et al. (2003) cite U.S. Mineral Management Service data from the Gulf of Mexico indicating that “by the time a well is 15 years old, there is a 50% probability that it will have measurable SCP in one or more of its casing annuli. However SCP may be present in wells of any age.”

Groundwater monitoring-well data from the immediate vicinity of hydrocarbon wells are very sparse. Van Stempvoort et al. (1996) selected oil and gas well sites

in the Lloydminster area (Alberta and Saskatchewan, Canada) with indications of seepage of natural gas through defective, permeable zones in the surface casing cement sheaths of these vertical wells into soil. These well sites were considered to also be susceptible to seepage of the gas into shallow aquifers. Monitoring wells were installed in shallow aquifers immediately adjacent to these hydrocarbon wells, and subsequent sampling indicated evidence for gas migration along well casings into the groundwater at several of these sites.

It is conceivable that at other well sites, where there is no detectable gas leakage at surface, annular gas flow could be leaking into shallow aquifers that have pore pressures less than the annular gas. This could result from an inadequate surface casing cement seal between an aquifer and a gas source below. Therefore, those wells with records of surface casing vent flow and/or SCP are also more likely to be those with gas seepage into any aquifer meeting this criterion because the aquifer’s capillary entry pressure to gas will be very low. This is one reason why regulators address risk mitigation by requiring operators to routinely monitor casing head pressures and report pressures exceeding predefined thresholds.

Cement grouting in a typical horizontal production well is usually conducted between both surface and intermediate casings and the shallow formations they penetrate to prevent hydrocarbon gases in the deeper formations from entering the casing or borehole annuli and traveling toward more shallow formations (Figure 2). Cement bonding between the well casing and rock is typically verified by a wireline acoustic logging tool known as a “cement bond log” (CBL), which will clearly identify the absence of a cement sheath over long pipe lengths of a few meters or more (i.e., “free pipe”). In many cases, but not always, geophysical logging is successful in identifying discontinuities in the cement sheaths (Boyd et al. 2006; also Claude Cooke Jr, Conroe, Texas, personal communication, November 28, 2012). Newer ultrasonic logging tools complement these acoustic logs but drilling-mud channels between the cement sheath and the rock wall are still not well imaged with logs in the opinion of logging experts consulted by the authors. If identified, these discontinuities can be plugged with injected cement by a process known as “remedial cementing” or “squeezing.”

There are little, if any, data to evaluate the radius of formation damage that may occur during drilling that is not sealed by cement grouting. Similarly, there is little information about the effect on the casing and surrounding cement of consecutive pressuring of the vertical casing through the shallow and intermediate zones due to progressive fracturing in multiple stages.

Improved cementation procedures (e.g., Dusterhoft et al. 2002; Ravi et al. 2002) and modern acoustic and ultrasonic tools will hopefully reduce the incidence of failure. However, as the Gulf of Mexico data (Brufatto et al. 2003) indicate, the aging of the cement sheath means that a CBL conducted at well completion cannot be relied upon after years of continuing production during which

time the casings may expand and contract with fracturing fluids and hot, pressurized oil and/or gas, thus stressing the annular cement sheath.

There are various potential reasons for inadequate cementation of well annuli (see Cooke et al. 1983; Dusseault et al. 2000; Bellabarba et al. 2008). The net effect of these failures is to create a condition that may allow pressurized gas—and possibly, although less likely, fracturing and formation fluids—to escape from the producing zone if appropriate pressure gradients exist. More typically, pressurized gas in shallower gas-rich formations, that is, the “intermediate zone” (Dusseault 2000; Muehlenbachs 2012), can enter the uncemented or compromised cement bonding in the casing annulus, and then migrate up the annulus behind the well casing. In either manner a scenario develops by which such gases, and possibly other fluids, could invade shallow aquifers.

Such problems were illustrated by gas releases from a vertical production well in Bainbridge Township (Ohio, USA) that caused numerous shallow water wells within the Berea Sandstone aquifer to become contaminated with natural gas. An Expert Panel reporting to the State Department of Natural Resources (Bair et al. 2010) concluded that there were three successive factors leading to the accident. First, there was inadequate cement grout present to safely isolate both the top of the Clinton sandstone reservoir zone and the overlying gas-bearing Newburg Formation. Second, hydraulic fracturing pressures breached the available cement and allowed gas to flow through fractured cement and into the open annulus above the Newburg. Third, a decision was made to shut in the resulting gas flow through the casing head. Had the casing head annulus valve not been closed and the well allowed to vent, pressure would not have been allowed to build up in the subsurface and gas would not have had sufficient pressure to migrate into water wells. Locally a structural dome within the Berea Sandstone aquifer acted as a gas trap resulting in longer-term gas release to the water wells.

The conclusions from the above examples of fugitive gas migration illustrate that for gas to migrate into shallow aquifers it requires a pathway (e.g., either an uncemented or incompletely cemented annulus), the presence of gas under pressure at or near the path through the annulus, and pressure build up below the surface casing shoe. For these reasons, casing pressures should be routinely monitored. If pressure exceeds certain critical levels then the gas must be vented to mitigate the risk of it escaping into the subsurface. Once vented, if SCP reoccurs, then appropriate measures need to be taken to mitigate the problem, for example, cementing off the nontarget gas-producing zones and determining if shallow groundwater has become contaminated by leak-off of casing gases. This pathway should receive more attention for potential migration of fracturing fluids and formation waters although migration periods for these fluids are expected to be limited to times of pressurization.

Fugitive Gas Leakage from Abandoned Wells

The risk of fugitive gas emissions (as well as formation water and fracturing fluid leakage) in areas with improperly plugged and abandoned wells installed during previous eras of oil and gas extraction is considerable based on the analysis of historic contamination incidents in Ohio and Texas by the Ground Water Protection Council (Kell 2011). For example, the Railroad Commission of Texas acknowledges that there are over 110,000 inactive wells in Texas plus another 7900 formally identified as orphan wells, that is, abandoned (Shields 2010). An estimate of the number of abandoned wells that exist in Alberta is 116,000 (Watson and Bachu 2007), and van Everdingen and Freeze (1971) estimated there were approximately 30,000 abandoned wells in the old oil and gas fields of southwestern Ontario. “Orphan well” programs operated by U.S. states and Canadian provinces seek to properly plug these wells; between 2002 and 2009 the Texan program plugged and abandoned 1500 such wells per year (Kell 2011). Several operators drilling in areas with known historic drilling activity are actively developing a variety of methods to pinpoint the location of old abandoned wells (McKee and Beasley 2012).

Improperly plugged and abandoned wells installed during previous eras of oil and gas extraction could pose a risk for shallow groundwater contamination with gases and fluids if the formations that they penetrate become re-pressurized as a result of either gas drilling, completion and well stimulation activities or deep well disposal practices. The contamination of a shallow alluvial water-supply aquifer near Fort Knox (Kentucky, USA) provides an example of formation water influx deteriorating groundwater quality. Here, chloride in excess of 10,000 mg/L discharged from abandoned exploration wells deep within the aquifer (Lyverse and Unthank 1988).

Similarly, Chafin (1994) describes gas wells in the San Juan basin in New Mexico and Colorado drilled in the 1930s that were abandoned and discharged methane into shallow groundwater (maximum measured groundwater concentration of 39 mg/L; with 25% of soil gas concentrations exceeding 100 mg/L_(gas)). Therefore regions of historical oil and gas exploration and production where unconventional gas development occurs may witness future problems of natural gas or formation fluid leakage.

Although not directly related to unconventional gas extraction, a fugitive gas release from natural gas storage in a salt cavern identified after natural gas explosions in 2001 in Hutchinson, Kansas provides insight into free gas transport in the subsurface (Allison 2001; Watney et al. 2003). Watney et al. (2003) concluded that a total of 3.5 million ft³ at 600 psi (100,000 m³ at 4 MPa) had migrated along the crest of an anticline at the contact between two shales at depths from 420 ft (130 m) below ground surface (bgs) at the cavern to 240 ft bgs (75 m) beneath the city. Leakage occurred through a casing failure that damaged an annular seal in a well penetrating the storage cavern. After reaching Hutchinson, the gas escaped by flowing upward through abandoned salt wells and into

buildings. The Kansas Geological Survey (Allison 2001; Watney et al. 2003) had great difficulty in identifying the thin dolostone units that transmitted the gas as they sought to drill venting wells to mitigate the problem. This indicates that the detection of deep gas migration pathways will probably not be straightforward and will require knowledge of the structural geology of the region and the location of existing operating and abandoned wells—both groundwater and hydrocarbon wells. Révész et al. (2010) and Bair et al. (2010) provide further examples of the difficulty of identifying gas migration pathways.

Interwellbore Communication

Cross-connection can also occur with active oil or gas wells in the neighboring area. Such cases have been reported in Alberta, including a recent case in which hydraulic fracturing in one well caused a blow-out in an adjacent oil well completed years earlier in the same formation (e.g., ERCB 2012a). The distance of such interwellbore communication (IWB) in Alberta is similar to that measured in the Barnett Shale play in Texas and appears to be up to 200 m (~600 ft) from the well being stimulated (M. Zoback, Stanford University, personal communication, November 30, 2012).

In addition, water wells can be pathways for migration of natural gas from shallow formations that contain coal seams (Armstrong et al. 2009). This is likely due to the fact that production from the water well itself (or any gas well) causes compressive stress redistribution around the well that in turn leads to a loss of the radial stress seal around the well and an opening up of natural fractures (Dusseault et al. 2000; M. Dusseault, University of Waterloo, personal communication, December 7, 2012). A technical review commissioned by the ECRB in Alberta determined that a 200 m (~600 ft) offset between a hydraulically fractured coal-bed gas well and a water well provides a sufficient safety margin to protect water wells from potential contamination (Taurus Reservoir Solutions Ltd. 2008).

Surface Spills and Infiltration of Produced Waters

The majority of examples of groundwater contamination from oil and gas operations arise from historically persistent problems with fluid containment at the surface. Leakage from surface storage has been a significant cause of groundwater contamination in the past, including saline contamination of alluvial groundwaters adjacent to oilfield brine-holding ponds (Pettyjohn 1982) and water wells (Novak and Eckstein; 1988). The storage of flow-back water may also pose risks from heavy metals, naturally occurring radioactive materials (NORMs; e.g., ^{226}Ra), and hydraulic fracturing chemicals.

On-site earth storage impoundments (“reserve pits”), typically constructed of compacted local clays and perhaps geosynthetic membranes to yield an expected hydraulic conductivity of approximately 10^{-9} m/s, are still used. Brine-induced hydraulic conductivity (K) increases due to clay shrinkage and fissuring in a salt-cavern brine

pond at Fort Saskatchewan (Alberta, Canada) were implicated in seepage into the underlying clay till, with permeameter-measured K values that increased from 10^{-11} to 10^{-9} m/s to approximately 10^{-8} m/s (Folkes 1982). These results caused regulatory concern because of the presence of a buried channel aquifer 30 m (90 ft) beneath the impoundments although no contamination was reported. These impoundments are also susceptible to overflow due to extreme precipitation events or to the failure to empty the impoundment over periods of several years. As a result, double-walled storage tanks are increasingly required by regulatory agencies to replace such holding ponds and reduce the potential for overflow due to extreme precipitation events or to the failure to empty the impoundment over periods of several years.

Holding ponds associated with coal-bed gas development in the Powder River Basin of Wyoming continue to be an area of active research because infiltration and chemical reactions between produced water, surface water, groundwater, and aquifer matrix can affect the quality of drinking water, stock water, and irrigation water locally used by ranchers. As a result, the Wyoming Department of Environmental Quality (2008) has established regulations governing both the location of storage ponds and monitoring of groundwater adjacent to ponds.

Gas Migration through Natural Faults and Fractures

While gas migration via abandoned wells and production well annuli is well documented, we know little about the potential for gas migration following stimulation of horizontal wells in unconventional gas plays through natural fracture or fault systems. Structurally induced fracture zones, such as those believed to have directed gas migration near Hutchinson, Kansas (Allison 2001; Watney et al. 2003), and local structural closures (e.g., the shallow anticline in the Berea Sandstone in Ohio; Bair et al. 2010) will be important in determining potential local and regional pathways for fugitive gas. In the Hutchinson case described above, the Kansas Geological Survey (Allison 2001; Watney et al. 2003) had difficulty identifying the gas migration pathway as they sought to drill venting wells to mitigate the problem. Ultimately, the pathway was identified as a 300 m (~1 000 ft) wide zone of fractured dolomite that was only 0.9 m (3 ft) thick with a fracture porosity of 2% that stretched 14 km (8.7 miles) along the crest of an anticline.

Numerous examples of structural pathways for gas migration have been identified in the Appalachian region (Scott and Rauch 1978; Beebe and Rauch 1979; Harrison 1983 1985; Rauch 1983, 1984; Rauch et al. 1984). Recent investigations of thermogenic gas migration in New York and Pennsylvania (Fountain and Jacobi 2000; Révész et al. 2010; Molofsky et al. 2011; Osborn et al. 2011; Warner et al. 2012) implicate gas migration along structural features as pathways for gas discharge to shallow groundwaters. For example, Fountain and Jacobi (2000) documented the presence of natural gas seepage from depth via the Clarendon-Linden fault zone in upstate New York. Molofsky et al. (2011) reported that 78% of the more than 1700

shallow water wells sampled as part of preshale gas assessments (2008–2011) in Susquehanna County, Pennsylvania, had detectable levels of dissolved methane (biogenic, thermogenic, and mixed). Although they were not able to statistically relate gas concentration to the location of existing gas wells, they demonstrated that water wells with elevated dissolved methane tend to be clustered near and within river valleys and their tributaries. Similar to Rauch's findings 30 years before (Rauch 1983, 1984; Rauch et al. 1984), this suggested a natural geologic origin of the gas in this area (as opposed to hydraulic fracture stimulated), possibly related to the surface expression of valleys carved into regional fracture networks.

The concept of gas flow by such "microseepage" has a long history in the oil and gas literature (e.g., Levorsen 1967; Hunt 1979; Stahl et al. 1981). Brown (2000) quantitatively evaluated the potential mechanisms of gas migration concluding that free-phase gas flow explains the observation of petroleum "microseeps." According to Brown, these seeps are a consequence of a relatively low capillary entry pressure for gas to penetrate water-wet fractures and will exhibit a flux rate governed by the cubic law (i.e., gas discharge $Q \sim [2b]^3$, where $2b$ is the fracture aperture). Even so, gas discharge via such fractures is "low enough so that petroleum accumulations can exist for geological time" without being depleted. Leakage of hydrocarbons through faults remains of intense interest to petroleum geologists (e.g., Ingram and Urai 1999; Aydin 2000; Cartwright et al. 2007).

Gorody (2012) has provided an extensive account of the processes by which methane migrates in porous and fractured rocks toward groundwater discharge areas. Of particular interest is his observation that gas breakthrough may occur in pulses due to changes in the pore pressure and the nonwetting phase pressure exerted by the buoyant gas. Gas migration can result in rapid temporary declines in gas flow, until gas accumulation and associated pressures in the fracture path recover to a sufficient level to again exceed the gas entry pressure of the fracture or porous medium. If gas flow is intermittent, a single sampling of a contaminated groundwater well is an inappropriate monitoring strategy.

Gas Migration Through Induced Fractures

Much of the public concern around unconventional gas development appears focused on hydraulic fracturing creating pathways for gas, formation water and fracturing chemicals from the usually deep target formation to shallow aquifers. There is no evidence that fracture propagation "out-of-zone" to shallow groundwater has occurred from deep (>1000 m or >3000 ft) shale gas reservoirs, although no scientifically robust groundwater monitoring to detect gas migration has been attempted to our knowledge. A weight-of-evidence is that such fracture propagation is unlikely in deep (>1 km) operations (ALL Consulting 2012; UK Royal Society/Royal Academy of Engineering 2012). Available evidence is largely related to measured or modeled fracture propagation as aforementioned.

This conclusion may not be true when shallow hydraulic fracturing occurs associated with coal-bed methane development because of the shallow depth of the coal formations. Hydraulic fracturing in shallow formations, in particular using nitrogen or propane fracturing fluids for coal-bed methane operations, has resulted in different interpretations of the occurrence of shallow groundwater contamination in Alberta, Canada (Blyth 2008; Tilley and Muehlenbachs 2011).

The one documented case (ERCB 2012b) in which a shallow aquifer became contaminated with hydraulic fracturing fluids was due to the accidental injection of hydraulic fracturing fluids directly into a sandstone at 136 m depth (443 ft depth) when the operators believed they had perforated the coiled tubing at 1500 m depth (4900 ft). Here a chain of human errors caused the shallow groundwater contamination but no vertical propagation of hydraulic fracturing fluids from depth was involved.

The totality of these findings suggests a low probability of shallow groundwater contamination by upward propagation of hydraulic fractures from deep shale gas plays. As noted above (see Interwellbore Communication), there is evidence of induced horizontal fracturing to approximately 200 m from the stimulated well. The potential for elevated pore-pressure transmission (rather than fracture propagation) beyond this distance through preexisting fracture or fault zones has been considered by geophysicists interested in remote triggering of earthquakes (Manga et al. 2012).

Monitoring and Behavior of Contaminants in Shallow Groundwater

Hydrocarbon Gases

The presence of methane in shallow groundwater is, by itself, not definitive evidence of contamination resulting from unconventional gas development. In many areas targeted for unconventional gas, elevated concentrations of methane have existed in shallow groundwater prior to any drilling activities. "Biogenic" methane can be generated in situ in shallow groundwater (e.g., by CO₂ reduction or acetate fermentation reactions) but gas occurrences in shallow aquifers can also result from upward migration of thermogenic or mixed thermogenic/biogenic methane (Barker and Fritz 1981; Révész et al. (2010); Bair et al. 2010).

Although it may be difficult to ascertain gas source(s), some well-constrained case studies are instructive. Fugitive gas (mainly methane) migrated along the annulus of an oil well and then migrated about 10 m laterally from the oil well into a buried sand and gravel aquifer near Lloydminster, Alberta, Canada (Van Stempvoort et al. 2005). In situ bacterial methane oxidation coupled with bacterial sulfate reduction occurring within a contaminated groundwater plume was identified by a depletion of the stable isotope ¹³C in bicarbonate and an enrichment of ³⁴S in residual sulfate in down-gradient groundwater monitoring wells. The authors concluded that these processes could

also be important near other oil and gas wells in western Canada and perhaps globally.

Forensic identification of stray or fugitive gas origin requires a comprehensive approach (e.g., Van Stempvoort et al. 2005; Révész et al. 2010; Tilley and Muehlenbachs 2011). In addition to the usual geochemical approach in groundwater quality investigations (e.g., measurement of pH, DO, Eh, major ions, and redox sensitive minor ions, such as Mn and Fe), a field investigation would also ideally include the following: (1) appropriate sampling techniques to collect representative groundwater samples of dissolved or free gas, (2) dissolved or free gas composition analyses, (3) estimation of in situ total dissolved gas pressure (Roy and Ryan, in press this issue), (4) determination of the stable isotope composition of gases; and (5) possibly the identification of microbial consortia responsible for catalyzing redox reactions. Inexpensive and reliable methods have been developed for dissolved gas sampling to determine composition (e.g., Gorody 2007; Hirsche and Mayer 2007). Compositional analyses for dissolved gas (Box 2) can follow different approaches and are increasingly undertaken at commercial laboratories.

Fingerprinting the chemical and isotopic compositions of natural gas associated with both shales and shallow groundwater is an effective tool for evaluating potential environmental impacts of hydraulic fracturing of horizontal wells in unconventional gas plays. Biogenic gases produced *in situ* in shallow aquifers are predominantly composed of CH₄ with low $\delta^{13}\text{C}$ (-50 to -110% VPDB) and $\delta^2\text{H}$ values (as low as -350% VSMOW). In contrast, thermogenic gases generated at elevated pressures and temperatures are usually composed of methane (C₁) and higher alkanes such as ethane (C₂), propane (C₃), and possibly butane (C₄) and pentane (C₅), with $\delta^{13}\text{C}$ values often ranging between -55 and -25% . Therefore, stable isotope analyses, wetness parameters and Bernard diagrams (see Box 1) when used together can be an effective tool to assess the sources of natural gas in shallow aquifers. If the chemical and isotopic compositions of natural gas in all gas-bearing formations are known, it may also be possible to identify the formation from which stray gases have been derived contaminating shallow groundwater with natural gas (e.g., Tilley and Muehlenbachs 2011). While natural gas occurrences in some formations, such as coal-bed methane in Alberta, are readily fingerprinted by geochemical and isotopic measurements (Cheung et al. 2010; Tilley and Muehlenbachs 2011), other formations display considerable variability in these parameters (Gorody 2012). Tilley and Muehlenbachs (2013) provide a comprehensive review of the isotope geochemistry of several United States and western Canadian shale-gas reservoirs.

A widely accepted methodology for sampling, analysis, and data interpretation would help to resolve uncertainties and disputes regarding impact of fugitive gases on shallow aquifers and their potential causes. The protocol presented in Gorody (2007) is one example that could be

advanced and adopted; additional field methods and isotopic tools could be employed where conditions warrant for interpretation of complex data (e.g., van Stempvoort et al. 2005; Hirsche and Mayer 2007; McLeish et al. 2007; Roy and Ryan 2010; Gorody 2012).

A particularly important component needed for the isotopic fingerprinting of gas-bearing formations is the characterization of $\delta^{13}\text{C}$ values of gases in drilling muds recovered from the vertical portion of energy wells (Rowe and Muehlenbachs 1999; Tilley and Muehlenbachs 2006, 2011). This would greatly facilitate the identification of sources of potential stray gas in shallow aquifers and may facilitate the remediation of gas leakage into aquifers, if necessary.

Formation Waters

Saline formation waters typically contain solutes that, when brought to the surface, can potentially contaminate soil and groundwater. These solutes are primarily sodium and chloride but may also include arsenic, barium and radium-226, the latter generated by the radioactive decay of uranium in shales. Because of the deleterious effects of saline formation waters or brines on activated sludge processes in municipal treatment plants, the disposal of brines is increasingly directed to injection wells or to recycling facilities where they exist (e.g., Pennsylvania and Texas).

Saline formation waters have recently become part of the shale-gas controversy due to the claims that Marcellus formation brines are migrating to shallow aquifers through pathways “unrelated to recent drilling activities” (Warner et al. 2012). Given that the Silurian sandstones and Devonian shales of the Appalachian basin have water-phase porosities approaching irreducible saturations (Soeder 1988; Ryder and Zagorski 2003), there is some question as to the availability of such brine for migration. Engelder (2012) suggests a higher brine saturation but also argues for “capillary binding” of the brine within the Marcellus shale. Nevertheless, geochemical characterization of formation waters should be part and parcel of the hydrogeological baseline reporting that will increasingly become standard if further disputes are to be rapidly and fairly resolved.

Fracturing Chemicals and Other Compounds of Interest

The US EPA (2011) is currently conducting research on hydraulic fracturing, specifically related to its potential impacts on drinking water. In part, it is anticipated that this study will determine whether some of the chemicals used in fracturing fluids can be detected in groundwater, and if so, obtain information about their fate and transport and toxicity. This study is using a combination of (1) analysis of existing data, (2) new case studies, both retrospective (studies at locations where hydraulic fracturing has already occurred) and prospective (collection of data at new sites prior to, during, and after hydraulic fracturing activities), (3) scenario evaluations, (4) laboratory studies, and (5) toxicity assessments.

The hydrogeological community has suitable expertise to evaluate the transport and fate of relevant chemicals in groundwater, including their attenuation by dispersion, sorption, and biodegradation. The behavior of some of the relevant chemicals (e.g., brine salts, aromatic hydrocarbons) in groundwater has already been well studied in other applications in contaminant hydrogeology. By contrast there is little or no peer-reviewed and published field data regarding the groundwater occurrence and fate of various anthropogenic chemicals that are widely used in unconventional natural gas production. These include various glycols, amines, and metal complexes used as corrosion inhibitors, some of which have been deemed “proprietary,” or metabolites and degradates that may form from these chemicals, for example, acrylamide. In many cases, assumptions about the biodegradability of the various chemical additives, if available, have been based on laboratory studies in oxygenated environments using samples of soil, surficial sediments and/or surface waters, which are not necessarily applicable to the deep subsurface (Van Stempvoort and Roy 2011). Also there is apparently very little information about groundwater contamination by and the fate of some of the less abundant chemicals that occur in produced gas and/or condensates (e.g., hydrocarbons that contain sulfur) or produced water (e.g., ²²⁶Ra, Ba, among others).

The peer-reviewed literature about groundwater monitoring programs at both conventional and unconventional natural gas production sites is sparse, suggesting that such monitoring is rarely conducted unless spills have been reported. Furthermore, many of the above chemicals are typically not included in groundwater monitoring programs. To address these science gaps, it would make sense to study the fate and transport of those chemicals considered to be threats to the environment and public health, as well as some chemicals that would be good tracers or indicators of the fluids produced or used in unconventional gas development.

Recommendations as to Research Programs

To support both sustainable development of unconventional gas and protection of groundwater resources, we identify two areas of hydrogeological research that will address key science gaps: (1) the characterization of the background or baseline conditions (including groundwater flow, geochemical and isotopic characterization, and gas pressure (P_{TDG}; Box 2) in shallow groundwater); and (2) field experiments and studies to understand better the processes by which natural gas, saline formation waters and fracturing chemicals may invade and contaminate shallow groundwaters and then be remediated where necessary. Laboratory experiments and computational studies will be needed to support this research into the transport and fate of natural gas, saline formation waters and fracturing chemicals into and within shallow groundwaters.

Baseline Groundwater Quality Mapping

Baseline or background testing of groundwater for methane concentrations and its carbon (and sometimes hydrogen) isotope ratios in some jurisdictions (e.g., ERCB 2006) is becoming standard practice in areas where unconventional gas development occurs. The aim is to determine a baseline of water quality screening parameters from which any perceived changes following the drilling and stimulation of wells in unconventional gas plays can be compared. Regulatory requirements to collect such data are principally used to address complaints. These baseline surveys tend to include existing water wells only, without use of groundwater profiling systems to detect spatial variability in free- and dissolved-gas phases, and usually fail to assess natural variations in concentrations and isotopic compositions of methane, and how these are affected by geographic region and/or geology, and with differences in aquifer properties, well construction, and pumping scenarios.

Generalized monitoring analytes useful for screening water quality are presented in Box 3 (*Forensic analysis of hydrocarbons in shallow groundwater and surface gas seeps*). This information could assist in rapid resolution in any disputes that arise. While domestic water well surveys provide useful analytical chemical data for public health authorities, the data are susceptible to gas exchange and microbially-catalyzed redox reactions within the well itself (Bair et al. 2010). These wells can also be poorly protected from surface contamination, poorly maintained and the source of the water is often uncertain. More comprehensive geochemical mapping could involve a time series of an expanded suite of parameters, ideally in a network of dedicated groundwater monitoring wells. The continued use of domestic or landowner wells requires careful consideration as they provide an initial screening of groundwater quality but one which is likely to reflect biases as identified above.

Box 3

Forensic Analysis of Hydrocarbons in Shallow Groundwater and Surface Gas Seeps

Forensic analyses of free and dissolved hydrocarbons in groundwater are designed to:

- Unambiguously identify the source(s) of stray hydrocarbons impacting surface and groundwater resources;
- Provide defensible data to demonstrate whether groundwater and surface water impacts are due to oil and gas operations, and if so, to determine when such impacts have been satisfactorily mitigated so that there is no

longer a threat to public health, safety, and the environment.

The approach is to sample potential gas sources within a certain radius of influence and to compare them with baseline and postimpact sample data of free and dissolved gases from affected water wells. If there is good pressure communication between a point source of natural gas and a gas seep, then the stable isotopic composition of the free gas phase at the seep tends to correspond precisely to that of the source. More often than not in such cases, the gas composition of both source and seep is also nearly identical. When gas contaminants occur in the dissolved phase, then source hydrocarbons are more likely to be influenced by dilution, alteration, and mixing.

Because of the hydrologic complexity of shallow groundwater environments, the objectives of a comprehensive sampling and analysis plan should strive to unravel three principal factors affecting the interpretation of results. These are dilution (Hirsche and Mayer 2007; Gorody 2012), mixing (Jenden et al. 1993; Tilley and Muehlenbachs 2006, 2011; Révész et al. 2010), and hydrocarbon oxidation (Barker and Fritz 1981; Coleman et al. 1988; Whiticar 1999).

Dilution of hydrocarbon contaminants in a groundwater plume depends on the size of a plume, plume velocity, adsorption effects within the aquifer matrix, dispersion and fluids incorporated and mixed along the migration path. Mixing occurs as a result of the interaction between dissolved gas plumes of multiple origins. For example, it is common to observe mixing between naturally occurring biogenic gas and contaminant thermogenic gas sources. Baseline samples provide the needed end-member dissolved hydrocarbon compositions required for mixing model calculations.

Hydrocarbon oxidation is principally mediated by bacteria. Ordinarily, hydrocarbon oxidation trends in gas composition and stable isotope data do not tend to appear until well after a contaminant point source has been mitigated, for example, a leaky gas well. However, hydrocarbon oxidation rates also vary depending on the size of a plume, plume velocity, the extent of the oxidation gradient near the leading edge of the plume, and the redox environment in the host aquifer. Furthermore, if the rate of fresh dissolved hydrocarbon influx into a water well is significantly greater than oxidation rates in the surrounding wellbore environment, then the chemical and isotopic composition of hydrocarbons is not significantly altered.

Demonstrating the effects of bacterially mediated hydrocarbon oxidation is one requirement needed

to demonstrate that a contaminant source has been mitigated. High oxidation rates will lower the concentration of dissolved hydrocarbons. However, when a contaminant plume mixes with aquifer fluids devoid of dissolved hydrocarbons in a water well, dilution could be mistaken for the effects of remediation. For this reason it is important to determine the composition of fluids hosting a contaminant plume and to differentiate those fluids, if possible, from fluids that may be derived from other aquifers supplying water to a water well.

Addressing the effects of dilution, mixing, and oxidation is best achieved by collecting multiple samples of both potential hydrocarbon point sources (produced hydrocarbons, hydrocarbons in annular spaces, and shallow gas obtained by sampling while drilling), and of shallow groundwater receptor sites (water and monitor wells, and hydrocarbon seeps). Using a variety of such sample types is vital to satisfactorily interpret the source of hydrocarbons in shallow groundwater environments.

Sampling available water wells within a radius of influence from potential contaminant point sources (e.g., commercial oil or gas wells) multiple times is most easily accomplished by collecting pre and postdrilling sample sets. Although providing detailed sampling protocols is beyond the scope of this paper, all sampling events should follow written, and preferably standardized, sampling and analysis plans to ensure that data quality is defensible. This includes routine collection and analysis of selected blind duplicate sample sets.

Minimum screening parameters needed to address the occurrence and source of free and dissolved hydrocarbons in groundwater samples should ideally include the following:

- dissolved methane, ethane, and BTEX concentrations;
- stable isotope analysis of carbon and hydrogen in both free and dissolved methane;
- stable isotope analysis of carbon in both free and dissolved ethane;
- fixed gases (including argon) and hydrocarbon gas chromatography of samples containing dissolved methane and ethane concentrations above a predetermined threshold or in free gas samples;
- charge-balanced major ion analyses;
- parameters useful for identifying the redox state of shallow groundwater samples; and
- routine monitoring, sampling, and analysis of gases derived from the headspace of a water well.

Forensic investigations designed to address impacts from potential point sources on shallow groundwater should include all the above parameters, and additional parameters to further characterize both fluid and hydrocarbon sources as needed. Parameter selection should be based on site and potential point source-specific criteria and may include one or more of the following:

- Volatile organic compounds (including benzene, toluene, ethylbenzene, *o*-xylenes, *m*-xylenes, *p*-xylenes, 1,2,4, and 1,3,5-trimethylbenzenes) and semi-volatile organic compound analysis using standard GC/MS methods;
- Stable isotope analyses of hydrogen and oxygen in water;
- Stable isotope analysis of carbon in dissolved inorganic carbon.

Minimum parameters useful for characterizing hydrocarbons in produced and bradenhead or casing-head gas samples ideally include the following:

- Fixed (including argon) and hydrocarbon gas chromatography;
- Stable isotope analysis of carbon in methane, ethane, propane, butane, and CO₂;
- Stable isotope analysis of hydrogen in methane;
- BTEX compounds (i.e., benzene, toluene, ethylbenzene, *o*-xylenes, *m*-xylenes, *p*-xylenes, 1,2,4, and 1,3,5-trimethylbenzenes) using standard GC/MS methods.

Given the potential role of fractures and structural features in gas migration to shallow aquifers, carefully designed and located groundwater monitoring instrumentation will likely be needed, particularly for research studies and dispute resolution. Depth discrete monitoring has long been used by those industries regulated under U.S. environmental laws (e.g., the Safe Drinking Water Act or SDWA, the Comprehensive Environmental Response, Compensation and Liability Act or CERCLA and the Resource Conservation and Recovery Act or RCRA) using multilevel well systems (e.g., Einarson 2006; Cherry et al. 2007; Mayer et al. 2008). Monitoring to detect upward migration of contaminants is unusual in contaminant hydrogeology. Lesage et al. (1991) presented an approach that was used to assess the potential for upward migration of refinery wastewaters following their deep-well injection; they employed the complementary use of deep, multilevel wells and shallow, conventional monitoring wells.

Experimental Field Studies

Further scientific investigation into the potential for groundwater contamination following unconventional gas development activities is warranted. At least three approaches to field programs are possible: (1) a forensic or “retrospective” analysis of existing cases of unconventional gas development, (2) an investigation that includes gathering of field data prior to the installation and stimulation of unconventional gas wells, and periodically during the subsequent production period, and (3) controlled experiments to understand processes that are believed to be responsible for or may result in groundwater contamination.

The U.S. Environmental Protection Agency study (US EPA 2011), which deals specifically with hydraulic fracturing, involves hydrogeologic field research components, including retrospective case studies at five developed sites with reported instances of water contamination, and two prospective case studies at sites where hydraulic fracturing will occur following baseline monitoring. Site identification, initial assessment and the first round of sampling have occurred for the five retrospective sites (includes oil, shale gas, and coal gas).

Rather than simply undertaking forensic or “retrospective” analyses of unconventional natural gas sites, an appropriate approach to understanding the potential propagation of natural gases into aquifers would be to design and conduct field-scale experiments in a controlled setting. A handful of prominent field sites with collaborative, long-term research programs have spawned dozens of research papers on the fate and transport of other contaminants, in particular chlorinated solvents and gasoline components, and many of the major advances in hydrogeology have occurred as a result of these integrated field-research programs (Anderson and McCray 2011).

A similar field-focused approach for unconventional gas development with hydraulic fracturing would allow engineers and geoscientists from industry to work with research hydrogeologists and environmental chemists to develop a greater understanding of how effective monitoring systems might be developed to detect potential migration and fate of gases and chemicals used in the hydraulic stimulation process. Controlled field experiments were critical to understanding the practice of hydraulic fracturing in the 1980s at U.S. Department of Energy’s Multiwell Experiment program in western Colorado (e.g., Lorenz et al. 1989; Warpinski 1990). Sites selected for this approach could include variable hydrogeologic settings in major play areas such as those in Rocky Mountain foothills in the Western Canadian sedimentary basin, the Front Range of Colorado, the Appalachian region of New York and Québec, and emerging CBM plays in Wyoming and Alberta.

Recent advances in carbon capture and geological storage and in unconventional oil and gas production have developed separately. Given the overlap in research needs for these activities, for instance with respect to potential gas leakage, there appear to be significant opportunities for technology transfers and other mutually beneficial and

synergetic interactions (Nicot and Duncan 2012). It will be essential that collaboration between government, industry, academia and other third party groups ensures experimental studies are conducted in a manner that inspires widespread credibility without politically motivated conflicts of interest. Furthermore, it will be necessary that the design, implementation and analysis of such studies are independently reviewed and verified by experts.

Industry has an opportunity to play a cooperative role in ensuring that unconventional natural gas production is environmentally safe and sustainable. We propose that working groups of environmental geoscientists and engineers from industry and academia cooperate to test and develop new methods to detect and monitor the presence of fugitive gas, saline water, and flowback chemicals in shallow groundwater at unconventional gas sites. Industry participation would also help to defer costs required for more comprehensive monitoring of shallow groundwater and soil coring of impoundments to address the fate of potentially hazardous chemicals in stored flow back and produced fluids. Other research objectives might also include the following: identification of gas and other fluids that may have escaped the production string of casings; improved understanding of cement curing and cement emplacement techniques; improved downhole monitoring of cement bonding; and testing the confinement of wastewaters injected into saline aquifers, depleted oil reservoirs, and other formations as proposed by Van Everdingen and Freeze (1971). Finally, it will be important to greatly expand the techniques available to hydrogeologists to undertake aquifer remediation in the event of contamination (e.g., Van Stempvoort et al. 2007a, 2007b).

Laboratory and Computational Experiments

There will be numerous reasons to conduct laboratory and numerical simulation experiments and investigations. For example, in order to design field experiments with a minimal risk of failure, it will be necessary to carefully study transport and attenuation processes of compounds of concern in the laboratory and by numerical simulation before undertaking field experiments under controlled conditions. Soil column studies and aquifer tank experiments of the fate and transport of fracturing chemicals can be used to identify the more mobile and recalcitrant compounds for field testing. Numerical simulations can also be used to evaluate risks of fluid migration through deep fault zones with known surface expressions based on parameters derived from the hydraulic testing of fault zones (e.g., Rafini and Larocque 2012).

Summary and Conclusions

This article has referred to issues that are not confined to unconventional gas extraction. It also mentioned issues that have arisen with conventional hydrocarbon extraction and which can be expected to occur with unconventional gas extraction. Articles on groundwater contamination arising from conventional oil and gas extraction sites have appeared infrequently in the two

journals of the NGWA (*Ground Water* and *Ground Water Monitoring & Remediation*). Notably, oil and gas exploration and production were exempted from U.S. Federal regulations (RCRA and CERCLA) in the 1970s and 1980s; perhaps in part as a result of that policy, “upstream” groundwater issues that arose during exploration and production—gas leakage from wells and contamination from impoundments—received relatively little research attention.

Consequently, less than 10 articles in total can be counted in both NGWA journals since the early 1980s on upstream oil and gas issues. By contrast, both journals have carried numerous articles on the characterization and remediation of sites contaminated by chlorinated solvents, gasoline, and other contaminants. This lack of “anticipatory research” was observed 30 years ago to have harmed groundwater protection (Brooks 1982) through limited research. Kell (2011) has emphasized in his review of groundwater investigations conducted by state oil and gas agencies in the USA that competent site investigation is the driving force for regulatory reform.

We identify several case histories (Table 3) involving the migration of natural gas to shallow aquifers, water wells, or buildings. Several of the examples indicate the long-standing problems arising from poorly completed oil or gas wells, while one identifies the importance of abandoned wells in gas migration. It is likely that the natural gas migrated as a buoyant free phase in all cases. While these case studies are the exception and not the rule, the migration of the gas through bedrock indicates the importance of fracture flow systems and the ability of hydrogeologists to identify those pathways in order to monitor them to the depth of surface casings, that is, the full depth of potentially potable groundwater. Table 3 represents a “canon” of peer-reviewed publications on this subject.

We have identified two areas where science gaps are evident and field-focused research is required: (1) baseline geochemical mapping and the development of problem-specific groundwater monitoring systems and networks; and (2) field testing of potential mechanisms by which hydrocarbon gases, saline fluids, and fracturing chemicals might invade and contaminate shallow groundwater and of methods of aquifer remediation. To support these research initiatives it will be necessary to undertake laboratory and computational studies to (1) design and analyze field experiments, (2) screen potential groundwater contaminants and (3) evaluate potentially vulnerable aquifers near fault zones with near-surface expression.

Thus we have illustrated the potential role of the hydrogeologists in identifying, characterizing, and monitoring aquifers deemed vulnerable to contamination by natural gas and perhaps other gas-field fluids and chemicals. All of these topics will require collaboration of engineers and geoscientists from industry with hydrogeologists and geochemists from the research community. These gaps in knowledge are harmful to the safe development of natural gas resources and the protection of groundwaters as well as to the social perception of their safe development.

Acknowledgments

The authors appreciate the comments of J.A. Cherry, B. Parker, T.M. Missimer, two anonymous reviewers, and those of Frank Schwartz, Editor-in-Chief of *Groundwater*.

References

- ALL Consulting. 2012. *The Modern Practices of Hydraulic Fracturing: A Focus on Canadian Resources*. Tulsa, Oklahoma.
- Allison, M.L. 2001. Hutchinson, Kansas: A geologic detective story. *Geotimes* October issue, www.geotimes.org/oct01/feature_kansas.html.
- Anderson, M., and J. McCray. 2011. Foreword: Lessons Learned About Contaminant Hydrogeology from Legacy Research Sites. *Ground Water* 49, no. 3: 617–619.
- Aravena, R., L.I. Wassenaar, and J.F. Barker. 1995. Distribution and isotopic characterization of methane in a confined aquifer in southern Ontario, Canada. *Journal of Hydrology* 173: 51–70.
- Armstrong, J., C. Mendoza, and A.W. Gorody. 2009. *Potential for Gas Migration due to Coalbed Methane Development*. Worley Parsons, Calgary, Alberta for Alberta Environment, Edmonton, Alberta.
- Aydin, A. 2000. Fractures, faults and hydrocarbon entrapment, migration and flow. *Marine and Petroleum Geology* 17: 797–814.
- Bair, E.S., D.C. Freeman, and J.M. Senko. 2010. Subsurface Gas Invasion, Bainbridge Township, Geauga County, Ohio. Expert Panel Technical Report. Submitted to Ohio Dept. of Natural Resources, <http://www.dnr.state.oh.us/bainbridge/tabid/20484/Default.aspx> (accessed May 12, 2011).
- Barker, J.F., and P. Fritz. 1981. The occurrence and origin of methane in some groundwater flow systems. *Canadian Journal of Earth Sciences* 18: 1802–1816.
- Barker, C. 1990. Calculated volume and pressure changes during the thermal cracking of oil and gas in reservoirs. *AAPG Bulletin* 74, no. 8: 1254–1261.
- Bellabarba, M. et al. 2008. Ensuring zonal isolation beyond the life of the well. *Schlumberger Oilfield Review* 20, no. 1: 18–22.
- Beebe, R.R., and H.W. Rauch. 1979. Lineaments and groundwater chemistry as exploration tools for Devonian shale gas in the midway-extra field of West Virginia. In *Proceedings of the Third Eastern Gas Shales Symposium*, ed. H. Barlow, 278–289. Morgantown, West Virginia: US Department of Energy.
- Bexte, D.C., M. Willis, G.G. De Bruijn, B. Eitzen, and E. Fouillard. 2008. Improved cementing practice prevents gas migration. *World Oil* 229, no. 6: 73–75.
- Beyerle, U., W. Aeschbach-Hertig, D.M. Imboden, H. Baur, T. Graf, and R. Kipfer. 2000. A mass spectrometric system for the analysis of noble gases and tritium from water samples. *Environmental Science and Technology* 34, no. 10: 2042–2050.
- Blyth, A. 2008. An Independent Review of Coalbed Methane Related Water Well Complaints Filed with Alberta Environment. Alberta Research Council, Edmonton, Alberta, 13p.
- Boyd, D., S. Al-Kubti, O.H. Khedr, N. Khan, K. Al-Nayadi, D. Degouy, A. Elkadi, and Z. Al Kindi. 2006. Reliability of Cement Bond Log Interpretations Compared to Physical Communication Tests Between Formations. Richardson, Texas: Society of Petroleum Engineers, SPE 101420.
- Bourgoyne, A.T., S.L. Scott, and W. Manowski. 1998. A Review of Sustained Casing Pressure Occurring on the OCS (Outer Continental Shelf). Submitted to the US Minerals Management Service, US Department of the Interior, Washington, D.C.
- Brooks, H. 1982. Science indicators and science priorities. *Science, Technology & Human Values* 7, no. 38: 14–31.
- Brown, A. 2000. Evaluation of possible gas microseepage mechanisms. *AAPG Bulletin* 84, no. 11: 1775–1789.
- Bruffatto, C. et al. 2003. From mud to cement—building gas wells. *Schlumberger Oilfield Review* 15, no. 3: 62–73.
- Cartwright, J., M. Huuse, and A. Aplin. 2007. Seal bypass systems. *AAPG Bulletin* 91, no. 8: 1141–1166.
- Chafin, D.T. 1994. Sources and migration pathways of natural gas in near-surface ground water beneath the Animas River Valley, Colorado and New Mexico. Water Resources Investigation Report 94-4006. Denver, Colorado: US Geological Survey.
- Cherry, J.A., B.L. Parker, and C. Keller. 2007. A new depth-discrete multilevel monitoring approach for fractured rock. *Ground Water Monitoring & Remediation* 27: 57–70.
- Cheung, K., P. Klassen, B. Mayer, F. Goodarzi, and R. Aravena. 2010. Major ion and isotope geochemistry of fluids and gases from coalbed methane and shallow groundwater wells in Alberta, Canada. *Applied Geochemistry* 25, no. 9: 1307–1329.
- Coleman, D.D., C.-L. Liu, and K.M. Riley. 1988. Microbial methane in the shallow Paleozoic sediments and glacial deposits of Illinois, USA. *Chemical Geology* 71, no. 1–3: 23–40.
- Cooke, C.E. Jr., M.P. Kluck, and R. Medrano. 1983. Field measurements and annular pressure and temperature during primary cementing. *Journal of Petroleum Technology* 35, no. 8: 1429–1438(SPE 11206).
- Curtis, J.B. 2002. Fractured shale-gas systems. *AAPG Bulletin* 86, no. 11: 1957–1980.
- Davies, R.J., S.A. Mathias, J. Moss, S. Hustoft, and L. Newport. 2012. Hydraulic fractures: How far can they go? *Marine and Petroleum Geology* 37, no. 1: 1–6.
- Desrocher, S. 1997. Isotopic and compositional characterization of natural gases in the lower and middle Triassic Montney, halfway, and Doig formations, Alberta Basin. M.Sc. thesis, Department of Geology and Geophysics, University of Calgary.
- Duan, Z., N. Møller, J. Greenberg, and J.H. Weare. 1992. The prediction of methane solubility in natural waters to high ionic strength from 0 to 250°C and from 0 to 1600 bar. *Geochemica et Cosmochimica Acta* 56, no. 4: 1451–1460.
- Duncan, P.M., and L. Eisner. 2010. Reservoir characterization using surface microseismic monitoring. *Geophysics* 75, no. 5: 75A139–75A146.
- Dusseault, M.B., M.N. Gray, and P. Nawrocki. 2000. *Why Oilwells Leak: Cement Behaviour and Long-term Consequences*. Richardson, Texas: Society of Petroleum Engineers, SPE 64733.
- Dusterhoft, D., G. Wilson, and K. Newman. 2002. *Field Study on the Use of Cement Pulsation to Control Gas Migration*. Richardson, Texas: Society of Petroleum Engineers, SPE 75689.
- Einarson, M. 2006. Multilevel ground-water monitoring. In *Practical Handbook of Environmental Site Characterization and Ground-Water Monitoring*, 2nd ed., D.M. Nielsen, 807–848. Boca Raton, Florida: CRC Taylor & Francis.
- Energy Resources Conservation Board (ERCB). 2012a. *Bulletin 2012–02. Hydraulic Fracturing: Interwellbore Communication between Energy Wells*. ERCB, Calgary, Alberta, Canada, January 23, 2012.
- Energy Resources Conservation Board (ERCB). 2012b. Caltex Energy Inc. Hydraulic Fracturing Incident: 16-27-068-10W6M, September 22, 2011. ERCB, Calgary, Alberta, Canada, December 20, 2012.
- Energy Resources Conservation Board (ERCB). 2011. Directive 55: Storage Requirements for the Upstream Petroleum Industry. ERCB, Calgary, Alberta, Canada, Addendum 2011-10-11.

- Energy Resources Conservation Board (ERCB). 2006. Directive 35: Baseline Water Well Testing Requirement for Coalbed Methane Wells Completed above the Base of Protection. ERCB, Calgary, Alberta, Canada. May 8, 2006.
- Engelder, T. 2012. Capillary tension and imbibitions sequester frack fluid in Marcellus gas shale. *Proceedings of National Academy of Science of United States of America* 109, no. 52: E3625.
- Fisher, K., and N. Warpinski. 2012. Hydraulic-fracture-height growth: Real data. *SPE Production & Operations* 27, no. 1: 8–19. Richardson, Texas: Society of Petroleum Engineers, SPE 145949.
- Folkes, D.J. 1982. Control of contaminant migration by the use of liners. *Canadian Geotechnical Journal* 19, no. 3: 320–344.
- Fountain, J.C., and R.D. Jacobi. 2000. Detection of buried faults and fractures using soil gas analysis. *Environmental and Engineering Geoscience* 6, no. 3: 201–208.
- Gardner, P., and D.K. Solomon. 2009. An advanced passive diffusion sampler for the determination of dissolved gas concentration. *Water Resources Research* 45, no. 6. DOI:10.1029/2008WR007399.
- Goodman, R.E. 1989. *Introduction to Rock Mechanics*, 2nd ed. New York: John Wiley & Sons.
- Gorody, A.W. 2012. Factors affecting the variability of stray gas concentration and composition in groundwater. *Environmental Geosciences* 19, no. 1: 17–31.
- Gorody, A.W. 2007. Recommended Sampling, Analysis, and Reporting Protocols for Baseline Groundwater Sampling in Advance of Coalbed Gas Development in the Telkwa Coal Field, British Columbia. Prepared for the British Columbia Ministry of Energy, Mines, and Petroleum Resources by Universal Geoscience Consulting, Inc., Houston, Texas.
- Groat, C.G., and T.W. Grimshaw. 2012. *Fact-Based Regulation for Environmental Protection in Shale Gas Development: Summary of Findings*. The Energy Institute, University of Texas at Austin, Austin, Texas. <http://energy.utexas.edu/>.
- Grossman, E.L., B.K. Coffman, S.J. Fritz, and H. Wada. 1989. Bacterial production of methane and its influence on ground-water chemistry in east-central Texas aquifers. *Geology* 17, no. 6: 495–499.
- Harrison, S.S. 1985. Contamination of aquifers by overpressuring the annulus of oil and gas wells. *Ground Water* 23, no. 3: 317–324.
- Harrison, S.S. 1983. Evaluating system of ground-water contamination hazards due to gas-well drilling on the glaciated Appalachian Plateau. *Ground Water* 21, no. 6: 689–700.
- Hill, R.J., D.M. Jarvie, J. Zumberge, M. Henry, and R.M. Pollastro. 2007. Oil and gas geochemistry and petroleum systems of the Fort Worth Basin. *AAPG Bulletin* 91, no. 4: 445–473.
- Hirsche, T., and B. Mayer. 2007. A Comprehensive Literature Review on the Applicability of Free and Dissolved Gas Sampling for Baseline Water Well Testing: Final Report. Edmonton, Alberta: Alberta Environment.
- Hitchon, B., G.K. Billings, and J.E. Klován. 1971. Geochemistry and origin of formation waters in the western Canada sedimentary basin; III, Factors controlling chemical composition. *Geochimica et Cosmochimica Acta* 35, no. 6: 567–598.
- Hunt, J.M. 1979. *Petroleum Geochemistry and Geology*. San Francisco, California: W.H. Freeman & Company.
- Ingram, G.M., and J.L. Urai. 1999. Top-seal leakage through faults and fractures: the role of mudrock properties. In *Muds and Mudstones: Physical and Fluid Flow Properties*, ed. A.C. Aplin, A.J. Fleet, and J.H.S. Macquaker, 125–135. Special Publications 158. London: Geological Society.
- Jenden, P.D., D.J. Drazan, and I.R. Kaplan. 1993. Mixing of Thermogenic Natural Gases in Northern Appalachian Basin. *AAPG Bulletin* 77, no. 6: 980–998.
- Johnson, E.G., and L.A. Johnson. 2012. Hydraulic fracture water usage in northeast British Columbia: locations, volumes and trends. In *Geoscience Reports 2012*, 41–63. Victoria, B.C., Canada: British Columbia Ministry of Energy and Mines.
- Kargbo, D.M., R.G. Wilhelm, and D.J. Campbell. 2010. Natural gas plays in the Marcellus shale: Challenges and opportunities. *Environmental Science and Technology* 44, no. 15: 5679–5684.
- Kampbell, D.H., and S.A. Vandegrift. 1998. Analysis of dissolved methane, ethane and ethylene in groundwater by a standard gas chromatographic technique. *Journal of Chromatographic Science* 36, no. 5: 253–256.
- Kaufman, P., G.S. Penny, and J. Paktinat. 2008. *Critical Evaluations of Additives Used in Shale Slickwater Fracs*. Richardson, Texas: Society of Petroleum Engineers, SPE 119900.
- Kell, S. 2011. State Oil and Gas Agency Groundwater Investigations and Their Role in Advancing Regulatory Reforms. A Two-State Review: Ohio and Texas. Prepared for the Ground Water Protection Council, August.
- Kelly, W.R., G. Matisoff, and J.B. Fisher. 1985. The effects of a gas well blow out on groundwater chemistry. *Environmental Geology & Water Science* 7, no. 4: 205–213.
- King, G.E. 2010. *Thirty Years of Shale Gas Fracturing: What have We Learned?* Richardson, Texas: Society of Petroleum Engineers, SPE 133456.
- Laughrey, C.D., and F.J. Baldassare. 1998. Geochemistry and origin of some natural gases in the plateau province, Central Appalachian Basin, Pennsylvania and Ohio. *AAPG Bulletin* 82, no. 2: 317–335.
- Lesage, S., R.E. Jackson, M.W. Priddle, P. Beck, and K.G. Raven. 1991. Monitoring shallow ground water for injected liquid industrial wastes, Sarnia, Canada. *Ground Water Monitoring Review* 11, no. 1: 151–159.
- Lestz, R.S., L. Wilson, R.S. Taylor, G.P. Funkhouser, H. Watkins, and D. Attaway. 2007. Liquid petroleum gas fracturing fluids for unconventional gas reservoirs. *Journal of Canadian Petroleum Technology* 46, no. 12: 68–72.
- Levorsen, A.I. 1967. *Geology of Petroleum*, 2nd ed. San Francisco, California: W.H. Freeman.
- Lorenz, J.C., N.R. Warpinski, P.T. Branagan, and A.R. Sattler. 1989. Fracture characteristics and reservoir behaviour of stress-sensitive fracture systems in flat-lying lenticular formations. *Journal of Petroleum Technology* 41, no. 6: 615–622 (Society of Petroleum Engineers, SPE 15244).
- Lyons, W.C., and G.J. Plisga (Eds) 2004. *Standard Handbook of Petroleum & Natural Gas Engineering*, 2nd ed. Gulf Professional Publishing (Elsevier) Sections 4.20 and 6.9.
- Lyverse, M.A., and M.D. Unthank. 1988. Assessment of Ground-Water Contamination in the Alluvial Aquifer near West Point, Kentucky. Water-Resources Investigation Report 88-4166. Louisville, Kentucky: US Geological Survey.
- Manga, M., I. Beresnev, E.E. Brodsky, J.E. Elkhoury, D. Elsworth, S.E. Ingebritsen, D.C. Mays, and C.-Y. Wang. 2012. Changes in permeability caused by transient stresses: Field observations, experiments and mechanisms. *Review of Geophysics* 50: 2011RG000382.
- Manning, A.H., D.K. Solomon, and A.L. Sheldon. 2003. Applications of a total gas pressure probe in ground water studies. *Ground Water* 41, no. 4: 440–448.
- Martini, A.M., L.M. Walter, T.C.W. Ku, J.M. Budai, J.C. McIntosh, and M. Schoell. 2003. Microbial production and modification of gases in sedimentary basins: A geochemical case study from a Devonian shale gas play, Michigan basin. *AAPG Bulletin* 87, no. 8: 1355–1375.
- Mayer, J.R., B.L. Parker, and J.A. Cherry. 2008. Detailed hydraulic head profiles as essential data for defining hydrogeologic units in layered fractured sedimentary rock. *Environmental Geology* 56, no. 1: 27–44.
- McKee, B., and C. Beasley. 2012. Use of remote sensing technologies to detect surface and near-surface stray gas

- occurrence and potential migration pathways in Tioga Co., Pa. In *Annual Meeting Abstracts*, p. 314, Geological Society of America, Charlotte, NC.
- McLeish, K., M.C. Ryan, and A. Chu. 2007. Integrated sampling and analytical approach for common groundwater dissolved gases. *Environmental Science and Technology* 41, no. 24: 8388–8393.
- MIT. 2011. The Future of Natural Gas: An Interdisciplinary MIT Study. MIT Energy Institute. web.mit.edu/mitei/research/studies/natural-gas-2011.shtml (accessed July 17, 2011).
- Molofsky, L.J., J.A. Connor, S.K. Farhat, A.S. Wylie, and T. Wagner. 2011. Methane in Pennsylvania water wells unrelated to Marcellus shale fracturing. *Oil & Gas Journal* 109, no. 49: 54–93.
- Muehlenbachs, K., 2012. Using stable isotope geochemistry to fingerprint fugitive gases from hydraulically fractured wells. Presentation at Hydraulic Fracture Stimulation: Science, Society & Environment, Canadian Society of Petroleum Geologists' Gussow Conference, Banff, Alberta, November 7.
- Myers, T. 2012. Potential contaminant pathways from hydraulically fractured shale to aquifers. *Ground Water* 50, no. 6: 872–882.
- National Energy Board. 2009. Energy brief: Understanding Canadian Shale Gas. Calgary, Alberta, Canada. <http://www.neb-one.gc.ca/clf-nsi/rnrgynfimt/nrgyprpt/ntrlgs/prmrndrstndngshlgs2009/prmrndrstndngshlgs2009nrgbrf-eng.pdf> (accessed March 12, 2013).
- Nicot, J.P., and I.J. Duncan. 2012. Common attributes of hydraulically fractured oil and gas production and CO₂ geological sequestration. *Greenhouse Gas Science & Technology* 2, no. 5: 352–368.
- Novak, S., and Y. Eckstein. 1988. Hydrochemical brine characterization and identification of brine contamination in aquifers. *Ground Water* 26, no. 3: 317–324.
- Orem, W.H., M.A. Voytek, E.J. Jones, H.E. Lerch, A.L. Bates, M.D. Bates, P.D. Warwich, and A.C. Clarke. 2007. Organic intermediates in the anaerobic biodegradation of coal to methane under laboratory conditions. *Organic Geochemistry* 41, no. 9: 997–1000.
- Osborn, S.G., and J.C. McIntosh. 2010. Chemical and isotopic tracers of the contribution of microbial gas in Devonian organic-rich shales and reservoir sandstones, northern Appalachian Basin. *Applied Geochemistry* 25, no. 3: 456–471.
- Osborn, S.G., A. Vengosh, N.R. Warner, and R.B. Jackson. 2011. Methane contamination of drinking water accompanying gas-well drilling and hydraulic fracturing. *Proceedings of the National Academy of Sciences of the United States of America* 108, no. 20: 8172–8176.
- Pettyjohn, W.A. 1982. Cause and effect of cyclic changes in ground-water quality. *Ground Water Monitoring & Remediation* 2, no. 1: 43–49.
- Rafini, S., and M. Larocque. 2012. Numerical modeling of the hydraulic signatures of horizontal and inclined faults. *Hydrogeology Journal* 20, no. 2: 337–350.
- Rauch, H.W. 1984. Use of lineaments as exploration tools for natural gas and ground water in Martin County, Kentucky. In *Proceedings of the International Symposium on Remote Sensing of the Environment, Third Thematic Conference: Remote Sensing for Exploration Geology*, vol. 1, 249–250. Ann Arbor, Michigan: Environmental Research Institute of Michigan.
- Rauch, H.W. 1983. An investigation of ground-water chemistry as an exploration tool for natural gas in Martin County, Kentucky. In *Proceedings of the Appalachian Basin Industrial Associates*, vol. 5, 127–139. Syracuse University.
- Rauch, H.W., K.G., Narotzky, J. Ragan, and D.J. Newton. 1984. Effect of short lineaments on gas well yield from Devonian shales in Eastern Kentucky, In *Proceedings of Workshop on Remote Sensing/Lineament Applications for Energy Extraction*, DOE/METC/84-9, 63–72. Morgantown, West Virginia: U.S. Department of Energy.
- Ravi, K., M. Bosma, and O. Gastebled. 2002. *Safe and Economic Gas Wells Through Cement Design for the Life of the Well*. Richardson, Texas: Society of Petroleum Engineers, SPE 75700.
- Révész, K.M., K.J. Breen, A.J. Baldassare, and R.C. Burruss. 2010. Carbon and hydrogen isotopic evidence for the origin of combustible gases in water-supply wells in north-central Pennsylvania. *Applied Geochemistry* 25, no. 12: 1845–1859.
- Rodriguez, N.D., and R.P. Philip. 2010. Geochemical characterization of gases from the Mississippian Barnett Shale, Fort Worth Basin, Texas. *AAPG Bulletin* 94, no. 11: 1641–1656.
- Rowe, D., and K. Muehlenbachs. 1999. Isotopic fingerprinting of shallow gases in the Western Canadian sedimentary basin: tools for the remediation of leaking heavy oil wells. *Organic Geochemistry* 30, no. 8: 861–871.
- Roy, J.W., and M.C. Ryan. 2010. In-well degassing issues for measurements of dissolved gases in groundwater. *Ground Water* 8, no. 6: 869–877.
- Royal Society/Royal Academy of Engineering. 2012. Shale gas extraction in the UK: A review of hydraulic fracturing. June 2012, London, UK. www.raeng.org.uk/shale.
- Rozell, D.J., and S.J. Reaven. 2012. Water pollution risk associated with natural gas extraction from the Marcellus Shale. *Risk Analysis* 32, no. 8: 1382–1393.
- Ryder, R.T., and W.A. Zagorski. 2003. Nature, origin, and production characteristics of the Lower Silurian regional oil and gas accumulation, central Appalachian basin, United States. *AAPG Bulletin* 87, no. 5: 847–872.
- Schoell, M. 1988. Multiple origins of methane in the Earth. *Chemical Geology* 71, no. 1–3: 1–10.
- Schnoor, J. 2012. Shale Gas and Hydrofracturing. *Environmental Science and Technology* 46, no. 9: 4686.
- Scott, D., and H.W. Rauch. 1978. Lineaments and ground-water quality as exploration tools for ground water and gas in the cottageville area of Western West Virginia. In *Preprints of Second Eastern Gas Shales Symposium*, 196–205. Morgantown, West Virginia: U.S. Department of Energy.
- Shields, C. 2010. Wells they leave behind. Fiscal Notes, August, Texas Comptroller of Public Accounts. www.window.state.tx.us/comptrol/fnotes/fn1008/wells.html (accessed February 19, 2013).
- Simpkins, W.W., and T.B. Parking. 1993. Hydrogeology and redox geochemistry of CH₄ in a Late Wisconsin till and loess sequence in central Iowa. *Water Resources Research* 29, no. 11: 3643–3657.
- Soeder, D.J. 1988. Porosity and permeability of Eastern Devonian gas shale. *SPE Formation Evaluation* 3, no. 1: 116–124.
- Stahl, W., E. Faber, B.D. Carey, and D.L. Kirksey. 1981. Near-surface evidence of migration of natural gas from deep reservoirs and source rocks. *AAPG Bulletin* 65, no. 9: 1543–1550.
- Stein, D., T.J. Griffin Jr., and D. Dusterhoft. 2003. Cement pulsation reduces remedial cementing costs. *Gastips* 9, no. 1: 22–24.
- Taurus Reservoir Solutions Ltd. 2008. Shallow nitrogen fracturing dimensions and groundwater protection: Evaluation of the ERCB Directive 27: Final Report to Alberta Energy Resources Conservation Board, p. 66.
- Taylor, S.W., B. Sherwood Lollar, and L.I. Wassenaar. 2000. Bacteriogenic ethane in near-surface aquifers: Implications for leaking hydrocarbon well bores. *Environmental Science and Technology* 34, no. 22: 4727–4732.
- Tilley, B., and K. Muehlenbachs. 2013. Isotope reversals and universal stages and trends of gas maturation in sealed,

- self-contained petroleum systems. *Chemical Geology* 339: 194–204.
- Tilley, B., S. McLellan, S. Hiebert, B. Quatero, B. Veilleux, and K. Muehlenbachs. 2011. Gas isotope reversals in fractured gas reservoirs of the western Canadian Footills: Mature shale gases in disguise. *AAPG Bulletin* 95, no. 8: 1399–1422.
- Tilley, B., and K. Muehlenbachs. 2011. Fingerprinting of gas contaminating groundwater and soil in a petroliferous region, Alberta, Canada. In *Proceedings, International Network of Environmental Forensics*, Cambridge, UK, July 25–27, 10 p.
- Tilley, B., and K. Muehlenbachs. 2006. Gas maturity and alteration systematic across the Western Canadian sedimentary basin from four mud gas isotope depth profiles. *Organic Geochemistry* 37, no. 12: 1857–1868.
- Tutuncu, A.N., C. Krohn, S. Gallinsky, J. Leveille, C. Esmersoy, and A.I. Mese. 2012. Environmental challenges in fracturing of unconventional resources. *The Leading Edge* 31, no. 8: 898–906.
- U.S. Department of the Interior (DOI). 2001. Investigation and mitigation of fugitive methane hazards in areas of coal mining. Office of Surface Mining Reclamation and Enforcement Appalachian Regional Coordinating Center, Pittsburgh, PA. 2001. <http://www.osmre.gov/resources/newsroom/News/Archive/2001/090601.pdf>
- US Energy Information Administration. 2012. Natural Gas Monthly, June 2010. Washington DC.
- United States Environmental Protection Agency (US EPA). 2011. *Plan to Study the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources*. Washington, D.C.: Office of Research and Development.
- US National Institute for Occupational Safety and Health (NIOSH). 1983. Comprehensive safety recommendations for land-based oil and gas well drilling. Publication number 83-127. <http://www.cdc.gov/niosh/docs/83-127/>.
- Van Everdingen, R.O. and R.A. Freeze. 1971. Subsurface Waste Disposal in Canada Injection of Liquid Industrial Waste in Deep Wells: A Preliminary Appraisal. Technical Bulletin No. 49, Inland Waters Branch, Environment Canada, Ottawa, Ontario, Canada.
- Van Stempvoort, D.R., and J.W. Roy. 2011. Potential impacts of natural gas production on groundwater quality in Canada and related research needs. Unpublished report, Environment Canada, Burlington, Ontario, Canada, 124p.
- Van Stempvoort, D., J.E. Armstrong, and B. Mayer. 2007a. Microbial reduction of sulfate injected to gas condensate plumes in cold groundwater. *Journal of Contaminant Hydrology* 92, no. 3–4: 184–207.
- Van Stempvoort, D., J.E. Armstrong, and B. Mayer. 2007b. Seasonal recharge and replenishment of sulfate associated with biodegradation of a hydrocarbon plume. *Ground Water Monitoring & Remediation* 27, no. 4: 110–121.
- Van Stempvoort, D., H. Maathuis, E. Jaworski, B. Mayer, and K. Rich. 2005. Oxidation of fugitive methane in ground water linked to bacterial sulfate reduction. *Ground Water* 43, no. 2: 187–199.
- Van Stempvoort, D.R., E.J. Jaworski, and M. Rieser. 1996. Migration of methane into ground water from leaking production wells near Lloydminster. Report for Phase 2 (1995). Publication No. 1996-0003, Canadian Association of Petroleum Producers, Calgary, Alberta, Canada.
- Warner, N.R., R.B. Jackson, T.H. Darrah, S.G. Osborn, A. Down, K. Zhao, A. White, and A. Vengosh. 2012. Geochemical evidence for possible natural migration of Marcellus Formation brine to shallow aquifers in Pennsylvania. *Proceedings of the National Academy of Sciences of the United States of America* 109, no. 30: 11961–11966.
- Warpinski, N.R. 2011. Measurements and observations of fracture height growth. Presented at US EPA Technical Workshop for the Hydraulic Fracturing Study: Chemical & Analytical Methods, Arlington, Virginia. <http://water.epa.gov/type/groundwater/uic/class2/hydraulicfracturing/hfworkshops.cfm#fdst>.
- Warpinski, N.R. 1990. Dual leakoff behaviour in hydraulic fracturing of tight, lenticular gas sands. *SPE Production Engineering* 5, no. 3: 243–252(SPE18259).
- Watney, W.L., A. Bynes, S. Bhattacharya, S. Nissen, and A. Anderson, A. 2003. Natural gas explosions in Hutchinson, Kansas: Geologic factors. Presentation to the North-Central GSA Conference, Kansas Geological Survey, Lawrence, Kansas.
- Watson, T., and S. Bachu. 2007. *Factors Affecting or Indicating Potential Wellbore Leakage*. Richardson, Texas: Society of Petroleum Engineers, SPE 106817.
- Wessels, S.A., A. De La Pena, M. Kratz, S. Williams-Stroud, and T. Jbeili. 2011. Identifying faults and fractures in unconventional reservoirs through microseismic monitoring. *First Break* 29: 99–104.
- Whiticar, M.J. 1999. Carbon and hydrogen isotope systematic of bacterial formation and oxidation of methane. *Chemical Geology* 161, no. 1–3: 291–314.
- Wyoming Department of Environmental Quality. 2008. *Compliance Monitoring and Siting Requirements for Unlined Impoundments Receiving Coalbed Methane Produced Water*. Laramie, Wyoming: Water Quality Division.
- Yager, R.M., and J.C. Fountain. 2001. Effect of natural gas exsolution on specific storage in a confined aquifer undergoing water level decline. *Ground Water* 39, no. 4: 517–525.
- Zoback, M.D., S. Kitasei, and B. Copithorne. 2010. Addressing the Environmental Risks from Shale Gas Development. Briefing paper for Worldwatch Institute.
- Zoback, M.D. 2010. *Reservoir Geomechanics*. Cambridge, UK: Cambridge University Press.
- Zoback, M.D., A. Kohli, K. Das, and M. McClure. 2012. *The Importance of Slow Slip on Faults During Hydraulic Fracturing Stimulation of Shale Gas Reservoirs*. Richardson, Texas: SPE 155475.