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OVERVIEW

Groundwater-quality hazards of methane leakage from hydrocarbon wells: A review of observational and numerical studies and four testable hypotheses

Amy K. Rice[1] | Greg Lackey[2] | James Proctor[3] | Kamini Singha[1,3,4]

[1]Hydrologic Science and Engineering Program, Colorado School of Mines, Golden, Colorado
[2]Civil, Environmental, and Architectural Engineering, University of Colorado, Boulder, Colorado
[3]Department of Geology and Geological Engineering, Colorado School of Mines, Golden, Colorado
[4]Department of Civil and Environmental Engineering, Colorado School of Mines, Golden, Colorado

Correspondence
Amy K. Rice, Hydrologic Science and Engineering Program, Colorado School of Mines, 1516 Illinois St., BE 214, Golden, CO 80401.
Email: amrice@mines.edu

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Methane leakage from hydrocarbon wells plays an important role in the groundwater-quality impacts of hydrocarbon development and presents a more likely hazard than hydraulic fracturing or formation fluids. Methane released from contaminated water wells has been linked with combustion risks and degraded water quality. Potentially, methane can serve as a precursor to other fluids associated with hydrocarbon extraction, such as volatile organics. In this review, we surveyed studies relating to contamination of drinking-water aquifers by methane gas from leaking hydrocarbon wells. Challenges associated with linking methane in groundwater to hydrocarbon extraction are identified, highlighting the need for groundwater-quality and well-integrity databases. Science-based policy recommendations are made, including deeper surface casings and greater cement coverage for wells with deviated wellbores, remediation of faulty abandoned wells, and increased gas-migration monitoring. We suggest four hypotheses to quantify risks to groundwater quality from methane leakage. First, differentiation between thermogenic methane occurring in groundwater due to natural migration and thermogenic methane present due to hydrocarbon development can be used to alleviate the need for baseline measurements of methane in groundwater. Second, methane newly discovered in freshwater aquifers is unlikely to have originated from leaks beginning decades ago. Third, pertaining to the zone separating methane leakage from groundwater, relative permeability will have a larger impact on plume diameter than heterogeneity in intrinsic permeability. Fourth, thermogenic methane in groundwater will serve as a precursor to benzene, toluene, ethybenzene, and xylene (BTEX) under conditions where methane and BTEX coexist in a hydrocarbon reservoir and leakage is transported primarily in the aqueous phase.

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benzene, toluene, ethybenzene, and xylene (BTEX), groundwater quality, hydraulic fracturing, methane leakage from oil and gas wells, stray gas or fugitive gas emissions

1 | INTRODUCTION

Widespread adoption of hydraulic fracturing and directional drilling has substantially increased the availability and use of natural gas (US Energy Information Administration - EIA, 2015, 2016). The elucidation of groundwater-quality hazards from natural gas wells is a relatively new research area, with the large majority of studies occurring within the last decade. Concerns related to groundwater quality mainly focus on fluids associated with hydraulic fracturing or formation fluids reaching drinking-water aquifers. Fluid migration can occur via infiltration of surface spills; leakage from wells due to casing and/or cement failure; or upward migration from deep reservoirs along faults, fractures, or degraded wells. Of these pathways, well integrity issues are considered the most challenging with respect to minimizing risk to groundwater quality because well integrity data are limited and transport mechanisms are not well understood (e.g., Dusseault, Jackson, & MacDonald, 2014; Jackson et al., 2013a; Lefebvre, 2017).

As the principal component of natural gas, methane is the substance most commonly associated with natural gas well leaks. Methane has a low solubility and is generally unreactive until dissolved, in which case methane tends to oxidize unless geochemical conditions in groundwater are strongly reducing. Methane is commonly regarded as nontoxic (e.g., Howarth, Santoro, & Ingraffea, 2011), but concerns associated with methane encroachment into aquifers include (a) combustion or hypoxia-tion dangers in enclosed spaces fed by methane-contaminated wells, (b) possible release of methane into the atmosphere, where it functions as a greenhouse gas with a global warming potential 34 times greater than CO_2 over a 100-year time period and 86 times greater over 20 years, (c) the geochemical evolution of groundwater leading to potential degradation of groundwater quality following the migration of aqueous-phase methane, and (d) methane's role as a potential precursor for other more hazardous fluids (e.g., benzene, xylene) (e.g., Duncan, 2015; IPCC, 2013; US Environmental Protection Agency - US EPA, 2013; Vidic, Brantley, Vandenbossche, Yoxtheimer, & Abad, 2013). Methane leaked in the subsurface is expected to migrate upward via buoyant advection and may, therefore, reach groundwater (Figure 1). Multiple studies have shown that, due to buoyancy, methane is a more likely aquifer contaminant than hydraulic fracturing fluids or brine (e.g., Kissinger et al., 2013; Nowamooz, Lemieux, Molson, & Therrien, 2015).

The transport of methane between deep hydrocarbon reservoirs and groundwater is complex because it involves multiphase, multicomponent flow through a variety of media: faulty cement, wellbore annuli, and heterogeneous formations, including faults and fracture networks. The complexities that arise even in simple geologic settings are illustrated by the findings of Cahill et al. (2017)), a field study in which methane was injected into a relatively homogeneous shallow sand aquifer.

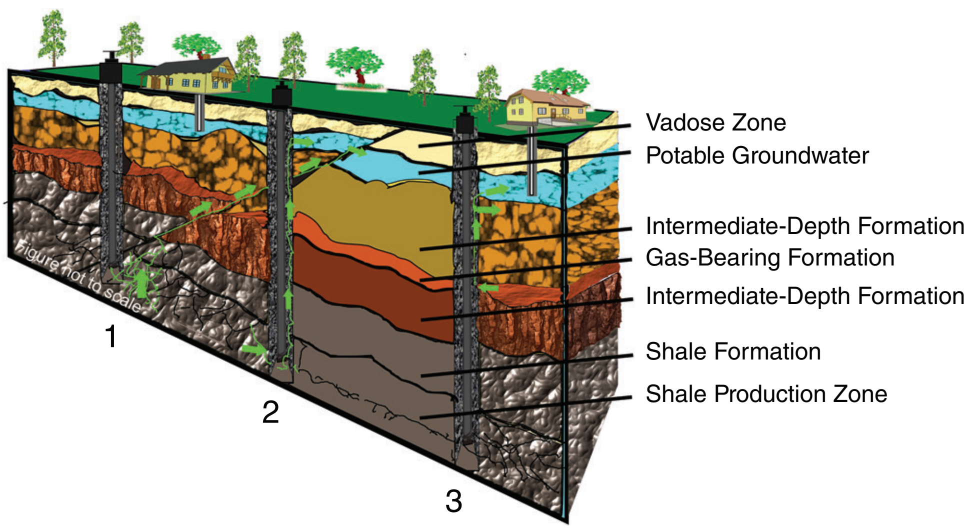

FIGURE 1 Overview of potential methane migration pathways (in green) to groundwater that can be linked to oil and gas operations. Well 1 shows stray gas migrating through fractures to an existing fault, which connects to groundwater (e.g., Cahill et al., 2017; Vengosh, Jackson, Warner, Darrah, & Kondash, 2014). Well 2 shows migration from a deep hydrocarbon reservoir or production casing leak through an open annulus and/or faulty annular cement to groundwater (e.g., Birdsell, Rajaram, Dempsey, & Viswanathan, 2015; Jacquet, 2014; Prpich, Coulon, & Anthony, 2016; Torres, Yadav, & Khan, 2015). Well 3 shows gas migration from an intermediate-depth gas-bearing formation (nonproduction) to groundwater via an open annulus and/or faulty annular cement (e.g., US Environmental Protection Agency - US EPA, 2016). Methane leakage into the matrix below groundwater is also shown, which can lead to groundwater contamination via buoyant advection through pores or fractures. Figure is not shown to scale

The authors showed that a larger than expected area was impacted by methane migration because of slight variations in grain-scale bedding, which hindered upward flow and encouraged the lateral movement (on the scale of 20 m) of free-phase gas. Along with additional controlled methane-release experiments, numerical modeling will play a large role in advancing conceptual models. However, a major challenge of numerically modeling methane migration is achieving an acceptably detailed characterization of the subsurface with respect to project goals, and incorporating the findings of observational studies to verify model results.

We build on a number of recent reviews dealing with environmental impacts of unconventional oil and gas development (e.g., Birdsell et al., 2015; Jackson et al., 2013b; Jacquet, 2014; Kahrilas, Blotevogel, Stewart, & Borch, 2015; Lefebvre, 2017; Prpich et al., 2016; Torres et al., 2015; US Environmental Protection Agency - US EPA, 2016; Vengosh et al., 2014). The major focus of these reviews has been to illuminate potential water quality hazards of hydrocarbon extraction, discuss likely contamination pathways, and highlight knowledge gaps relating to transport. None have exclusively discussed transport of methane from leaking wells to groundwater. Here, we specifically focus on the role of methane in the study of groundwater-quality hazards from natural gas wells. This review is also informed by work synthesizing data on methane in the environment (e.g., Allen, 2014; Brantley et al., 2018; Dusseault et al., 2014; Howarth et al., 2011; IPCC, 2013; Rahm & Riha, 2014; US Environmental Protection Agency - US EPA, 2016; Vidic et al., 2013). Moreover, through a new synthesis, we provide perspective on unresolved questions associated with observational studies of methane in groundwater and how numerical modeling and new observations could be used to address them. This review looks to encourage a shift in popular and scientific focus from less probable groundwater-contamination scenarios, such as by fracturing fluids, which would require unique geologic and hydrologic circumstances for large-scale migration to occur (e.g., Gassiat, Gleeson, Lefebvre, & McKenzie, 2013; Reagan, Moridis, Keen, & Johnson, 2015) and to emphasize the most likely subsurface risk to groundwater quality from oil and gas extraction: methane migration from leaking wells.

We present challenges associated with linking methane concentrations in groundwater to deep hydrocarbon reservoirs and provide science-based policy recommendations. Numerical modeling studies on fluid migration to groundwater resulting from hydrocarbon development are reviewed, and we predict how numerical models will be used to better evaluate groundwater-quality impacts of hydrocarbon extraction. Potential effects of methane leaked from hydrocarbon wells on aquifer geochemistry are presented to examine the environmental impacts of methane leakage apart from its assumed function as a precursor for other fluids. Finally, we present four hypotheses resulting from our synthesis.

1.1 | Observational and field studies

Methane is ubiquitous in the subsurface. Determining the origin of methane in groundwater is often difficult because methane migration may occur from formations at varying depths along an assortment of natural or anthropogenic pathways. It also can be sourced in situ from microbial activity. However, the presence of methane in the shallow subsurface in the vicinity of oil and gas operations may be indicative of a nearby well leak. In this section, we examine how detailed data collection has been used to gain insight into the origin of methane in the shallow subsurface in regions with heavy oil and gas development. We argue that extensive, publicly available groundwater-quality data taken before and after oil and gas development and well-integrity information (i.e., surface casing pressure or vent flow) are necessary to evaluate the environmental impact of hydrocarbon extraction.

1.2 | Challenges of data availability and interpretation

Isotopic analysis of methane is an integral part of groundwater-quality data collection in regions of oil and gas development (Harkness et al., 2017). Methane in aquifers is often naturally sourced from relatively shallow microbial methanogenesis. Methane derived from microbes is termed microbial or biogenic. Thermogenic methane is typically associated with deeper hydrocarbon production zones, where it is produced through the breakdown of organic matter under high temperatures (Schoell, 1988; Whiticar, 1999). There is also evidence that, in some regions, thermogenic methane can be found in the shallow subsurface where erosion has removed the previously existing overlying sediment that had once provided the conditions necessary for its creation (Lavoie et al., 2016).

It is possible to differentiate between microbial and thermogenic methane by evaluating isotope ratios of carbon ($\delta^{13}C$-CH_4) and hydrogen (δ^2H-CH_4). Conclusions based on isotopic evidence can be supported by the isotopic composition and presence or absence of other components of natural gas, such as higher-chain hydrocarbons (ethane, propane, butane, and pentane), of which ethane is the most abundant (e.g., Schoell, 1988; Whiticar, 1999). The presence of thermogenic methane in an aquifer may indicate that gas has leaked upward from the deep subsurface through a pathway created by nearby oil and gas operations (e.g., Lefebvre, 2017; Reagan et al., 2015; Schoell, 1988). However, this is not the only mechanism for thermogenic methane to reach shallow groundwater. A number of studies have shown that thermogenic methane can migrate naturally into shallow aquifers in some regions through deeply circulating groundwater flow paths (e.g., Baldassare, Mccaffrey, & Harper, 2014; Moritz et al., 2015). Gases from intermediate formations, which have compositional and isotopic characteristics distinct from production gas and may be thermogenic in origin, can also leak into the shallow subsurface through pathways created by oil and gas operations (e.g., Jackson, Vengosh, et al., 2013a). Geochemical and physical processes, such as oxidation and diffusion, can also change the isotopic signature and alter the composition of microbial and thermogenic gas (Alperin, Reeburgh, & Whiticar, 1988; Prinzhofer & Pernaton, 1997; Whiticar & Faber, 1986). These factors confound investigations into the origin of methane in the subsurface. Therefore, researchers attempting to assess widespread impacts of oil and gas drilling on groundwater quality are forced to rely on a broad variety of geochemical techniques. These include analyses of major cations and anions, tritium (^{3}H), stable isotopes of lithium ($\delta^{7}Li$), boron ($\delta^{11}B$), and carbon ($\delta^{13}C$-DIC), and the elemental and isotopic compositions of helium, neon, and argon in addition to the compositional and isotopic analyses of natural gas. These techniques and their applications are thoroughly described and demonstrated by Harkness et al. [2017].

The challenge in identifying relationships between oil and gas drilling and stray methane in the subsurface is best illustrated by the studies that have investigated the issue as it relates to northeastern Pennsylvania (e.g., Hammond, 2016; Jackson, Vengosh, et al., 2013a; Molofsky, Connor, Farhat, Wylie, & Wagner, 2011; Molofsky, Connor, Wylie, Wagner, & Farhat, 2013; Osborn, Vengosh, Warner, & Jackson, 2011; Siegel, Azzolina, Smith, Perry, & Bothun, 2015). Osborn et al. (2011) and Jackson, Vengosh, et al. (2013a) collected samples from water wells in regions with active (northeastern Pennsylvania) and nonactive (New York, where hydraulic fracturing currently is not allowed) unconventional oil and gas operations. The authors identified the presence of methane in the majority (>80%) of the tested-water wells and, through compositional and isotopic analyses, showed an increasing risk of thermogenic methane contamination in water wells with close proximity to oil and gas wells. These findings were challenged by Molofsky et al. (2011, 2013) and Siegel et al. (2015), who analyzed large data sets (n = 1,701 and 11,309, respectively) of predrill groundwater samples collected by oil and gas operators in northeastern Pennsylvania. No regional trends were identified between the proximity of water wells to oil and gas operations and stray methane contamination. Instead, topography and groundwater geochemistry were identified as influencing methane concentration, suggesting natural migration of thermogenic methane from the deep subsurface into shallow groundwater (Molofsky et al., 2013; Siegel et al., 2015).

Despite the conflicting narratives of the studies investigating the relationship between oil and gas drilling and groundwater contamination in northeastern Pennsylvania, these findings are not mutually exclusive. Instead, they describe a complex system in which methane migrates into shallow aquifers both naturally through deeply circulating groundwater upwelling in valleys and unnaturally via enhanced pathways created by oil and gas drilling (e.g., Dusseault et al., 2014; Ingraffea, Wells, Santoro, & Shonkoff, 2014; Jackson et al., 2014; Kang et al., 2014, 2016; Lackey, Rajaram, Sherwood, Burke, & Ryan, 2017; Pétron et al., 2014; Watson & Bachu, 2009). Molofsky et al. (2013) and Siegel et al. (2015) had access to data sets large enough to investigate regional trends of methane occurrence in groundwater. However, these studies lack the detailed isotopic measurements necessary to distinguish between natural and anthropogenically induced methane migration. Furthermore, they analyze private databases maintained by oil and gas companies, which lack the transparency of publicly available data sets (Siegel et al., 2015). Osborn et al. (2011) and Jackson, Gorody, et al. (2013b) performed gas compositional and isotopic analyses, but these studies were limited by the size of their sampling data sets (n = 68 and 141) and therefore could not investigate regional-scale trends.

To properly investigate both regional trends of methane occurrence as well as incidents of groundwater contamination, a sufficiently large, detailed, and publicly available groundwater quality database is needed. Li and Carlson (2014) and Sherwood et al. (2016) demonstrated the value of such a database through their analysis of groundwater sampling records collected in the Colorado Oil and Gas Conservation Commission (COGCC) online database. In 2005, the COGCC passed a groundwater sampling regulation that required operators to sample water wells within a one-half mile radius of a proposed oil and gas well and perform gas composition and stable isotope analyses on hydrocarbons present in the sample if methane is found in concentrations greater than 1 mg/L (e.g., COGCC, n.d.; Li & Carlson, 2014; Li, Son, & Carlson, 2016; Sherwood et al., 2016). Through analysis of these records in the Wattenberg Field of Colorado, Sherwood et al. (2016) showed that methane contamination in the region was found to be predominantly microbial in origin (n = 169) with fewer (n = 42) water wells impacted by thermogenic methane (Sherwood et al., 2016). Unlike northeastern Pennsylvania, natural migration of thermogenic methane has not been observed in the Wattenberg Field, thus its presence in drinking water is attributed to oil and gas operations and additional geochemical analyses (e.g., noble gas isotopes) are not necessary to confirm groundwater contamination (Darrah, Vengosh, Jackson, Warner, & Poreda, 2014; Harkness et al., 2017; Sherwood et al., 2016). No regional-scale relationships were observed between the concentrations and isotopic characteristics of methane and their proximity to the nearest oil and gas well in the Wattenberg (Li & Carlson, 2014). Isolated incidents of well-integrity loss among older wells installed before modern regulations were identified as the primary source of thermogenic methane contamination and newer horizontal drilling was not found to increase the rate of groundwater contamination in the region over the years considered (1988–2014) (Lackey et al., 2017; Sherwood et al., 2016).

The baseline sampling requirements in Colorado do not include many of the advanced geochemical analyses proven to be effective at determining the origin of methane in regions where natural thermogenic methane migration complicates investigations into the groundwater-quality impacts of oil and gas drilling (Darrah et al., 2014; Harkness et al., 2017). However, inclusion of these analyses in baseline sampling efforts would be impractical and potentially only necessary in areas where other lines of evidence suggest that groundwater contamination from oil and gas drilling is an issue. Currently, Colorado is the only state that makes detailed records of large-scale baseline groundwater-quality sampling publicly available (e.g., Davies et al., 2014; Lackey et al., 2017; Sherwood et al., 2016).

Lack of available data has been a considerable impediment to the evaluation of the impacts of oil and gas operations on groundwater quality (e.g., Soeder, 2015). Efforts are underway in many regions to identify the potential groundwater-quality impacts of oil and gas drilling and evaluate background concentrations and characteristics of methane in shallow aquifers (e.g., Humez et al., 2016; LeDoux et al., 2016; McMahon, Thomas, & Hunt, 2013b; Moritz et al., 2015; Nicot, Mickler, et al., 2017; Nicot, Larson, et al., 2017b, 2017a; Rivard et al., 2014; Wright, McMahon, Mueller, & Clark, 2012). These data should be gathered into publicly available databases where they can properly inform regional-scale investigations about the relationship between oil and gas drilling and groundwater contamination.

1.3 | Anthropogenically induced pathways of methane migration

Despite the considerable challenges associated with identifying the origin of methane in aquifers, some incidents of methane contamination in groundwater in Ohio (Bair, Freeman, & Senko, 2010), Colorado (McMahon, Thomas, & Hunt, 2013a; Sherwood et al., 2016; Thyne, 2014), Wyoming (Acton Mickelson Environmental, Inc., 2016; Digiulio & Jackson, 2016), and Alberta, Canada (Tilley & Muehlenbachs, 2012) have been determined to be associated with oil and gas activities. In all of these incidents, a faulty or improperly constructed oil and gas wellbore was the primary pathway through which stray methane escaped from the deep subsurface into shallow groundwater (Figure 2(a)).

Indeed, a number of studies have appropriately identified the risks posed by faulty oil and gas wells and have emphasized the importance of assessing the frequency with which wells lose integrity and mechanisms by which gas migration occurs (Dusseault et al., 2014; Ingraffea et al., 2014; Jackson et al., 2014; Kang et al., 2014, 2016; Pétron et al., 2014). Oil and gas wells that have structural-integrity loss typically exhibit surface casing pressure (SfCP) if the surface casing annulus is sealed at the wellhead, or surface-casing vent flow (SCVF) if the annulus is left unsealed (Figure 2(b)) (Dusseault et al., 2014; Lackey et al., 2017; Watson & Bachu, 2009). Local regulations determine whether operators leave the annuli of their wells sealed or unsealed (Dusseault et al., 2014; Lackey et al., 2017). Vertically mobile methane can escape the well and contaminate the surrounding subsurface if gas migration below the surface casing, SfCP-induced gas

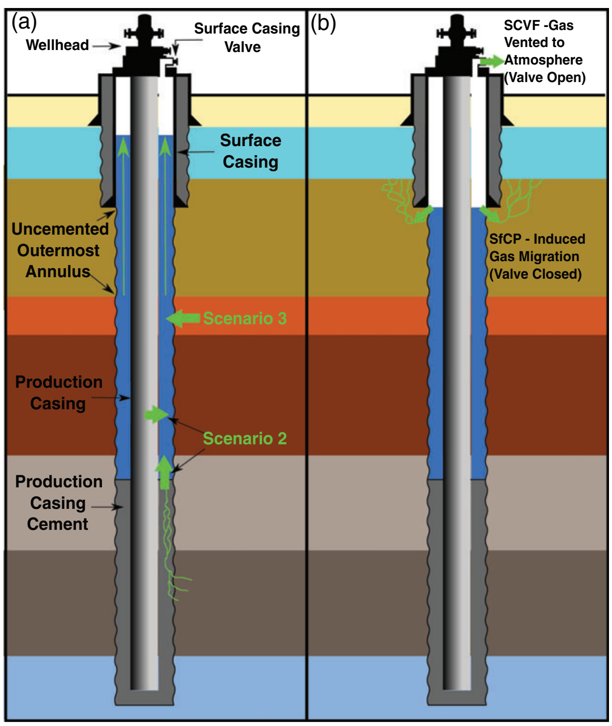

FIGURE 2 (a) Major well components are identified and mechanisms for gas migration along faulty or degraded hydrocarbon wellbores are illustrated. Scenarios associated with methane leakage to groundwater shown in Figure 1 are highlighted, including migration from deep hydrocarbon reservoirs (Scenario 2) and gas migration from an intermediate-depth gas-bearing formation (Scenario 3). (b) Gas well integrity loss can lead to either surface-casing pressure (SfCP) or surface-casing-vent flow (SCVF), depending on gas venting at the surface

migration, or dissolved transport takes place (Figure 1) (Lackey et al., 2017). Leaving the well annuli unsealed at the surface prevents the buildup of pressure at the wellhead and removes the possibility of SfCP-induced gas migration. However, it does not prevent gas migration below the surface casing or dissolved transport (Bachu, 2017). Similar to the paucity of publicly available groundwater quality data, there are few existing oil and gas databases that contain detailed well integrity information (Davies et al., 2014; Lackey et al., 2017). Currently, only the Alberta Energy Regulator, British Columbia Oil and Gas Commission, and COGCC maintain publicly available databases with records of SCVF or SfCP (Lackey et al., 2017; Tao & Bryant, 2014). Gas migration monitoring in the soil surrounding oil and gas wells is only required in Alberta. Other regions rely on baseline groundwater sampling to detect gas migration from faulty oil and gas wells (Bachu, 2017; Sherwood et al., 2016).

While SfCP and SCVF indicate integrity loss, not all wells with compromised structural integrity contaminate groundwater (Bachu, 2017; Lackey et al., 2017; Watson & Bachu, 2009). Of the 446,289 wells in Alberta, approximately 4.9% (~21,868) have exhibited SCVF and 0.73% (3,276) have exhibited gas migration. A small portion (1,040) of wells with SCVF also exhibited gas migration, indicating that most cases of well integrity loss in Alberta do not also result in groundwater contamination (Bachu, 2017). Rather, gas migration is predominantly influenced by well type and underlying geology. Thermal heavy oil and bitumen wells in Alberta are more prone to gas migration than conventional wells, and the majority (90%) of wells exhibiting gas migration are drilled through shallow coal seams (Bachu, 2017), which is suggestive of anthropogenically induced migration of methane gas along well annuli from coal deposits to the surface.

Watson and Bachu (2009) and Bachu (2017) analyzed SCVF and gas-migration records collected by the Alberta Energy Regulator, and found that wells installed with intervals of uncemented casing or deviated wellbores are more prone to losing integrity and developing SCVF (Watson & Bachu, 2009). Similarly, Lackey et al. (2017) electronically mined SfCP test data from reports in the COGCC database and analyzed SfCP in a subset of the Wattenberg Field in Colorado. They found that 3,047 (77.7%) of the 3,923 wells tested exhibited nonzero SfCP and 270 (6.9%) exhibited SfCP critical or above, indicative of a high risk of causing SfCP-induced gas migration. These authors concluded that wellbore deviation, with higher frequencies of SfCP occurrence in horizontal and deviated wells as opposed to vertical wells, and geographic location are the most significant influences on well integrity loss. Although newer unconventional wells with deviated wellbores lose integrity more frequently than older conventional wells (Bachu, 2017; Lackey et al., 2017; Watson & Bachu, 2009), Lackey et al. (2017) showed that they pose less of a threat to groundwater than legacy wells in the Wattenberg Field. Legacy wells in Colorado, installed before modern regulations, were constructed with shorter surface casings than modern wells. In many cases, surface casing length was not sufficient to protect the deepest drinking water aquifer in the region. The majority of newer unconventional wells in the Wattenberg Field are built with surface casings that exceed regulatory standards (Stone, Eustes, & Fleckenstein, 2016), which reduces the risk of SfCP-induced gas migration, and are often cemented above the bottom of the surface casing, which removes the possibility of SfCP-induced gas migration all together (Lackey et al., 2017).

Well-integrity loss has been studied in other regions as well, most notably Pennsylvania (Considine, Watson, Considine, & Martin, 2013; Davies et al., 2014; Ingraffea et al., 2014; Vidic et al., 2013). However, because SCVF/SfCP and gas migration data are not collected by the Pennsylvania Department of Environmental Protection, studies have largely analyzed violation records and inspector notes. Estimated frequencies of integrity loss in Pennsylvania range between 2.0 and 6.6% (Considine et al., 2013; Davies et al., 2014; Ingraffea et al., 2014; Vidic et al., 2013). While overall integrity-loss rates can be estimated from violation records and inspector notes, these documents are not quantitative indicators of integrity loss and thus provide less insight into the degree of integrity loss than records of SCVF/SfCP. Regardless, Ingraffea et al. (2014) showed that unconventional wells installed in northeastern Pennsylvania had the highest risk of losing integrity as compared to conventional wells in the southwestern portion of the state, fitting with the findings from Alberta and Colorado.

Evidence from Watson and Bachu (2009) showed an increased incidence of integrity loss among abandoned wells in Alberta, suggesting that well-integrity and gas-migration monitoring should continue beyond the economic lifetime of a well. Unfortunately, this poses a unique challenge as it is estimated that millions of abandoned wells exist, a portion of which have no documentation; even their location may be unknown (Boothroyd, Almond, Qassim, Worrall, & Davies, 2016; Kang et al., 2014, 2016). Outside of Alberta, little data have been collected on abandoned oil and gas wells; however, studies of methane leakage from abandoned wells have been undertaken in Pennsylvania and the United Kingdom (Boothroyd et al., 2016; Kang et al., 2014, 2016). Kang et al. (2014, 2016) found that abandoned wells contribute a significant portion (5–8%) of anthropogenic methane emissions in Pennsylvania and Boothroyd et al. (2016) showed that abandoned wells in the United Kingdom appear to lose integrity within a decade of decommissioning.

Leakage along hydrocarbon wells is also of concern for carbon sequestration efforts, and estimates of hydrocarbon well integrity and predictions relating to carbon dioxide (CO_2) leakage along wellbores occur in the carbon capture and storage literature (e.g., Crow, Carey, Gasda, Williams, & Celia, 2010; Gasda, Nordbotten, & Celia, 2009; Nordbotten, Celia, Bachu, & Dahle, 2005). Like methane, CO_2 is a buoyant gas in the subsurface, but comparisons pertaining to transport of methane and CO_2 are inexact partially due to the lower solubility, density, and viscosity of methane as compared to CO_2 (e.g., Kang, 2014; Nordbotten, Celia, & Bachu, 2005) and the potential for supercritical CO_2 and/or CO_2-saturated formation water to cause well-cement degradation (e.g., Zhang & Bachu, 2011). Subsurface source zones also differ for these gases (e.g., shale-gas reservoirs vs. formations used for carbon sequestration). However, some insights gained from CO_2 sequestration studies may be applied to methane leakage to identify processes leading to wellbore failure (e.g., Zhang & Bachu, 2011) and provide estimates of well abandonment (e.g., Gasda, Bachu, & Celia, 2004). For example, in a study examining CO_2 leakage risk in the Alberta Basin, Gasda et al. (2004) found that preferential pathways for flow were associated with interfaces between well casing and cement, interfaces between cement and formation rock, or degraded or poorly emplaced cement. Also, a study using wellbore logging tools, in situ point and average permeability measurements, and laboratory tests on sidewall cores of well casing, cement, mud, and the formation surrounding five wells indicated that eccentric placing of well casings (e.g., imperfectly centered production casing, resulting in thin cement coverage in part of the annular region) is a major risk factor for leakage (Duguid et al., 2017). The authors found that casing eccentricity is associated with creation of preferential pathways for flow, which increase effective permeability of annular cement by several orders of magnitude (Duguid et al., 2017). Formation of preferential flow pathways and increases in effective permeability of cement are directly applicable to analysis and simulation of methane migration.

1.4 | Concluding remarks on observational studies

We make a number of recommendations in support of calls for science-based oil and gas policy (e.g., Nicot, 2017). Higher frequencies of integrity loss among wells with deviated wellbores, a key component of newer unconventional wells, suggest that wells constructed in this manner should be built with deeper surface casings and greater production casing cement coverage to prevent SfCP-induced stray gas migration. In regions that require annuli to be left unsealed at the surface (e.g., Pennsylvania and Alberta), more work needs to be done to quantify greenhouse-gas emissions from SCVF and efforts should be encouraged to prevent, capture, or flare stray gas releases (e.g., Brandt et al., 2014; Pétron et al., 2012, 2014). A greater focus is needed on locating undocumented abandoned wells, monitoring abandoned wells for integrity loss and gas migration, and targeting problem wells for remediation to meet modern regulatory standards. These findings, along with the geographic dependence of integrity loss, make it clear that SfCP and SCVF monitoring should be expanded to all regions with oil and gas development. Gas-migration monitoring in soils surrounding the wellbore, in a manner similar to what is done in Alberta, should also be considered in the United States to allow quantification of the relationship between well-integrity loss and groundwater contamination and to help prevent future incidents of groundwater contamination. Fundamentally, detailed, publicly available baseline and postproduction groundwater-quality data and measurements of SfCP or vent flow should be undertaken in all regions with oil and gas development.

2 | MODELING STUDIES: UNPACKING ASSUMPTIONS TO INFORM CONCEPTUAL MODELS OF METHANE MIGRATION

In conjunction with observational studies, numerical models are useful to elucidate the groundwater-quality impacts of hydrocarbon development. We focus on the evolution of assumptions used to create numerical models of subsurface methane transport. Our goals are: (a) to investigate which assumptions are useful and (b) to predict how numerical models will be used to better evaluate the relationship between groundwater quality and oil and gas extraction. We begin by discussing why simplifying assumptions are needed to numerically model these systems. We then provide a critical review of assumptions relating to porous media attributes and multiphase flow in the context of subsurface transport of fluids associated with oil and gas development to groundwater. We conclude with a discussion of insights on hydrocarbon/groundwater systems gained through numerical modeling efforts.

2.1 | Modeling studies and assumptions

Quantitative analysis of subsurface methane migration is complex, potentially involving advective, diffusive, and reactive transport of multiple pressure and temperature-dependent phases (e.g., gas and liquid) and components (e.g., methane, air, and water vapor in the gas phase). For computational studies of methane leakage from natural gas wells, the size of the model may be prohibitive: the scale needs to be large enough to capture deep hydrocarbon production zones and shallow drinking-water aquifers, typically separated by hundreds to thousands of meters. Meanwhile, discretization must be small enough to accurately resolve the edges of a migrating methane plume and potentially a wellbore. Modern computation currently cannot handle detailed analysis of methane migration at such large scales and small resolutions inexpensively. Therefore, recent advances in numerical assessment of methane migration have been predicated on a continually evolving understanding of how simplifying assumptions impact estimation of methane migration upward over thousands of meters from hydrocarbon reservoirs to groundwater (Table 1). This section will discuss the progression of model assumptions leading up to the simulation of methane leakage from hydrocarbon wellbores.

2.2 | Models of fluid migration associated with hydrocarbon development, not including simulation of methane migration

Myers (2012b) was among the first to use numerical modeling to examine groundwater quality impacts of modern oil and gas development. He simulated transport of hydraulic fracturing fluids from the Marcellus Shale to a freshwater aquifer along a fully connecting, vertical fault. Myers found that advective transport from hydraulically fractured hydrocarbon reservoirs to groundwater in his model could occur in less than 10 years. This work was criticized for simplified assumptions pertaining to the region of the Marcellus; contested assumptions include the presence of the fully penetrating vertical fault, single-phase flow in water-saturated, homogeneous porous media, and an upward hydraulic gradient driving flow (e.g., Flewelling & Sharma, 2014; Saiers & Barth, 2012). Replying to Saiers & Barth (2012), Myers (2012a) defended this work, highlighting the use of sensitivity analysis to explore contaminant transport through a complex, data-sparse region.

More recent studies have provided more complex conceptual formulations, albeit still employing some of the assumptions used by Myers (2012b). Gassiat et al. (2013) examined contamination of groundwater from hydraulic fracturing at depth via transmissive faults and fractures in a generic sedimentary basin. Their model was loosely based on the Utica shale in the St. Lawrence Lowlands, Québec, Canada. Gassiat et al. found that groundwater contamination could occur in less than 1,000 years under specified assumptions, including the presence of a high permeability fault, hydraulic fracturing in the upper portion of the shale near the fault, and high overpressure in the shale formation. As the authors state, these results are of limited applicability due to use of a two-dimensional model, which implies an infinitely extensive fault, and single-phase flow.

Continuing the effort to constrain fluid transport from deep oil and gas reservoirs, Brownlow et al. (2016) focused on unintended migration along hydrocarbon wells. They used a three-dimensional, single-phase model to examine leakage into groundwater from abandoned wells in the Eagle Ford Shale play in south Texas. They included abandoned wells that were converted to water wells for livestock and domestic supply in their model, and concluded that this abandonment procedure presented increased contamination risk to groundwater resources. However, the assumption of single-phase flow and site-specific parameterization limits transferability to other sites or systems.

The role of the subsurface porous matrix also plays a critical role in fluid migration from deep hydrocarbon reservoirs to groundwater. Birdsell et al. (2015) utilized a single-phase, three-dimensional model to investigate the effects of the various phases of hydraulic fracturing operations (hydraulic fracturing fluid injection, well shut-in, production, and abandonment) on flow of fluids from the Marcellus Shale to groundwater with and without a highly permeable pathway. They found that inclusion of porous matrix imbibition and well suction from the production phase in their simulations reduced the risk of groundwater contamination by up to a factor of 10, as defined by the cumulative mass of a fracturing-fluid tracer reaching

TABLE 1 Simplifying assumptions used in computational studies of fluid migration to groundwater from hydrocarbon reservoirs

Author	Driving force	Dimensions	Permeable pathway	Homogeneous permeability	Single phase	Methane migration
Myers (2012b)	ΔH imposed at boundaries	3	Yes	Yes	Yes	No
Kissinger et al. (2013)	ΔP from injection, reservoir P	3	Yes	No (layers)	Yes/no	Yes
Gassiat et al. (2013)	Reservoir P	2	Yes	Yes	Yes	No
Birdsell et al. (2015)	ΔH imposed at boundaries	3	Yes	Yes	Yes	No
Nowamooz et al. (2015)	Buoyancy, Reservoir P	3	Yes	Yes	No	Yes
Reagan et al. (2015)	Buoyancy, ΔP from injection/production	3	Yes	Yes	No	Yes
Brownlow, James, and Yelderman Jr. (2016)	Induced ΔH	3	Yes	No (layers)	Yes	No
Raynauld et al. (2016)	Regional ΔH, density effects, topography	2	No	No (layers)	Yes	Yes (dissolved)
Rice, McCray, and Singha (2018)	Buoyancy, reservoir P	3	No	No (correlated random variation)	No	Yes

groundwater 1,000 years after the beginning of extraction operations. These results highlight a simplifying assumption used in prior studies: neglecting imbibition. The numerical model employed single-phase analysis with a semianalytical, one-dimensional solution for two-phase flow used as a general sink term for imbibition.

2.3 | Models of fluid migration associated with hydrocarbon development, including simulation of methane migration

Numerical models that incorporate methane migration show methane arriving at groundwater in greater volumes than other fluids associated with hydrocarbon development. Kissinger et al. (2013) were the first to simulate methane transport associated with hydrocarbon development in a groundwater-quality study. They explored several flow paths for hydraulic fracturing fluid, brine, and methane and performed simulations to estimate how these fluids could leak into shallower layers in North Rhine-Westphalia and Lower Saxony, Germany. Their results indicated that transport of substantial quantities of gas-phase methane and small quantities of liquid-phase contaminants to groundwater can occur if a fully connecting permeable pathway is assumed, with methane transport requiring low gas-phase residual saturation in the pathway. Kissinger et al. (2013) used three-dimensional meshes, multiphase flow (allowing them to determine the importance of gas-phase residual saturation), and physically plausible driving forces for their site, thus avoiding assumptions criticized in earlier studies with the exception of the fully connecting pathway. The authors stressed that their results are not sufficient to assess risk to groundwater due to high levels of parameter and scenario uncertainty, an important limitation of models intended as case studies.

Pathways of methane migration have been the major focus of subsequent numerical studies. Reagan et al. (2015) used a three-dimensional, multiphase model to investigate gas and water migration from deep hydrocarbon reservoirs to groundwater. The initial condition used in these simulations is a hydrostatic pressure profile with no overpressure in the shale-gas reservoir. Other studies have concluded that overpressure in the shale-gas reservoir is an important intial condition with respect to upward fluid migration along a permeable feature (e.g., Gassiat et al., 2013; Nowamooz et al., 2015). Reagan et al. (2015) focused on the relative importance of transport along faults or fractures compared to transport along natural gas wells, and concluded that transport along wells presented the greater hazard to groundwater quality than transport along faults and fractures. This is due to the larger overall volume of voids in faults and fractures as compared to void spaces in well annuli, even given greater intrinsic permeability of faults and fractures compared to wells. Gas transport through a lower-porosity connecting feature conveys more methane to an aquifer since less gas is stored within the feature, a conclusion that is supported by studies of fluid migration in fault zones and fracture networks.

Following Reagan et al. (2015), several authors focused on the role of the wellbore as the primary pathway for fluid migration from deep hydrocarbon reservoirs to groundwater. Nowamooz et al. (2015) modeled brine and methane leakage rates along a decommissioned wellbore in the St. Lawrence Lowlands of Québec. Unlike Reagan et al. (2015), these authors simulated overpressure in the shale-gas formation driving upward methane and brine migration along a faulty wellbore. Similar to Reagan et al. (2015), Nowamooz et al. (2015) found that cementation quality and hydrodynamic properties of the well annulus control travel times of methane from hydrocarbon production zones to groundwater. Travel times for methane in their simulations ranged from a few months to 30 years. The authors varied the permeability and initial gas saturation of the source zone Utica Shale, which is homogenous over the 1,000 m radius of the simulated domain. They found that, for most cases, leakage at the base of a freshwater aquifer was sustained for the 100-year duration of their simulations. These findings are at odds with Reagan et al. (2015), who concluded that methane flow to groundwater was more apt to be transient. The differences are due largely to disparity in conceptual models, specifically in assumed extent, permeability and presence/absence of overpressure in hydrocarbon source zones. Rice et al. (2018) examined the role of multiphase analysis on methane migration from a leaking wellbore to groundwater without an explicitly permeable pathway, but rather through an intact matrix. They demonstrated that changes in parameters impacting capillarity and relative permeability strongly influence the volume of methane reaching groundwater. Relative permeability of methane is dependent on gas-phase saturation and thus requires multiphase analysis. They also concluded that methane leakage from natural gas wellbores at depths potentially conducive to leakage can reach groundwater in less than 1 year, highlighting the need for hydrogeological characterization of formations between groundwater and hydrocarbon production zones. The major simplifying assumption in this study is source zone pressure sustained over the 100-year duration of the simulations, as in Nowamooz et al. (2015).

2.4 | Concluding remarks on numerical studies

The appropriate application of simplifying assumptions dominates debates on how best to apply numerical techniques to investigate groundwater-quality impacts of hydrocarbon development. For example, single-phase models are useful to reduce computational cost (e.g., Birdsell et al., 2015). However, multiphase models allow more realistic consideration of gas-phase relative permeability and analysis of density and viscosity effects associated with multiple interacting phases (e.g., Rice et al., 2018). To include methane in models, multiphase analysis is necessary to capture gas- and aqueous-phase flow. Subsurface homogeneity is another simplifying assumption that persists in current studies. The importance of heterogeneity in permeability to single-phase transport through porous media is well-known (e.g., Bear, 1972; Freeze & Cherry, 1979). For the added complexity of multiphase systems, the role of heterogeneity in permeability is as consequential, but less well characterized.

Modeling studies investigating of the relative importance of processes and parameters associated with methane migration will be useful because these systems are often complex and poorly characterized, making model calibration difficult or impossible in most cases. Data are often lacking or sparse pertaining to (a) groundwater chemistry, including baseline measurements before hydrocarbon development begins and continued monitoring after production ends and (b) characterization of formations below groundwater where wellbore leakage may occur. However, more accurate models might be achieved if regulations were changed to require dedicated wells installed to monitor groundwater quality up- and down-gradient from oil and gas wells (Jackson, Vengosh, et al., 2013a). For example, Soeder (2015) analyzed groundwater for major and minor cations, metals, anions, bicarbonate, dissolved methane and benzene, toluene, ethybenzene, and xylene (BTEX), total organic carbon, and isotopes of carbon, hydrogen, and strontium to provide baseline concentrations of fluids of interest to with respect to fluid migration from boreholes to groundwater. Current practice is to collect samples from domestic water wells in close proximity to drilling, which depends on existence of such wells and cooperation from landowners. In multiple cases, requests to sample nearby water wells have been refused; some landowners may view groundwater monitoring as hostile to hydrocarbon extraction (Soeder, 2015).

Another major challenge facing computational studies of subsurface flow and transport, including methane migration, is achieving the appropriate degree of complexity with respect to model structure (parameterization, dimensionality, grid resolution, etc.) and which processes are simulated. Decisions on which simplifying assumptions are useful should be based on study goals, with additional levels of complexity systematically identified as informative (e.g., Freedman et al., 2017). Complexities may be selected based on observations and predefined error tolerances, based on study goals, between observations and model output. Additional data on formations separating hydrocarbon wells from groundwater should also be used to inform models of methane migration due to wellbore leakage. Oil and gas operators regularly collect data on production zones parameters such as porosity and permeability. Similar measurements of the intermediate zones should be undertaken. Finally, additional laboratory (e.g., Zhang & Yu, 2016) and controlled-release experiments (e.g., Cahill et al., 2017) are needed to identify the relative importance of parameters (e.g., water saturation, source pressure, capillary pressure/saturation parameters) and processes (e.g., sorption, mobile–immobile transport) impacting methane migration from hydrocarbon wellbores to groundwater in real systems. For numerical models of hydrocarbon well leakage of methane, testing model results against data is challenging due to spatial and temporal variability in methane concentrations in groundwater and the short durations of most methane concentration records. With an increasing amount of data available, model verification procedures are expected to become more common and provide insight on which processes and elements of model structure are most instructive.

Many of the issues and outstanding challenges discussed above will become more tractable as computational resources continue to improve (e.g., Hayley, 2017). "Early" studies of groundwater-quality impacts of oil and gas development are only 6 years old as of this writing. Continual evaluation and use of only the most necessary simplifying assumptions is a vital task in the progression of the state of the science of fluid migration from hydrocarbon reservoirs to groundwater. Toward these goals, it will be vital to strengthen interdisciplinary collaborations linking petrophysical, geomechanical, and hydrogeological aspects of these problems.

3 | STUDIES ON GEOCHEMICAL REACTIONS OF METHANE IN GROUNDWATER SYSTEMS

Methane in groundwater sourced from natural gas well leakage can influence aquifer geochemistry. Kelly, Matisoff, and Fisher (1985)) provide an early description of the geochemical impacts of natural gas well leakage. They examined perturbations in groundwater chemistry caused by a gas well blow-out that introduced a large amount of methane into a shallow freshwater aquifer in Ohio. They saw elevated levels of Fe^{2+}, Mn^{2+}, Ca^{2+}, sulfide, alkalinity, and pH, and lowered levels of dissolved oxygen, SO_4^{2-}, and NO_3^- in wells affected by methane leakage. Using equilibrium thermodynamic models, the authors attributed these changes to methane oxidation, sulfate reduction, and reduction and dissolution of iron and manganese oxides. Changes in chemical variables were so considerable that the authors suggested using anomalous increases in pH, decreases in Eh, and complete or nearly complete reduction of SO_4^{2-} to HS^-, NO_3^- to NH_4^+, and reduction of Fe and Mn oxides leading to precipitation of Fe and Mn to inform hydrocarbon exploration about promising locations for drilling.

A review of more recent studies indicates methane leakage can have a profound impact on groundwater chemistry, but the changes rarely present substantial health hazards (e.g., Duncan, 2015; US Environmental Protection Agency - US EPA, 2013).

Methane is a common component of landfill leachate, the groundwater-quality impacts of which have been studied extensively (e.g., Christensen et al., 2001; Grossman, Cifuentes, & Cozzarelli, 2002; Kjeldsen et al., 2002; Nikiema, Brzezinski, & Heitz, 2007; Renou, Givaudan, Poulain, Dirassouyan, & Moulin, 2008). Comparisons between landfill leachate and gas-well leakage are approximate due to tendencies of landfill leachate toward more diffuse sources, different fluid compositions, and shorter transport distances to groundwater as compared to leaking wells. However, natural attenuation via anaerobic methane oxidation has been repeatedly shown to provide an important sink for landfill methane in groundwater systems (e.g., Grossman et al., 2002; Nikiema et al., 2007), a fate expected to be shared by thermogenic methane (e.g., Roy et al., 2016).

Oxidation of methane in groundwater from hydrocarbon well leakage has been related to bacterial sulfate reduction and sulfide production (Van Stempvoort, Maathuis, Jaworski, Mayer, & Rich, 2005). Methane oxidation can occur relatively quickly. Published maximum methane oxidation rates in groundwater vary by orders of magnitude (3.21×10^{-8} to 4.25×10^{-3} kg m^{-3} d^{-1}) with oxidation rates dependent on factors such as dissolved methane and sulfate concentrations and groundwater temperature (Roy, Molson, Lemieux, Van Stempvoort, & Nowamooz, 2016). However, in simulations parameterized based on a field site in Alberta with a relatively high maximum oxidation rate (1×10^{-3} kg m^{-3} d^{-1}), Roy et al., (2016) found that methane concentration decreased from 110 mg/L (i.e., solubility) to 10 mg/L in 5 years. In addition to consumption of methane and sulfate, Wolfe and Wilkin (2017) observed groundwater chemistry variability, which they linked to methane migration from a coalbed production zone in Colorado. Changes included production of higher molecular weight hydrocarbons and a shift in carbon, oxygen, and sulfur isotopes present in groundwater. They also failed to observe mobilization of heavy metals from soil grains, providing evidence against the hypothesis that redox changes due to methane leakage from hydrocarbon wells are associated with release of heavy metals into aquifers. Dissolution of aquifer solids is likely discouraged by microbial production of hydrogen sulfide, which stabilizes metals such as arsenic and lead in soil grains (Wolfe & Wilkin, 2017). Molofsky et al. (2016) looked for groundwater-quality factors that can be used to predict the presence of methane in the region of the Marcellus Shale. They identified three factors that, when combined, had strong predictive capability of methane contamination: low NO_3^- and SO_4^{2-} redox condition (similar to Kelly et al. (1985)), water rich in sodium, and a valley location.

Modeling studies have sought to extend applicability of observations by examining the geochemical impact of methane leakage in hypothetical aquifers. For example, Schwartz (2015) simulated theoretical leakage of methane gas caused by hydraulic fracturing. He modeled major constituents of groundwater and the seven most hazardous trace elements found naturally in groundwater (As, Cd, Cr, Ni, Pb, Se, and U). His results show depletion of the most of the hazardous elements due to methane leakage as acidity and oxygen fugacity decrease. Desorption reactions of Cr and Se from soil grains are also observed, but the author concluded that this is a minor risk (Schwartz, 2015). Roy et al. (2016) examined whether confined or unconfined aquifers are more susceptible to methane contamination. They found that methane oxidation attenuates methane concentrations from natural gas well leakage in both confined and unconfined aquifers, but methane contamination was more extreme in confined aquifers due to lack of venting to the atmosphere. The authors urged analysis of natural background aquifer geochemistry combined with numerical modeling for aquifer vulnerability assessment in regions of oil and gas development (Roy et al., 2016).

3.1 | Concluding remarks on geochemical studies

Methane oxidation leading to attenuation of methane is likely in groundwater, often accompanied by sulfate reduction and the production of dissolved sulfide. It appears improbable that the dissolution of soil grains, by, for example, the reduction of ferric iron in iron hydroxides, will lead to heavy-metal mobilization (Wolfe & Wilkin, 2017). However, Ziegler, McGuire, and Cozzarelli (2015) observed As and trace-element mobilization due to the introduction of other hydrocarbons besides methane to sediments. The authors conclude that trace-element mobilization can occur in systems with biodegradation of organic matter, suggesting that mobilization of heavy metals due to methane encroachment warrants further study under iron-reducing conditions. Confined aquifers are more susceptible to stray gas contamination than unconfined aquifers (Roy et al., 2016; Sherwood et al., 2016), and therefore should be a focus of future geochemical studies.

4 | IDEAS FOR ADVANCEMENT AND FOUR TESTABLE HYPOTHESES

We examine critical open questions and suggest important topics for future research to quantify risks to groundwater quality from methane leakage associated with hydrocarbon development. The first challenge we discuss is investigation of methane migration along natural pathways to better distinguish between naturally and anthropogenically induced methane contamination, for example, by testing whether fault and fracture networks are necessary for gas migration from deep reservoirs (e.g., Molofsky et al., 2011). The second challenge is improving estimates of when leaking hydrocarbon wells will lead to observed methane concentrations in groundwater and what factors influence plume size. The last issue we explore here is discovering whether methane concentrations in groundwater can be linked to contamination from BTEX compounds, which are toxic components of natural gas. For each idea, we highlight a testable hypothesis emerging from current work.

Hypothesis 1: *Differentiation between thermogenic methane occurring in groundwater due to natural migration from deep hydrocarbon reservoirs and thermogenic methane present from wellbore leakage or transport along induced fractures can be used to alleviate the need for baseline measurements of methane concentrations in groundwater.*

The foremost challenge for observational studies is parsing out the origin of methane discovered in groundwater. Thermogenic methane that reaches groundwater via natural migration (i.e., via naturally occurring faults and fractures or slow migration through the matrix and not induced by oil and gas development) can add noise to the signal of methane sourced from oil and gas extraction (e.g., Raynauld et al., 2016), especially if natural and anthropogenically induced migration are associated with the same source formation. Also, thermogenic methane sourced from formations shallower than the shale-gas formation can be present in groundwater. Thermogenic methane from intermediate sources can be distinguished from shale gas if variations in isotopic signatures with depth are known. Numerical studies have focused on anthropogenically induced methane migration (Table 1) (e.g., Gassiat et al., 2013; Nowamooz et al., 2015), with no work on groundwater-quality impacts of natural methane migration. Computational work exploring this phenomenon, including elucidation of the hallmarks of natural migration such as expected isotopic fractionation of natural gas following migration from deep production zones along varying flow paths (e.g., Alperin et al., 1988; Schoell, 1988; Whiticar, 1999; Whiticar & Faber, 1986), probable shapes of breakthrough curves, and concentrations of methane and other natural gas components associated with natural migration, would be of value to observational scientists as they investigate plausible sources of methane in groundwater (e.g., Gross et al., 2013; Iverach, Beckmann, Cendón, Manefield, & Kelly, 2017; Li et al., 2016; Molofsky et al., 2013; Osborn et al., 2011; Rogers, Burke, Osborn, & Ryan, 2015; Sherwood et al., 2016), usually without access to baseline methane concentrations before hydrocarbon development began (e.g., Huang, Li, Pang, Wang, & Yang, 2017; Smedley, Ward, Bearcock, & Bowes, 2017; Soeder, 2015). Identifying methane source zone parameters, including methane pressure and the source formation extent and permeability, will be a challenging aspect of this work and a topic appropriate for interdisciplinary collaborations, for example, among hydrogeologists and petrophysics experts or hydrocarbon exploration researchers.

Hypotheses 2 and 3 deal with temporal and spatial aspects of methane migration, which are often related. We discuss them together below.

Hypothesis 2: *For most wellbore leakage scenarios, methane will reach groundwater within months or years, so methane newly discovered in freshwater aquifers is unlikely to have originated from legacy wells with leaks beginning decades ago.*

Hypothesis 3: *At a given (i) depth, (ii) source pressure, and (iii) mean intrinsic permeability, methane plume diameter following leakage from a faulty wellbore will vary primarily as a function of the relative permeability of the porous media separating a leak source zone from groundwater. For gas-phase methane leakage from a hydrocarbon wellbore, relative permeability will have a larger impact on plume diameter than any other porous media parameter, including heterogeneity in intrinsic permeability of the intervening media.*

Methane flow rates from leaking hydrocarbon wells to groundwater vary in both time and space. No observational studies to date have presented subsurface methane flow rates associated with wellbore leakage. Also, with the exception of the controlled-release experiment of Cahill et al. (2017), the spatial footprint of methane leakage (e.g., processes controlling expected plume size) has not been explored. Computational studies presenting methane flow rates due to well leakage (e.g., Nowamooz et al., 2015; Reagan et al., 2015) assume spatial homogeneity in permeability and no "anomalous" transport due, for example, to mobile and immobile zones, and, therefore, generally can be interpreted as conservative cases (i.e., tending to minimize travels times and maximize concentrations arriving at aquifers). Currently, methane plume size and travel time distributions are not well predicted (e.g., Rice et al., 2018). It is expected that future studies will focus on the influence of processes and porous media and fractured rock properties tending to attenuate methane concentrations and/or decrease travel times, and which would serve to illuminate the connection between well integrity loss and stray gas migration (e.g., SfCP-induced gas migration; e.g., Lackey et al., 2017; Sherwood et al., 2016). Relative permeability of the formation surrounding a leaking hydrocarbon wellbore is important because it can impact effective permeability by orders of magnitude, as a function of phase saturation. Therefore, proportionally minor changes in relative permeability can have a large influence on methane gas-phase migration.

Hypothesis 4: *Thermogenic methane in groundwater will serve as a precursor to BTEX under conditions where methane and BTEX co-occur in a hydrocarbon reservoir and leakage from hydrocarbon wellbores is transported primarily in the aqueous phase.*

Minor constituents of natural gas may include aromatics such as BTEX, with natural gas composition of these compounds varying by reservoir (e.g., Faramawy, Zaki, & Sakr, 2016). In dry gas reservoirs (i.e., reservoirs where methane occurs without condensate or liquid hydrocarbons, with a typical gas-to-oil ratio >100,000; Schlumberger, n.d.), BTEX is unlikely to co-occur with methane. BTEX compounds are highly toxic, with nervous system damage or increased risk of cancer reported for low concentrations (maximum contaminant levels are: benzene: 5 ppb; toluene: 1000 ppb; ethylbenzene: 700 ppb; and xylene: 10,000 ppb) (US Environmental Protection Agency - US EPA, 2013) BTEX in groundwater has been linked with surface spills associated with hydrocarbon extraction (Gross et al., 2013); loss of well integrity during hydraulic fracturing operations (Digiulio & Jackson, 2016); and, in modeling results of transport in aquifers, predicted to reach domestic water wells setback from oil and gas wells (Rogers et al., 2015). Benzene is concerning in groundwater due to its high toxicity and mobility: benzene is 10 times more soluble than ethylbenzene or xylenes and is considered highly mobile in soil (K_{oc} = 59) (Williams, Ladd, & Farmer, 2006). However, benzene is volatile and degrades quickly (on the order of days) in the gas phase. The residence time of methane in the atmosphere is on the order of a decade (Howarth et al., 2011; IPCC, 2013). Due to differences in parameters impacting environmental fate and transport, it is unknown under what conditions benzene and other BTEX compounds originating from oil and gas reservoirs may be found with thermogenic methane in groundwater. Future studies elucidating the relationship between BTEX and thermogenic methane in aquifers would allow the use of methane as a precursor for these compounds: as the majority constituent of natural gas and generally conservative with regard to transport, methane concentrations from leakage are likely to be higher and thus easier to measure.

5 | CONCLUSIONS

This review has served to highlight the most likely subsurface risk to groundwater quality from oil and gas development: methane leakage from hydrocarbon wells, which is more probable than contamination by production fluids. Methane is commonly found in groundwater, but it can be difficult to link to oil and gas development. Here, we outline the state of the science with respect to data collection and numerical modeling associated with methane migration in oil and gas systems. Fluid transport from deep hydrocarbon reservoirs to groundwater is a different sort of problem than those encountered by traditional hydrogeological models due, for example, to the presence of upward migration over thousands of meters and need for multiphase analysis. Most studies indicate that long-term methane migration along wellbores presents a bigger threat than migration during active operations (e.g., Zhang & Soeder, 2016) or along faults (Reagan et al., 2015). Postproduction wells, especially those abandoned using older, less-stringent regulations or with unknown locations, are shown to present the greater risk to groundwater as compared to active wells.

We suggest that there is a need for publicly available, standardized data of groundwater methane concentrations that are collected through a standard sampling protocol and controlled for quality. Water-quality data, including detailed gas compositional and isotopic measurements of methane, should be linked to oil and gas databases that include construction, completion, remediation, and violation records. Efforts should also be made to expand SfCP and SCVF testing and include these records in publicly available oil and gas databases, as they are easily measured indicators of well integrity. Regulators should also consider monitoring the soil around oil and gas wells for gas migration (as done in Alberta) as a more effective method for detecting leakage from faulty wellbores than sampling nearby groundwater wells. Furthermore, we recommend that wells with deviated wellbores associated with directional drilling be constructed to higher standards (as has been done in the Wattenberg Field of Colorado), which include deeper surface casings and greater cement coverage along the wellbore, to decrease the likelihood of methane leakage into groundwater. In states that require well annuli to remain unsealed, we support efforts to prevent stray gas venting to the atmosphere by capturing or flaring methane emissions. Sources of thermogenic methane in groundwater would be clarified by data collected by operators regarding the varying isotopic signature of methane with depth. We also highlight the need for locating and remediating problematic abandoned wells.

We recommend modeling efforts focused on minimizing computational cost while capturing processes substantially impacting methane migration. For example, a lack of data on formations between hydrocarbon production zones and groundwater has limited modeling that examines hydrocarbon well leakage (e.g., Lavoie et al., 2014; Rice et al., 2018). We suggest modeling studies designed to identify which observations in these formations would be most informative, with respect to specific parameters and spatial and temporal discretization of measurements. Furthermore, we recommend additional modeling work to evaluate the role of heterogeneity in porous media properties such intrinsic and relative permeability, porosity, and initial aqueous saturation. Multiphase analysis allows simulation of methane gas transport through variably water-saturated media, including more accurate characterization of relative permeability and evaluation of density effects than single-phase analysis. Both single- and multiphase studies indicate that long-term transport via faulty wellbores, including annular transport, provides the greatest risk of groundwater contamination, emphasizing potentially large hazards associated with faulty legacy and postproduction wells. We stress the need for interdisciplinary collaborations, for example, among petrophysical, geomechanical, and hydrogeological researchers, to advance the state of the science with regard to numerical modeling of subsurface methane migration.

Methane oxidation in groundwater has been observed with sulfate reduction and production of sulfide and multiple other changes to aquifer geochemistry, including elevated levels of alkalinity and pH and lowered dissolved oxygen. Mobilization of heavy metals due to, for example, reduction of iron in soil grains has not been observed or shown in modeling studies. However, trace-element mobilization has been linked to introduction of other hydrocarbons to aquifers. In regions with high-risk of methane leakage to groundwater, aquifer hydrogeochemical characterization should be accompanied by simulation of likely methane leakage scenarios.

Looking forward, we present four new hypotheses emerging from the state of the science: (a) differentiation between thermogenic methane occurring in groundwater due to natural migration from deep hydrocarbon reservoirs and thermogenic methane present from wellbore leakage or transport along induced fractures can be used to alleviate the need for baseline measurements of methane concentrations in groundwater; (b) For most wellbore leakage scenarios, methane will reach groundwater within months or years, so methane newly discovered in freshwater aquifers is unlikely to have originated from persistent leaks beginning decades ago; (c) At a given (i) depth, (ii) source pressure, and (iii) mean intrinsic permeability, methane plume diameter following leakage from a faulty wellbore will vary primarily as a function of the relative permeability of the porous media separating a leak source zone from groundwater. For gas-phase methane leakage from a hydrocarbon wellbore, relative permeability will have a larger impact on plume diameter than any other porous media parameter, including heterogeneity in intrinsic permeability of the intervening media; and (d) thermogenic methane in groundwater will serve as a precursor to BTEX under conditions where methane and BTEX co-occur in a hydrocarbon reservoir and leakage from hydrocarbon wellbores is transported primarily in the aqueous phase. These hypotheses highlight some of the greatest research needs in the field of methane migration due to hydrocarbon wellbore leakage, which include evaluating the origin of methane in groundwater, analyzing spatial and temporal aspects of subsurface methane transport, and determining the impact of hydrocarbon well leakage on aquifer geochemistry and groundwater quality. Advances in each of these areas will be possible through interdisciplinary collaborations and closer integration of observations and numerical modeling.

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CONFLICT OF INTEREST

The authors have declared no conflicts of interest for this article.

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