

***A critical review of state-of-the-art and emerging approaches to identify  
fracking-derived gases and associated contaminants in aquifers***

J. C. McIntosh<sup>1,\*</sup>, M. J. Hendry<sup>2</sup>, C. Ballentine<sup>3</sup>, R. S. Haszeldine<sup>4</sup>, B. Mayer<sup>5</sup>, G. Etiope<sup>6</sup>, M. Elsner<sup>7</sup>, T. H. Darrah<sup>8</sup>, A. Prinzhofer<sup>9</sup>, S. Osborn<sup>10</sup>, L. Stalker<sup>11</sup>, O. Kuloyo<sup>12</sup>, Z.-T. Lu<sup>13</sup>, A. Martini<sup>14</sup>, B. Sherwood Lollar<sup>15</sup>

<sup>1</sup>Department of Hydrology and Atmospheric Sciences, University of Arizona, Tucson, AZ 85721, USA

<sup>2</sup>Department of Geological Sciences, University of Saskatchewan, Saskatoon, SK S7N 5E2, Canada

<sup>3</sup>Department of Earth Sciences, University of Oxford, Oxford OX1 3AN, United Kingdom

<sup>4</sup>School of GeoSciences, University of Edinburgh, Edinburgh EH9 3FE, United Kingdom

<sup>5</sup>Department of Geoscience, University of Calgary, Calgary, AB T2N 1N4, Canada

<sup>6</sup>Istituto Nazionale di Geofisica e Vulcanologia, Sezione Roma 2, Italy, and Faculty of Environmental Science and Engineering, Babes-Bolyai University, Cluj-Napoca, Romania.

<sup>7</sup>Chair of Analytical Chemistry and Water Chemistry, Technical University of Munich, Germany

<sup>8</sup>Divisions of Solid Earth Dynamics and Water, Climate and the Environment, School of Earth Sciences, Ohio State University, Columbus, OH 43210, USA

<sup>9</sup>GEO4U, Rio de Janeiro, Brazil

<sup>10</sup>Department of Geological Sciences, California State Polytechnic University, Pomona, CA 91768, USA

<sup>11</sup>CSIRO Energy, Kensington, WA 6151, Australia

<sup>12</sup>Department of Geoscience, University of Calgary, Calgary, AB T2N 1N4, Canada

<sup>13</sup>Hefei National Laboratory for Physical Sciences at the Microscale, CAS Center for Excellence in Quantum Information and Quantum Physics, University of Science and Technology of China, Hefei 230026, China

<sup>14</sup>Department of Geology, Amherst College, Amherst, Massachusetts 01002, USA

<sup>15</sup>Department of Earth Sciences, University of Toronto, Toronto, ON M5S 3B1, Canada

\*Corresponding author: Jennifer McIntosh, email: [mcintosh@hwr.arizona.edu](mailto:mcintosh@hwr.arizona.edu); phone: 1-520-626-2282

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## **ABSTRACT:**

High-volume, hydraulic fracturing (HVHF) is widely applied for natural gas and oil production from shales, coals or tight sandstone formations in the United States, Canada, and Australia, and is being widely considered by other countries with similar unconventional energy resources. Secure retention of fluids (natural gas, saline formation waters, oil, HVHF fluids) during and after well stimulation is important to prevent unintended environmental contamination, and release of greenhouse gases to the atmosphere. Here, we critically review state-of-the-art techniques and promising new approaches for identifying oil and gas production from unconventional reservoirs to resolve whether they are the source of fugitive methane and associated contaminants into shallow aquifers. We highlight future research needs and propose a phased program, from generic baseline to highly specific analyses, to inform HVHF and unconventional oil and gas production and impact assessment studies. These approaches may also be applied to broader subsurface exploration and development issues (e.g., groundwater resources), or new frontiers of low-carbon energy alternatives (e.g., subsurface H<sub>2</sub> storage, nuclear waste isolation, geologic CO<sub>2</sub> sequestration).

## **1. INTRODUCTION**

Hydraulic fracturing of subsurface geologic formations by multi-stage injection of high-volume, high-pressure fluids, chemical additives and proppants, typically in horizontal wellbores, has opened up previously inaccessible oil and natural gas resources for production on an unprecedented global scale over the past decade.<sup>1</sup> Yet, concerns exist about potential negative impacts of high-volume hydraulic fracturing (HVHF) on the environment, such as chemical contamination of groundwater and accumulation of flammable gases in drinking-water aquifers.<sup>2</sup> Despite this, and knowing the large

number of wells that have been drilled in the United States, Canada and elsewhere, there are relatively few documented instances of surface water and shallow groundwater contamination by accidental release of HVHF fluids<sup>3-6</sup> and produced waters<sup>4,7-10</sup> associated with unconventional oil and gas production. Leakage of natural gas from HVHF reservoirs into shallow aquifers has been documented in a few cases of poor well construction<sup>3,11-16</sup> and possibly leakage along fractures.<sup>3</sup> These reported instances account for ~<4.5% of all HVHF wells.<sup>3,11,15</sup> In cases of suspected contamination, identifying the sources and extent of contamination related to HVHF and oil and gas production is often challenging because of the lack of baseline data prior to HVHF, adequate subsurface hydrogeologic and well construction information, and appropriate geochemical and isotopic tracer data. For these reasons, there is continued debate about the magnitude and scale of environmental impacts from HVHF.<sup>7,11,17-26</sup>

Robust scientific assessment of these important issues will require development of best practice standards for appropriate geochemical and isotopic sampling strategies (e.g. fluid types, density and type of wells),<sup>27</sup> effective natural tracers for determining and distinguishing the source of both fugitive and natural fluids, and strategies for establishing baseline conditions prior to energy development. In addition, tracer results should ideally be combined with other complimentary data, such as HVHF well casing integrity, hydrogeologic context (e.g., characteristics of aquifers and confining units between shallow aquifers and target HVHF reservoirs, including natural gas accumulations), and the presence of microbial communities that can generate and/or degrade hydrocarbons. This paper seeks to provide a starting point for development of a robust best practice approach to monitoring HVHF impacts, which may be applied more broadly to other subsurface resource extraction and related storage issues relevant to the current hydrocarbon-based global economy as well as the transition to a more renewable energy-based future.

Currently, a combination of fluctuating oil and gas prices, and the introduction of moratoria and formal reviews on exploration or use of HVHF methods, have slowed production in the United States,

Canada, Scotland, France, Germany, and Australia. Some countries, such as South Africa and China, are commencing production using HVHF, while others are still considering development of unconventional energy resources (e.g. England). There is an opportunity for the scientific community to provide guidance on the best methods for evaluating fugitive gas leakage and HVHF fluid or produced waters contamination of groundwater, including establishment of pre-drill baseline conditions, recommendations for monitoring during and post-HVHF, and evaluation of alleged cases of contamination.

Building from established approaches (e.g., geochemical, isotopic, microbial), novel technologies for tracing environmental contaminants associated with HVHF are rapidly advancing. Recent development of new naturally occurring isotope tracers (i.e., clumped isotopes of hydrocarbons), high-resolution datasets of natural gases and associated fluids with depth, and incorporation of noble gas geochemistry and microbiology with more traditional hydrogeological and geochemical approaches are particularly promising analytical tools for identifying sources of fluids in the subsurface and providing the critical information and interpretational baseline for quantitatively assessing impact and contamination. Here, we critically review techniques for tracing the origin, transport, and fate of natural gas, saline waters, and fluids injected during HVHF, starting with the current state-of-the-art and subsequently focusing on emerging approaches. We highlight future research needs and opportunities throughout. We also propose a phased analytical program for groundwater monitoring with increasing levels of complexity and cost of analyses that can be applied to specific conditions and localities and provide a strategic conceptual framework for broader issues of subsurface exploration and development (e.g. groundwater resource development, subsurface storage).

**1.1. HVHF-associated sources of contamination.** Sources of hydrocarbons and contaminants from HVHF associated with oil and gas production include the release of: (1) flammable natural gas, including

methane (CH<sub>4</sub>) and higher chain hydrocarbons, such as ethane (C<sub>2</sub>H<sub>6</sub>, commonly termed C<sub>2</sub>) and propane (C<sub>3</sub>H<sub>8</sub>, termed C<sub>3</sub>); and (2) produced liquids, including oil, saline formation water (naturally occurring waters sometimes containing elevated levels of naturally occurring radioactive materials (NORMs) emplaced within sediments and trapped during the formation of rock layers), and HVHF fluids (fluids injected during HVHF) <sup>4,5,12–14</sup> into shallow aquifers. Oil and gas wells are usually completed at considerable depth (up to several km below surface), although ~6% of wells in the United States have been hydraulically fractured shallower than 900 m,<sup>28</sup> and in some cases zones of HVHF coincide with zones of fresh and brackish water resources.<sup>29</sup> Casing or well sealing (i.e. cementing) failures have the potential to act as short-circuit conduits for the flow and mixing of many different fluids from multiple geologic formations and multiple gas, water and oil sources.<sup>13,30–32</sup> In some cases, fugitive natural gas and/or saline formation waters may originate from non-target formations above or below the hydrocarbon production zone.<sup>14,22,28,33</sup> Upward leakage along well bores is, therefore, a likely pathway for the migration of fugitive fluids into shallow aquifers (**Fig. 1**).<sup>11,13,14,30–32,34</sup>

Stray formation waters, HVHF fluids, and natural gas can also migrate into potable aquifers via vertical leakage along faults or zones of intense fracturing, via imperfectly sealed abandoned wells, or from underground gas storage facilities (**Fig. 1**).<sup>2,11,14,16,24,35–38</sup> Accidental surface spills of HVHF chemicals and produced fluids can contaminate local environments, including surface waters and shallow aquifers.<sup>7,10,21,39</sup> In some jurisdictions, disposal of flow-back water and produced fluids from hydraulically fractured boreholes may not be injected into the subsurface and require additional costs of special facilities to eliminate all salinity, chemical additives and NORMs before surface discharge.<sup>40</sup> In other jurisdictions, surface discharge of treated HVHF fluids and hyper-saline brines may introduce contaminants, including metals, organic compounds, and NORMs into surface waters, streambed sediments, and soils with potential for infiltration to groundwater.<sup>41,42</sup>

**1.2. Natural Gas and Brine Seepage.** Natural migration of hydrocarbons to the Earth's surface (in the form of seeps, gas vents, mud volcanoes, gas-rich springs, or diffuse microseepage) is a common and widespread process in petroliferous basins.<sup>43,44</sup> To a lesser extent, saline formation waters associated with hydrocarbons can also migrate into near-surface environments.<sup>45</sup> Fluid migration pathways between and among source rocks, reservoirs, and shallow aquifers, can exist naturally (e.g. along faults of multiple scales, or through fractured formations; **Fig. 1**) and identifying sources and conduits can be complex. They can include multiple gas sources generated in the subsurface by abiotic, thermogenic and/or microbial processes, which can be mixed within geologic formations (source rocks or reservoirs) or along migration pathways in the absence of any drilling or HVHF activities.<sup>46</sup> In addition, gases sourced from depth can mix with microbial gases generated in shallow aquifers and result in natural gases with hydrocarbon fingerprints of indeterminate origin, which are further modified by transformation under variable reducing/oxidizing conditions.<sup>24,43,44,47,48</sup> Salinization of freshwater aquifers by natural migration of saline formation waters or dissolution of evaporites is also common in many sedimentary environments.<sup>36,49</sup> Alternatively, application of road salt in the winter, seawater intrusion in coastal areas, and discharge of sewage effluent can also increase the salinity in potable aquifers.<sup>50</sup>

**1.3. Importance of Baseline Characterization Studies.** Distinguishing between natural pathways and sources of hydrocarbons and associated contaminants (e.g. salinity), historical anthropogenic activity (e.g. coal mining, conventional oil and gas), and more recent HVHF impacts requires an understanding of the temporal and spatial hydrogeology, as well as the use of appropriate natural geochemical and isotopic tracers. Thus, it is essential that baseline characterization and post-HVHF investigations in areas of proposed unconventional energy development include a thorough assessment of natural gas, heavier organic compounds, and saline formation water systems, including multiple sources and mixing of gases,

and other anthropogenic sources of salinity. Currently, there are few studies that define background characteristics of natural gas (and other water quality indicators) in aquifers in the context of potential environmental impacts from HVHF and other oil and gas activities.<sup>7,18,23,24,47,51–56</sup> In addition, little information is typically available on other sources of fluids unrelated to HVHF activities (e.g. gas reservoirs overlying shale gas production zones, saline formation waters<sup>29</sup>, soil gases and hydrocarbon seeps) or on the migratory pathways for the gas and salinity.

It is important to note that establishment of baseline conditions does not necessarily represent “pristine” conditions, but rather the conditions prior to drilling followed by HVHF upon which impacts are evaluated. For example, there is a long legacy of coal mining, and conventional oil and gas production in many basins where HVHF is now occurring, as well as underground gas storage facilities.<sup>35</sup> Microbial gas leakage due to natural methanogens in soil zones,<sup>57</sup> or from anthropogenically enhanced methanogenesis due to landfill<sup>58</sup> or nitrate contamination plumes<sup>59</sup> can also introduce CH<sub>4</sub> into aquifers. Therefore, it is essential that baseline groundwater characteristics are established prior to HVHF activities from as many access points as possible at multiple surface and subsurface sites, either via existing landowner or municipal water supply wells, or from monitoring wells in close proximity to oil and gas wells. Previous studies reported fugitive CH<sub>4</sub> leakage into water supply wells within 1-3 km of Marcellus Shale gas wells in northeastern Pennsylvania.<sup>3,13</sup> However, due to aquifer heterogeneities and factors controlling contaminant transport, 1-3 km may or may not be the appropriate monitoring well radius from unconventional gas wells in other parts of the Appalachian Basin or in other oil/gas regions.<sup>60</sup> Specific recommendations on monitoring well spacing for California and the Northern Territory of Australia are discussed in *Section 4.2.1.* below.

Similar to groundwater, soils surrounding oil and gas wells, pipelines, storage ponds, and surface waters within impacted watersheds should be sampled prior to HVHF activities. Repeated groundwater, surface water and soil sampling followed by a comprehensive geochemical, isotopic and microbial

assessment, as outlined below, affords the opportunity to generate scientifically defensible baseline data, based on which potential negative environmental impacts can be quantitatively assessed through continued sampling and analyses during and after HVHF activities.

## 2. ESTABLISHED TECHNIQUES FOR TRACING CONTAMINATION

**2.1. Fugitive gases.** Measuring natural gas concentration (and oil, in the case of oil shale) in groundwater is essential to define baseline conditions prior to drilling, to monitor potential changes during HVHF and subsequent hydrocarbon production, and when contamination is suspected. However, gas abundance alone (e.g., <sup>20</sup>) is an unreliable indicator and additional geochemical attributes are needed as described below. It is important to note that CH<sub>4</sub> and heavier hydrocarbon concentrations in aquifers can vary markedly over time, depth and distance due to transport, microbial and oxidative attenuation of natural gas plumes, and activities that are unrelated to HVHF associated with oil and gas production.<sup>61,62</sup> Changes to atmospheric or hydrostatic pressure (e.g. drought) and other disturbance (e.g. groundwater pumping) can impact relative concentrations of hydrocarbons.<sup>14,47,54</sup> Therefore, it is important to undertake appropriate spatio-temporal sampling to monitor CH<sub>4</sub> (and other tracers) in HVHF areas. Sampling protocols need to be robust, repeatable and reproducible, and care must be taken to select the most appropriate sampling techniques.<sup>16,63–65</sup>

Analysis of the stable natural abundance carbon ( $\delta^{13}\text{C}$ ) and hydrogen ( $\delta^2\text{H}$ ) isotope ratios of CH<sub>4</sub> (C<sub>1</sub>) and higher chain hydrocarbons (C<sub>2+</sub>) in addition to their molecular ratios are a necessary but often insufficient step towards distinguishing sources of many natural gases.<sup>66–70</sup> Interpretations of gas isotope signatures commonly rely on empirically-derived “fingerprinting” diagrams based on CH<sub>4</sub> to C<sub>2+</sub> (C<sub>1</sub>/C<sub>2+</sub>) ratios versus  $\delta^{13}\text{C}$  of CH<sub>4</sub> (referred to as ‘Bernard diagrams’ (**Fig. 2a**); <sup>66</sup>) or plots of  $\delta^2\text{H}$  versus  $\delta^{13}\text{C}$  of CH<sub>4</sub> (called ‘Schoell diagrams’; <sup>67</sup>) (**Fig. 2b**). The empirical data used to build some of these interpretive



models are often based on thermogenic gas data from a limited number of basins with conventional oil and gas occurrences and microbial gas data from near-surface environments (e.g., wetlands and marine sediments), which may not be useful in all geographic cases nor fully applicable to unconventional energy resources.<sup>71</sup> Due to the increasing sensitivity of analytical instrumentation for chemical and C and H isotopic analyses, and to the increasing size of a global gas isotope database, the historically distinctive graphical regimes of “microbial”, “thermogenic” and “abiotic” gases now overlap substantially (**Fig. 2**), rendering single-tracer (e.g., only hydrocarbons) isotopic characterization of gas samples problematic in many hydrogeological settings.<sup>46,72</sup> Mixing of variable gas sources with potentially different isotopic signatures in the subsurface is common and adds a further potential complication.<sup>7,23,24,37</sup>

The role of secondary processes, such as migration and microbial oxidation of hydrocarbons can further alter initial gas isotope values and C<sub>1</sub>/C<sub>2</sub>+ ratios,<sup>73,74</sup> obfuscating the source of the gas. This is especially true for both unconventional reservoirs and groundwater systems, where <sup>13</sup>C-depleted microbial CH<sub>4</sub> is often continuously being introduced to the system (via in situ methanogenesis in aquifer zones, coal seams, or from other underlying geologic formations<sup>57</sup>), possibly overprinting fugitive gas signatures. Methanogenic environments often contain a mixture of archaea (e.g. acetoclastic and hydrogenotrophic methanogens) that use different carbon substrates and impart different C isotope fractionations leading to different δ<sup>13</sup>C-CH<sub>4</sub> values (**Fig. 2b**).<sup>71</sup> Removal of CH<sub>4</sub> via aerobic or anaerobic microbial oxidation imparts a strong <sup>13</sup>C-enrichment in the remaining CH<sub>4</sub> and can sometimes be identified by unusually high δ<sup>13</sup>C values and concomitant H<sub>2</sub>S contamination in case that methane oxidation is coupled with bacterial sulfate reduction.<sup>75</sup>

At baseline conditions, C<sub>2</sub> concentrations in shallow aquifers are typically low (<0.1 mole %),<sup>57</sup> and C<sub>3</sub> is rarely detected (e.g. <sup>52</sup>). The presence of these higher chain hydrocarbons in groundwater may indicate the introduction of thermogenic gases; however, there is evidence that C<sub>2</sub> can be generated by

microbial processes<sup>57,76</sup> though typically with much higher  $C_1/C_{2+}$  ratios than for thermogenic gas sources. In addition, gas diffusion can sometimes cause migrated thermogenic or microbial gases ( $C_1$ - $C_{5+}$ ) to have lower  $\delta^{13}C$  and  $\delta^2H$  values and higher  $C_1/C_{2+}$  ratios than the initial gas source<sup>45,77–79</sup> though this is typically only observed in low permeability rocks such as shales. Differential solubility and adsorption during gas advection along more permeable rocks and fractures can increase  $C_1/C_{2+}$  ratios.<sup>80</sup> The net result is that migrated hydrocarbons, such as ones that have naturally seeped into shallow aquifers, may have higher  $C_1/C_{2+}$  ratios and measurable decreases in  $\delta^{13}C$ - $CH_4$  values compared to the original reservoir gas composition (**Fig. 2a**).<sup>16,81</sup> In light of these multiple processes, it is important to interpret  $CH_4$  isotopic signatures in context with more traditional lines of evidence, including molecular and isotopic compositions of  $C_2$  and  $C_3$ , and gases up to  $C_5$  (the pentane series), production history and geologic context. With the addition of emerging techniques discussed below, this information can provide more insight and sensitivity and specificity to establishing source attribution of fugitive gases.

**2.2. Produced waters.** Measuring total dissolved solids and major ion chemistry readily identifies the increase of salinity in fresh groundwater, but these methods alone cannot reliably distinguish between different sources of salinity.<sup>50</sup> For example, saline groundwater derived from road salt dissolution versus leakage (natural or anthropogenic) of basinal brines or mixing with sewage effluent or drilling fluids can all be dominated Na and Cl, but their  $\delta^{18}O$  values may be distinct. Major ion chemistry and water stable isotope ratios ( $\delta^{18}O$  and  $\delta^2H$ ) may not be able to distinguish between basinal brines from particular geologic formations with great specificity, as most basinal brines are Na-Cl or Ca-Cl type waters derived from evaporated paleoseawater and modified by water-rock-microbial reactions over geologic timescales (e.g. <sup>82</sup>). Further analysis, including trace ions, dissolved organic composition (DOC), radionuclides and various isotopes of these minor components can be effective additional tracers.

Injected HVHF fluids are typically composed of local freshwater (including groundwater) and

increasingly also saline groundwater sources mixed with sand and added chemicals.<sup>83</sup> After drilling and HVHF is completed, wells are dewatered to produce oil/gas and recover HVHF fluids, although much of the HVHF fluids remain within the formation.<sup>84</sup> The initial flowback waters are relatively dilute, similar in composition to the HVHF fluids; however, salinities quickly increase after a few days of production. The increase in salinity of produced waters is primarily from mixing of HVHF fluids with ambient saline formation waters released from shale fractures and pore spaces as a result of HVHF, or from connectivity with adjacent formations.<sup>84,85</sup>

Measurement of minor element concentrations (i.e. Br, Li, B, I), dissolved carbon species (TC, TIC, TOC), stable isotopes of water and dissolved components ( $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$ ,  $\delta^{13}\text{C}$ ,  $\delta^7\text{Li}$ ,  $\delta^{11}\text{B}$ ,  $\delta^{34}\text{S}$ ), and radiogenic isotopes ( $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $^{228}\text{Ra}/^{226}\text{Ra}$ ,  $^{129}\text{I}/\text{I}$ ), coupled with major ion chemistry can all help to distinguish various sources of salinity in produced waters and identify potential contamination in shallow aquifers, soils, or surface waters related to HVHF.<sup>7,39,86–89</sup> Analysis of other geochemical parameters, such as naturally occurring radioactivity (e.g. Ra,  $^{222}\text{Rn}$ ), ammonium, trace metals, and specific organic compounds, (often in high concentrations in HVHF produced waters), are also important for monitoring water quality impacts,<sup>36,39,42</sup> particularly for the BTEX group (benzene, toluene, ethylbenzene and xylene).<sup>90</sup>

In addition to determining the extent of saline water contamination of shallow aquifers from surface spills or subsurface HVHF leakage, it can be important to identify which formation the saline fluid is coming from in order to attribute and mitigate HVHF contamination or leakage issues. Radiogenic strontium ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) isotopes have been used to differentiate fluids from specific formations in the Appalachian Basin and are particularly sensitive tracers for fluid mixing.<sup>36,39,91–93</sup> For example, formation waters from the Marcellus Shale are relatively unradiogenic compared to brines from overlying Upper Devonian shales and Pennsylvanian coalbeds. Therefore, less than ~0.001% of Marcellus Shale brine would need to be introduced into shallow groundwater to detect a significant shift in

<sup>87</sup>Sr/<sup>86</sup>Sr ratios.<sup>36,94</sup> However, if there is future oil/gas production from other formations in the area with similar Sr isotope ratios (e.g. Utica Shale, Appalachian Basin;<sup>36</sup>), Sr isotopes may become a non-unique tracer of fluid sources. In such cases, other tracers, such as Ra, Li, B and/or I isotopes may be employed. The Marcellus Shale is highly radioactive (up to 18,000 picocuries/L of total radium) with relatively low <sup>228</sup>Ra/<sup>226</sup>Ra compared to other oil/gas producing formations within the Appalachian Basin.<sup>95</sup> Iodine isotopes (<sup>129</sup>I/I) and I/Br ratios of Marcellus Shale formation waters are also distinct compared to other geologic formations and shallow groundwater in the Appalachian Basin<sup>86,91</sup> and investigating these tracers in other basins could be of value. Li and B isotopes, combined with Li/Cl and B/Cl ratios, show promise for identifying HVHF fluids that have reacted with clay-rich formations, such as organic-rich shales.<sup>7,39,87</sup>

Determining the apparent age of groundwater in HVHF impacted shallow aquifers is an important consideration for characterizing fluid mixing and hydrogeologic conditions, the timescales of processes and systems response to remediation, and potential dispersion of any contamination related to HVHF fluids and oil/gas production. Well-established isotopic techniques for groundwater ‘dating’ include <sup>14</sup>C, <sup>3</sup>H, <sup>3</sup>H/<sup>3</sup>He, SF<sub>6</sub>, <sup>36</sup>Cl, and <sup>4</sup>He,<sup>96,97</sup> while the analyses of <sup>4</sup>He and other radiogenic noble gases (e.g. <sup>21</sup>Ne\*, <sup>40</sup>Ar\*, <sup>129</sup>Xe, <sup>134</sup>Xe, <sup>136</sup>Xe) have recently been developed as promising tracers of older geological fluids in the crystalline basement.<sup>98</sup>

**2.3. Organic chemicals in formation water and HVHF additives.** Characterization of volatile organic analytes (VOA) and water-soluble organics is another important approach to define the impacts of HVHF fluids. The exact mixture of chemicals used for HVHF can be proprietary, but increasingly the chemistry of these compounds are being disclosed (e.g., FracFocus database [[www.fracfocus.org](http://www.fracfocus.org)] or may be mandatory in some jurisdictions (e.g., Western Australia; Department of Mines Chemical Disclosures, 2013). The chemical composition of the additives varies to some extent based on the local geology

(mineralogy, formation water chemistry, porosity, permeability, etc.), and the occurrence of some chemicals in combination may nonetheless serve as an indicator of HVHF activities as described below.

Based on FracFocus reports, more than 70 % of all HVHF operations use short chain alcohols (methanol, ethanol, isopropanol) and petroleum hydrocarbons (similar to those in the formation water). More than 50 % employ ethoxylated alcohols and nonylphenols, about 30% use persulfate or peroxodisulfate, while greater than 50 % report using organic acids. Other frequently reported chemical HVHF additives include (polyalkoxylated) amines, quaternary ammonium compounds as clay stabilizers, complexing agents for scale and iron control, as well as biocides.<sup>83</sup> In addition to the HVHF additives, petroleum hydrocarbon blends of short and longer chain alkanes, cycloalkanes and aromatic hydrocarbons are often naturally present in formation waters in oil/gas reservoirs in varying concentrations.<sup>3,4,99,100</sup> The range of compounds depends on the thermal maturity, source, and depositional environment of the organic matter, and any secondary effects (e.g. biodegradation of oil, water washing, evaporation, secondary migration, etc.). When HVHF additives act on these natural compounds in saline groundwater, halogenated substances may form which may be additional indicator compounds of HVHF activities.<sup>101–103</sup>

In the event of leakage (e.g. mobilization of natural gas, saline formation waters, or HVHF fluids) organic geochemical and isotopic analysis of these species can be used to identify the zones from which the natural gas or heavier hydrocarbons may originate.<sup>3,4</sup> Standard methods such as gas chromatography (GC) or GC-mass spectrometry (GC-MS) of isolated organics from oil, gas or formation water samples are routine and can be employed to understand provenance. The advent of comprehensive two dimensional gas chromatography- mass spectrometry (GCxGC-MS) of isolated fractions can provide additional information, and this method has become increasingly available in academic and service-based laboratories.<sup>3,4</sup> Lighter hydrocarbons (i.e. volatile and often toxic species of these substances, such as BTEX compounds) can also be identified by routine analysis of VOA by GC-MS.

Obtaining baseline analyses from shallow aquifers, HVHF target formations, and available boreholes prior to drilling, and from the well to be stimulated (before commencing HVHF stimulation) would provide highly applicable baseline information and is recommended as a vital step, as many of these substances are naturally occurring and may have additional anthropogenic sources. A method that has also become routine is GC-isotope ratio-MS, which can provide further information by measuring stable carbon and hydrogen isotope values for difference chemicals, typically n-alkanes. In addition, the application of high-resolution or ultrahigh-resolution mass spectrometry can provide value insight into complex mixtures of organic contaminants (e.g., naphthenic acids) found in potentially impacted groundwater.<sup>3,101,104</sup> Ongoing advances in new analytical methods can be incorporated in future evaluations, and may indicate that there could be a place for archiving samples appropriately for future investigations if required.

### **3. EMERGING METHODS TO ASSESS HVHF IMPACTS**

Several new chemical and isotopic approaches have recently been developed and/or applied and are particularly promising for identifying sources of fluids and their migration mechanisms and pathways from deep reservoirs to shallow aquifers and the atmosphere in situations where the traditional tracers produce ambiguous results. Clumped isotopes of CH<sub>4</sub> and noble gases show promise for more definitively distinguishing sources of natural gas (i.e. microbial from thermogenic and abiotic), removal via various oxidation pathways, and fingerprinting gases from specific oil/gas reservoirs based on their formation temperatures.<sup>105–107</sup> High-resolution molecular and isotopic profiles of hydrocarbons obtained during oil/gas drilling provide information about potential gas sources and fingerprints, particularly from intermediate gas-bearing zones between target reservoirs and shallow aquifers.<sup>78</sup> Advanced microbiological techniques allow characterization of microbial communities responsible for

CH<sub>4</sub> generation and hydrocarbon oxidation, and their response to introduction of HVHF fluids. Development of laser-based approaches for measuring noble gas radionuclides in groundwater provides more robust residence time constraints for potentially HVHF-impacted aquifers.<sup>108</sup> More broadly, these emerging approaches may be applied to other subsurface extraction and storage issues, including new frontiers of energy and renewable alternatives (e.g. subsurface storage of H<sub>2</sub>, anthropogenic CO<sub>2</sub>, and/or nuclear waste).

**3.1. High-resolution Gas Profiles.** A key pre-requisite for identifying sources of fugitive gas leakage associated with HVHF is the high-resolution determination of concentrations and C (and H) isotopic compositions of hydrocarbon gases from the surface to the target reservoir. This can be achieved by using continuous mud-gas logging techniques and/or discrete, high-resolution, gas, core or cuttings samples followed by chemical and isotopic analyses either in the field or the laboratory. During mud-gas logging, hydrocarbon concentrations are measured in real time on gases released from drilling fluids during rotary drilling using a field gas chromatograph (GC). Mud gas concentrations can be corrected for rate of drilling, volume of drill fluid, and amount of atmospheric air contamination to generate in situ dissolved gas profiles.<sup>45,64,78</sup> Recently, new laser-based technologies have been applied to measure real-time  $\delta^{13}\text{C}$ -CH<sub>4</sub> values during mud gas logging, providing continuous gas isotope data.<sup>78</sup> In addition, a GC Infrared Isotope Ratio technique has been designed to measure  $\delta^{13}\text{C}$  values of C<sub>1</sub>-C<sub>3</sub> gases during mud-gas logging. Despite the utility of these data, high-resolution  $\delta^{13}\text{C}$ -C<sub>1-3</sub> and in situ concentration depth profiles are not routinely collected in the oil and gas industry. Broader application of this approach would provide both key baseline data on gas source(s) as well as identify sweet-spots for hydrocarbon production, and have the potential to later identify the depth from which fugitive gas leakage or natural seepage may occur (**Fig. 3a**).<sup>109</sup> Sample collection is routine with mud-gas logging; limitations to this approach would be the cost of gas isotope analyses, which are going down with development and

refinement of laser-based approaches. The cost of these analyses is relatively insignificant compared to the cost of drilling oil and gas wells. The average completion cost for an on-shore unconventional oil or natural gas well in the United States was \$2.9 to 5.6 million in 2016.<sup>110</sup>

**3.2. Clumped isotopes of hydrocarbons.** A recent innovation in CH<sub>4</sub> isotope geochemistry is the use of clumped isotopes of CH<sub>4</sub> and other hydrocarbons. Clumped CH<sub>4</sub> isotopes are the rare isotopic species that contain two heavy isotopes from among the heavy carbon isotope (<sup>13</sup>C) and the heavy hydrogen isotope (<sup>2</sup>H, or D) and form highly stable bonds (e.g. <sup>13</sup>CH<sub>3</sub>D, <sup>12</sup>CH<sub>2</sub>D<sub>2</sub>). The presence of multiple heavy isotopes makes the bond more stable, locking in the thermal conditions at the time of formation (up to at least ~250°C) - a principle that provides a quantitative geothermometer for CH<sub>4</sub> in certain cases - with the potential to pinpoint specific gas reservoirs based on thermal maturation and burial histories of source rocks in basins(Fig. 3b).<sup>105–107,111,112</sup>

New research on <sup>13</sup>CH<sub>3</sub>D (the least rare clumped CH<sub>4</sub> isotopologue) demonstrated the applicability of the geothermometer approach for a variety of thermogenic gas fields, and for coalbed CH<sub>4</sub> and gas hydrates.<sup>107,112</sup> In addition, theoretical, field and laboratory measurements have

demonstrated that information from clumped CH<sub>4</sub> isotopes extends beyond temperature estimates.<sup>105–</sup>

<sup>107</sup> These insights are two-fold. On the one hand, <sup>13</sup>CH<sub>3</sub>D data have demonstrated that kinetic isotope effects may override equilibrium effects (e.g. in the case of microbial methanogenesis) and thereby provide information on rates and timing of methanogenesis as well as insight into ambient environmental conditions (in particular regarding associated water, or H<sub>2</sub> concentrations).<sup>105,106</sup>

Furthermore, other clumped isotopes (e.g. <sup>12</sup>CH<sub>2</sub>D<sub>2</sub>) provide insight about reaction kinetics, CH<sub>4</sub> oxidation, transport, and in particular, better resolution of gas mixing.<sup>107</sup> Extension of the clumped isotope approach to propane is in an exploratory stage, but may provide additional insight into effects of biodegradation in thermogenic reservoirs.<sup>113</sup> Information gleaned from clumped isotopes (e.g.,



pathways, mixing, and temperature of gas formation) may help overcome some of the uncertainties with traditional gas isotope fingerprinting approaches (Section 2.1). Laboratory culturing experiments and broader application of clumped isotopes in different subsurface environments are needed to better interpret clumped isotope results, such as equilibrium versus kinetic isotope effects. Development of laser-based approaches will reduce costs for clumped isotope analysis of methane and likely make this technique more widely accessible. At this stage there are no commercial laboratories offering clumped isotopes of methane analysis.

**3.3. Microbiological techniques for characterizing community response.** New, rapid and relatively inexpensive microbial sequencing techniques have opened the possibility of using DNA profiling to document stray gas and/or fluid exposure in an aquifer.<sup>114</sup> The entire DNA in an aquifer sample (metagenomics), or sections of Bacterial or Archaeal DNA (e.g. 16S rRNA gene unique to each group), can be targeted to characterize in situ microbial communities.<sup>115</sup> Genes most highly expressed under certain redox conditions (metatranscriptomics) or amino acids produced due to gene expression (metaproteomics) can also be detected and monitored to investigate microbial community responses to environmental changes (e.g. introduction of fugitive gases or HVHF fluids). In addition, shifts in microbial cell numbers and population structure can be monitored by fluorescence-based techniques including fluorescent in situ hybridization (FISH), flow cytometry and fluorescence-activated cell sorting (FACS).<sup>116–118</sup> Natural abundance stable isotope (<sup>13</sup>C) and radiocarbon (<sup>14</sup>C) analyses of microbial biomarkers, such as phospholipid fatty acids (PFLAs) can also provide insights into microbial carbon cycling and hydrocarbon biodegradation.<sup>119,120</sup>

In CH<sub>4</sub>-containing shallow groundwater, these techniques are applied to detect methanogenic, and/or methanotrophic microorganisms responsible for in situ microbial CH<sub>4</sub> production or CH<sub>4</sub> oxidation, respectively. Since microbial activity can alter groundwater geochemistry and the δ<sup>13</sup>C and

$\delta^2\text{H}$  values of hydrocarbon gas compounds, microbiological analyses can support or clarify geochemical and isotopic indicators (including clumped isotopes) of biogeochemical  $\text{CH}_4$  cycling and redox conditions in groundwater.<sup>54</sup> This approach has been successfully applied for research purposes where groundwater samples were collected for analysis,<sup>54</sup> and for monitoring laboratory-scale methane contamination experiments. However, it is not yet fully integrated for in situ field applications particularly due to the time required and multiple steps involved to extract and sequence DNA, as well as to analyze the data generated. Nevertheless, with recent advancements regarding the emergence of hand-held DNA sequencers, it may be possible to apply these techniques directly at a contaminated site in the near future.

**3.4. Noble gas tracers of fluid sources and transport mechanisms.** Noble gases are inert, conservative and naturally occurring tracers that can provide unique insight into subsurface fluid (gas, liquid hydrocarbons, and water) sources and transport mechanisms, although to date they have not been widely applied in HVHF studies. Noble gases have three sources: i) the atmosphere, usually introduced into subsurface systems dissolved in meteoric water (groundwater or marine pore fluids); ii) radiogenic noble gases produced by natural radioactive decay processes in the subsurface; and iii) noble gases sourced from magmatic fluids. The isotopic composition of each of these noble gas sources is distinct, well-defined and quantifiable, hence analysis of noble gas isotopes can quantitatively resolve each of these inputs.<sup>121</sup>

Distinguishing between anthropogenic-induced deep fluid input into near-surface groundwater and natural migration pathways will inevitably depend upon the nature, timing, and location of HVHF activity and local temporal and geological context. Atmospheric and radiogenic noble gases each impart critical information about these various factors. For example, because natural variations in atmospheric noble gases incorporated into crustal fluids are relatively minor and fractionate only by well-constrained

physical mechanisms (e.g., diffusion, phase partitioning), they provide a key reference point for determining the additional amounts of radiogenic noble gases, and  $^4\text{He}$  in particular, that might be in excess of that introduced during natural recharge of meteoric water or gas-water interactions.

In combination, atmospheric and radiogenic noble gases permit mean residence time estimations of groundwater, pore fluids, and hydrocarbon gases.<sup>96</sup> For old groundwater, where the rate of  $^4\text{He}$  accumulation in the water is known, excess  $^4\text{He}$  provides information about the mean residence time of the groundwater.<sup>96</sup> In near-surface aquifers, concentrations of excess  $^4\text{He}$  are generally low compared to fluids deeper in sedimentary basins (e.g. saline formation waters, hydrocarbons released by HVHF and conventional oil and gas deposits). Localized deep fluid contributions to shallow water systems can be identified from anomalous  $^4\text{He}$  groundwater concentrations, and by correlation with other indicators such as Br or dissolved hydrocarbon gases.<sup>22,24,122</sup> This can aid in the de-convolution of mixing between shallow microbial gases ( $^4\text{He}$ -poor),<sup>7,14,24</sup> the effects of hydrocarbon oxidation,<sup>7,24</sup> and mechanisms of hydrocarbon transport to shallow aquifers and surficial seeps (**Fig. 3c**).<sup>4,7,14,24</sup>

The relative abundance of atmospheric noble gases also records information about the relative proportions of natural gas and water (dissolved vs. free-gas migration, super-saturation), the extent of gas-water interactions (e.g., stripping during fugitive gas transport), and the length-scale and mechanism of fluid transport to a potentially impacted aquifer.<sup>4,7,13,14,33,123</sup> For example, near-surface aquifers that are equilibrated with a free (deeper) gas (or oil) phase will contain concentrations of atmosphere-derived noble gases lower than those predicted based on recharge alone.<sup>7,14,33,124</sup>

Wider application of noble gases in hydrocarbon systems and overlying aquifers is needed to better characterize sources of fluids and migration pathways in instances of contamination. Additional research is also needed to better characterize noble gases in produced waters, which have only recently been measured,<sup>125</sup> versus more common measurements of noble gases in produced gases. Analytical technology for measuring noble gases has greatly improved over the last ~5 years with introduction of

automated sample processing lines, improved mass spectrometer stability, and multi-collection methods improving sample throughput and analytical precision, while reducing analytical costs.

**3.5. Dating Groundwater by ATTA.** Development of a new laser-based atom counting method called ATTA (Atom Trap Trace Analysis) has made it feasible to analyze isotope tracers  $^{85}\text{Kr}$  (half-life  $t_{1/2} = 10.7$  years),  $^{39}\text{Ar}$  ( $t_{1/2} = 269$  years), and  $^{81}\text{Kr}$  ( $t_{1/2} = 230,000$  years) in order to determine the mean residence time of HVHF-associated groundwater and trace its flow pathways, with each isotope covering a distinct age range around the respective half-life.<sup>108</sup> Combined with  $^{14}\text{C}$  ( $t_{1/2} = 5,700$  years), the tracers together cover an age range from a few years to 1.3 million years. They may also aid the calibration of the  $^4\text{He}$  flux method,<sup>126</sup> which can extend the range beyond 1.3 million years. Being chemically inert, the noble gas tracers have well-determined, near uniform distributions in the atmosphere, and relatively simple transport processes underground. For the latest generation of ATTA instruments, each analysis requires a sample of 10 – 40 liters of water. Dating takes three steps: 1) sampling is usually performed at the well with a membrane-contactor-based gas collector; 2) the extracted gas is brought back to the lab and chemically purified; 3) the purified krypton or argon is injected into the ATTA apparatus for isotope analysis. Additional research is needed to reduce sample volumes to be able to ‘date’ pore waters from core materials, low permeability formations, fractures, etc. Advances are also being made to reduce sample analysis time.

#### **4. A PHASED ANALYTICAL PROGRAM TO IDENTIFY POTENTIAL CONTAMINATION**

Given the wide range of naturally occurring tracers and contaminants discussed above, and related emerging techniques for identification, it may be difficult for industry and regulatory authorities to assess which analyses could provide the most effective and appropriate baseline and ongoing

information prior to, during, and after HVHF operations. It is impractical and expensive to prescribe or undertake the full suite of available analyses on all samples in a given jurisdiction, and it may be unclear which analyses would aid a progressive investigation in a case of contamination. A key goal of this paper is to provide guidance and a strategic roadmap through the use of these various approaches and techniques, as often cases may be quite site-specific.

#### **4.1. Practical Application**

Looking to parallel industries such as Carbon Capture and Storage, where risk-based assessment has emerged as a successful regulatory approach,<sup>127,128</sup> many jurisdictions have taken a risk-based approach for conducting baseline evaluations or environmental risk assessments and investigations to reduce environmental hazards from HVHF.<sup>129,130</sup> Broadly speaking, this means that a proponent of a project and the regulator would be focused primarily on the features of a site, license, or permit area that could result in a loss of containment of HVHF fluids, produced waters, or natural gas. This risk-based approach is strongly informed by the development of a geological models (both static and dynamic) particular to the area of investigation, which is part of a defined license or permitted area.

Thus, the first step is to build a conceptual model of hydrogeology, geochemistry and gases; all fluid analyses and inferred flow pathways and cross-connections are rooted in a holistic understanding of the physical and chemical framework of the geological and hydrological architecture. A suite of analytical and investigatory techniques of fluids, as reviewed here, are then available. However, how does a regulatory authority assess what baseline information is necessary to be acquired in advance of drilling, HVHF stimulation, and oil and gas production? Which analyses should be specified to a developer that may aid a progressive investigation in the event of an incident? In the section below, we try to address these questions and propose a staged analytical approach or workflow for how organizations might conduct a range of evaluations related to HVHF and oil and gas activities.

#### **4.2. Phased Analytical Approach**

We propose the following phased approach for conducting hydrogeological, microbiological, and geochemical evaluations to provide essential, but fit-for-purpose scientific data: baseline information obtained 'Pre-Drilling'; during 'Drilling, during and soon after HVHF, Routine Operation (oil and gas production), and Post-Closure of Oil/Gas Operations'; in the case of 'Suspected Contamination'; and for the 'Most Advanced Investigation' (**Fig. 4**). This phased approach moves from simple, routine and low-cost analyses to more detailed, expensive and specialized ones on an as-needed basis, where problem-specific detailed investigations may require more experience and greater expertise.

**Figure 4** includes the most widely used and practicable methodologies currently available, many of which have come from traditional industry practices in defining potential reserves and would in many cases be part of an overall evaluation phase. Knowledge of the geologic context, including hydrogeologic, structural, stratigraphic and lithologic (e.g. porosity, permeability, TOC, thermal maturity) factors of the target reservoir and overlying formations, and production history are a critical corollary for a thorough interpretation of geochemical and isotopic data – and the two are iterative. For example, a hydrogeologic, structural and stratigraphic conceptual model is essential for effective planning purposes of both drilling and oil and gas exploration leading to HVHF, and for the execution of a geochemical characterization (or tracer) program. The results of the tracer program will test and provide the quantitative basis for confirmation or further revision of the conceptual model and improve the resource evaluation of a prospective area.

To assess potential environmental impacts of HVHF using best practice requires three components:

- (1) Baseline sampling of shallow groundwater and chemical and isotopic characterization of groundwater in the vicinity of operations prior to HVHF. Good accuracy and precision is

important as case-study experience with CO<sub>2</sub> tracking shows that subsequent legalistic challenges will probe the limits of reliability.<sup>131,132</sup>

(2) For a subset of oil/gas wells drilled, mud-gas logs from the surface to the production zone can characterize natural gas occurrences throughout the intermediate zone between the target oil/gas formation and shallow aquifers;

(3) After HVHF, the flowback and produced waters and gas should be collected, and chemically and isotopically characterized over time.

Taken together, the data provide a degree of assurance to the operator, regulator and community that any future contamination or impact can be effectively assessed and sources attributed and apportioned, and strategic mitigation and remediation plans can be put in place if necessary.

**4.2.1. Routine Baseline Characterization.** For baseline characterization, local groundwater (monitoring and/or domestic wells, springs) and existing oil/gas wells can be sampled in the vicinity of proposed HVHF activities, including lateral reaches of deviated HVHF boreholes. Characterization or prior knowledge of regional groundwater flow is important to design adequate well sampling plans both up- and down-gradient of proposed HVHF activities, including availability and construction of domestic wells. This baseline data on groundwater would ideally be combined with independent geophysical surveying to detect faults and fractures; and more complex analysis of regional rock stress at the affected depths – to enable prediction of seismic hazard and fracture direction and extent.

There are currently no federal regulations in place in the United States for routine baseline sampling prior to HVHF activities, except in cases where diesel fuel is injected for HVHF. However, individual states may have their own monitoring requirements. For example, since 2015, the California State Water Resources Control Board has required groundwater monitoring in areas of oil and gas well

stimulation.<sup>133</sup> Domestic well owners in California can request water quality testing by the state, before and after HVHF, if their well is within 457 m of an unconventional oil or gas well.<sup>60</sup>

In the UK, basic analyses (major ion chemistry and CH<sub>4</sub> abundance) relevant to establishment of baseline conditions are undertaken and compiled by the British Geological Survey, and CH<sub>4</sub> in groundwater is monitored for 12 months before HVHF. Monitoring of groundwater chemistry is not required, although declaration of all HVHF fluid ingredients is compulsory, along with close monitoring of seismicity induced during operations. If challenges occur during or after HVHF operations, the developer may be requested by the Regulator to make additional or advanced analyses at their own expense. Or, in the case of a court-based legal challenge, the developer will need to defend their position, and the State or individual organization may provide much more advanced geochemical information on a case-by-case need.

In Australia, several states and territories have enacted moratoria to enable formal evaluations of the impacts of HVHF onshore. The “Scientific Inquiry into Hydraulic Fracturing in the Northern Territory”, reported in March 2018, resulted in 135 recommendations. One recommendation included in the introduction of Strategic Regional Environmental and Baseline Assessment (SREBA) to obtain relevant pre-development baseline information. The committee recommended “comprehensive regional baseline datasets are essential to underpin modelling of the possible impacts of any new industry and to inform the site-specific quantitative risk assessments that are being conducted by industry and being submitted to regulators for assessment”.<sup>134</sup> Groundwater monitoring within 10-20 m of planned shale gas wells or well pads, prior to and especially during HVHF, was recommended using multi-level monitoring wells that penetrate the full depth of potable aquifers.<sup>134</sup>

The costs of establishing baseline knowledge will vary depending on the geographic location of the HVHF activity, such that it might be borne by the operator/producer conducting the drilling operations possibly under the conditions of the petroleum license, or the State, as an environmental



protection service to incumbent citizens, businesses or Natural Capital. In the case of the Northern Territory, companies have worked with state government to support regional baseline surveys in key areas of interest.

In the case of baseline characterization, a range of routine analyses of water and gas (**Fig. 4**) are commercially available at reasonable cost and provide fundamental information about the environmental conditions, including sources of gas, water, solutes, and carbon-bearing compounds, providing baseline information. Many of these more routine methods will also be applicable to the post-closure monitoring activities in cases where no unintended releases occurred during HVHF activities (i.e. the highest risk point in the lifecycle of a HVHF stimulated well) and operation.

**4.2.2. Additional Pre-HVHF Baseline Analyses.** If boreholes are drilled to investigate shale hydrocarbons, they typically undergo detailed data acquisition during the drilling phase, including wireline geophysical logging, mud gas logging (from surface to total depth), flowback fluids from initial production and produced waters and gas. For added robustness in characterization of multiple sources of natural gas in the subsurface, besides gases in target unconventional reservoirs, and potential sources of hydrocarbons in shallow aquifers, we recommend analyzing mud gases for gas composition and  $\delta^{13}\text{C}$  of  $\text{CH}_4$  and  $\text{C}_{2+}$  with depth from the near-surface through intermediate zones to target formations (**Fig. 4**).

Characterization of volatile and non-volatile organics can also help identify sources of organic compounds that may be of concern to human health or the environment. While some of these analyses need to be conducted within specific time periods for some regulatory reporting (e.g., organic samples that may be subject to degradation), water and gas samples can also be archived for some later analyses for targeted investigations (as described below) or analyzed in the future as new techniques are developed (e.g. clumped isotopes of higher chain hydrocarbons). For example, natural gas and noble gas

samples may be archived for years if stored in gas-tight cannisters or copper tubes, respectively. These investigations may be conducted in areas of special interest from an environmental or social perspective, to provide assurance to stakeholders prior to engaging in operations.

**4.2.3. Targeted Investigations.** In the case of suspected contamination of shallow groundwater, characterization of additional natural tracers can be considered, as outlined in the middle column in **Figure 4**. These include the application of multiple tracers that are, in most cases, widely available geochemical and isotopic techniques. These can be used in targeted investigations to provide more quantitative differentiation of sources and transport of natural or HVHF-related fluids, and may help resolve issues, such as source attribution or apportionment, or define the need for further investigations. Some of these analytical methods may only be relevant in specific geologic environments. For example, analysis of NORMs would only be relevant in environments containing radioactive shales or where mobilization of in situ naturally occurring radioactive material might be present. Most of these techniques can be obtained from commercial laboratories, though in some locations, they may only be found at research institutions, as the methods transition from research-based to routine, commercial application. While more expensive on a per sample basis than more routine analyses, it is important to view the cost of these more innovative techniques in the context of overall investigation costs. If a limited number of targeted analyses can reduce risk and uncertainty by ruling out potential sources of contamination and/or pathways of contaminant movement, the overall cost savings may be large.

**4.2.4. Emerging Opportunities for New Techniques.** The emerging opportunities outlined in the third column in **Figure 4** are highly sophisticated approaches (e.g. microbiological characterization) and in some cases at the frontiers of research development (e.g. clumped isotopes of hydrocarbons;  $^{81}\text{Kr}$  and

<sup>39</sup>Ar by ATTA). These methods are particularly promising for determining the residence time of fluids in groundwater systems and identifying the sources (natural or anthropogenic) and fate of hydrocarbons in shallow aquifers. Yet, they are not likely to be included in state/province or federally regulated monitoring programs at this stage, as they are not available at commercial laboratories and require more complex interpretation.

## **5. BROADER APPLICATION**

An improved understanding of the behavior and applicability of natural tracers of hydrocarbons, salinity, and organics associated with HVHF fluids in the environment will aid scientific and regulatory evaluation of natural systems prior to HVHF, in monitoring during and after HVHF, and in investigation of alleged HVHF incidents, leakage or spills. It may also aid countries or states/provinces in their decision to retain, impose, or lift moratoria on HVHF. In addition, the techniques and phased analytical program outlined in this paper can be applied to other subsurface exploration and development issues, such as extraction of fresh and brackish water resources, in situ mining, long-term storage of anthropogenic waste products (e.g., produced waters, CO<sub>2</sub>, spent nuclear fuel), and shorter-term storage of alternative energy sources (e.g., natural gas, H<sub>2</sub>).

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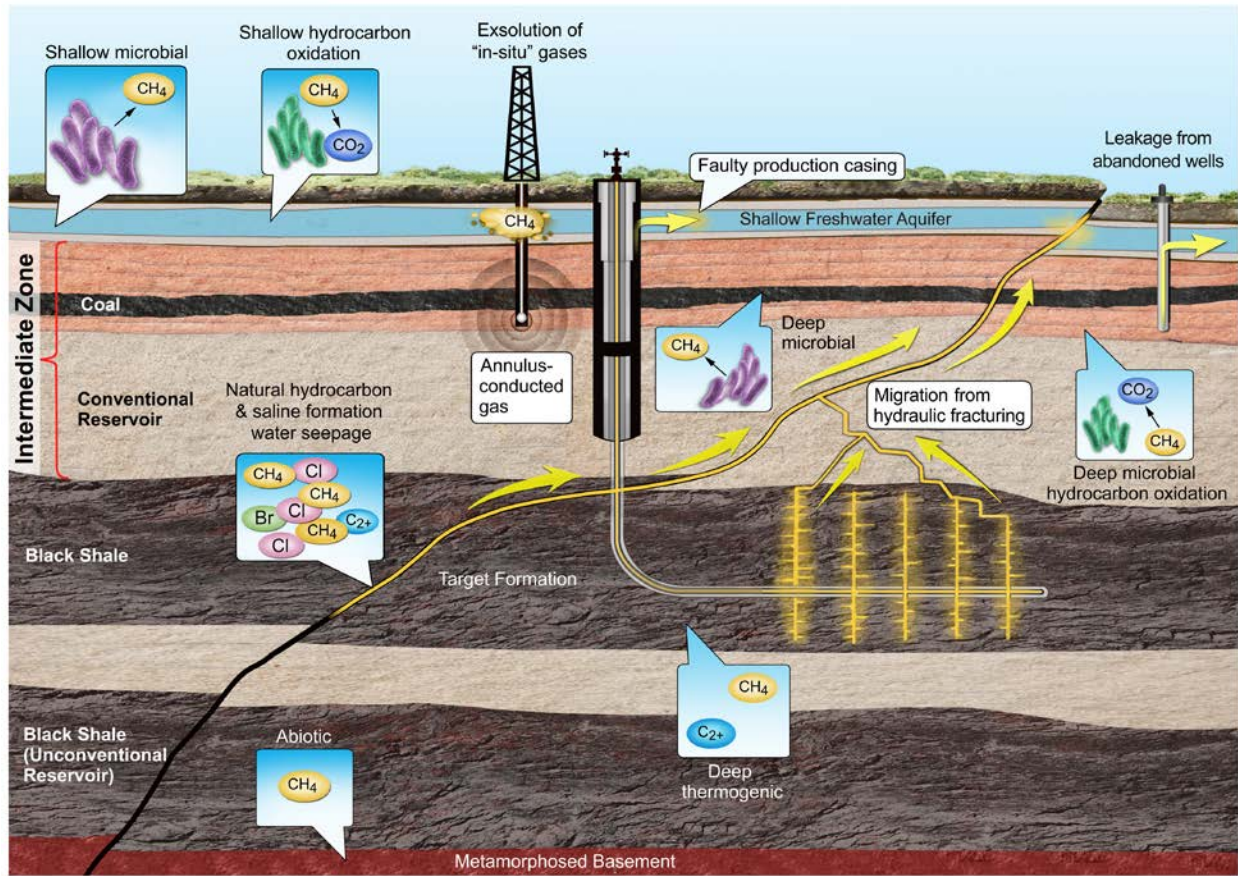
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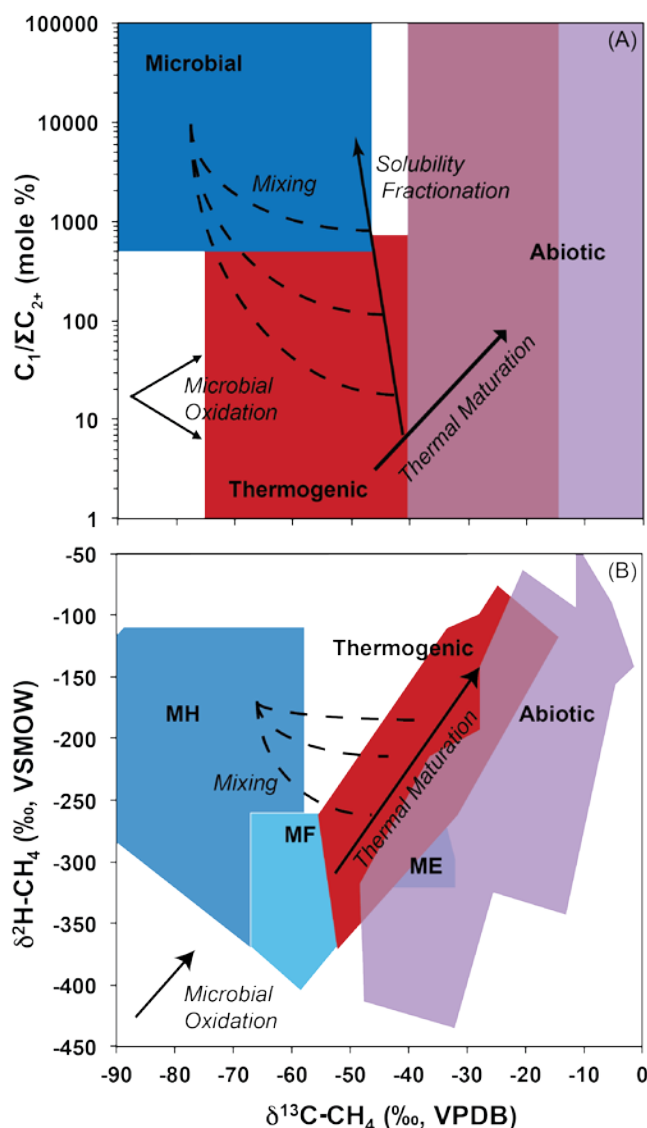
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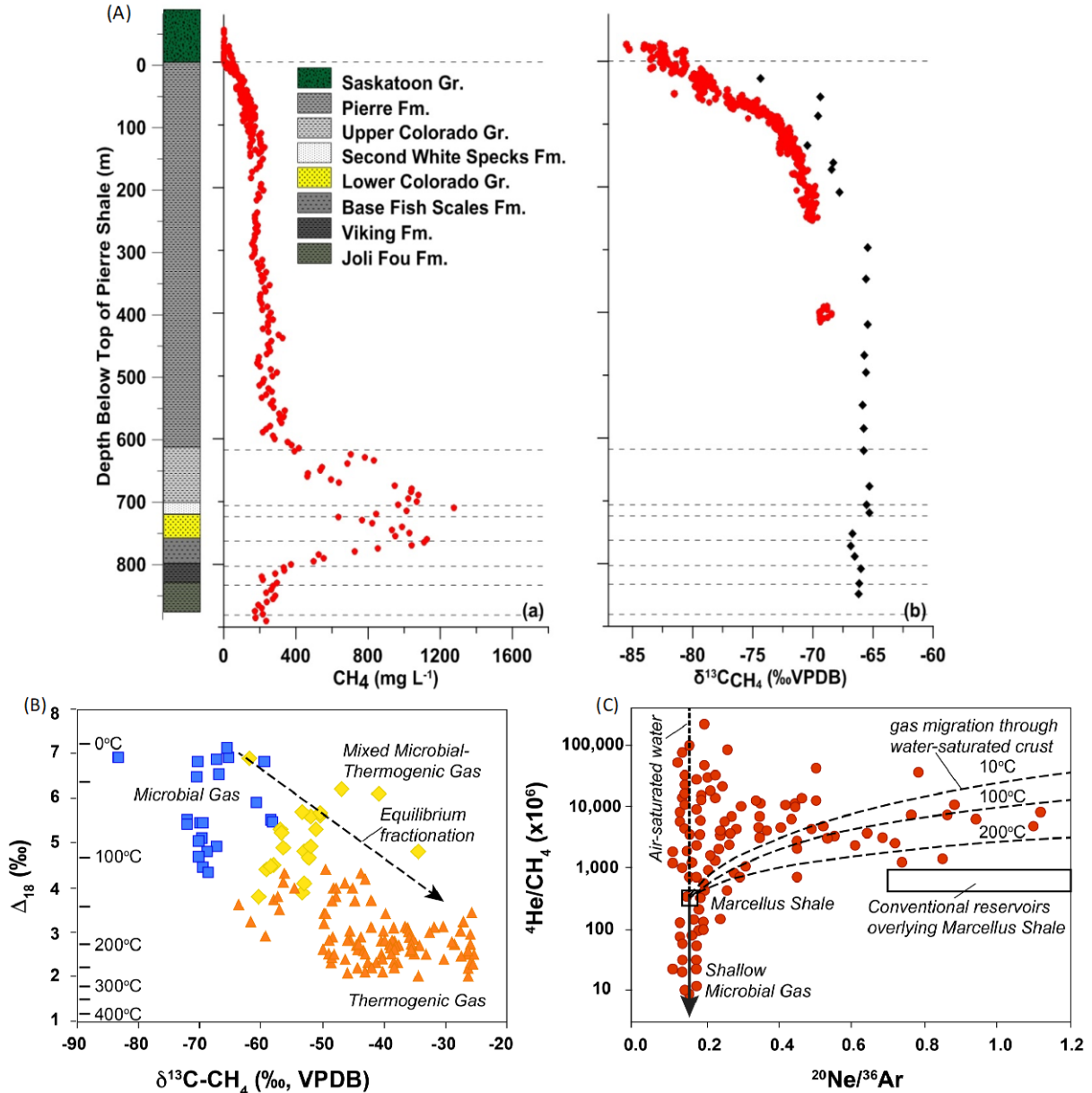
# Figures and Figure Captions



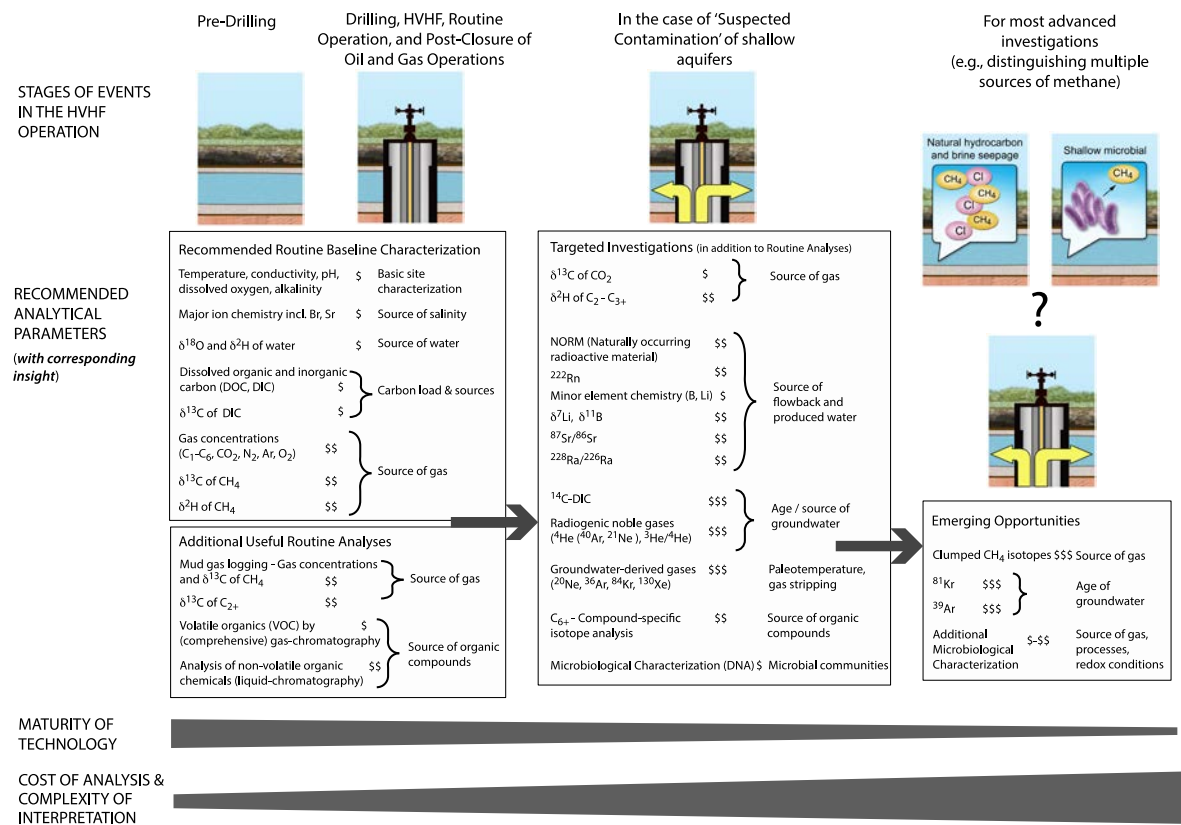
**Fig. 1:** Conceptual model of sources and pathways of natural gas and associated formation water migration from multiple reservoirs at depth in geologic basins into shallow groundwaters, and biodegradation of hydrocarbons via aerobic and/or anaerobic microbial oxidation; modified from <sup>14</sup>.



**Fig. 2:** Traditional hydrocarbon gas isotope fingerprinting approaches for determining sources of natural gas in hydrocarbon reservoirs and near-surface environments. (A) 'Bernard diagram' showing ratio of methane ( $C_1$ ) to higher chain hydrocarbons ( $C_{2+}$ ) versus carbon stable isotope value of methane in microbial, thermogenic and abiotic gases <sup>72</sup>. (B) 'Schoell diagram' showing range of hydrogen versus carbon stable isotope values of methane for the multiple sources of natural gas <sup>67</sup>, modified from <sup>46,112</sup>. Separate fields are shown for microbial gas generated via hydrogenotrophic methanogenesis (MH), acetate fermentation (MF), and methanogenesis in evaporitic environments (ME) <sup>112</sup>. The considerable overlap in the C and H stable isotope values of methane for microbial versus thermogenic and/or abiotic gas sources, and multiple physical, chemical and biological processes that modify the initial gas composition (i.e., ratio of methane to higher chain hydrocarbons) and isotope signatures (shown in black lines) can make it challenging to identify the source of contamination in near-surface environments.



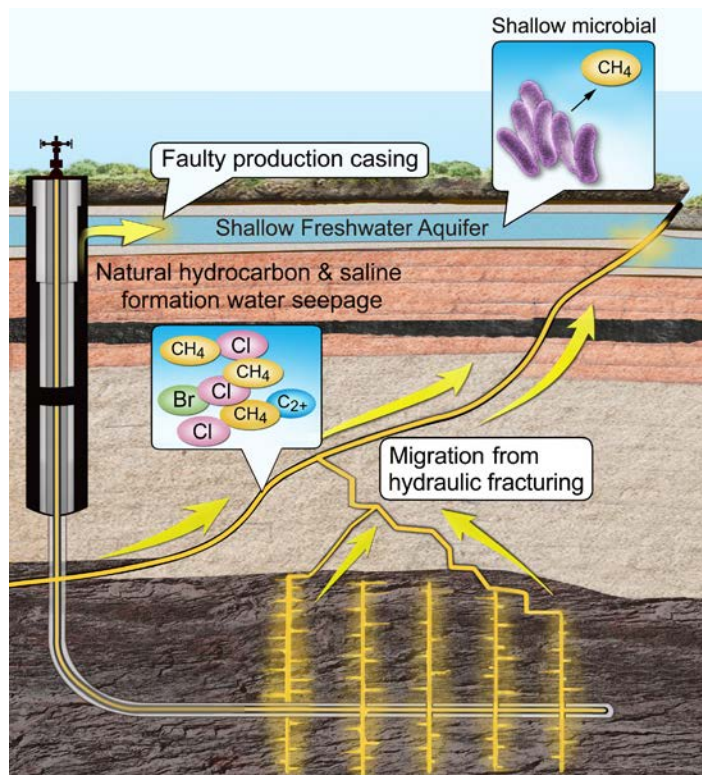
**Fig. 3:** Emerging approaches for better characterizing natural or fugitive gas sources, transport mechanisms, and ultimate fate in near-surface environments. (A) High-resolution depth profile example of methane concentration and isotopic signature through Quaternary deposits and Cretaceous shales in the Williston Basin, modified from <sup>78</sup>. The red circles represent gas samples collected and analyzed during mud-logging using an in-line methane isotope analyzer, while the blue diamonds are discrete samples collected during mug-gas logging and later analyzed in the laboratory. (B) Clumped isotope of methane ( $\Delta_{18}$ ) values and corresponding, inferred paleotemperature of formation versus C stable isotope of methane values, for gas samples from known microbial, thermogenic, and mixed microbial-thermogenic fields <sup>105–107,111,135–137</sup>. (C) Noble gas signatures of dissolved gases in shallow groundwater overlying an area of shale gas production in the Appalachian Basin showing mixing between shallow microbial gas, and gases derived from the Marcellus Shale and overlying conventional gas reservoirs, modified from <sup>7,24</sup>.



**Fig. 4:** Recommended phased analytical approach for groundwater monitoring prior to the onset of high-volume hydraulic fracturing (HVHF) operations, during HVHF and oil/gas operations, in the case of suspected contamination, and for the most advanced investigations in the cases of multiple sources of contamination. Analyses move from simple, routine and low-cost (\$) to more detailed, expensive (\$-\$-\$-\$) and specialized ones on an as-needed basis. Analytical costs generally range between <\$50 USD (\$), \$50-250 USD (\$\$), and >\$250 USD (\$\$\$). The techniques and phased analytical approach can be broadly applied to other subsurface resource development (e.g., groundwater resources) and storage issues (e.g.,  $\text{CO}_2$  sequestration, nuclear waste isolation,  $\text{H}_2$  storage).



1087 TOC Graphic:  
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