Potential impacts of shale gas development on inorganic groundwater chemistry: Implications for environmental baseline assessment in shallow aquifers

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ABSTRACT: The potential contamination of shallow groundwater with inorganic constituents is a major environmental concern associated with shale gas extraction through hydraulic fracturing. However, the impact of shale gas development on groundwater quality is a highly controversial issue. The only way to reliably assess whether groundwater quality has been impacted by shale gas development is to collect pre-development baseline data against which subsequent changes in groundwater quality can be compared. The objective of this paper is to provide a conceptual and methodological framework for establishing a baseline of inorganic groundwater quality in shale gas areas, which is becoming standard practice as a prerequisite for evaluating shale gas development impacts on shallow aquifers. For this purpose, this paper first reviews the potential sources of inorganic contaminants in shallow groundwater from shale gas areas. Then, it reviews the previous baseline studies of groundwater geochemistry in shale gas areas, showing that a comprehensive baseline assessment includes documenting the natural sources of salinity, potential geogenic contamination and potential anthropogenic influences from legacy contamination and surface land use activities that are not related to shale gas development. Based on this knowledge, best practices are identified in terms of baseline sampling, selection of inorganic baseline parameters and definition of threshold levels.
INTRODUCTION

The exploitation of shale gas through horizontal drilling and high-volume hydraulic fracturing has raised environmental concerns over the contamination of water resources. Of particular concern is the potential contamination of shallow groundwater, which is a major source of water for domestic and public supply in many parts of the world. The main risks for groundwater quality near hydraulic fracturing operations arise from 1) the upward migration of gas and flowback/produced fluids along improperly cased/cemented gas wells and 2) the infiltration of contaminated fluids related to surface spills and leaks. Other possible pathways for upward migration of fluid and gas include abandoned leaky oil and gas wells and natural faults, while the vertical propagation of induced hydraulic fractures to overlying shallow aquifers is considered highly unlikely. To date, much concern has focused on the potential contamination of shallow groundwater with methane and organic chemicals used in hydraulic fracturing (HF) fluids. However, there is increasing evidence that inorganic compounds may pose the greatest risk to groundwater quality in shale gas development areas due to their toxicity, mobility and persistence in the environment. Inorganic contaminants present in fluids associated with shale gas production include primarily major and minor elements such as Cl, Na, Ba, Sr, B and Mn, radionuclides such as Ra-226, Ra-228 and U-238, and trace metals/metalloids such as As, Cd, Cr, Ni, Pb, Sb and Se. These geogenic elements can exceed concentrations that are considered harmful to human health and the environment. Therefore, research efforts are needed to better understand the impacts of shale gas development on inorganic constituents in groundwater.

The impact of shale gas development on groundwater quality has been a controversial issue in the scientific community over the last decade. In the course of this debate, it became apparent that comparing pre- versus post-drilling data is the only way to unequivocally conclude whether groundwater quality has been impacted by shale gas development. Hence, there has been a call for the collection of geochemical baseline data, prior to shale gas development, based on which potential future impacts could be quantitatively evaluated through monitoring during and after shale gas exploitation. The term “geochemical baseline” can be defined as the concentration and, if applicable, isotope ratio range of a substance in a delimited area and depth interval over a specific period of time. It differs from the “natural geochemical background” that refers to the concentration range of a substance in a pristine environment, i.e. unaffected by anthropogenic influence. As part of environmental baseline assessment, a number of geochemical baseline studies have emerged in recent years in shale gas development areas.
significant amount of inorganic chemical data is now available, both related to the shallow groundwater and flowback/produced water from various shale gas production sites. However, these baseline studies have followed different approaches, as there is no consensus on the collection of baseline data, including sampling network design, sampling duration/frequency or geochemical parameters to measure.\textsuperscript{15} As collecting baseline data is becoming common practice, there is a need to develop a standard approach for pre-development baseline assessment in areas where shale gas development is proposed. Moreover, it is also critical to establish sound regulations for baseline requirements, as shale gas regulations are not well developed and highly variable within and between countries, provinces and states.\textsuperscript{1}

The main purpose of this paper is to develop a conceptual and methodological framework to improve the baseline assessment of shallow groundwater quality in areas of shale gas development. For this purpose, this paper first reviews the potential sources of inorganic groundwater contaminants associated with shale gas extraction, with the aim of identifying the important environmental factors for baseline assessment. Then, it provides a critical review of the baseline studies of inorganic groundwater chemistry that have been conducted in shallow aquifers overlying shale gas areas. Considering the potential sources of contamination and previous baseline studies, we propose best practice recommendations for baseline assessment of inorganic constituents in shallow groundwater in areas targeted for shale gas development. Given the large literature on unconventional shale gas development from industrial, governmental and academic sources, this paper focuses predominantly on recent peer-reviewed publications based on the collection of empirical evidence which, in contrast to theoretical or conceptual studies, can support the quantitative assessment of baseline groundwater quality.\textsuperscript{24} Priority was also given to baseline studies conducted prior to any shale gas activity compared to baseline studies that collected geochemical data after shale gas drilling had commenced in the area.\textsuperscript{25-27}

2. GEOLOGICAL AND GEOCHEMICAL CHARACTERISTICS OF SHALE RESERVOIRS

In this paper, the term “shale” refers generically to fined-grained sedimentary rock formations, while the term “black shale” is used to designate fine-grained organic-rich sedimentary rocks containing unconventional oil and gas resources. These tight rock formations include siltstones, carbonate mudstones and “true” shales which are usually defined as mudrocks with > 75% clay contents exhibiting fissility.\textsuperscript{28} Shales are characterised by very low matrix permeability ($K < 10^{-18}$ m$^2$) and fluid migration occurs mainly along fractures, laminations and bedding planes.\textsuperscript{29,30} Extracting natural gas from black shales is only economically feasible by artificially increasing the permeability using horizontal drilling and hydraulic fracturing techniques.\textsuperscript{2,29,31} Hydraulic fracturing consists of injecting pressurised fluids into low-permeability reservoirs to open existing or new
fractures. The fluids used for hydraulic fracturing are composed primarily of water (80-90 wt. %) and proppant such as sand or ceramic (10-20 wt. %) with small proportions of chemical additives (0.5%-3 wt. %). Chemical additives include a wide range of compounds that can serve as surfactants, gelling and foaming agents, friction reducers, crosslinkers, breakers, biocides, corrosion inhibitors and clay stabilizers, among others. The depth of shale gas reservoirs typically varies between 1000 and 3500 m, although shale reservoirs have been hydraulically fractured as shallow as 200 m in some basins (e.g. Antrim Shale, Michigan Basin, USA; New Albany Shale, Illinois Basin, USA). Shale gas formations (production zone in Figure 1) are generally overlain by a variety of sedimentary deposits that can provide traps and seals for conventional oil and gas resources (intermediate zone in Figure 1).

Shales are primarily composed of clay minerals (i.e. illite, mixed-layer illite/smectite, smectite, kaolinite, chlorite) and quartz, and can contain significant proportions of other minerals such as feldspars (i.e. K-feldspars, plagioclase), micas (i.e. biotite, muscovite) and carbonate minerals (i.e. calcite, dolomite, siderite, ankerite). Formed under reducing conditions, black shales contain abundant organic matter (> 2% total organic carbon) and sulphide minerals, primarily pyrite. Black shales are commonly enriched in trace elements that are primarily associated with sulphide minerals and to a lesser degree with organic matter and clay minerals. In particular, black shales are often enriched in trace metals and metalloids such as As, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, U, V and Zn and may contain significant contents of naturally-occurring radioactive material (NORM). The high levels of radioactivity result from the natural abundance of U-238 and Th-232 and their decay products including isotopes of Ra, Po, Rn and Pb in many organic-rich shale formations. It is noteworthy that black shales can host sulphide ore deposits that usually contain very high contents of trace metals and metalloids. As a result of water-rock interactions, elevated concentrations of trace metals/metalloids have been reported in shallow groundwater associated with organic-rich shale occurrences. However, the concentrations of a number of trace metals/metalloids and NORMs were likely limited by sequestration in Fe-Mn oxyhydroxides and clay minerals in shallow oxidising groundwater, and by sulphide mineral and organic matter stability in reducing groundwater.
Figure 1. Conceptual model of the potential processes for inorganic groundwater contamination associated with shale gas extraction. The direct and indirect effects are related to shallow groundwater quality. Direct effects refer to the input of inorganic contaminants into shallow groundwater; indirect effects refer to the triggering of geochemical mechanisms affecting the inorganic chemistry of shallow groundwater. In this worst-case scenario, the shale gas well integrity is compromised due to casing failures. The abandoned oil and gas well is improperly plugged. Drilling wastes are improperly disposed and leached by rainwater. The release of wastewater is related to on-site spills, overflowing and leaking storage pits (other pathways include the release of untreated or inadequately treated wastewater and road spreading).

3. POTENTIAL SOURCES OF INORGANIC CONTAMINANTS IN SHALLOW GROUNDWATER

3.1. Direct release of dissolved inorganic contaminants

3.1.1. Major constituents in flowback/produced water

The release of contaminated fluids associated with shale gas development may directly affect the quality of shallow groundwater in shale gas areas. Significant volumes of flowback and produced waters are generated during shale gas extraction (hundreds to tens of thousands of m$^3$ per well) $^{50,51}$. Flowback waters return to the surface a few days to a few weeks following hydraulic fracturing and prior to gas production, while produced water is co-produced continuously with the gas once the well is placed into production $^{33,50}$. The distinction between flowback and produced waters is neither obvious nor clearly defined, and most studies have reported flowback/produced water data without distinction $^{34,50}$. Flowback and produced waters generally
consist of highly mineralised Na-(Ca)-Cl waters (thousands to hundreds of thousands ppm total dissolved solids or TDS) with high levels of alkaline earth elements (Ca, Sr, Ba, Ra), alkali elements (Na, K, Li) and halides (Cl, Br), and moderate to low concentrations of dissolved inorganic carbon and sulphate (Figure 2). The salinity of flowback/produced water rapidly increases with time after hydraulic stimulation, which is attributed to an increasing proportion of natural formation brines. Saline formation waters are commonly found at depth in sedimentary basins and likely originated as evaporated seawater further modified by water-rock interactions and dilution processes in the shale gas reservoir itself or in adjacent units.

The concentrations of a number of inorganic constituents in flowback/produced waters exceed international standards and guidelines for drinking water and environmental protection. Due to the highly saline nature of these fluids, the contamination of shallow groundwater by only a small quantity (a few percent) of these highly saline fluids can cause concentrations to exceed drinking water standards. The elevated total dissolved solids related to Na, Ca and Cl contents are likely to make the water unsuitable for drinking purpose (i.e. TDS > 1,000 ppm). However, the greatest risks to human health are related to the high concentrations of Ba, radioactive Ra (Ra-226 and Ra-228), B and F. As shown in Figure 2, the levels of Ba, Ra and B in flowback/produced waters can exceed the WHO drinking water standards by more than three orders of magnitude. Although there is no WHO guideline for Mn and Sr, concentrations as high as tens of ppm Mn and thousands of ppm Sr may pose a risk to human health. Elevated concentrations of the alkaline earth elements Sr, Ba and Ra in flowback/produced waters have been attributed to 1) the limited precipitation of sulphate minerals (e.g. barite, celestite) due to strongly reducing conditions and elevated temperatures in the reservoir and 2) the increased competition for sorption sites on clay minerals and organic matter due to high ionic strength of the fluids. There is still a debate whether Ba and Ra in flowback/produced water are derived from formation brines or are released from black shales during hydraulic fracturing. Elevated B concentrations are thought to result either from carbonate dissolution or desorption from clays. To our knowledge, no information is currently available regarding the mobilisation of F and Mn in flowback/produced waters.

It is important to note that the isotopic composition of produced formation waters and its dissolved constituents has been extensively investigated. Produced formation waters are generally characterised by elevated $\delta^2$H and $\delta^{18}$O values of water and variable isotopic compositions of dissolved elements ($^{87}$Sr/$^{86}$Sr, $\delta^{11}$B, $\delta^{7}$Li, $^{228}$Ra/$^{226}$Ra, $\delta^{138}$Ba) depending of the shale rock composition and reactions during water-rock interaction.
Figure 2. Concentration ranges of selected major inorganic constituents, NORMs and trace elements in flowback/produced water. Red marker = WHO drinking-water guideline value; orange marker = WHO health-based value; violet marker = WHO screening levels. Data from Abualfaraj et al. 13; Barbot et al. 72; Cantlay et al. 73; Capo et al. 67; Chapman et al. 68; Gao et al. 69; Haluszczak et al. 52; Huang et al. 70; Lester et al. 74; Liu et al. 75; Ni et al. 58; Osselin et al. 54; Osselin et al. 76; Phan et al. 77; Phan et al. 65; Rosenblum et al. 78; Rowan et al. 55; Tasker et al. 71; Ziemkiewicz and He 33.

3.1.2. Trace element release during fluid-shale interactions

As mentioned in section 2, black shales are often enriched in trace metals/metalloids and radionuclides associated with sulphide minerals, organic matter and clay minerals. These hazardous elements may be released as a result of black shale interaction with hydraulic fracturing fluids and with rainwater during drill cutting disposal. Flowback/early-produced waters have been found to contain elevated concentrations of trace metals/metalloids such as As, Cd, Ni, Pb, Sb and Se (Figure 2). The release of inorganic constituents during shale-fluid interaction as a result of the hydraulic fracturing process has been mainly investigated through laboratory experiments 11,53,62,64,79–89 and recently by exploring the geochemical and isotopic composition of flowback/early-produced water (δ⁳⁴S-SO₄, δ¹⁸O-SO₄, δ²H-δ¹⁸O of water, δ¹⁵N-NO₃, δ¹⁸O-NO₃, δ¹⁵N-NH₄, δ¹³C-
DIC, $^{14}$C-DIC, $^{\delta}$Li, $^{\delta}$B, $^{87}$Sr/$^{86}$Sr) $^{53,65,76}$. Most of the experimental studies have used geochemical and/or mineralogical characterisation combined with batch experiments on core samples to assess major controls on element mobility including shale mineralogy, solution pH, redox conditions, ionic strength, solid to liquid ratio and presence of specific chemical additives.

Batch leachate and flowback water chemistry suggested that the oxidation of pyrite and organic matter may release trace metals/metalloids in the early stage of hydraulic fracturing $^{11,65,79,81,84,85,89}$ (Figure 1). Trace metals/metalloids can also be transported in flowback/produced waters through mechanical detachment of particulate sulphide grains $^{90}$. Sulphide grains can be subsequently dissolved under oxidising conditions, releasing trace metals/metalloids into waste fluids. In addition, U is likely to be released from the shale after reaction with HF fluid due to the dissolution of carbonate and metal oxide/phosphate minerals as well as the desorption from clay minerals $^{80}$. Under acidic conditions caused by sulphide oxidation and the absence of buffering minerals (i.e. carbonates), high concentrations of trace elements may result from the dissolution of Fe-Mn oxyhydroxides, which are major sinks for trace metals/metalloids $^{84}$. Trace element concentrations appear to decrease in the later stages of production, as produced water contains progressively more saline, strongly reducing formation waters with low metal/metalloid concentrations $^{65,76}$. Overall, hydraulic fracturing processes are designed to ensure the development of an effective fracture network through physical modification of the rock structure and mineral dissolution, which is necessarily associated with elevated concentrations of dissolved constituents and contaminants $^{76}$.

The drilling and completion of shale gas wells can generate large volumes of drilling wastes $^{42,77}$. Drilling wastes consist of drill cuttings (shale rock pieces) usually enriched in trace metals/metalloids and/or NORMs, as well as residual drilling muds which often contain elevated Ba (barite used as weighting agent) and various organic chemicals such as base oil, polymers and biocides $^{42,91}$. The leaching of poorly-managed drilling wastes by rainwater may release toxic elements into shallow groundwater through run-off (Figure 1). Based on leaching experiments, several studies have evaluated the potential for the release of toxic trace elements and NORMs from exposing shale cuttings to surface conditions $^{39,43,77,92-94}$. These studies revealed that the oxidative dissolution of sulphide minerals and organic matter may be a significant source of dissolved trace metals/metalloids (e.g. As, Cd, Mo, Ni and Zn) in leachates (Figure 1). Furthermore, the oxidation of sulphide minerals may form acid rock drainage in material with low neutralising capacity and promote the release of cationic metals such as Ni, Co, Cd, Pb and Zn $^{28,93,94}$. Trace metals/metalloids associated with Fe-Mn oxyhydroxides and iron(III)-bearing clays are also likely to be mobilised under reducing conditions such as anaerobic landfill conditions $^{42}$ (Figure 1). Moreover, the dissolution of carbonate minerals and the oxidation of organic matter and/or U oxides associated with organic matter may release U, which can persist in solution under oxidising conditions $^{77}$. Experimental studies have found that U-238 and U-234 are readily
leachable in drill cuttings, particularly under low pH conditions. In contrast to flowback/produced waters, Ra-226 levels are generally low in leachates from drill cuttings, probably due to co-precipitation of Ra with secondary sulphates. However, significant amounts of Ra and Ba may be released from cation exchange sites (e.g. clays, organic matter) with increased ionic strength of the leachate water and from barite dissolution under reducing conditions. Overall, the improper management and disposal of drilling wastes may pose risks similar to those occurring in waste rock piles from base and precious metal mining in black shales. In addition, the leaching of organic chemicals contained in drilling wastes could directly and/or indirectly impact shallow groundwater quality (section 3.2.2).

3.2. Indirect release of dissolved inorganic contaminants through changes in geochemical conditions

3.2.1. Fugitive gas

Shale gas operations can cause the migration of natural gas (primarily methane) from deep and intermediate non-target zones to shallow aquifers, particularly in cases where casing/cement failures occur along well bores. Fugitive gas migration into shallow aquifers can produce secondary water quality impacts associated with the mobilisation of trace metals/metalloids and other redox-sensitive species (Figure 1). In steady-state CH₄-rich groundwater, trace metals/metalloids generally occur at low dissolved concentrations as a result of sulphide mineral and organic matter stability and carbonate mineral precipitation. However, in originally CH₄-free groundwater systems, the introduction of CH₄ can lead to the mobilisation of elements present in the aquifer material due to changes in physico-chemical conditions. Experimental injection studies have shown that aerobic CH₄ oxidation driven by O₂ first leads to acidification of groundwater due to increased CO₂ and subsequent potential release of hazardous trace elements, as also suggested by the documented impacts of CO₂ leakage from carbon sequestration. Once O₂ is depleted, the reductive dissolution of Fe-Mn oxyhydroxides associated with anaerobic CH₄ oxidation may release sorbed metals/metalloids, while increased pH may promote desorption of oxyanion-forming trace elements such as As, Mo, Sb and Se. Anaerobic CH₄ oxidation has been reported to increase pH, alkalinity and the concentrations of reduced species (e.g. NH₄, Fe, Mn and H₂S) in previous studies of shallow groundwater affected by gas leakage from oil and gas wells completed in conventional and unconventional reservoirs and by gas well blowouts. Microbially-mediated Mn, Fe and SO₄ reduction may lead to the formation of zones with high concentrations of dissolved metal and/or sulphide species, depending on the availability of electron acceptors in the aquifer. The migration of CH₄ into oxidising groundwater will likely result in the prevalence of mildly oxidising conditions favourable for the mobilisation of some trace metals and metalloids. It is important to note that brine migration into shallow aquifers may also increase the mobility of trace elements by introducing...
competing ions for sorption sites. The indirect effects of CH₄ leakage are likely to be highly site-specific, depending on the aquifer mineralogy and hydrogeological characteristics.

### 3.2.2. Surface operations

Surface activities associated with shale gas development may indirectly affect the inorganic quality of shallow groundwater. Several studies have identified shale gas surface operations as the source of organic contaminants in shallow groundwater including gasoline, diesel range organic compounds, BTEX and ethylene glycol. Organic contamination of groundwater is generally related to accidental surface spills and leaks which have been reported for some US shale gas sites (Figure 1). Fracturing fluids and flowback/produced waters can contain a wide range of anthropogenic and geogenic organic compounds.

Synthetic chemicals consist primarily of hydraulic fracturing additives that belong to different classes of organic compounds such as alcohols, polymers, hydrocarbons and acids. Geogenic organic compounds mainly consist of aliphatic compounds such as light hydrocarbon gases (e.g. methane, ethane, propane) and aromatic hydrocarbons such as benzene, toluene, ethylbenzene and xylene (BTEX). Moreover, a number of transformation products resulting from the degradation of organic substances are present in flowback/produced waters such as organic acids, acetate and halogenated compounds. The biodegradation of these organic compounds can produce secondary water quality impacts, similar to those produced by CH₄ oxidation (section 3.2.1) (Figure 1). For example, an experimental injection study showed that the biodegradation of BTEX and ethanol coupled with Fe reduction released naturally-occurring As, Co, Cr and Ni to groundwater. Moreover, groundwater depletion may occur in shale gas areas where large volumes of groundwater are withdrawn for hydraulic fracturing. The associated water table decline increases the exposure of aquifer minerals to O₂, which diffuses through the water-unsaturated zone. These conditions may promote the release of trace metals/metalloids through sulphide mineral and organic matter oxidation.

### 4. BASELINE STUDIES OF SHALLOW GROUNDWATER GEOCHEMISTRY IN SHALE GAS AREAS

#### 4.1. Naturally-occurring sources

#### 4.1.1. Sources of salinity

A number of studies have recently investigated the sources of shallow groundwater salinity in shale gas areas. In some areas, groundwater salinity is derived exclusively from (meteoric) water-rock interaction in the unsaturated zone and the shallow aquifer. This is the case in upland bedrock and karst aquifers where low-salinity Ca-(Mg)-HCO₃ waters occur predominantly as a result of carbonate dissolution. Na-HCO₃ waters also commonly occur further along the flow path in...
sedimentary aquifers as a result of Na-Ca ion exchange and in bedrock aquifers through Na-silicate weathering\textsuperscript{15,20,114}. In such fresh waters (< 500 ppm TDS), brine contamination can easily be detected based on changes in total dissolved solids and concentrations of dissolved elements such as Cl, Br, Ba and Sr.

In other areas however, brine contamination may be more difficult to identify due to the originally high salinity of groundwater (> a few thousand ppm TDS). In particular, the natural migration of formation brines into shallow aquifers has been identified as a major source of salinity in shallow groundwater from several shale gas basins including the Appalachian Basin (USA)\textsuperscript{115,116}, the Karoo Basin (South Africa)\textsuperscript{21,117} and the St. Lawrence Lowlands (Canada)\textsuperscript{15} (Figure 3). The mineralised waters derived from mixing with formation brines are characterised by TDS values from thousands to tens of thousands ppm associated with high concentrations of Cl, Br, Na, Ba, Li, Sr and CH\textsubscript{4}, and are generally found in aquifers in valley bottoms and fractured zones. Structural and geochemical evidence suggests that formation brines naturally migrate through faults and fractures along deformational features\textsuperscript{106,116}. These areas have been suggested to be at greater risk of contamination by upward fluid migration due to the occurrence of conductive pathways between deep formations and shallow aquifers, although the time scale for potential brine migration is poorly constrained\textsuperscript{59,106} (Figure 1). A number of geochemical and isotopic tools have been applied to detect brine contribution to shallow groundwater in shale gas basins including concentrations and ratios of dissolved ions such as Cl, Br, Ba, Na, Li, Sr and I, stable and radiogenic isotopes of dissolved elements ($\delta^{11}$B, $\delta^{7}$Li, $^{87}$Sr/$^{86}$Sr, $^{228}$Ra/$^{226}$Ra) and elemental and isotopic compositions of noble gases ($^3$He, $^4$He, $^{20}$Ne, $^{21}$Ne, $^{22}$Ne, $^{36}$Ar, $^{38}$Ar, $^{40}$Ar)\textsuperscript{21,59,115,117–121}. Stable isotope ratios of water have been found to be less sensitive to small contributions of brines, in comparison with isotopes of dissolved constituents\textsuperscript{59}.

Other natural sources of salinity may complicate the detection of brine contamination in shallow aquifers. These salinity sources may include evaporite dissolution and contribution of residual seawater introduced in the aquifer during Quaternary transgressions\textsuperscript{15,111}. In some cases, groundwater salinity may originate from surficial aquifers, as is the case for mineralised groundwater (> 1000 ppm TDS) originating from glacial deposits in Alberta\textsuperscript{122}. Although not yet documented in baseline studies, natural sources of salinity may also include seawater intrusion in coastal areas and evaporation in arid and semi-arid shale gas areas such as in northern China, north-western India and central Argentina\textsuperscript{123}.  

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Figure 3. Conceptual model of the sources of groundwater contaminants affecting the baseline conditions in shallow aquifers in shale gas development areas. The listed contaminants are not exhaustive.

4.1.2. Geogenic contaminants

Naturally-occurring inorganic contaminants are common in shallow groundwater in sedimentary basins and generally exhibit a high spatial variability of their dissolved concentrations (Figure 3). However, little consideration has been given to geogenic contaminants in baseline studies, although this can be a major source of controversy regarding subsequent impacts, or the lack thereof, of shale gas development on groundwater quality. The baseline studies conducted so far have generally attributed the occurrence of hazardous inorganic constituents to natural processes including formation water migration and water-rock interaction with shallow aquifer materials. However, no detailed geochemical investigations of the sources and distribution of these geogenic contaminants were conducted in these studies. Elevated trace element concentrations at baseline conditions have been reported in bedrock groundwater from shale gas development areas, such as As and Mn in the Appalachian Basin and As, Be and Mo in the Permian Basin. In addition, baseline studies of shallow aquifers have reported elevated concentrations of potentially toxic minor elements including F, Ba and B. Due to environmental concerns
related to radioactive elements in shales, natural radioactivity and radionuclide activities (Rn-222, Ra-226, Ra-228) have been recently evaluated in shallow groundwater from the Karoo Basin (South-Africa)\textsuperscript{19}, the Carboniferous Maritime Basin (Canada)\textsuperscript{22} and the Sichuan Basin (China)\textsuperscript{128}. The reported levels of radium were generally low, whereas several sites had radon levels above the WHO reference level (100 Bq/L) in shallow aquifers of the Karoo Basin\textsuperscript{19}.

4.2. Anthropogenic contamination

4.2.1. Legacy of hydrocarbon resource extraction

Shallow groundwater may be affected by anthropogenic contamination prior to shale gas development. In hydrocarbon basins, legacy contamination from coal mining, coalbed methane exploitation and conventional oil and gas extraction may further complicate the identification of shale gas development impacts on groundwater quality\textsuperscript{58,129} (Figure 3). Mine drainage is likely to release toxic metals/metalloids into shallow groundwater around coal mines\textsuperscript{95}. Previous studies have identified coal-mine drainage by relatively high SO\textsubscript{4} and low Br and Ba concentrations as compared to saline fluids associated with oil and gas production\textsuperscript{3,130,131}. Conventional oil and gas development may have contaminated shallow groundwater mainly due to surface spills (e.g. hydrocarbons, produced waters) and upward migration of saline fluids along improperly cased/cemented wells and unplugged or improperly plugged abandoned wells\textsuperscript{132}. Differentiating between produced waters from conventional and unconventional hydrocarbon reservoirs is challenging, although ratios of major ions and isotopic compositions of Sr, B, Li, Ba and Ra can provide a unique fingerprint for each reservoir\textsuperscript{58,63,66,68,71,73,129,133}. However, the distinction between produced waters from conventional and unconventional reservoirs is not always possible due to geochemical overlaps\textsuperscript{58,59,133}. To our knowledge, no pre-development baseline investigations have documented legacy groundwater contamination from previous hydrocarbon operations in shale gas development areas.

4.2.2. Surface contamination

In rural areas, groundwater obtained from domestic/farm wells may be impacted by surface contamination sources such as de-icing road salts, septic tank effluents and agricultural residues\textsuperscript{121,134} (Figure 3). As a result, shallow groundwater may contain a number of dissolved contaminants prior to shale gas development including chloride, sodium, nitrate and pesticides. Landfill leachates and agricultural residues can also cause elevated CH\textsubscript{4} concentrations in groundwater\textsuperscript{17,118}. Baseline studies of shallow aquifers have often used major and minor ion concentrations to distinguish between surface contamination and natural sources of salinity. For instance, domestic and agricultural contamination has been commonly identified using NO\textsubscript{3} concentrations\textsuperscript{113,121,135}. Road salt contamination have often been detected using ion ratios such as Br/Cl and (Ba+Sr)/Mg, as de-icing salts are
usually composed of halite and thus contain low levels of Br, Ba and Sr. However, the application of ion ratios can be limited by minor element concentrations being below the quantification limit. The delineation of surface contamination of shallow groundwater is greatly complicated by the use of oil and gas wastewaters on roads for de-icing or dust suppression in some regions. Importantly, surface contamination effects have been spatially correlated with land use (e.g. road network, agriculture) and hydrogeological conditions (e.g. confinement conditions, flow path).

5. RECOMMENDATIONS FOR BASELINE ASSESSMENT BEST PRACTICE IN SHALE GAS DEVELOPMENT AREAS

5.1. Groundwater sample collection

5.1.1. Sampling infrastructure

Baseline groundwater samples can be obtained from a variety of sampling infrastructures including existing private and public water-supply wells, natural springs, as well as dedicated observation (monitoring) wells (Figure 3). To date, private domestic/farm wells have been predominantly used for the collection of baseline groundwater data. The reason for the extensive use of private wells is the opportunity for low-cost and rapid data acquisition over large spatial areas. Shale gas development occurs predominantly in rural areas where private wells are a major source of drinking water. In addition, the collection of well water continually used for domestic purposes provides information directly related to public health in shale gas regions. However, groundwater data obtained from private wells may have a number of limitations for baseline characterisation including 1) inadequate spatial distribution, 2) limited geological, hydrogeological and infrastructure information (e.g. well depth, water inflow, stratigraphy) and 3) non-representative geochemical conditions (e.g. surface contamination, gas exchange, microbially-catalysed redox reactions, mixing of groundwater from different aquifers or aquifer sections).

In contrast, dedicated observation wells can provide high-quality water chemistry data from desired locations and depths (e.g. multi-level wells), with detailed geological, hydrogeological and infrastructure information for interpreting the data. However, data acquisition from purpose-drilled wells is still very limited since installation of such wells is rarely required by regulatory agencies. The main limitation of such infrastructures is the cost of installation. Although sophisticated monitoring systems such as multi-level wells can be expensive, shallow single-depth observation wells are not very costly and can often provide valuable information on groundwater quality. Such simple sampling infrastructures may consist of standpipe piezometers in unconsolidated sediments and open boreholes in bedrock formations. The primary limitation of such observation
wells is that the collected samples are representative of the upper part of the shallow aquifer and may be a mixture of groundwater from different aquifer sections. In addition, it is noteworthy that sampling non-pumping observation wells requires more time and equipment than sampling domestic wells using the pre-installed pump. An important aspect is that baseline groundwater observation wells can be used for long-term monitoring programmes, that may be required or desirable during and after shale gas production. Therefore, investing in well-designed and effective shallow groundwater monitoring systems can be cost-effective in the long run, as it provides evidence for regulatory compliance and, where it occurs, early detection of leakage events that may require remedial action. Multi-level wells are particularly well-suited to monitor the migration of fluids and gases over the full depth of shallow aquifers. In addition, depth discrete sampling is useful to investigate potential variation in baseline chemistry and redox conditions with depth, which can be difficult to obtain using other types of sampling infrastructures.

5.1.2. Sampling network

An optimal sampling network should allow for the collection of baseline groundwater data at the site-scale, in close proximity to the shale gas wells (tens to hundreds of meters), and at the basin-scale, over the whole area targeted for shale gas development (few kilometres to tens of kilometres). The sampling network is to be designed based on the conceptual model/understanding of the groundwater system, which depends on the existing knowledge of the geology (structure, stratigraphy, lithology, mineralogy), groundwater flow directions, natural background groundwater quality and pollution sources. At the site-scale, collecting baseline data is critical owing to the specific risks of groundwater contamination associated with shale gas operations (Figure 1). However, the presence of a sufficient number of existing groundwater wells in close proximity to shale gas extraction sites is unlikely and therefore the installation of new observation wells may be required to collect sufficient groundwater data. The installation of groundwater monitoring wells adjacent to future shale gas well pads has been stressed by several authors. Furthermore, shallow groundwater observation wells would be highly desirable at locations adjacent to potential surface contamination sources such as wastewater storage and drilling waste disposal. In this respect, knowledge of local groundwater flow direction is valuable, in particular the location along the flow path relative to the potential contamination sources (upgradient/downgradient).

At the basin-scale, the baseline groundwater sampling network should provide a representative number of sampling sites for each relevant aquifer unit (e.g. karst aquifers, alluvial aquifers, bedrock aquifers). The number of sampling wells should increase with the size, heterogeneity (e.g. structure, mineralogy, groundwater flow conditions) and vulnerability of the aquifer units. Potential contamination areas should be covered with a high density of wells, particularly deformation zones which
may act as preferential migration pathways for deep fluids. For the purpose of ensuring a good spatial coverage, baseline groundwater collection sites will likely need to take advantage of natural springs and existing wells. Shale gas regulations may require that existing water-supply wells be tested within a specified radius from the proposed shale gas well (e.g. 610 m in Pennsylvania, 805 m in Colorado). Although such baseline groundwater data are valuable, the baseline sampling area needs to be delineated based on the best understanding of the groundwater system and should be expanded in most cases to collect sufficient baseline data. Observation wells from regional to national groundwater quality monitoring networks can be used to obtain baseline groundwater samples, as such wells are generally well-documented. The provenance of well water should be clearly identified to avoid attributing samples to the wrong aquifer or to avoid analysis of mixed groundwater samples from different aquifer units. In remote areas, the absence of existing groundwater wells can be a severe limitation for collecting sufficient baseline data, even though groundwater contamination in such areas would have limited implications for public health. In such cases, a number of groundwater observation wells in the vicinity of the shale gas well pads should be ideally installed to obtain baseline data for relevant aquifer units (Figure 3).

5.2. Baseline groundwater data

5.2.1. Selected baseline parameters

Geochemical baseline groundwater studies should provide a set of scientifically-defensible data for standard baseline parameters. The purpose is to provide the key baseline information on groundwater chemistry based on parameters being commonly measured at reasonable cost. Table 1 presents a selection of standard hydrochemical parameters that are recommended for routine measurements of the baseline characterisation of groundwater geochemistry in shale gas areas. The selected parameters provide information on 1) geochemical conditions (i.e. redox, acidity/alkalinity, mineralisation), 2) sources of dissolved constituents (section 4), 3) baseline levels against which any future changes can be compared and 4) sample quality control (i.e. analytical consistency).
Table 1. Selection of standard hydrochemical parameters for baseline characterisation of groundwater geochemistry in shale gas development areas.

<table>
<thead>
<tr>
<th>Parameter Category</th>
<th>Parameters</th>
<th>Information</th>
</tr>
</thead>
<tbody>
<tr>
<td>Field measurements</td>
<td>T, Specific conductance, pH, Eh, O₂</td>
<td>Geochemical conditions, quality control</td>
</tr>
<tr>
<td>Dissolved major and minor constituents</td>
<td>B, Ba, Br, Ca, Cl, DIC, DOC, F, Fe, HCO₃, I, K, Mg, Mn, Na, NH₄, NO₃, PO₄, Si, SO₄, S₉₉, Sr</td>
<td>Geochemical conditions, sources of dissolved constituents, baseline levels, quality control</td>
</tr>
<tr>
<td>Trace element concentrations</td>
<td>Al, As, Be, Cd, Cr, Co, Cu, Hg, Li, Mo, Ni, Pb, Sb, Sn, Se, V, U, Zn</td>
<td>Geochemical conditions, baseline levels</td>
</tr>
<tr>
<td>NORMs</td>
<td>Gross alpha, gross beta, Ra-226, Ra-228, Rn-222, U-238</td>
<td>Baseline levels</td>
</tr>
<tr>
<td>Dissolved C₁-C₃ alkane concentrations</td>
<td>CH₄, C₂H₆, C₃H₈</td>
<td>Baseline levels, gas origin</td>
</tr>
<tr>
<td>Stable isotopic composition of CH₄</td>
<td>δ¹³C₄H₄, δ³²H₄</td>
<td>Methane origin</td>
</tr>
</tbody>
</table>

*Although not the focus of this study, organic parameters are to be added to this list of standard parameters to obtain a comprehensive baseline assessment.

This core set of baseline parameters is intentionally limited in order to keep costs manageable and to focus efforts towards a better spatial coverage and higher measurement frequency. However, additional tracers can be measured in groundwater samples from selected sites to gain insight into specific geochemical processes such as brine migration, methane origin and pollution with organic compounds. These additional tools can include a wide range of more complex and costly tracer analyses such as gas elemental concentrations (N₂, CO₂, He, Ne, Ar) and noble gas isotope ratios (³⁷He/⁴⁰He, ²⁰Ne/²²Ne, ²¹Ne/²²Ne, ²⁰Ne/³⁶Ar, ⁴⁰Ar/³⁶Ar), carbon and hydrogen isotopes of C₂, CO₂ and DIC (δ¹³C-C₂H₆, δ¹³C-C₃H₈, δ¹³C-CO₂, δ¹³C-DIC, δ³⁷H-C₂H₆, δ³⁷H-C₃H₈), radiocarbon (¹⁴C-DIC) and isotope ratios of Sr, B, Li, Ra and Ba (⁸⁷Sr/⁸⁶Sr, δ¹¹B, δ⁷Li, ²²⁸Ra/²²⁶Ra, δ¹³⁸Ba). Isotope compositions of sulphur (δ³⁴S-SO₄, δ¹⁸O-SO₄) and nitrogen-containing compounds (δ¹⁵N-NO₃, δ¹⁸O-NO₃) can be valuable tools for assessing redox processes such as sulphide oxidation as well as denitrification and bacterial sulphate reduction potentially triggered by methane intrusion into shallow aquifers. McIntosh et al. recently reviewed well-established and emerging techniques that can be applied for monitoring hydraulic fracturing impacts on shallow groundwater. It is important to keep in mind that new and more advanced, but also more costly techniques can be implemented once contamination is suspected based on standard parameter monitoring. Additional parameters can be determined on samples collected specifically for these analyses or on archived samples.

A comprehensive baseline assessment requires that organic compounds be added to the list of measured parameters. It is difficult to select specific baseline organic parameters as organic additives and natural organic compounds are numerous and
the exact mixture of HF additives is often unknown, especially at the time of the baseline assessment. Nevertheless, a number of organic and inorganic additives commonly used in hydraulic fracturing can be determined including alcohols, persulfates and organic acids\textsuperscript{17,32,34}. Organic compounds that are resistant to biodegradation and commonly detected in flowback waters are to be measured preferentially\textsuperscript{13,108}. In addition, baseline measurements should include geogenic organic compounds that may be released in shallow groundwater in the vicinity of shale gas operations such as kerosene, BTEX and mixed alkanes\textsuperscript{108}.

Moreover, it is pertinent to note that complementary data can be collected during baseline groundwater sampling campaigns, such as groundwater levels and mineralogical data of shallow aquifer rocks. For example, geochemical and mineralogical data can be obtained from rock samples collected from outcrops and from drilling cores of observation wells. Such complementary data can be helpful to improve the conceptual hydrogeochemical model and to interpret future monitoring groundwater data.

In rare cases, baseline groundwater data can be directly obtained from existing datasets related to established monitoring networks (see section 5.3). An example of such a monitoring network is the governmental Groundwater Observation Well Network (GOWN) in Alberta (Canada) that consists of over 250 high-quality groundwater monitoring wells completed in particular aquifer units. The associated database contains a comprehensive range of hydrochemical parameters including dissolved gases and isotopic parameters that have been routinely measured for many years\textsuperscript{99}.

5.2.2. Threshold levels

An ultimate objective of environmental baseline assessment is to establish threshold levels for each relevant groundwater constituent above which contamination by shale gas-related activities is likely. These threshold values are unrelated to health-based drinking water standards and can be defined as the upper limit of baseline variation\textsuperscript{18,140}. For an individual monitoring site, the baseline values vary within the min-max range and the threshold level corresponds to the maximum value. The concentration range reflects the temporal variability in groundwater chemistry, as evaluated with multiple sampling events over a defined baseline monitoring period. A baseline monitoring period of at least one year has been suggested to capture seasonal variations\textsuperscript{136,137}. A longer baseline monitoring period would increase the chance of detecting maximum variability but is likely to interfere with the shale gas development schedule. The sampling frequency should depend on the groundwater system characteristics. For example, a deep confined aquifer will require lower sampling frequencies than a small shallow unconfined aquifer, the latter being more sensitive to recharge variations and surface contamination\textsuperscript{140}. Montcoudiol et al.\textsuperscript{138} recommended the collection of at least six samples evenly distributed throughout the year for baseline assessment. However, high sampling frequencies may be difficult to achieve for some private wells due to potentially limited accessibility. It is important to note that these considerations apply to regular groundwater sampling for routine laboratory analysis that is currently used for most
chemical parameters, while in-situ sensor technology is usually used for continuous monitoring of physico-chemical parameters.

Threshold levels also need to be derived for each relevant aquifer unit at the basin-scale, i.e. within a radius of few kilometres to tens of kilometres depending on the density of sampling sites. Such threshold levels will serve to identify potential contamination at sampling sites for which no baseline data are available (i.e. not sampled during baseline characterisation). Such thresholds need to integrate the spatio-temporal variability in groundwater chemistry at the scale of the aquifer unit. To establish meaningful threshold values, appropriate statistical techniques should be applied to representative hydrochemical data from individual sampling sites. A discussion of the statistical methods used to determine threshold values is beyond the scope of this paper. However, statistical techniques must be able to identify outliers to avoid setting too high, non-representative threshold levels. For this purpose, a statistically sufficient number of samples should be available per aquifer unit (ideally from over 20 sampling sites). Moreover, analytical techniques with low detection limits are required for a number of key parameters in order to avoid problems associated with a large proportion of non-detects. In some cases, it may be preferable to exclude groundwater samples that are significantly affected by local surface contamination and therefore unrepresentative of regional groundwater quality, such as those obtained from domestic/farm wells with integrity issues.

The baseline groundwater assessment procedure is summarised as a flow chart in Figure 4.
5.3. Alternative methods in the absence of pre-drilling data

Until very recently, baseline groundwater data were rarely collected prior to shale gas development. In the absence of pre-development data collection, three major methods have been suggested for estimating baseline groundwater chemistry: existing (historical) records, reference (analogue) sites and equilibrium geochemical modelling. The comparison of baseline historical and post-drilling data has been used to evaluate the impacts of shale gas activities on groundwater in several studies. However, this comparison is rarely possible due to no or only sparsely available historical groundwater chemistry data. Pre-1990 datasets often have limited hydrochemical parameters and uncertainties related to sampling (e.g. filtration, well...
purging), measurement methods and detection limits. More recent datasets from groundwater quality monitoring programmes often lack some key baseline parameters, as such programmes were generally established for regular monitoring of drinking water quality. Notably, the concentrations of dissolved gases and NORMs are rarely measured in routine groundwater monitoring programmes that usually focus on the concentrations of major constituents and a selection of minor/trace elements. Moreover, changes in groundwater chemistry may have occurred in an area since data collection as a result of more recent anthropogenic contamination unrelated to shale gas development and/or natural variability. Therefore, uncertainties associated with historical data increase with time and question the validity of using datasets containing samples obtained at different times, often many years apart. Although existing records are unlikely to provide suitable baseline groundwater data, they can provide qualitative information to improve the conceptual hydrogeochemical model and to design baseline groundwater sampling networks for specific hydrocarbon resource plays (section 5.1.2).

In the absence of any data, spatial comparisons have been made between active shale gas extraction sites and non-active reference sites. In general, reference sites are located adjacent to active sites to maximise the similarity in environmental conditions and for practical reasons (e.g. sampling). However, although this method can provide useful information, the data comparison will always be undermined by differences related to hydrogeological characteristics and sampling conditions (e.g. well characteristics, number of samples). Finally, geochemical modelling can be an effective tool to predict the baseline concentrations of various dissolved constituents in aquifers and to distinguish groundwater contamination associated with shale gas development by deviations from the predicted baseline conditions. For example, Wen et al. used equilibrium calculations to predict fugitive gas contamination based on CH₄, Fe and SO₄ concentrations. Humez et al. used logistic regression to estimate baseline methane concentrations from groundwater chemical data in areas without dissolved gas measurements. However, estimating baseline conditions using geochemical modelling requires field data and the quantification of anthropogenic sources. Geochemical models can be valuable to improve the site conceptual model, but do not produce empirical data that can be used to derive threshold values. The major limitations of these *a posteriori* methods further emphasise the importance of collecting pre-drilling baseline groundwater data in areas of future shale gas development.

6. **RESEARCH PERSPECTIVES**

This critical review highlighted a number of knowledge gaps both related to inorganic contamination processes and baseline groundwater assessment in shale gas areas. The research on environmental impacts of shale gas development is only in its infancy and more laboratory and field studies are needed to further characterise the fate of inorganic contaminants associated
with flowback/produced fluids and drilling wastes. These studies should collect high-quality empirical data to document both the potential direct and indirect impacts of shale gas development on groundwater quality. In particular, valuable information can be obtained from groundwater monitoring at instrumented field sites such as the Marcellus Shale Energy and Environment Laboratory. An improved understanding of the risks to groundwater quality is critical to better protect groundwater resources and to establish a reliable baseline. In that respect, the review of recent baseline groundwater studies identified a lack of consideration for 1) the geogenic contamination of shallow groundwater in shale gas areas and 2) the establishment of threshold levels for critical groundwater constituents such as Cl, Na, Ba, Ra, F, As and Mn. To fill these gaps, future studies should conduct in-depth investigations of the distribution and sources of inorganic groundwater constituents in areas of future shale gas development. Moreover, further research is needed to establish a list of organic parameters to be measured as part of baseline characterisation. More broadly, future research should be directed towards establishing a generic and flexible approach for baseline assessment of groundwater quality in shallow aquifers, including the development of reliable methods for the identification of threshold levels. In this way, relevant high-quality information would be collected to allow scientifically defensible assessment of potential future impacts on groundwater quality, such as those associated with shale gas development. Finally, it is important to mention that future baseline studies will be largely guided by policy and regulatory frameworks in different countries, provinces and states. In addition to scientific baseline requirements, a number of policy issues need to be addressed by regulatory authorities, including the funding of baseline assessment, the requirement for landowners to conduct baseline testing and the public availability of baseline data.

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