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**SECURE – Subsurface Evaluation of Carbon capture  
and storage and Unconventional risks**

**REPORT ON SYNERGIES OF ENVIRONMENTAL  
BASELINE STRATEGIES FOR CCS AND SHALE  
GAS PLAYS**

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## Public introduction

Subsurface Evaluation of CCS and Unconventional Risks (SECURE) is gathering unbiased, impartial scientific evidence for risk mitigation and monitoring for environmental protection to underpin subsurface geoenergy development. The main outputs of SECURE comprise recommendations for best practice for unconventional hydrocarbon production and geological CO<sub>2</sub> storage. The project is funded from June 2018–May 2021.

The project is developing monitoring and mitigation strategies for the full geoenergy project lifecycle; by assessing plausible hazards and monitoring-associated environmental risks. This is achieved through a programme of experimental research and advanced technology development that includes demonstration at commercial and research facilities to formulate best practice. We will meet stakeholder needs; from the design of monitoring and mitigation strategies relevant to operators and regulators, to developing communication strategies to provide a greater level of understanding of the potential impacts.

The SECURE partnership comprises major research and commercial organisations from countries that host shale gas and CCS industries at different stages of operation (from permitted to closed). We are forming a durable international partnership with non-European groups; providing international access to study sites, creating links between projects and increasing our collective capability through exchange of scientific staff.

## Executive report summary

Environmental baseline assessment is a key aspect of shale gas (SG) development and carbon capture and storage (CCS) activities. The environmental baseline is defined as the environmental conditions prior to any SG or CCS activities, and includes naturally-occurring conditions and the influence of previous or ongoing anthropogenic activity in the area. SG and CCS both utilise the deep sub-surface and therefore share some common strategies regarding environmental baseline assessment.

This report highlights synergies of environmental baseline strategies for SG and CCS, in relation to groundwater and ground gas. It should be noted that monitoring air quality and seismicity are also important aspects of environmental baseline strategies for both industries, but these are beyond the scope of this report. The synergies identified for environmental baseline strategies for SG and CCS are: i) the design of the sampling network, including the use of pre-existing wells and drilling dedicated monitoring wells; ii) the spatial distribution of the sampling network, to ensure baseline data are collected from all relevant major hydrogeological units at appropriate depths; iii) the selection of geochemical parameters to measure, with consideration of site-specific mineralogy; iv) defining threshold values for geochemical parameters that can be used to identify change and/or potential contamination that may arise from industrial activities; v) strategies for, and challenges of, characterising retrospectively the environmental baseline for sites where this was not completed before industrial activity began.

The identification of these synergies between SG and CCS for environmental baseline assessment promotes knowledge sharing between industries. The potential benefits of this could be more rapid advances in research, best practice and development of regulations for both industries. This could enable more robust baseline datasets to be collected, which would lead to a better understanding of contamination risks that may arise.



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# 1 Introduction

This report draws together evidence from the international literature regarding environmental baseline monitoring for shale gas (SG) development using hydraulic fracturing and carbon capture and storage (CCS). Many international investigations have been carried out, including several previous EC-funded studies (M4ShaleGas, ShaleXEnvironment, Fracrisk and SHEER on shale gas and RISCs, the EU Demonstration Project Network and ULTimate CO<sub>2</sub> on CCS) as well as numerous other studies where shale gas and CCS operations have conducted or tested. The environmental baseline monitoring requirements from these studies have been evaluated for both industries to identify synergies between the two. These synergies highlight areas where expertise from one industry can be applied to the other, which provides the opportunity to enhance the development of environmental baseline monitoring for both industries through shared learning.

SG and CCS both utilise the deep sub-surface, therefore, two key areas of concern related to both activities are i) the contamination of shallow groundwater, and; ii) leakage of ground gases into the environment (primarily CH<sub>4</sub> and other hydrocarbons for SG and CO<sub>2</sub> for CCS). This report focuses on environmental baseline monitoring strategies for assessing groundwater quality and ground gas. The wider remit of environmental baseline monitoring for both industries encompasses air quality and seismicity as well, but these factors are beyond the scope of this report. It is important to define what is meant by the environmental baseline and any related monitoring. The following definitions are used for this report:

**Environmental baseline:** the environmental baseline defines the environmental conditions prior to any SG or CCS activities commencing. In addition to natural environmental conditions, the environmental baseline also includes any influence of previous anthropogenic activity on the environment in the area of interest (e.g. historical mining sites). The baseline provides key information for refining the conceptual model of a site before industrial works begin.

**Environmental baseline monitoring:** environmental baseline monitoring is monitoring of environmental parameters to establish the environmental baseline. The environmental baseline is not a static entity. Therefore, a monitoring period of sufficient length is required to establish and characterise the spatial and temporal variability of the baseline. From these data, appropriate threshold values for parameters of concern can be established. The purpose of the threshold is to allow identification of any change to the baseline and/or contamination that may arise from the CCS and SG activities. Some solutes and gases may be naturally-occurring in the environment or be related to previous anthropogenic activities and it is important to distinguish between these different sources (McIntosh et al., 2019; Schlömer et al., 2014; Sharma et al., 2009; Vengosh et al., 2014).

Ideally, the environmental baseline should be established before any industrial activities begin. However, that is not always done, particularly with older sites in countries with historically little/no regulation or rapid development of the industry (Klusman, 2003; Richardson et al., 2013; Smyth et al., 2009). Where not carried out, attempts have been made to establish an environmental baseline after operations have begun, by using any available historical data for the site or studying a reference site, with similar hydrogeochemical settings but no CCS or SG facilities (Barth-Naftilan et al., 2018; Gao et al., 2020; Hildenbrand et al., 2016; Reilly et al., 2015; Smyth et al., 2009; Wen et al., 2019a).

In order for the environmental baseline to be utilised, environmental monitoring must continue throughout all stages of operation and decommissioning of a site. The monitoring data from operational phases is to be compared against the defined thresholds, to identify any deviation from the baseline conditions or other adverse effects and ensure compliance with risk mitigation measures and regulations.

Regulations for CCS and SG are currently not well-developed in all but a few places and there is currently no EU Directive for SG. The EU CCS Directive (2009/31/EC) states the need for environmental monitoring at all stages of the lifecycle of a storage site (baseline, operational and post-operational), but does not specify best-practice details and specific parameters to measure. Instead, the Directive states that “the choice of monitoring technology shall be based on best practice available at the time of design” (Annex II (1.1)).

The current status of development regarding best-practice guidelines for both CCS and SG presents the opportunity to assess current progress for both industries and identify synergies between them. This report explores synergies related to environmental baseline monitoring for assessing groundwater quality and ground gas, with the aim of understanding where there can be mutual benefit to both industries by sharing of knowledge and solutions.



## **1.1 REPORT STRUCTURE, AIMS AND OBJECTIVES**

The key components of environmental baseline monitoring for SG and CCS are summarised in Sections 2 and 3. The main objective of this report, to identify synergies between environmental baseline monitoring strategies for CCS and SG, is discussed in Section 4. These synergies could lead to efficiencies within the research, development and practice for both industries. A selection of case studies is included in Appendix 1. These provide examples that relate to the key concepts discussed in this report.

The report is structured as follows:

- Section 2 - The key components of environmental baseline monitoring for SG
- Section 3 - The key components of environmental baseline monitoring for CCS
- Section 4 - Synergies between environmental baseline monitoring for SG and CCS
- Section 5 - Conclusions
- Appendix 1 – SG and CCS Case Studies



## 2 Environmental baseline assessment for shale gas

### 2.1 POTENTIAL SOURCES OF CONTAMINATION IN THE SHALLOW SUB-SURFACE

#### 2.1.1 Flowback and produced waters

##### 2.1.1.1 NATURALLY-OCCURRING INORGANIC CONTAMINANTS

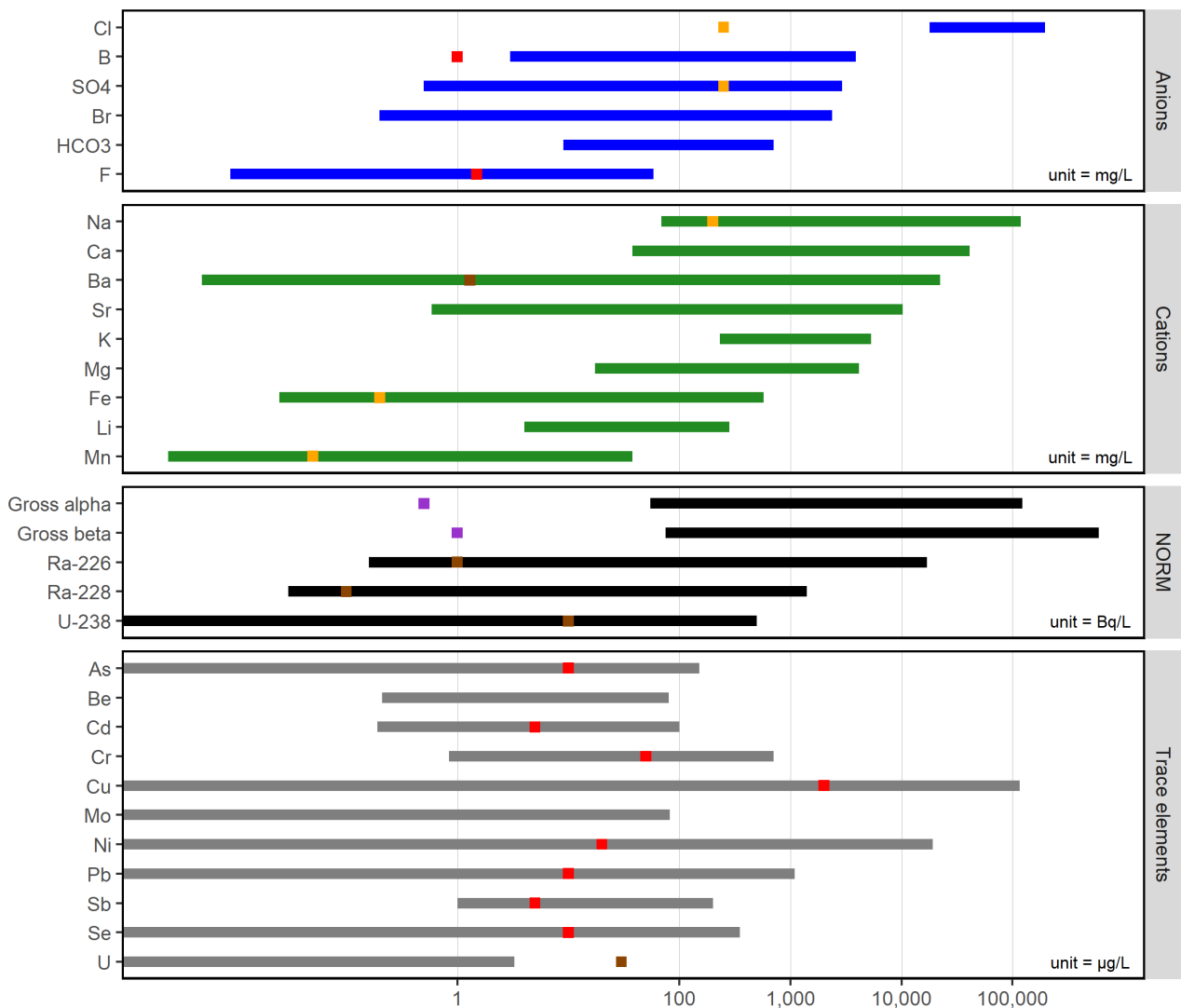
Significant volumes of flowback and produced waters are generated during SG extraction (Kondash et al., 2017). Flowback waters return to the surface a few days to a few weeks following hydraulic fracturing and prior to gas production, while produced water is co-produced continuously with the gas once the well is placed into production. Flowback and produced waters may contain elevated concentrations of inorganic constituents originating from saline formation waters and shale-fluid interactions during the hydraulic fracturing process. These mineralised fluids generally consist of saline Na-(Ca)-Cl waters with high levels of alkaline earth elements (Ca, Sr, Ba, Ra), alkali elements (Na, K, Li) and halides (Cl, Br), and low concentrations of carbonates and sulphates (Figure 1). The salinity of flowback/produced waters rapidly increases with time after hydraulic stimulation, which is attributed to an increasing proportion of natural formation brines (Osselin et al., 2018; Haluszczak et al., 2013; Rowan et al., 2015). Formation brines are thought to be derived from evaporated seawater further modified by water-rock interactions and dilution processes in the gas shale itself or in adjacent units (Engle et al., 2016; Engle and Rowan, 2014; Ni et al., 2018; Rowan et al., 2015; Warner et al., 2012).

The concentrations of the majority of inorganic constituents in flowback and produced waters exceed international standards and guidelines for drinking water and environmental protection. The contamination of shallow groundwater by only a small quantity of these highly saline fluids can cause concentrations to exceed drinking-water and environmental standards. The most concerning concentrations for human health are those of Na, Cl, Ba and Ra, and to a lesser degree, SO<sub>4</sub>, Sr, B, Br and Mn (Figure 1). Elevated concentrations of the alkaline earth elements Sr, Ba and Ra have been attributed to 1) the limited precipitation of sulphate minerals (e.g. barite, celestite) due to warm and strongly reducing conditions, and 2) the increased competition for sorption sites onto clay minerals and organic matter due to high ionic strength (Fan et al., 2018; Tieman et al., 2020). Recent studies suggest that significant amounts of Ba and Ra could be released in flowback/produced waters as a result of hydraulic fracturing processes (Renock et al., 2016; Landis et al., 2018). From an isotopic perspective, formation and produced waters have been characterised by enriched stable isotopes of water ( $\delta^2\text{H}$ ,  $\delta^{18}\text{O}$ ) and variable isotopic compositions of solutes ( $^{87}\text{Sr}/^{86}\text{Sr}$ ;  $\delta^{11}\text{B}$ ;  $\delta^7\text{Li}$ ;  $^{228}\text{Ra}/^{226}\text{Ra}$ ;  $\delta^{138}\text{Ba}$ ) depending of the shale rock composition and reactions during water-rock interaction (Engle et al., 2016; Osselin et al., 2018; Tasker et al., 2020; Tieman et al., 2020; Capo et al., 2014; Chapman et al., 2012; Gao et al., 2020; Huang et al., 2020; Rowan et al., 2015).

Moreover, gas-rich shales are often enriched in toxic trace elements and radionuclides associated with organic matter, sulphide and clay minerals. These hazardous elements may be released as a result of shale interaction with hydraulic fracturing fluid. The inorganic chemistry of flowback and early-produced waters have been characterised by elevated concentrations of trace elements such as Be, Cd, Cr, Cu, Mo, Ni, Pb, Sb, Se and U (Abualfaraj et al., 2014; Lester et al., 2015; Ziemkiewicz and He, 2015). The release of inorganic constituents during shale-fracturing fluid interaction has been mainly investigated by laboratory experiments (Harrison et al., 2017; Marcon et al., 2017; Mehta and Kocar, 2019; Pearce et al., 2018; Wang et al., 2015; Wilke et al., 2015; Wang et al., 2016b; Li et al., 2017; Wilke et al., 2018; Landis et al., 2018; Renock et al., 2016; Pilewski et al., 2019) and more recently by exploring the geochemical and isotopic composition of flowback and produced waters ( $\delta^{34}\text{S}_{\text{SO}_4}$ ,  $\delta^{18}\text{O}_{\text{SO}_4}$ ,  $\delta^2\text{H}$ - $\delta^{18}\text{O}$  of water,  $\delta^7\text{Li}$ ,  $\delta^{11}\text{B}$ ,  $^{87}\text{Sr}/^{86}\text{Sr}$ ) (Osselin et al., 2019; Phan et al., 2020). Most of the experimental studies 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 the presence of specific chemical additives. In the initial stage of hydraulic fracturing, batch leachate and produced water chemistry suggested that the oxidation of pyrite and organic matter may release trace metals (Harrison et al., 2017; Wilke et al., 2015; Mehta and Kocar, 2019; Pearce et al., 2018; Phan et al., 2020). The physical detachment of particulate sulphide grains may also be a significant process for trace metal transport in flowback and produced waters (Kreisserman and Emmanuel, 2018). Under acidic conditions associated with the absence of buffering minerals, elevated dissolved trace metals may occur as a result of the dissolution of Fe-Mn oxyhydroxides, which are major sinks for trace metals (Mehta and Kocar, 2019). Trace metal concentrations appear to decrease in the later stage of production, as produced water is diluted by saline formation waters (Osselin et



al., 2019). Overall, hydraulic fracturing processes are designed to ensure the development of an effective fracture network through physical modification of the rock and mineral dissolution, which is necessarily associated with high concentrations of dissolved elements, including hazardous contaminants (Osselin et al., 2019).



**Figure 1: Concentration range of selected major inorganic constituents, NORM and trace elements in flowback/produced water. Red marker = EU drinking-water standard (chemical parameter); orange marker = EU indicator parameter; brown marker = WHO guideline value; Violet marker = WHO screening levels. Data from Abualfaraj et al. (2014); Barbot et al. (2013); Cantlay et al. (2020a); Capo et al. (2014); Chapman et al. (2012); Gao et al. (2020); Haluszczak et al. (2013); Huang et al. (2020); Liu et al. (2020); Ni et al. (2018); Osselin et al. (2018); Phan et al. (2015); Rosenblum et al. (2017); Rowan et al. (2015); Tasker et al. (2020); Ziemkiewicz and He (2015); Lester et al. (2015); Osselin et al. (2019); Phan et al. (2020).**

#### 2.1.1.2 ANTHROPOGENIC AND GEOGENIC ORGANIC CONTAMINANTS

Fracturing fluids and flowback waters can contain a wide range of anthropogenic and geogenic organic compounds. Man-made organic compounds consist primarily of hydraulic fracturing additives that are used for a variety of purposes. These may include friction reducers, crosslinkers, breakers, corrosion and scale inhibitors, clay stabilizers, surfactants and biocides (Elsner and Hoelzer, 2016; Stringfellow et al., 2014). The organic additives belong to a diverse class of compounds (e. g. alcohols, polymers, hydrocarbons, acids) and





include a number of toxic substances (Elsner and Hoelzer, 2016; Stringfellow et al., 2014; Brantley et al., 2014).

Geogenic organic compounds mainly consist of aliphatic compounds such as light gases (e.g. methane, ethane, propane) and aromatic hydrocarbons such as benzene, toluene, ethylbenzene, xylene (BTEX) (Luek and Gonsior, 2017). Moreover, a number of transformation products resulting from the degradation of organic substances are present in flowback and produced waters such as organic acids, acetate and halogenated compounds (Luek and Gonsior, 2017; Elsner and Hoelzer, 2016).

The leakage of fracturing fluid and flowback/produced water may directly and indirectly affect the quality of shallow groundwater due to the presence of organic compounds. Several studies have identified SG activities as the source of toxic organic substances in shallow groundwater including gasoline and diesel range organic compounds, BTEX and ethylene glycol (Drollette et al., 2015; Gross et al., 2013; Llewellyn et al., 2015). Moreover, the biodegradation of organic compounds may produce secondary water-quality impacts, similar to those produced by methane oxidation (see 2.2.2). 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 (Ziegler et al., 2015).

A number of organic compounds are readily biodegradable, which can explain their decreasing concentrations in flowback/produced waters, and the reduction of groundwater contamination risk (Elsner and Hoelzer, 2016).

## 2.1.2 Fugitive gas

### 2.1.2.1 METHANE CONTAMINATION

Shallow groundwater may be contaminated by the upward migration of free and/or dissolved methane resulting from SG exploitation. A number of studies have attributed high CH<sub>4</sub> concentrations in groundwater to SG development (Jackson et al., 2013a; Llewellyn et al., 2015; Osborn et al., 2011; Darrah et al., 2014; Sherwood et al., 2016). Based on the hydrocarbon abundance and CH<sub>4</sub> isotopes, Osborn et al. (2011) and Jackson et al. (2013a) concluded that the increased concentrations of thermogenic gas near gas well sites are related to fugitive gas contamination. Using noble gas and their isotopic compositions, Darrah et al. (2014) identified several clusters of groundwater wells that exhibited evidence for fugitive gas contamination.

It is noteworthy that the origin of methane in groundwater near SG sites is highly controversial in the US, a number of studies attribute the occurrence of hydrocarbons to natural processes, unrelated to SG activities (Molofsky et al., 2013; Siegel et al., 2015a; Zhu et al., 2018). Flux of methane gas naturally along fault zones and unrelated to shale-gas development have also been recorded (Boothroyd et al., 2017). Methane in groundwater is not considered a health hazard for ingestion, but its degassing and accumulation in confined spaces may pose a risk of explosion or asphyxiation (Bell et al., 2017; Osborn et al., 2011).

### 2.1.2.2 INDIRECT IMPACTS OF FUGITIVE GAS MIGRATION

Fugitive gas migration into shallow aquifers can produce secondary water-quality impacts associated with the mobilisation of trace elements and other redox-sensitive species. In steady-state, CH<sub>4</sub>-rich groundwater, trace elements generally occur at low dissolved concentrations as a result of organic matter and sulphide stability, and the precipitation of carbonate minerals (Darvari et al., 2018). However, in originally CH<sub>4</sub>-free groundwater systems, the introduction of methane can lead to the mobilisation of elements present in the shallow aquifer material due to changes in Eh-pH conditions.

Experimental injection studies have shown that aerobic CH<sub>4</sub> oxidation driven by O<sub>2</sub> first leads to carbonic acidification and potential release of hazardous trace elements (Cahill et al., 2017), as suggested by the documented impacts of CO<sub>2</sub> leakage from carbon sequestration (Qafoku et al., 2017). Once O<sub>2</sub> is depleted, the reduction of Fe-Mn oxyhydroxides associated with anaerobic CH<sub>4</sub> oxidation may release sorbed metals, while increased pH may promote the desorption of oxyanion-forming trace elements (e. g. As, Mo, Sb, Se).

Anaerobic CH<sub>4</sub> oxidation has been reported to increase pH, alkalinity and the concentrations of reduced species (e. g. NH<sub>4</sub>, Fe, Mn and H<sub>2</sub>S) in previous studies of shallow groundwater affected by gas leakage from conventional and unconventional wells (Van Stempvoort et al., 2005; Woda et al., 2018; Wolfe and Wilkin, 2017) and by gas well blowout (Kelly et al., 1985; Schout et al., 2018). Microbially-mediated Mn, Fe and SO<sub>4</sub> reduction may lead to the formation of zones with high concentrations of dissolved metal/metalloid and/or sulphide species, depending of the availability of electron acceptor in the aquifer (Woda et al., 2018). The migration of methane in oxidising groundwater will likely result in the prevalence of mildly oxidising conditions favourable for the mobilisation of some trace metals. It is important to note that formation brines may also



increase the mobility of trace metals by introducing dissolved CH<sub>4</sub> and competing ions for sorption sites. The indirect effects of CH<sub>4</sub> leakage are likely to be highly site-specific, depending on the aquifer composition and hydrogeological characteristics (Forde et al., 2019).

### 2.1.3 Drilling-waste leachates

The leaching of poorly-managed drilling wastes by rainwater may release toxic elements into shallow groundwater through runoff. Drilling wastes consist of drill cuttings (shale rock pieces) sometimes enriched in trace metals/metalloids and/or radionuclides (Eitrheim et al., 2016; Phan et al., 2015; Walter et al., 2012), as well as residual drilling muds which often contain elevated Ba contents (weighting agent) and various organic chemicals such as base oil, polymers and biocides (Stuckman et al., 2019; Mikos-Szymańska et al., 2018).

Based on leaching experiments, several studies have evaluated the potential for the release of toxic trace elements and radionuclides from the exposition of shale cuttings to surface conditions (Phan et al., 2015; Lavergren et al., 2009; Yu et al., 2014; Piszcz-Karaś et al., 2016; Eitrheim et al., 2016; Johnson and Graney, 2015). These studies revealed that the oxidative dissolution of sulphide minerals and organic matter may be a significant source of trace metals (e. g. As, Cd, Mo, Ni and Zn) in leachates. Furthermore, the oxidation of sulphide minerals may form acid rock drainage in material with low neutralising capacity and promote the release of cationic metals (e. g. Ni, Co, Cd, Pb, Zn) (Yu et al., 2014; Chermak and Schreiber, 2014; Piszcz-Karaś et al., 2016). The dissolution of carbonate minerals may release U, which can persist in solution under oxidising conditions (Phan et al., 2015). Significant amounts of Ba may be desorbed from exchangeable sites (e. g. clays, organic matter) with increased ionic strength (Phan et al., 2015; Stuckman et al., 2019). Trace metals associated with Fe-Mn oxyhydroxides and iron(III)-bearing clays are also likely to be mobilised under reducing conditions such as anaerobic landfill conditions (Stuckman et al., 2019).

Overall, the improper disposal of drilling wastes may pose risks similar to those occurring in waste rock piles from base- and precious-metal mining in black shales (e. g. Nordstrom et al., 2015; Parviainen and Loukola-Ruskeeniemi, 2019). In addition, the leaching of organic chemicals contained in drilling wastes could directly and/or indirectly impact shallow groundwater quality (Section 2.1.2).

### 2.1.4 Contaminant pathways

Flowback and produced waters have the potential to impact shallow groundwater as a result upward migration due to well integrity issues (e.g. improperly cased/cemented gas wells), conductive fractures, accidental spills, leaks and surface run-off, and wastewater discharge (Vengosh et al., 2014; Davies et al., 2014; Dilmore et al., 2015; Garcia-Aristizabal et al., 2017). In addition, methane contamination has mainly been linked to the migration of gas from deep target and intermediate non-target formations due to well integrity issues related to casing or cement failures (Jackson et al., 2013b; Darrah et al., 2014; Brantley et al., 2014). Methane migrating along well bores may intersect shallow to intermediate flow paths via bedrock fractures (Llewellyn et al., 2015). Alternatively, shallow groundwater contamination by upward propagation of induced hydraulic fractures from the target formation is considered unlikely (Jackson et al., 2013b). Organic pollution is likely to occur from accidental surface spills and leaks, which have been widely reported at SG sites (Patterson et al., 2017; Maloney et al., 2017).

## 2.2 BASELINE STUDIES FOR SHALE GAS

### 2.2.1 Naturally-occurring potential contaminants

#### 2.2.1.1 ORIGIN OF METHANE

Methane (C<sub>1</sub>) and higher-chain hydrocarbons (C<sub>2+</sub>) are often naturally present in shallow groundwater from SG basins. The occurrence and origin of CH<sub>4</sub> in groundwater has been the focus of most of the baseline studies published to date (SG case studies 1, 2, 3 and 4). Unfortunately, many studies have been conducted in areas where SG extraction has already commenced, and, therefore, it remains uncertain whether the data in many examples represent geochemical conditions unaffected by SG activities (e. g. Zhu et al., 2018; Siegel et al., 2016; Molofsky et al., 2013; Huang et al., 2017b; Humez et al., 2016).

However, an increasing number of pre-drilling baseline studies have reported dissolved CH<sub>4</sub> concentrations exceeding 1 mg/L in undeveloped areas (Bordeleau et al., 2018a; Currell et al., 2017; Harkness et al., 2018; Moritz et al., 2015; McIntosh et al., 2014; Rivard et al., 2018; Ward et al., 2020b). In groundwater, CH<sub>4</sub> may have a biogenic origin, related to microbial activity, or a thermogenic origin, related to thermal decomposition



of organic matter. Biogenic CH<sub>4</sub> is mostly associated with shallow anaerobic environments; while thermogenic CH<sub>4</sub> is formed at depths of several hundred metres to kilometres in the subsurface, such as in oil and gas fields (Bell et al., 2017; McPhillips et al., 2014).

To determine the origin of CH<sub>4</sub>, baseline studies have traditionally used the ratio of methane to higher-order hydrocarbons (C<sub>1</sub>/C<sub>2+</sub>) and stable isotopic composition of CH<sub>4</sub> ( $\delta^{13}\text{C}_{\text{CH}_4}$ ,  $\delta^2\text{H}_{\text{CH}_4}$ ) (Bordeleau et al., 2018a; Currell et al., 2017; Schloemer et al., 2018; McPhillips et al., 2014). Based on these data, baseline studies have suggested that shallow groundwater contains predominantly biogenic CH<sub>4</sub> (Bordeleau et al., 2018a; Currell et al., 2017; Schloemer et al., 2018; McIntosh et al., 2014).

Elevated concentrations of biogenic CH<sub>4</sub> are likely to be associated with 1) organic-rich lithology (e.g. peat or alluvial deposits), and 2) geochemically evolved groundwater located in downgradient areas (valley bottoms) (McIntosh et al., 2014; McPhillips et al., 2014). However, thermogenic gas has also been observed in the shallow sub-surface as a result of upward migration from deep formations or uplift of gas-bearing formations that were previously located in the deep sub-surface (Eymold et al., 2018; Moritz et al., 2015; Bordeleau et al., 2018a). In relation to this, the occurrence of high thermogenic CH<sub>4</sub> concentrations have been correlated with 1) organic-rich shale or coal bed units, 2) deformation features such as fracture/fault zones, and 3) water types derived from mixing with deep brines (e. g. Na-Cl) (Harkness et al., 2018; Kreuzer et al., 2018; Moritz et al., 2015). However, methane isotopic data and C<sub>1</sub>/C<sub>2+</sub> ratios are often subject to uncertainties due to secondary processes such as mixing, migration and microbial oxidation (McIntosh et al., 2019).

To reduce these uncertainties, additional isotopic and geochemical indicators have been applied such as stable carbon isotopes of dissolved inorganic carbon ( $\delta^{13}\text{C}_{\text{DIC}}$ ), stable isotopic composition of heavier aliphatic hydrocarbons (e.g.,  $\delta^{13}\text{C}_{\text{C}_2\text{H}_6}$ ), methane radiocarbon ( $^{14}\text{C}_{\text{CH}_4}$ ), and noble gas elemental and isotope geochemistry (Eymold et al., 2018; Bordeleau et al., 2018a; Rivard et al., 2018). Recent baseline studies have also documented the temporal variability of CH<sub>4</sub> concentrations and isotopic composition (Rivard et al., 2018; Currell et al., 2017; Loomer et al., 2018; Schloemer et al., 2018; Ward et al., 2020b; Smedley et al., 2017). These studies indicated that CH<sub>4</sub> concentrations can vary substantially over time, changing by up to several orders of magnitude at some sites. Temporal variations of methane were mostly attributed to changes in groundwater flow conditions and associated redox conditions, and dependent on hydrogeological conditions (e.g. aquifer depth, confinement and permeability) (Schloemer et al., 2018; Loomer et al., 2018). Alternatively, isotopic composition of CH<sub>4</sub> is generally more stable, in particular for the situation where there are elevated methane concentrations (Rivard et al., 2018; Currell et al., 2017). The lack of variation in isotope composition was interpreted as limited variability in the CH<sub>4</sub> source over time (Currell et al., 2017).

#### 2.2.1.2 SOURCES OF INORGANIC CONTAMINANTS

The natural occurrence of saline waters and inorganic (geogenic) contaminants may complicate the identification of groundwater contamination by SG development. A number of studies have recently investigated the salinity sources in shallow groundwater from SG basins (SG case studies 5, 6 and 7). In some areas, groundwater salinity is derived exclusively from meteoric water interaction with shallow aquifer material.

This is the case in upland bedrock and karst aquifers where low-salinity Ca-HCO<sub>3</sub> waters occur predominantly as a result of carbonate dissolution (Gao et al., 2020; Huang et al., 2020; Rhodes and Horton, 2015; Bordeleau et al., 2018b; Li et al., 2016). Na-HCO<sub>3</sub> waters also commonly occur further along the flow path in sedimentary aquifers as a result of Na-Ca exchange and in bedrock aquifers through Na-silicate weathering (Down et al., 2015; Bordeleau et al., 2018b). In such groundwaters, brine contamination can easily be detected based on changes in major- and minor-element concentrations 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. In particular, the migration of formation brines into shallow aquifers has been identified as a major source of salinity in groundwater from several SG basins including the Appalachian Basin (USA) (Kreuzer et al., 2018; Harkness et al., 2017), the Karoo Basin (South Africa) (Eymold et al., 2018; Harkness et al., 2018) and the St. Lawrence Lowlands (Canada) (Bordeleau et al., 2018b). The mineralised waters derived from mixing with formation brines are characterised by relatively high concentrations of Cl, Na, Br, Ba, B, Li, Sr and hydrocarbons (methane, ethane and propane).

Recent structural and geochemical evidence suggests that in some geological settings, formation brines naturally migrate through faults and fractures along deformational features (Kreuzer et al., 2018; Llewellyn, 2014). A number of geochemical and isotopic tools have been applied to detect natural brine migration into shallow aquifers including ion concentrations and ratios (Cl, Br, Ba, Na, Li, Sr, I), stable and radiogenic isotopes of dissolved elements ( $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $\delta^{11}\text{B}$ ,  $\delta^7\text{Li}$ ,  $^{228}\text{Ra}/^{226}\text{Ra}$ ) and elemental and isotopic compositions of noble gas ( $^3\text{He}$ ,  $^4\text{He}$ ,  $^{20}\text{Ne}$ ,  $^{21}\text{Ne}$ ,  $^{22}\text{Ne}$ ,  $^{36}\text{Ar}$ ,  $^{38}\text{Ar}$ ,  $^{40}\text{Ar}$ ) (Harkness et al., 2018; Harkness et al., 2017; Eymold et al., 2018;



Kreuzer et al., 2018; Warner et al., 2012; Darrah et al., 2015; Lautz et al., 2014; Reilly et al., 2015; Lu et al., 2015). Stable isotopes of water are less sensitive to small contributions of brines, in comparison with isotopes of dissolved elements (Warner et al., 2012). Other salinity sources may also complicate the detection of brine contamination such as evaporite dissolution and residual seawater introduced in the aquifer during marine transgressions (Bordeleau et al., 2018b; Loomer et al., 2019).

Elevated concentrations of geogenic contaminants are common in groundwater from sedimentary basins, and generally exhibit a high spatial variability. However, the distribution and sources of geogenic contaminants have been addressed in a limited number of baseline studies, and this remains a major source of controversy regarding the impacts of SG development on groundwater quality (Fontenot et al., 2013; McHugh et al., 2014; Kinchy, 2019). The few studies available have generally attributed the occurrence of hazardous inorganic constituents to natural processes, without thorough investigation of the geochemical sources. The most probable sources include the migration of saline formation waters and water-rock interaction with shallow aquifer solids (SG case studies 5 and 6). Elevated trace-element concentrations have been reported in bedrock groundwater from SG areas, in particular As and Mn in the Appalachian Basin (Down et al., 2015; Harkness et al., 2017; Wen et al., 2019a; Siegel et al., 2015b), and As, Be and Mo in the Permian Basin (Hildenbrand et al., 2016). In addition, baseline studies have reported hazardous concentrations of minor elements such as F, Ba and B (Kreuzer et al., 2018; Harkness et al., 2018; McMahan et al., 2015; Hildenbrand et al., 2015). Due to environmental concerns related to radioactive shales, natural radioactivity and radionuclide activities ( $^{222}\text{Rn}$ ,  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$ ) have been recently evaluated in the Karoo Basin (South-Africa) (Botha et al., 2019), the Carboniferous Maritime Basin (Canada) (Lagacé et al., 2018) and the Sichuan Basin (China) (Huang et al., 2017a).

## 2.2.2 Anthropogenic contamination

### 2.2.2.1 LEGACY OF HYDROCARBON RESOURCE EXTRACTION

Shallow groundwater may be affected by anthropogenic contamination prior to SG development. In many areas, shale gas exploration is taking place in regions of former deep coal-mining, and there is a shale gas resource in many areas that have been drilled for conventional hydrocarbons (e.g., north Nottinghamshire, UK and the central belt of Scotland). Consequently, in some hydrocarbon basins, legacy contamination from coal mining and conventional oil and gas extraction may further complicate the identification of SG development impacts on groundwater quality (Tisherman and Bain, 2019; Ni et al., 2018). Mine drainage is likely to release toxic metals and metalloids in shallow groundwater around coal mines (Nordstrom et al., 2015). Previous studies have identified coal-mine drainage by relatively high  $\text{SO}_4$  and low Br and Ba concentrations as compared to oil and gas brines (Cantlay et al., 2020b; Brantley et al., 2014; Pelak and Sharma, 2014).

Shallow groundwater may also be impacted by fluid and gas migration along improperly sealed abandoned oil and gas wells. Unplugged wells can particularly act as conduits for upward migration of hydrocarbons (Jackson et al., 2013b; Kang et al., 2014). In addition, groundwater quality may have been affected by produced formation waters from conventional oil and gas wells in some areas. Differentiating between produced waters from conventional and unconventional reservoirs is challenging, although elemental ratios and isotopic compositions (Sr, B, Li, Ba, Ra) have been used to provide a unique fingerprint for each reservoir (Phan et al., 2016; Chapman et al., 2012; Tieman et al., 2020; Warner et al., 2014; Tasker et al., 2020; Cantlay et al., 2020a; Tisherman and Bain, 2019; Ni et al., 2018). However, the distinction is not always possible due to geochemical overlaps (Ni et al., 2018; Phan et al., 2016; Warner et al., 2012). To our knowledge, no pre-SG baseline investigations have documented convincing legacy contamination from conventional hydrocarbon operations in SG areas.

### 2.2.2.2 SURFACE CONTAMINANTS

In rural areas, domestic/farm wells are commonly impacted by surface contamination sources such as de-icing road salts, septic tank effluents and agricultural residues (Jackson and Heagle, 2016; Reilly et al., 2015). In baseline studies, surface contamination has often been identified using major- and minor-ion concentrations (SG case studies 7). For instance, domestic and agricultural contamination has been detected using  $\text{NO}_3$  concentrations (Johnson et al., 2015; Reilly et al., 2015; Li et al., 2016). Road salt contamination has been identified using elemental ratios such as Br/Cl and (Ba+Sr)/Mg, as halite used for de-icing contains low levels of Br, Ba and Sr (Down et al., 2015; Johnson et al., 2015; Lautz et al., 2014).

The application of ratios can be limited by minor element concentrations being below the quantification limit (Johnson et al., 2015; Down et al., 2015). However, the detection of surface contamination is greatly



complicated by the use of oil and gas wastewaters on roads for de-icing or dust suppression in some regions outside Europe (Tasker et al., 2018; Wen et al., 2019a).

Moreover, elevated CH<sub>4</sub> concentrations can be related to contamination by landfill leachate (or gas) migration or agricultural residues (Darrah et al., 2015; McIntosh et al., 2019). Importantly, surface sources are spatially correlated with land-use (e. g. road network, agriculture) and hydrogeological conditions (e.g. confinement conditions, regional flow path) (Bordeleau et al., 2018b; Wen et al., 2019a). Such spatial information is of critical importance for baseline characterisation. Surface contaminants should also be considered for onshore CCS (Section 3.3.2).



## 3 Environmental baseline assessment for CCS

### 3.1 POTENTIAL SOURCES OF CONTAMINATION IN THE SHALLOW SUB-SURFACE

#### 3.1.1 Mechanisms of CO<sub>2</sub> leakage and brine intrusion from onshore CCS sites

The main causes for concern regarding groundwater contamination from onshore CCS sites are leakage of CO<sub>2</sub> and brine displacement into overlying aquifers. Groundwater contamination is a risk to the environment and where the shallow groundwater provides potable water supply, there is also a risk to human health (Lions et al., 2014). The accumulation of CO<sub>2</sub> gas in the shallow subsurface can also cause degradation of ecosystems, with impacts on vegetation growth and the potential to cause an asphyxiation risk in confined spaces (e.g. tunnels, basements or mines). This section summarises the potential sources and processes that can lead to groundwater contamination, and the key components of environmental baseline monitoring for CCS that have been developed to date.

CO<sub>2</sub> can leak from a CCS site as either supercritical CO<sub>2</sub> (scCO<sub>2</sub>), or as dissolved-phase CO<sub>2</sub> in formation fluid, which is commonly brine. To date, CO<sub>2</sub> leakage from onshore CCS sites has been reported to be low (Jenkins et al., 2015). However, given that CO<sub>2</sub> storage will be required to last for thousands of years, even the earliest established CCS sites are in very early stages of their anticipated lifecycle. If CCS is to become a widely used technology then CO<sub>2</sub> leakage from some storage sites could be expected (Holloway et al., 2007). CO<sub>2</sub> leakage from CCS is a major concern, particularly with respect to potable groundwater in overlying aquifers (Harvey et al., 2013). Impacts on groundwater quality need to be understood to minimise the risk of contamination and facilitate the acceptance of CCS as a viable solution to mitigate climate-change impacts (CCS case studies 1 and 2). However, baseline studies have not always been undertaken, especially for older CCS sites. In this case, any other existing historical hydrogeochemical data from the area can be used, or monitoring can be undertaken with consideration that industrial operations have already begun (CCS case study 3 and 4).

There are two main types of CO<sub>2</sub> leakage that can occur from a CCS site: i) gradual, longer-term leaks into overlying strata via natural pathways or abandoned wells and ii) sudden, short-duration well blowouts. This report only considers long-term, gradual CO<sub>2</sub> leakages, as this mechanism is of most relevance to groundwater quality and is also applicable to brine intrusion. A well blowout is related to a rapid release of gas to the atmosphere and most likely bypass groundwater. Slow leakages and slow gas accumulation are the main concern for groundwater and ground gas. These gradual leaks are at risk of going undetected without effective environmental baseline and ongoing monitoring. Well blowouts typically release CO<sub>2</sub> to the atmosphere and are rare, albeit high-risk if they do occur (Holloway et al., 2007; Jordan and Benson, 2008).

Gradual migration and leakage of CO<sub>2</sub> and brine can occur due to geological features such as faults and fractures in the formation and cap rock, well-integrity problems or poorly-plugged abandoned wells (Celia and Nordbotten, 2009; Holloway et al., 2007; IPCC, 2005). The chance of these types of leakage is considered to be low, and the impact of such a leak would be dependent on site-specific characteristics (e.g. geology, hydrogeology), the nature of the leak (e.g. flux) and the sensitivity of receptors (e.g. principal aquifer providing potable water) (Xiao et al., 2016; Bachu and Watson, 2009). In areas where there is a history of extensive oil and gas exploitation, the high density of abandoned wells can increase the risk of leakage via this route (Gasda et al., 2004). Failure of injection wells can also create CO<sub>2</sub> leakage pathways, but this has reduced with the introduction of regulations and improved engineering standards. The lowest rates occur at injection wells that are constructed for the purpose, instead of those converted for CCS activities (Bachu and Watson, 2009).

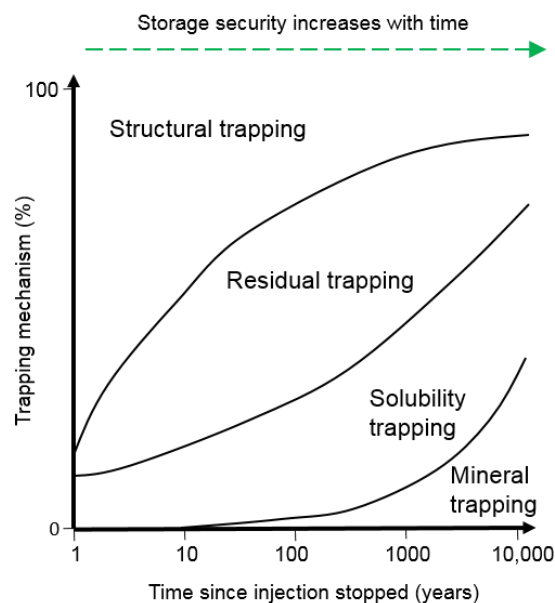
The density of scCO<sub>2</sub> is lower than that of water, therefore scCO<sub>2</sub> will rise through the target formation from the point of injection to the cap rock. The highest risk of CO<sub>2</sub> leakage is during the injection phase, due to the increased pressure in the formation and the initial reliance on structural and stratigraphic trapping of the freshly injected CO<sub>2</sub> (Figure 2) (Streit et al., 2005). After the injection period, the reduction in pore pressure will reduce the risk of migration of CO<sub>2</sub>, both dissolved and supercritical, and the reduction of geomechanical stress will also reduce the chance of a fracture pathway being created or reactivated (Holloway et al., 2007; Streit et al., 2005).

Increased pressure caused by the injection of CO<sub>2</sub> can also result in brine from the target formation being displaced upwards into the shallow aquifer (Oldenburg and Rinaldi, 2010). Brine density is controlled by salinity and temperature. Therefore the salinity of the brine, in combination with the amount of pressure exerted on it, will determine the amount of the brine displacement. Highly saline, dense fluid, experiencing low over-pressure



will tend to reach a new hydrostatic equilibrium within the conduit that has provided the pathway for intrusion. Lower-salinity fluid exposed to high pressure is likely to reach the overlying aquifer and the flow could persist. The density of the brine is likely to confine it to the lower part of the aquifer, although upconing could result from groundwater pumping (Neymeyer et al., 2007). The nature of the fault or fracture network may also influence the extent to which brine is displaced; wider fault zones could reduce the likelihood of brine displacement because the larger area (within the fault zone) can accommodate the brine better (Keating et al., 2013). In narrow faults, brine is more easily forced upwards and is therefore more easily displaced.

Over time, several mechanisms combining physical, chemical and biological factors can contribute to improving the stability of CO<sub>2</sub> storage (Figure 2) (Holloway et al., 2007; Förster et al., 2006; IPCC, 2005). Residual/capillary trapping, solubility trapping and mineral trapping all develop with increasing time since initial CO<sub>2</sub> injection. This is important because the storage of CO<sub>2</sub> will need to be successful for thousands of years to truly become a mitigation option for climate change. Residual/capillary trapping is a physical, hydrodynamic trapping mechanism that immobilises CO<sub>2</sub> by trapping in capillaries and pore space. This occurs as the injected CO<sub>2</sub> moves through the porous rock. Solubility trapping refers to the dissolution of CO<sub>2</sub> into formation fluid. CO<sub>2</sub>-rich water is more dense than the surrounding formation fluid and therefore sinks through the aquifer, further decreasing the risk of leakage and also causing a convective current within the aquifer which aids further dissolution of CO<sub>2</sub> (Lindenberg and Bermago, 2003). However, it will take between 5,000 and 50,000 years for the majority of CO<sub>2</sub> to dissolve into an aquifer (Lindenberg and Bermago, 2003). Mineral trapping occurs through the formation of solid carbonate minerals, which binds the CO<sub>2</sub> into the rock formation (Lindenberg and Bermago, 2003).



**Figure 2: Different mechanisms of CO<sub>2</sub> trapping and their relative importance over time. Adapted from IPCC (2005).**

### 3.1.2 Hydrogeochemical impacts of CO<sub>2</sub> leakage and brine intrusion

In the case of CO<sub>2</sub> leakage into an overlying aquifer, CO<sub>2</sub> will dissolve into the groundwater as described above. However, when this occurs outside of the designated CCS formation, this can have impacts on groundwater quality. Mobilisation of contaminants and their impacts on groundwater is the main concern regarding leakage of CO<sub>2</sub> from an onshore CCS storage site (Figure 3) (Newmark et al., 2010; Harvey et al., 2013) (CCS case studies 4, 5 and 6).

Dissolution of CO<sub>2</sub> in groundwater causes a reduction in pH which can initiate geochemical reactions including adsorption/desorption and dissolution/precipitation (Trautz et al., 2013). This can either be beneficial or detrimental, depending on the naturally-occurring compounds in the aquifer and how they react to the CO<sub>2</sub> leakage (Harvey et al., 2013). Mobilisation of major elements (e.g. Ca, Mg, K and Na), minor elements (e.g. Fe, Mn, Al and Ba) and trace elements (e.g. As, Pb and Cd) can occur through desorption or dissolution (Qafoku et al., 2017). These elements of concern are usually naturally present in the aquifers but may not be mobile or present in high concentrations under prevailing natural geochemical conditions. Their mobilisation



can have negative consequences for groundwater quality and drinking-water quality. However, CO<sub>2</sub> solubility is reduced when the salinity of the formation water is high, which consequently reduces the extent of pH decrease (Horner et al., 2015).

The mineralogy of the aquifer is important in determining the extent of increased acidity from a CO<sub>2</sub> leak (CCS case study 5). Formations containing calcite have been shown to experience a smaller or no decline in pH due to the natural buffering capacity of the calcite (Lawter et al., 2016; Wang et al., 2016a; Wunsch et al., 2014; Wunsch et al., 2013). Where sediment contains no calcite, groundwater can become more acidic and reactive minerals may release solutes through dissolution or desorption. However, calcite may also be detrimental to groundwater quality, potentially releasing contaminants such as As, Mn, Ba and Ni during dissolution of carbonate rocks (Kirsch et al., 2014; Wunsch et al., 2014; Wunsch et al., 2013; Lu et al., 2009).

As with CO<sub>2</sub> leakage impacts, site-specific properties such as mineralogy are a key factor in determining the impact of intrusion of brine into an aquifer (Qafoku et al., 2017). Analogous with produced fluids from SG operations, displaced brine can introduce toxic trace elements (e.g. Cd and As) into a shallow aquifer (Shao et al., 2015) and their fate is dependent on subsequent geochemical reactions with aquifer materials.

In some circumstances, brine extraction could be a possibility to increase the capacity for CO<sub>2</sub> storage without breaching the reservoir pressure limit for CO<sub>2</sub> injection, and to manage pressure in the reservoir (Jahediesfanjani et al., 2019; González-Nicolás et al., 2019).

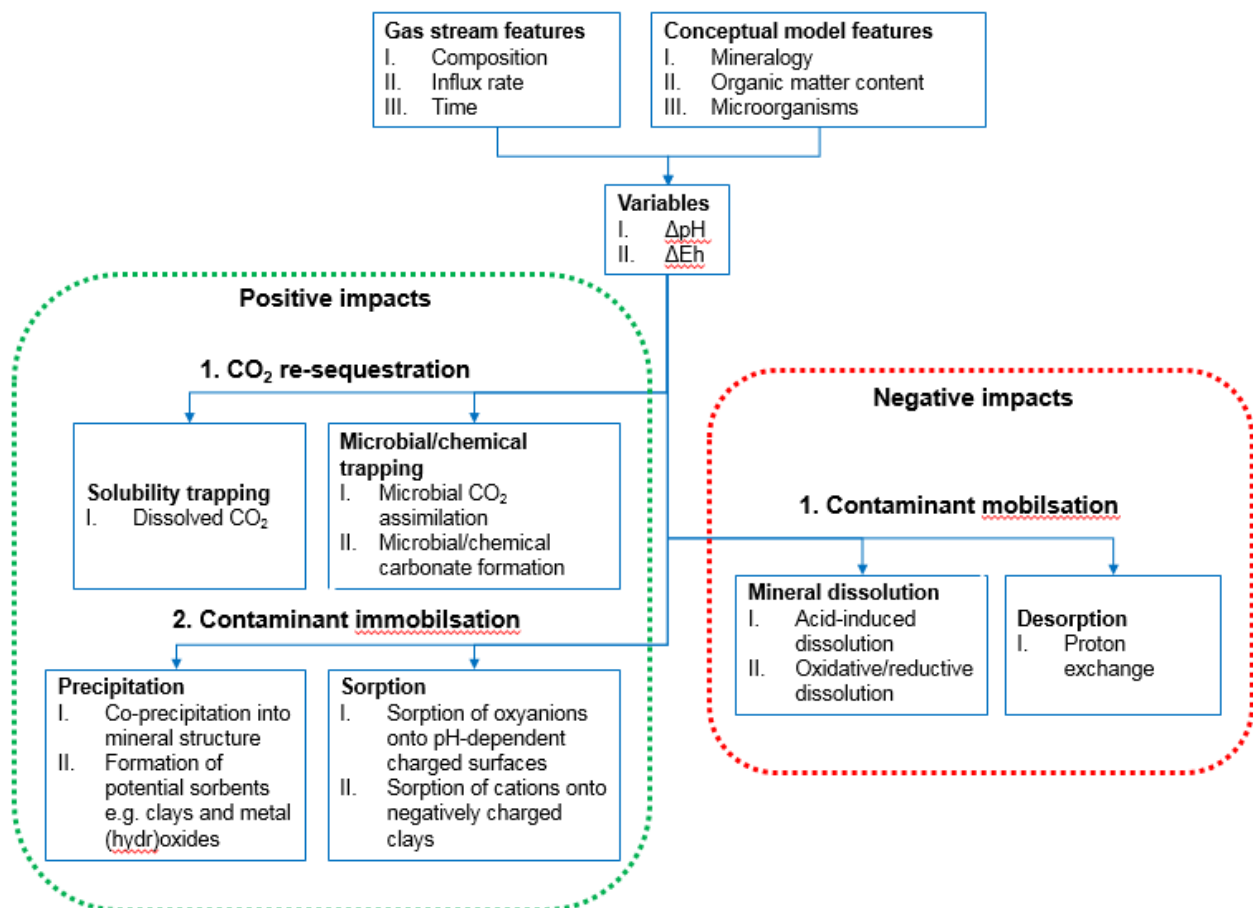


Figure 3: Conceptual framework to assess the positive and negative impacts of CO<sub>2</sub> in the shallow sub-surface, in relation to the hydrogeochemistry of a site. Adapted from Harvey et al. (2013).





## 3.2 BASELINE STUDIES FOR CCS

### 3.2.1 Naturally-occurring potential contaminants

#### 3.2.1.1 GROUND GAS EMISSIONS AND DISSOLVED GASES

CO<sub>2</sub> can be emitted from natural gas repositories, and natural emissions have been used to understand the potential impacts of leakage from a CO<sub>2</sub> storage site (Holloway et al., 2007). Naturally-occurring CO<sub>2</sub> migration in sedimentary basins is likely to be along faults and be low-flux, which imitates the expected characteristics of gradual CO<sub>2</sub> leaks from a repository, for example, dissolved-phase CO<sub>2</sub> can be discharged at the ground surface via springs. Volcanic areas, which experience large, infrequent CO<sub>2</sub> release to the atmosphere, are generally not targeted for CCS (IEAGHG, 2005).

The importance of determining baseline CO<sub>2</sub> concentrations is highlighted by an example from Weyburn, Canada CCS facility (CCS case study 1), where a local landowner claimed that CO<sub>2</sub> leakage was causing detrimental impacts to his land and property (Beaubien et al., 2013). In this case, noble gases and stable-isotope data were used to confirm that the CO<sub>2</sub> was not of a deep subsurface origin (Gilfillan et al., 2017).

Using isotopic and trace gas composition is recommended for identifying the origin of any CO<sub>2</sub> detected (Flude et al., 2017; Darling et al., 2018). For the In Salah CO<sub>2</sub> storage project in Algeria, perfluorocarbon compounds were added to the injected CO<sub>2</sub> as a tracer to aid with detection of breakthroughs for comparison with modelling of CO<sub>2</sub> migration within the repository (Ringrose et al., 2013) (CCS case study 7). The frequency and spatial distribution of sampling is important: ideally, continuous sampling at strategically selected sites should be undertaken (CCS case study 8).

CO<sub>2</sub> gas, both naturally-occurring and from a CO<sub>2</sub> leak, can also be converted to methane due to microbial activity in certain environmental conditions. This means that elevated methane concentrations could also indicate a CO<sub>2</sub> leak. In addition, research has investigated the possibility of purposefully converting stored CO<sub>2</sub> into methane within a repository, and then extracting it as a recycled energy source (Kuramochi et al., 2013; Shao et al., 2015). This could potentially improve the economic viability of CCS. Therefore, monitoring for methane gas should also be considered as it could either be a proxy indicator for a CO<sub>2</sub> leak, or if conversion to methane in the repository is undertaken, monitoring would allow identification of a potential methane leak from the storage site.

#### 3.2.1.2 MINERALOGY-BASED HYDROGEOCHEMICAL PARAMETERS AND INDIRECT IMPACTS OF FUGITIVE GAS LEAKAGE

The specific conditions in the aquifer at the storage site and the surrounding area need to be considered before injection begins. This is to establish baseline conditions (Holloway et al., 2007; Gaus, 2010; Chadwick et al., 2007) (CCS case studies 9 and 10). Key factors to consider are the system properties, parameters and variables associated with deleterious outcomes described in Figure 3 (Harvey et al., 2013).

The site-specific mineralogy of any overlying shallow aquifer is vital in determining the potential impact from CO<sub>2</sub> leakage, as described in Section 3.1. Therefore, detailed characterisation of the overlying aquifer(s) is essential, to understand how the groundwater system(s) would respond. Regarding mineralogy of the aquifer, assessing the quantity of any carbonate minerals present can determine the pH buffering capacity, which is the primary control on mobilisation of contaminants. The type of carbonate compounds will also indicate if toxic elements are likely to be released as a result of carbonate dissolution. It is also important to identify the presence of any elements in the rock that are immobile under natural or prevailing conditions, but would be toxic if mobilised by exposure to increased acidity.

Groundwater sampling to establish the environmental baseline should include monitoring pH, Eh and solutes relevant to subsurface CO<sub>2</sub> release (Figure 3). Even where the aquifer has a natural capacity to buffer pH, there will be a time lag between the initial leakage and establishing a new equilibrium.

However, there are several factors that may mitigate the impacts of a CO<sub>2</sub> leak and therefore make it difficult to detect. These include mixing and dilution of CO<sub>2</sub>-impacted groundwater with the surrounding, un-impacted aquifer, pH buffering, limited trace-metal presence in aquifers and/or secondary precipitation of trace metals (Keating et al., 2009). The design of the sampling infrastructure and frequency should take into account these factors to reduce the risk of a CO<sub>2</sub> leak remaining undetected.



### 3.2.2 Anthropogenic contamination

Potential CCS sites are subject to sources of anthropogenic contamination in similar ways to SG sites. The legacy of natural resource extraction and presence of surface contaminants described in section 2.2 are also relevant here. For example, surface hydrocarbon spills can cause anomalous concentrations of hydrocarbon gases (Beaubien et al., 2013). It is important to consider the impacts of any historical or current anthropogenic activities prior to CCS development, to ensure that if any environmental degradation occurs, the source can be identified correctly. This is particularly important for the public acceptance, development of policy, and regulatory approval of CCS.

## 4 Synergies between SG and onshore CCS for environmental baseline monitoring

### 4.1 INTERNATIONAL STANDARDS

International guidance (ISO standards) on installation of groundwater monitoring points (boreholes), groundwater monitoring and complying with thresholds are applicable to both SG and onshore CCS monitoring activities (ISO 5667-22:2010; ISO 5667-3:2012; ISO 5667-6:2016; ISO 5667-11:2009; ISO 5667-14:2016; ISO 5667-20:2008). This guidance should be used as the starting point for designing a monitoring programme.

The EU Water Framework Directive (WFD) (2000/60/EC) and the EU Groundwater Directive (GWD) (2006/118/EC) provide a series of objectives for Member States regarding the management of water resources and groundwater. The associated Common Implementation Strategy (CIS) documents provide guidance on how to meet the WFD and GWD objectives (European Communities, 2007a,b,c; European Communities, 2009; European Communities, 2010). The guidelines emphasise the importance of developing and using a conceptual model of the hydrogeological system to frame the monitoring programme. The conceptual model can inform the sampling network and monitoring programme requirements including locations, depths, number of sampling sites, parameter selection, sampling frequency and duration of the baseline monitoring period. The development of a conceptual model is iterative, and any baseline data collected will further improve the understanding of the conceptual model. This may lead to refinement of sampling networks and monitoring programmes.

### 4.2 GROUNDWATER SAMPLE COLLECTION

#### 4.2.1 Sampling infrastructures

Groundwater samples for assessing baseline conditions can be obtained from a variety of sampling infrastructures including existing private and public water-supply wells, existing oil and gas wells, and natural springs, as well as dedicated observation (monitoring) wells (Figure 4). To date, pre-existing private domestic/farm wells have played an important role in baseline characterisation for SG and CCS (e. g. Down et al., 2015; Harkness et al., 2017; Worth et al., 2014; Siegel et al., 2015b). The reason for the extensive use of private wells is the low-cost and rapid data acquisition over large areas (Rivard et al., 2018). In addition, the collection of well water continually used for domestic purposes provides information directly related to public health in SG regions (Jackson et al., 2013b). However, private well data may have a number of limitations for baseline characterisation including 1) inadequate spatial distribution, 2) limited geological, hydrogeological and infrastructure information (e.g. casing depth, water inflow, stratigraphy) (Jackson and Heagle, 2016; Soeder, 2015; Rivard et al., 2018).

In contrast, dedicated observation wells can provide high-quality water chemistry data from desired locations and depths, with detailed geological, hydrogeological and infrastructure information for interpreting the data. However, data acquisition from purpose-drilled observation wells is still very limited (e. g. Montcoudiol et al., 2019; Bordeleau et al., 2018b; Rivard et al., 2018). The main limitation of such infrastructure is the cost, but, although sophisticated monitoring systems can be expensive, shallow observation wells consisting of a simple tube are affordable and can provide valuable information in many cases. It should also be borne in mind that investment in well-designed and effective monitoring infrastructure at the outset can lead to significant cost savings in the long run, as it provides evidence to demonstrate on-going regulatory compliance and, where it occurs, early detection of leakage events that require remedial action. Several large-scale commercial CCS projects have included financial resources to drill dedicated wells for monitoring, which have also been

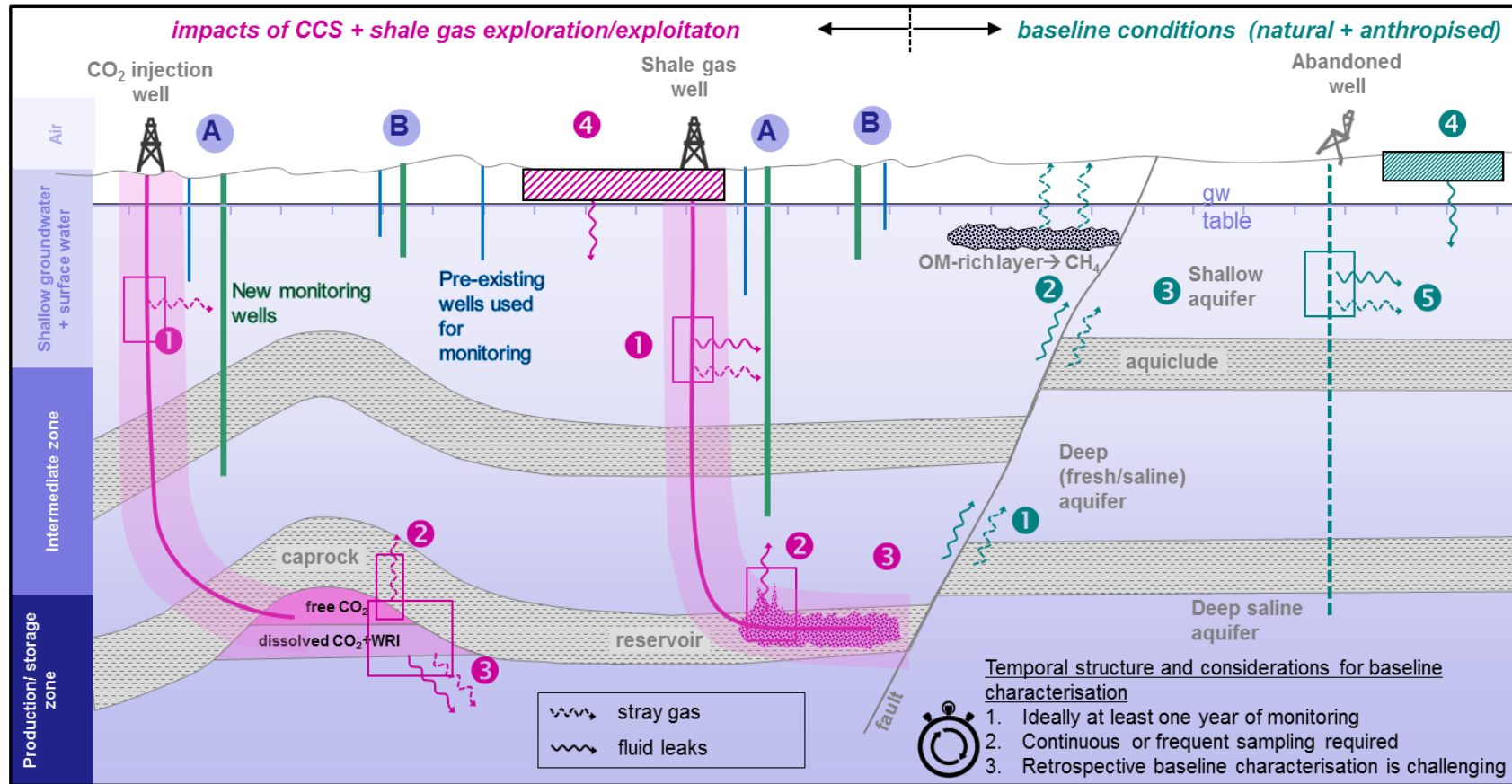


supplemented by sampling from existing wells (e.g. CCS case studies 7 and 9). Dedicated wells for baseline monitoring purposes have also been drilled in the Vale of Pickering, UK as part of a SG project, and following several years of experience of monitoring the baseline and transition to operational monitoring, detailed recommendations for environmental monitoring have been developed (Ward et al., 2020a). It is recommended, where possible, to drill some dedicated sampling wells for characterising the environmental baseline. The conceptual model should be used to select the optimal location for any purpose-drilled well. Wells should be sited in key areas, where the data collected can improve the conceptual model, for example, siting in a relevant hydrogeological unit where there is currently little data. The integrity of purposefully drilled wells is generally superior to re-purposed existing wells (Jordan and Benson, 2008). Manceau et al. (2015) investigated the influence that temperature and pressure can have on well integrity.

#### 4.2.2 Sampling network

An optimal sampling network should allow for the collection of baseline data at the site-scale, in close proximity to the SG well or CCS injection wells (tens to hundreds metres), and at the basin-scale, over the whole area targeted for SG or CCS development (up to several tens of kilometres) (Figure 4). The conceptual model should be used to inform the details of the network. At the site-scale, collecting baseline data is critical, owing to the specific risks of contamination including fluid and gas leakage along SG production and CCS injection wells, surface spills and leaks. However, the presence of existing wells on extraction and injection sites is unlikely and new observation wells may be required to collect groundwater data. The installation of monitoring wells adjacent to production and injection wells has been stressed by several authors (Jackson et al., 2013b; Soeder, 2015; McIntosh et al., 2019; Mathieson et al., 2011). Furthermore, shallow observation wells would be required at locations adjacent to potential surface sources such as wastewater storage and drilling waste disposal at SG sites.

Knowledge of groundwater flow is important for optimising the installation/selection of sampling wells, in particular the well location along the flow path relative to the potential contamination sources (upgradient/downgradient) (Soeder, 2015; McIntosh et al., 2019). At the basin-scale, the baseline network should provide a representative number of sampling sites for each relevant major hydrogeological unit (CCS case study 6) (section 4.2.2). In addition, potential contamination areas should be targeted, particularly deformation zones which may act as preferential migration pathways (e.g. SG case studies 1, 3 and 5). For this purpose, baseline data collection will likely need to take advantage of natural springs and existing wells. It is noteworthy that domestic/farm wells should be chosen carefully to minimise sampling in wells with integrity issues (Rivard et al., 2018; Jackson and Heagle, 2016; Jordan and Benson, 2008; Mathieson et al., 2011). Selection of appropriate monitoring locations and depths can simplify data analysis. Schlömer et al. (2014) developed criteria to assess the effectiveness of monitoring sites based on CO<sub>2</sub> concentrations and variability (CCS case study 8). Purpose-drilled wells will also provide the benefits of dedicated sampling wells described in section 4.1.1.



Geochemical baseline characterisation

- |   |   |
|---|---|
| <ol style="list-style-type: none"> <li>1 Natural analogues for gas emissions: leakage from deep aquifers</li> <li>2 Natural analogues for gas emissions: biogenic sources</li> <li>3 Aquifer mineralogy – used for selection of geochemical parameter to monitor</li> </ol> | <ol style="list-style-type: none"> <li>4 Anthropogenic impacts: surface run-off from industrial activity</li> <li>5 Anthropogenic impacts: leakage from previously abandoned wells</li> </ol> |
|---|---|

Sampling network infrastructure and spatial distribution

- A Monitoring in close proximity to injection/extraction well
- B Regional scale monitoring
- A + B Ensure sampling is completed in all major hydrogeological units

Potential sources of contamination from SG and CCS activities

- 1 Leakage from injection/extraction well
- 2 Leakage out of reservoir formation
- 3 Fluid-water-rock interactions, with potential for migration
- 4 Surface spills of drilling waste (for SG)

**Figure 4: Synergies between SG and CCS for environmental baseline assessment and potential sources of contamination from industrial activity**



### 4.3 BASELINE GROUNDWATER DATA

#### 4.3.1 Selected geochemical parameters

Geochemical baseline studies should provide a set of data for standard parameters (Figure 4). These parameters must give key baseline information on groundwater chemistry, while being commonly measured at reasonable cost. The principle of measuring a suite of geochemical parameters is to characterise the hydrochemical environment in the aquifer and spatial and temporal variability in concentrations that are important as change indicators, change in this case being the impact from SG or CCS operations. Table 1 summarises key parameters that should be considered for environmental baseline monitoring. A comprehensive suite of parameters is ideal to provide a robust baseline dataset (CCS case studies 1 and 2). Flude et al. (2017) found that a lack of baseline data for noble gases limited the interpretation of monitoring results after CO<sub>2</sub> injection had begun (CCS case study 10). However, for regulatory compliance purposes, a reduced list of parameters may be established (Ward et al., 2020a). For example, CCS baseline monitoring parameters associated with the carbonate system are particularly important because of the role of pH buffering capacity in mitigating a CO<sub>2</sub> leak (CCS case study 5). For SG, monitoring methane is a critical parameter. For both SG and CCS, monitoring of salinity would be important. Each could provide direct evidence of contamination and provide early warnings of potential environmental risk. The conceptual model should be used to inform which parameters are important for a specific site.

**Table 1: Parameters to consider for environmental baseline monitoring for SG and CCS**

Parameter	Example
<b>Field measurements</b>	Temperature, SEC, pH, Eh, O <sub>2</sub>
<b>Dissolved major and minor elements</b>	B, Ba, Ca, Cl, DIC, DOC, F, Fe, K, HCO <sub>3</sub> , Mg, Mn, Na, NH <sub>4</sub> , NO <sub>3</sub> , PO <sub>4</sub> , Si, SO <sub>4</sub> , S <sub>tot</sub> , Sr
<b>Trace-element concentrations</b>	Al, As, Be, Cd, Cr, Co, Cu, Hg, Li, Mo, Ni, Pb, Sb, Sn, Se, V, Zn
<b>Radioactivity and radionuclide elements</b>	Ra, Rn, Th, U
<b>Dissolved gases and hydrocarbons</b>	CO <sub>2</sub> , C <sub>1</sub> -C <sub>3</sub> alkanes (methane, ethane and propane), BTEX, TPH
<b>Stable isotopic composition of CH<sub>4</sub> and CO<sub>2</sub></b>	$\delta^{13}\text{C}_{\text{CH}_4}$ , $\delta^2\text{H}_{\text{CH}_4}$ , $\delta^{13}\text{C}_{\text{CO}_2}$ , $\delta^{18}\text{O}_{\text{CO}_2}$
<b>Gas</b>	CO <sub>2</sub> (for CCS) and CH <sub>4</sub> gas (for SG and CCS)

Measured parameter values provide baseline levels against which any future changes will be compared, particularly for hazardous minor and trace elements. Field measurements provide additional information to interpret potential changes in geochemical conditions, such as those associated with brine and fugitive-gas migration, and for quality assurance purposes. This can also improve the conceptual model. Hydrocarbon concentrations and stable isotopic CH<sub>4</sub> and CO<sub>2</sub> compositions are crucial to assess changes in methane and/or carbon dioxide origin and detect fugitive-gas contamination. Additional tracers can be measured to gain insight into specific geochemical processes such as brine migration, methane origin and organic pollution (e.g. SG case studies 1, 5 and 9). These additional tools include a range of more complex and costly tracers that can be measured at a limited number of sites. McIntosh et al. (2019) recently reviewed well-established and emerging techniques that can be applied as additional tracers for baseline characterisation. However, most of these techniques can be implemented when contamination is suspected based on standard parameter monitoring.

Moreover, geochemical and mineralogical composition of shallow aquifer rocks should be included in any academic baseline characterisation. Rock data can be relevant for interpreting potential changes in groundwater quality, in particular the bulk geochemistry and mineralogical speciation of hazardous minor and trace elements. These data can be used to inform the conceptual model and identify which specific parameters are present that may be of concern if mobilised by a change in hydrogeochemical conditions (CCS case study 6). Geochemical and mineralogical data can be obtained from rock samples collected during the drilling of observation wells and/or exploration/production SG wells. Similarly to groundwater chemistry data, rock data should be representative of the different aquifer lithologies at the basin-scale. It is noteworthy that any other



geological information needs to be considered for interpreting geochemical data and developing a good understanding of baseline conditions.

#### 4.3.2 Threshold values

The ultimate objective of environmental baseline assessment is to establish an understanding of the hydrogeological system that allows any changes arising from SG or CCS operations to be identified (Montcoudiol et al., 2017). When considering what constitutes change, the criteria need to be agreed in advance of baseline monitoring to ensure the correct data are being collected. Both SG and CCS operations are primarily in the deep sub-surface and environmental monitoring is at much shallower depths. Therefore, early change detection is essential to implement effective remediation measures. As part of the change detection process, threshold values can be established, and might be required by regulators. If exceeded, these might simply indicate a change is taking place or that contamination of shallow groundwater by SG and CCS activities is occurring or could be expected if conditions continue to deteriorate (upward trend). For example, research has shown that CO<sub>2</sub> soil gas concentrations above 10% could be of concern for terrestrial ecosystems (RISCS, 2014). The threshold corresponds to the upper limit of baseline variation (Reimann and Garrett, 2005).

Historically, methane gas has not widely been measured directly in groundwater, although methane is detectable in the many hydrogeological environments (Darling and Gooddy, 2006; Bell et al., 2017). This highlights the importance of establishing a baseline, especially for such a crucial parameter that could indicate both methane leakage and CO<sub>2</sub> that has been converted to methane.

A robust baseline dataset is also vital for investigating any alleged leakages from industrial activities (CCS case study 1, SG case studies 6 and 9) (Beaubien et al., 2013). Site-specific threshold values (for an individual well) can be determined for each constituent, which can account for spatial variability between observation wells considered to be sited at key locations (e.g. in close proximity to industrial activities). The baseline concentration range needs to be calculated, taking into account the temporal variability in groundwater chemistry. For this purpose, a data collection period of at least one year, with multiple sampling, has been suggested as a requirement to capture the seasonal variations (Soeder, 2015; Rivard et al., 2018; Ward et al., 2020a). However, a longer data collection period of 2 -5 years could be beneficial and might be necessary (RISCS, 2014). The longer the baseline monitoring period, the greater the chance of detecting maximum temporal variability and assessing the influence of any non-SG and CCS effects such as land-use change or climate variations (e.g. drought or flood periods affecting groundwater recharge patterns) that may influence key geochemical indicators. The cyclical nature (wavelength and magnitude) of natural processes, and their influence on environmental variability, can also be better understood. In terms of sampling frequency, Montcoudiol et al. (2019) recommended the collection of at least six samples evenly distributed throughout the year in observation wells for a SG baseline assessment and this can also be used as a guide for CCS. The number of samples ultimately required will depend on the observed temporal variability and the level of confidence required in the evaluation. Measurement uncertainties need to be considered when evaluating the temporal variability, especially when applying statistical analyses for small datasets (Montcoudiol et al., 2019) and when relying on repurposed domestic wells due to integrity problems, as mentioned in section 4.1.1 (Jackson and Heagle, 2016).

High sampling frequencies can be difficult to achieve in private wells due to potentially limited availability/access to suitable monitoring sites. A more rigorous approach would be to install continuous monitoring stations, which could improve the resolution and increase the volume of baseline data (RISCS, 2014) (CCS case study 8), though these have their own drawbacks in terms of reliability, maintenance and calibration requirements, and cost. For such continuous monitoring, it would be optimal to drill dedicated boreholes for installation of equipment for automatic measurement.

A statistical baseline model can be developed for sites that show large variations that do not appear to originate from seasonal variation or other temporal trends (Ward et al., 2020a). This could also be used to establish generic threshold values need to be derived at the basin-scale for evaluation of data for sampling sites, namely those that have not previously been characterised during baseline assessment. Previously sampled wells will have their own site specific thresholds already established. Considering the spatial variability of hydrogeological conditions, generic thresholds need to be determined for each hydrogeological unit of interest. To establish meaningful generic threshold values for use by regulators, appropriate statistical techniques should be applied to representative hydrogeochemical data (Reimann et al., 2005; Parrone et al., 2019). To undertake this, a statistically sufficient number of samples should be available per hydrogeological unit. Statistical techniques must be able to identify outliers to avoid setting too high, non-representative threshold values (Last et al., 2016). In some cases, it may be preferable to exclude samples that are clearly affected by



local contamination and are therefore not representative of regional groundwater quality (Jackson and Heagle, 2016).

#### 4.4 ALTERNATIVE METHODS IN THE ABSENCE OF PRE-DRILLING DATA

Until very recently, baseline data were not routinely collected prior to SG development, and early CCS projects also lacked dedicated baseline monitoring (CCS case studies 3 and 4). In the absence of pre-development data, three methods have been suggested for estimating baseline water chemistry: historical records, reference (analogue) sites, and equilibrium geochemical modelling (Nordstrom, 2015; Smyth et al., 2009). The comparison of historical baseline and post-drilling data has been used to evaluate the impacts of SG and CCS activities on groundwater in several studies (Burton et al., 2016; Reilly et al., 2015; Wen et al., 2019a; Smyth et al., 2009). In the EU, potable groundwater will already be monitored to ensure compliance with the WFD (2000/60/EC) and this can be used to provide some pertinent hydrogeochemical information. In addition, the GWD requires background studies to be conducted to determine the naturally occurring hydrogeochemistry and the relevance of any generic thresholds. However, this comparison is not always possible due to no or only sparse historical groundwater-chemistry data being available. Historical datasets often have limited hydrochemical parameters and uncertainties related to sampling (filtration, well purging), measurement methods and detection limits (Johnson et al., 2015; Reilly et al., 2015; McHugh et al., 2014). For example, methane gas has been shown to occur naturally in many hydrogeological environments, but until recently, little has been known about natural dissolved methane occurrence because groundwater sampling has rarely measured it directly and it has no reliable geochemical proxy (Darling and Goody, 2006). However, methane can be a key indicator of leakage and contamination that may occur from a SG or CCS site and if no dedicated baseline characterisation has taken place prior to industrial activity, it could be difficult to identify the origin of methane observed during an operational or post-operational phase.

Moreover, changes in groundwater chemistry may have occurred in an area since the sampling of evaluated data as a result of more recent anthropogenic contamination 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. If historical data are unlikely to provide suitable baseline data, they can provide qualitative information to inform the development of a conceptual model of use for designing a sampling network and interpreting baseline data. In the absence of any data, spatial comparisons have been made between an active site and non-active reference sites for SG (Fontenot et al., 2013; Gao et al., 2020; Osborn et al., 2011) and this could also be applied to CCS sites. In general, reference sites are located adjacent to active sites to optimise comparable environmental conditions, as well as for practical reasons (e.g. sampling) (SG case study 10). However, although this method can provide useful information, the data comparison will always be undermined by uncertainties related to hydrogeological characteristics and sampling conditions (e.g. well characteristics, number of samples) (Soeder, 2015; McHugh et al., 2014). Finally, geochemical modelling can be an effective tool to detect groundwater contamination associated with SG and CCS development. For example, Wen et al. (2019b) used equilibrium calculations to detect fugitive gas contamination based on methane, iron and sulphate concentrations for a SG project. However, estimating baseline conditions using geochemical modelling precisely requires field data and the quantification of anthropogenic sources (Nordstrom, 2015). The major limitations of these *a posteriori* methods further emphasise the importance of collecting pre-drilling baseline data in areas of future SG and CCS development.



## 5 Conclusion

SG and CCS are two relatively new industries, where regulations worldwide are still being established. Both industries utilise the deep sub-surface and therefore share some common objectives and strategies regarding environmental baseline assessment. The environmental baseline is defined as the environmental conditions prior to any SG or CCS activities, and includes naturally-occurring conditions and the influence of previous or ongoing anthropogenic activity in the area. This report highlights synergies between SG and CCS in relation to environmental baseline strategies and focuses on groundwater quality and ground gas. It is important to note that monitoring of air quality and seismicity could also be included in the wider remit of the environmental baseline. However, these factors are beyond the scope of this report.

International guidance (ISO standards) on monitoring groundwater and installation of groundwater monitoring points (boreholes) are applicable to both SG and CCS monitoring activities and this guidance should form the starting point for designing a monitoring programme. It is important to develop a conceptual model for the system, which can inform the requirements for a sampling network and monitoring programme. The collection of baseline data will, in turn, improve the conceptual model, which may lead to refinement of the sampling network and monitoring programme. More widely, the following synergies between environmental baseline strategies for SG and CCS have been identified for:

- i) The design of the sampling network in terms of utilising existing wells and drilling of new bespoke wells for baseline characterisation;
- ii) Consideration of the spatial distribution of the sampling network and ensuring sampling is undertaken at suitable depths and in all relevant major hydrogeological units of interest;
- iii) The selection of hydrogeochemical parameters to be tested for, including consideration of aquifer mineralogy to determine exactly which parameters will be most indicative of contamination at a given site;
- iv) The process of defining threshold values for water parameters against which operational and post-operational monitoring data can be assessed to identify any impact. This requires temporal variation of the environmental baseline to be characterised and therefore the baseline data collection programme should ensure sufficient frequency of sampling for an appropriate duration to allow sufficiently robust statistical change detection. Continuous sampling methodologies deployed for at least one year are recommended;
- v) It is recommended to establish the environmental baseline conditions before industrial activity, but this has not always been undertaken (commonly for older sites). In this case, the use of historical data for the region, or using monitoring data for a different region with a similar hydrogeochemical setting, for reference, can provide some indication of baseline conditions.

Both industries will face challenges and opportunities as they continue to develop. The benefit of identifying synergies between SG and CCS promotes knowledge sharing and technology transfer between industries. This could lead to more rapid advances in research, best practice and development of regulations across both industries and help inform policy development. Regarding environmental baseline assessment, this has the potential to reduce costs and improve the quality of data collection and interpretation. This could result in a more robust baseline dataset and a better understanding of the contamination risks that may occur from deep-subsurface industrial activity.





# Appendix 1

## SG CASE STUDIES

<p><b>SG case study 1</b></p> <p><b>Focus:</b> Groundwater geochemistry and methane</p>
<p><b>Name of project/ facility:</b> Saint-Édouard, Quebec, Canada</p> <p>(Note: this project is located in the same sedimentary basin as case studies 2 and 3, although these case studies are part of different projects and have different objectives and study areas within the basin)</p> <p><b>Type of project:</b> Public research (governmental institution)</p> <p><b>Institution/ company:</b> Geological Survey of Canada</p> <p><b>Type of facility/ sampling site:</b> Observation wells, private wells</p> <p><b>Size of study area:</b> 500 km<sup>2</sup></p> <p><b>Pre-development baseline:</b> No - specific objective of the project</p> <p><b>Hydraulic fracturing:</b> None (moratorium, as at 2010)</p> <p><b>Amount of shale gas extracted:</b> none</p> <p><b>Aim of project/ research:</b> Establish geochemical baseline for methane and dissolved inorganic constituents; evaluate natural upward deep fluid migration.</p> <p><b>Main findings/ relevance to baseline monitoring:</b></p> <ul style="list-style-type: none"><li>• Pre-development baseline data for methane and major ion chemistry.</li><li>• Methane concentrations vary widely in relation with water type, aquifer confinement conditions and bedrock geology.</li><li>• Two distinct sources of salinity in shallow groundwater: residual paleo seawater and formation brines.</li><li>• Evidence of migration of deep formation brines in faulted areas.</li></ul> <p><b>Related publication(s):</b></p> <p>Bordeleau, G., Rivard, C., Lavoie, D., Lefebvre, R., Malet, X., Ladeveze, P., 2018b. Geochemistry of groundwater in the Saint-Edouard area, Quebec, Canada, and its influence on the distribution of methane in shallow aquifers. Applied Geochemistry, 89: 92-108</p>



## SG Case Study 2

**Focus:** Groundwater geochemistry and methane

**Name and location of project/ facility:** Southwestern Ontario, Canada

(Note: this project is located in the same sedimentary basin as case studies 1 and 3, although these case studies are part of different projects and have different objectives and study areas within the basin)

**Type of project for data collection:** Public research (governmental institutions)

**Institution/ company:** University of Arizona, United States Geological Survey, Geological Survey of Canada, Ontario Geological Survey, California State Polytechnic University.

**Type of facility/ sampling site:** Domestic, farm and monitoring wells

**Size of study area:**  $\approx 23,000 \text{ km}^2$

**Pre-development baseline:** No - objective of the project.

**Hydraulic fracturing:** None

**Amount of shale gas extracted:** none

**Aim of project/ research:** Understand the origin and distribution of natural gas and brine in shallow aquifers; establish baseline data on groundwater chemistry.

**Main findings/ relevance to baseline monitoring:**

- High  $\text{CH}_4$  levels were found in  $\text{Na-HCO}_3\text{-Cl}$  groundwater, depleted in Ca, Mg and  $\text{SO}_4$  as a result of cation exchange with clays, and bacterial sulfate reduction and methanogenesis.
- $\text{CH}_4$  is primarily microbial in origin, associated with organic-rich shale-bearing formations and lack of alternative electron acceptors.
- A few samples showed Na-Cl-Br evidence for mixing with basinal brines, indicating local areas of natural brine leakage into shallow aquifers.

**Related publication(s):**

McIntosh, J.C., Grasby, S.E., Hamilton, S.M., Osborn, S.G., 2014. Origin, distribution and hydrogeochemical controls on methane occurrences in shallow aquifers, southwestern Ontario, Canada. Applied Geochemistry, 50: 37-52.



### SG Case Study 3

**Focus:** Groundwater methane

**Name and location of project/ facility:** St. Lawrence Lowlands, Quebec, Canada

(Note: this project is located in the same sedimentary basin as case studies 1 and 2, although these case studies are part of different projects and have different objectives and study areas within the basin)

**Type of project for data collection:** Academic research

**Institution/ company:** Concordia University, Université du Québec à Montréal, Institut national de la recherche scientifique.

**Type of facility/ sampling site:** Private, municipal and observation wells.

**Size of study area:** 15 435 km<sup>2</sup>

**Pre-development baseline:** No - objective of the project

**Hydraulic fracturing:** None (moratorium)

**Amount of shale gas extracted:** none

**Aim of project/ research:** Document baseline concentrations and sources of dissolved hydrocarbon gases.

**Main findings/ relevance to baseline monitoring:**

- Baseline concentrations of methane in shallow aquifers of the St. Lawrence Lowlands.
- The  $\delta^{13}\text{C}$  signature of methane suggests that a significant proportion of samples are of thermogenic origin, in relation with migration along natural faults.
- Mixing, migration, and oxidation processes likely affected the chemical and isotopic composition of the gases, making it difficult to determine their origin.
- Methane levels are mainly controlled by the composition of the bedrock, local redox conditions and water flow patterns and confinement (residence time).

**Related publication(s):**

Moritz, A., Helie, J.F., Pinti, D.L., Larocque, M., Barnetche, D., Retailleau, S., Lefebvre, R., Gelinas, Y., 2015. Methane Baseline Concentrations and Sources in Shallow Aquifers from the Shale Gas-Prone Region of the St. Lawrence Lowlands (Quebec, Canada). *Environmental Science & Technology*, 49(7): 4765-4771.



#### SG Case Study 4

**Focus:** Groundwater methane

**Name and location of project/ facility:** Northeastern Pennsylvania, USA

(Note: this project is located in the same sedimentary basin as case studies 8 and 9, although these case studies are part of different projects and have different objectives and study areas within the basin)

**Type of project for data collection:** Private research (oil and gas company, consulting firm)

**Institution/ company:** GSI Environmental Inc., Cabot Oil and Gas Corporation.

**Type of facility/ sampling site:** Private wells

**Size of study area:**  $\approx 1,500 \text{ km}^2$

**Pre-development baseline:** Shale gas extraction commenced without baseline data collection in PA. Objective of the project: establish baseline data without substantial gas extraction activities (2008-2011).

**Hydraulic fracturing:** Yes

**Amount of shale gas extracted:** Significant volumes of shale gas extracted

**Aim of project/ research:** Evaluate the sources of methane in groundwater.

**Main findings/ relevance to baseline monitoring:**

- Methane concentrations are high
- The high concentrations have been controversial; Osborn et al. (2011) concluding they were SG-related; Molofsky et al. (2013) that they are natural
- Methane is either thermogenic, likely originating from Upper Devonian deposits overlying the Marcellus shale, or microbial, originating from anaerobic groundwater units with long residence times
- Natural methane concentrations are associated with valleys and chemically evolved groundwater, rather than shale-gas extraction activities.

**Related publication(s):**

Osborn, S. G., Vengosh, A., Warner, N. R. & Jackson, R. B. 2011. Methane contamination of drinking water accompanying gas-well drilling and hydraulic fracturing. *Proceedings of the National Academy of Sciences of the United States of America*, 108, 8172-8176.

Molofsky, L.J., Connor, J.A., Wylie, A.S., Wagner, T., Farhat, S.K., 2013. Evaluation of Methane Sources in Groundwater in Northeastern Pennsylvania. *Ground Water*, 51(3): 333-349.



### SG Case Study 5

**Focus:** Groundwater geochemistry and methane

**Name and location of project/ facility:** Karoo Basin, South Africa

**Type of project for data collection:** Public/ private research (governmental institution, universities, consulting firm).

**Institution/ company:** Ohio State University, Duke University, Stellenbosch University, Groundwater Africa, CSIR Natural Resources and the Environment.

**Type of facility/ sampling site:** Deep boreholes; natural springs; shallow drinking-water or agricultural wells.

**Size of study area:**  $\approx 200,000 \text{ km}^2$

**Pre-development baseline:** No - objective of the project.

**Hydraulic fracturing:** No fracking (prior to unconventional drilling)

**Amount of shale gas extracted:** none

**Aim of project/ research:** Establish geochemical baseline for shallow groundwater; evaluate natural brine migration contamination into shallow aquifers.

**Main findings/ relevance to baseline monitoring:**

- Groundwater geochemistry is influenced by three end-members: a shallow dilute Ca-HCO<sub>3</sub> water type, a deep fossil Na-HCO<sub>3</sub>-Cl water type, and a deep saline CH<sub>4</sub>-rich Na-Cl water type.
- Dolerite intrusions likely provide preferential pathways for the upward migration of deep saline waters to the shallow aquifers.
- Elevated levels of geogenic contaminants (CH<sub>4</sub>, B, F) in shallow groundwater are related with the migration of saline water from depth and the interactions of migrated fluids with volcanic intrusions.
- B and Sr isotopes are not well suited to identify contamination from future shale gas development in the Karoo Basin.

**Related publication(s):**

Harkness, J.S., Swana, K., Eymold, W.K., Miller, J., Murray, R., Talma, S., Whyte, C.J., Moore, M.T., Maletic, E.L., Vengosh, A., 2018. Pre-drill groundwater geochemistry in the Karoo Basin, South Africa. *Groundwater*, 56(2): 187-203.



### SG Case Study 6

**Focus:** Groundwater geochemistry

**Name and location of project/facility:** Pennsylvania, eastern Ohio and north-central West Virginia, USA

**Type of project for data collection:** Private research (oil and gas company, consulting firm, environmental services company, university)

**Institution/ Company:** Syracuse University, Chesapeake Energy Corporation, Enviro Clean Products and Services, AECOM Technology Corporation.

**Type of facility/ sampling site:** Domestic/ stock water wells

**Size of study area:**  $\approx 150,000 \text{ km}^2$

**Pre-development baseline:** Shale gas extraction commenced without baseline data collection in PA, OH and WV. Specific objective of the project.

**Hydraulic fracturing:** Yes

**Amount of shale gas extracted:** Significant volumes of shale gas extracted.

**Aim of project/research:** Establish the baseline concentrations of major ions and metals; compare these constituent concentrations to drinking-water-quality standards.

**Main findings/ relevance to baseline monitoring:**

- Groundwater commonly exceeds drinking-water guidelines for inorganic contaminants as a result of natural processes.
- Water-quality exceedances relate to factors such as the sample location within the groundwater flow system, the groundwater chemical type, the geologic unit producing the water, and/or the topographic position (valley vs. upland).
- Recent pre-drilling geochemical data are similar to historical data which pre-date most unconventional shale gas development.
- Underlying fresher groundwater, the saline waters is considered to be naturally-occurring connate brine or salt water which has not been flushed by circulating meteoric water; rather than vertical migration of salt water from deep strata.

**Related publication(s):**

Siegel, D.I., Smith, B., Perry, E., Bothun, R., 2015b. Pre-drilling Water-Quality Data of Groundwater Prior to Shale Gas Drilling in the Appalachian Basin: The Chesapeake Energy Corporation DataSet. Applied Geochemistry, 63: 37-57.



### SG Case Study 7

**Focus:** Radium in groundwater

**Name and location of project/ facility:** Southeastern New Brunswick, Canada

**Type of project for data collection:** Academic research

**Institution/ company:** Université de Moncton

**Type of facility/ sampling site:** Private domestic wells

**Size of study area:**  $\approx 2,000 \text{ km}^2$

**Pre-development baseline:** No - objective of the project.

**Hydraulic fracturing:** Limited to McCully Gas Field, Kings County. No fracking in Kent and Albert counties.

**Amount of shale gas extracted:** unknown

**Aim of project/ research:** Establish  $^{226}\text{Ra}$  baseline in groundwater; characterize  $^{226}\text{Ra}$  spatial distribution and temporal variability; characterize  $^{226}\text{Ra}$  partitioning between dissolved phase and particulate forms; understand the mechanisms controlling  $^{226}\text{Ra}$  mobility under natural environmental settings.

**Main findings/ relevance to baseline monitoring:**

- $^{226}\text{Ra}$  levels were generally low, stable over time, and randomly distributed.
- $^{226}\text{Ra}$  was essentially observed in the dissolved phase.
- The highest  $^{226}\text{Ra}$  levels are associated with high hardness, and/or high concentrations of individual alkaline earth elements (i.e. Mg, Ca, Sr, Ba), high concentrations of Mn and Fe, and low pH.
- $^{226}\text{Ra}$  could serve as an indicator of environmental impact from shale gas extraction.

**Related publication(s):**

Lagacé, F., Foucher, D., Surette, C., Clarisse, O., 2018. Radium geochemical monitoring in well waters at regional and local scales: an environmental impact indicator-based approach. *Chemosphere*, 205: 627-634.

**SG Case Study 8**

**Focus:** Groundwater geochemistry

**Name and location of project/ facility:** Northeastern Pennsylvania, USA

(Note: this project is located in the same sedimentary basin as case studies 4 and 9, although these case studies are part of different projects and have different objectives and study areas within the basin)

**Type of project for data collection:** Academic research

**Institution/ company:** Kent State University

**Type of facility/ sampling site:** Private domestic wells

**Size of study area:** 10,344 km<sup>2</sup>

**Pre-development baseline:** Shale gas extraction commenced without baseline data collection in PA.

**Hydraulic fracturing:** Yes

**Amount of CO<sub>2</sub> injected/ shale gas extracted:** Significant volumes of shale gas extracted.

**Aim of project/ research:** Determine the contamination sources in well water.

**Main findings/ relevance to baseline monitoring:**

- Private well water is not contaminated by flowback fluids from drilling and fracturing processes.
- Some wells are suspected to be contaminated by animal waste, septic effluent, or road salt.
- Comparison with historical data (1980s) suggest that the majority of wells are geochemically similar to historical groundwater wells.

**Related publication(s):**

Reilly, D., et al. (2015). Identification of local groundwater pollution in northeastern Pennsylvania: Marcellus flowback or not? *Environmental Earth Sciences* 73(12): 8097-8109.





### SG Case Study 9

**Focus:** Groundwater geochemistry and hydrocarbons

**Name and location of project/ facility:** Marcellus Shale Region, Northeastern Pennsylvania and Southern New York, U.S.A.

(Note: this project is located in the same sedimentary basin as case studies 4 and 8, although these case studies are part of different projects and have different objectives and study areas within the basin)

**Type of project for data collection:** Public research (governmental institution)

**Institution/ company:** United States Geological Survey.

**Type of facility/ sampling site:** Private domestic wells

**Size of study area:**  $\approx 6,500 \text{ km}^2$

**Pre-development baseline:** No pre-development baseline in PA - Shale gas extraction commenced without baseline data collection. Recent baseline studies exist in Southern NY.

**Hydraulic fracturing:** Intensive fracking in PA. No fracking in NY.

**Amount of shale gas extracted:** Significant volumes in PA. None in NY.

**Aim of project/ research:** Determine if hydrocarbons related to UOG activities are present in upland groundwater.

**Main findings/ relevance to baseline monitoring:**

- Natural mixing with brine and hydrocarbons from deep formations is less common in upland areas compared to valleys, making easier the identification of shale gas impacts on groundwater quality in these areas.
- One proximal sample (<1 km) contains thermogenic  $\text{CH}_4$  that appears to have been mobilized by shale-gas production activities.
- Modelled groundwater-age distributions calibrated to  $^3\text{H}$ ,  $\text{SF}_6$ , and  $^{14}\text{C}$  concentrations are useful to determine if groundwater recharged before or after shale-gas development.

**Related publication(s):**

McMahon, P. B., Lindsey, B. D., Conlon, M. D., Hunt, A. G., Belitz, K., Jurgens, B. C., Varela, B. A., 2019. Hydrocarbons in Upland Groundwater, Marcellus Shale Region, Northeastern Pennsylvania and Southern New York U.S.A. Environ. Sci. Technol. 53, 8027– 8035.

**SG Case Study 10**

**Focus:** Groundwater and produced water geochemistry

**Name of project/ facility:** Changning County , Sichuan, China

**Type of project for data collection:** Public research (governmental institutions)

**Institution/ company:** PetroChina Research Institute of Petroleum Exploration and Development, China Earthquake Administration, Duke University.

**Type of facility/ sampling site:** Shale gas wells; gas-water separators or storage ponds; karst caves.

**Size of study area:**  $\approx 250 \text{ km}^2$

**Pre-development baseline:** No - comparison between an active and a non-active reference area.

**Hydraulic fracturing:** Yes (unknown date)

**Amount of shale gas extracted:** unknown

**Aim of project/ research:** Establish geochemical baseline for shallow groundwater; evaluate potential contamination of shallow groundwater caused by shale gas development.

**Main findings/ relevance to baseline monitoring:**

- Baseline groundwater chemistry in karst aquifers corresponds to low salinity Ca-HCO<sub>3</sub> to Ca-Mg-HCO<sub>3</sub> water types.
- No contamination of shallow groundwater based on geochemical data, Sr isotope ratios, and volatile organic compounds.
- Br/Cl and <sup>87</sup>Sr/<sup>86</sup>Sr ratios are useful indicators to evaluate the migration of produced waters in shallow aquifers in Changning field gas area.

**Related publication(s):**

Gao, J., Zou, C., Li, W., Ni, Y., Liao, F., Yao, L., Sui, J., Vengosh, A., 2020. Hydrochemistry of flowback water from Changning shale gas field and associated shallow groundwater in Southern Sichuan Basin, China: Implications for the possible impact of shale gas development on groundwater quality. *Sci Total Environ*, 713: 136591.



## CCS CASE STUDIES

<b>CCS Case Study 1</b>
<b>Focus:</b> Ground gas and groundwater
<b>Name and location of project/facility :</b> IEA Weyburn CO <sub>2</sub> Monitoring and Storage Project, Canada
<b>Type of project:</b> Research project undertaken alongside commercial scale CCS
<b>Institution/company:</b> International Energy Agency Greenhouse Gas Research and Development Programme (IEA GHG)
<b>Type and scale of facility:</b> Commercial enhanced oil recovery (EOR)
<b>Pre-development baseline:</b> Yes
<b>Date of first CO<sub>2</sub> injection:</b> 2000
<b>Amount of CO<sub>2</sub> injected:</b> more than 16Mt by June 2010
<b>Aim of project/research:</b> Consideration of the hydrogeological and hydrogeochemical baseline conditions of the reservoir and potential impact on reservoir performance (plus other objectives not associated with baseline monitoring) and long term monitoring results
<b>Main findings/ relevance to baseline monitoring:</b> <ul style="list-style-type: none"><li>• Dissolved gases can be used as tracers to identify potential transport pathways</li><li>• Comparison of baseline and operational phase data for soil gas and carbon isotopes has been used to verify there is no evidence for CO<sub>2</sub> leakage</li><li>• The importance of baseline data was highlighted when a landowner reported that an alleged leak had caused damage to private assets, but monitoring data showed this was not the case</li><li>• Modelling of regional groundwater flow can predict the direction of CO<sub>2</sub> migration</li><li>• 10 years of groundwater quality monitoring found no significant change in hydrochemistry in relation to CO<sub>2</sub> storage; approximately 60 wells were sampled seven times throughout a decade</li></ul>
<b>Related publication(s):</b> <p>Riding, J. B. &amp; Rochelle, C. A. 2005. The IEA Weyburn CO<sub>2</sub> Monitoring and Storage Project. Final Report of the European Research Team. British Geological Survey Research Report RR/05/03 54pp.</p> <p>Beaubien, S. E., Jones, D. G., Gal, F., Barkwith, A. K. A. P., Braibant, G., Baubron, J. C., Ciotoli, G., Graziani, S., Lister, T. R., Lombardi, S., Michel, K., Quattrocchi, F. &amp; Strutt, M. H. 2013. Monitoring of near-surface gas geochemistry at the Weyburn, Canada, CO<sub>2</sub>-EOR site, 2001–2011. <i>International Journal of Greenhouse Gas Control</i>, 16, S236-S262.</p> <p>Rostron, B. &amp; Whittaker, S. 2011. 10+ years of the IEA-GHG Weyburn-Midale CO<sub>2</sub> monitoring and storage project: Successes and lessons learned from multiple hydrogeological investigations. <i>Energy Procedia</i>, 4, 3636-3643.</p>



## CCS Case Study 2

**Focus:** Groundwater and ground gas

**Name and location of project/facility :** CO2SINK, Ketzin, Germany

**Type of project:** Pilot study – field laboratory

**Institution/company:** EU's first research and development study on in-situ testing of a proposed CCS site

**Pre-development baseline:** Yes

**Date of first CO<sub>2</sub> injection:** June 2008

**Amount of CO<sub>2</sub> injected:** after 1 year, approximately 18,000 t

**Aim of project/research:** Baseline characterisation

### Main findings/ relevance to baseline monitoring:

- Hydrochemical baseline monitoring was undertaken to provide data for comparison with continued monitoring during later phases, to ensure detection of a CO<sub>2</sub> leak if it occurred
- Hydraulic connection between shallow and deeper aquifers was investigated and used for modelling groundwater flow
- Baseline CO<sub>2</sub> gas flux in the shallow aquifer was also characterised
- The model results were to be used in the risk assessment to identify the potential impact of a CO<sub>2</sub> leak into shallow groundwater
- CO<sub>2</sub> leakage is considered unlikely, but the risk assessment and monitoring improves societal acceptance and confidence in CCS as a viable climate change mitigation strategy
- Baseline data to inform groundwater risk assessments should include a full suite of methods to assess geology, geophysics, mineralogy, geochemistry and groundwater flow pathways

### Related publication(s):

Förster, A., Norden, B., Zinck-Jørgensen, K., Frykman, P., Kulenkampff, J., Spangenberg, E., Erzinger, J., Zimmer, M., Kopp, J., Borm, G., Juhlin, C., Cosma, C.-G. & Hurter, S. 2006. Baseline characterization of the CO2SINK geological storage site at Ketzin, Germany. *Environmental Geosciences*, 13, 145-161.

Würdemann, H., Möller, F., Kühn, M., Heidug, W., Christensen, N. P., Borm, G. & Schilling, F. R. 2010. CO2SINK—From site characterisation and risk assessment to monitoring and verification: One year of operational experience with the field laboratory for CO<sub>2</sub> storage at Ketzin, Germany. *International Journal of Greenhouse Gas Control*, 4, 938-951.



### CCS Case Study 3

**Focus:** Ground gas

**Name and location of project/facility:** Rangely, Colorado, USA

**Type of project:** Research undertaken alongside active commercial activity

**Institution/company:** Research funded by US Department of Energy grant to Colorado School of Mines

**Type and scale of facility:** Commercial scale CO<sub>2</sub>-enhanced oil recovery (EOR)

**Size of CCS facility:** 78 km<sup>2</sup>

**Pre-development baseline:** No – a control area with similar geological characteristics was set up for this research project

**Date of first CO<sub>2</sub> injection:** 1986

**Amount of CO<sub>2</sub> injected:** 23 million metric tonnes of purchased CO<sub>2</sub> between 1986 and 2003 – date of publication. This does not include Carbon dioxide returned to the surface via production wells which is separated and reinjected

**Aim of project/research:** methodology for detecting microseepage at large-scale (field study at existing CCS site)

**Main findings/ relevance to baseline monitoring:**

- CO<sub>2</sub> ground gas concentration varies seasonally due to climatic variations – reduced root respiration and microbial oxidation of organic matter in winter
- No baseline monitoring undertaken but this study estimates the rate of CO<sub>2</sub> leakage that is occurring using baseline data from a similar geological setting
- “Estimated microseepage to the atmosphere of approximately 400 metric tonnes of CH<sub>4</sub>/a from the 78 km<sup>2</sup> area of the Rangely field. Preliminary estimates of deep-sourced CO<sub>2</sub> losses are <3800 tonnes/a, based on stable isotope measurements of soil gases.” (Klusman, 2003).

**Related publication(s):**

Klusman, R. W. 2003. Rate measurements and detection of gas microseepage to the atmosphere from an enhanced oil recovery/sequestration project, Rangely, Colorado, USA. *Applied Geochemistry*, 18, 1825-1838.



#### CCS Case Study 4

**Focus:** Groundwater

**Name and location of project/facility :** SACROC oilfield in Scurry County, Texas, USA

**Type of project:** Laboratory and field studies

**Institution/company:** Field studies funded by U.S. Department of Energy (DOE) regional carbon sequestration partnership programs and industrial sponsors

**Type and scale of facility:** Enhanced Oil Recovery (EOR)

**Size of CCS facility:** ~90 mi<sup>2</sup>

**Pre-development baseline:** Compiled from historic records, no dedicated baseline was characterised before injection commenced

**Date of first CO<sub>2</sub> injection:** 1972

**Amount of CO<sub>2</sub> injected:** 150 MMt, but approximately 50% has been recovered

**Aim of project/research:** Research questions: (1) Can changes in chemistry of fresh water aquifers provide evidence of CO<sub>2</sub> leakage from deep injection/sequestration reservoirs containing brine and or hydrocarbons? (2) What parameters can we use to assess potential impacts to water quality? (3) If CO<sub>2</sub> leakage to freshwater aquifers occurs, will groundwater quality be degraded and if so, over what time period?

#### **Main findings/ relevance to baseline monitoring:**

- No dedicated pre-CO<sub>2</sub> injection baseline was characterised, therefore historical records had to be used. For some parameters, such as pH, data were available dating back to 1936
- Laboratory batch experiments showed geochemical reactions to the dissolution of CO<sub>2</sub> into freshwater within hours or days of exposure to CO<sub>2</sub>
- A decrease in pH was observed and cation concentrations for Ba, Ca, Fe, Mg, Mn, and Sr increased by over an order of magnitude
- Field study included sampling 68 wells and one spring on five separate occasions between 2006 and 2008
- Results of field sampling within the SAROC boundary were compared with results from outside the boundary and no evidence was found of preferential groundwater degradation inside the boundary

#### **Related publication(s):**

Smyth, R. C., Hovorka, S. D., Lu, J., Romanak, K. D., Partin, J. W., Wong, C. & Yang, C. 2009. Assessing risk to fresh water resources from long term CO<sub>2</sub> injection–laboratory and field studies. *Energy Procedia*, 1, 1957-1964.



### CCS Case Study 5

**Focus:** Groundwater

**Name and location of project/facility :** Gulf Coast region, not linked to a specific CCS facility

**Type of project:** Research project

**Institution/company:** Gulf Coast Carbon Center, Bureau of Economic Geology, Jackson School of Geosciences, The University of Texas

**Type and scale of facility:** N/A

**Size of CCS facility:** N/A

**Pre-development baseline:** N/A

**Date of first CO<sub>2</sub> injection:** N/A

**Amount of CO<sub>2</sub> injected:** N/A

**Aim of project/research:** Assess potential impact of CO<sub>2</sub> leakage into potable groundwater in aquifers that overlie potential CCS repositories that were being investigated in the region

**Main findings/ relevance to baseline monitoring:**

- Significant risks to groundwater quality resulting from carbonate dissolution, driven by increased acidity from CO<sub>2</sub> dissolution
- Some cations became permanently elevated (e.g. Ca, Mg, Si, K, Sr, Mn, Ba, Co, B and Zn)
- Carbonates were the source of elevated Ca and Mg
- Mineral buffering can reduce the rate of cation release
- Some trace solutes increased in concentration and then subsequently decreased due to mitigation by mineral buffering causing adsorption (e.g. Fe, Al, Mo, U, V, As, Cr, Cs, Rb, Ni, and Cu)

**Related publication(s):**

Lu, J., Partin, J. W., Hovorka, S. D. & Wong, C. 2009. Potential risks to freshwater resources as a result of leakage from CO<sub>2</sub> geological storage: a batch-reaction experiment. *Environmental Earth Sciences*, 60, 335-348.

**CCS Case Study 6****Focus:** Groundwater**Name and location of project/facility :** Quest CCS Project, Alberta, Canada**Type of project:** Commercial**Institution/company:** Shell**Type and scale of facility:** Commercial**Pre-development baseline:** Yes**Aim of project/research:** Baseline assessment – groundwater physical and geochemical properties**Main findings/ relevance to baseline monitoring:**

- Hydrogeochemical monitoring forms a key aspect of the measurement, monitoring and verification (MMV) process
- Shallow hydrogeology has been characterised for four aquifers overlying the CCS site
- Historical data and purposefully collected baseline data have been used to assess the hydrogeological baseline conditions
- Indicator parameters were selected for monitoring that would identify migration of CO<sub>2</sub>, based on the geochemical baseline data and expected CO<sub>2</sub>-aquifer interactions

**Related publication(s):**

Brydie, J., Jones, D., Jones, J. P., Perkins, E., Rock, L. & Taylor, E. 2014. Assessment of Baseline Groundwater Physical and Geochemical Properties for the Quest Carbon Capture and Storage Project, Alberta, Canada. *Energy Procedia*, 63, 4010-4018.





### CCS Case Study 7

**Focus:** Groundwater and ground gas

**Name and location of project/facility :** In Salah, Algeria

**Type of project:** Research alongside commercial activity

**Institution/company:** Joint Industry Project (JIP): BP, Sonatrach and Statoil

**Type and scale of facility:** Industrial scale CCS

**Pre-development baseline:** Yes

**Date of first CO<sub>2</sub> injection:** 2004

**Amount of CO<sub>2</sub> injected:** over 3.8Mt

**Aim of project/research:** Lessons learnt and knowledge transfer regarding CCS monitoring and verification programmes

#### **Main findings/ relevance to baseline monitoring:**

- Site-specific characteristics need to be considered, there is no general approach to designing a monitoring and verification programme
- Five wells were drilled specifically for groundwater monitoring (~350 m deep)
- It is vital to establish both local and regional hydrogeological and hydrochemical baseline characteristics
- Several ground gas surveys were completed
- More baseline data is needed for natural CO<sub>2</sub> emissions in different environments, and understanding of temporal variability
- Core samples were analysed for several reservoir intervals and the cap rock
- Understanding of rock mineralogy and expected interactions with formation fluid is vital

#### **Related publication(s):**

Mathieson, A., Midgely, J., Wright, I., Saoula, N. & Ringrose, P. 2011. In Salah CO<sub>2</sub> Storage JIP: CO<sub>2</sub> sequestration monitoring and verification technologies applied at Krechba, Algeria. *Energy Procedia*, 4, 3596-3603.

Ringrose, P. S., Mathieson, A. S., Wright, I. W., Selama, F., Hansen, O., Bissell, R., Saoula, N. & Midgley, J. 2013. The In Salah CO<sub>2</sub> Storage Project: Lessons Learned and Knowledge Transfer. *Energy Procedia*, 37, 6226-6236.



### CCS Case Study 8

**Focus:** Ground gas

**Name and location of project/facility:** CO<sub>2</sub> Large-Scale Enhanced Gas Recovery in the Altmark Natural Gas Field (CLEAN) Altmark area, Northern Germany

**Type of project:** Research project alongside commercial facility

**Institution/company:** Commercial facility: GDF SUEZ E&P Deutschland GmbH in cooperation with Vattenfall Europe AB.

Research project: Institute for Geosciences and Natural Resources

**Pre-development baseline:** Yes, the subject of this research project

**Date of first CO<sub>2</sub> injection:** 2008

**Amount of CO<sub>2</sub> injected:** none, the injection permission was not granted due to public opposition and political resistance

**Aim of project/research:** Develop and assess the effectiveness of a ground gas monitoring network

#### **Main findings/ relevance to baseline monitoring:**

- One of the largest continuous baseline datasets recorded worldwide – 4 year duration
- Continuous monitoring of soil gas using an economic system, minimal maintenance and facilitates automatic transfer of data
- Site specific variability in CO<sub>2</sub> concentrations at shallow depths (1-3m)
- Continuous long term monitoring is needed to quantify natural variation of CO<sub>2</sub>
- Selection of appropriate monitoring sites and depths can simplify data analysis – criteria were developed to rate the effectiveness of monitoring sites based on CO<sub>2</sub> concentrations and variability
- Below the biologically active soil zone, CO<sub>2</sub> concentrations are stable (over more than 1 year)
- Modelling showed the stable baseline CO<sub>2</sub> concentrations were sensitive to leakages

#### **Related publication(s):**

Schlömer, S., Möller, I. & Furche, M. 2014. Baseline soil gas measurements as part of a monitoring concept above a projected CO<sub>2</sub> injection formation—A case study from Northern Germany. *International Journal of Greenhouse Gas Control*, 20, 57-72.



### CCS Case Study 9

**Focus:** Methodology for establishing an environmental baseline

**Name and location of project/facility :** Aquistore, Canada

**Type of project:** Independent research and monitoring project, undertaken alongside active commercial activity at a coal power plant

**Institution/company:** Petroleum Technology Research Centre (not-for-profit corporation), with public and private sponsors and collaboration with research institutes. Research is led by Aquistores Science and Engineering Research Committee

**Type and scale of facility:** Commercial scale project, part of SaskPower's Boundary Dam Integrated CCS Demonstration project, which is the world's first fully integrated CCS demonstration project from a coal power plant

**Pre-development baseline:** Yes, this was developed as an essential part of this project

**Date of first CO<sub>2</sub> injection:** 2015

**Amount of CO<sub>2</sub> injected: Aim of project/research:** Design and field test a measurement, monitoring and verification (MMV) program, to enable early detection of CO<sub>2</sub> leakages and therefore minimise risk

#### **Main findings/ relevance to baseline monitoring:**

- Geological and hydrogeological site characterisation was undertaken prior to drilling, drilling core then provided extra geological information about target formations, cap rock and transitions between strata. Side wall cores were also taken during rotary drilling;
- A detailed MMV program was established which included a suite of methods to develop an integrated conceptual model;
- For groundwater:
  - 20 dedicated wells were drilled for groundwater sampling, in addition to the use of 20 existing wells, either domestic or owned by the nearby coal power plant
  - The 40 groundwater wells were sampled during three baseline surveys – parameters measured included major, minor and trace elements, and carbon and oxygen stable isotopes;
- For ground gas:
  - 50 probes sampled for 20-30 mins at a time for each sampling round for: He, H<sub>2</sub>, CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>S, C1-G7, hydrocarbons, δ<sup>13</sup>C and δ<sup>14</sup>C
  - A survey of 100 sites of 1 m depth were used for soil gas analysis of: CH<sub>4</sub>, CO<sub>2</sub>, δ<sup>13</sup>CH<sub>4</sub>, N<sub>2</sub>, and Ar
  - Continuous measurements taken simultaneously for CO<sub>2</sub> and CH<sub>4</sub>

#### **Related publication(s):**

Worth, K., White, D., Chalaturnyk, R., Sorensen, J., Hawkes, C., Rostron, B., Johnson, J. & Young, A. 2014. Aquistore Project Measurement, Monitoring, and Verification: From Concept to CO<sub>2</sub> Injection. *Energy Procedia*, 63, 3202-3208

Rostron, B., White, D., Hawkes, C. & Chalaturnyk, R. 2014. Characterization of the Aquistore CO<sub>2</sub> project storage site, Saskatchewan, Canada. *Energy Procedia*, 63, 2977-2984.



### CCS Case Study 10

**Focus:** Ground gas – CO<sub>2</sub> baseline and noble gases

**Name and location of project/facility :** CO<sub>2</sub>CRC Otway Project, Victoria, Australia

**Type of project:** Demonstration project

**Institution/company:** Collaborative research project including government, industry and academic institutions

**Pre-development baseline:** Yes, this began in 2006 for ground gas and hydrogeochemistry and cores were analysed when drilling commenced

**Date of first CO<sub>2</sub> injection:** 2008

**Aim of project/research:** Demonstrate the viability of CCS under Australian conditions

**Main findings/ relevance to baseline monitoring:**

- Naturally occurring CO<sub>2</sub> in the shallow subsurface meant that a rigorous baseline characterisation was required
- Regional scale survey undertaken to determine the origin and distribution of natural CO<sub>2</sub>
- Sampling conducted at several times throughout the year to account for temporal variability
- However, Flude et al. (2017) found in a later study that the lack of baseline data for noble gases limited the interpretation of changes to the noble gas fingerprint of the CO<sub>2</sub> injected plume during migration through the reservoir.

**Related publication(s):**

Sharma, S., Cook, P., Berly, T. & Lees, M. 2009. The CO<sub>2</sub>CRC Otway Project: Overcoming challenges from planning to execution of Australia's first CCS project. *Energy Procedia*, 1, 1965-1972.

Flude, S., Györe, D., Stuart, F. M., Zurakowska, M., Boyce, A. J., Haszeldine, R. S., Chalaturnyk, R. & Gilfillan, S. M. V. 2017. The inherent tracer fingerprint of captured CO<sub>2</sub>. *International Journal of Greenhouse Gas Control*, 65, 40-54.



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