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**REPORT ON INTEGRATED MULTI-TRACER
FINGERPRINTING OF GAS AND FLUID MIGRATION
IN GROUNDWATER IN RELATION TO SHALE GAS
EXPLORATION AND CARBON STORAGE**

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Public introduction

Monitoring of groundwater chemistry in connection with new subsurface geoenergy activities, notably unconventional hydrocarbons (shale gas) and CO₂ storage, is important to ensuring the activities are and remain safe and groundwater remains protected. Monitoring of groundwater helps to establish chemical compositions before any activities start as well as to determine whether any changes have occurred throughout operations and post-closure.

Chemical and especially isotopic compositions can help to characterise and distinguish shallow groundwater, which is typically fresh, and deep subsurface fluids connected to hydrocarbon or CO₂ storage reservoirs, which are typically saline. Chemical and isotopic tracers can help to determine the origins of deep fluids, their modes of evolution and any pathways towards the near-surface. A number of stable and radiogenic isotopes are potentially useful for discriminating processes, including isotopes of oxygen, hydrogen, carbon, sulphur, lithium, boron, strontium, radium and the noble gases. This report details four case studies in the context of unconventional hydrocarbon and CCS research that have used a toolbox of chemical and isotopic tracers to establish local geochemical conditions and provide insights into subsurface processes and potential pathways. The toolbox has helped to augment environmental monitoring and assessment capability for subsurface energy activities.



Executive report summary

Understanding the environmental risks of new deep subsurface geogeneity activities such as onshore unconventional hydrocarbon operations and carbon capture and storage (CCS) is important to minimising the risks and ensuring maintenance of safe systems. A key part of that understanding is monitoring of the shallow subsurface, particularly groundwater which acts as a major source of water supply, but also of shallow gases. Monitoring of groundwater chemistry including major ions, trace elements and element ratios can reveal much information about fluid sources and geochemical reactions. However, isotopic compositions of many of the key constituents of groundwaters and deep fluids can potentially provide greater resolution on their provenance, flowpaths, residence times and interactions, especially when the difference between compositions of shallow fresh groundwaters and deep fluids is large. Key diagnostic isotopes in the unconventional hydrocarbon and CCS context include $\delta^{18}\text{O}_{\text{H}_2\text{O}}$, $\delta^{18}\text{O}_{\text{SO}_4}$, $\delta^2\text{H}_{\text{H}_2\text{O}}$, $\delta^2\text{H}_{\text{CH}_4}$, $\delta^{13}\text{C}_{\text{DIC}}$, $\delta^{13}\text{C}_{\text{CH}_4}$, $\delta^{13}\text{C}_{\text{CO}_2}$, $\delta^{34}\text{S}_{\text{SO}_4}$, $\delta^7\text{Li}$, $\delta^{11}\text{B}$, $^{87}\text{Sr}/^{86}\text{Sr}$, $^{228}\text{Ra}/^{226}\text{Ra}$, $^3\text{He}/^4\text{He}$, $^{40}\text{Ar}/^{36}\text{Ar}$ and $^4\text{He}/^{20}\text{Ne}$.

This report details some of the most useful trace-element and isotopic tracers for use in investigations to develop understanding of fluids in the deep subsurface. The report describes four case studies from experimental or commercial operations: those related to the unconventional hydrocarbon baseline at Vendsyssel, Denmark and the Vale of Pickering, UK, and cases related to onshore CCS at Svelvik, Norway and Otway, Australia. The studies suggest that a combination of chemical and multi-isotope tracers is likely the most effective way of identifying fluid provenance and tracing pathways but the most valuable tracers are likely to vary and be site-specific.



Contents

Public introduction	ii
Executive report summary	i
Contents	ii
1 Introduction	1
2 Contaminant tracers	2
2.1 Chemical compositions and ratios	2
2.2 Isotopic tracers	2
3 Case studies	6
3.1 Hydrocarbon baseline: Vendsyssel, Denmark	6
3.2 Hydrocarbon baseline: Vale of Pickering, UK	8
3.3 Carbon storage: Svelvik, Norway	9
3.4 Carbon storage: Otway, Australia.....	11
4 Conclusions	12
Acknowledgements	13
5 References	14

FIGURES

Figure 1. Distributions of SO ₄ , S (sulphide), CH ₄ and δ ³⁴ S in groundwaters from the Kimmeridge Clay/superficial and Corallian aquifers of the Vale of Pickering.....	8
Figure 2. C1/C2 ratios (mol) vs δ ¹³ C _{CH4} compositions and δ ¹³ C _{CH4} vs δ ² H _{CH4} compositions of groundwaters from the Kimmeridge Clay/superficial and Corallian aquifers of the Vale of Pickering; plot fields after (Whiticar, 1999)	9
Figure 3. δ ¹³ C and δ ¹⁸ O isotopic compositions of gas in borehole BH01 before, during and after CO ₂ injection at the Svelvik site in 2011. All plots from Jones et al. (2014) (Creative Commons CC-BY 3.0)	10



1 Introduction

Concerns for the protection of groundwater quality, including in drinking-water aquifers, have long accompanied developments in deep subsurface energy facilities. Developments in onshore unconventional hydrocarbons and CCS require assessment and mitigation of the potential environmental impact of the development, including that on groundwater. Groundwater monitoring is a key component of groundwater protection and helps to establish pre-development conditions, detect any changes that may occur during operation and development, and facilitate satisfactory site closure and decommissioning. Monitoring also plays a key role in providing reassurance to regulators and local communities that the CCS or unconventional hydrocarbon activities have not impacted on the environment (de Caritat et al., 2013; Hortle et al., 2011).

In the context of both onshore unconventional hydrocarbons and onshore CCS, baseline monitoring needs to be capable of identifying and characterising initial conditions, using appropriate analytes, frequency of measurement, spatial spread and analytical sensitivity. For both baseline and operational monitoring, important indicators for unconventional hydrocarbon investigation include major ions, dissolved gases and organic compounds. For CCS, CO₂ is a key primary analyte, though inorganic solutes also help to determine water-rock reaction processes.

CCS operations require monitoring targeted at both the deep subsurface to assess reservoir performance and establish leakage early-warning systems, and monitoring of the shallow subsurface to establish any environmental impacts (e.g. Dillen et al., 2009). The nature of monitoring will also be determined by the locations and types of storage reservoir. Deep storage of CO₂ has been considered for depleted hydrocarbon reservoirs and deep saline aquifers, the latter considered to have much the greater capacity for storage globally (Michael et al., 2010). Storage may also be onshore or offshore, with Europe having a much greater tendency to favour offshore projects. Examples of large commercial operations in saline aquifers onshore include In Salah, Algeria, while operations in onshore depleted hydrocarbon reservoirs include Weyburn, USA. Operations at Otway, Australia, involved both depleted hydrocarbon reservoirs and saline aquifers (Michael et al., 2010). Examples of offshore commercial CO₂ storage operations include Sleipner in the Norwegian North Sea and Snøhvit in the Norwegian Barents Sea. While these have less relevance for near-surface environmental monitoring, they can provide extra insights into deep subsurface processes and pathways and data to inform onshore monitoring in a CCS context. Onshore experimental CCS pilots such as Ketzin, Germany and Svelvik, Norway provide extra insights. Information from natural CO₂ analogues can also be of value in assessing processes and likely diagnostic tracers (Gal et al., 2011).

For onshore unconventional hydrocarbons, there has been considerable need to establish baseline conditions in groundwater in overlying aquifers before hydraulic fracturing operations to understand pre-existing compositions and counter incorrect attributions of natural groundwater-quality characteristics to development activities. The presence of any legacy contaminants from older conventional hydrocarbon development also needs to be factored in to such baseline groundwater-quality assessments. This can be a particular challenge since groundwater in organic-rich and deeper aquifers typically contains naturally-occurring methane and increased salinity (Barth-Naftilan et al., 2018; Harkness et al., 2017).

Leakage of injected CO₂ in a CCS operation could occur via the host formation cap rock, or via faults or fractures, or via deep wells, including abandoned wells (Humez et al., 2014a). Processes in the host formation include water-rock reactions related to changing equilibrium by added CO₂, overpressure of the formation and potential for mobilisation of in-situ saline formation fluids. Potential geochemical impacts of supercritical CO₂ injection include mineral dissolution/precipitation reactions in response to changes in pH, carbonate equilibrium and potentially changing redox conditions, sorption/desorption reactions in relation to changing pH and redox conditions, and further reactions arising from changing ionic strength if mixing with formation fluids is involved. Precipitation of the mineral dawsonite has long been suggested as a geochemical response to injected CO₂ but its formation is also widely debated and the mineral is rarely found (e.g. Takaya et al., 2019). CCS storage reservoirs vary considerably in storage depth (650–3100 m), with resulting temperature and pressure variations. Most to date have been installed in silicate formations with only a few in carbonate systems (Michael et al., 2010). The complex geochemical interactions involved mean that numerous solutes could be of value to investigate and monitor in the context of CCS operations. These include especially CO₂, pH/Eh and inorganic solutes.

Similar complexities in terms of monitoring reactions related to unconventional hydrocarbon development also apply. Concerns for leakage of products of hydraulic fracturing at depth (UK legislation requires the minimum



depth for hydraulic fracturing in the UK to be 1000 m, National Audit Office (2019)) could potentially include leakage via source-rock faults and fractures, especially any faults reactivated by the hydraulic fracturing operations, as well as leakage via abandoned wells. Here, geochemical reactions in sources and pathways involve impacts of leakage of methane and higher alkanes, potential for mobilisation of NORM (naturally-occurring radioactive materials) and potential for mobilisation of saline formation water and flowback. Monitoring for hydrocarbon gases (and CO₂), pH/Eh, inorganic solutes including salinity indicators, and organic compounds are relevant in this context. Monitoring of diagnostic compounds in hydraulic fracturing fluid might also be informative.

With each type of subsurface development, reactions and impacts on fluid compositions vary according to local conditions including rock types, pathways, contaminant fluids and aquifer types. A varied toolbox of chemical and isotopic techniques has been used over the years for investigating groundwater characteristics, residence times, potential pathways and provenance in the context of both unconventional hydrocarbons and CCS. This report details some of the more useful tools and approaches to characterising groundwater chemistry and signatures of potential contaminants. It also describes findings from a number of case studies on the application of environmental tracers for monitoring related to CO₂ storage and unconventional hydrocarbon activities.

2 Contaminant tracers

2.1 CHEMICAL COMPOSITIONS AND RATIOS

Chemical compositions of groundwaters and deep brines can be diagnostic of provenances and fluid flow paths in both unconventional hydrocarbon and CCS settings. Formation and flowback fluids are highly saline and may contain high concentrations of some trace metals and NORM (Zhang et al., 2015). Deep formation and flowback fluids from unconventional hydrocarbon areas of the USA are saline (<30 g/L in Colorado) (Kharaka et al., 2019) to hypersaline (TDS >50 g/L) (Chapman et al., 2012; Warner et al., 2014). Formation fluids from reservoir gas fields of Iran also have TDS >50 g/L (Bagheri et al., 2014; Zhang et al., 2015). Such compositions are highly distinctive from those of modern shallow fresh groundwater and major and trace elements can be effective in identifying them.

Evaluation of contaminants from leakage or water-rock reactions has been carried out via laboratory experiments (Little and Jackson, 2010), modelling (Gaus et al., 2005; Nickerson and Risk, 2013) or field trials (Humez et al., 2014b; Kharaka et al., 2010). Major ions give a picture of principal minerals and geochemical reactions, though relations may be complex. High concentrations of DIC can be indicative of microbial metabolic reactions in organic-carbon-rich formations (Martini et al., 2003). Trace elements such as REE have been found to be potentially diagnostic as tracers of deep brines, for example in CCS applications (McLing et al., 2014).

A number of trace-element ratios have also been found to be diagnostic of provenance and pathways of saline fluids, including Sr/Ca, Ba/Sr, Na/Cl and Br/Cl. For example, Br/Cl ratios have been used to characterise deep brines, with high Br/Cl ratios (Vengosh et al., 2014) and low Na/Cl ratios relative to modern seawater being attributed to evaporation of seawater beyond halite saturation (Warner et al., 2012).

2.2 ISOTOPIC TRACERS

Chemical compositions and element ratios provide useful information on water-rock reactions and distinctions between different bodies of groundwater and brine, but difficulties can arise with ascribing unambiguous sources on the basis of chemical compositions alone. Isotopic tracers have potential to provide a greater resolution on likely processes and can be powerful when used in combination with chemical compositions.

A number of isotopic tracers have been used for assessing sources and pathways of deep saline fluids, including in assessing cases of surface and near-surface contamination of freshwater (Chapman et al., 2012). Some studies have found that isotopic tracers are capable of distinguishing signatures of conventional reservoir brines from unconventional shale-gas brines (Tasker et al., 2020; Vengosh et al., 2015). Isotopic data could also increase confidence in source apportionment and process understanding in cases of litigation (Hammond et al., 2020).



A range of isotopic tracers have been used in shale-gas and CCS-related studies. Their value for diagnostic purposes is likely to vary from region to region depending on geological and hydrogeological circumstances, and potential impacts of in-situ alteration, but combinations of isotopic tracers can and have proven effective.

2.2.1 Oxygen and deuterium in water

Oxygen is a component of both water and CO₂ and its isotopic composition can therefore be a useful tracer in some applications. Its signature is usually appraised alongside that of H₂ as the other water component. The water isotopes $\delta^{18}\text{O}$ and $\delta^2\text{H}$ have long been used to distinguish between meteoric water and seawater in hydrogeological studies. They may also be of value in studies of groundwater residence time and can give useful insight into temperature and altitude of recharge (Clark and Fritz, 1997).

The stable isotopes of O and H have been applied to problems identifying brines in groundwater mixtures but some studies have found the method insufficiently sensitive to distinguish compositional changes from brine inputs (Warner et al., 2014). Warner et al. (2012) concluded that large inputs of Appalachian brine (>20%) to shallow groundwater would be needed before a change would be registered in the $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta^2\text{H}_{\text{H}_2\text{O}}$ ratios in the Appalachian Basin of Pennsylvania.

2.2.2 Boron

Boron is a relatively incompatible element in most silicate minerals and a number of boron minerals are soluble; hence, boron is mobile in the aqueous environment. Boron can adsorb to clays and be present in kerogen (Williams et al., 2015). A relatively large mass difference between ¹⁰B and ¹¹B results in significant fractionation in nature and production of an observed range of $\delta^{11}\text{B}$ isotopic compositions in water of some 145 ‰ (Barth-Nettilan et al., 2018; Vengosh et al., 1991; Xiao et al., 2013). Variations in B isotopic composition also relate to variations in initial source compositions. The large variations make $\delta^{11}\text{B}$ a useful tracer and numerous studies have used it for distinguishing B sources including surface pollutants such as wastewater (Bassett et al., 1995; Vengosh et al., 1994), seawater intrusion and brine influx and for interpreting sediment depositional environments (Xiao et al., 2013).

Dissolved boron is dominated by borate B(OH)₃ at pH values <9, and B(OH)₄⁻ at more alkaline pH (Takeno, 2005). Isotopic fractionation is caused by exchange between the two species and fractionation also occurs during evaporation, adsorption/coprecipitation, volatilisation and biological processes (Pennisi et al., 2006; Vengosh et al., 1991; Xiao et al., 2013). Fractionation has been associated with pH-dependent adsorption of B to humic acid (Lemarchand et al., 2005) and clays (Williams et al., 2001). Preferential incorporation of ¹⁰B into clays during diagenesis can cause an increase in $\delta^{11}\text{B}$ in the residual porewater (Spivack et al., 1987; Vengosh, 1998).

Depleted $\delta^{11}\text{B}$ compositions typify non-marine borate and igneous minerals, while enriched compositions have been associated with salt-lake brines, oilfield brines and evaporated seawater (Williams et al., 2001; Xiao et al., 2013). Dissolution of igneous rocks gives $\delta^{11}\text{B}$ compositions of around -3 to +3 ‰, domestic wastewater around -15 to +10 ‰ and brines of +40 ‰ and higher. Due to long residence time, B in modern open seawater has a fairly constant isotopic composition of around +39.6 ‰ (Foster et al., 2010).

Stable isotopes of boron have been used in a number of unconventional hydrocarbon studies to distinguish the compositions of formation brines. Flowback fluids from Marcellus and Fayetteville Shales had $\delta^{11}\text{B}$ (+25–31 ‰) compositions distinct from surface water $\delta^{11}\text{B}$ (+8–20 ‰) and from conventional oil and gas $\delta^{11}\text{B}$ (+36–51 ‰) compositions (Warner et al., 2014). The large variations in $\delta^{11}\text{B}$ have proven highly effective in saline water investigations although low concentrations of B in freshwater can limit detection and resultant precision on $\delta^{11}\text{B}$ compositions (Xiao et al., 2013).

2.2.3 Lithium

As with B, Li is mobile in water but can adsorb to clays, oxides and organic matter. The light stable isotopes of lithium are also strongly fractionated in nature. Incorporation of Li into clay minerals and adsorption onto clays, oxides and organic matter involves preferential incorporation of ⁶Li leaving a residual fluid enriched in ⁷Li (and enriched $\delta^7\text{Li}$ compositions) (Négrelet et al., 2010; Phan et al., 2016; Steinhöfel et al., 2021; Williams and Hervig, 2005). Lithium adsorbs to kerogen, producing a typically depleted kerogen isotopic composition ($\delta^7\text{Li}$ +4 to -32 ‰) (Williams et al., 2015). Organic carbon sources are typically depleted in both Li and B isotopic compositions relative to both natural water and minerals (Williams et al., 2015). Most silicate rocks have $\delta^7\text{Li}$ compositions of around -20 to +10 ‰ (Négrelet et al., 2010).



Isotopic compositions of Li have like B proven useful in unconventional hydrocarbon studies for tracing and distinguishing formation brines and highlighting differences from shallow fresh groundwater. Marcellus and Fayetteville flowback fluids for example were shown to have distinctive $\delta^7\text{Li}$ (6–10 ‰) compositions compared to conventional hydrocarbon fluids ($\delta^7\text{Li}$ 10–23 ‰) and surface water ($\delta^7\text{Li}$ 17–30 ‰) (Phan et al., 2016; Warner et al., 2014). Warner et al. (2014) suggested that both B and Li in the formation fluids were mobilised from exchange sites on clay minerals, although Phan et al. (2016) found negligible amounts of exchangeable Li on clays, with sequential extraction showing dominance of Li in structural positions in Marcellus clays and feldspars. The Li isotopic composition of open seawater is around 31 ‰ (Millot et al., 2004; Nishio and Nakai, 2002).

2.2.4 Strontium

Isotopic compositions of Sr can be useful in tracing water-rock reactions in aquifers (Frost and Toner, 2004) and deep formations (Smalley et al., 1992), as well as in distinguishing surface pollutants (Brinck and Frost, 2007; Christian et al., 2011). Unlike the light elements, the isotopic composition of Sr, expressed as the ratio $^{87}\text{Sr}/^{86}\text{Sr}$, is not fractionated by evaporation, precipitation or microbiological activity (Brinck and Frost, 2007; Chapman et al., 2012), although fractionation can occur by dissolution or cation-exchange reactions (Johnson and DePaolo, 1997). The method has the advantage that small variations in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio can be measured precisely (e.g. ± 0.00001) by mass spectrometry and Sr is easily detected in both fresh groundwater and saline fluids.

Isotopic compositions of Sr have been found useful in the context of formation water identification and discrimination in groundwater. Formation water typically has high concentrations of dissolved Sr and distinctive isotopic compositions such that small quantities of contaminant inputs to groundwater can be identified (Chapman et al., 2012; Harkness et al., 2017; Warner et al., 2012). Chapman et al. (2012) for example reported a narrow range of $^{87}\text{Sr}/^{86}\text{Sr}$ for production brines from the Marcellus Shale (0.710148–0.711183) and was able to distinguish the ratios from those of modelled Devonian seawater, local coal-mine drainage and brines from other local Devonian formations.

2.2.5 Carbon, hydrogen and oxygen isotopes of dissolved gases

Carbon, H and O in dissolved CH_4 and CO_2 have a wide range of isotopic compositions and have been used widely to differentiate evolution, pathways and provenance in situations relevant to both unconventional hydrocarbon exploration and CO_2 storage (e.g. Flude et al., 2017; Humez et al., 2014a).

Methane and higher alkane gases are commonly classified as biogenic or thermogenic based on hydrocarbon ratios (C1/C2) and C and H isotopic compositions. Biogenic gas, produced via microbial activity, may include small proportions of higher alkanes but is overwhelmingly dominated by methane (C1/C2 >5000) and has depleted $\delta^{13}\text{C}_{\text{CH}_4}$ (-55 ‰ or less) isotopic signatures. In contrast, thermogenic gas, produced by thermal cracking of kerogen, typically has a larger proportion of ethane (C2), and higher alkanes and therefore lower C1/C2 ratios (<5000), with more enriched $\delta^{13}\text{C}_{\text{CH}_4}$ (greater than -55 ‰) and $\delta^2\text{H}$ (typically greater than -300 ‰) isotopic ratios (Martini et al., 2003; Whiticar et al., 1986). Compositions of $\delta^{13}\text{C}_{\text{CH}_4}$ (and of $\delta^{13}\text{C}_{\text{C}_2\text{H}_6}$) become more enriched with increasing thermal maturity (Harkness et al., 2017).

Stable C and H isotopic signatures have been used to discriminate differing methane production pathways and substrates in sedimentary environments (Bernard et al., 1976; Whiticar et al., 1986). Carbon stable isotopic ratios can be especially helpful for discriminating geogenic forms of methane, while H isotopic ratios provide helpful information for discriminating biogenic methane metabolic production pathways, notably in distinguishing between acetate fermentation and CO_2 reduction pathways. However, complications occur as isotopic ratios vary according to factors including substrate original compositions and thermal maturity (Martini et al., 2003; Wang et al., 2015; Wei et al., 2019), kinetic isotope effects, temperature and reaction rates (Whiticar, 1999). Isotopic compositions can also be modified as a result of subsequent diagenetic and microbial processes including aerobic/anaerobic oxidation, and sulphate reduction (Coleman et al., 1981; Harkness et al., 2017; Martini et al., 1998; Martini et al., 2003). Ratios of C1/C2 are also impacted by oxidation reactions due to preferential loss of CH_4 relative to hydrocarbons of higher molecular weight (Whiticar, 1999). The physical separation of methanogenesis and methane oxidation reactions may be very small and localised (Whiticar, 1999).

In some studies, clumped isotopes of methane, such as $^{13}\text{CH}_3^2\text{H}$ and $^{12}\text{CH}_2^2\text{H}_2$ isotopologues may prove useful as geothermometers and have provided further resolution on relative influences of biogenic and thermogenic methanogenesis (Stolper et al., 2015). Biogenic methane typically forms at temperatures less than 80°C and thermogenic at greater than 60°C and, as clumped-isotope ordering that formed in isotopic equilibrium without



subsequent isotopic exchange is a function of its formation temperature, this may help to discriminate (Douglas et al., 2017; Stolper et al., 2015). Values are expressed in Δ_{18} notation, analogous to other isotopic delta values, from which a formation temperature can be estimated. The Stolper et al. (2015) study found that within the Antrim Shale, USA, both biogenic and thermogenic methane were present in fluids from different boreholes and that Δ_{18} -based fluid temperatures correlated with C_1/C_{2+} ratios, $\delta^2H_{H_2O}$ ratios and $\delta^2H_{CH_4}$ ratios. The temperature dependence of clumped-isotopic compositions is not specific to methane and could be applied to other molecules including CO_2 (Douglas et al., 2017; Eiler, 2007). Nonetheless, clumped-isotope analysis is specialist and as yet has not been adopted widely.

The $\delta^{13}C$ stable-isotopic composition of CO_2 is also potentially important for the understanding of processes pertaining to unconventional hydrocarbon research (Martini et al., 1998). Enrichment of $\delta^{13}C$ in both CO_2 and co-produced DIC and are noted to be a strong signal of microbial methane oxidation (Barker and Fritz, 1981; Martini et al., 2003). The composition of $\delta^{13}C_{CO_2}$ and its relation with $\delta^{13}C_{CH_4}$ in groundwater may also be a useful tool in distinguishing CO_2 reduction from acetate fermentation pathways (Li et al., 2020).

The $\delta^{13}C$ isotopic composition of CO_2 is one of the most important direct tracers in CCS research (Clark and Fritz, 1997; Shan et al., 2019; Shin et al., 2020). Some studies have also found $\delta^{18}O$ isotopic ratios to be a useful CO_2 tracer in CCS applications (Humez et al., 2014a), although others have found the $\delta^{18}O$ less useful as a conservative tracer due to rapid (hours to days) isotopic exchange between the CO_2 and water (Mayer et al., 2015).

In CCS applications the $\delta^{13}C_{CO_2}$ ratio is useful provided that the injected gas has a signature distinct from other ambient sources of CO_2 (Mayer et al., 2015; Schulz et al., 2012). The $\delta^{13}C$ composition of injected CO_2 is mainly dependent on the feedstock, although post-injection reactions including adsorption can fractionate the aqueous CO_2 compositions (Flude et al., 2016; Larson and Breecker, 2014). The isotopic composition of CO_2 derived from fossil fuels including oil is expected to be depleted (ca. -25 ‰ or lighter) (Hoefs, 2018). Nowak et al. (2014) found that the composition of oil-derived CO_2 injected at the Ketzin CCS site in Germany averaged -30.9 ‰; CO_2 injected from a natural-gas reservoir averaged -3.5 ‰. Evidence of a CO_2 leak in the surrounding groundwater is strengthened if a change in $\delta^{13}C_{CO_2}$ composition is accompanied by an increase in DIC concentration (Mayer et al., 2015). By contrast, the $\delta^{13}C$ composition of magmatic CO_2 is reported to be enriched (around -4 ‰) (Sano et al., 2020).

In groundwater close to a demonstration CO_2 injection site at Tomakomai in Hokkaido, Japan, shifts in both $\delta^{13}C_{CO_2}$ and total DIC were tentatively attributed to the injection process inducing an earthquake some 32 km from the injection site and prompting fluid migration (Sano et al., 2020). Around 300 kilotons of CO_2 produced as a by-product of hydrogen production at an oil refinery, purified (amine scrubbed) and compressed, were injected slowly into two subcoastal aquifers between April 2016 and December 2019. The earthquake occurred in September 2018. Groundwater from a borehole 13 km away from the injection site had $\delta^{13}C_{CO_2}$ compositions close to -17.8 ‰ from mid 2015 to early 2018, but decreased to -18.8 ‰ subsequently, with an increase in total DIC concentration in late 2018 (Sano et al., 2020). The groundwater also showed an associated decrease in ^{14}C activity over the time interval. The decreasing $\delta^{13}C$ compositions and ^{14}C activity were taken to be due to migration of the injected isotopically-depleted, ^{14}C -dead CO_2 towards the monitoring borehole. Assuming a model flowpath of 30 km length between injection site and groundwater borehole, a relatively rapid fluid velocity of around 40 m/day was postulated (Sano et al., 2020).

2.2.6 Radium

Uranium is commonly found in relatively large proportions in shale and so data for U and its decay products can be useful tools in investigations of shale-gas fluid migration. The nuclides of Ra, ^{226}Ra and ^{228}Ra are the disintegration products of ^{238}U and ^{232}Th respectively. In groundwater, they are mobilised by alpha recoil and desorption from and dissolution of minerals in the host aquifer. Isotopes of Ra have proven to be useful tracers for distinguishing saline formation waters from shallow fresh groundwaters. Appalachian brines from the Marcellus Formation of Pennsylvania for example, have high activities of ^{226}Ra and ^{228}Ra (55–115 Bq/L) and low $^{228}Ra/^{226}Ra$ ratios (0.12–0.73), while shallow groundwater has low combined Ra activities (<0.2 Bq/L) (Warner et al., 2012). Fayetteville shale produced waters from Arkansas have ^{226}Ra and ^{228}Ra activities of (0.5–10 Bq/L) and even lower ratios (0.1–0.5) compared to the Appalachian brines (Warner et al., 2013). Tasker et al. (2020) concluded that $^{228}Ra/^{226}Ra$ ratios were among the best isotopic ratios to distinguish Marcellus from Utica/Point Pleasant Shale in the USA as their signatures were most distinctive.



2.2.7 Noble gases

Isotopes of the noble gases, especially He, Ne and Ar, have been used as tracers in a number of studies of deep hydrocarbon fluids and CCS. Their attraction as tracers owes especially to their inert nature, rarity and well-characterised and distinctive isotopic compositions in the atmosphere, crust and mantle. The noble gases present in subsurface fluids derive from a combination of atmospheric gases incorporated at the time of sediment deposition or recharged subsequently via groundwater, the mantle and gases derived radiogenically (e.g. ^4He and ^{21}Ne produced by radioactive decay of U and Th) (Ballentine et al., 2002). The ratios of $^3\text{He}/^4\text{He}$, $^{40}\text{Ar}/^{36}\text{Ar}$ and $^4\text{He}/^{20}\text{Ne}$ can identify the sources of gases and evaluate the atmospheric influence on deep gas compositions (Li et al., 2020). As ^4He is radiogenic, its accumulation in groundwater can also serve as an indicator of residence time assuming no other subsurface sources, although as ^4He ages are typically higher than obtained using other groundwater dating methods (Andrews and Lee, 1979), inputs of ^4He from such sources appears common (Morikawa et al., 2008).

The $^3\text{He}/^4\text{He}$ ratio of geological materials (R) is typically expressed relative to the atmospheric ratio (R_a). The $^3\text{He}/^4\text{He}$ ratio in the atmosphere (R_a) is 1.39×10^{-6} (Kotarba and Nagao, 2008; Sano and Wakita, 1985). The $^3\text{He}/^4\text{He}$ ratio of the crust is $\leq 10^{-7}$ while the mantle (represented by MORB) typically has $^3\text{He}/^4\text{He}$ ratios $\geq 10^{-5}$, (Kotarba and Nagao, 2008; Ozima and Podosek, 2002; Porcelli and Ballentine, 2002). As R/R_a , the typical ratio of the crust is approximately 0.025, while that of the mantle averages around 8.75 (Kotarba and Nagao, 2008).

The atmospheric ratio of $^{40}\text{Ar}/^{36}\text{Ar}$ is around 296 and of $^4\text{He}/^{20}\text{Ne}$ around 0.318 (Kotarba and Nagao, 2008; Sano and Wakita, 1985). The crust has $^{40}\text{Ar}/^{36}\text{Ar} \geq 5000$ while the mantle typically has $^{40}\text{Ar}/^{36}\text{Ar}$ ratios $\geq 10,000$; $^4\text{He}/^{20}\text{Ne}$ ratios for the crust and mantle have been estimated as 100,000 (Kotarba and Nagao, 2008; Porcelli and Ballentine, 2002; Sano and Wakita, 1985).

Kotarba and Nagao (2008) reported high $^4\text{He}/^{20}\text{Ne}$ ratios of 1040–41,200 and low $^3\text{He}/^4\text{He}$ ratios of 0.017–0.10 in natural gases and oil-dissolved gases from Flysch and Mesozoic Basement of the Carpathian Foredeep of Poland and Ukraine. They linked the high ratios of the former to lack of atmospheric inputs and low ratios of the latter to lack of mantle inputs of ^3He , with dominance of ^4He of radiogenic origin in the crust.

Shallow groundwaters, mostly from drinking-water wells (Cl concentrations up to 2400 mg/L) in the Northern Appalachian Basin of West Virginia, are reported to have R/R_a ($^3\text{He}/^4\text{He}$) ratios from 1.021 to 0.0166, reflecting a range of compositions from atmospheric plus a small proportion of tritiogenic ^3He , to crustal compositions (Harkness et al., 2017). Decreasing $^3\text{He}/^4\text{He}$ ratios correlated with increasing ^4He concentrations and increasing $^4\text{He}/^{20}\text{Ne}$ ratios. $^{40}\text{Ar}/^{36}\text{Ar}$ ratios ranged between 294.5 and 308. Dissolved CH_4 was present at concentrations greater than 1 mg/L in 34% of the analysed groundwaters and concentrations were highest in the more saline groundwaters (with Cl >50 mg/L). The data supported an inference that saline groundwater likely derived by migration of CH_4 -rich brines, probably from coal horizons at depth (Harkness et al., 2017).

Noble gases are potentially also valuable as tracers in gas leakage scenarios in a CCS context. It can be assumed that CO_2 injected into a deep storage formation will also contain atmospheric noble gases which may contrast their compositions with those of noble gas contributions from the mantle or from the deeper crust derived via U, Th and K decay (Flude et al., 2017; Humez et al., 2014a). Spiking of injected CO_2 with noble gases can also aid in distinguishing end members (Roberts et al., 2017).

Concentrations of noble gases in CO_2 storage facilities will be controlled by the capture method. Concentrations in amine-stripped CO_2 are likely to be low and the isotopic ratios determined by the nature of the feedstock (Flude et al., 2016). Noble gas isotopic compositions in CO_2 derived from fossil fuels may contain radiogenic components that should be distinctive as tracers of leakage in shallow groundwater conditions (Flude et al., 2016).

3 Case studies

3.1 HYDROCARBON BASELINE: VENDSYSSEL, DENMARK

The Cambro-Ordovician Alum Shale, an organic-rich black shale deposit, underlies large parts of Sweden, Denmark and Norway. One of three licences for unconventional hydrocarbon exploration of the formation in Denmark was issued for Vendsyssel in North Jutland, Denmark, in 2010. The Vendsyssel-1 (VDS-1) exploration borehole was drilled in 2015 by TOTAL, in association with the Danish state oil company, Nordsofonden. The borehole was 3564 m deep and proved some 39 m of high-TOC (up to 9%) shale deposit,



overlain by 35 m of low-TOC (around 2%) shale. Investigations showed the exploration borehole produced low gas recovery due to poor gas content and porosity and the formation was thinner than expected, certainly in comparison to analogous units in Poland (Schovsbo and Jakobsen, 2019). No further commercial exploration tests were carried out on the borehole by the company and the borehole was plugged and abandoned later the same year. A moratorium on onshore hydraulic fracturing for shale-gas exploration was issued for Denmark in 2012, although previously issued licences remained valid (EC, 2016).

During the drilling and post-drilling phases, samples of mud gas were collected from the VDS-1 borehole for chemical and isotopic analysis by TOTAL (Kloppmann, 2021). Samples of groundwater were also collected from four shallow (<100 m deep) groundwater observation boreholes. Mud gases had methane as the dominant hydrocarbon (>99%) at depths less than 1300 m in the recovered Pleistocene, Cretaceous and Jurassic argillaceous formations, below which higher alkanes (ethane and higher) became detectable. Ratios of hydrocarbons ($C_1/(C_2+C_3)$) fell from 65 in the Jurassic Fjerritslev shales (ca. 1300 m), to 3 in the Permo-Carboniferous formations (ca. 3000 m) and increased to 10 and 19 in the Rastrites Shale (ca. 3400 m) and Alum Shale formations (>3500 m) respectively. Butane was only detectable in the depth range 2800–3420 m (Kloppmann, 2021).

The $\delta^{13}C$ isotopic compositions of methane in the mud gases from the Mesozoic formations in VDS-1 showed biogenic signatures (less than -55 ‰) (Whiticar, 1999), including -70 ‰ for the Chalk Group and around -65 ‰ for the Fjerritslev Shale. Palaeozoic shale had more enriched compositions (around -44 ‰ for Permo-Carboniferous and Silurian formations and -38 ‰ for the Rastrites and Alum shale formations), suggesting increasing maturity with increasing depth. The Jurassic shales were considered as early mature, the Permo-Carboniferous and Silurian as mature and Rastrites and Alum shales late mature (Kloppmann, 2021). Ratios of $\delta^{13}C_{CH_4}$ and $\delta^{13}C_{C_2H_6}$ in the mud gases increased with depth in the Permo-Carboniferous and Silurian formations, reflecting increasing gas maturity (Berner and Faber, 1996), but the trend changed in the underlying Alum Shale, with $\delta^{13}C_{C_2H_6}$ becoming more depleted. This reversal was attributed by Kloppmann (2021) to radiolysis of kerogen by uranium, present in the shale with an average abundance of 100 mg/kg. Radiolytic reactions have been noted to produce gases with increasingly depleted ^{13}C compositions (Dahl et al., 1988).

The shallow groundwater from the four observation boreholes was reducing to strongly reducing with presence of NH_4 and compositions indicative of sulphate reduction in two of the four. One was brackish while the others were fresh. The groundwaters had a large range of $C_1/(C_2+C_3)$ ratios (2 to 4500), with a $\delta^{13}C_{CH_4}$ range of -75 to -49 ‰ and $\delta^2H_{CH_4}$ of -253 to -226 ‰ (Kloppmann, 2021). Two of the boreholes had groundwater containing high methane and low higher alkane concentrations, with the more depleted $\delta^{13}C_{CH_4}$ and $\delta^2H_{CH_4}$ compositions consistent with a biogenic methane source. These compare with shallow groundwater from other sites in the Vendsyssel-Kattegat area, which had CH_4 as the dominant hydrocarbon, with $\delta^{13}C_{CH_4}$ ratios of -63.6 to -89.2 ‰ and $\delta^2H_{CH_4}$ of -177 to -228 ‰, consistent with a biogenic source in the Upper Pleistocene marine sediments, produced via CO_2 reduction (Jorgensen et al., 1990).

The other two observation boreholes around the VDS-1 borehole investigated by Kloppmann (2021) had groundwater with detectable concentrations of higher alkanes (C_2 – C_6), one of which had the more enriched $\delta^{13}C_{CH_4}$ and $\delta^2H_{CH_4}$, and each resembling a composition closer to thermogenic. The latter two groundwater types were taken to reflect a mixture between shallow groundwater in the Quaternary units and hydrocarbons from deeper formations, notably the Permo-Carboniferous and Upper Silurian shales (Kloppmann, 2021). This raised the prospect of dissolved-gas compositions at shallow levels evolving by migration of deep fluids along fractures, the authors speculating that fracture activation could have been through past isostatic readjustments or movements induced during drilling.

Compositions of $^{87}Sr/^{86}Sr$ in the shallow groundwaters around VDS-1 lay in the range 0.7095 to 0.7104, close to values for other groundwaters in North Jutland and slightly more radiogenic than modern Baltic seawater (0.709370 ± 0.000054). The small distinction between the compositions in the four groundwaters despite variable hydrocarbon compositions and salinities rendered the Sr isotopes less useful for discriminating processes in the system (Kloppmann, 2021). Compositions of $\delta^{34}S$ suggested that a combination of sulphide oxidation and sulphate reduction had affected the shallow groundwaters.

Values for $\delta^{11}B$ in the groundwaters were 4–31 ‰, the higher end approaching that of modern seawater (39.6 ‰). Values for δ^7Li were 18–27 ‰, the higher end also approaching the modern seawater composition of 31 ‰. Groundwater compositions were taken to reflect a combination of seawater influence and ion exchange of B and Li on Quaternary clay minerals. Taken in combination, the B and Li isotopic compositions could be seen to be distinctive from USA Fayetteville and Marcellus flowback fluids ($\delta^{11}B$ ca. 25–35 ‰, δ^7Li



ca 5–15 ‰ and of particular potential value for provenance discrimination in a shale-gas investigation (Kloppmann, 2021).

3.2 HYDROCARBON BASELINE: VALE OF PICKERING, UK

Conventional gas has been exploited from boreholes in the Vale of Pickering, North Yorkshire, since the 1990s, with hydrocarbon reserves from both Zechstein carbonates and Carboniferous sandstone. Conventional gas reserves have since reduced and gas exploitation has all but ceased in the Vale of Pickering fields.

In 2016, a licence to explore for shale gas by hydraulic fracturing was issued by the UK government for a borehole at Kirby Misperton in the central part of the Vale of Pickering. The operator, Third Energy, had drilled an exploratory vertical borehole (KM8) in 2013 to prove geological formations and carry out preliminary hydrocarbon investigations. The borehole penetrated to 3100 m, to include the target Upper Viséan Bowland Shale Formation and Upper Viséan sandstone. Hydraulic fracturing was planned for five vertical sections of the borehole (Third Energy, 2017). In 2018, the government delayed consent for hydraulic fracturing operations to begin at the site, pending financial checks. The company was sold to an affiliate of an American company in 2019. Consent to begin operations has not been provided since.

Hydraulic fracturing did proceed at an alternative site in Lancashire, north-west England, during 2018 and 2019, although induced seismic activity associated with both those activities forced an early cessation of hydraulic fracturing. As a result of the seismic events at the Lancashire site, a moratorium on shale-gas exploration was issued for England in November 2019. This brought England in line with the other three nations of the United Kingdom in establishing onshore moratoria for hydraulic fracturing.

The Vale of Pickering hosts aquifers in superficial Quaternary glaciolacustrine and fluvioglacial deposits, as well as more permeable units within the underlying Jurassic Kimmeridge Clay. These formations provide local private supplies for domestic and agricultural use. A number of the existing shallow boreholes (<60 m deep) abstract water from a combination of superficial and Kimmeridge Clay groundwater. Underlying the Kimmeridge Clay and cropping out around the periphery of the Vale of Pickering is the Jurassic Corallian Limestone aquifer. The peripheral outcrop and subcrop areas underlying the edge of the Kimmeridge Clay form a regional water supply for the towns and villages. In the central part of the vale, in the area occupied by KM8, the Corallian Limestone is deep (top around 200 m), downfaulted and its groundwater of poor quality, being brackish and alkaline (SEC around 3000 $\mu\text{S}/\text{cm}$, pH around 10).

High concentrations of dissolved methane (up to 75 mg/L) are a feature of both parts of the Kimmeridge Clay/superficial aquifer and the underlying Corallian Limestone in the central part of the vale. Concentrations are low or undetectable (<0.7 mg/L) in groundwater from the Corallian Limestone around the periphery at outcrop or subcrop, where groundwaters are oxic or mildly reducing. High concentrations of CH_4 are associated with SO_4 -reducing groundwater conditions as evidenced by strong sulphide smell in many and a negative association between SO_4 and S^{2-} , low SO_4 concentrations where CH_4 concentrations are high, and enriched $\delta^{34}\text{S}$ isotopic compositions of reduced low- SO_4 groundwaters (Figure 1). Groundwater having undergone SO_4 reduction is a key feature of the high- CH_4 groundwaters, suggesting CH_4 formation in situ (Wen et al., 2019).

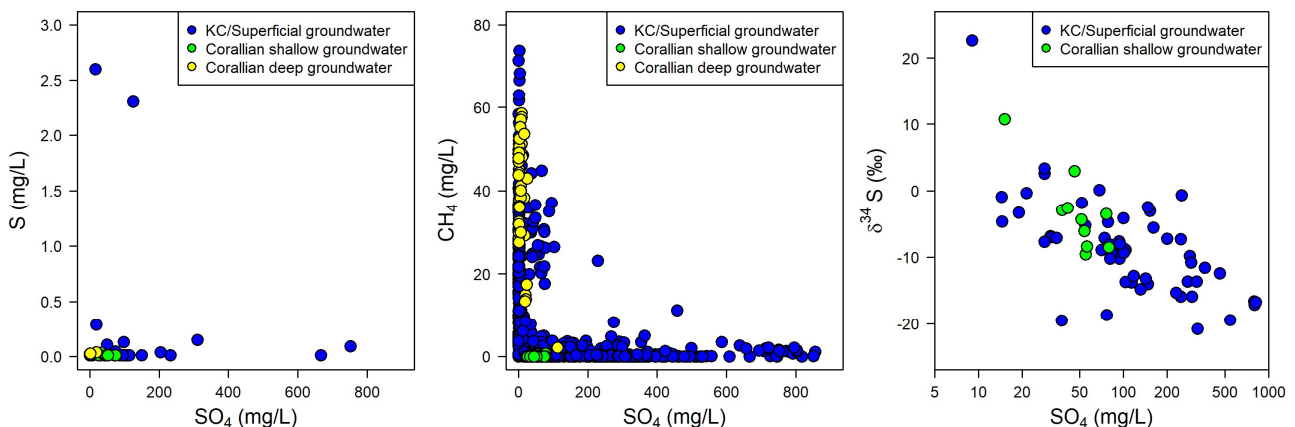


Figure 1. Distributions of SO_4 , S (sulphide), CH_4 and $\delta^{34}\text{S}$ in groundwaters from the Kimmeridge Clay/superficial and Corallian aquifers of the Vale of Pickering



Proportions of dissolved CH₄ in the groundwaters are large relative to the higher alkanes, such that C1/C2 ratios are greater than 90 in most and up to 170,000. Stable isotopic compositions of $\delta^{13}\text{C}_{\text{CH}_4}$ are depleted, mostly in the range -50 ‰ to -90 ‰. These compositions indicate a biogenic signature for the CH₄ (Figure 2) although a few points plot to more enriched $\delta^{13}\text{C}$ isotopic composition, potentially suggesting a degree of CH₄ oxidation in some samples (Martini et al., 2003; Whiticar et al., 1986). The relationship between $\delta^{13}\text{C}_{\text{CH}_4}$ and $\delta^2\text{H}_{\text{CH}_4}$ indicates that compositions are dominantly consistent with generation of CH₄ by CO₂ reduction (Figure 2).

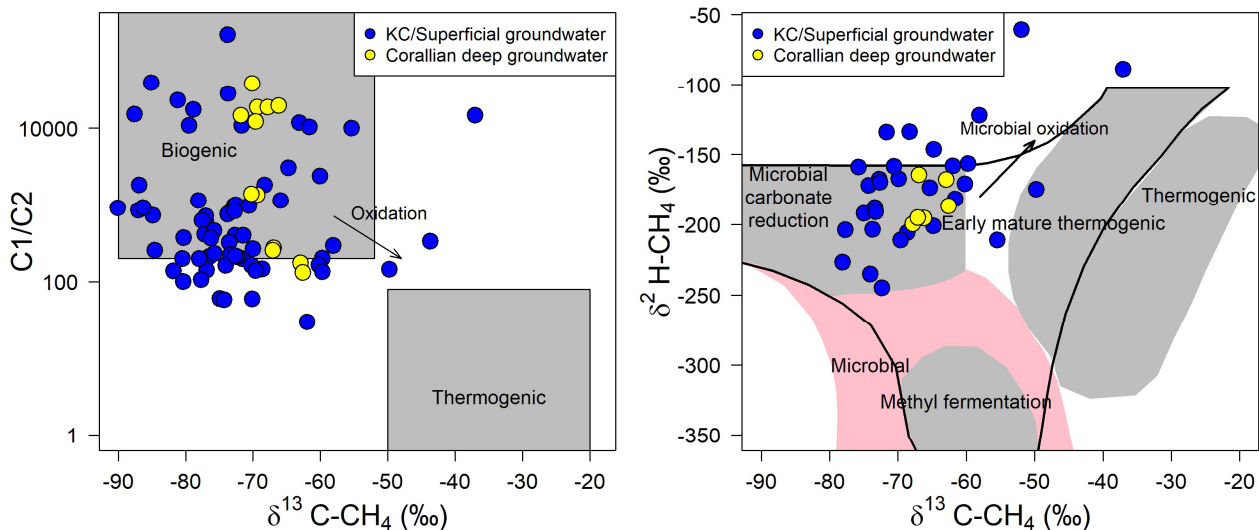


Figure 2. C1/C2 ratios (mol) vs $\delta^{13}\text{C}_{\text{CH}_4}$ compositions and $\delta^{13}\text{C}_{\text{CH}_4}$ vs $\delta^2\text{H}_{\text{CH}_4}$ compositions of groundwaters from the Kimmeridge Clay/superficial and Corallian aquifers of the Vale of Pickering; plot fields after (Whiticar, 1999)

The high CH₄ concentrations of the Vale of Pickering groundwaters therefore appear to have been produced in situ by microbial mediation with little evidence for upward migration of ex-situ thermogenic gases. Establishing this baseline condition in the groundwater CH₄ compositions would be important in the event of any future exploration for subsurface unconventional hydrocarbon resources.

3.3 CARBON STORAGE: SVELVIK, NORWAY

The small field-scale experimental site at Svelvik, Norway, formed a study area for experiments on the superficial injection of CO₂ into unconsolidated Quaternary sediments. The site was set up to investigate a superficial system with potential for rapid observable changes and appropriate monitoring approaches. The study was conducted by nine Norwegian partners, coordinated by SINTEF Petroleum Research with a partner and community agreement forming the CO₂FieldLab Project in 2007 (Denchik et al., 2014; Dillen et al., 2009).

The site in Oslofjord, some 50 km south of Oslo, is well-characterised. The superficial deposits consist of a central ridge of porous and permeable Holocene fluvio-glacial sand and gravel with overlying silts and clays along the lower-lying margins. These deposits overlie Permian sedimentary rocks and granite at some 300–400 m depth (Humez et al., 2014b). The ridge lies at 70 m above sea level, and groundwater level around 60 cm below surface at the ridge. The central ridge forms an unconfined aquifer, with confined sections below the marginal clays. Groundwater consists of fresh water overlying salt water with an interface at around 12 m depth. Site set up involved installation of a central inclined injection borehole as well as four groundwater monitoring boreholes (Dillen et al., 2009; Humez et al., 2014b).

In an injection experiment carried out in 2011, CO₂ (1.67 t) was injected at a wellhead pressure of 1.9–2 bar over 6 days into the 45°-inclined borehole to a target depth of 20 m (Humez et al., 2014b; Jones et al., 2014). Groundwater data from one of four monitoring boreholes at the site showed the greatest evidence of reaction following the injection and became the focus of investigations. Injected CO₂ was found to migrate from 20 m into the sand aquifer at around 10 m depth. Groundwater at 10 m depth in the monitoring borehole showing greatest change had a pH drop (8.2 to 6.1) and increase in alkalinity (240 mg/L to 1400 mg/L) in response to the CO₂ injection. For the other two depths, pH decreased then recovered to baseline values and alkalinity increased before dropping back to baseline concentrations (Humez et al., 2014b).



Groundwater showed a strong positive correlation between Cl and SO₄ ($R^2 = 0.99$), suggesting that both behaved conservatively and were the result of two-component mixing (Humez et al., 2014b). Multi-tracer indicators of controlling mineral reaction processes (major ions, trace elements, $\delta^{34}\text{S}_{\text{SO}_4}$, $\delta^{18}\text{O}_{\text{SO}_4}$, $\delta^{18}\text{O}_{\text{H}_2\text{O}}$, $\delta^2\text{H}_{\text{H}_2\text{O}}$, $\delta^{13}\text{C}_{\text{DIC}}$, $\delta^7\text{Li}$, $\delta^{11}\text{B}$, $^{87}\text{Sr}/^{86}\text{Sr}$) demonstrated the mixing was between seawater and a freshwater end member, and that compositions were controlled by mineral dissolution/precipitation reactions and cation exchange (Humez et al., 2014b).

Gas monitoring at 50 cm depth in a 2 m borehole (BH01) some 20 m north-west of the injection well identified changes in the gas $\delta^{13}\text{C}_{\text{CO}_2}$ and $\delta^{18}\text{O}_{\text{CO}_2}$ ratios over the duration of the experiment. Injected CO₂ had a $\delta^{13}\text{C}_{\text{CO}_2}$ composition of -30.4 ‰ and $\delta^{18}\text{O}_{\text{CO}_2}$ of +12.9 ‰ with atmospheric values at -13.7 ‰ and +28.6 ‰ respectively (Jones et al., 2014). Gas CO₂ concentrations did not vary significantly in BH01 from atmospheric values during the course of the experiment but $\delta^{13}\text{C}_{\text{CO}_2}$ compositions showed a decrease from atmospheric values to injection CO₂ values before recovering to natural atmospheric compositions three days after the cessation of CO₂ injection. Compositions of $\delta^{18}\text{O}_{\text{CO}_2}$ increased from atmospheric values at the start to +78 ‰ before returning towards atmospheric compositions some days after injection ceasing (Figure 3). The $\delta^{18}\text{O}_{\text{CO}_2}$ composition could not be explained by simple binary mixing of CO₂ gases. Equilibrium between CO₂ and H₂O causing a shift in $\delta^{18}\text{O}$ composition (without changing $\delta^2\text{H}$) was invoked. At low temperature, water has a depleted $\delta^{18}\text{O}$ signature while CO₂ is enriched in $\delta^{18}\text{O}$ (Jones et al., 2014) (Figure 3).

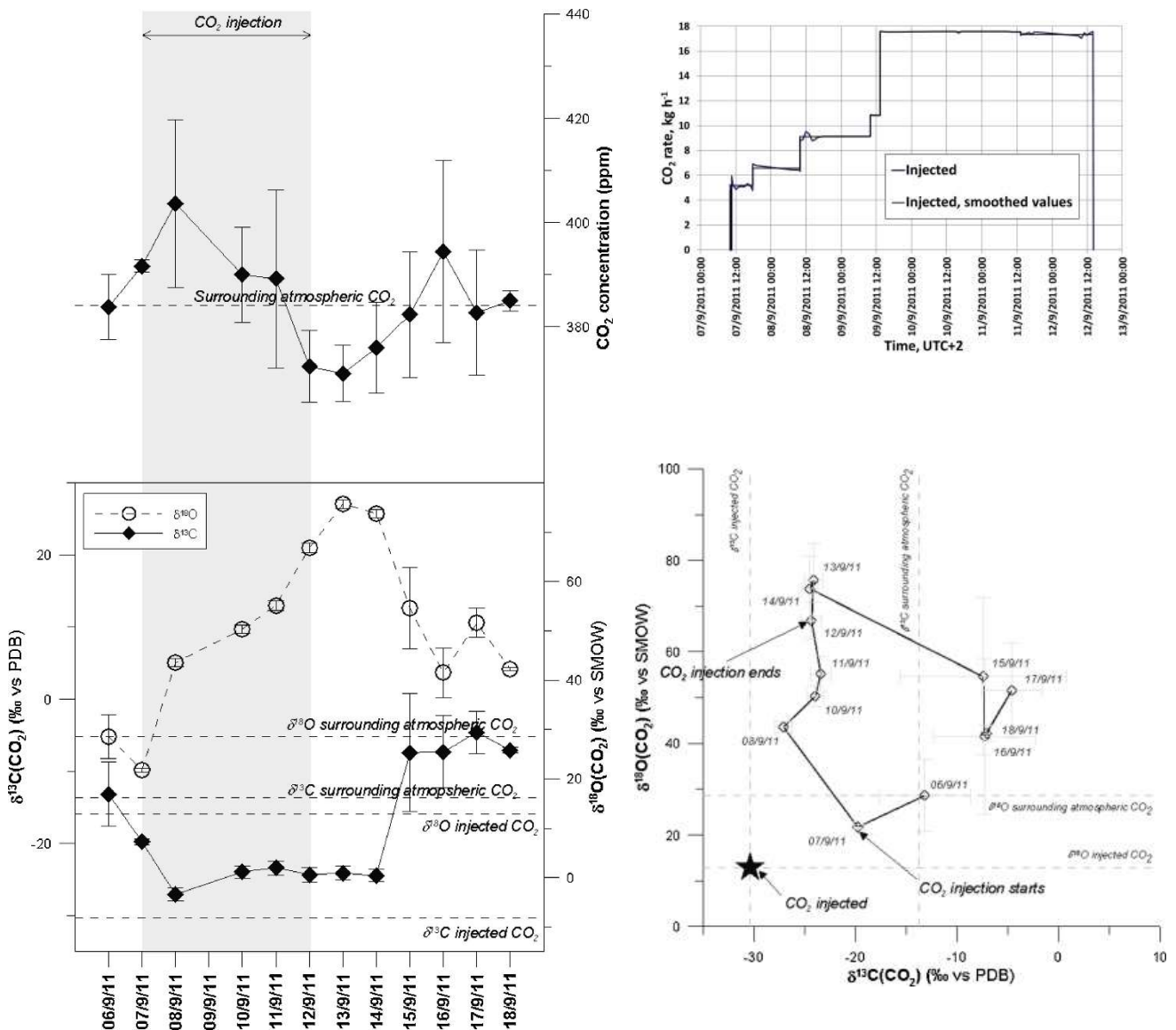


Figure 3. $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ isotopic compositions of gas in borehole BH01 before, during and after CO₂ injection at the Svelvik site in 2011. All plots from Jones et al. (2014) (Creative Commons CC-BY 3.0)



3.4 CARBON STORAGE: OTWAY, AUSTRALIA

The Cooperative Research Centre for Greenhouse Gas Technologies (CO2CRC) owns and has been operating the Otway International Test Centre in south-west Victoria, Australia since 2003. This research facility now provides seven purpose-drilled CO₂ storage wells for injection and monitoring, supply of CO₂, a variety of storage reservoir types, a seismic monitoring array, regulatory approvals, and support of local communities to undertake CCS research. The CO2CRC group works with industry, research partners and governments to study CCS (CO2CRC, 2020, 2021; Jenkins et al., 2012). Part of the CO2CRC remit involves research on safe CO₂ injection, use and storage and development of methodologies for monitoring and verification (CO2CRC, 2020; Hortle et al., 2011). Operations at the Otway site began by injecting CO₂ into a depleted hydrocarbon reservoir in 2008 (Sharma et al., 2009) and with subsequent injection into an overlying saline aquifer (Michael et al., 2010).

CO2CRC began searching for a research site with a CO₂ source located close to suitable geological storage in 2004. The Otway site in Victoria, Australia was purchased along with two adjacent petroleum tenements. One contained a well which was the source of CO₂-rich gas for injection, and the other contained a production well near the crest of a depleted reservoir structure which was to be converted for monitoring. A third well was drilled for injection. The injection well was drilled 308 m downdip from the monitoring well, with injection at a depth of 2,003–2014 m into the Cretaceous Waarre-C Formation (CO2CRC, 2021; Dance, 2013; Jenkins et al., 2012).

The Waarre gas reservoir had produced natural gas in 2002–2003. The reservoir is a 25–30m thick sandstone, fault-bounded on three sides and capped by mudstone. The bounding faults terminate in the mudstone, preventing migration. The existing production well represents the only feasible risk of leakage. The reservoir has an estimated capacity of 150 kt of CO₂, which comfortably exceeds the targets of the project. The structure of the faults would ensure the stored CO₂ plume would have a footprint of 0.5 km² (Jenkins et al., 2012).

Two water-supply (including potable water) aquifers overlie the reservoir, separated by at least 1000 m of alternating aquifers and aquitards. The most productive is the unconfined to semi-confined Miocene Port Campbell Limestone, which is used for irrigation, dairy and domestic purposes. The deeper Eocene Dilwyn Formation aquifer (ca. 600–850 m) has previously been used for urban water supply. While site characterisation suggested that the risk to these aquifers from a migrating CO₂ plume is low, the presence of such resources provides the opportunity to demonstrate the integrity of CO₂ storage (de Caritat et al., 2013).

Monitoring at the Otway site includes integrity monitoring, which uses seismic techniques to ensure a CO₂ plume is stable; and assurance monitoring of groundwater, soil gas, and atmospheric gases to demonstrate that the CCS activities provide safe and effective CO₂ storage. It was important to establish the baseline chemistry of the two overlying aquifers, continue monitoring to identify any changes, and if so to understand their causes (de Caritat et al., 2013; Underschultz et al., 2011).

Experimentation at the Otway site has been conducted in three stages. Stage 1 was completed in 2009 and involved injection, storage and monitoring of 65 kt injected CO₂ to a depleted natural gas reservoir. The Otway Stage 2 Project was completed in 2019 and involved injection, storage and monitoring of 15 kt injected CO₂ into an overlying saline aquifer. The Otway Stage 3 Project is ongoing and aims to research ways to reduce the cost and environmental footprint of CCS (CO2CRC, 2020, 2021). Published research for the monitoring of groundwaters is mainly limited to the Otway Stage 1 Project.

The Stage 1 groundwater monitoring programme at Otway included biannual geochemical sampling, hourly water-level monitoring, and headspace gas sampling of the Dilwyn aquifer. Baseline groundwater conditions prior to CO₂ injection were established at the Otway site over nearly two years. The first samples were taken in June 2006, with data from five sampling trips attained prior to CO₂ injection. Sampling continued biannually until March 2011 which meant samples were taken before, during, and after injection. The sampling network consisted of 28 existing boreholes, most of which were shallow (<100 m), extending into the Port Campbell Limestone, and within 3 km of the injection site. Three of the boreholes were within 10 km and were deeper (800–850m), extending into the Dilwyn aquifer (de Caritat et al., 2013; Hortle et al., 2011).

Sampling began at each site once the measured physicochemical parameters of the pumped water stabilised. Analytes included major ions and trace elements, Fe²⁺, and isotopic compositions of δ¹⁸O_{H2O} and δ²H_{H2O}, δ¹³C_{DIC}, δ¹⁸O_{DIC}, δ³⁴S_{SO4} and δ¹⁸O_{SO4} (de Caritat et al., 2013). Port Campbell Limestone groundwaters were found to be brackish (SEC 800–3900 μS/cm), cool (T 12.9–22.5°C) and of near-neutral pH (pH 6.62–7.45), while Dilwyn Formation groundwaters were fresher (SEC 505–1470 μS/cm), warmer (T 42.5–48.5°C) and more alkaline (pH 7.43–9.35) (de Caritat et al., 2013).



The baseline $\delta^{13}\text{C}_{\text{DIC}}$ in the groundwaters varied between -15.4‰ and -9.4‰ in the Port Campbell Limestone aquifer and between -21.2‰ and -11.6‰ in the Dilwyn Aquifer. de Caritat et al. (2013) concluded that the Port Campbell groundwaters were consistent with dissolution of marine carbonate (ca. 0‰) by H_2CO_3 , while the more depleted compositions of the Dilwyn groundwaters reflected a contribution from organic C (-23‰). Isotopic compositions of $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ were -5.1‰ to -3.3‰ for Port Campbell Limestone groundwaters and -5.6‰ to -4.7‰ for the Dilwyn Formation groundwaters. These values deviated from the local meteoric water line, a deviation that was attributed to evaporation or evapotranspiration (de Caritat et al., 2013).

The injected CO_2 had a more enriched $\delta^{13}\text{C}$ value (-6.7‰) than that recorded in the natural baseline, so any CO_2 leakage would cause an increase in $\delta^{13}\text{C}_{\text{DIC}}$ as well as increase in HCO_3^- and associated chemical changes due to pH adjustments over time (de Caritat et al., 2013).

In the Otway case there were no statistically significant changes in chemical compositions between the pre- and post- injection chemical data. Any minor changes were generally in the opposite direction expected for any impact from CO_2 influx to the aquifer. It was concluded that this probably represented a minor dilution effect, resulting from increased rainfall during the monitoring period. Likewise, stable-isotopic compositions of DIC, SO_4 or H_2O in the groundwaters showed little discernible change during the course of the injection or subsequently (de Caritat et al., 2013). Groundwater levels also remained constant in both aquifers throughout drilling, pumping and injection activities and despite an increase in rainfall over the length of the project (de Caritat et al., 2013; Underschultz et al., 2011). The significance of establishing a robust baseline that includes as much natural variability as possible (e.g. droughts, seasonality etc) over a long time period was considered critical (de Caritat et al., 2013).

Headspace gas samples were also taken from the three Dilwyn Formation aquifer boreholes in Stage 1 to detect tracer compounds and CO_2 content. The tracers SF_6 , Kr, and C^2H_4 (deuterated methane) were added to the injected CO_2 . All analyses of these tracers, for both pre- and post- injection samples, were undetected. These data are considered to be of low significance given that initial results suggested that CO_2 measurements were impacted by sampling activities (Hortle et al., 2011).

The injected tracer compounds were also used in other strands of the Stage 1 monitoring programme to confirm breakthrough of injected CO_2 , and as part of soil gas and atmospheric monitoring. Direct measurement of reservoir fluids at the reservoir monitoring borehole is the primary method used to confirm containment of injected CO_2 . The injected tracers ensure that any detection of injected CO_2 is unambiguous (Boreham et al., 2011; Jenkins et al., 2012; Stalker et al., 2015).

Between 2007 and 2012, a baseline and assurance monitoring soil gas survey was undertaken at the Otway site. Sampling was carried out annually, and analysis suggested that there was a shallow source of soil CO_2 , e.g. biological respiration. The concentrations were highly variable over the study period. No deep source of CO_2 , either from the injected CO_2 or other sources, was apparent in the soil-gas samples. While the isotopic composition of the injected CO_2 was distinct from that of local biological respiration, the tracers added to the injected CO_2 could be used to help distinguish any leaked CO_2 (Schacht and Jenkins, 2014).

Atmospheric concentrations and fluxes of CO_2 , isotopic composition ($\delta^{13}\text{C}_{\text{CO}_2}$), and tracers of injected gas (SF_6 , C^2H_4) or combustion (CO) were monitored at a site 700 m to the north-east of the Otway injection well. These were compared to long-term baseline measurements from a site in Tasmania. The results showed large diurnal and seasonal variations in CO_2 , and much of the variability could be modelled. In favourable conditions, small CO_2 emissions, such as emissions from the drilling process or nearby small industry were detected, and confirmed by tracers and modelling. This confirms the atmospheric monitoring has sufficient sensitivity to identify spatially small CO_2 emitters (Jenkins et al., 2012).

None of the assurance monitoring techniques has detected any anomalies at Otway that would indicate the presence of injected CO_2 outside the storage reservoir (Jenkins et al., 2012).

4 Conclusions

A large number of chemical and isotopic tracers in groundwater and gases have potential application in the context of identifying provenance and detailing subsurface migration pathways, mixing and biogeochemical reactions. This report has outlined some of the most commonly applied tracers in the fields of unconventional hydrocarbons and CO_2 storage. Major ions, trace elements and element ratios can be of significant value in identifying subsurface geochemical reactions, but a number of isotopes have provided extra improved insights



into fluid provenance, residence time, migration pathways and mixing processes that can add significant resolution. Stable isotopes of O, H, C, S, Sr, B, Li, Ra and noble gases have proven effective as fluid tracers in number of investigations, although which combinations of tracers are most diagnostic is likely to be location-specific.

Case studies are outlined for two areas originally planned for unconventional hydrocarbon exploration (Vendsyssel, Denmark and Vale of Pickering, UK) and two associated with onshore CO₂ storage (Svelvik, Norway and Otway, Australia). All demonstrate from chemical and isotopic evidence the importance of establishing regional groundwater baseline conditions ahead of any proposed new subsurface geenergy activity.

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