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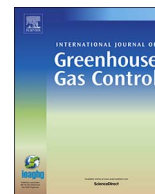
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Using noble gas fingerprints at the Kerr Farm to assess CO₂ leakage allegations linked to the Weyburn-Midale CO₂ monitoring and storage project



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ABSTRACT

For carbon capture and storage technology to successfully contribute to climate mitigation efforts, the stored CO₂ must be securely isolated from the atmosphere and oceans. Hence, there is a need to establish and verify monitoring techniques that can detect unplanned migration of injected CO₂ from a storage site to the near surface. Noble gases are sensitive tracers of crustal fluid input in the subsurface due to their low concentrations and unreactive nature. Several studies have identified their potential to act as tracers of deep fluid migration to the shallow subsurface, but they have yet to be used in a contested situation. In January 2011 it was reported extensively in global media that high CO₂ concentrations in soils and related groundwater pollution had been identified on a farm property belonging to the Kerr family, located near to the town of Weyburn in Saskatchewan, Canada. The origin of this CO₂ pollution was cited to be the nearby Weyburn-Midale CO₂ Monitoring and Storage Project. Here, as part of an investigation funded independently of the Weyburn-Midale field operators, we present $\delta^{13}\text{C}_{\text{DIC}}$, $^3\text{He}/^4\text{He}$, $^4\text{He}/^{20}\text{Ne}$, ^{20}Ne , ^{36}Ar , ^{40}Ar and Kr measured in waters obtained from four groundwater wells located on and surrounding the Kerr property. We aim to establish if stable carbon and noble gas natural tracers are effective at determining if migration of CO₂ from the storage project was responsible for the alleged high CO₂ concentrations and water pollution measured on the Kerr farm. We compare the stable carbon isotope and noble gas ‘fingerprints’ of the Kerr groundwaters to those expected in a water equilibrated with the atmosphere under local recharge conditions, the produced CO₂ obtained from production wells, and the CO₂ injected into the Weyburn and Midale oil fields. We find that the stable carbon isotope data do not constrain the origin of the dissolved CO₂ in the Kerr groundwaters. Due to low noble gas concentrations in the captured CO₂ we are unable to completely rule out the presence of 20–34% contribution from injected CO₂ to the groundwaters surrounding the Kerr property. However, we find that all of the Kerr groundwater samples exhibit noble gas fingerprints that would be expected in a shallow groundwater in contact with the atmosphere and hence there is no evidence for the addition of a deep radiogenic component or dilution from the addition of a gas phase low in atmospheric derived noble gases. Our findings corroborate previous studies that indicate that elevated CO₂ concentrations found on the Kerr property are almost certainly of biological origin, and not migrated from the deep subsurface. The comprehensive follow up to these CO₂ leakage allegations outlined in this study provides a robust framework for responses to any future leakage allegations at CO₂ storage sites and further highlights that no single technique can categorically identify the origin of CO₂ in the shallow subsurface. Hence, it is essential that the full range of geochemical tracers (stable carbon and ^{14}C isotopes, noble gases, water chemistry, process based gas ratios) are integrated with a good understanding of geological and engineering data in response to CO₂ leakage allegations in the future.

1. Introduction

For Carbon Capture and Storage (CCS) technology to be routinely

deployed evidence is required that large volumes of CO₂ can be injected into the subsurface and securely retained. This evidence base can only be provided through evaluation of the containment performance of

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both natural CO₂ reservoirs (Miocic et al., 2013, 2016) and through the evaluation of the security of engineered CO₂ storage sites (Wolaver et al., 2013). Around the world several large scale CO₂ injection projects have been initiated to provide this evidence base. The largest of these is operating at the Weyburn and Midale oil fields in Saskatchewan, Canada, where CO₂ has been introduced into the Weyburn field since 2000, and the Midale field since 2005, to both increase oil recovery, termed CO₂-enhanced oil recovery (EOR), and for storage purposes (Whittaker et al., 2011). The injected CO₂ is sourced from the Dakota Gasification plant in North Dakota and is pumped some 320 km to the oil fields, and ~20 Mt of CO₂ had been injected by the start of 2011 (Whittaker et al., 2011). Currently, 2.4 Mt/year and 0.4 Mt/year of CO₂ are injected into the Weyburn and Midale oil fields, respectively, and it is intended that in excess of 40 Mt of CO₂ will be stored in the fields in total (IEA Greenhouse Gas Programme, 2004).

There are many natural sources of CO₂ within the crust with overlapping geochemical signatures, including breakdown of carbonate minerals or cements, biological activity or hydrocarbon oxidation (Romanak et al., 2014; Wycherley et al., 1999). This makes it extremely difficult to unequivocally detect the small releases of anthropogenic CO₂ that could arise from a diffuse leakage of CO₂ from a storage site. Hence, there is a need to establish and verify monitoring techniques that can detect any unplanned migration of CO₂ from a storage site to the near surface. The requirement for such leakage assessment techniques was clearly demonstrated in January 2011, when landowners living near the International Energy Agency Greenhouse Gas (IEAGHG) Weyburn–Midale CO₂ Monitoring and Storage Project in Saskatchewan, Canada, announced to international media that CO₂ was leaking into the soil and groundwater on their property.

These allegations were based on a soil gas study undertaken over the property in the summer of 2010 by a geochemical consultancy, Petro-Find GeoChem Ltd. This study found that soil gas CO₂ concentrations averaged ~2.3%, and recorded a soil gas anomaly of ~11% measured in the northern portion of the property (Lafleur, 2010). Petro-Find attributed the source of this soil gas anomaly to the CO₂ injected into the nearby Weyburn-Midale CO₂-EOR field based on the measured range of stable carbon isotope ratios ($\delta^{13}\text{C}$) of soil gas being between –21.6 and –22.9‰, similar to the $-20.4 \pm 0.4\text{‰}$ values of the CO₂ injected into the EOR reservoir (Lafleur, 2010).

The Petroleum Technology Research Centre (PTRC), which is responsible for the environmental monitoring of the CO₂ storage project, immediately published a science based response refuting the allegations. This stated that Petro-Find had not taken into account similar soil gas $\delta^{13}\text{C}$ (CO₂) values observed in prairie soils comparable to those on the Kerr property measured on a control site some distance away from the CO₂-EOR field (Rubin and Zhai, 2012), and that there are several other natural sources that could account for the measured $\delta^{13}\text{C}$ (CO₂) values (NETL, 2010; Petroleum Technology Research Centre, 2011). Whilst this went some way to addressing the public fears that the CO₂ leakage allegations raised, there was a clear need for both the fledgling CO₂ storage industry and the local community to have the allegations independently investigated in order to establish if there was any validity to them.

Following the allegations, three separately funded, and independently conducted investigations were launched. The first of these was undertaken by European scientists who had completed 10 years of near-surface monitoring at the nearby Weyburn-Midale CO₂ EOR field (Beaubien et al., 2013). A second study was commissioned by the Weyburn field operators, Cenovus Energy Inc. (Cenovus), and undertaken by three third parties external to Cenovus; TRIUM Environmental, Chemistry Matters and TERA Environmental Consultants. Once completed, the TRIUM Environmental and Chemistry Matters site investigation was then independently reviewed by the PTRC. A third study was co-ordinated by the International Performance Assessment Centre for Geological Storage of CO₂ (IPAC-CO₂), a not-for-profit research and development organisation founded in 2008. IPAC-CO₂ was

established to fill a gap in the understanding and assessment of risk and performance in the Carbon Capture and Storage chain by providing independent, objective information, best practices, advice and assessments to governments and industry (ZeroCO₂.no, Accessed 1st March, 2016). IPAC-CO₂ was funded by Royal Dutch Shell and the Government of Saskatchewan, and hosted at the University of Regina (Saskatchewan, Canada). Prior to the Kerr allegations, IPAC-CO₂ developed an Incident Response Protocol (IRP) that would be implemented if there were allegations of CO₂ leakage at a CCS project (Sherk, 2011). This IRP provided a framework and foundation for the Kerr investigation which comprised three distinct activities undertaken on the Kerr property and surrounding area; (i) chemical analysis of soil gases (Romanak et al., 2014), (ii) stable C isotope and noble gas analysis of the shallow groundwaters (this study), (iii) hydrogeological analysis (Wolaver et al., 2011).

Here, we present measurements of the $\delta^{13}\text{C}$ values of DIC and noble gas measurements ($^3\text{He}/^4\text{He}$, $^4\text{He}/^{20}\text{Ne}$, Ne, Ar and Kr) from waters obtained from four groundwater wells located on and surrounding the Kerr property. We compare these measurements to the geochemical fingerprints expected in a water equilibrated with the atmosphere and those measured in the injected CO₂ and fluids produced from the Weyburn CO₂-EOR reservoir. We use this comparison to assess the role that inherent stable C isotopes and noble gas fingerprints can play in evaluating the validity of the allegations of leakage on the Kerr property.

2. Investigation background

2.1. Scientific background

$\delta^{13}\text{C}_{\text{DIC}}$ measurements have been extensively used in tracing CO₂ injected into the Weyburn field and other CO₂ storage test sites (Johnson et al., 2009; Raistrick et al., 2006). They have proved to be effective at tracking the migration and fate of CO₂ injected into the Weyburn-Midale field (Mayer et al., 2013) and at several shallow CO₂ leakage monitoring pilot projects (Jones et al., 2015; McAlexander et al., 2011; Moni and Rasse, 2014; Schulz et al., 2012). However, the effectiveness of $\delta^{13}\text{C}_{\text{DIC}}$ as a sole means to track the migration of CO₂ injected at depths in excess of a 100 m to the shallow subsurface has yet to be fully quantified (Mayer et al., 2015). CO₂, for example, is both highly soluble and reactive in shallow systems (e.g. Gilfillan et al., 2009) which limits the sensitivity of early seepage detection. There are many sources of DIC in subsurface waters, including the weathering of carbonate and silicate minerals by acid rain, the breakdown of organic matter and plant respiration. Each of these processes leads to wide and overlapping $\delta^{13}\text{C}_{\text{DIC}}$ ranges, meaning the typical range in natural subsurface waters is –5 to –25‰ (Kendall et al., 1995), which is within the range observed when fossil fuel derived CO₂ equilibrates with water (Flude et al., 2016; Petroleum Technology Research Centre, 2011).

Noble gases are intimately associated with all natural and engineered CO₂ occurrences, being trace components in the gas mixture in parts per billion quantities. There are three distinct sources of noble gases within the subsurface, namely the crust, the mantle and the atmosphere, and these can be discriminated and “fingerprinted” by both their isotopic compositions and abundance ratios of each isotope (Ballentine et al., 2002; Gilfillan et al., 2014; Holland and Gilfillan, 2013). Helium, in particular has proved to be effective at tracing deep input to shallow systems due to its extremely low concentration in the atmosphere of 5.2 parts per million (Torgersen et al., 1992). This low abundance allows the presence of small additional quantities of helium above the atmospheric level to be readily resolved. There are only two helium sources that result in concentrations above the atmospheric level in subsurface fluids. Helium produced through the radiogenic decay of U and Th in the crust, which yields the ^4He isotope, with the other source in crustal fluids being the mantle (Ballentine and Burnard, 2002). Helium derived from the Earth’s mantle is contrastingly rich in

the ^3He isotope, and widely contributes to sedimentary fluids (Ballentine et al., 2002; Kennedy and van Soest, 2007; Marty et al., 1992; Oxburgh et al., 1986; Marty et al., 1993; Ballentine et al., 2002; Kennedy and van Soest, 2007). Differing helium inputs from these distinct sources results in a range of $^3\text{He}/^4\text{He}$ ratios being observed in fluids present in almost all sedimentary basins (Ballentine et al., 2002; Castro et al., 1998).

The use of noble gases in tracing CO_2 origins and its fate within natural CO_2 accumulations and hydrocarbon reservoirs has been demonstrated in a number of studies (Gilfillan et al., 2008; , 2009; Györe et al., 2015; Holland and Gilfillan, 2013; Nimz and Hudson, 2005; Zhou et al., 2012). Recent work has shown that noble gases can trace CO_2 dissolved in the groundwater migrating to the surface above the St. Johns Dome natural CO_2 reservoir in Arizona (Gilfillan et al., 2011). The noble gas composition of shallow groundwaters and surface waters found above this natural CO_2 reservoir exhibited low $^3\text{He}/^4\text{He}$ ratios, and elevated $^4\text{He}/^{20}\text{Ne}$ ratios, indicating a clear link to the noble gas composition measured in CO_2 in the deep reservoir below (Gilfillan et al., 2011). This link has been further corroborated by recent cation and trace element analysis of springs and groundwaters in the vicinity of the St. Johns CO_2 reservoir, which confirmed the presence of an additional dissolved CO_2 component in the shallow groundwaters (Keating et al., 2014).

Noble gas fingerprinting techniques have also recently been used to identify micro-seepage of CO_2 and CH_4 above the Teapot Dome oil field in Wyoming (Mackintosh and Ballentine, 2012). This study found that $^3\text{He}/^4\text{He}$ ratios in the soils gas were considerably below the atmospheric ratio, due to the addition of a radiogenic ^4He component, which was also reflected by elevated ^4He concentrations and $^4\text{He}/^{20}\text{Ne}$ ratios relative to atmospheric values. Mackintosh and Ballentine (2012) concluded that the detection of crustal-sourced helium micro-seepage into water saturated systems will be enhanced by two orders of magnitude compared with soil gases. This is due to the low solubility of helium in water which results in a baseline concentration which is two orders of magnitude lower than the expected atmospheric ^4He concentration in a soil gas (Mackintosh and Ballentine, 2012).

Additionally, noble gases have recently proved to be effective at identifying the source of fugitive CH_4 contamination of groundwaters overlying the Marcellus and Barnett shale formations related to shale gas extraction (Darrah et al., 2014), and in resolving the origin of naturally elevated CH_4 levels of shallow groundwaters in the northern Appalachian basin (Darrah et al., 2015). These studies highlighted that groundwater wells with high CH_4 concentrations, located close to gas production wells, had elevated concentrations of ^4He and below expected concentrations of ^{20}Ne and ^{36}Ar (Darrah et al., 2014). The elevated ^4He concentrations were attributed to the presence of thermogenic derived CH_4 gas, whilst the lower than expected concentrations of ^{20}Ne and ^{36}Ar in the waters were attributed to the migrated methane gas having significantly lower ^{20}Ne and ^{36}Ar concentrations than a groundwater in contact with the atmosphere. This results in the migrating methane ‘stripping’ out the ^{20}Ne and ^{36}Ar as noble gases are more soluble in methane than in water. The process is identical to the stripping of formation waters which has been observed in natural CO_2 reservoirs (Gilfillan et al., 2008, 2009; Zhou et al., 2012) and recently in a CO_2 -EOR field (Györe et al., 2017, 2015). This noble gas stripping process provides an additional means to test for the presence of a deep subsurface sourced gas that is depleted in atmospheric noble gases.

2.2. Approach

We aimed to evaluate the effectiveness of $\delta^{13}\text{C}_{\text{DIC}}$, $^3\text{He}/^4\text{He}$, $^4\text{He}/^{20}\text{Ne}$, Ne, Ar and Kr fingerprints in determining the validity of the allegations of CO_2 leakage made on the Kerr property. To achieve this we undertook measurements of a suite of noble gases and C stable isotope tracers from three different sources: (i) CO_2 injected into the field (injected CO_2); (ii) fluids produced from the field (produced CO_2);

(iii) groundwaters at the Kerr property and surrounding area (Kerr groundwaters). We aimed to determine if migration CO_2 originating from either the CO_2 injected into, or CO_2 contained in the fluids produced from the Weyburn field was responsible for the alleged elevated CO_2 concentrations on the Kerr property. To do this we compare the noble gas and C isotope fingerprints between type (i), (ii) samples to those of type (iii), the Kerr groundwaters.

Based on the studies outlined in the Scientific Background section we hypothesise that any external CO_2 addition to the Kerr groundwaters, bar those of shallow subsurface biologic processes, would result in either the addition of crustal derived ^4He and/or a depletion in the main atmospheric derived noble gases of ^{20}Ne , ^{36}Ar , ^{40}Ar and Kr. The addition of a crustal radiogenic ^4He component can be identified by elevated $^4\text{He}/^{20}\text{Ne}$ ratios above those of the atmosphere and/or a reduction in $^3\text{He}/^4\text{He}$ ratios below those of atmospheric values. We focus on the Kerr groundwaters as opposed to soil gases based on the study of Mackintosh and Ballentine (2012) which showed helium anomalies would be enhanced by two orders of magnitude compared with soil gases as a result of the low solubility of helium in water.

3. Methods

Sample collection was undertaken over a period of three days in late June 2011, some 11 months following the soil gas sampling undertaken in the previous summer on which the leakage allegations were based (Lafleur, 2010). Samples of injected CO_2 were collected from a the sampling port of a Cenovus injection well (Well ID – 101/12-04-006-13 W2/0) located approximately 10 km northwest of the Kerr quarter. A sample of CO_2 separated from the produced reservoir fluids (produced gas, water and oil) was collected from the sampling port of the flowline emerging from a Cenovus satellite processing facility located at 16-30-05-13 (Fig. 1). This flowline contained produced gas separated by the first stage separation system at the satellite site from the oil, gas and water collected from 14 production wells that surrounded the Kerr property. Gases were collected from both the pressurised injection well and the satellite processing facility flow line using a high pressure to low pressure step down regulator, allowing gas collection at slightly above atmospheric pressure in 70 cm long vacuum tight copper tubes held in aluminium clamps. Shallow groundwaters were collected from the domestic groundwater well on the Kerr farm, two domestic groundwater wells on the adjacent Thackeray farm and the IPAC No. 1 monitoring well which was drilled during the sampling program. This was located as close to the maximum CO_2 anomaly reported by Petro-Find as possible given the underlying ground conditions required for the drilling rig (Lafleur, 2010) (Fig. 1). All of the wells were of standard shallow groundwater bored type construction, drilled using a rotary bucket auger and completed with PVC casing utilising a sand screen at the base. Each well was 0.762 m in diameter, ranging in depth below ground surface from 3.09 m (Thackeray Farm Well) to 12.29 m (Thackeray House Well). Groundwater was encountered between 1.76 m (IPAC ~ 1 monitoring well) and 3.56 m below ground level. Samples were collected from the base of the well water volumes using a peristaltic pump, with each well being pumped until water chemistry parameters stabilised before sample collection.

$\delta^{13}\text{C}$ (CO_2) values of the gas samples and $\delta^{13}\text{C}_{\text{DIC}}$ values of the waters were determined at the University of Rochester using a Delta S (Finnigan) mass spectrometer and the analytical error was $\pm 0.2\%$. Standard extraction and purification procedures were used (Jenden et al., 1993) and the ratios are expressed as $\delta^{13}\text{C} \text{‰ V-PDB}$. The dissolved gases were extracted on a stainless steel and 1720 glass extraction line at the University of Rochester using standard procedures (Poreda et al., 2004). Noble gas isotopic ratios ($^3\text{He}/^4\text{He}$, $^{20}\text{Ne}/^{22}\text{Ne}$, $^{21}\text{Ne}/^{22}\text{Ne}$, $^{40}\text{Ar}/^{36}\text{Ar}$, $^{38}\text{Ar}/^{36}\text{Ar}$) and elemental abundances (^4He , ^{20}Ne , ^{40}Ar and Kr) were determined on the University of Rochester’s VG 5400 mass spectrometer, using established techniques (Poreda and Farley, 1992). Bulk gases were purified by consecutive exposure to a Zr-

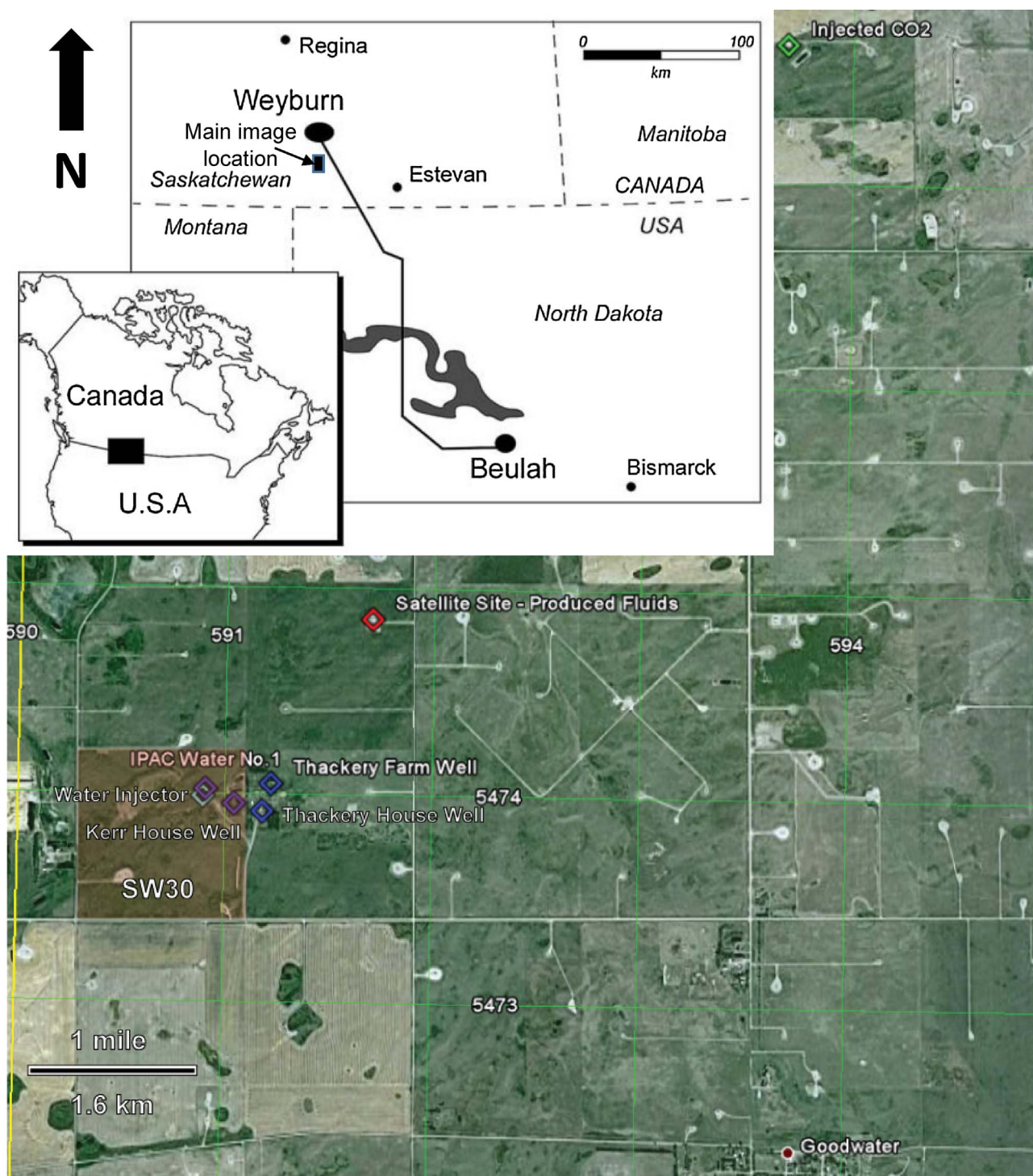


Fig. 1. Location Map (inset) showing the location of the Weyburn-Midale CO₂ Storage and Monitoring Project and the approximate location of the CO₂ pipeline which transports CO₂ to the field from Beulah, North Dakota after (Emberley et al., 2004). Main image is an aerial photograph showing the localities of the wells sampled in this study in relation to the town of Goodwater and the Kerr property (SW30). Grid lines indicate the UTM grid, aerial photograph courtesy of Google.

Al getter (SAES ST-707) held at 450 °C and a SAES SORB-AC cartridge held at 250 °C then cooled to 25 °C. This was followed by the sequential trapping of Ar into an activated charcoal finger at liquid N₂ temperature (−178 °C) and the He and Ne into an activated charcoal finger at −261 °C. He was released from the cryogenic finger at −242 °C and expanded into the spectrometer and measured, followed by Ne and Ar analyses. He, Ne, Ar, and Kr concentrations were determined by comparison to an air standard of known volume (0.77 cm³). Helium isotope ratios were normalized using a Rochester air standard. Neon isotope

ratios were corrected for interference by measurement of ⁴⁰Ar²⁺ and CO₂²⁺ (⁴⁰Ar²⁺ was typically < 0.4% of total ²⁰Ne signal on the faraday cup and CO₂²⁺ was below detection limits for ²²Ne). The two sigma analytical error for the ³He/⁴He ratio is approximately 0.5% and those for both the ⁴⁰Ar/³⁶Ar and He/Ne isotope ratios were 0.2%, and 0.3% for ³⁸Ar/³⁶Ar and 1% for ²⁰Ne/²²Ne, ²¹Ne/²²Ne and ²⁰Ne/³⁶Ar and 1.5% for all noble gas abundances. Helium isotope ratios (³He/⁴He) are expressed relative to the ratio in air ($R_a = R_{\text{measured}}/R_{\text{air}}$ where $R_{\text{air}} = 1.399 \times 10^{-6}$). All other ratios are absolute values. The

majority of the duplicate sample ratios and concentrations are within 5% of each other. Two sigma errors to the last significant figure are reported for both gas ratios and concentrations and these may be taken as limits of detection for small associated data values.

We report the concentrations of noble gases dissolved in water, rather than the concentrations of noble gases in the headspace gas degassed from the waters. This is because the amount of headspace (ie non noble gas) gases exsolved from the Kerr groundwaters was insufficient to obtain high quality ratio concentrations of noble gases relative to the total exsolved gas. However, the concentration of the individual noble gases degassed from the water samples was sufficient for high quality analysis to be performed; hence these concentrations are presented relative to the amount of water degassed. Reporting the dissolved noble gas concentration in groundwaters in this manner is standard practice in shallow groundwaters where small quantities of dissolved gases are present (Kipfer et al., 2002).

To allow direct comparison between the different sample types, and to detect any external input to the Kerr groundwaters from the Weyburn EOR operations, we calculate the noble gas concentration in water that would arise from equilibrium of the noble gases within the injected and produced CO₂ with a shallow groundwater in the area surrounding the Kerr property. Using the average measured groundwater well water temperature of 14.3 °C (IPAC-CO₂, 2011), pressure of 0.101 MPa (1 atm) and salinity value of 0.02 Molar NaCl (equivalent to the average TDS value of 1034 mg l⁻¹, (IPAC-CO₂, 2011)) we calculate the Henry's constants using empirical equations (Crovetto et al., 1982; Smith, 1985). Under these conditions the calculated Henry's constants for He, Ne, Ar, Kr and Xe are 14.12, 11.69, 3.41, 1.80 and 1.19 GPa, respectively.

We also calculate the expected concentration and isotope ratio ranges of atmosphere-derived noble gases dissolved in the groundwater, known as air-saturated water (ASW). These concentrations and ratios were obtained using established solubility equilibrium techniques (Kipfer et al., 2002), taking the range of regional recharge conditions of 10–25 °C (Environment Canada), an average site altitude of 580 m and assumed an entrained excess air Ne component of between 10–45%. Excess air is the term given to explain the common observation that groundwaters contain atmosphere derived noble gases in excess, resulting in dissolved noble gas concentrations which are significantly larger than the expected calculated solubility equilibrium concentrations (Kipfer et al., 2002). Excess air is measured relative to Ne concentrations and is typically in the range of 10–50% (Kipfer et al., 2002). As the excess air contribution only effects the atmosphere-derived noble gases, this phenomenon will not impact on the detection of a radiogenic ⁴He noble gas component in the groundwaters.

4. Results

4.1. $\delta^{13}\text{C}$ (CO₂) and $\delta^{13}\text{C}_{\text{DIC}}$ values

The measured $\delta^{13}\text{C}$ (CO₂) of the CO₂ injected into the Weyburn field of $-21.2 \pm 0.2\text{‰}$ is similar to the average value of $-20.4 \pm 0.3\text{‰}$ previously reported from analysis of 8 samples of injected CO₂ and 8 samples of recycled CO₂ from the Weyburn reservoir collected between 2000 and 2010 (Mayer et al., 2013). The measured produced CO₂ $\delta^{13}\text{C}$ (CO₂) duplicate values obtained in this study were -14.8 and $-12.4 \pm 0.2\text{‰}$ (Table 1), somewhat above the range of -16.5 and -17.7‰ observed by Mayer et al. (2013) in the final stage of their study of produced gases from the Weyburn field in late 2010. The sampled Kerr groundwaters exhibit $\delta^{13}\text{C}_{\text{DIC}}$ values ranging from $-13.4 \pm 0.2\text{‰}$ to $-19.0 \pm 0.2\text{‰}$ (Table 1).

4.2. Noble gas concentrations

⁴He concentrations exhibit marked distinctions depending on sample type (Fig. 2). The lowest concentration of

$41.63 \pm 0.5 \mu\text{m}^3\text{kg}^{-1}$ is that calculated for a shallow groundwater which has equilibrated with the injected CO₂ (see Methods). The groundwaters sampled from the wells on and around the Kerr property (the Kerr groundwaters) exhibit a range of 39.2 ± 0.6 to $86.9 \pm 1.3 \mu\text{m}^3\text{kg}^{-1}$ which is almost identical to the air saturated water (ASW) concentration range of 42.1 ± 0.6 to $85.8 \pm 1.2 \mu\text{m}^3\text{kg}^{-1}$. This indicates that there is no presence of ⁴He in excess of the concentration calculated for equilibrium dissolution of atmospheric noble gases into a groundwater under the recharge conditions present at the study site (see Methods). The ⁴He concentration of a shallow ground water in equilibrium with the produced CO₂ is two orders of magnitude higher than the values recorded from the Kerr groundwaters, ranging from 7634 ± 115 to $18313 \pm 275 \mu\text{m}^3\text{kg}^{-1}$.

²⁰Ne, ³⁶Ar, ⁴⁰Ar and Kr in the shallow subsurface are primarily derived from the atmosphere. Similar to ⁴He, the lowest ²⁰Ne, ³⁶Ar, (Fig. 3) ⁴⁰Ar (Fig. 2) and Kr concentrations are those for a formation water in equilibrium with the injected CO₂. However, in contrast to ⁴He, the next lowest ²⁰Ne, ³⁶Ar, ⁴⁰Ar and Kr concentrations are those calculated for a shallow groundwater water in equilibrium with produced CO₂ from the Weyburn field (Table 2). The highest noble gas concentrations are those measured in the Kerr groundwaters, which overlap with the calculated ASW range (Table 1 and Figs. 2 and 3).

4.3. Noble gas isotope ratios

⁴He/²⁰Ne ratios exhibit considerable variation depending on sample type. The lowest ratios are those observed in the Kerr groundwaters which vary from 0.248 ± 0.006 to 0.403 ± 0.010 , overlapping with the ASW range of 0.288 ± 0.007 – 0.325 ± 0.01 (Fig. 4). The injected CO₂ exhibits a higher ratio of 12.6 ± 0.3 , with the duplicate produced CO₂ samples ranging from 1000 ± 21 to 1488 ± 31 , significantly above the calculated air saturated water (ASW) range (Fig. 4). The above ASW ratios of the produced CO₂ indicate an excess of ⁴He above atmospheric levels.

³He/⁴He vary considerably between the different sample types, with the lowest values of 0.173 ± 0.001 and $0.179 \pm 0.001 R_a$ (where R_a is the air ³He/⁴He ratio of 1.399×10^{-6}) being observed in the CO₂ produced from the Weyburn field (Fig. 5). The CO₂ injected into the Weyburn field has a slightly higher ratio of $0.193 \pm 0.001 R_a$. The range observed in the Kerr groundwaters of 0.880 ± 0.004 to $1.103 \pm 0.006 R_a$ is significantly above that of the other samples (Fig. 5).

Other noble gas ratios of the Kerr groundwaters are within the range expected for ASW; the ²¹Ne/²²Ne are within 2 sigma error of the ASW ratio of 0.0290 ± 0.003 . ⁴⁰Ar/³⁶Ar are also all within error of the calculated ASW range of 294 – 296 ± 1 . The only non-atmospheric ratios observed are ²⁰Ne/²²Ne that range from 9.96 ± 0.10 to 10.15 ± 0.10 , in excess of the air ratio of 9.80 ± 0.08 . The elevation of ²⁰Ne/²²Ne is a common observation in natural groundwaters and is thought to be the result of a solubility controlled fractionation process, where ²⁰Ne dissolves preferentially to ²²Ne (Zhou et al., 2005).

5. Discussion

5.1. Comparison of results to previous measurements from the Weyburn CO₂-EOR field

For logistical and budgetary reasons it was not possible to undertake sampling in the area on and surrounding the Kerr property on multiple occasions, over an extended period. Whilst this is an obvious limitation of our study, Mayer et al. (2013) have produced an extensive compilation of both $\delta^{13}\text{C}$ (CO₂) and $\delta^{13}\text{C}$ of DIC from both injected CO₂ and produced fluid samples collected at the Weyburn field over a 10 year period from 2000 to 2010. Our measured $\delta^{13}\text{C}$ (CO₂) of the injected CO₂ of $-21.2 \pm 0.2\text{‰}$ is comparable to the average value of $-20.4 \pm 0.3\text{‰}$ previously reported from analysis of 8 samples of

Table 1

Sample location, type, noble gas and carbon isotope ratio measurements, values in brackets are 2 sigma error margins to last significant figure.

Sample Name	Location (UTM zone 13)	Sample Type	$^3\text{He}/^4\text{He}$ (R _a)	$^{20}\text{Ne}/^{22}\text{Ne}$	$^{21}\text{Ne}/^{22}\text{Ne}$	$^{40}\text{Ar}/^{36}\text{Ar}$	$^4\text{He}/^{20}\text{Ne}$	$^{20}\text{Ne}/^{36}\text{Ar}$	$^{84}\text{Kr}/^{36}\text{Ar}$	$\delta^{13}\text{C}_{\text{DIC}}$ (‰)
101/12-04-006-13 W2/0	593685 5477689	Injected CO ₂	0.193 (1)	10.24 (2)	0.0295 (1)	352.9 (7)	14.5 (3)	0.940 (9)	0.147 (2)	-21.2 (2) ⁺
16-30-05-13 No. 1	591704 5474850	Produced CO ₂	0.173 (1)	9.82 (2)	0.0280 (1)	524.7 (10)	1149 (20)	0.192 (2)	0.0313 (3)	-14.8 (2) ⁺
16-30-05-13 No. 2	591704 5474850	Produced CO ₂	0.179 (1)	9.87 (2)	0.0288 (1)	529.0 (11)	1710 (30)	0.229 (2)	0.0055 (1)	-12.4 (2) ⁺
Thackery Farm Well No. 1	591223 5474051	Groundwater	0.880 (4)	9.96 (2)	0.0292 (1)	294.9 (6)	0.248 (4)	0.202 (2)	0.0256 (3)	-16.8 (2)
Thackery Farm Well No. 2	591223 5474051	Groundwater	1.034 (5)	10.10 (2)	0.0292 (1)	297.4 (6)	0.357 (6)	0.174 (2)	0.0251 (3)	-16.0 (2)
Thackery House Well	591183 5473918	Groundwater	1.079 (5)	10.15 (2)	0.0293 (1)	294.8 (6)	0.313 (5)	0.142 (2)	0.0305 (3)	-16.2 (2)
Kerr Well Water No. 1	591046 5473954	Groundwater	1.103 (6)	10.14 (2)	0.0293 (1)	297.5 (6)	0.403 (7)	0.190 (2)	0.0256 (3)	-19.0 (2)
Kerr Well Water No. 2	591046 5473954	Groundwater	0.914 (5)	10.13 (2)	0.0291 (1)	297.3 (6)	0.379 (7)	0.156 (2)	0.0260 (3)	-15.9 (2)
IPAC Water No. 1	590907 5474023	Groundwater	0.897 (4)	10.05 (2)	0.0293 (1)	294.9 (6)	0.312 (5)	0.145 (2)	0.0314 (3)	-13.4 (2)
101/06-30-005-13W 2/0	590895 5473977	Injected Water	0.295 (1)	10.31(2)	0.0287 (1)	303.9 (6)	1.42 (3)	0.460 (5)	0.0262 (3)	-20.7 (2)
Air Saturated Water (ASW) 15 °C	-	0% Excess Air Ne	1.000 (5)	9.80 (8)	0.0290 (1)	296.1 (6)	0.254 (7)	0.141 (1)	0.0401 (2)	-
Air Saturated Water (ASW) 15 °C	-	45% Excess Air Ne	1.000 (5)	9.80 (8)	0.0290 (1)	294.1 (6)	0.286 (8)	0.221 (2)	0.0357 (2)	-
Air Saturated Water (ASW) 25 °C	-	0% Excess Air Ne	1.000 (5)	9.80 (8)	0.0290 (1)	296.1 (6)	0.273 (9)	0.169 (4)	0.0371 (2)	-
Air Saturated Water (ASW) 25 °C	-	45% Excess Air Ne	1.000 (5)	9.80 (8)	0.0290 (1)	293.8 (6)	0.296 (10)	0.254 (6)	0.0328 (2)	-

⁺ This value is the $\delta^{13}\text{C}$ (CO₂) of the CO₂ injected into the Weyburn oil reservoir for EOR.

* Both of these are $\delta^{13}\text{C}$ (CO₂) measurements of the CO₂ in the fluids produced from Well 16-30-05-13, which contained the separated gases from 14 producing oil wells at the Weyburn field.

Air saturated water (ASW) noble gas ratios calculated using an average elevation of 580 m above Sea Level (canmaps.com) and a groundwater recharge temperature range of 15 – 25 °C (Environment Canada) assuming 0% and 45% excess air Ne, using the methods outlined by Kipfer et al. (2002).

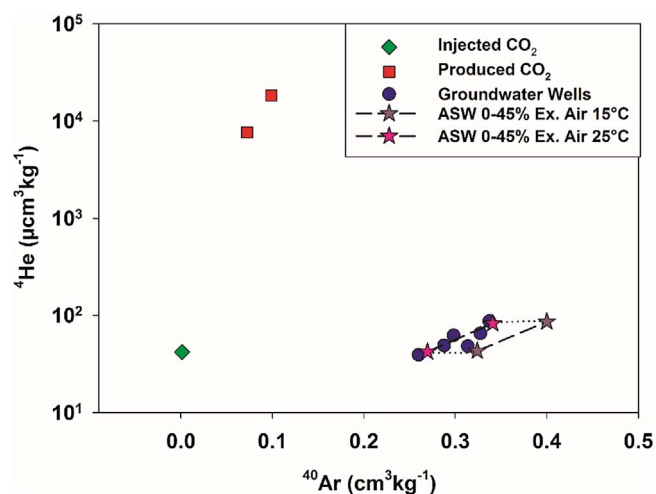


Fig. 2. ^4He plotted against ^{40}Ar for the Kerr groundwaters, CO₂ and fluids produced from the Weyburn field. ^4He and ^{40}Ar are both produced in the crust by radioactive decay, and so are more abundant in deep derived fluids. The Kerr groundwater samples plot within the concentrations expected in a shallow groundwater, termed air saturated water (ASW), recharging under the summer temperature conditions experienced in Saskatchewan (15–25 °C), including a typical excess air component of 10–45%. All analytical error bars are smaller than printed symbols.

source CO₂ and 8 samples of injected CO₂ (which includes the source CO₂ and a small recycled component) from the Weyburn reservoir collected between 2000 and 2010 (Mayer et al., 2013). This indicates that our injected CO₂ sample is representative of the CO₂ injected into the Weyburn field over its history.

The produced CO₂ $\delta^{13}\text{C}$ (CO₂) duplicate values obtained in this study were -14.8 and -12.4 ± 0.2‰ (Table 1), somewhat above the range of -16.5 and -17.7‰ observed by Mayer et al., 2013 in the final stage of their study of produced gases from the Weyburn field in late 2010. This variation can be explained by the fact that we sampled from a satellite site producing fluids from a suite of injection wells located nearest to the Kerr property which is part of flood phase 1C rather than those of phase 1A sampled by Mayer et al. (2013). Injection of CO₂ into the Phase 1A area of the field commenced in 2000, with injection into the Phase 1C portion of the field commencing in 2003

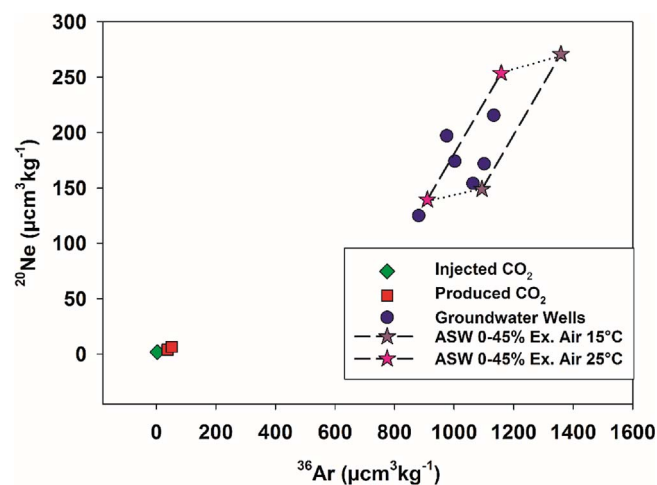


Fig. 3. ^{20}Ne plotted against ^{36}Ar for the Kerr groundwaters, CO₂ injected and fluids produced from the Weyburn field. Both ^{20}Ne and ^{36}Ar in shallow groundwaters are primarily derived from the atmosphere. The Kerr groundwater samples plot within the expected concentrations in a shallow groundwater, bar one sample (Thackery House well), which shows a slight depletion in ^{20}Ne compared to the calculated ASW range. Both ^{20}Ne and ^{36}Ar values in the produced fluids and the injected CO₂ are two orders of magnitude lower than those measured in the Kerr groundwaters. All analytical error bars are smaller than printed symbols.

(Chalaturnyk and Durocher, 2005). Mayer et al. (2013) show that $\delta^{13}\text{C}$ (CO₂) values decrease from the reservoir baseline value of -12.7‰ over time throughout their study, as more of the injected CO₂ reaches the production wells, and a similar evolution would be expected in the phase 1C region of the field.

Whilst it would obviously have been beneficial to undertake multiple measurements of the CO₂ injected into and CO₂ produced from the Weyburn CO₂-EOR field, the above comparison shows that the samples we have collected are representative of the range of CO₂ injected and CO₂ produced from the Weyburn field since CO₂ injection commenced in 2000 (Mayer et al., 2013).

Table 2

Noble gas and HCO₃⁻ concentrations, values in brackets are 2 sigma error margins to last significant figure.

Sample Name	Sample Type	⁴ He (μcm ³ kg ⁻¹)	Ne (μcm ³ kg ⁻¹)	²⁰ Ne (μcm ³ kg ⁻¹)	⁴⁰ Ar (cm ³ kg ⁻¹)	³⁶ Ar (μcm ³ kg ⁻¹)	Kr ((μcm ³ kg ⁻¹))
101/12-04-006-13 W2/0	Injected CO ₂	41.8 (4)	3.64 (4)	3.13 (5)	0.00431 (4)	12.21 (3)	5.99 (6)
16-30-05-13 No. 1 ⁺	Produced CO ₂	7634 (76)	8.40 (8)	7.63 (10)	0.0724 (7)	138 (2)	14.4 (2)
16-30-05-13 No. 2 ⁺	Produced CO ₂	18313 (183)	13.5 (2)	12.3 (17)	0.0986 (10)	186 (2)	3.44 (4)
Thackery Farm Well No. 1	Groundwater	48.8 (5)	217 (3)	197 (3)	0.288 (3)	976 (10)	43.9 (5)
Thackery Farm Well No. 2	Groundwater	62.1 (7)	192 (2)	174 (3)	0.298 (3)	1003 (10)	44.2 (5)
Thackery House Well	Groundwater	39.2 (4)	137 (2)	125 (2)	0.260 (3)	882 (9)	47.2 (5)
Kerr Well Water No. 1	Groundwater	86.9 (9)	237 (3)	215 (3)	0.337 (4)	1133 (12)	51.0 (6)
Kerr Well Water No. 2	Groundwater	65.1 (7)	189 (2)	171 (3)	0.327 (4)	1101 (11)	50.3 (5)
IPAC Water No. 1	Groundwater	48.1 (5)	169 (2)	154 (2)	0.314 (4)	1064 (11)	58.7 (6)
101/06-30-005-13W 2/0	Injected Water	288 (3)	223 (3)	202 (3)	0.134 (2)	440 (5)	20.2 (2)
Air Saturated Water (ASW) 15 °C	0% Excess Air Ne	42.9 (6)	165 (4)	149 (4)	0.324 (3)	1094 (6)	42.6 (3)
Air Saturated Water (ASW) 15 °C	45% Excess Air Ne	85.8 (12)	299 (7)	271 (7)	0.400 (3)	1359 (12)	48.0 (4)
Air Saturated Water (ASW) 25 °C	0% Excess Air Ne	42.1 (6)	154 (4)	139 (5)	0.270 (3)	910 (20)	33.7 (3)
Air Saturated Water (ASW) 25 °C	45% Excess Air Ne	82.3 (12)	280 (6)	253 (8)	0.341 (8)	1159 (26)	36.7 (4)

⁺ Noble gas concentrations for groundwater in equilibrium with the produced CO₂ and injected CO₂ calculated from original gas concentrations using the average groundwater temperature of 14.3 °C, salinity of 0.02 Molar NaCl and pressure of 0.101 MPa, as measured during this study.

[^] Air saturated water concentrations calculated using an average elevation of 580 m above Sea Level (canmaps.com) and a groundwater recharge temperature range of 15–25 °C (Environment Canada) assuming 0% and 45% excess air Ne.

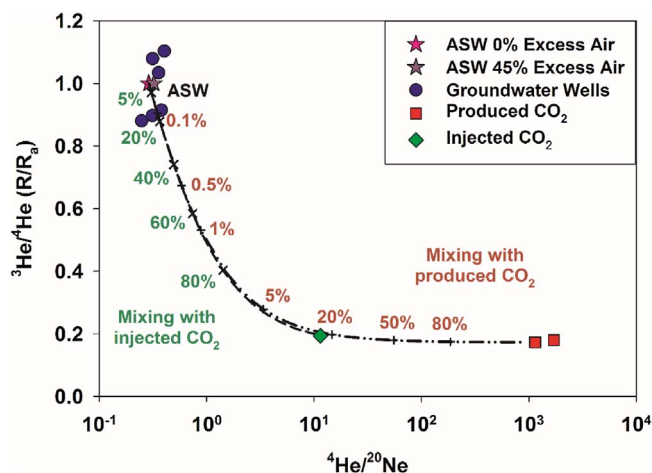


Fig. 4. ³He/⁴He plotted against ⁴He/²⁰Ne for the Kerr groundwaters and CO₂ injected into the Weyburn field. Three of the groundwater samples exhibit above ASW ³He/⁴He ratios. The ⁴He/²⁰Ne ratio of ASW is well constrained at 0.15–0.17 under the recharge conditions experienced in the summer in Saskatchewan. High ²⁰Ne content relative to ⁴He is a strong indicator of atmospheric input. The produced CO₂ and injected CO₂ exhibit ⁴He/²⁰Ne well above those of ASW. All analytical error bars are smaller than printed symbols.

5.2. δ¹³C_{DIC} values

Mayer et al. (2013) found that as CO₂ concentrations increased at the Weyburn production wells, the δ¹³C CO₂ values progressively approached those of the injected CO₂ (−20.4 ± 0.3‰ from the 16 samples outlined previously). Using their measured reservoir pH values they predicted that the δ¹³C of DIC in equilibrium with the injected CO₂ would be −19 ± 2‰. However, they found that their measured values approached a value of only −16‰, indicating that there was an additional HCO₃⁻ source with elevated δ¹³C DIC values within the reservoir. Increasing concentrations of calcium and magnesium provided independent evidence that calcite and dolomite dissolution had generated additional HCO₃⁻, resulting in a contribution of HCO₃⁻ with a δ¹³C_{DIC} value of +3‰.

Hence, the difference of δ¹³C of DIC (composed of DIC in isotopic equilibrium with injected CO₂ and DIC derived from carbonate dissolution) and δ¹³C of injected CO₂ was +4.4‰. “In order to allow direct comparison to the measured δ¹³C DIC values in the Kerr groundwaters we use this fractionation value to calculate the δ¹³C_{DIC} which would be produced in water in equilibrium with CO₂ which has the

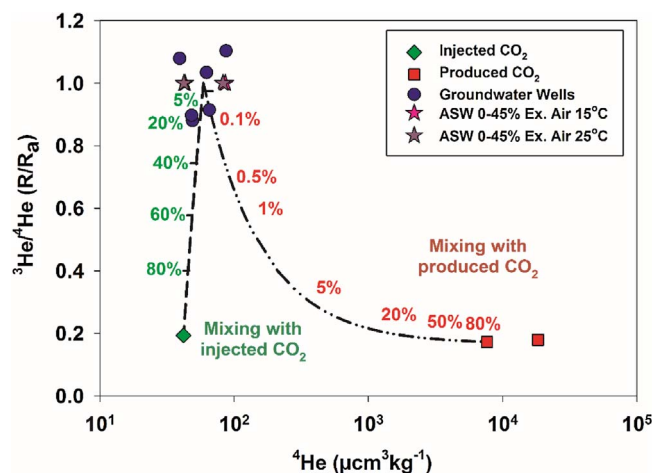


Fig. 5. ³He/⁴He plotted against ⁴He in the injected and produced CO₂ from the Weyburn field and the sampled groundwaters surrounding the Kerr property. All of the shallow groundwater samples exhibit ⁴He concentrations that are within the range expected in ASW. Mixing lines on the plot depict the trend which would result from mixing a groundwater with the best case ASW ³He/⁴He ratio of 1 R_a and the average ⁴He concentration measured in the Kerr groundwaters, with the CO₂ injected into and produced from the Weyburn field. All analytical error bars are smaller than printed symbols.

δ¹³C (CO₂) of both the injected (−21.2 ± 0.2‰) and produced CO₂ (−14.8 and −12.4 ± 0.2‰). Using this fractionation value we calculate a δ¹³C_{DIC} value of −16.8 ± 0.2‰ for water in contact with the injected CO₂ and a δ¹³C_{DIC} range of −10.4 to −8.0 ± 0.2‰ for water in contact with the produced CO₂.

The range of δ¹³C_{DIC} values measured in the Kerr groundwaters of −13.4 ± 0.2‰ to −19.0 ± 0.2‰, overlaps with that of water in contact with the injected CO₂ and is distinct from those exhibited by water in contact with the produced CO₂. This indicates that there is a potential link between the δ¹³C_{DIC} values in the Kerr groundwaters and the injected CO₂. However, this is not an unequivocal link as there are multiple sources of DIC in shallow groundwaters, with each of the sources exhibiting overlapping δ¹³C_{DIC} ranges. This results in a typical δ¹³C_{DIC} range in natural subsurface waters of −5 to −25‰ (Kendall et al., 1995). Hence, natural soil processes including plant respiration, dissolution of carbonate minerals and bacterial activity could account for the range of −13.4 ± 0.2‰ to −19.0 ± 0.2‰ observed in the Kerr groundwaters (Hendry et al., 1999; Keller and Bacon, 1998; Petroleum Technology Research Centre, 2011; Romanak et al., 2014).

Mayer et al. (2015) have undertaken a comprehensive review of the

usefulness of the stable isotope composition of CO₂ for leakage monitoring at CO₂ storage sites, which concluded that δ¹³C can be a useful tracer if values in the injected CO₂ are distinct from those of baseline δ¹³C (CO₂, DIC) at the CCS site by more than 10‰. Extensive soil gas measurements were undertaken in the vicinity of the Weyburn CO₂-EOR field prior to CO₂ injection commencing in 2001 and after 10 years of injection in 2011 (Beaubien et al., 2013). Beaubien et al. (2013) found that regional δ¹³C CO₂ soil gas values ranged from −17.3 to −23.1‰, overlapping with the range measured on the Kerr property of −21.7 to −22.7‰ by Romanak et al. (2014) and the average value of the injected CO₂ of −20.4 ± 0.3‰ as reported by Mayer et al. (2013). These studies highlight that δ¹³C measurements alone cannot be used as a distinctive means to determine the origin of CO₂ measured on the Kerr property as also outlined by a recent signal to noise analysis (Risk et al., 2015).

5.3. Mixing modelling

Noble gases offer an additional means of pinpointing gas sources, due to the distinct deep crustal origin of ⁴He and the atmospheric source of ²⁰Ne and ³⁶Ar. Our results show that all of the noble gas concentrations and isotope ratios measured in the Kerr shallow groundwater samples are within the calculated ASW ranges (the values resulting from dissolution of atmospheric noble gases into shallow groundwater), bar those of ²⁰Ne/²²Ne and a single sample which plots below the ASW range of ²⁰Ne and ³⁶Ar (Thackeray House Well). This observation implies that there is no additional source of noble gases to these groundwaters bar equilibration with the atmosphere. This is distinct from observations of elevated ⁴He concentrations and depleted ²⁰Ne and ³⁶Ar values in studies where deep gas migration to the shallow subsurface has been documented (Darrah et al., 2015; Darrah et al., 2014; Gilfillan et al., 2011).

However, three of the Kerr groundwater samples exhibit below ASW ³He/⁴He ratios which could indicate an additional low ³He/⁴He component to these waters (Mackintosh and Ballentine, 2012). In order to fully resolve the presence of any non-atmospheric contribution to these groundwater samples, we now model how ⁴He concentrations, ³He/⁴He and ⁴He/²⁰Ne ratios of ASW would evolve through mixing with either the injected or produced CO₂ from the Weyburn field. As the ASW noble gas fingerprint is determined by the solubility equilibration of the noble gases in contact with the atmosphere (see Methods) under the local recharge conditions, ASW is the accepted standard for a shallow groundwater which is uncontaminated from any other inputs (Kipfer et al., 2002). Using these three end members, mixing lines for both ratio–ratio plots and ratio–element plots can be plotted using established techniques (Langmuir et al., 1978). The direct comparison of these mixing models with the Kerr groundwater noble gas composition allows resolution of the possible contribution to the waters from both the injected or produced CO₂.

5.4. ³He/⁴He ratios and ⁴He concentrations

In Fig. 5 a plot of ³He/⁴He and ⁴He of the Kerr groundwaters is shown. Mixing lines on the figure depict the calculated trends which would result from mixing of the CO₂ injected into, and the CO₂ produced from the Weyburn field with a shallow groundwater with an ASW ³He/⁴He (1 R_a) and the average ASW ⁴He concentration. Tick marks indicate the portion of ⁴He originating from either the CO₂ injected or CO₂ produced from the Weyburn field on the mixing lines presented. Three of the measured groundwaters contain an excess of ³He relative to the predicted concentration in ASW, resulting in ³He/⁴He ratios above the ASW ratio of 1 R_a. This can be explained by the presence of ³He originating from the decay of tritium which was emitted to the atmosphere as a result of nuclear weapons testing from the 1950s to 1980s (Happell et al., 2004). This additional ³He component is variable and creates some uncertainty around the baseline

³He/⁴He ratio of the groundwater in the region. Hence, to account for this variation we also use the higher value of 1.1 R_a as a worst case scenario for assessing the portion of noble gases originating from either the CO₂ produced from, or injected into, the Weyburn field.

The three Kerr groundwaters with below ASW ³He/⁴He ratios lie close to the two mixing lines plotted. The concentration of ⁴He measured in the fluids produced from the Weyburn field is two orders of magnitude higher than the atmospheric value, as a result of crustal radiogenic contributions from interaction with the crustal fluids present in the EOR field (Fig. 5). This is reflected in the higher than ASW ⁴He/²⁰Ne and lower than ASW ³He/⁴He ratios exhibited by the produced CO₂ gas sample (Fig. 4). Using the mixing model presented allows us to resolve that the Kerr groundwater with the lowest ³He/⁴He could conceivably contain a maximum 0.14% contribution to ⁴He from the produced fluids using the best case ³He/⁴He endmember (1 R_a) or a 0.25% contribution using the worst case ³He/⁴He endmember (1.1 R_a).

Fig. 5 highlights that a 20% contribution using the best ³He/⁴He (1 R_a) end member and a 32% contribution in the worst case (1.1 R_a) end member contribution to the Kerr groundwaters from the injected CO₂ could account for the lowest ³He/⁴He ratio observed. This is a reflection of the ⁴He concentration of the injected CO₂ being at the lower range of the ASW concentration expected in the shallow groundwaters recharging at the summer temperatures experienced in Saskatchewan.

5.5. ³He/⁴He and ⁴He/²⁰Ne ratios

Plots of ³He/⁴He against ⁴He/²⁰Ne ratios of the Kerr groundwaters, along with measured ratios in the CO₂ produced and injected into the Weyburn EOR field are shown in Fig. 4. Mixing lines are shown with tick marks indicating the portion originating from either the CO₂ injected or produced from the Weyburn EOR field. The ⁴He/²⁰Ne ratios measured in samples of the produced and injected CO₂ into the Weyburn field are above the ASW range of 0.288 ± 0.001–0.322 ± 0.001, and all of the Kerr groundwaters exhibit ⁴He/²⁰Ne ratios which are within error of the calculated ASW range (Fig. 4).

Using the mixing model presented allows determination that the Kerr groundwater with the lowest ³He/⁴He and highest ⁴He/²⁰Ne ratios indicates a maximum of a 0.14% contribution, in the best case scenario, to 0.25% in a worst case scenario, to the ⁴He concentration from the produced CO₂. Fig. 5 also shows that using the best case (1 R_a) and worst case (1.1 R_a) ³He/⁴He end member, a 20%–32% contribution to the measured ³He/⁴He and ⁴He/²⁰Ne of the Kerr groundwaters could originate from the CO₂ injected into the Weyburn field could account for the lowest ³He/⁴He and highest ⁴He/²⁰Ne ratio observed.

5.6. ²⁰Ne, ³⁶Ar, ⁴⁰Ar, ⁸⁴Kr concentrations

The concentrations of the noble gases heavier than He in the Kerr groundwaters are all within the expected ASW range, bar a single sample that exhibits a ²⁰Ne concentration that is below the ASW range (Thackeray House Well). This is significant as the ²⁰Ne, ³⁶Ar, ⁴⁰Ar and ⁸⁴Kr concentrations measured in the produced and injected gases and injected water are considerably lower than those in the Kerr groundwaters. Hence, if there was addition of a component of the produced or injected gases from the Weyburn field to the Kerr groundwaters it would be expected that the concentrations of ²⁰Ne, ³⁶Ar, ⁴⁰Ar and ⁸⁴Kr would be lower than that of ASW. Whilst the Thackeray House well does exhibit a below ASW ²⁰Ne concentration it also has an above ASW ³He/⁴He ratio, and shows a ⁴He/²⁰Ne ratio which is within the ASW range. Additionally this groundwater sample does not have an elevated ⁴He or a depleted ³⁶Ar concentration compared to the predicted ASW range.

Recent work using noble gases to investigate the contamination of groundwaters by natural gas from unconventional gas production in the USA has shown that well waters with high methane concentrations,

located close to gas production wells, have below ASW concentrations of ^{20}Ne and ^{36}Ar (Darrah et al., 2014). This is a result of the fugitive methane containing insignificant concentrations of groundwater derived ^{20}Ne and ^{36}Ar concentrations and consequently the migrating methane 'strips' out these noble gases from the groundwaters. This occurs as the noble gases are much more soluble in CH_4 than in water and is identical to the stripping of formation waters which has been observed in natural CO_2 reservoirs (Gilfillan et al., 2008; Gilfillan et al., 2009; Zhou et al., 2012) and recently in a CO_2 -EOR field (Györe et al., 2015). Noble gases are also considerably more soluble in CO_2 than water (Warr et al., 2015) so the presence of an active flux of CO_2 to the Kerr groundwaters would be expected to lower the concentration of both ^{20}Ne and ^{36}Ar by a similar 'stripping' process.

Additionally, the groundwater samples with elevated CH_4 concentrations reported by Darrah et al. (2014) also exhibited above ASW $^4\text{He}/^{20}\text{Ne}$ ratios, as a result of the presence of increased levels of radiogenic ^4He which had migrated from depth (Darrah et al., 2014). A similar trend has recently been observed in naturally methane rich shallow aquifers of the Appalachian Basin (Darrah et al., 2015). Elevated $^4\text{He}/^{20}\text{Ne}$ ratios were also observed in all of the spring and well water samples collected from directly above the St. Johns Dome CO_2 reservoir, whilst three springs located away from the reservoir had ASW $^4\text{He}/^{20}\text{Ne}$ ratios (Gilfillan et al., 2011). The Appalachian study of the tracing fugitive CH_4 contamination of groundwaters and previous noble gas measurements in both groundwaters at St. Johns (Gilfillan et al., 2011) and soil gases at Teapot Dome (Mackintosh and Ballentine, 2012) shows that $^4\text{He}/^{20}\text{Ne}$ ratios are a sensitive tool to identify the migration of any deep gas input into the shallow subsurface. Hence, if CO_2 from depth were migrating to the shallow groundwaters on the Kerr Farm, elevated $^4\text{He}/^{20}\text{Ne}$ ratios would be expected to be observed in the groundwater samples based on these previous studies.

5.7. Limitations of this study and recommendations for future application of noble gas tracers in contested situations

The absence of elevated $^4\text{He}/^{20}\text{Ne}$ ratios in the Kerr groundwaters corresponds to the ^4He , ^{20}Ne , ^{36}Ar , ^{40}Ar , ^{84}Kr concentration measurements, showing that there is limited evidence of migration of the injected or produced CO_2 from the Weyburn field into the Kerr groundwaters. However, we are unable to rule out a best case possibility of a 0.14%, and a worst case possibility of a 0.25%, contribution to the groundwater sample with the lowest $^3\text{He}/^4\text{He}$ ratio from the produced fluids, or a 20% to 32% contribution from the injected CO_2 to the sample with the lowest $^3\text{He}/^4\text{He}$ ratio. The inability to firmly rule out a significant contribution to the Kerr groundwaters from the injected CO_2 is a key limitation of our study and is due to the low helium concentrations measured in the injected CO_2 . This is most likely to be the result of the solubility based capture method used to extract the CO_2 from the gasification process, which results in the majority of the insoluble ^4He being lost as it is not captured by the capture technique and hence is vented with the non-captured flue gas (Flude et al., 2016).

As we find no evidence of a ^4He component above that of ASW we conclude that the below ASW $^3\text{He}/^4\text{He}$ ratios are most probably the result of measured low ^3He concentrations, a potential reflection of increased analytical error in measuring such small amounts of ^3He in the waters. This is due to the extremely low concentration of ^3He in ASW of 60–120 parts per trillion and highlights that $^3\text{He}/^4\text{He}$ ratios are not a robust means to assess the presence of, or lack of presence of a radiogenic component in this study. We therefore recommend that future investigations of this type focus on $^4\text{He}/^{20}\text{Ne}$ ratios, which is a more sensitive and robust measure of the presence of a non-atmospheric radiogenic component and also avoids the complication of elevated baseline $^3\text{He}/^4\text{He}$ ratios due to the presence of tritium derived ^3He .

Whilst we have included the injected CO_2 end member to make a robust assessment of all of the possible sources of CO_2 near to the Kerr Farm it is not necessarily valid. The nearest CO_2 injection well to the

Kerr quarter is located some 1.4 km away and CO_2 injection at this location ceased in 2005 (Cenovus Energy Inc., 2011). The section of the Weyburn EOR field located directly beneath the Kerr property has remained under water injection throughout extraction operations of the oil field since the 1960's (Sherk et al., 2011). Hence, we believe it to be unlikely that injected CO_2 could migrate over 1.5 km laterally and through ~1.5 km of overburden without encountering formation water containing an excess ^4He fingerprint inherited from the radiogenic decay process. Given that CO_2 is an excellent solvent (Warr et al., 2015) and has been shown to strip out radiogenic noble gases from formation waters (Darrah et al., 2015; Darrah et al., 2014; Gilfillan et al., 2008; Györe et al., 2015) we would expect any migrated injected CO_2 to obtain a radiogenic fingerprint high in ^4He . This would result in above atmospheric $^4\text{He}/^{20}\text{Ne}$ and below atmospheric $^3\text{He}/^4\text{He}$ ratios, similar to those of the produced CO_2 . We do not observe any presence of a radiogenic fingerprint in any of the Kerr groundwater samples.

In light of our findings, we recommend that further investigation into the composition of captured CO_2 is needed to quantify how useful noble gases will be in tracking injected CO_2 within CO_2 storage reservoirs and identifying how quickly the radiogenic fingerprint of the storage reservoir is inherited by injected CO_2 . We also recommend that operators of CO_2 injection sites establish both the geochemical baseline of their reservoir prior to CO_2 injection, and routinely monitor the geochemical fingerprint of the CO_2 injected, including both stable carbon and noble gas isotopic measurements. This comprehensive geochemical database could then be used as a robust reference basis for geochemical investigations should allegations of leakage be made.

5.8. Comparison with findings from other studies completed on the Kerr site

Our interpretation that there is no evidence of migration of the CO_2 injected into or produced from the Weyburn EOR field into the Kerr groundwaters is further corroborated by comparison with the results of separate investigations into the allegations of CO_2 contamination on the Kerr property. ^{14}C measurements were a key component of the investigation instigated by the field operators, Cenovus, by TRIUM Environmental Inc. This study analysed radiocarbon within 78 samples of soil gases over the entire of the Kerr quarter and found that these contained high levels of ^{14}C , indicating a recent carbon source. The ^{14}C values measured were identical to those measured on a control site well outside of the Cenovus CO_2 -EOR operations, whilst ^{14}C measurements from CO_2 originating from the Dakota gasification plant and the recycled gas injected into the Weyburn field showed that these contained no measurable ^{14}C (Cenovus Energy Inc., 2011). This showed that the CO_2 contained in the soil gases overlying the Kerr property had to have a recent, 'living' high ^{14}C source, rather than a 'dead' non ^{14}C containing fossil fuel origin.

Further support to the lack of evidence of CO_2 migration from depth is provided by the relationship between the concentration of O_2 and N_2 with CO_2 in the soil gas samples in both the investigation performed on behalf of the field operators (Cenovus Energy Inc., 2011) and that performed by IPAC- CO_2 (Romanak et al., 2014). The Cenovus funded study found that soil gas CO_2 measurements for both the Kerr Quarter and two off site control localities were in natural equilibrium with N_2 and O_2 , providing an indication of the origin of the CO_2 . If the CO_2 was from a natural biogenic soil respiration process, O_2 is consumed to yield CO_2 within the soil due to plant and microbial respiration activity. As a result of this consumption of O_2 its concentration decreases, whilst CO_2 is produced and its concentration increases. N_2 concentration is unaffected in that natural process. In contrast, if the injected, industrial source CO_2 was migrating to surface soils, N_2 concentrations would decrease as it is displaced from the soil by the anthropogenic CO_2 . No such change in N_2 concentrations was observed in either the Cenovus or IPAC- CO_2 funded studies (Cenovus Energy Inc., 2011; Romanak et al., 2014). In addition, seasonality of soil gas CO_2 concentrations was suggested in the Cenovus study as soil gas CO_2 concentrations measured

in September were lower than those in August. This is indicative of a natural cycle where plant and microbial based activity declines as summer ended and winter approached (Cenovus Energy Inc., 2011).

6. Conclusions

We conclude that the carbon isotope data do not constrain the origin of elevated dissolved CO₂ concentrations in the Kerr groundwaters, due to the lack of a distinct fingerprint between the injected and produced CO₂ relative to that of baseline values in the shallow subsurface in the region. Our combined noble gas fingerprints show no evidence of the presence of noble gases from the injected CO₂, or from the CO₂ produced from the Weyburn CO₂ Enhanced Oil Recovery field, within the groundwaters surrounding the Kerr property. All of the Kerr groundwater samples exhibit noble gas fingerprints which would be expected in shallow groundwaters and show no evidence for the addition of a deep radiogenic component or dilution from the addition of a gas phase low in atmospheric derived noble gases.

However, we are unable to categorically rule out a best case possibility of a 0.14%, and a worst case possibility of a 0.25%, contribution to the groundwater sample with the lowest ³He/⁴He ratio from the produced fluids, or a 20%–32% contribution from the injected CO₂ to this sample. The inability to firmly rule out a significant contribution to the Kerr groundwaters from the injected CO₂ is a key limitation of the noble gas fingerprinting technique used in this study. This is the result of low helium concentrations measured in the injected CO₂, most probably due to the solubility based capture method used to capture the CO₂. However, we believe it is unlikely that injected CO₂ could migrate from the nearest CO₂ injection well (some 1.5 km away, and at a depth of 1.5 km) without encountering formation water rich in radiogenic noble gases and inheriting a radiogenic fingerprint high in ⁴He and with a low ³He/⁴He ratio, similar to that of the produced CO₂.

We also determine that ⁴He/²⁰Ne ratios are a more robust indicator of the lack of a deep radiogenic component in the Kerr groundwaters than ³He/⁴He ratios. This is due to a combination of the difficulties in measuring the extremely small amounts of ³He present in the groundwaters and complications in determining the baseline ³He/⁴He ratio as a result of the presence of tritogenic derived ³He. Additionally, there is a significantly larger sensitivity in using ⁴He/²⁰Ne ratios, as opposed to ³He/⁴He ratios, as there is a considerably larger range between deep radiogenic fluids and groundwaters in equilibration with the atmosphere (Risk et al., 2015). Hence, we recommend that future investigations of near-surface contamination by deep fluids utilising noble gases focus on ⁴He/²⁰Ne ratios and ⁴He concentrations as opposed to ³He/⁴He ratios.

Combining the conclusions of our study with the findings of the hydrological and soil gas analysis undertaken as a separate strand of the IPAC-CO₂ investigation, indicates the CO₂ found on the Kerr property is of biological origin (IPAC-CO₂, 2011; Romanak et al., 2014). This corroborates the findings of the Cenovus commissioned study into the allegations, which used ¹⁴C data to show that the CO₂ present on the Kerr property was of modern origin as opposed to the geologically old CO₂ injected into the Weyburn field (Cenovus Energy Inc., 2011). Hence, it is clear that the integration of the full range of geochemical tracers (stable carbon and ¹⁴C isotopes, noble gases, water chemistry, process based gas ratios) is the most effective means to understand the CO₂ source and refute the leakage allegations made at the Kerr Farm. Therefore, future investigations into allegations of CCS related CO₂ leakage should use a similar comprehensive range of geochemical tools and integrate them with a good understanding of geological and engineering data at the site.

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