

REPORT ON NOBLE GAS, CARBON STABLE ISOTOPE AND HCO_3
MEASUREMENTS FROM THE KERR QUARTER AND SURROUNDING
AREA, GOODWATER, SASKATCHEWAN

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THE KERR INVESTIGATION: FINAL REPORT

1. SUMMARY

Here we report noble gas and carbon stable isotope measurements from four groundwater wells surrounding the Kerr quarter, near Goodwater in Saskatchewan. These are compared to the noble gas and carbon isotope compositions measured from fluids sampled from a production well, and CO₂ and water sampled from Enhanced Oil Recovery (EOR) injection wells associated with the Weyburn oil field, located near the Kerr quarter. To determine if migration of dissolved CO₂ from the Weyburn oil field is responsible for the alleged CO₂ anomaly measured in soil gases on the Kerr quarter and surrounding area, we compare the suite of noble gas and carbon stable isotope tracers in the water and CO₂ injected deep into the oil field, with the fluids produced from the field and with the noble gases and carbon isotopes measured in the groundwater wells.

“We find no evidence in any of the noble gas data within the groundwaters surrounding the Kerr quarter that there is a detectible presence of noble gases derived from the deep injected water or CO₂ or the fluids produced from the Weyburn Field. The absence of crustal derived noble gases derived from depth means that there is no evidence of the migration of CO₂ from the Weyburn oil field into the groundwater on the Kerr quarter or surrounding area.”

Dr. Stuart Gilfillan,
University of Edinburgh



Dr. George (Jerry) Sherk, Chief Operating Officer of IPAC-CO₂ Research Inc., and Dr. Stuart Gilfillan of the University of Edinburgh (right) took samples in June from the Kerr farm water well.

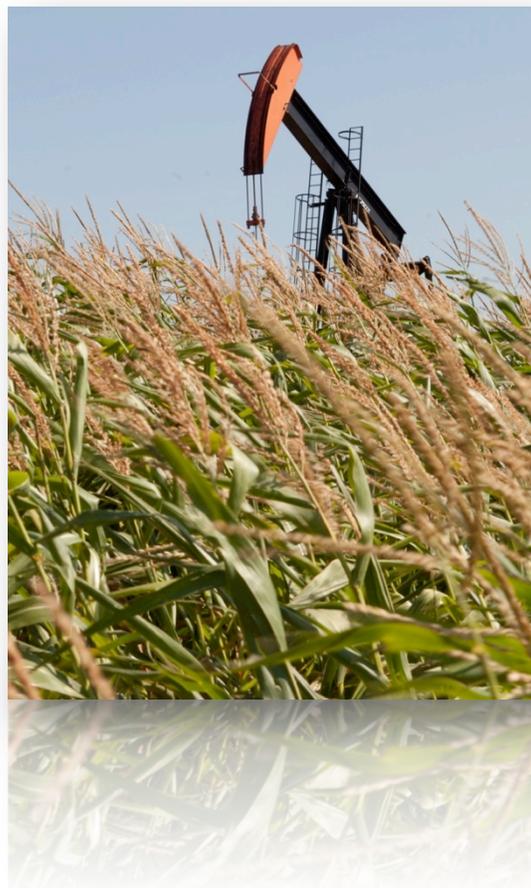
While the carbon isotope data does not clearly distinguish between the different samples, we find no evidence in any of the noble gas data within the groundwaters surrounding the Kerr quarter that there is a detectable presence of noble gases from the deep injected water or CO₂ or the fluids produced from the Weyburn field. The absence of crustal noble gases derived from depth means that there is no evidence of the migration of CO₂ from the Weyburn oil field into the groundwater on the Kerr quarter or surrounding area.

2. BACKGROUND

In January 2011 it was extensively reported in Canadian and global news media that the Kerr family were forced to move from their property located above the Weyburn oil field as a result of an alleged leakage of CO₂ which had been injected into the oil field below to enhance oil recovery (EOR). A geochemical consultant from Petro-Find, who was hired on behalf of the Kerr's, reported measurements of $\delta^{13}\text{C}$ (CO₂) isotope values in soil gases rich in CO₂, which he claimed to be similar to those of the CO₂ injected into the deep oil reservoir (Lafleur, 2010). The Petroleum Technology Research Centre (PTRC), who is responsible for the environmental monitoring of the Weyburn CO₂-EOR and storage operation, published a detailed science-based response. This correctly stated that Petro-Find had not taken into account similar soil gas $\delta^{13}\text{C}$ (CO₂) ratios observed in prairie soils comparable to those found on the Kerr property (e.g. Keller and Bacon, 1998; Hendry, 1999).

Petro-Find also failed to mention that $\delta^{13}\text{C}$ (CO₂) is not a unique tracer and that several other natural sources could have accounted for the measured isotope values (PTRC, 2011). While this response went some way to addressing the public fears raised by the alleged CO₂ leak, it is clear that more must be done to fully account for the safety and security of the CO₂ stored at Weyburn. It is imperative for both the project and the local community that there is an independent investigation into the alleged leak to establish whether there is any truth in the allegations.

Noble gases are intimately associated with all natural and engineered CO₂ occurrences, and are trace components mixed into the gas mixture in parts per billion quantities. The noble gases are extremely powerful tracers of both CO₂ source, and the subsurface processes that act on CO₂. This is because there are only 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 their isotopic compositions and abundance ratios.





Dr. Stuart Gilfillan (left) and Dr. George (Jerry) Sherk check their monitoring equipment.



Dr. George (Jerry) Sherk carefully deposits a hose into a water well.

Crustal noble gases, such as ^4He and ^{40}Ar , are produced by the radioactive decay of uranium, thorium and potassium within the crust (Ballentine and Burnard, 2002). Mantle derived noble gases, such as ^3He , were trapped within the mantle during the accretion of the Earth and have been degassing ever since (Ballentine, et al., 2002). Atmospheric noble gases, such as ^{20}Ne and ^{36}Ar enter the subsurface dissolved in the groundwater via meteoric recharge (Ballentine, et al., 2002). The distinct elemental and isotopic composition of these three noble gas components allows the contribution from each source to be determined and provides detailed information on the source and transport processes associated with the CO_2 .

Noble gases have been widely used to trace regional flows of groundwater in numerous locations (Castro and Goblet, 2003; Castro et al., 1998). Several studies have successfully demonstrated the potential of noble gases to trace the origins of CO_2 and its fate within reservoirs (Gilfillan et al., 2008; Gilfillan et al., 2009; Lafortune et al., 2009; Nimz and Hudson, 2005). Recent research has shown that noble gases can be used to trace diffuse CO_2 migrating from a natural deep CO_2 reservoir through the subsurface to the surface at St. Johns Dome in Arizona (Gilfillan et al., 2011).

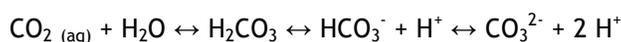
Noble gases in trace quantities, therefore, can be used to identify the origins of CO_2 at the land surface. Hence, to determine the origin of the alleged CO_2 anomaly measured in soil gases on the Kerr quarter, the trace noble gases can be measured. We made measurements of a suite of noble gas and carbon stable isotope tracers from four different sources:

- 1) the water injected into the oil field
- 2) the CO_2 injected into the oil field
- 3) the fluids produced from the field
- 4) the Kerr and Thackery quarter groundwater well waters

We test the hypothesis that migration of dissolved CO₂, which originates either from the free phase CO₂ or water injected into the Weyburn oil field or from the CO₂ contained in the produced fluids, is responsible for the CO₂ anomaly at the surface. If this is the case we should be able to match the noble gas and carbon isotope fingerprints from either samples 1, 2 or 3 to those present in the type 4 samples, the Kerr and Thackery ground waters. We focus on dissolved CO₂ as no free phase CO₂ was present in the sampled wellwaters.

3. SAMPLE COLLECTION AND ANALYTICAL TECHNIQUES

Dr. Stuart Gilfillan conducted a field sampling campaign in late June 2011, which was supervised by IPAC-CO₂ staff and Dr. Janis Dale from the University of Regina. The sampling was conducted after one week of dry weather that was preceded by a two-week period of very intense rainfall, where 161.6mm of rain fell between June 7 and 21 (Environment Canada). This was over double the average normal June monthly rainfall in the region. To assess the effect that this rainfall had on the dissolved CO₂ content of the ground waters surrounding the Kerr quarter, we collected three samples from the Kerr house well during the noble gas sampling program. CO₂ is soluble in water but also reacts with it to form several species; dissolved CO₂ (CO_{2(aq)}) carbonic acid (H₂CO₃), bicarbonate (HCO₃⁻) and carbonate (CO₃²⁻), which interact with water as follows:



At the pH range of the water contained in the Kerr well (7.8 to 8) the overwhelming majority of the dissolved CO₂ will speciate to the bicarbonate ion (HCO₃⁻). Hence, to see how the heavy rainfall had affected the dissolved CO₂ concentrations in the Kerr well we had the HCO₃⁻ concentrations measured by two separate laboratories. BDS laboratories in Qu'Appelle analyzed one of the samples and the University of Rochester, New York analyzed the other two (Table 1).

Table 1. HCO₃⁻ concentrations measured in the Kerr House well since 2002 compared with the values recorded during the noble gas sampling program

Date	Oct 2002	May 2003	Nov 2003	Aug 2003	Jun 2005	Jul 2008	Jun 2011	Jun 2011
Source	EnCana	EnCana	EnCana	McDonald & Assc.	EnCana	SRC Analytical	BDS Labs*	University of Rochester*
pH	7.8	8.0	7.8	7.6	8.0	8.26	7.8	-
HCO ₃ ⁻ (mg/l ³)	308	211	259	272	262	251	351	376 & 410

*Data from this study

The results in Table 1 clearly show that the HCO₃⁻ concentrations were slightly higher during our sampling program compared to previous analyses, indicating that there was more CO₂ dissolved in the well water. This confirmed that the dissolved CO₂ concentration was not diluted by the heavy rainfall.

It had actually increased, possibly due to the slightly acidic rain water dissolving carbonate minerals present in the soil.

Gas samples for noble gas analysis were collected from a Cenovus CO₂ injection well (Well ID-101/12-04-006-13 W2/0) located approximately six miles northwest of the Kerr quarter, and duplicate samples were collected from a Cenovus production satellite site well (Well ID 16-30-05-13) (Fig. 1). This well contained produced gas separated from the oil from 14 production wells surrounding the Kerr quarter. The gases were collected in 75 cm long copper tubes held in aluminium clamps (Fig. 2). Gases were sampled at slightly over atmospheric pressure via a regulator fitted to the wellhead with a high pressure hosing connecting the copper tube to the regulator. A 20 cm length of high pressure hosing was connected to the other end of the copper tube to prevent turbulent back mixing of atmospheric gases into the sample. Gas was flowed through the copper tube for five minutes to further ensure that all atmospheric gases had been removed from the tube. The tube clamp farthest from the well was then closed, followed by the remaining clamp ensuring that the copper was cold welded to form a leak tight sealed sample for analysis.

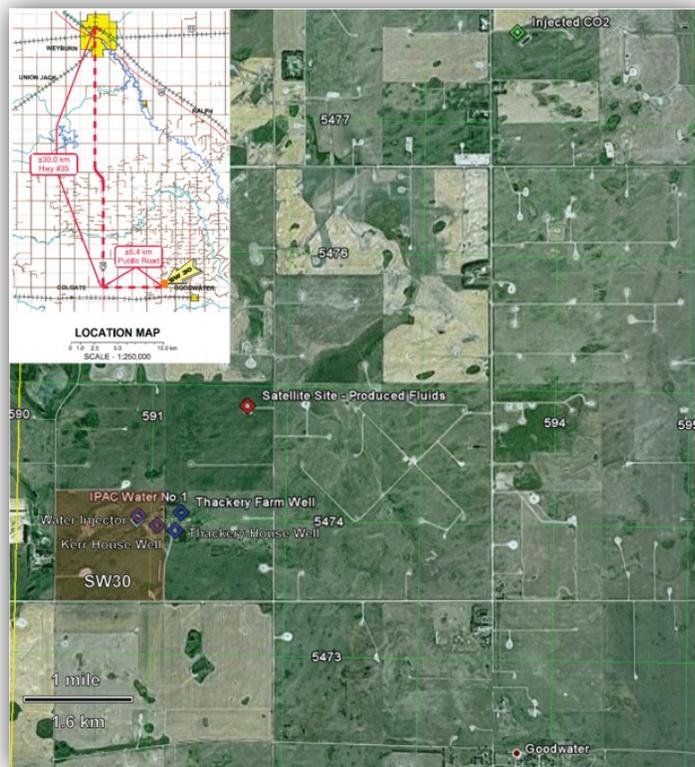


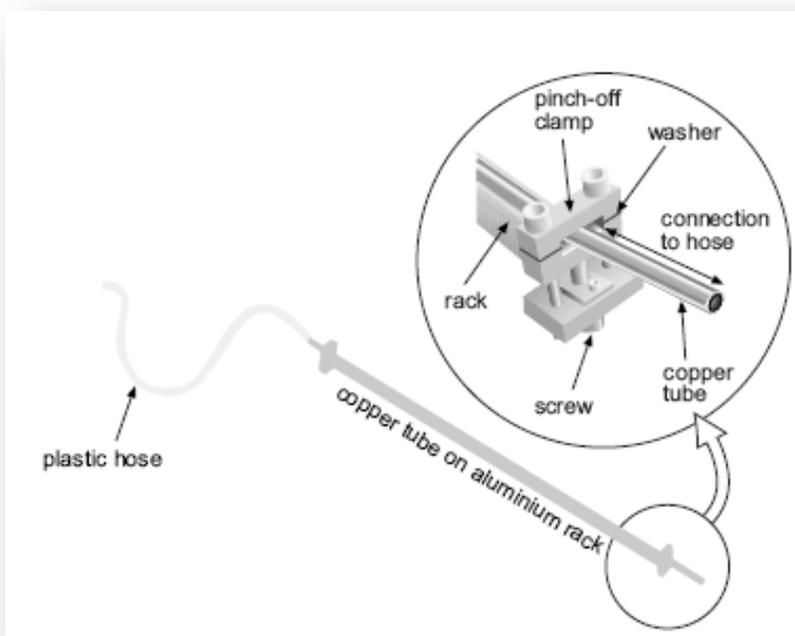
Fig. 1. Location Map (inset) showing the location of the Kerr quarter relative to Weyburn and aerial photograph (main image) showing the localities of the wells sampled in this study in relation to the town of Goodwater and the Kerr quarter.

Water samples were also collected in June 2011 in a similar fashion from a Cenovus water injection well on the Kerr quarter (Well ID-101/06/30-005-13W 2/0), the domestic groundwater well on the Kerr farm, two domestic groundwater wells on the adjacent Thackery farm and the IPAC No. 1 monitoring well which was drilled during the sampling program. This was located close to the CO₂ anomaly reported by LaFleur (2010) (Fig 2). For all of the samples, water was pumped directly from the sampled well via a weighted length of plastic tubing using a peristaltic pump, through the 75 cm length of copper tube (Fig. 3). Water was pumped from approximately 50 cm above the measured bottom of the well for a period of five minutes to flush out any atmospheric contamination. The copper tube clamp farthest from the well head was then closed, followed by the remaining clamp ensuring that the copper was cold welded to form a leak tight, sealed water sample for analysis.

$\delta^{13}\text{C}$ (CO₂) ratios of the gas samples and $\delta^{13}\text{C}_{\text{DIC}}$ ratios of the waters were determined at the University of Rochester using a Delta S (Finningan) mass spectrometer. Standard extraction and purification procedures were used and the ratios are expressed as $\delta^{13}\text{C}$ ‰ V-PDB. The analytical error was ± 0.2 ‰.

Isotopic ratios (³He/⁴He, ²⁰Ne/²²Ne, ²¹Ne/²²Ne, ⁴⁰Ar/³⁶Ar, ³⁸Ar/³⁶Ar) and elemental abundances (⁴He, ²⁰Ne, ⁴⁰Ar) 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-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. The 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 (0.77cm³). Helium isotope ratios were normalized using a Rochester air standard.

Fig. 2. Schematic of the apparatus used for noble gas sampling with copper tubing. The plastic hose is attached directly to the wellhead using a suitable regulator. CO₂ gas is allowed to flow through the copper tube until sample collection is complete. The tubing is then crimped at both ends.



Neon isotope ratios were corrected for interference by measurement of $^{40}\text{Ar}^{2+}$ and CO_2^{2+} ($^{40}\text{Ar}^{2+}$ was typically $< 0.4\%$ of total ^{20}Ne signal on the faraday cup and CO_2^{2+} was below detection limits for ^{22}Ne). The analytical error for the $^3\text{He}/^4\text{He}$ ratio is approximately 0.5% and those for both the $^{40}\text{Ar}/^{36}\text{Ar}$ and He/Ne isotope ratios were 0.2%, and 0.3% for $^{38}\text{Ar}/^{36}\text{Ar}$. Helium isotope ratios ($^3\text{He}/^4\text{He}$) 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 per cent 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.



Fig. 3. Photograph of Dr. Jerry Sherk of IPAC-CO₂ assisting with the collection of a water sample for noble gases at the Kerr groundwater well. The peristaltic pump, hosing and copper tube clamp are clearly shown.

4. RESULTS



Dr. Stuart Gilfillan records a depth measurement taken by drilling contractor Al Bjornson of Estevan, Sk.

Table 2 documents the location and type of sample collected along with noble gas and carbon isotope ratios. Table 3 shows the noble gas and HCO_3^- concentrations of the samples. 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 that were reported in the St. Johns study of Gilfillan et al., (2011). This is because the amount of bulk (i.e. non-noble gas) gases dissolved in the groundwaters was too low for useful noble gas concentrations in the gas phase to be reported. However, the amount of noble gases present in the groundwater was sufficient for high quality analyses to be obtained. To compare the produced CO_2 and injected CO_2 concentrations to those of the ground waters, we had to calculate the noble gas concentrations for waters in equilibrium with the produced CO_2 and injected CO_2 gas samples from the measured gas phase concentrations.

This is a straightforward process using the established Henry's constants for the noble gases along with the Weyburn reservoir temperature of 62°C , salinity of 2.07 Molar NaCl and the lithostatic pressure calculated from the average reservoir depth of 1400m (Cantucci et al. 2009) using established methods (Kipfer et al, 2002).

We also calculated 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 calculated using established solubility equilibrium techniques as outlined in Kipfer et al., (2002). We used the regional recharge conditions consisting of a range of recharge temperatures from 10 to 25°C (Environment Canada), the average site altitude of 580m and assumed an entrained excess air Ne component of between 0 to 50%. Excess air is the term given to account for the significantly above solubility predicted air noble gas concentrations, which are frequently measured in groundwater samples. It is measured relative to Ne concentrations and is typically in the range of 10 to 50% (Kipfer et al, 2002). These calculated values are reported as ASW in Table 2 and 3 and shown as ASW on the graphs.

4.1. $\delta^{13}\text{C}$ (CO_2) and $\delta^{13}\text{C}_{\text{DIC}}$ Isotopes

The measured $\delta^{13}\text{C}$ (CO_2) from the injected CO_2 of $-21.2 \pm 0.2 \text{ ‰}$ is similar to the value of $20.4 \pm 0.4 \text{ ‰}$ previously reported from analysis of 12 samples taken over 40 months of injection by Raistrick et al., (2006). It should be noted that the CO_2 being injected into the Weyburn Oil field at the time of sampling consisted entirely of recycled CO_2 which had been produced from the field, processed and then re-injected. This was due to landslide damage caused by heavy rain in the previous week to the bulk CO_2 pipeline from the Dakota gasification plant, which meant that the pipeline was shut and no CO_2 from the gasification plant was being injected. However, as almost all of the CO_2 within the Weyburn field originates from the Dakota gasification plant and the $\delta^{13}\text{C}$ (CO_2) value is similar to that measured previously in 12 samples over a 40 month injection period (Raistrick et al., 2006), we conclude that this is a representative sample of the CO_2 injected into the field since 2000.

The produced fluid well $\delta^{13}\text{C}_{\text{DIC}}$ duplicate values were -14.7 and $-12.3 \pm 0.2 \text{ ‰}$. Both of these $\delta^{13}\text{C}_{\text{DIC}}$ values have been calculated from measured $\delta^{13}\text{C}$ (CO_2) using the CO_2 gas to DIC fractionation factor of 0.03‰ . This combined fractionation factor takes into account the proportion of gaseous CO_2 which dissolves to HCO_3^- and H_2CO_3 at the nearest measured reservoir fluid pH of 5.52 and the Weyburn reservoir temperature of 62°C (Cantucci et al., 2009). The sampled groundwater wells exhibit $\delta^{13}\text{C}_{\text{DIC}}$ values ranging from $-13.4 \pm 0.2 \text{ ‰}$ to $-19.0 \pm 0.2 \text{ ‰}$, slightly overlapping with the range observed in the CO_2 produced from the reservoir, but above that of the injected CO_2 .



Dr. George (Jerry) Sherk (left), Dr. Stuart Gilfillan and Thomas Ogilvie, a University of Regina geology student, take a break from the hot summer sun.

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

Name	Location (UTM zone 13)	Type	³ He/ ⁴ He (R/R _s)	²⁰ Ne/ ²² Ne	²¹ Ne/ ²² Ne	⁴⁰ Ar/ ³⁶ Ar	⁴ He/ ² °Ne	²⁰ Ne/ ^{β6} Ar	⁸⁴ Kr/ ^{β6} Ar	δ ¹³ C _{DIC} (‰)
101/12-04-006-13 W2/o	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 #1	591223 5474051	Groundwater	0.880 (4)	9.96 (2)	0.0292 (1)	294.9 (6)	0.24 (8)	0.202 (2)	0.0256 (3)	-16.8 (2)
Thackery Farm Well #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 #1	591046 5473954	Groundwater	1.103 (6)	10.14 (2)	0.0293 (1)	297.5 (6)	0.40 (3)	0.190 (2)	0.0256 (3)	-19.0 (2)
Kerr Well Water #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 #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/o	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) 10°C [^]	-	0% Excess Air Ne	1.000 (5)	9.80 (8)	0.0290 (1)	296.1 (6)	0.25 (4)	0.141 (1)	0.0401 (2)	-
Air Saturated Water (ASW) 10°C [^]	-	50% Excess Air Ne	1.000 (5)	9.80 (8)	0.0290 (1)	294.1 (6)	0.28 (6)	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 [^]	-	50% Excess Air Ne	1.000 (5)	9.80 (8)	0.0290 (1)	293.8 (6)	0.29 (6)	0.254 (6)	0.0328 (2)	-

⁺ This value is the δ¹³C (CO₂) of the CO₂ injected into the Weyburn oil reservoir for EOR.

^{*}Both of these δ¹³C_{DIC} values have been calculated from measured δ¹³C (CO₂) using the CO₂ gas to DIC fractionation factor of 0.03‰ calculated using the Weyburn reservoir temperature of 62 °C and the nearest measured reservoir pH of 5.52 from Well w04 reported in Cantucci et al., (2009).

[^] Air saturated water noble gas ratios calculated using an average elevation of 580m above Sea Level (canmaps.com) and a groundwater recharge temperature range of 10 -25 °C (Environment Canada) assuming 0% and 50% excess air Ne, using the methods outlined by Kipfer et al., (2002).

Table 3 Noble gas and HCO₃ concentrations, values in brackets are 2 sigma error margins to the last significant figure

Name	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)	⁸⁴ Kr (µcm ³ kg ⁻¹)	HCO ₃ ⁻ (mg l ⁻¹)
101/12-04-006-13 W2/o	Injected CO ₂	24.7 (3)	1.88 (2)	1.71 (3)	0.00117 (2)	3.33 (3)	1.14 (2)	0.648 (9)	-
16-30-05-13-#1	Produced CO ₂	4516 (45)	4.32 (4)	3.93 (6)	0.0197 (2)	37.6 (4)	2.74 (3)	1.56 (3)	915*
16-30-05-13-#2	Produced CO ₂	10833 (108)	6.96 (7)	6.33 (9)	0.0269 (3)	50.8 (5)	0.654 (7)	0.372 (5)	915*
Thackery Farm Well #1	Groundwater	48.8 (5)	217 (3)	197 (3)	0.288 (3)	976 (10)	44 (5)	25.0 (4)	632
Thackery Farm Well #2	Groundwater	62.1 (7)	192 (2)	174 (3)	0.298 (3)	1003 (10)	44 (5)	25.2 (4)	880
Thackery House Well	Groundwater	39.2 (4)	137 (2)	125 (2)	0.260 (3)	882 (9)	47 (5)	26.9 (4)	562
Kerr Well Water #1	Groundwater	86.9 (9)	237 (3)	215 (3)	0.337 (4)	1133 (12)	51 (5)	29.0 (4)	410
Kerr Well Water #2	Groundwater	65.1 (7)	189 (2)	171 (3)	0.327 (4)	1101 (11)	50 (5)	28.6 (4)	376
IPAC Water #1	Groundwater	48.1 (5)	169 (2)	154 (2)	0.314 (4)	1064 (11)	59 (6)	33.4 (5)	494
101/06-30-005-13W 2/o	Injected Water	288 (3)	223 (3)	202 (3)	0.134 (2)	440 (5)	20 (2)	11.5 (2)	194
Air Saturated Water (ASW) 10°C [^]	0% Excess Air Ne	40.6 (6)	-	160 (6)	0.336 (4)	1133 (6)	-	45.4 (4)	-
Air Saturated Water (ASW) 10°C [^]	50% Excess Air Ne	91.6 (13)	-	320 (7)	0.426 (3)	1448 (13)	-	51.8 (5)	-
Air Saturated Water (ASW) 25°C [^]	0% Excess Air Ne	39.3 (6)	-	144 (5)	0.251 (3)	848 (19)	-	31.5 (3)	-
Air Saturated Water (ASW) 25°C [^]	50% Excess Air Ne	85.0 (12)	-	287 (9)	0.332 (8)	1131 (25)	-	37.1 (4)	-

* Taken from the nearest reservoir well water sample from Well w04 completed by Cantucci et al., (2009).

+ Noble gas concentrations for waters in equilibrium with the produced CO₂ and injected CO₂ calculated from original gas concentrations using the reservoir temperature of 62 °C, salinity of 2.07 Molar NaCl and the lithostatic pressure calculated from the average reservoir depth of 1400m.

[^] Air saturated water concentrations calculated using an average elevation of 580m above Sea Level (canmaps.com) and a groundwater recharge temperature range of 10 -25 °C (Environment Canada) assuming 0 per cent and 50 per cent excess air.

Fig. 4 illustrates that there is no clear relationship between HCO_3^- concentrations and the $\delta^{13}\text{C}_{\text{DIC}}$ both within the groundwater wells and with the produced fluids and injected water.

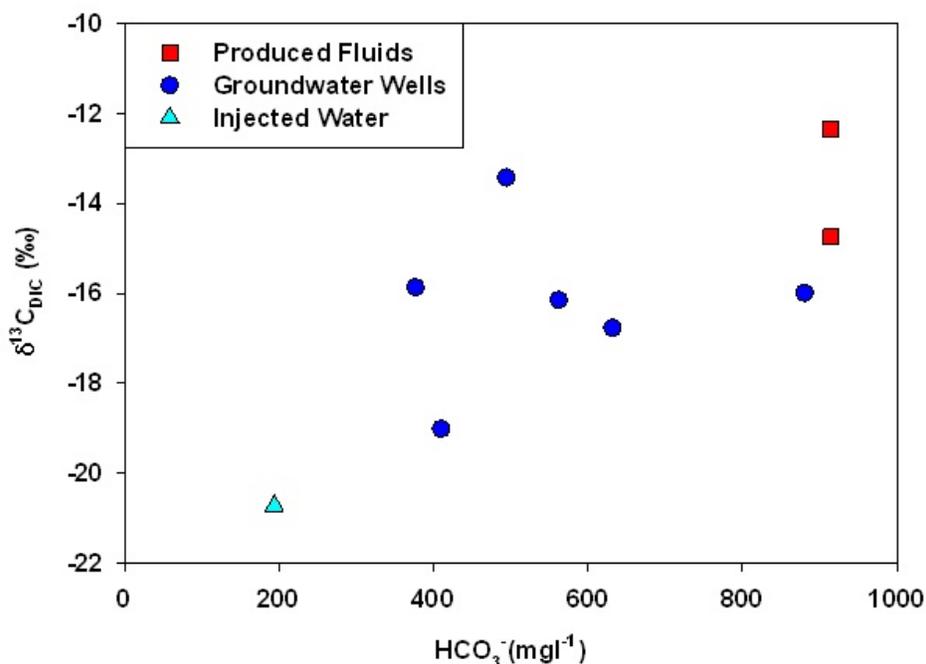


Fig. 4. $\delta^{13}\text{C}_{\text{DIC}}$ variation plotted against HCO_3^- concentrations for the produced fluids, groundwater wells and injected water samples. There is no clear correlation between the HCO_3^- concentration of the waters sampled and measured $\delta^{13}\text{C}_{\text{DIC}}$. The range of $\delta^{13}\text{C}_{\text{DIC}}$ values observed in the samples overlaps slightly with the measured range in the produced fluids, but the $\delta^{13}\text{C}_{\text{DIC}}$ observed in the injected water is distinct. Whilst there appears to be a casual correlation between the low $\delta^{13}\text{C}_{\text{DIC}}$ measured in the injected water, the groundwater samples and the higher values measured in the produced fluids, this is not statistically significant. The trend exhibits an R^2 value of 0.48 meaning that more than fifty percent of the data can be attributed to unknown inherent variability. The R^2 value drops to 0.44 if the slightly anomalous low $\delta^{13}\text{C}_{\text{DIC}}$ value of -19 ‰ measured in the duplicate sample Kerr Well No. 1 is discounted. All errors are smaller than printed symbols.

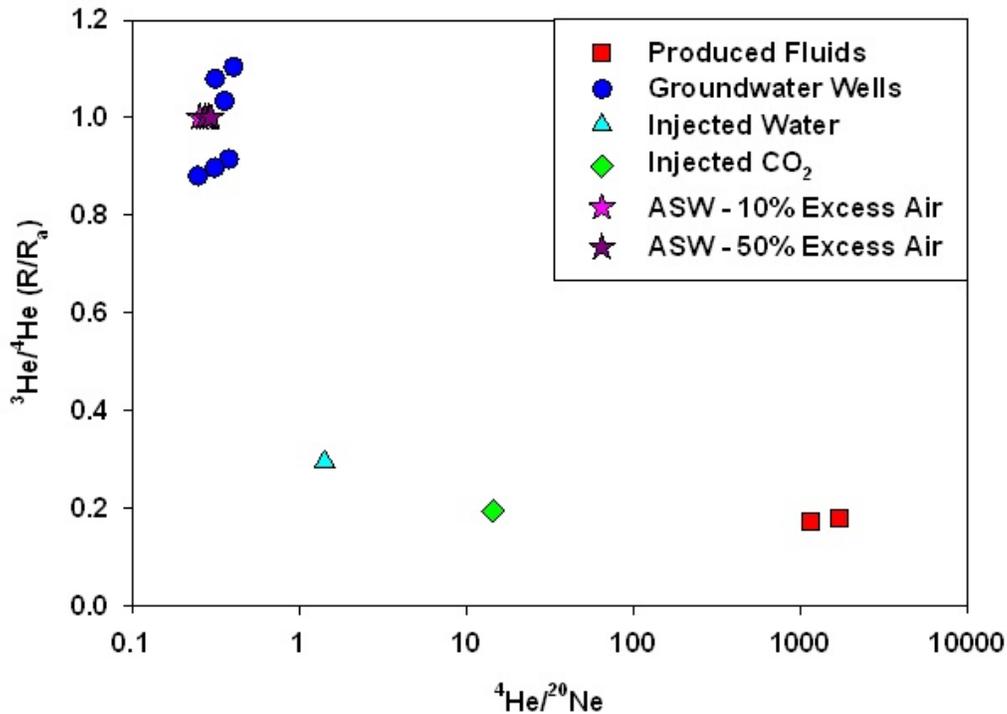


Fig. 5. $^3\text{He}/^4\text{He}$ ratio plotted against $^4\text{He}/^{20}\text{Ne}$ ratio. The produced CO₂ and injected CO₂ exhibit ratios well in excess of the air saturated water values. The groundwater wells are extremely close to the air saturated water (ASW) ratio range indicating that almost all of the He they contain is of atmospheric origin. Air saturated water is the calculated equilibrium ratios of the air derived noble gases in a groundwater at the field site recharge conditions. All errors are smaller than printed symbols.

4.2. Helium

The observed $^4\text{He}/^{20}\text{Ne}$ ratios in the injected CO₂ and duplicate produced fluid samples are significantly above the calculated air saturated water range of 0.250 to 0.296 (Fig. 5). This indicates that atmospheric He inputs to these samples are minimal. The injected water $^4\text{He}/^{20}\text{Ne}$ ratio of 1.42 indicates that there is a small amount of atmospheric ^4He input in this sample. However, it is still above the range of 0.248 to 0.403 that is observed in the groundwater samples. This range overlaps with the air saturated water range and indicates that almost the entire of the He dissolved in the groundwaters are of atmospheric origin.

Similarly, there is a distinct difference in $^3\text{He}/^4\text{He}$ ratios throughout the sample types, with the lowest values of 0.173 and 0.179 R_a being observed in the produced CO_2 from the Weyburn field (Fig. 5). The injected CO_2 has a similar, albeit slightly higher ratio of 0.193 R_a . The injected water sample is higher again at 0.295 R_a . The range observed in the groundwater samples of 0.897 to 1.103 R_a is significantly above the ratios observed in the other samples and is consistent with the $^4\text{He}/^{20}\text{Ne}$ ratios in indicating that almost the entire of the He in the groundwater samples originates from the atmosphere.

^4He concentrations also exhibit marked distinctions depending on sample type (Fig. 6). The lowest concentration is that of $24.7 \mu\text{m}^3\text{kg}^{-1}$ calculated for water equilibrated with the injected CO_2 . The groundwater samples exhibit a range of 39.2 to $86.9 \mu\text{m}^3\text{kg}^{-1}$ that is similar to the calculated air saturated water concentration range of 39.3 to $91.6 \mu\text{m}^3\text{kg}^{-1}$. This shows that there is no significant addition of ^4He to the groundwater samples. Measured ^4He concentration in the injected water is an order of magnitude higher at $288 \mu\text{m}^3\text{kg}^{-1}$, with the calculated ^4He concentrations of water in equilibrium with the produced fluid samples being over another order of magnitude higher, ranging from 4516 to $10833 \mu\text{m}^3\text{kg}^{-1}$.

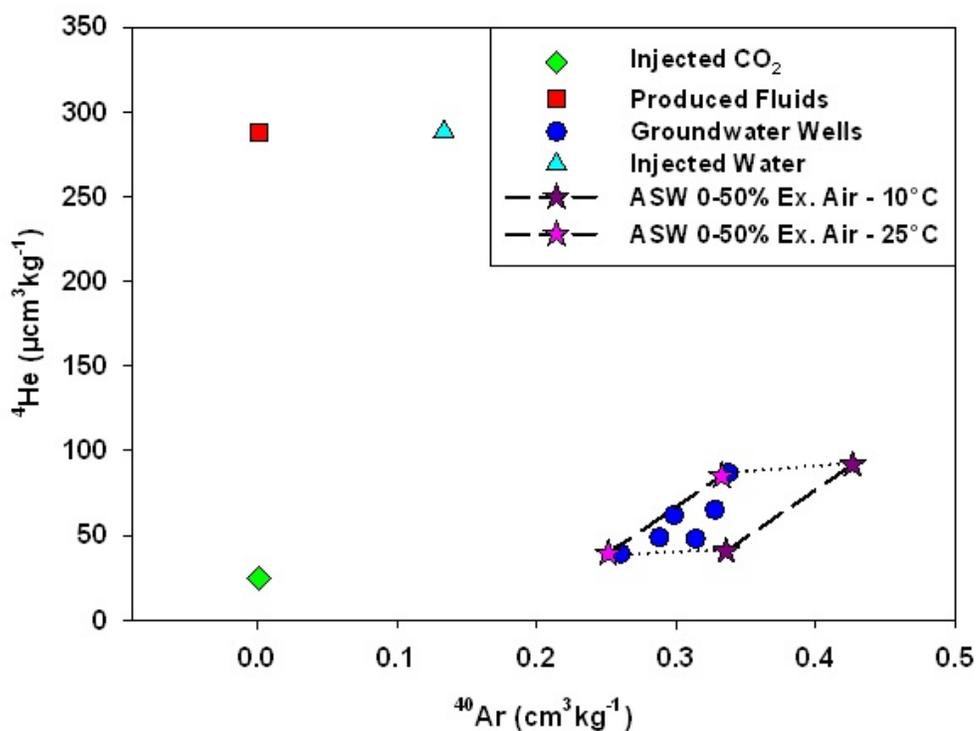


Fig. 6. ^4He concentration plotted against ^{40}Ar concentration. ^4He and ^{40}Ar are both produced in the crust by radioactive decay. All of the groundwater samples plot within the air saturated water (ASW) concentrations indicating that there is no input of crustal ^4He and the ^{40}Ar is entirely derived from the atmosphere. The lower ASW concentrations are those with no excess air component and the higher values are those with a 50% excess air component. Excess air is the term given to account for the significantly above solubility predicted air noble gas concentrations that are frequently measured in groundwater samples. It is measured relative to Ne concentrations and is typically in the range of 10 to 50% (Kipfer et al, 2002).

4.3. Neon

As with ^4He , the lowest ^{20}Ne concentration of $1.71 \mu\text{cm}^3\text{kg}^{-1}$ is that calculated for water equilibrated with the injected CO_2 (Fig. 7). The next lowest are those calculated for water equilibrated with the duplicate produced fluid samples, which range from 3.93 to $6.33 \mu\text{cm}^3\text{kg}^{-1}$. Both of these are two orders of magnitude lower than the Ne concentrations measured in the groundwater samples which range from 125 to $215 \mu\text{cm}^3\text{kg}^{-1}$, similar to both the range of calculated air saturated water concentrations range of 144 to $320 \mu\text{cm}^3\text{kg}^{-1}$ and the concentration of the injected water of $203 \mu\text{cm}^3\text{kg}^{-1}$. ^{20}Ne is primarily derived from the atmosphere, and hence the concentration range observed reinforces a deduction that the groundwater samples contain only atmospheric noble gases (Fig. 7).

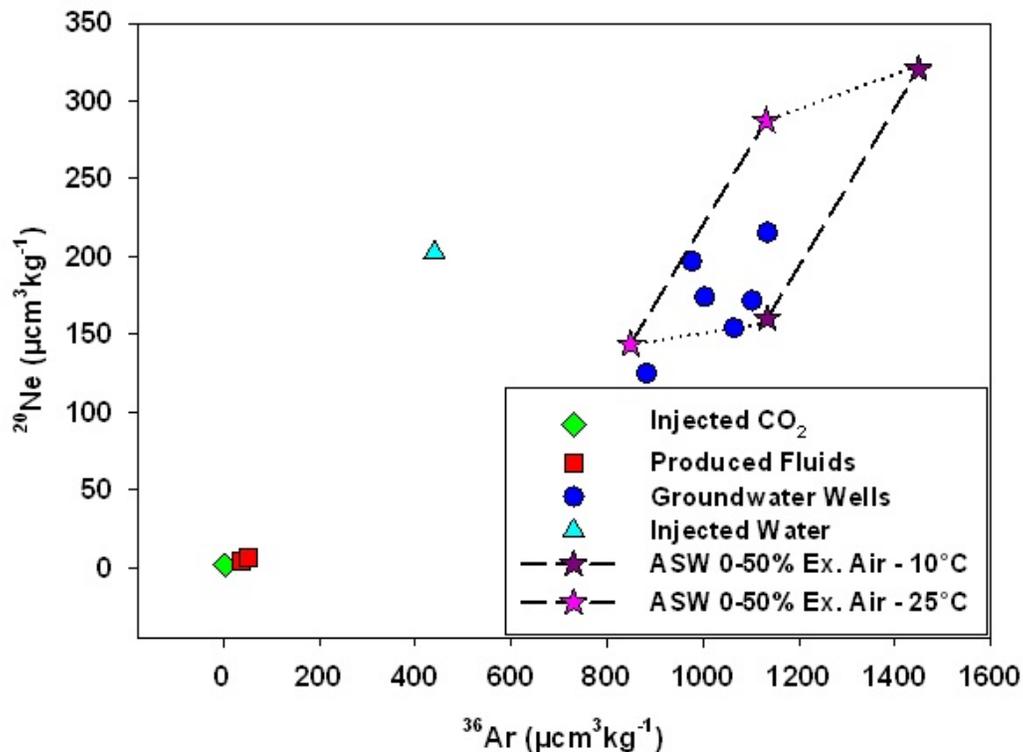


Fig. 7. ^{20}Ne concentrations plotted against ^{36}Ar concentrations. Both ^{20}Ne and ^{36}Ar are primarily derived from the atmosphere. There is a pronounced difference in concentrations between the produced fluids and injected CO_2 , the injected water and the groundwater samples. All but one of the groundwater samples can be explained by the calculated air saturated water concentration range, indicating that all of the ^{20}Ne and ^{36}Ar in the waters is atmosphere derived. All errors are smaller than printed symbols.

With the exception of the $^{20}\text{Ne}/^{22}\text{Ne}$ range of 9.82 to 9.87 exhibited by the produced CO_2 , the majority of the measured ratios are in excess of the air ratio of 9.80 ± 0.08 . This includes both the injected water ratio of 10.31 and the injected CO_2 value of 10.24. The ratios measured in the groundwaters are slightly lower, ranging from 9.96 to 10.15, but are still above the air ratio. The elevation of $^{20}\text{Ne}/^{22}\text{Ne}$ ratios is a common observation in natural groundwaters that has been observed at the San Juan methane gas field in Colorado and at the Green River Springs in Utah and is thought to be the result of a solubility controlled fractionation process (Zhou et al., 2005). The $^{21}\text{Ne}/^{22}\text{Ne}$ ratios of all of the samples are within error of the air ratio of 0.0290 ± 0.0003 .

4.4. Argon

As with ^4He and Ne , the lowest ^{40}Ar concentration of $0.00117 \mu\text{cm}^3\text{kg}^{-1}$ is that calculated for water in equilibrium with the injected CO_2 under reservoir conditions (Fig. 5). The next highest concentrations are those calculated for water in contact with the produced fluids from the Weyburn field, which range from 0.0197 to $0.0269 \mu\text{cm}^3\text{kg}^{-1}$. The injected water has an order of magnitude higher ^{40}Ar concentration at $0.134 \mu\text{cm}^3\text{kg}^{-1}$. The higher concentrations of 0.288 to $0.337 \mu\text{cm}^3\text{kg}^{-1}$ are observed in the groundwater wells, within the calculated air saturated water range of 0.251 to $0.426 \mu\text{cm}^3\text{kg}^{-1}$. ^{36}Ar concentrations show extremely similar concentration groups, with the lowest observed in the calculated water concentration equilibrated with the injected CO_2 and the highest being those observed in the groundwater wells (Fig. 7).

$^{40}\text{Ar}/^{36}\text{Ar}$ ratios of the groundwater wells are all within error of the calculated air saturated water range of 293.8 to 296.1 ± 0.5 , again indicating that the Ar is derived entirely from the atmosphere. The injected water ratio is slightly above the air saturated water ratio at 303.9 , with the next highest being the ratio measured in the injected CO_2 of 352.9 . The highest $^{40}\text{Ar}/^{36}\text{Ar}$ ratios measured was that of the produced fluids with the two duplicate samples exhibiting consistent ratios of 524.7 and 529.0 .

4.5. Krypton

The lowest ^{84}Kr concentrations are those calculated for water in equilibrium with the injected CO_2 ($0.648 \mu\text{cm}^3\text{kg}^{-1}$) and produced fluids (0.372 to $1.56 \mu\text{cm}^3\text{kg}^{-1}$) (Fig. 8). These are an order of magnitude lower than the injected water ^{84}Kr concentration of $11.5 \mu\text{cm}^3\text{kg}^{-1}$. This in turn is more than half of the concentration measured in the groundwaters which range from 26.9 to $33.4 \mu\text{cm}^3\text{kg}^{-1}$, overlapping with the calculated air saturated water range of 31.5 to $51.8 \mu\text{cm}^3\text{kg}^{-1}$.

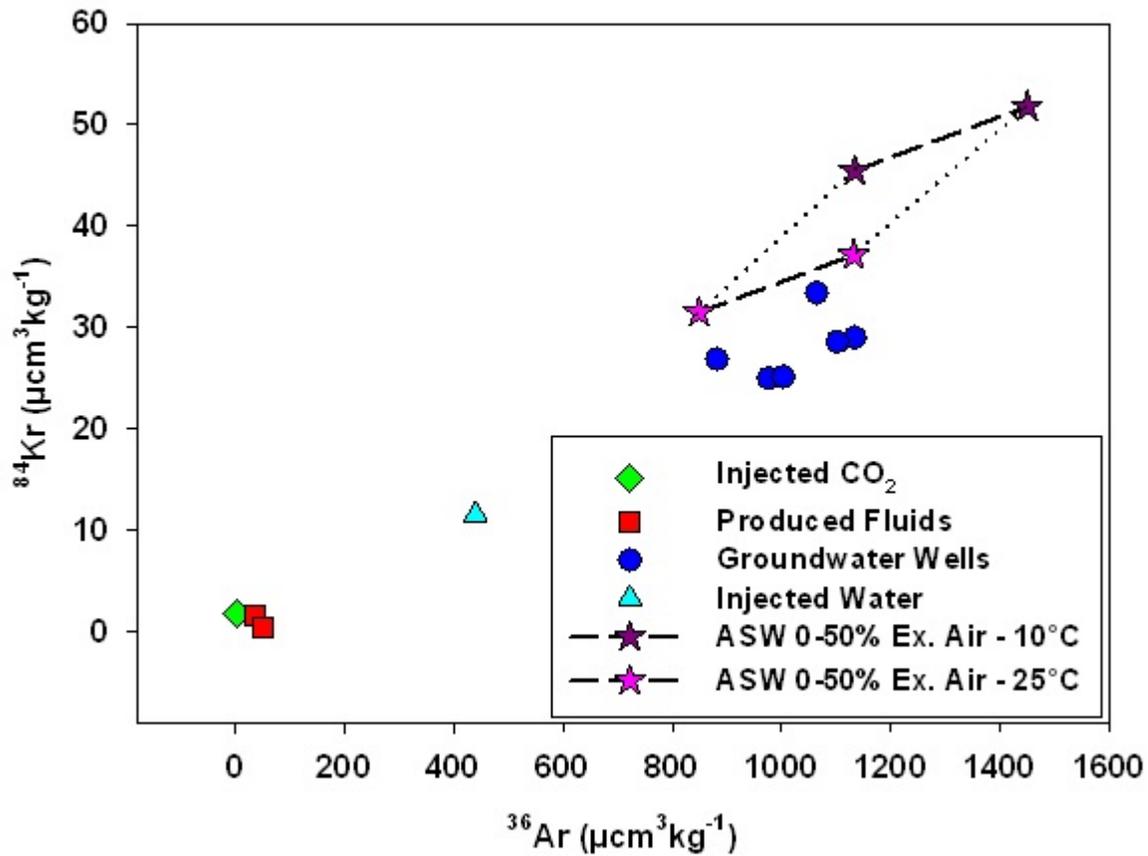


Fig. 8. Plot of ^{84}Kr against ^{36}Ar illustrating that the groundwater samples exhibit ^{84}Kr concentrations that are slightly below the calculated air saturated water range. However, they are still an order of magnitude above the injected water concentration and several orders above the injected CO₂ and produced fluid concentrations. All errors are smaller than printed symbols.

5. DISCUSSION

It is readily apparent that almost all the noble gas concentrations and isotope ratios, bar those of $^{20}\text{Ne}/^{22}\text{Ne}$, measured in the groundwater samples are within or very close to the calculated air saturated water ranges. That suggests that there is no component of deep CO_2 containing crustal derived noble gases in these shallow samples. To highlight this we now focus on comparing the results from this study to those measured at the natural CO_2 rich groundwater springs at St. Johns Dome, Arizona. Recent noble gas measurements of the St. Johns springs has shown a clear link between their noble gas composition and that of the CO_2 contained in the deep St. Johns Dome CO_2 reservoir (Gilfillan et al., 2011).

“It is readily apparent that almost all the noble gas concentrations and isotope ratios, bar those of $^{20}\text{Ne}/^{22}\text{Ne}$, measured in the groundwater samples are within or very close to the calculated air saturated water ranges. That suggests that there is no component of deep CO_2 containing crustal derived noble gases in these shallow samples. “

5.1. Relationship of HCO_3^- to $\delta^{13}\text{C}$ and $^3\text{He}/^4\text{He}$ ratios

$\delta^{13}\text{C}$ measurements on DIC have been extremely useful in tracing CO_2 injected in the Weyburn EOR field and other CO_2 storage test sites (Raistrick et al 2006). However, there are many sources of dissolved inorganic carbon in subsurface waters, with each exhibiting overlapping $\delta^{13}\text{C}$ ranges. The typical $\delta^{13}\text{C}$ values of DIC in subsurface waters are in the range of -5 to -25 ‰ (Kendall et al., 1995). The primary reactions which produce DIC are the weathering of carbonate minerals by acid rain, the weathering of silicate minerals by carbonic acid produced by the dissolution of biogenic soil CO_2 by percolating rain water and the weathering of carbonate minerals by carbonic acid. All of the above could account for the $\delta^{13}\text{C}$ isotope range observed in the groundwaters sampled around the Kerr quarter. There is no clear relationship between the HCO_3^- concentration and the $\delta^{13}\text{C}_{\text{DIC}}$ is present (Fig. 4) implying that there is no relationship between the $\delta^{13}\text{C}$ isotopes and the amount of dissolved CO_2 in the groundwater.

Significantly, there is also no relationship between the $^3\text{He}/^4\text{He}$ ratio and HCO_3^- concentrations measured in the groundwaters in this study (Fig. 9). This is in stark contrast to the systematic relationship observed between HCO_3^- concentration and $^3\text{He}/^4\text{He}$ ratios in the St. Johns surface springs and groundwater wells (Fig. 10), where there is a clear link between shallow samples and deep sources of CO_2 and He. The St. Johns samples show a clear distinction between the above atmospheric ratios measured in three anomalous spring water samples, and the significantly below atmosphere $^3\text{He}/^4\text{He}$ ratios measured in all of the other samples (Fig. 10). The majority of the St. Johns water samples exhibit higher HCO_3^- concentrations which correspond to lower $^3\text{He}/^4\text{He}$ ratios and show a clear trend towards the lower $^3\text{He}/^4\text{He}$ and higher HCO_3^- concentrations recorded in the deep CO_2 well water. While the HCO_3^- concentrations measured in the groundwater wells around the Kerr quarter are similar to those of the St. Johns samples, there is no evidence of a trend towards the low $^3\text{He}/^4\text{He}$ ratios and high HCO_3^- concentrations measured in the produced CO_2 from the Weyburn field (Fig. 9 & 10).

Fig. 9. $^3\text{He}/^4\text{He}$ ratios plotted against HCO_3^- concentrations in the produced reservoir fluids, groundwater wells and water injected into the reservoir surrounding the Kerr quarter. The black dash line indicates the air $^3\text{He}/^4\text{He}$ value of $1R_a$. All of the groundwater wells have $^3\text{He}/^4\text{He}$ ratios that are close to the air ratio and exhibit no relationship between HCO_3^- concentrations and the $^3\text{He}/^4\text{He}$ ratio.

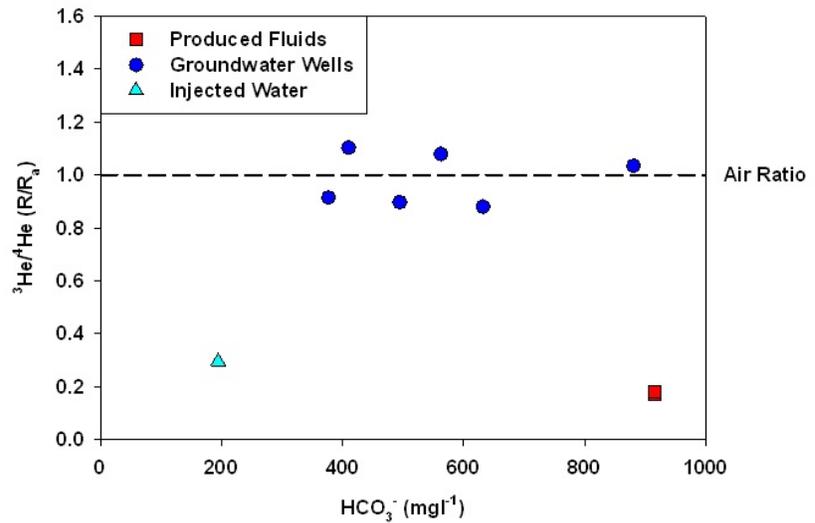
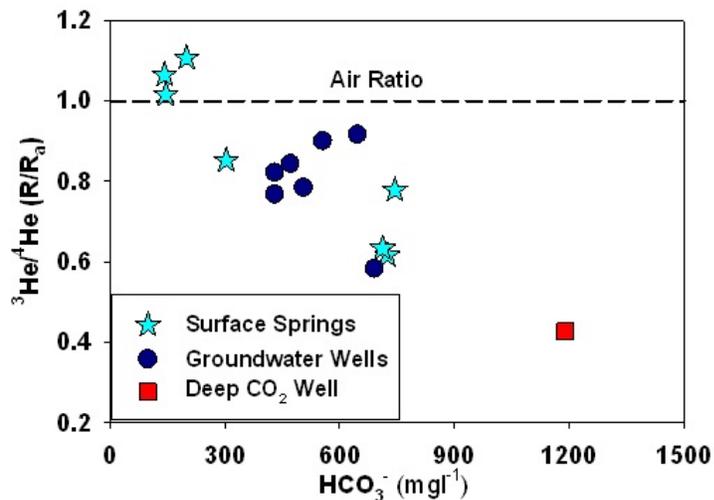


Fig. 10. $^3\text{He}/^4\text{He}$ ratios plotted against HCO_3^- concentrations for the surface springs, groundwater wells and CO_2 well sampled around St. Johns Dome. The black dash line indicates the air $^3\text{He}/^4\text{He}$ value of $1R_a$. There is a clear distinction between the above air ratios measured in three anomalous spring water samples; Willowbank Spring, 24 Bar Ranch and New Mexico Spring, caused by the addition of tritogenic ^3He and the below air $^3\text{He}/^4\text{He}$ ratios measured in the other samples. There is also a correlation between increasing HCO_3^- concentrations and $^3\text{He}/^4\text{He}$ decreasing toward the values measured in the deep CO_2 reservoir.



5.2. ^4He concentrations and $^3\text{He}/^4\text{He}$ ratios

As a result of light mass of He atoms they are not retained by the Earth's gravitational field and so are lost from the atmosphere to space. This means that the atmosphere is not a significant source of He into groundwater. ^4He predominately originates from the radioactive decay of uranium and thorium in the Earth's crust and builds up in deep groundwaters over time (Torgersen and Clark, 1985). Hence, it is not surprising that the concentration of ^4He measured in the fluids from the Weyburn field is two orders of magnitude higher than the concentration in the atmosphere (Fig. 11). This is also reflected in the considerably higher than air saturated water He/Ne ratios exhibited by the produced fluids (Fig. 5). The addition of crustal derived ^4He can also account for the higher ^4He concentration than air saturated water concentrations measured in the injected water. All of the groundwater wells surrounding the Kerr quarter show ^4He concentrations that are comparable to air saturated water values. This along with the air saturated water He/Ne ratios strongly implies that there is no additional source of ^4He from depth to the groundwaters.

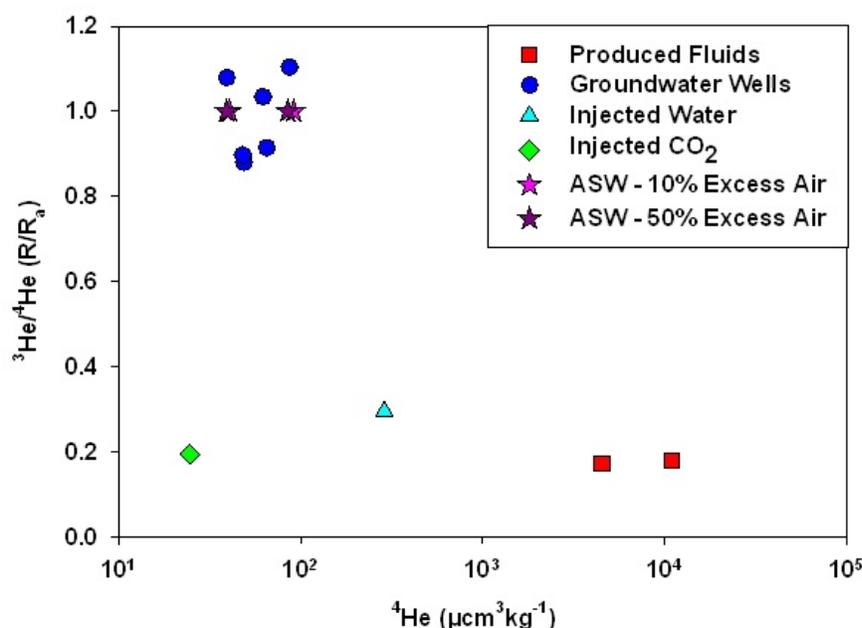


Fig. 11. $^3\text{He}/^4\text{He}$ plotted against ^4He concentrations in the produced reservoir fluids, groundwater wells and water injected into the reservoir surrounding the Kerr quarter. It is readily apparent that all of the groundwater samples exhibit ^4He concentrations that are within the air saturated water concentrations and there is no correlation to the either the injected water, injected CO_2 or produced fluids from the Weyburn oil field.

There is also no relationship between $^3\text{He}/^4\text{He}$ ratios and the concentration of ^4He in the groundwaters. This strongly implies that there is no addition of deep crustal ^4He to the sampled waters surrounding the Kerr quarter and indicates that there is no migration of fluids from depth into the sampled wells. This is again in contrast to the clear relationship between decreasing $^3\text{He}/^4\text{He}$ and increasing ^4He concentrations observed in the St. Johns study (Fig. 12). Fig. 12 illustrates that the low $^3\text{He}/^4\text{He}$ and high ^4He within the groundwater wells and majority of surface springs (except for the anomalous springs) can be explained by simple mixing between deep well water, which exhibits low $^3\text{He}/^4\text{He}$ ratios and high ^4He values, and varying amounts of shallow groundwater that has an atmospheric $^3\text{He}/^4\text{He}$ ratio and ^4He concentration.

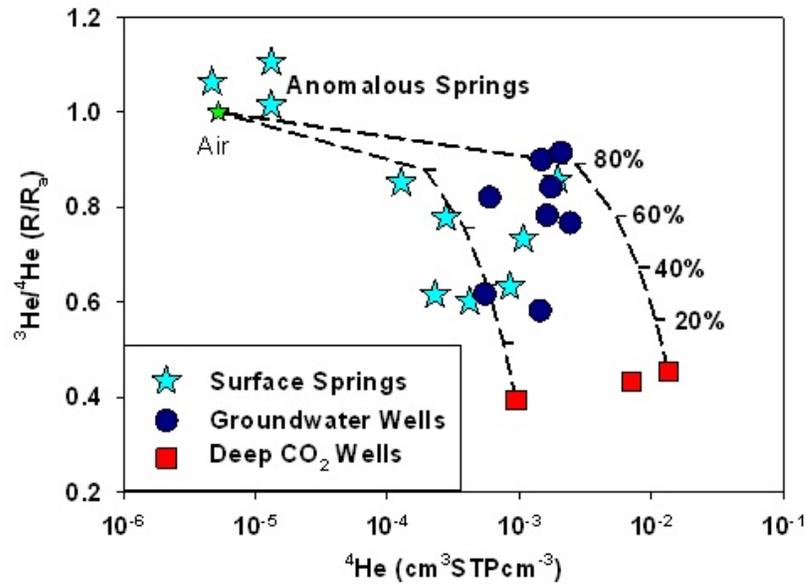


Fig. 12. $^3\text{He}/^4\text{He}$ plotted against ^4He for the St. Johns samples. Also plotted are mixing lines illustrating the mixing between different compositions of deep groundwater measured from wells, to 100% air. The low $^3\text{He}/^4\text{He}$ and high ^4He within the groundwater wells and majority of surface springs can be explained by simple mixing between the $^3\text{He}/^4\text{He}$ and ^4He values measured in the deep CO_2 wells and varying amounts of air (per cent air indicated on tick marks). This proves that the excess ^4He component entrained at depth is retained and not lost on migration of the waters to the surface. No such relationship is apparent in the samples from the Kerr study.

5.3. Ne, Ar and Kr ratios and Concentrations

With the exception of the slightly above air $^{20}\text{Ne}/^{22}\text{Ne}$ ratios and slightly below ^{84}Kr concentrations exhibited by the groundwater wells, the $^{20}\text{Ne}/^{22}\text{Ne}$ and $^{40}\text{Ar}/^{36}\text{Ar}$ ratios and ^{20}Ne , ^{36}Ar and ^{40}Ar concentrations are within air saturated water range (Figs 6-8). This indicates that the noble gases in groundwaters surrounding the Kerr quarter are of atmospheric origin and do not contain a measurable amount of radiogenic noble gases from depth. This reinforces the conclusions made from the He data that there is no additional source of noble gases to the groundwater samples other than the atmosphere.

6. CONCLUSIONS

All of the noble gas concentrations and the majority of noble gas ratios measured in the groundwaters from wells surrounding the Kerr quarter are within or very close to the air saturated values. There is no evidence in any of the noble gas data that there is any significant presence of deep crustal derived noble gases within the ground waters surrounding the Kerr quarter. The absence of crustal derived noble gases means that there is no evidence of the migration of deep CO₂ from the Weyburn oil field into the groundwater on the Kerr quarter or the surrounding area.

“The absence of crustal derived noble gases means that there is no evidence of the migration of deep CO₂ from the Weyburn oil field into the groundwater on the Kerr quarter or the surrounding area.”

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