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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

34 atmosphere under local recharge conditions, the produced CO₂ obtained from production
35 wells, and the CO₂ injected into the Weyburn and Midale oil fields. We find that the stable
36 carbon isotope data do not constrain the origin of the dissolved CO₂ in the Kerr groundwaters.
37 Due to low noble gas concentrations in the captured CO₂ we are unable to completely rule out
38 the presence of 20 to 34% contribution from injected CO₂ to the groundwaters surrounding the
39 Kerr property. However, we find that all of the Kerr groundwater samples exhibit noble gas
40 fingerprints that would be expected in a shallow groundwater in contact with the atmosphere
41 and hence there is no evidence for the addition of a deep radiogenic component or dilution
42 from the addition of a gas phase low in atmospheric derived noble gases. Our findings
43 corroborate previous studies that indicate that elevated CO₂ concentrations found on the Kerr
44 property are almost certainly of biological origin, and not migrated from the deep subsurface.
45 The comprehensive follow up to these CO₂ leakage allegations outlined in this study provides
46 a robust framework for responses to any future leakage allegations at CO₂ storage sites and
47 further highlights that no single technique can categorically identify the origin of CO₂ in the
48 shallow subsurface. Hence, it is essential that the full range of geochemical tracers (stable
49 carbon and ¹⁴C isotopes, noble gases, water chemistry, process based gas ratios) are
50 integrated with a comprehensive understanding of geological and engineering data in
51 response to CO₂ leakage allegations in the future.

52 **1. Introduction**

53 For Carbon Capture and Storage (CCS) technology to be routinely deployed evidence is
54 required that large volumes of CO₂ can be injected into the subsurface and securely retained.
55 This evidence base can only be provided through evaluation of the containment performance
56 of both natural CO₂ reservoirs (Miocic et al., 2013; Miocic et al., 2016) and through the
57 evaluation of the security of engineered CO₂ storage sites (Wolaver et al., 2013). Around the
58 world several large scale CO₂ injection projects have been initiated to provide this evidence
59 base. The largest of these is operating at the Weyburn and Midale oil fields in Saskatchewan,
60 Canada, where CO₂ has been introduced into the Weyburn field since 2000, and the Midale
61 field since 2005, to both increase oil recovery, termed CO₂-enhanced oil recovery (EOR), and
62 for storage purposes (Whittaker et al., 2011). The injected CO₂ is sourced from the Dakota
63 Gasification plant in North Dakota and is pumped some 320 km to the oil fields, and ~20 Mt of
64 CO₂ had been injected by the start of 2011 (Whittaker et al., 2011). Currently, 2.4 Mt/year and
65 0.4 Mt/year of CO₂ are injected into the Weyburn and Midale oil fields, respectively, and it is
66 intended that in excess of 40 Mt of CO₂ will be stored in the fields in total (IEA Greenhouse
67 Gas Programme, 2004).

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

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

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

98 Following the allegations, three separately funded, and independently conducted
99 investigations were launched. The first of these was undertaken by European scientists who
100 had completed 10 years of near-surface monitoring at the nearby Weyburn-Midale CO₂ EOR
101 field (Beaubien et al., 2013). A second study was commissioned by the Weyburn field
102 operators, Cenovus Energy Inc. (Cenovus), and undertaken by three third parties external to

103 Cenovus; TRIUM Environmental, Chemistry Matters and TERA Environmental Consultants.
104 Once completed, the TRIUM Environmental and Chemistry Matters site investigation was then
105 independently reviewed by the PTRC. A third study was co-ordinated by the International
106 Performance Assessment Centre for Geological Storage of CO₂ (IPAC-CO₂), a not-for-profit
107 research and development organisation founded in 2008. IPAC-CO₂ was established to fill a
108 gap in the understanding and assessment of risk and performance in the Carbon Capture and
109 Storage chain by providing independent, objective information, best practices, advice and
110 assessments to governments and industry (ZeroCO2.no, Accessed 1st March 2016). IPAC-
111 CO₂ was funded by Royal Dutch Shell and the Government of Saskatchewan, and hosted at
112 the University of Regina (Saskatchewan, Canada). Prior to the Kerr allegations, IPAC-CO₂
113 developed an Incident Response Protocol (IRP) that would be implemented if there were
114 allegations of CO₂ leakage at a CCS project (Sherk, 2011). This IRP provided a framework
115 and foundation for the Kerr investigation which comprised three distinct activities undertaken
116 on the Kerr property and surrounding area; (i) chemical analysis of soil gases (Romanak et
117 al., 2014), (ii) stable C isotope and noble gas analysis of the shallow groundwaters (this study),
118 (iii) hydrogeological analysis (Wolaver et al., 2011).

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

126 **2. Investigation Background**

127 *2.1. Scientific Background*

128 $\delta^{13}\text{C}_{\text{DIC}}$ measurements have been extensively used in tracing CO₂ injected into the Weyburn
129 field and other CO₂ storage test sites (Johnson et al., 2009; Raistrick et al., 2006). They have
130 proved to be effective at tracking the migration and fate of CO₂ injected into the Weyburn-
131 Midale field (Mayer et al., 2013) and at several shallow CO₂ leakage monitoring pilot projects
132 (Jones et al., 2015; McAlexander et al., 2011; Moni and Rasse, 2014; Schulz et al., 2012).
133 However, the effectiveness of $\delta^{13}\text{C}_{\text{DIC}}$ as a sole means to track the migration of CO₂ injected
134 at depths in excess of a 100 m to the shallow subsurface has yet to be fully quantified (Mayer
135 et al., 2015). CO₂, for example, is both highly soluble and reactive in shallow systems (e.g.
136 Gilfillan et al., 2009) which limits the sensitivity of early seepage detection. There are many
137 sources of DIC in subsurface waters, including the weathering of carbonate and silicate

138 minerals by acid rain, the breakdown of organic matter and plant respiration. Each of these
139 processes leads to wide and overlapping $\delta^{13}\text{C}_{\text{DIC}}$ ranges, meaning the typical range in natural
140 subsurface waters is -5 to -25‰ (Kendall et al., 1995), which is within the range observed
141 when fossil fuel derived CO_2 equilibrates with water (Flude et al., 2016; Petroleum Technology
142 Research Centre, 2011).

143 Noble gases are intimately associated with all natural and engineered CO_2 occurrences, being
144 trace components in the gas mixture in parts per billion quantities. There are three distinct
145 sources of noble gases within the subsurface, namely the crust, the mantle and the
146 atmosphere, and these can be discriminated and “fingerprinted” by both their isotopic
147 compositions and abundance ratios of each isotope (Ballentine et al., 2002; Gilfillan et al.,
148 2014; Holland and Gilfillan, 2013). Helium, in particular has proved to be effective at tracing
149 deep input to shallow systems due to its extremely low concentration in the atmosphere of 5.2
150 parts per million (Torgersen et al., 1992). This low abundance allows the presence of small
151 additional quantities of helium above the atmospheric level to be readily resolved. There are
152 only two helium sources that result in concentrations above the atmospheric level in
153 subsurface fluids. Helium produced through the radiogenic decay of U and Th in the crust,
154 which yields the ^4He isotope, with the other source in crustal fluids being the mantle (Ballentine
155 and Burnard, 2002). Helium derived from the Earth’s mantle is contrastingly rich in the ^3He
156 isotope, and widely contributes to sedimentary fluids (Ballentine et al., 2002; Kennedy and
157 van Soest, 2007; Marty et al., 1992; Oxburgh et al., 1986); Marty et al., 1993; Ballentine et al.,
158 2002; Kennedy and van Soest, 2007). Differing helium inputs from these distinct sources
159 results in a range of $^3\text{He}/^4\text{He}$ ratios being observed in fluids present in almost all sedimentary
160 basins (Ballentine et al., 2002; Castro et al., 1998).

161 The use of noble gases in tracing CO_2 origins and its fate within natural CO_2 accumulations
162 and hydrocarbon reservoirs has been demonstrated in a number of studies (Gilfillan et al.,
163 2008; Gilfillan et al., 2009; Györe et al., 2015; Holland and Gilfillan, 2013; Nimz and Hudson,
164 2005; Zhou et al., 2012). Recent work has shown that noble gases can trace CO_2 dissolved
165 in the groundwater migrating to the surface above the St. Johns Dome natural CO_2 reservoir
166 in Arizona (Gilfillan et al., 2011). The noble gas composition of shallow groundwaters and
167 surface waters found above this natural CO_2 reservoir exhibited low $^3\text{He}/^4\text{He}$ ratios, and
168 elevated $^4\text{He}/^{20}\text{Ne}$ ratios, indicating a clear link to the noble gas composition measured in CO_2
169 in the deep reservoir below (Gilfillan et al., 2011). This link has been further corroborated by
170 recent cation and trace element analysis of springs and groundwaters in the vicinity of the St.
171 Johns CO_2 reservoir, which confirmed the presence of an additional dissolved CO_2 component
172 in the shallow groundwaters (Keating et al., 2014).

173 Noble gas fingerprinting techniques have also recently been used to identify micro-seepage
174 of CO₂ and CH₄ above the Teapot Dome oil field in Wyoming (Mackintosh and Ballentine,
175 2012). This study found that ³He/⁴He ratios in the soils gas were considerably below the
176 atmospheric ratio, due to the addition of a radiogenic ⁴He component, which was also reflected
177 by elevated ⁴He concentrations and ⁴He/²⁰Ne ratios relative to atmospheric values. Mackintosh
178 and Ballentine (2012) concluded that the detection of crustal-sourced helium micro-seepage
179 into water saturated systems will be enhanced by two orders of magnitude compared with soil
180 gases. This is due to the low solubility of helium in water which results in a baseline
181 concentration which is two orders of magnitude lower than the expected atmospheric ⁴He
182 concentration in a soil gas (Mackintosh and Ballentine, 2012).

183 Additionally, noble gases have recently proved to be effective at identifying the source of
184 fugitive CH₄ contamination of groundwaters overlying the Marcellus and Barnett shale
185 formations related to shale gas extraction (Darrah et al., 2014), and in resolving the origin of
186 naturally elevated CH₄ levels of shallow groundwaters in the northern Appalachian basin
187 (Darrah et al., 2015). These studies highlighted that groundwater wells with high CH₄
188 concentrations, located close to gas production wells, had elevated concentrations of ⁴He and
189 below expected concentrations of ²⁰Ne and ³⁶Ar (Darrah et al., 2014). The elevated ⁴He
190 concentrations were attributed to the presence of thermogenic derived CH₄ gas, whilst the
191 lower than expected concentrations of ²⁰Ne and ³⁶Ar in the waters were attributed to the
192 migrated methane gas having significantly lower ²⁰Ne and ³⁶Ar concentrations than a
193 groundwater in contact with the atmosphere. This results in the migrating methane 'stripping'
194 out the ²⁰Ne and ³⁶Ar as noble gases are more soluble in methane than in water. The process
195 is identical to the stripping of formation waters which has been observed in natural CO₂
196 reservoirs (Gilfillan et al., 2008; Gilfillan et al., 2009; Zhou et al., 2012) and recently in a CO₂-
197 EOR field (Györe et al., 2017; Györe et al., 2015). This noble gas stripping process provides
198 an additional means to test for the presence of a deep subsurface sourced gas that is depleted
199 in atmospheric noble gases.

200 2.2. Approach

201 We aimed to evaluate the effectiveness of $\delta^{13}\text{C}_{\text{DIC}}$, ³He/⁴He, ⁴He/²⁰Ne, Ne, Ar and Kr
202 fingerprints in determining the validity of the allegations of CO₂ leakage made on the Kerr
203 property. To achieve this we undertook measurements of a suite of noble gases and C stable
204 isotope tracers from three different sources: (i) CO₂ injected into the field (injected CO₂); (ii)
205 fluids produced from the field (produced CO₂); (iii) groundwaters at the Kerr property and
206 surrounding area (Kerr groundwaters). We aimed to determine if migration CO₂ originating
207 from either the CO₂ injected into, or CO₂ contained in the fluids produced from the Weyburn

208 field was responsible for the alleged elevated CO₂ concentrations on the Kerr property. To do
209 this we compare the noble gas and C isotope fingerprints between type (i), (ii) samples to
210 those of type (iii), the Kerr groundwaters.

211 Based on the studies outlined in the Scientific Background section we hypothesise that any
212 external CO₂ addition to the Kerr groundwaters, bar those of shallow subsurface biologic
213 processes, would result in either the addition of crustal derived ⁴He and/or a depletion in the
214 main atmospheric derived noble gases of ²⁰Ne, ³⁶Ar, ⁴⁰Ar and Kr. The addition of a crustal
215 radiogenic ⁴He component can be identified by elevated ⁴He/²⁰Ne ratios above those of the
216 atmosphere and/or a reduction in ³He/⁴He ratios below those of atmospheric values. We focus
217 on the Kerr groundwaters as opposed to soil gases based on the study of Mackintosh and
218 Ballentine (2012) which showed helium anomalies would be enhanced by two orders of
219 magnitude compared with soil gases as a result of the low solubility of helium in water.

220 **3. Methods**

221 Sample collection was undertaken over a period of three days in late June 2011, some 11
222 months following the soil gas sampling undertaken in the previous summer on which the
223 leakage allegations were based (Lafleur, 2010). Samples of injected CO₂ were collected from
224 a the sampling port of a Cenovus injection well (Well ID - 101/12-04-006-13 W2/0) located
225 approximately 10 km northwest of the Kerr quarter. A sample of CO₂ separated from the
226 produced reservoir fluids (produced gas, water and oil) was collected from the sampling port
227 of the flowline emerging from a Cenovus satellite processing facility located at 16-30-05-13
228 (Fig. 1). This flowline contained produced gas separated by the first stage separation system
229 at the satellite site from the oil, gas and water collected from 14 production wells that
230 surrounded the Kerr property. Gases were collected from both the pressurised injection well
231 and the satellite processing facility flow line using a high pressure to low pressure step down
232 regulator, allowing gas collection at slightly above atmospheric pressure in 70 cm long vacuum
233 tight copper tubes held in aluminium clamps. Shallow groundwaters were collected from the
234 domestic groundwater well on the Kerr farm, two domestic groundwater wells on the adjacent
235 Thackeray farm and the IPAC No. 1 monitoring well which was drilled during the sampling
236 program. This was located as close to the maximum CO₂ anomaly reported by Petro-Find as
237 possible given the underlying ground conditions required for the drilling rig (Lafleur, 2010) (Fig.
238 1). All of the wells were of standard shallow groundwater bored type construction, drilled using
239 a rotary bucket auger and completed with PVC casing utilising a sand screen at the base.
240 Each well was 0.762 m in diameter, ranging in depth below ground surface from 3.09 m
241 (Thackery Farm Well) to 12.29m (Thackery House Well). Groundwater was encountered
242 between 1.76m (IPAC ~1 monitoring well) and 3.56m below ground level. Samples were

243 collected from the base of the well water volumes using a peristaltic pump, with each well being
244 pumped until water chemistry parameters established before sample collection.

245 $\delta^{13}\text{C}$ (CO_2) values of the gas samples and $\delta^{13}\text{C}_{\text{DIC}}$ values of the waters were determined at
246 the University of Rochester using a Delta S (Finningan) mass spectrometer and the analytical
247 error was ± 0.2 ‰. Standard extraction and purification procedures were used (Jenden et al.,
248 1993) and the ratios are expressed as $\delta^{13}\text{C}$ ‰ V-PDB. The dissolved gases were extracted
249 on a stainless steel and 1720 glass extraction line at the University of Rochester using
250 standard procedures (Poreda et al., 2004). Noble gas isotopic ratios ($^3\text{He}/^4\text{He}$, $^{20}\text{Ne}/^{22}\text{Ne}$,
251 $^{21}\text{Ne}/^{22}\text{Ne}$, $^{40}\text{Ar}/^{36}\text{Ar}$, $^{38}\text{Ar}/^{36}\text{Ar}$) and elemental abundances (^4He , ^{20}Ne , ^{40}Ar and Kr) were
252 determined on the University of Rochester's VG 5400 mass spectrometer, using established
253 techniques (Poreda and Farley, 1992). Bulk gases were purified by consecutive exposure to
254 a Zr-Al getter (SAES ST-707) held at 450°C and a SAES SORB-AC cartridge held at 250°C
255 then cooled to 25°C . This was followed by the sequential trapping of Ar into an activated
256 charcoal finger at liquid N_2 temperature (-178°C) and the He and Ne into an activated charcoal
257 finger at -261°C . He was released from the cryogenic finger at -242°C and expanded into the
258 spectrometer and measured, followed by Ne and Ar analyses. He, Ne, Ar, and Kr
259 concentrations were determined by comparison to an air standard of known volume (0.77
260 cm^3). Helium isotope ratios were normalized using a Rochester air standard. Neon isotope
261 ratios were corrected for interference by measurement of $^{40}\text{Ar}^{2+}$ and CO_2^{2+} ($^{40}\text{Ar}^{2+}$ was typically
262 < 0.4 % of total ^{20}Ne signal on the faraday cup and CO_2^{2+} was below detection limits for ^{22}Ne).
263 The two sigma analytical error for the $^3\text{He}/^4\text{He}$ ratio is approximately 0.5% and those for both
264 the $^{40}\text{Ar}/^{36}\text{Ar}$ and He/Ne isotope ratios were 0.2 %, and 0.3 % for $^{38}\text{Ar}/^{36}\text{Ar}$ and 1 % for
265 $^{20}\text{Ne}/^{22}\text{Ne}$, $^{21}\text{Ne}/^{22}\text{Ne}$ and $^{20}\text{Ne}/^{36}\text{Ar}$ and 1.5 % for all noble gas abundances. Helium isotope
266 ratios ($^3\text{He}/^4\text{He}$) are expressed relative to the ratio in air ($R_a = R_{\text{measured}} / R_{\text{air}}$ where $R_{\text{air}} = 1.399$
267 $\times 10^{-6}$). All other ratios are absolute values. The majority of the duplicate sample ratios and
268 concentrations are within 5 % of each other. Two sigma errors to the last significant figure are
269 reported for both gas ratios and concentrations and these may be taken as limits of detection
270 for small associated data values.

271 We report the concentrations of noble gases dissolved in water, rather than the concentrations
272 of noble gases in the headspace gas degassed from the waters. This is because the amount
273 of headspace (ie non noble gas) gases exsolved from the Kerr groundwaters was insufficient
274 to obtain high quality ratio concentrations of noble gases relative to the total exsolved gas.
275 However, the concentration of the individual noble gases degassed from the water samples
276 was sufficient for high quality analysis to be performed; hence these concentrations are
277 presented relative to the amount of water degassed. Reporting the dissolved noble gas

278 concentration in groundwaters in this manner is standard practice in shallow groundwaters
279 where small quantities of dissolved gases are present (Kipfer et al., 2002).

280 To allow direct comparison between the different sample types, and to detect any external
281 input to the Kerr groundwaters from the Weyburn EOR operations, we calculate the noble gas
282 concentration in water that would arise from equilibrium of the noble gases within the injected
283 and produced CO₂ with a shallow groundwater in the area surrounding the Kerr property.
284 Using the average measured groundwater well water temperature of 14.3°C (IPAC-CO₂,
285 2011), pressure of 0.101 MPa (1 atm) and salinity value of 0.02 Molar NaCl (equivalent to the
286 average TDS value of 1034 mg l⁻¹, (IPAC-CO₂, 2011)) we calculate the Henry's constants using
287 empirical equations (Crovetto et al., 1982; Smith, 1985). Under these conditions the calculated
288 Henry's constants for He, Ne, Ar, Kr and Xe are 14.12, 11.69, 3.41, 1.80 and 1.19 GPa,
289 respectively.

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

303 **4. Results**

304 *4.1. δ¹³C (CO₂) and δ¹³C_{DIC} Values*

305 The measured δ¹³C (CO₂) of the CO₂ injected into the Weyburn field of -21.2 ± 0.2 ‰ is similar
306 to the average value of -20.4 ± 0.3 ‰ previously reported from analysis of 8 samples of
307 injected CO₂ and 8 samples of recycled CO₂ from the Weyburn reservoir collected between
308 2000 and 2010 (Mayer et al., 2013). The measured produced CO₂ δ¹³C (CO₂) duplicate values
309 obtained in this study were -14.8 and -12.4 ± 0.2 ‰ (Table 1), somewhat above the range of
310 -16.5 and -17.7 ‰ observed by Mayer et al., (2013) in the final stage of their study of produced
311 gases from the Weyburn field in late 2010. The sampled Kerr groundwaters exhibit δ¹³C_{DIC}
312 values ranging from -13.4 ± 0.2 ‰ to -19.0 ± 0.2 ‰ (Table 1).

313 *4.2. Noble Gas Concentrations*

314 ⁴He concentrations exhibit marked distinctions depending on sample type (Fig. 2). The lowest
315 concentration of $41.63 \pm 0.5 \mu\text{cm}^3\text{kg}^{-1}$ is that calculated for a shallow groundwater which has
316 equilibrated with the injected CO₂ (see Methods). The groundwaters sampled from the wells
317 on and around the Kerr property (the Kerr groundwaters) exhibit a range of 39.2 ± 0.6 to 86.9
318 $\pm 1.3 \mu\text{cm}^3\text{kg}^{-1}$ which is almost identical to the air saturated water (ASW) concentration range
319 of 42.1 ± 0.6 to $85.8 \pm 1.2 \mu\text{cm}^3\text{kg}^{-1}$. This indicates that there is no presence of ⁴He in excess
320 of the concentration calculated for equilibrium dissolution of atmospheric noble gases into a
321 groundwater under the recharge conditions present at the study site (see Methods). The ⁴He
322 concentration of a shallow ground water in equilibrium with the produced CO₂ is two orders of
323 magnitude higher than the values recorded from the Kerr groundwaters, ranging from $7634 \pm$
324 115 to $18313 \pm 275 \mu\text{cm}^3\text{kg}^{-1}$.

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

332 *4.3. Noble Gas Isotope Ratios*

333 ⁴He/²⁰Ne ratios exhibit considerable variation depending on sample type. The lowest ratios
334 are those observed in the Kerr groundwaters which vary from 0.248 ± 0.006 to 0.403 ± 0.010 ,
335 overlapping with the ASW range of 0.288 ± 0.007 - 0.325 ± 0.01 (Fig. 4). The injected CO₂
336 exhibits a higher ratio of 12.6 ± 0.3 , with the duplicate produced CO₂ samples ranging from
337 1000 ± 21 to 1488 ± 31 , significantly above the calculated air saturated water (ASW) range
338 (Fig. 4). The above ASW ratios of the produced CO₂ indicate an excess of ⁴He above
339 atmospheric levels.

340 ³He/⁴He vary considerably between the different sample types, with the lowest values of 0.173
341 ± 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
342 in the CO₂ produced from the Weyburn field (Fig. 5). The CO₂ injected into the Weyburn field
343 has a slightly higher ratio of $0.193 \pm 0.001 R_a$. The range observed in the Kerr groundwaters
344 of 0.880 ± 0.004 to $1.103 \pm 0.006 R_a$ is significantly above that of the other samples (Fig. 5).

345 Other noble gas ratios of the Kerr groundwaters are within the range expected for ASW; the
346 ²¹Ne/²²Ne of are within 2 sigma error of the ASW ratio of 0.0290 ± 0.003 . ⁴⁰Ar/³⁶Ar are also all

347 within error of the calculated ASW range of 294 to 296 ± 1. The only non-atmospheric ratios
348 observed are $^{20}\text{Ne}/^{22}\text{Ne}$ that range from 9.96 ± 0.10 to 10.15 ± 0.10 , in excess of the air ratio
349 of 9.80 ± 0.08 . The elevation of $^{20}\text{Ne}/^{22}\text{Ne}$ is a common observation in natural groundwaters
350 and is thought to be the result of a solubility controlled fractionation process, where ^{20}Ne
351 dissolves preferentially to ^{22}Ne (Zhou et al., 2005).

352 **5. Discussion**

353 *5.1. Comparison of results to previous measurements from the Weyburn CO₂-EOR field*

354 For logistical and budgetary reasons it was not possible to undertake sampling in the area on
355 and surrounding the Kerr property on multiple occasions, over an extended period. Whilst this
356 is an obvious limitation of our study, Mayer et al., (2013) have produced an extensive
357 compilation of both $\delta^{13}\text{C}$ (CO₂) and $\delta^{13}\text{C}$ of DIC from both injected CO₂ and produced fluid
358 samples collected at the Weyburn field over a 10 year period from 2000 to 2010. Our
359 measured $\delta^{13}\text{C}$ (CO₂) of the injected CO₂ of -21.2 ± 0.2 ‰ is comparable to the average value
360 of -20.4 ± 0.3 ‰ previously reported from analysis of 8 samples of source CO₂ and 8 samples
361 of injected CO₂ (which includes the source CO₂ and a small recycled component) from the
362 Weyburn reservoir collected between 2000 and 2010 (Mayer et al., 2013). This indicates that
363 our injected CO₂ sample is representative of the CO₂ injected into the Weyburn field over its
364 history.

365 The produced CO₂ $\delta^{13}\text{C}$ (CO₂) duplicate values obtained in this study were -14.8 and $-12.4 \pm$
366 0.2 ‰ (Table 1), somewhat above the range of -16.5 and -17.7 ‰ observed by Mayer et al.,
367 2013 in the final stage of their study of produced gases from the Weyburn field in late 2010.
368 This variation can be explained by the fact that we sampled from a satellite site producing
369 fluids from a suite of injection wells located nearest to the Kerr property which is part of flood
370 phase 1C rather than those of phase 1A sampled by Mayer et al., (2013). Injection of CO₂ into
371 the Phase 1A area of the field commenced in 2000, with injection into the Phase 1C portion
372 of the field commencing in 2003 (Chalaturnyk and Durocher, 2005). Mayer et al., (2013) show
373 that $\delta^{13}\text{C}$ (CO₂) values decrease from the reservoir baseline value of -12.7 ‰ over time
374 throughout their study, as more of the injected CO₂ reaches the production wells, and a similar
375 evolution would be expected in the phase 1C region of the field.

376 Whilst it would obviously have been beneficial to undertake multiple measurements of the CO₂
377 injected into and CO₂ produced from the Weyburn CO₂-EOR field, the above comparison
378 shows that the samples we have collected are representative of the range of CO₂ injected and
379 CO₂ produced from the Weyburn field since CO₂ injection commenced in 2000 (Mayer et al.,
380 2013).

381 5.2. $\delta^{13}\text{C}_{\text{DIC}}$ Values

382 Mayer et al. (2013) found that as CO_2 concentrations increased at the Weyburn production
383 wells, the $\delta^{13}\text{C}$ CO_2 values progressively approached those of the injected CO_2 (-20.4 ± 0.3
384 ‰ from the 16 samples outlined previously). Using their measured reservoir pH values they
385 predicted that the $\delta^{13}\text{C}$ of DIC in equilibrium with the injected CO_2 would be -19 ± 2 ‰.
386 However, they found that their measured values approached a value of only -16 ‰, indicating
387 that there was an additional HCO_3^- source with elevated $\delta^{13}\text{C}$ DIC values within the reservoir.
388 Increasing concentrations of calcium and magnesium provided independent evidence that
389 calcite and dolomite dissolution had generated additional HCO_3^- , resulting in a contribution of
390 HCO_3^- with a $\delta^{13}\text{C}_{\text{DIC}}$ value of $+3$ ‰.

391 Hence, the difference of $\delta^{13}\text{C}$ of DIC (composed of DIC in isotopic equilibrium with injected
392 CO_2 and DIC derived from carbonate dissolution) and $\delta^{13}\text{C}$ of injected CO_2 was $+4.4$ ‰. In
393 order to allow direct comparison to the measured $\delta^{13}\text{C}$ DIC values in the Kerr groundwaters
394 we use this fractionation value to calculate the $\delta^{13}\text{C}_{\text{DIC}}$ which would be produced in water in
395 equilibrium with CO_2 which has the $\delta^{13}\text{C}$ (CO_2) of both the injected (-21.2 ± 0.2 ‰) and
396 produced CO_2 (-14.8 and -12.4 ± 0.2 ‰). Using this fractionation value we calculate a $\delta^{13}\text{C}_{\text{DIC}}$
397 value of -16.8 ± 0.2 ‰ for water in contact with the injected CO_2 and a $\delta^{13}\text{C}_{\text{DIC}}$ range of -10.4
398 to -8.0 ± 0.2 ‰ for water in contact with the produced CO_2 .

399 The range of $\delta^{13}\text{C}_{\text{DIC}}$ values measured in the Kerr groundwaters of -13.4 ± 0.2 ‰ to $-19.0 \pm$
400 0.2 ‰, overlaps with that of water in contact with the injected CO_2 and is distinct from those
401 exhibited by water in contact with the produced CO_2 . This indicates that there is a potential
402 link between the $\delta^{13}\text{C}_{\text{DIC}}$ values in the Kerr groundwaters and the injected CO_2 . However, this
403 is not an unequivocal link as there are multiple sources of DIC in shallow groundwaters, with
404 each of the sources exhibiting overlapping $\delta^{13}\text{C}_{\text{DIC}}$ ranges. This results in a typical $\delta^{13}\text{C}_{\text{DIC}}$
405 range in natural subsurface waters of -5 to -25 ‰ (Kendall et al., 1995). Hence, natural soil
406 processes including plant respiration, dissolution of carbonate minerals and bacterial activity
407 could account for the range of -13.4 ± 0.2 ‰ to -19.0 ± 0.2 ‰ observed in the Kerr
408 groundwaters (Hendry et al., 1999; Keller and Bacon, 1998; Petroleum Technology Research
409 Centre, 2011; Romanak et al., 2014).

410 Mayer et al., (2015) have undertaken a comprehensive review of the usefulness of the stable
411 isotope composition of CO_2 for leakage monitoring at CO_2 storage sites, which concluded that
412 $\delta^{13}\text{C}$ can be a useful tracer if values in the injected CO_2 are distinct from those of baseline
413 $\delta^{13}\text{C}$ (CO_2 , DIC) at the CCS site by more than 10 ‰. Extensive soil gas measurements were
414 undertaken in the vicinity of the Weyburn CO_2 -EOR field prior to CO_2 injection commencing in
415 2001 and after 10 years of injection in 2011 (Beaubien et al., 2013). Beaubien et al., (2013)

416 found that regional $\delta^{13}\text{C}$ CO_2 soil gas values ranged from -17.3 to -23.1 ‰, overlapping with
417 the range measured on the Kerr property of -21.7 to -22.7 ‰ by Romanak et al., (2014) and
418 the average value of the injected CO_2 of -20.4 ± 0.3 ‰ as reported by Mayer et al., (2013).
419 These studies highlight that $\delta^{13}\text{C}$ measurements alone cannot be used as a distinctive means
420 to determine the origin of CO_2 measured on the Kerr property as also outlined by a recent
421 signal to noise analysis (Risk et al., 2015).

422 *5.3. Mixing Modelling*

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

434 However, three of the Kerr groundwater samples exhibit below ASW $^3\text{He}/^4\text{He}$ ratios which
435 could indicate an additional low $^3\text{He}/^4\text{He}$ component to these waters (Mackintosh and
436 Ballentine, 2012). In order to fully resolve the presence of any non-atmospheric contribution
437 to these groundwater samples, we now model how ^4He concentrations, $^3\text{He}/^4\text{He}$ and
438 $^4\text{He}/^{20}\text{Ne}$ ratios of ASW would evolve through mixing with either the injected or produced
439 CO_2 from the Weyburn field. As the ASW noble gas fingerprint is determined by the solubility
440 equilibration of the noble gases in contact with the atmosphere (see Methods) under the
441 local recharge conditions, ASW is the accepted standard for a shallow groundwater which is
442 uncontaminated from any other inputs (Kipfer et al., 2002). Using these three end members,
443 mixing lines for both ratio-ratio plots and ratio-element plots can be plotted using established
444 techniques (Langmuir et al., 1978). The direct comparison of these mixing models with the
445 Kerr groundwater noble gas composition allows resolution of the possible contribution to the
446 waters from both the injected or produced CO_2 .

447 *5.4. $^3\text{He}/^4\text{He}$ ratios and ^4He concentrations*

448 In Fig. 5 a plot of $^3\text{He}/^4\text{He}$ and ^4He of the Kerr groundwaters is shown. Mixing lines on the
449 figure depict the calculated trends which would result from mixing of the CO_2 injected into, and

450 the CO₂ produced from the Weyburn field with a shallow groundwater with an ASW ³He/⁴He
451 (1 R_a) and the average ASW ⁴He concentration. Tick marks indicate the portion of ⁴He
452 originating from either the CO₂ injected or CO₂ produced from the Weyburn field on the mixing
453 lines presented. Three of the measured groundwaters contain an excess of ³He relative to the
454 predicted concentration in ASW, resulting in ³He/⁴He ratios above the ASW ratio of 1 R_a. This
455 can be explained by the presence of ³He originating from the decay of tritium which was
456 emitted to the atmosphere as a result of nuclear weapons testing from the 1950s to 1980s
457 (Happell, 2004). This additional ³He component is variable and creates some uncertainty
458 around the baseline ³He/⁴He ratio of the groundwater in the region. Hence, to account for this
459 variation we also use the higher value of 1.1 R_a as a worst case scenario for assessing the
460 portion of noble gases originating from either the CO₂ produced from, or injected into, the
461 Weyburn field.

462 The three Kerr groundwaters with below ASW ³He/⁴He ratios lie close to the two mixing lines
463 plotted. The concentration of ⁴He measured in the fluids produced from the Weyburn field is
464 two orders of magnitude higher than the atmospheric value, as a result of crustal radiogenic
465 contributions from interaction with the crustal fluids present in the EOR field (Fig. 5). This is
466 reflected in the higher than ASW ⁴He/²⁰Ne and lower than ASW ³He/⁴He ratios exhibited by
467 the produced CO₂ gas sample (Fig. 4). Using the mixing model presented allows us to resolve
468 that the Kerr groundwater with the lowest ³He/⁴He could conceivably contain a maximum 0.14
469 % contribution to ⁴He from the produced fluids using the best case ³He/⁴He endmember (1 R_a)
470 or a 0.25 % contribution using the worst case ³He/⁴He endmember (1.1 R_a).

471 Figure 5 highlights that a 20 % contribution using the best ³He/⁴He (1 R_a) end member and a
472 32 % contribution in the worst case (1.1 R_a) end member contribution to the Kerr groundwaters
473 from the injected CO₂ could account for the lowest ³He/⁴He ratio observed. This is a reflection
474 of the ⁴He concentration of the injected CO₂ being at the lower range of the ASW concentration
475 expected in the shallow groundwaters recharging at the summer temperatures experienced in
476 Saskatchewan.

477 5.5. ³He/⁴He and ⁴He/²⁰Ne ratios

478 Plots of ³He/⁴He against ⁴He/²⁰Ne ratios of the Kerr groundwaters, along with measured ratios
479 in the CO₂ produced and injected into the Weyburn EOR field are shown in Figure 4. Mixing
480 lines are shown with tick marks indicating the portion originating from either the CO₂ injected
481 or produced from the Weyburn EOR field. The ⁴He/²⁰Ne ratios measured in samples of the
482 produced and injected CO₂ into the Weyburn field are above the ASW range of 0.288 ± 0.001
483 - 0.322 ± 0.001, and all of the Kerr groundwaters exhibit ⁴He/²⁰Ne ratios which are within error
484 of the calculated ASW range (Fig. 4).

485 Using the mixing model presented allows determination that the Kerr groundwater with the
486 lowest $^3\text{He}/^4\text{He}$ and highest $^4\text{He}/^{20}\text{Ne}$ ratios indicates a maximum of a 0.14 % contribution, in
487 the best case scenario, to 0.25 % in a worst case scenario, to the ^4He concentration from the
488 produced CO_2 . Figure 5 also shows that using the best case (1 R_a) and worst case (1.1 R_a)
489 $^3\text{He}/^4\text{He}$ end member, a 20 % to 32 % contribution to the measured $^3\text{He}/^4\text{He}$ and $^4\text{He}/^{20}\text{Ne}$ of
490 the Kerr groundwaters could originate from the CO_2 injected into the Weyburn field could
491 account for the lowest $^3\text{He}/^4\text{He}$ and highest $^4\text{He}/^{20}\text{Ne}$ ratio observed.

492 5.6. ^{20}Ne , ^{36}Ar , ^{40}Ar , ^{84}Kr Concentrations

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

504 Recent work using noble gases to investigate the contamination of groundwaters by natural
505 gas from unconventional gas production in the USA has shown that well waters with high
506 methane concentrations, located close to gas production wells, have below ASW
507 concentrations of ^{20}Ne and ^{36}Ar (Darrah et al., 2014). This is a result of the fugitive methane
508 containing insignificant concentrations of groundwater derived ^{20}Ne and ^{36}Ar concentrations
509 and consequently the migrating methane 'strips' out these noble gases from the groundwaters.
510 This occurs as the noble gases are much more soluble in CH_4 than in water and is identical to
511 the stripping of formation waters which has been observed in natural CO_2 reservoirs (Gilfillan
512 et al., 2008; Gilfillan et al., 2009; Zhou et al., 2012) and recently in a CO_2 -EOR field (Györe et
513 al., 2015). Noble gases are also considerably more soluble in CO_2 than water (Warr et al.,
514 2015) so the presence of an active flux of CO_2 to the Kerr groundwaters would be expected to
515 lower the concentration of both ^{20}Ne and ^{36}Ar by a similar 'stripping' process.

516 Additionally, the groundwater samples with elevated CH_4 concentrations reported by Darrah
517 et al., (2014) also exhibited above ASW $^4\text{He}/^{20}\text{Ne}$ ratios, as a result of the presence of
518 increased levels of radiogenic ^4He which had migrated from depth (Darrah et al., 2014). A
519 similar trend has recently been observed in naturally methane rich shallow aquifers of the

520 Appalachian Basin (Darrah et al., 2015). Elevated $^4\text{He}/^{20}\text{Ne}$ ratios were also observed in all of
521 the spring and well water samples collected from directly above the St. Johns Dome CO_2
522 reservoir, whilst three springs located away from the reservoir had ASW $^4\text{He}/^{20}\text{Ne}$ ratios
523 (Gilfillan et al., 2011). The Appalachian study of the tracing fugitive CH_4 contamination of
524 groundwaters and previous noble gas measurements in both groundwaters at St. Johns
525 (Gilfillan et al., 2011) and soil gases at Teapot Dome (Mackintosh and Ballentine, 2012) shows
526 that $^4\text{He}/^{20}\text{Ne}$ ratios are a sensitive tool to identify the migration of any deep gas input into the
527 shallow subsurface. Hence, if CO_2 from depth were migrating to the shallow groundwaters on
528 the Kerr Farm, elevated $^4\text{He}/^{20}\text{Ne}$ ratios would be expected to be observed in the groundwater
529 samples based on these previous studies.

530 *5.7. Limitations of this study and recommendations for future application of noble gas tracers* 531 *in contested situations*

532 The absence of elevated $^4\text{He}/^{20}\text{Ne}$ ratios in the Kerr groundwaters corresponds to the ^4He ,
533 ^{20}Ne , ^{36}Ar , ^{40}Ar , ^{84}Kr concentration measurements, showing that there is limited evidence of
534 migration of the injected or produced CO_2 from the Weyburn field into the Kerr groundwaters.
535 However, we are unable to rule out a best case possibility of a 0.14 %, and a worst case
536 possibility of a 0.25 %, contribution to the groundwater sample with the lowest $^3\text{He}/^4\text{He}$ ratio
537 from the produced fluids, or a 20 % to 32 % contribution from the injected CO_2 to the sample
538 with the lowest $^3\text{He}/^4\text{He}$ ratio. The inability to firmly rule out a significant contribution to the
539 Kerr groundwaters from the injected CO_2 is a key limitation of our study and is due to the low
540 helium concentrations measured in the injected CO_2 . This is most likely to be the result of the
541 solubility based capture method used to extract the CO_2 from the gasification process, which
542 results in the majority of the insoluble ^4He being lost as it is not captured by the capture
543 technique and hence is vented with the non-captured flue gas (Flude et al., 2016).

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

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

555 injection well to the Kerr quarter is located some 1.4 km away and CO₂ injection at this location
556 ceased in 2005 (Cenovus Energy Inc., 2011). The section of the Weyburn EOR field located
557 directly beneath the Kerr property has remained under water injection throughout extraction
558 operations of the oil field since the 1960's (Sherk et al., 2011). Hence, we believe it to be
559 unlikely that injected CO₂ could migrate over 1.5 km laterally and through ~1.5 km of
560 overburden without encountering formation water containing an excess ⁴He fingerprint
561 inherited from the radiogenic decay process. Given that CO₂ is an excellent solvent (Warr et
562 al., 2015) and has been shown to strip out radiogenic noble gases from formation waters
563 (Darrah et al., 2015; Darrah et al., 2014; Gilfillan et al., 2008; Györe et al., 2015) we would
564 expect any migrated injected CO₂ to obtain a radiogenic fingerprint high in ⁴He. This would
565 result in above atmospheric ⁴He/²⁰Ne and below atmospheric ³He/⁴He ratios, similar to those
566 of the produced CO₂. We do not observe any presence of a radiogenic fingerprint in any of the
567 Kerr groundwater samples.

568 In light of our findings, we recommend that further investigation into the composition of
569 captured CO₂ is needed to quantify how useful noble gases will be in tracking injected CO₂
570 within CO₂ storage reservoirs and identifying how quickly the radiogenic fingerprint of the
571 storage reservoir is inherited by injected CO₂. We also recommend that operators of CO₂
572 injection sites establish both the geochemical baseline of their reservoir prior to CO₂ injection,
573 and routinely monitor the geochemical fingerprint of the CO₂ injected, including both stable
574 carbon and noble gas isotopic measurements. This comprehensive geochemical database
575 could then be used as a robust reference basis for geochemical investigations should
576 allegations of leakage be made.

577 *5.8. Comparison with findings from other studies completed on the Kerr site*

578 Our interpretation that there is no evidence of migration of the CO₂ injected into or produced
579 from the Weyburn EOR field into the Kerr groundwaters is further corroborated by comparison
580 with the results of separate investigations into the allegations of CO₂ contamination on the
581 Kerr property. ¹⁴C measurements were a key component of the investigation instigated by the
582 field operators, Cenovus, by TRIUM Environmental Inc. This study analysed radiocarbon
583 within 78 samples of soil gases over the entire of the Kerr quarter and found that these
584 contained high levels of ¹⁴C, indicating a recent carbon source. The ¹⁴C values measured were
585 identical to those measured on a control site well outside of the Cenovus CO₂-EOR operations,
586 whilst ¹⁴C measurements from CO₂ originating from the Dakota gasification plant and the
587 recycled gas injected into the Weyburn field showed that these contained no measurable ¹⁴C
588 (Cenovus Energy Inc., 2011). This showed that the CO₂ contained in the soil gases overlying

589 the Kerr property had to have a recent, 'living' high ^{14}C source, rather than a 'dead' non ^{14}C
590 containing fossil fuel origin.

591 Further support to the lack of evidence of CO_2 migration from depth is provided by the
592 relationship between the concentration of O_2 and N_2 with CO_2 in the soil gas samples in both
593 the investigation performed on behalf of the field operators (Cenovus Energy Inc., 2011) and
594 that performed by IPAC- CO_2 (Romanak et al., 2014). The Cenovus funded study found that
595 soil gas CO_2 measurements for both the Kerr Quarter and two off site control localities were in
596 natural equilibrium with N_2 and O_2 , providing an indication of the origin of the CO_2 . If the CO_2
597 was from a natural biogenic soil respiration process, O_2 is consumed to yield CO_2 within the
598 soil due to plant and microbial respiration activity. As a result of this consumption of O_2 its
599 concentration decreases, whilst CO_2 is produced and its concentration increases. N_2
600 concentration is unaffected in that natural process. In contrast, if the injected, industrial source
601 CO_2 was migrating to surface soils, N_2 concentrations would decrease as it is displaced from
602 the soil by the anthropogenic CO_2 . No such change in N_2 concentrations was observed in
603 either the Cenovus or IPAC- CO_2 funded studies (Cenovus Energy Inc., 2011; Romanak et al.,
604 2014). In addition, seasonality of soil gas CO_2 concentrations was suggested in the Cenovus
605 study as soil gas CO_2 concentrations measured in September were lower than those in August.
606 This is indicative of a natural cycle where plant and microbial based activity declines as
607 summer ended and winter approached (Cenovus Energy Inc., 2011).

608 **6. Conclusions**

609 We conclude that the carbon isotope data do not constrain the origin of elevated dissolved
610 CO_2 concentrations in the Kerr groundwaters, due to the lack of a distinct fingerprint between
611 the injected and produced CO_2 relative to that of baseline values in the shallow subsurface in
612 the region. Our combined noble gas fingerprints show no evidence of the presence of noble
613 gases from the injected CO_2 , or from the CO_2 produced from the Weyburn CO_2 Enhanced Oil
614 Recovery field, within the groundwaters surrounding the Kerr property. All of the Kerr
615 groundwater samples exhibit noble gas fingerprints which would be expected in shallow
616 groundwaters and show no evidence for the addition of a deep radiogenic component or
617 dilution from the addition of a gas phase low in atmospheric derived noble gases.

618 However, we are unable to categorically rule out a best case possibility of a 0.14 %, and a
619 worst case possibility of a 0.25 %, contribution to the groundwater sample with the lowest
620 $^3\text{He}/^4\text{He}$ ratio from the produced fluids, or a 20 % to 32 % contribution from the injected CO_2
621 to this sample. The inability to firmly rule out a significant contribution to the Kerr groundwaters
622 from the injected CO_2 is a key limitation of the noble gas fingerprinting technique used in this
623 study. This is the result of low helium concentrations measured in the injected CO_2 , most

624 probably due to the solubility based capture method used to capture the CO₂. However, we
625 believe it is unlikely that injected CO₂ could migrate from the nearest CO₂ injection well (some
626 1.5 km away, and at a depth of 1.5 km) without encountering formation water rich in radiogenic
627 noble gases and inheriting a radiogenic fingerprint high in ⁴He and with a low ³He/⁴He ratio,
628 similar to that of the produced CO₂.

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

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

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842 **Figure Captions**

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

849 **Figure 2.** ⁴He plotted against ⁴⁰Ar for the Kerr groundwaters, CO₂ and fluids produced from
850 the Weyburn field. ⁴He and ⁴⁰Ar are both produced in the crust by radioactive decay, and so
851 are more abundant in deep derived fluids. The Kerr groundwater samples plot within the
852 concentrations expected in a shallow groundwater, termed air saturated water (ASW),
853 recharging under the summer temperature conditions experienced in Saskatchewan (15 – 25
854 °C), including a typical excess air component of 10 - 45 %. All analytical error bars are smaller
855 than printed symbols.

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

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

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

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