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Application of noble gas tracers to identify the retention mechanisms of CO2 migrated from a deep reservoir into shallow groundwater

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Title   Application of noble gas tracers to identify the retention mechanisms of CO2 migrated from a deep reservoir into shallow groundwater

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Abstract

Carbon Capture and Storage (CCS) is a valuable climate-mitigation technology, which offers the potential to cost-effectively reduce the emissions associated with the burning of fossil fuels. However, there is a potential risk of a small portion of the stored CO2 unintentionally migrating from a storage site to a shallow groundwater aquifer which is the final retaining zone for any migrated CO2 before it escapes to the atmosphere. Hence, it is imperative to identify the physical retention mechanisms of CO2 within a shallow aquifer. In this study 1.70×10^2 kg of CO2 and noble gas tracers (He, Ar and Kr) were continuously injected into a groundwater aquifer over 28 days with the aim of identifying the mechanisms and amount of CO2 retention. Among the tracers, Kr was found to be the earliest indicator of CO2 migration. The other tracers – He and Ar – arrived later and exhibited diluted signals. The diluted signals were attributed to degassing of the plume mass (1.6% of CO2) during the early stages of CO2 migration. Diffusion accelerated the dilution of the lighter elements at the plume boundaries. Consequently, the clear relation of the noble gases with the CO2 proved that degassing and mixing primarily control the mass retention of CO2 in shallow groundwater, and the relative importance of these processes varies along the evolving path of migrating CO2.

Keywords	CCS; monitoring; CO2 leakage; noble gas tracing; artificial tracer; geochemical monitoring
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Suggested reviewers	Greg Holland, Finlay Stuart, Stephanie Flude, Domokos Gyore

Submission Files Included in this PDF

File Name [File Type]

Cover letter.docx [Cover Letter]

Response to Reviewers.docx [Response to Reviewers]

[1] Ju et al.,_revised.docx [Review Reports]

Highlights_revised.docx [Highlights]

[2] Ju et al.,_revised.docx [Manuscript File]

Figure1.tif [Figure]

Figure2.tif [Figure]

Figure3.tif [Figure]

Figure4_revised.tif [Figure]

Figure5.tif [Figure]

Figure 6_revised.tif [Figure]

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Figure10.tif [Figure]

Figure11.tif [Figure]

Figure12.tif [Figure]

declaration-of-competing-interests.docx [Conflict of Interest]

Credit Author Statement.docx [Author Statement]

Supplementary Material.docx [Supplementary Material]

To view all the submission files, including those not included in the PDF, click on the manuscript title on your EVISE Homepage, then click 'Download zip file'.

Research Data Related to this Submission

Data set   https://data.mendeley.com/datasets/hrydvx2xgp/1

The dataset associated with the mass balance calculation

You can find all the dataset associated with the mass balance calculation (Figure 8~12).

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Editors-in-chief

International Journal of Greenhouse Gas Control

Dear Editors-in-chief,

RE: Manuscript by Ju, Gilfillan, Lee …. et al. "**Application of noble gas tracers to identify the retention mechanisms of CO_2 migrated from a deep reservoir into shallow groundwater**"

Once again, we would like to thank the associate editor and all the reviewers for very informative and constructive comments for the improvement of our manuscript. We tried to respond to every comment by the reviewers and incorporated the responses into the revised manuscript. You can find all details in the 'Response to Reviewers.docx' file listing all the comments and responses.

I hope the revised manuscript is suitable for publication in the *International Journal of Greenhouse Gas Control*.

Sincerely,

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[Reviewer 1]

Once again, we thank Reviewer #1 for his/her very detailed reading of our manuscript and associated comments and suggestions. Please see our responses below with the revised version of the manuscript ([1] Ju et al.,_revised).

Specific comments

Introduction

1) Line 40 (Languages)

- RESPONSE: CHANGES MADE.
- It has been modified as below:
- From: "This leaked CO2 could potentially migrate through geological conduits such as permeable faults and/or abandoned wells resulting in the deterioration of fresh water resources above the CO2 reservoir"
- To: "This CO2 could potentially migrate through geological conduits such as permeable faults and/or abandoned wells resulting in the deterioration of fresh water resources above the CO2 reservoir" (Lines 40–42 in [1]).

2) Line 70 (Languages)

- RESPONSE: CHANGES MADE.
- It has been modified as below:
- From: "The degree of solubility trapping has also been determined using noble gases, through identification of the fractionation of naturally present noble gas tracers due to the partitioning of the noble gases into groundwater present within the reservoir formations"
- To: "The degree of solubility trapping has also been determined using noble gases, through identification of the degree of partitioning of the noble gases into groundwater present within the reservoir formations" (Lines 69–71 in [1]).

Materials and methods

3) Line 145 (Languages)

- RESPONSE: CHANGES MADE.
- It has been modified as below:
- From: "The SMWs are located along the created groundwater flow, while PS-04 was upgradient relative to the CO2 injection point."
- To: "The SMWs are located along the created groundwater flow pathway, while PS-04 was up-gradient relative to the CO2 injection point." (Lines 143–144 in [1])

4) Line 147 (Languages)

- RESPONSE: CHANGES MADE.
- It has been modified as below:
- From: "The well BS-09 was intended to capture the preferential movement of a released CO2 along a high connectivity zone between injection well and BS-09, identified in the work of Ju et al. (2019)."
- To: "The well BS-09 was intended to capture the preferential movement of the released CO2 along a high connectivity zone between injection well and BS-09, identified in the work of Ju et al. (2019)." (Lines 144–146 in [1])

5) Line 229 (Languages)

- RESPONSE: CHANGES MADE.
- It has been modified as below:
- From: "…before samples injection into the RGA200 mass spectrometer (Stanford Research Systems, California, USA)."
- To: "…before sample injection into the RGA200 mass spectrometer (Stanford Research Systems, California, USA) for analysis." (Lines 229–230 in [1])

Results

6) Line 376-377 (Languages)

- RESPONSE: CHANGES MADE.
- It has been modified as below:
- From: "This was attributed to dilution of CO2 plume along a concentration gradient"
- To: "This was attributed to the Kr taking a less distributed pathway through the subsurface than the other tracers, and a result of the dilution of CO2 plume along the concentration gradient" (Lines 370–372 in [1]).

7) Line 389-391 (Languages)

- RESPONSE: CHANGES MADE.
- It has been modified as below:
- From: "Note that SMW 4-2 showed a stronger signal at the plateau than SWM 3-2 did (Figure 6), implied a low conductivity zone existing and hindering the SMW 3-2 from capturing a CO2 plume efficiently. This result was consistent with the observations made in alkalinity and pCO2 (Figure 5)."
- To: "It is worth noting that SMW 4-2 exhibited a higher concentration of Kr once the tracers arrived than SWM 3-2 (Figure 6), implying that a low conductivity zone hinders well SMW 3-2 from capturing the full CO2 plume. This result was consistent with the observations made in alkalinity and pCO2 (Figure 5)." (Lines 383–386 in [1])

8) Line 403 (Languages)

- RESPONSE: CHANGES MADE.
- It has been modified as below:
- From: "In the final stage of BTCs, the plume tail is recorded in all of the monitoring wells through the decrease of noble gas concentration resulting after the injection at the IW ceased."
- To: "In the final stage of BTCs, the plume tail is recorded in all of the monitoring wells through the decrease of noble gas concentrations after injection at the IW ceased." (Lines 397–399 in [1])

Conclusions

9) Line 603-604 (Languages)

- RESPONSE: CHANGES MADE.
- It has been modified as below:
- From: "Around the leak point, CO2 degassing dominantly occurred from a dissolved plume of high gas pressure, suggesting a near-surface monitoring network is necessary for capturing the active "vertical" movement of degassed budget in this area."

- To: "Our findings indicate that around the injection point, CO2 degassing dominantly occurs from the dissolved plume due to the high gas pressure, suggesting a near-surface monitoring network is necessary for capturing the active "vertical" movement of degassed budget in this area." (Lines 595–598 in [1])

[Reviewer 2]

Once again, we thank Reviewer #2 for his/her very detailed reading of our manuscript and associated comments and suggestions. Please see our responses below with the revised version of the manuscript ([1] Ju et al.,_revised).

General observations

The authors have made changes that have improved the manuscript significantly. I have a couple substantial comments however that need attention.

- RESPONSE: CHANGES MADE.
- We sincerely appreciate your thorough review. Please find detailed responses below.

Major comments

Results

1) **Table 1** has several errors. First, the exponents for the values were not fully updated and so the results are non-sensical.

- RESPONSE: CHANGES MADE.
- My apologies for the confusion. The exponents have been fully updated according to your comment (Table 1 in [1]).

   Second, the data originally shown for "% lost" were not updated when the column title was changed to "% remaining".

- RESPONSE: CHANGES MADE.
- My apologies for the confusion. The column has been updated according to the changed title (Table 1 in [1]).

2) A major conclusion of this work is that the Kr plume front precedes the CO2 plume front. However, that is difficult to see based on comparisons of Figs. 5 and 6. Perhaps you could add a BTC figure that plots these two gases at the higher time resolution of Fig. 6, to help convince the reader that Kr precedes CO2. It might work to add pCO2 to Fig. 6, but it might also be too difficult to see with all four gases plotted.

- RESPONSE: CHANGES MADE.
- Thank you for the beneficial comment. This has been modified according to your suggestions in the revised version of the manuscript (Figure 6 in [1]).
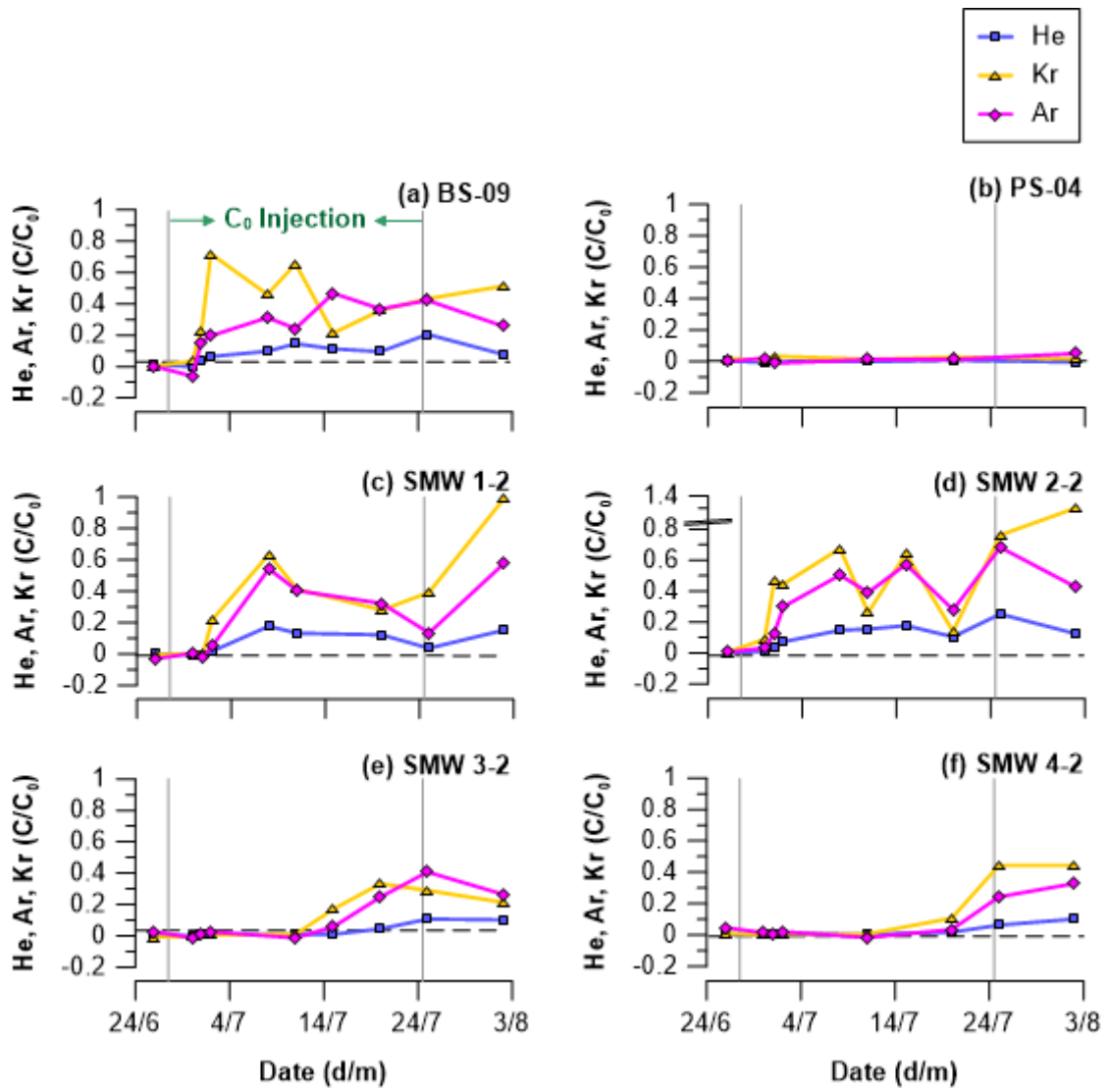
Figure R1 Original version of Figure 6.
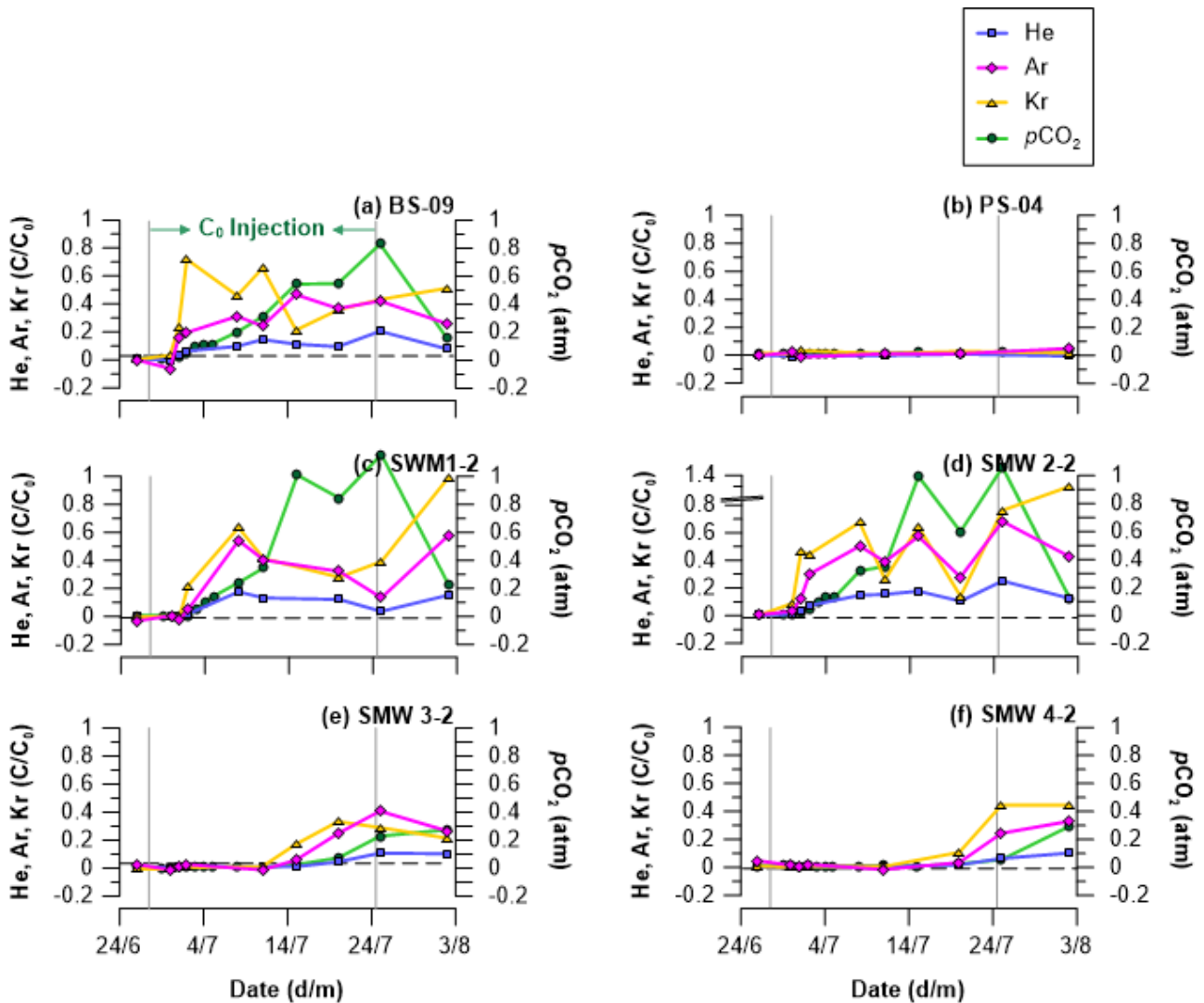
Figure R2 Modified version of Figure 6.

Specific comments

We sincerely appreciate the English corrections. All of your suggestions have been accepted and reflected in the revised version of the manuscript.

Introduction

3) **Line 82-83** change to read " . . . and ASW. Differences in the noble gas contents of these samples stemmed from . . ."

- RESPONSE: CHANGES MADE.
- It has been modified according to your comment (Lines 86–87 in [1]).

4) **Line 98** delete "artificial" (there is no such thing as an artificial noble gas!

- RESPONSE: CHANGES MADE.
- It has been modified according to your comment (Line 102 in [1]).

Materials and methods

5) **Line 152** delete "works".

- RESPONSE: CHANGES MADE.
- It has been modified according to your comment (Line 166 in [1]).

6) **Line 200** change to read "Figure 3. Schedule for water sample collection during the CO2 injection test"

- RESPONSE: CHANGES MADE.
- It has been modified according to your comment (Lines 206–207 in [1]).

7) **Line 222** change to read " . . . before sample injection . . ."

- RESPONSE: CHANGES MADE.
- It has been modified according to your comment (Line 229 in [1]).

Results

8) **Line 246** change to read "However, prior to the experiment the hydrostatic pressure data showed a stable correlation with atmospheric pressure changes and no irregular turbulence . . ."

- RESPONSE: CHANGES MADE.
- It has been modified according to your comment (Lines 254–256 in [1]).

9) **Line 256** delete "to"

- RESPONSE: CHANGES MADE.
- It has been modified according to your comment (Line 264 in [1]).

10) **Line 257** change to read "In contrast, wells SMW 3-2 . . ."

- RESPONSE: CHANGES MADE.
- It has been modified according to your comment (Lines 264–265 in [1]).

11) **Line 344** change to read "The pH also decreased noticeably, . . ."

- RESPONSE: CHANGES MADE.
- It has been modified according to your comment (Line 352 in [1]).

12) **Figure 6** Still need to change the order of the noble gases in the figure legend so that they align with atomic mass (i.e., He, Ar, Kr).

- RESPONSE: CHANGES MADE.
- The legend has been modified according to your suggestion (Figure 6 in [1]).

Discussion

13) **Figure 8, 9, 10 and 11** Vertical axis title is only partly shown.

- RESPONSE: EXPLAINED.
- They look okay in both word and pdf format. In case, the figures were also uploaded to the website as a separate file.

Conclusions

14) Line 562 change to read: ". . . plume and the other . . ."

- RESPONSE: CHANGES MADE.
- It has been modified according to your comment (Line 580 in [1]).

15) Line 592 change to read " . . . just a few meters from the leak point . . ."

- RESPONSE: CHANGES MADE.
- It has been modified according to your comment (Line 611 in [1]).

16) Line 596 spelling of "gaseous"

- RESPONSE: CHANGES MADE.
- It has been modified according to your comment (Line 615 in [1]).

17) Line 596-597 change to read " . . . pathways in the vadose zone depending on the . . ."

- RESPONSE: CHANGES MADE.
- It has been modified according to your comment (Lines 615–616 in [1]).

1 **Application of noble gas tracers to identify the retention mechanisms of CO$_2$ migrated from a**

2 **deep reservoir into shallow groundwater**

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17

Abstract

Carbon Capture and Storage (CCS) is a valuable climate-mitigation technology, which offers the potential to cost-effectively reduce the emissions associated with the burning of fossil fuels. However, there is a potential risk of a small portion of the stored CO_2 unintentionally migrating from a storage site to a shallow groundwater aquifer. The shallow groundwater which is the final retaining zone for any migrated CO_2 before it escapes into the atmosphere. Hence, it is imperative to To identify the physical retention mechanisms of CO_2 within a shallow aquifer. In this study 1.70x10^2 kg of CO_2 and noble gas tracers (He, Ar and Kr) were continuously injected into a groundwater aquifer over 28 days with the aim of identifying the mechanisms and amount of CO_2 retention. Among the tracers, Kr was found to be the earliest indicator of CO_2 migration. The other tracers – He and Ar – arrived later and exhibited diluted signals. The diluted signals were attributed to degassing of the plume mass (1.6% of CO_2) during the early stages of CO_2 migration. Diffusion accelerated the dilution of the lighter elements at the plume boundaries. Consequently, the clear relation of the noble gases with the CO_2 proved that degassing and mixing primarily control the mass retention of CO_2 in shallow groundwater, and the relative importance of these processes is differentiated varies along the evolving path of migrating CO_2.

Keywords: CCS; monitoring; CO_2 leakage; noble gas tracing; artificial tracer; geochemical monitoring

1. Introduction

Carbon Capture and Storage (CCS) is a climate change mitigation technology that comprises the capture of CO_2 from an industrial point source, such as a power plant or refinery, transport of the captured CO_2 to a storage site followed by the injection of the captured CO_2 into deep geological strata for permanent disposal (IPCC, 2005). However, there is a potential risk that a small portion of the mobile CO_2 in a storage site could accidently migrate out of the subsurface reservoir and inadvertently reach shallower levels of the subsurface (Alcalde et al., 2018). This ~~leaked~~ CO_2 could potentially migrate through geological conduits such as permeable faults and/or abandoned wells resulting in the deterioration of fresh water resources above the CO_2 reservoir (Harvey et al., 2012; IEAGHG, 2011; Lemieux, 2011; Lion et al., 2014) and ~~in the~~ leakage of a small portion of the CO_2 into the atmosphere (Ide et al., 2006; IPCC, 2005). Recently, the Weyburn-Midale (Canada) CO_2 monitoring and storage project faced allegations that leakage of CO_2 injected into the Weyburn-Midale oil field for Enhanced Oil Recovery (EOR) and storage was causing a deterioration of the groundwater quality on a farm located above the field (Beaubien et al., 2013; Gilfillan et al., 2017).

A variety of geochemical tools have been used to verify CO_2 storage security and track the fate of CO_2 injected for storage. These include CO_2 soil gas and groundwater concentrations, stable C and O isotopes within the CO_2, on-site monitoring parameters (pH, alkalinity, ORP, EC, temperature and DO), inert gas tracers, major and trace ions and radiocarbon (^{14}C) (Flude et al., 2016; Lee et al., 2016). Soil gas and dissolved CO_2 concentrations in groundwater can provide a direct tracer of CO_2 migration, allowing discrimination of different CO_2 origins and providing a means to establish the mass balance of CO_2 present in the groundwater system (Ballentine et al., 2001; Beaubien et al., 2014; Gilfillan et al., 2011; Lollar et al., 1997; Sathaye et al., 2016). Recent developments in on-site monitoring technologies now allow the continuous measurement of a number of parameters (e.g. alkalinity, T, EC, pH) which can be used to establish the overall distribution and temporal evolution of a small CO_2 plume within a shallow groundwater aquifer (Lee et al., 2016). Noble gases are characterized by their inert behavior, which makes them ideal tracers within a subsurface system. This inertness means that noble gases are

61 conservative tracers and do not partake in the chemical reactions that dilute the CO_2 leakage signals and

62 hence are capable of providing a robust means to distinguish between natural and stored CO_2 (Risk et

63 al., 2015).

64 Noble gas tracing techniques have been used to track both the fate and migration pathways of

65 injected CO_2 in reservoirs. Within a typical porous CO_2 storage reservoir, CO_2 is retained by a

66 combination of structural, residual and solubility trapping mechanisms (Alcalde et al., 2018; Holland

67 and Gilfillan, 2013; IPCC, 2005). Recent experiments at the CO2CRC Otway Demonstration site for

68 CO_2 storage in Australia have used Kr and Xe as conservative tracers to determine the degree of residual

69 trapping within a porous saline formation, using a numerical mass balance approach (LaForce et al.,

70 2014). The degree of solubility trapping has also been determined using noble gases, through

71 identification of the degree of ~~fractionation of naturally present noble gas tracers due to the~~ partitioning

72 of the noble gases into groundwater present within the reservoir formations (Ballentine et al., 1991;

73 Brennwald et al., 2005; Gilfillan et al., 2008, 2009; 2014; Pinti and Marty, 1995; Zhou et al., 2005).

74 Noble gas tracers are also suitable for monitoring the vertical migration of the reservoir CO_2,

75 thanks to the compositional difference of natural noble gas tracers between storage reservoir and the

76 near surface environment (Mackintosh and Ballentine, 2012). Gilfillan et al. (2011) applied noble gas

77 tracing tools to constrain the nature of CO_2 leakage into shallow groundwater and surface water bodies.

78 ~~The~~ Further work by Gilfillan et al., (2017) used inherent tracers residing in ~~a~~ the Weyburn-Midale

79 injection and storage project reservoir ~~CO_2 reservoir provided a means~~ to show that CO_2 migration

80 from ~~a~~ the deep reservoir into the shallow aquifer system had not occurred ~~near an artificial CO_2~~

81 ~~injection site at the Weyburn-Midale Storage and Monitoring project~~. This work found that ~~as~~the noble

82 gas composition in the groundwater samples above the CO_2 injection and storage project did not vary

83 over a typical background level of a shallow aquifer, ~~that is, the~~of Air Saturated Water (ASW) with an

84 excess air component of up to 45% (Gilfillan et al., 2017). Recent work by Flude et al. (2016) and Flude

85 et al. (2017) evaluated the inherent tracing ability of noble gases focusing on the compositional

86 difference of them between captured CO_2, the subsurface storage reservoir, air and ASW. ~~The~~

87 ~~distinguished composition of~~Differences in the noble gas~~es~~ contents of these samples~~between the~~

88 ~~sampled gases~~ stemmed from the different CO_2 capturing processes and what controls the composition

89 of noble gas tracer in a stored fluid (e.g. gas stripping of reservoir water and/or interaction with

90 radiogenic components).

91   The concept of inert tracers was extended to artificial enhancement studies, involving the

92 addition of inert gas tracers such as SF_6 and noble gases to the injected CO_2 in CCS storage. This aimed

93 to provide a much clearer distinction between the injected CO_2 and that naturally present in the

94 subsurface and so improving the monitoring efficiency (Myers et al., 2013; Nimz and Hudson, 2005).

95 For example, noble gases have been previously used as artificial tracers to indicate CO_2 leakage

96 pathways in the vadose zone (Cohen et al., 2013; Rillard et al., 2015) and in the aquifer system (Lu et

97 al., 2012; Nimz and Hudson, 2005; Stalker et al., 2009). In the CO_2-Vadose project, undertaken at a test

98 CO_2 release site in France, the lighter noble gases (He and Ne) were found to have the fastest arrival

99 time in monitoring wells due to their higher diffusion coefficient and low solubility within the soil water

100 compared to the CO_2 and other tracers (Cohen et al., 2013). In contrast, the heavier noble gas tracers

101 (Kr and Xe) exhibited the fastest arrival in the aquifer system due to their solubility in groundwater

102 compared to other noble gases following the artificial injection into a deep reservoir (~2 km) (Stalker

103 et al., 2015). In a recent test, a small amount of CO_2 (16.9 kg) spiked with ~~artificial~~ noble gas was

104 released into a shallow aquifer at Korea CO_2 Storage Environmental Management (K-COSEM) study

105 site, in order to understand the behavior of the leaked plume in the shallow groundwater system. This

106 study identified that the mass distribution of the leaked CO_2 is predominantly controlled by the

107 solubility of the individual noble gases and mixing processes during the limited time of monitoring

108 work (i.e. 4 months) (Ju et al., 2019).

109   The shallow groundwater is the final zone encountered by migrating CO_2 before it is lost into

110 the vadose zone and atmosphere. Furthermore, this reservoir is directly linked into the human activity,

111 hence, should be protected from a potential leakage of stored CO_2 (Lee et al., 2016). While noble gas

112 tracers have proven useful to monitor leaked CO_2 plume in shallow aquifer systems (Flude et al., 2016;

113 2017), this has only been demonstrated on a few occasions, for example, in a natural CO_2 production

114 site using inherent noble gases (Gilfillan et al., 2011), in a CO_2 injection test site using artificially

115 enhanced noble gases (Ju et al., 2019) and to rule out CO_2 migration in a shallow aquifer above an

116 actual CO_2 storage reservoir using inherent noble gases (Gilfillan et al., 2017), as described above. In

117 this study, we presents the results of applying noble gases to a CO_2 injection test into a near-surface

118 aquifer. This artificial CO_2 migration test aims to mimic a situation where a measurable amount of CO_2

119 (1.70×10^2 kg) has migrated from a deep CO_2 storage reservoir into a shallow groundwater aquifer. This

120 study aims focuses onto determininge the amount of CO_2 retained in the groundwater and the

121 mechanisms controlling the migration of the CO_2 plume using noble gas tracers. A mass balance model

122 was constructed based on the partitioning coefficients of noble gas tracers in a gas-water system, to

123 understand and to quantify the final retention of the injected CO_2 within the shallow aquifer system.

124 **2. Materials and methods**

125 **2.1 Site description**

126 The Korea CO_2 Storage Environmental Management (K-COSEM) Research Center has

127 installed a controlled CO_2 release experiment at Eumseong gun (county) of South Korea (Figure 1). The

128 geology at the field experimental site includes three different subsurface media, firstly consisting of a

129 weathered soil layer composed of medium to coarse grained silty sand (0–30 m below ground surface

130 (bgs)), followed by weathered biotite granite (30–70 m bgs), and finally consolidated biotite granite

131 (starting at 70 m bgs) (Lee et al., 2017; Ju et al., 2018a). The water level was located at the 16.0–18.4

132 m bgs and the hydraulic conductivity of the aquifer was estimated from pumping tests, ranging from

133 1.7×10^{-5} cm/s for the consolidated bedrock to 2.0×10^{-4} cm/s for the weathered layer. Prior to the

134 commencement of the experiment, the groundwater was flowing from the northwest toward the

135 southeast following a hydraulic gradient of 0.003 (i.e., the regional flow in Figure 1a).

136 At the K-COSEM site, a total of 24 monitoring wells had been installed in the shallow aquifer

137 (i.e. < 15 m below the water table) including the injection well (IW), partially screened (PS), boreholes

138 (BH), borehole screened (BS) and saturated zone monitoring wells (SMWs) (Figure 1a). Each saturated

139   zone monitoring well (SMW) contained several screened multi-depth monitoring wells for groundwater

140   monitoring at different depths (Figure 1f). In this CO_2 injection study, the IW and six monitoring wells

141   (PS-04, SMW1 to 4, BS-04, -09 and -10) were employed for the CO_2 injection experiment (Figure 1b).

142   The wells BS-04 and BS-10 located at both ends of the monitoring range were used to create an induced

143   pressure gradient field by pumping out groundwater at a down-gradient location (BS-10) and successive

144   injection in at an up-gradient location (BS-4) (Figure 1c). The SMWs are located along the created

145   groundwater flow pathway, while PS-04 was up-gradient relative to the CO_2 injection point. The well

146   BS-09 was intended to capture the preferential movement of a the released CO_2 along a high

147   connectivity zone between injection well and BS-09, identified in the work of Ju et al. (2019). Details

148   on the study site and monitoring network can also be found in previous works (Lee et al., 2017; Lee et

149   al., 2018; Ju et al., 2018b; Ju et al., 2019).

150
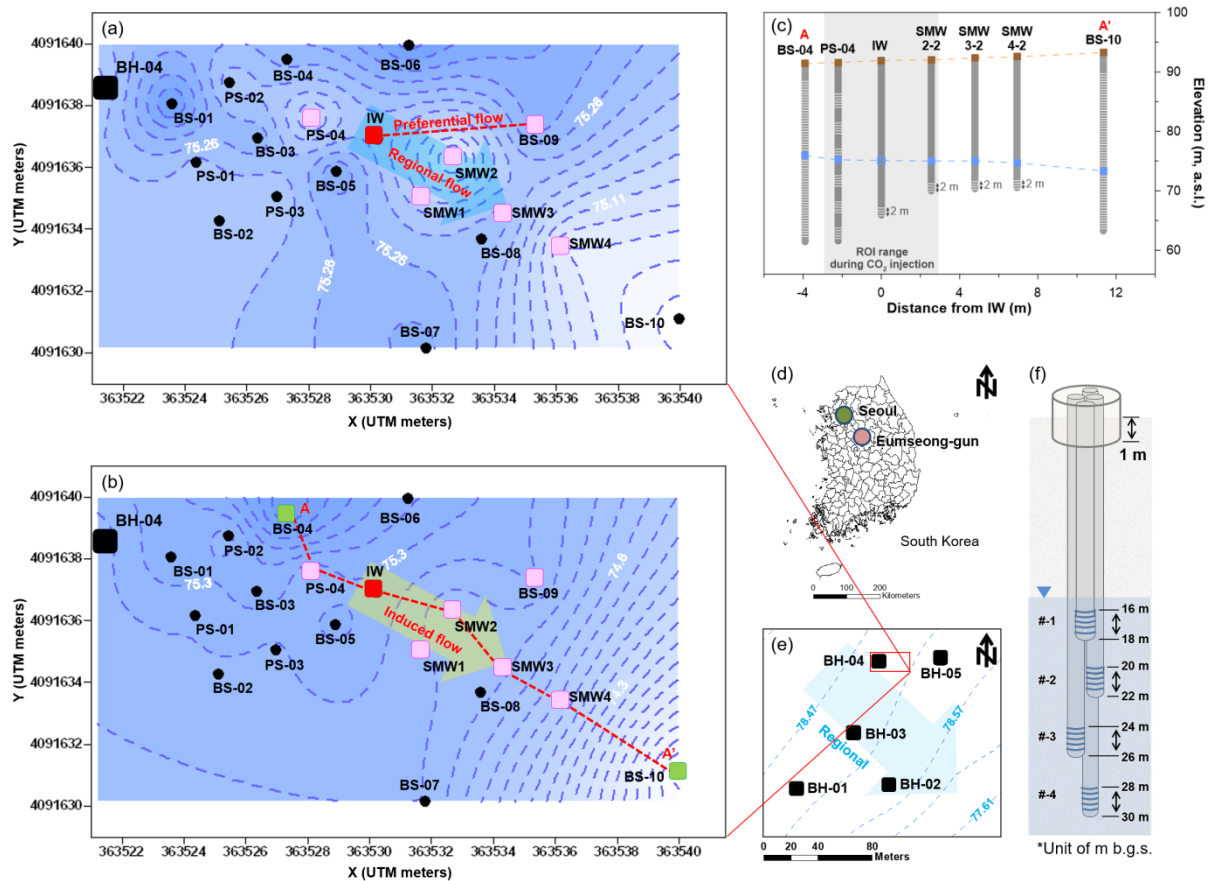
Figure 1. Maps of the study site. Figures on the left show (a) natural ~~pressure gradient~~regional groundwater flow ~~field~~ (shown as a blue-colored arrow) before enhanced groundwater circulation using the wells BS-04 and BS-10, where a preferential path exists in this field due to local hydrogeological heterogeneity (16 May 2016), (b) induced pressure gradient field (shown as a green-colored arrow) after the pumping out and pumping in using the two wells (see green squares) (4 July 2016). Note that the induced flow was intended to speed up the plume migration along the groundwater flow (i.e., regional flow in [a]). Pink squares represent the wells used for monitoring ~~works~~; a red square represents the injection well (IW). Figures on the right show (c) a cross-section view along the induced pressure gradient (4 July 2016), (d) the location map of the study area, (e) the contours of groundwater levels obtained by kriging using 17 wells surrounding the study site (7 March 2015), and (f) the structure of each saturated zone monitoring well (SMW) containing a bundle of four screened pipes with different lengths.

163   **2.2   Artificial injection**

164   **2.2.1   Induced pressure gradient field**

165   The CO_2 injection was undertaken in the induced pressure gradient field to reinforce the

166   groundwater flow, therefore, to speed up the CO_2 plume migration (Figure 2c). The hydraulic pressure

167   gradient was achieved by ~~enhancing~~ groundwater circulation ~~work~~, consisting of water production and

168   reinjection using the BS-04 and BS-10 wells located at both ends of the monitoring network (Figure

169   2c). A total of 24.0 m^3/d of groundwater was pumped from BS-10 and reinjected into BS-04 (Figure

170   2c). A period of 1 month was required to stabilize the pressure gradient (22 May 2017 to 27 June 2017).

171   The pressure gradient was steeper near the injection site and production points (i.e. the BS-04 and BS-

172   10), with the average gradient being 0.18 (Figure 2c). The circulation was maintained until 17

173   September 2017.
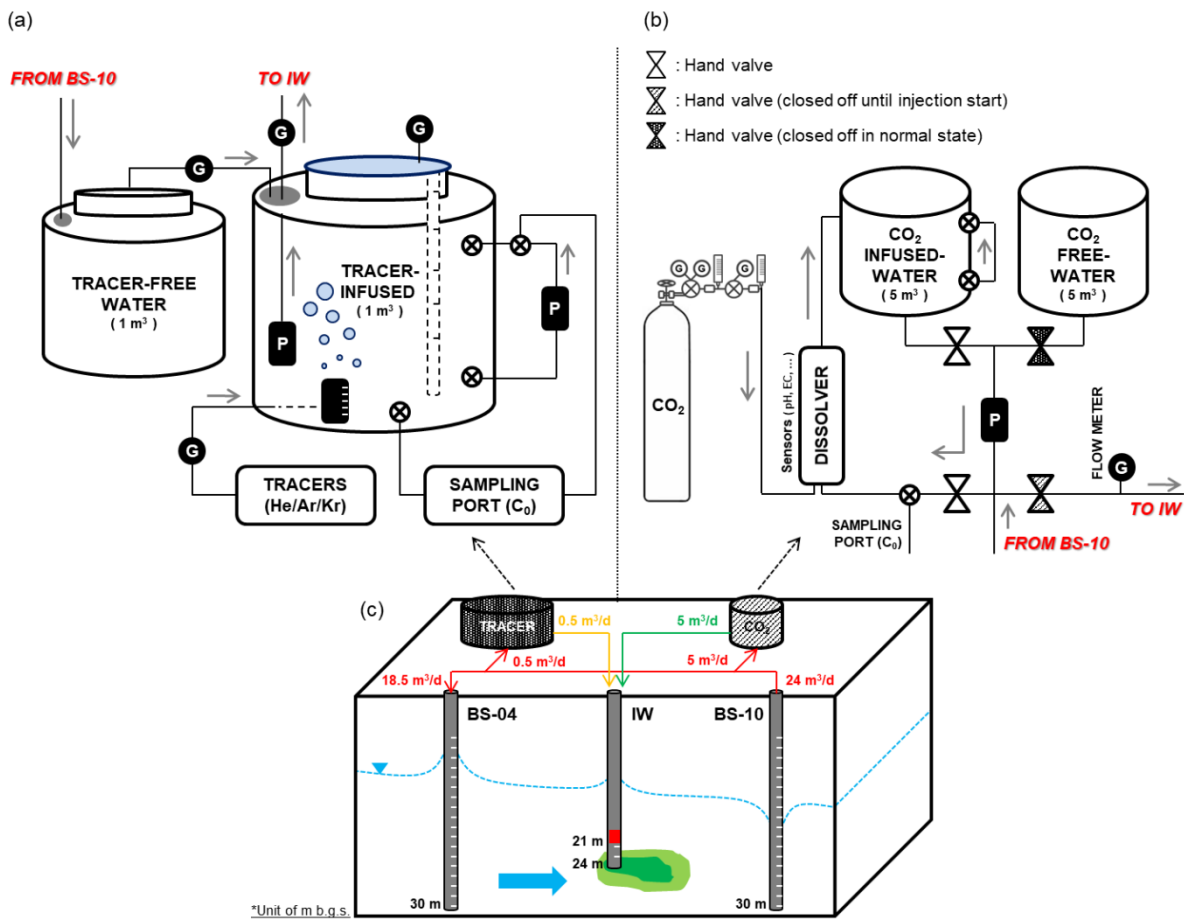
174

175   **Figure 2**. Injection systems for the artificial CO_2 release experiment. (a) tracer-infused groundwater

176   was prepared in a 1 m³ tank and (b) CO_2-infused groundwater was prepared in a 5 m³ tank. (c) gas-

177   charged groundwater was continuously released into the induced pressure gradient field through the

178   IW.

179   **2.2.2 Injection**

180   To prepare the injection water, the water flux sent to BS-04 (24.0 m³/d) was reduced to 18.5

181   m³/d and 5.5 m³/d of groundwater was sent into the injection tank (Figure 2c). 5.0 m³/d of groundwater

182   was sent into the CO_2 dissolver tank (Figure 2b) and 0.5 m³/d of tracer–enhanced water was prepared

183   in the other tank (Figure 2a). The CO_2-infused groundwater was prepared in the 5 m³ tank equipped

184   with the circulation pump, CO_2 dissolver, water sampling port and flow meter (Figure 2b). Injection

185   was initiated when the CO_2 concentration reached the equilibrium state (termed C_0). To ensure that the

186   equilibrium concentration was maintained, alkalinity, pH, EC, DO, ORP, temperature, salinity, TDS

187   was continuously monitored with real time measurement devices such as YSI (YSI Inc./Xylem Inc.,

188   USA), LTC Levelogger Junior (Solinist, Canada) and SH-300-DS (SOHA TECH, Inc., Korea) while

189   circulating water within the tank using a pump (Figure 2b). These measurements showed that it took

190   approximately 24 hours to achieve the equilibrium state. The noble gas infused groundwater was also

191   prepared one day ahead of the injection test. Approximately 0.5 m³/d of groundwater was pumped into

192   the 1 m³ of closed tank equipped with the circulation pump, tracer tank, water sampling port and flow

193   meter (Figure 2a). ~~Tracers~~ The injected tracers were a mixture of He (0.2 vol. %), Ar (99.4 vol. %), and

194   Kr (0.4 vol. %) and were injected through a flowmeter and diffuser (AS-10 3/8) into the 1 m³ dissolver

195   tank. The infused liquids were first injected into the subsurface on 27 June 2017 and continued to be

196   injected for 27 days until 24 July 2017. Samples for initial concentration analyses (i.e. C_0) were

197   collected during the injection event and through the sampling ports (Figures 2a and b). Injection took

198   place at 4.5–7.5 m below the water table (corresponding to 21–24 m bgs) in an isolated zone below a

199   packer (Figure 2c). The ambient surface weather conditions during the injection event were 20.4–26.9°C

200   without precipitation. The injection rate was controlled by a submersible and controllable quantitative

201   pump (model MP1, Grundfos, Denmark) at a constant rate of 5.5 m³/d (Figure 2c).

2.3 Real-time monitoring

Real-time monitoring data was collected from 17 May 2017 to 13 October 2017 (Figure 3). Over this period, hydraulic pressure (P), temperature (T) and electrical conductivity (EC) were measured in-situ using the LTC Levelogger Junior (Solinist, Canada) and the barometric state was monitored at the same time using the Barologger Edge (Solinist, Canada) at 10 minute intervals.
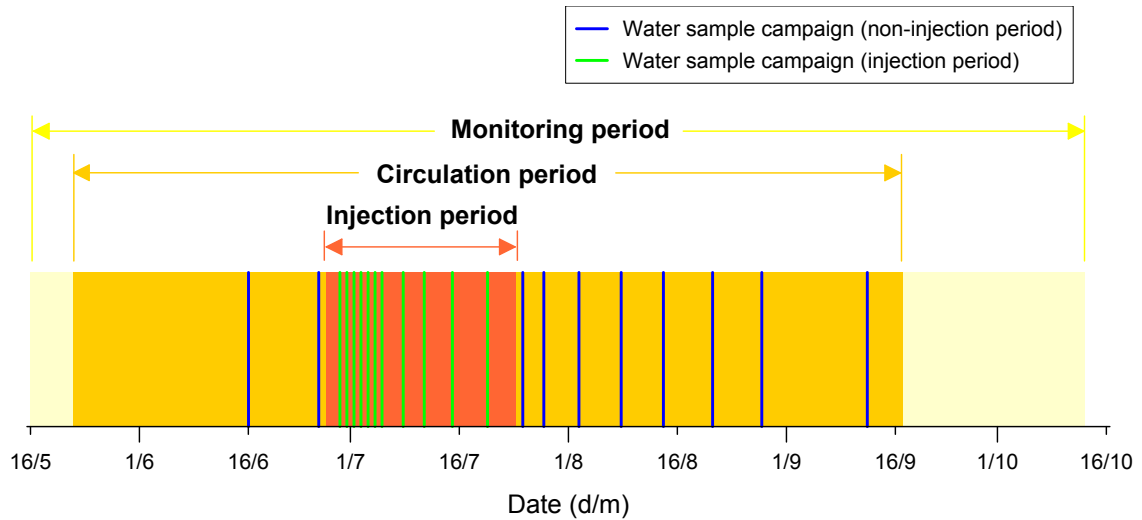
Figure 3. Record for monitoring worksSchedule for water sample collection during the artificial CO$_2$ injection test.

2.4 Water sampling campaign

2.4.1 Baseline survey period

Water samples were collected using a Waterra Inertial Pump with PowerPack PP-1 (Wattera, Canada) to obtain baseline data before the CO$_2$ injection. The local baseline of the pCO$_2$ was obtained on two occasions through water sampling between 16 June 2017 and 26 June 2017 (Figure 3). The baseline for the noble gas tracers was determined by a single water-sampling operation on 26 June 2017 (Figure 3). Alkalinity was determined in the field site by acid titration method with 0.05 N HNO$_3$. The pH and temperature were also measured in-situ using a portable water quality meter (YSI ProDSS, YSI Inc./Xylem Inc., USA). The noble gas samples were collected using a standard copper tube of 28 cm^3 and a pinch-off clamp set.

2.4.2 Injection and post-injection period

Data acquisition after the CO_2 injection was conducted in the same manner as the baseline data collection. Water samples were collected on 19 occasions following the injection event, over 76 days from 27 June 2017 to 12 September 2017 (Figure 3).

2.5 Laboratory analyses

2.5.1 Noble gas

The noble gas samples were analyzed in the noble gas analysis laboratory at the Korea Polar Research Institute (KOPRI) using an automated system as outlined in Stanley et al. (2009) and Kim et al. (2016). Gases were first extracted from a groundwater sample under high vacuum condition ($\sim10^{-7}$ mbar) and stored in an aluminosilicate glass ampoule (Lott and Jenkins, 1998). Excessive water vapor, active gases, and condensable gases were then removed using cryogenic traps and a series of hot and cold Zr-Al alloy getters (St 101, SAES Getters S.p.A., Italy) before samples injection into the RGA200 mass spectrometer (Stanford Research Systems, California, USA) for analysis. The noble gases, He, Ne, Ar, and Kr were calibrated against air standards of 0.9 and 2.7 cm^3 STP, to cover the wide range of the tracer enhanced injection water. The discrepancy between duplicate samples was less than 5% (Ju et al., 2019).

2.6 Analytical methods

2.6.1 pCO_2 calculation

pCO_2 values for the sampled waters were calculated using the monitored parameters of alkalinity, pH, and temperature. Alkalinity, pH and temperature were measured in-situ. Using these data a robust calculation for pCO_2 value was made using the program PHREEQC Version 3 (Parkhurst and Appelo, 2013).

2.6.2 Mass balance model

At the early stage of the CO_2 injection, the CO_2 plume is unstable with a high partial pressure, resulting in a degree of CO_2 degassing. Hence, CO_2 bubbles rise freely from the brine with a proportion of the CO_2 remaining in the dissolved phase. During the degassing period, the free-phase CO_2 strips out

246 the dissolved, relatively insoluble noble gases, especially the lighter elements (He and Ne), leaving the

247 system relatively enriched in the heavier noble gases (Ar, Kr, Xe) (Ballentine et al., 2002; Holland and

248 Gilfillan, 2013). Based on the degree of this enrichment, we can inversely constrain the mass balance

249 of the CO_2 plume in terms of the degassing process (see the Appendix A ~~Mass~~ mass balance model for
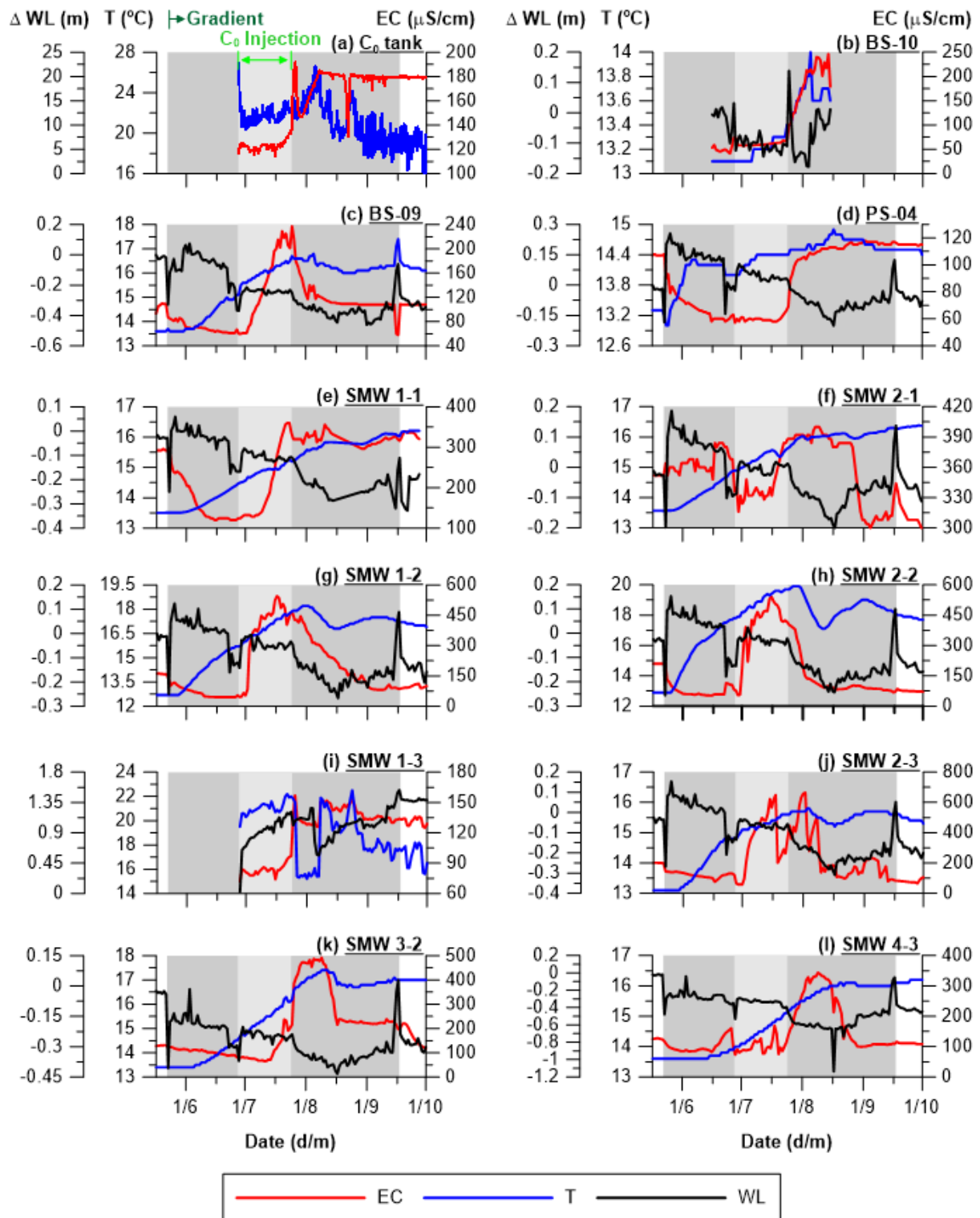
250 detailed explanation).

3 Results

3.1 Prior to CO_2 injection

253   Pressure and temperature changes result in the degassing of insoluble substances from the

254 groundwater system. At the K-COSEM test site, the groundwater level shows a clear decreasing trend

255 due to large-scale water consumption from nearby industrial complexes (Figure 4) (Ju et al., 2019).

256 However, prior to the experiment the hydrostatic pressure data ~~does not record any irregular turbulence~~

257 ~~prior to the experiment and maintained~~showed a stable correlation with ~~the~~ atmospheric pressure

258 changes and no irregular turbulence (Supplementary Figure S1). Groundwater temperatures

259 corresponded to normal seasonal values ranging between 12.7 to 13.6°C (Figure 4).

260   The induced pressure gradient commenced on the 22 May 2017 as a result of the onset of water

261 circulation (Figure 3c). Perturbations were detected in the water level (WL), temperature (T), and

262 electrical conductivity (EC) values during the initiation of water circulation (see the start points of dark

263 grey zone in Figure 4). The pressure turbulence was most noticeable within the monitoring wells located

264 inside the radius of influence (ROI) area both of the pumping (BS-10) and injection wells (BS-04). For

265 example, PS-04, SMW 1 series and SMW 2 series wells showed an instant pressure increase after the

266 circulation commenced, as they are located near ~~to~~ the injection well (BS-04) (Figure 4d–j). In

267 ~~Contrastingly~~contrast, wells SMW 3-2 and 4-3 showed an abrupt decrease in pressure, as a result of

268 their location near to well BS-10 where water was extracted (Figure 4k and l). Well BS-09 also

269 displayed a modest increase in pressure 9 days after water circulation commenced (specifically on 31

270 May 2017) (Figure 4c). Temperature within all monitoring wells showed an overall increase after the

271 water circulation regime started (see the start points of dark grey zone in Figure 4). This is most likely
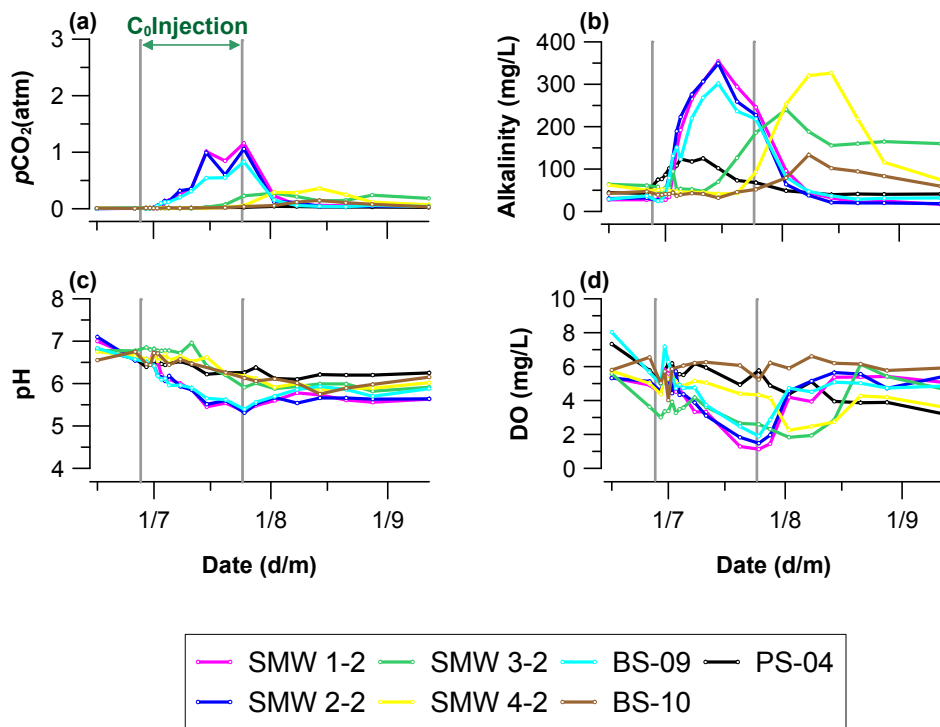
272   linked to the groundwater for injection having resided in the surface tank at temperatures warmer (i.e.,

273   17.1 to 28.6°C) than those of the subsurface groundwaters (i.e., 13.3°C) for the day prior to re-injection

274   into the subsurface. The EC showed the overall decreasing trend in the initial circulation period as the

275   re-injected water (BS-10) has a relatively low EC background compared to the other wells, with the

276   exception of well SMW 2-1 (Figure 4).

Figure 4. Water level (WL), temperature (T) and electrical conductivity (EC) data. Measurements were completed in the monitoring wells continuously using a LTC data logger. The groundwater circulation was initiated at 22 May 2017 (dark grey shaded zone) and the CO_2 injection started at 27 June 2017 and kept going till 24 July 2017 (light grey shaded zone).

282   As outlined previously, two water sampling campaigns were conducted during the circulation

283   period and prior to CO_2 injection commenced, in order to establish the groundwater baseline

284   composition (16 June 2017 and 26 June 2017) (Figure 3). The baseline alkalinity values were relatively

285   low (27.5–64.1 mg/L), DO exhibited a wide variation (3.6–8.0), pH was weakly acidic (6.5–7.1) and

286   pCO_2 was relatively low (0.0–0.01 atm) prior to CO_2 injection (Figure 5). All of the parameters were

287   close to the baseline values of low carbonate levels in the biotite granite protolith (Ju et al., 2019).

288

289   **Figure 5.** pCO_2, pH, alkalinity and DO values. The grey vertical lines represent the injection period.

290   During the water circulation period, pH exhibited an overall decreasing trend as the low-pH

291   water was pumped out from the down-gradient well (BS-10) and reinjected into the up-gradient well

292   (BS-04) (Figure 5c). DO also exhibited a decreasing trend as groundwater was re-equilibrated in the

293   warm surface temperature (17.1–28.6°C) before being injected into the well BS-04 (Figure 4d). pCO_2

294   and alkalinity showed minor variation across the monitored region depending on the groundwater flow

295   direction and the initial C parameter distributions (Figure 4a and b).

296   Mean He, Ar and Kr concentrations measured before the injection commenced were 5.43×10^{-8}

297   cm^3 STP/g_{H2O}, 3.72×10^{-4} cm^3 STP/g_{H2O} and 9.80×10^{-8} cm^3 STP/g_{H2O}, respectively. These are close

298   to the Air Saturated Water (ASW) value at the temperature condition (i.e. 13.3°C) of study site—such

299   as 4.58×10^{-8} cm^3 STP/g_{H2O}, 3.58×10^{-4} cm^3 STP/g_{H2O} and 8.30×10^{-8} cm^3 STP/g_{H2O} for He, Ar and

300   Kr values, respectively (Kipfer et al., 2002).

3.2 Injection fluid

302   The gas-infused groundwater was released into the IW from 27 June 2017 to 24 July 2017

303   (Figure 3). The CO_2–infused groundwater (C_0) collected from the 5 m^3 tank (Figure 2b) was initially

304   below the saturation point (0.40 atm) for 11 days after the injection (29 June 2017 to 8 July 2017), and

305   reached to the over-saturation state (> 2.3 atm) about 18 days after the injection on 15 July 2017 (Figure

306   5a). This CO_2 variation can be attributed to an accidentally reduced water flux going into the CO_2 tank,

307   causing a decrease of the water level, resulting in altering of the C system balance in CO_2 tank. For the

308   same reason, the pH and DO initially maintained 5.0 and 3.9 mg/L but showed a sudden decrease to 4.2

309   and 0.5 mg/L on the 15 July 2017. Water samples collected from the 1 m^3 tank (C_0) (Figure 2a) were

310   analyzed for their He, Ar and Kr concentrations, and reported at 2.92×10^{-5} cm^3 STP/g_{H2O}, 2.26×10^{-2}

311   cm^3 STP/g_{H2O} and 4.95×10^{-5} cm^3 STP/g_{H2O}, respectively. The noble gas concentrations lie between

312   fully saturated and Air Saturated Water (ASW) levels, and thus they will remain dissolved in the

313   groundwater system unless being exposed to low partial pressure conditions such as air bubbles or the

314   vadose zone interface (i.e. water table) (Ju et al., 2019).

3.3 Post injection

3.3.1 P, T and EC

317   Pressure turbulence was observed in all monitoring wells prior to the initiation of CO_2 injection

318   (Figure 4), which can be attributed to the change in water volume from 24.0 m^3/d to 18.5 m^3/d for

319   preparing the gas-infused water of 5.5 m^3 (C_0) before CO_2 injection within the circulation system (see

320   the section 2.2.2 Injection for detailed explanation). Minor changes in temperature were observed inside

321   the Radius of Influence (ROI) zone of IW such as PS-04, BS-09, SMW 1 and SMW 2 (Figure 4c~j).

322   The temperature showed a gradual increase since the groundwater circulation initiated in which the

323   SMW 2-2 showed the highest increase of up to +7.0°C and followed by SMW1-2 (+5.5°C), SMW 3-2

324   (+4.0°C), BS-09 (+3.8°C) and the others (< +2.8°C) (Figure 4). The higher increase in the temperature

325   of BS-09 indicates a preferential flow gradient still exists in the study site even after the formation of

326   the induced pressure gradient (Figure 1a). In EC data, the most prominent signals were recorded at

327   SMW 1-2 (+464 µS/cm, +472%), SMW 2-2 (+447 µS/cm, +368%), SMW 2-3 (+531 µS/cm , +301%),

328   SMW 3-2 (+383 µS/cm, +250%) with the others showing a less pronounced change (< +129%). These

329   observations were consistent with temperature data, exhibiting the greatest change in the SMW #-2

330   wells. This indicated that the CO_2 plume moved horizontally from the injection depth of 21–24 m to the

331   screen depth of SMW #-2 (i.e., 20–22 m) (Figure 1c). The response in EC is clearly different to that of

332   temperature as a notable increase in EC was only observed after CO_2 injection occurred. This is because

333   EC is the function of geochemical interaction between the CO_2 water and the rock materials (Vialle et

334   al., 2014). In the groundwater flow regime, the SMW series wells, BS-09 and BS-10 are located ahead

335   of the migration direction of the IW, which is illustrated by the clearly increasing EC trend (Figure 1b).

336   Alternatively, well PS-04 is located upgradient from the CO_2 injection point, resulting in a gradual

337   lowering of the EC trend after the CO_2 injection was initiated as there is no communication between

338   this well and the CO_2 rich-water (Figure 1b).

3.3.2 pCO_2, pH, alkalinity and DO

340   As expected, the chemical elements exhibited strong signals correlating with the CO_2 plume

341   arrival. The parameters are presented as breakthrough curves (BTCs) (Figure 5). Note that for the

342   SMWs, the parameters represent the data from the injection depth (i.e., SMW #-2) only, as this

343   generated the largest signals among all depths. The pCO_2 produced the strongest signal at SMW 1-2

344   (+1.15 atm, +25,385%) which was followed by SMW 2-2 (+1.05 atm, +18,067%), BS-09 (+0.82 atm,

345   +12,631%), SWM 4-2 (+0.35 atm, +3,746%) and the others wells (< +2,923%) (Figure 5a). The

346   pronounced response of pCO_2 compared to other parameters is attributed to its low baseline

347   concentration (0.0–0.01 atm) (Risk et al., 2015). Alkalinity also showed significant increases with the

348   arrival of the injected CO_2, particularly in wells SMW 1-2 (+326.4 mg/L, +1,189%), SMW 2-2 (+318.0

349 mg/L, +1,017%), BS-09 (+269.2 mg/L, +821%), SMW 4-2 (+270.0 mg/L, +478%) with other wells

350 showing smaller, but measureable changes (< +286%) (Figure 5b). Alkalinity gradually increases with

351 the chemical interactions between the CO_2 plume and the aquifer materials similar to the EC. The small

352 differences in response to CO_2 injection between EC and alkalinity can be attributed to the geochemical

353 variation of the study site resulting in different CO_2 related buffering capacities (Sechriest, 1960).
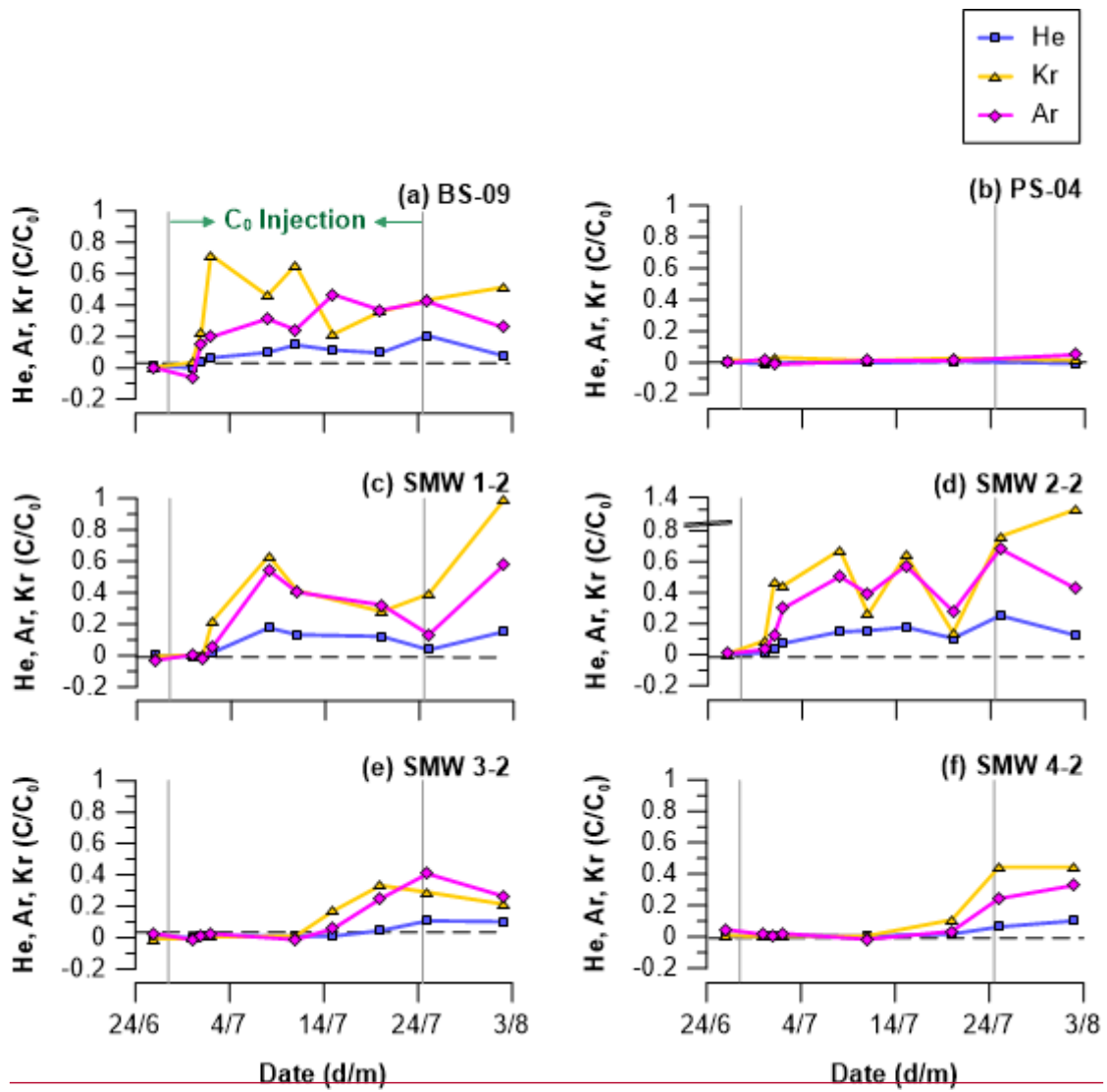
354   The pH also ~~showed~~ decreased noticeably, changing by -1.5 units at SMW 2-2, which was

355 followed by -1.5 units at SMW 1-2, -1.4 units at SMW 2-3, -1.3 units at BS-09 and > -0.96 units at the

356 others (Figure 5c). The DO showed relatively modest change by up to -4.0 mg/L (-78%) at SMW 1-2

357 which was followed by BS-09 (-4.9 mg/L, -72%), SMW 2-2 (-3.7 mg/L, -72%), SMW 3-2 (-2.8 mg/L,

358 -60%) and the others (< -58%) (Figure 5d). In this experimental setting, the DO evolves with the three-

359 component groundwater mixing between low-DO water volumes (re-injection water at BS-04 and

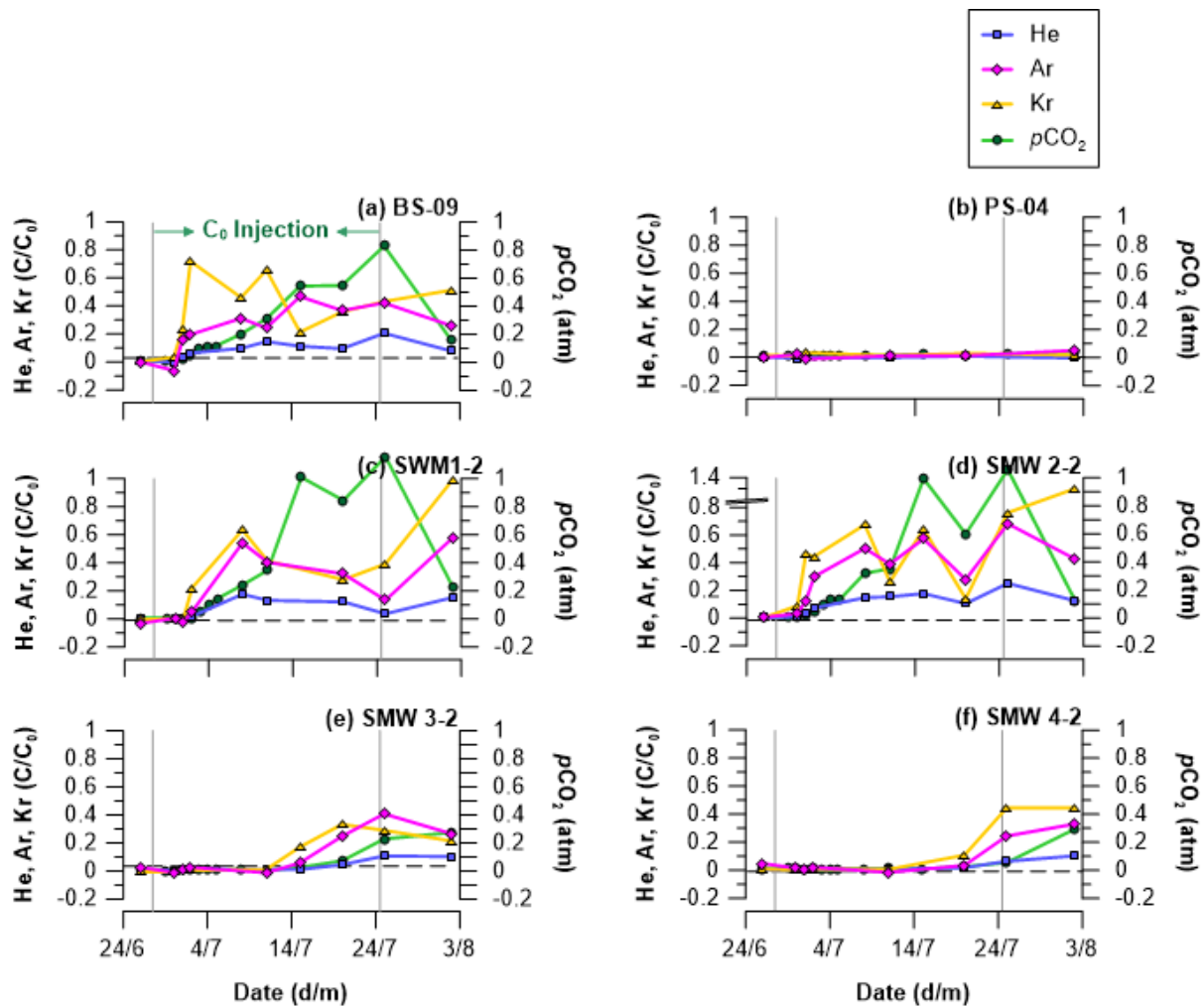360 injection water at IW) and high-DO water volume (local groundwater) (Figure 2).

3.3.3   Noble gas tracers

362   The measured concentrations of He, Ar and Kr tracers are presented in BTCs (Figure 6). The

363 concentration was normalized to the injection amount (C_0) after the background portion (i.e.

364 atmospheric origin) was subtracted from both monitored (C) and initial concentration (C_0), to simply

365 define the CO_2 arrival as a positive signal. Note that for the SMWs, the parameters present the data

366 from the injection depth (i.e., SMW #-2) only, as this exhibited the largest signals of all depths. As a

367 result, the tracers successfully produced the strong positive signals with the CO_2 plume arrival in the

368 BTCs (Figure 6). The tracer concentrations exhibited variable arrival times and concentrations due to

369 the CO_2 plume following different flow paths within the heterogeneous groundwater system at the site,

370 similar to ~~what was~~the findings of ~~described by~~ Kilgallon et al. (2018), Lee et al. (2017), Lu et al. (2012)

371 and Stalker et al. (2015). Most importantly, Kr showed the earliest arrivals through all monitoring wells

372 compared to the He and Ar tracer. This was attributed to the Kr taking a less distributed pathway through

373 the subsurface than the other tracers, and a result of the dilution of CO_2 plume along ~~a~~ the concentration

374 gradient (see the discussion section 4.1.2 Diffusion process controlling the efficiency of noble gas

375   tracing).

376   The tracers associated with the CO_2 plume were firstly detected in SMW 2-2 (+4 d) followed

377   by BS-09 (+4 d), SMW 1-2 (+5 d), SMW 3-2 (+18 d) and SMW 4-2 (+23 d) (Figure 6a, c, d, e and f).

378   The strongest signal was recorded at SMW 2-2 (+1,430% for He, +322% for Ar and +6,904% for Kr)

379   suggesting the majority of the CO_2 plume moved along the induced groundwater pressure gradient

380   (Figure 6). A portion of the tracers also moved toward BS-09 and produced a strong signal in spite of

381   ~~its longer~~being a greater ~~moving~~ distance away from the injection point (5.2 m) than that of SWM 1-1

382   and SMW 2-2 (2.6 m). This can be~~,~~ attributed to the preferential flow path~~way present~~ in the study site

383   (Figure 1a) (Ju et al., 2019; Lu et al., 2012). Well PS-04 did not record the presence of any tracers

384   during the injection period due to its location behind the IW in the groundwater flow direction (Figure

385   1b). ~~Note~~ It is worth noting that SMW 4-2 ~~showed~~ exhibited ~~a stronger signal~~a higher concentration of

386   Kr once the tracers arrived ~~at the plateau~~ than SMW 3-2 ~~did~~ (Figure 6), ~~implied~~ implying that a low

387   conductivity zone ~~existing and hindering~~ hinders well~~the~~ SMW 3-2 from capturing ~~a~~ the full CO_2 plume

388   ~~efficiently~~. This result was consistent with the observations made in alkalinity and pCO_2 (Figure 5).
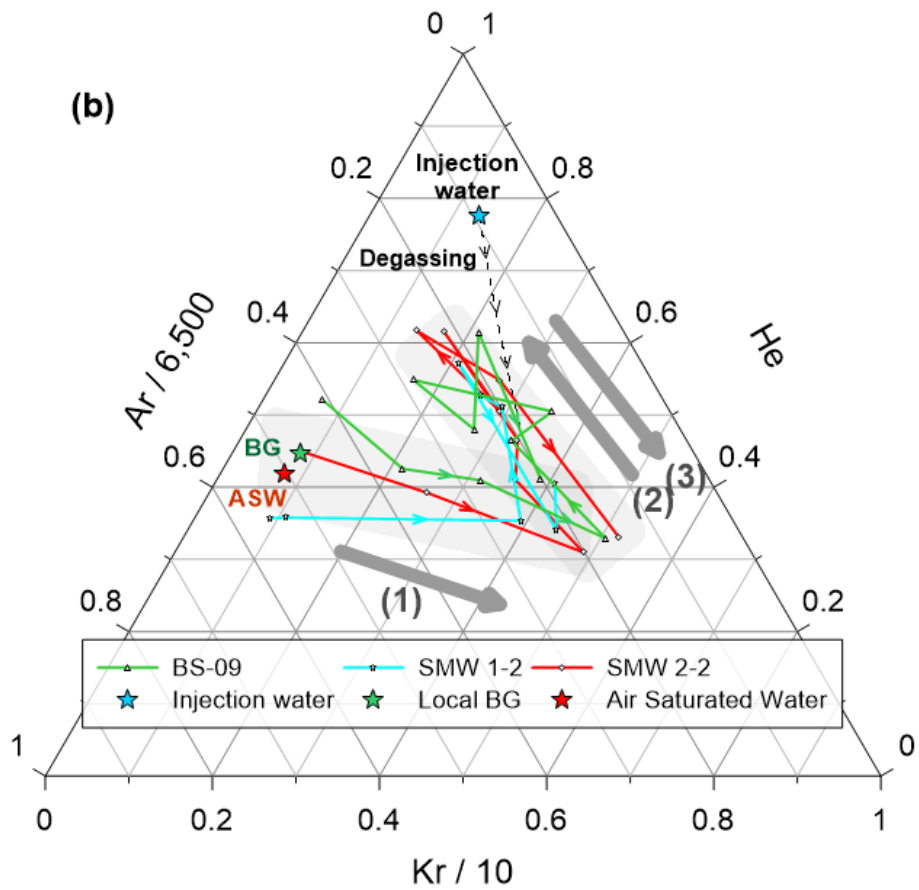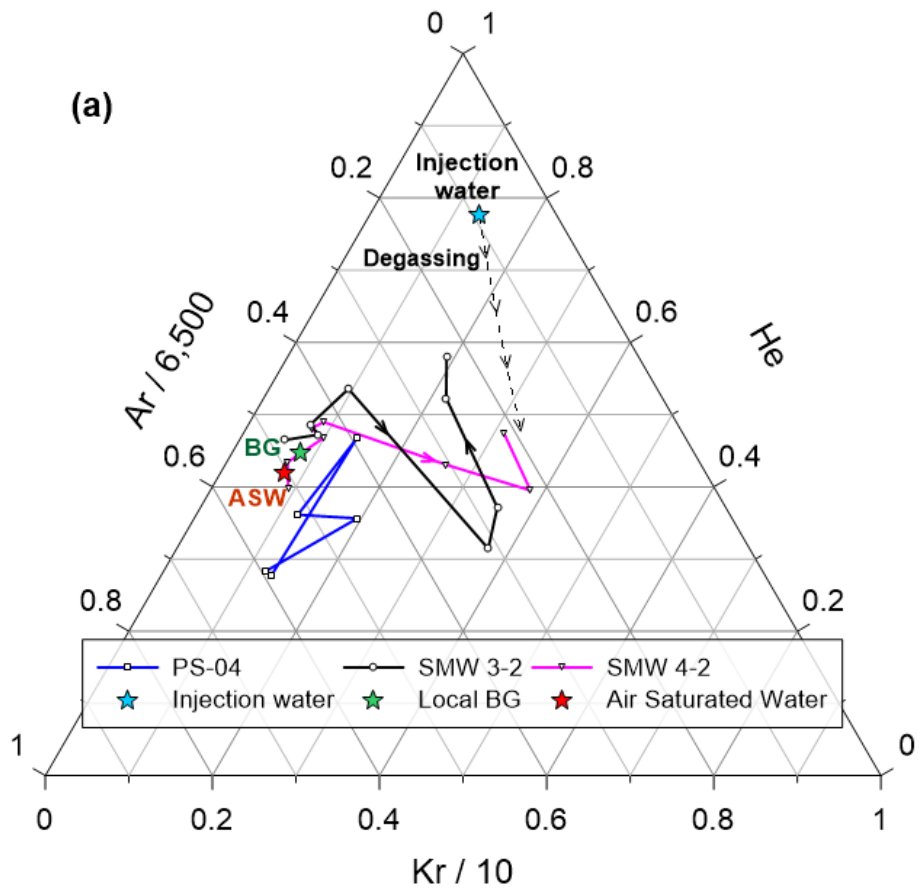
Figure 6. ~~Noble g~~Gas tracer concentration during the experiment. Noble gas was presented as C/C_0 (see the text for details) with pCO_2. The grey vertical lines show the start and end of the injection period. The Air Saturated Water (ASW, black dotted horizontal line) was calculated according to Kipfer et al. (2002) to indicate the local background level of noble gas tracers.

As the injection water gradually approached the monitoring network, the observation wells captured the temporal evolution of the CO_2 plume. In the early stage of BTCs, Kr showed the fastest arrival time compared to the other tracers for all monitoring wells (Figure 6). This was followed by an increase in Ar and He concentrations, with both parameters soon reaching their peak concentration within a few days (Figure 6). In the final stage of BTCs, the plume tail is recorded in all of the monitoring wells through the decrease of noble gas concentrations ~~resulting~~ after ~~the~~ injection at the IW ceased. However, it can be observed that the concentration increased in the last stage of the BTCs for monitoring wells adjacent to IW (Figure 6c and d). This can be ~~attributed to the circulation injection

403   system of this experiment. In the final stage of the injection period (4 days before the end of injection),

404   the tracer-charged plume had reached BS-10 (Figure 4b). As water was still being produced for the

405   reinjection at the IW, a portion of the CO_2 plume was returned back into the injection tank containing

406   the- artificial noble gas tracers. Note that heavier components such as Ar and Kr acted as an early

407   warning tracer for CO_2 arrival in every monitoring well during the monitoring period. This was

408   attributed to physical mechanisms affecting the distribution of the dissolved gases (see the section 4.1.2

409   Diffusion process controlling the efficiency of noble gas tracing).

Figure 7. Noble gas ternary diagram showing the two groups of wells categorized by their response. (a) monitoring wells which showed no concentration change from background level (i.e., PS-04) or only an early-stage evolution (i.e., SMW 3-2 and SMW 4-2). (b) monitoring wells that showed a three-step evolution as located close to the injection point (i.e., SMW 1-2 and SMW 2-2) and located in a preferential migration path (i.e., BS-09). The early-stage CO_2 plume is characterized by high Kr concentration (Arrow 1), the plume then gradually increases in He and Ar concentrations (Arrow 2). In the final stage, it becomes rich in Kr again, following the cessation of injection (Arrow 3). The peak composition was different from that of injection water due to initial degassing loss.

The consistent temporal evolution of the recorded noble gas concentrations within the six monitoring wells is depicted in the ternary diagram of Figure 7. The local BG (i.e., green star) represents the average of background level of individual monitoring wells. Prior to the CO_2 plume arrival, each monitoring well plots near to the Air Saturated Water (ASW) level. The initial arrival of the CO_2 plume was marked by a significant increase in Kr in all monitoring wells (see the arrow 1 in Figure 7) which corresponds to the early stage evolution in the BTCs (Figure 6). Note that PS-04 did not exhibit a response after injection. Following the arrival of the Kr tracer, the He and Ar concentrations within the monitoring wells increase as the plume center approached, converging at a single point (Figure 7). However, the concentrations of noble gas tracers at the peak concentrations were lower than those at the time of injection. They were 73.6–88.3% (He), 26.2–55.5% (Ar), and 0–65.5% (Kr) of the initial concentrations. The lower concentrations can be attributed to the degassing loss of the injection fluid (Sathaye et al., 2016), explained in more detail in the section 4.1.1. This degassing process controls the overall retention amount of the injected CO_2. The composition of the plume tail captured in the monitoring wells was similar to the composition of the plume front, characterized by a high Kr concentration (Figure 7).

3.4 Following injection

The ~~C₀~~CO_2 injection ceased~~stopped~~ after 28 days ~~of injection~~ (27 June 2017 to 24 July 2017) (Figure 3). This corresponds to the point where the monitoring parameters start to change at the BS-10

437 (Figure 4b and 5). In this moment, the slight increase of EC was also observable in the CO_2 tank as CO_2

438 water re-entered the injection tank (Figure 4a). ~~Accordingly~~Additionally, -PS-04 also showed a minor

439 increase in EC at the termination period due to the re-circulation of CO_2 injected water (Figure 4d).

440 From this point (24 July 2017), the groundwater circulation system was modified to avoid the re-

441 enhancement of the CO_2 plume. Another local groundwater from BH-03 was prepared and from then

442 onwards substituted the circulation portion going to the BS-04 (Figure 1e and 2c).

3.5 Following groundwater circulation

444 The groundwater circulation ended on 17 September 2017, 56 days after CO_2 injection stopped

445 and 118 days after groundwater circulation commencement (Figure 3). The pressure turbulence was

446 observable in all monitoring wells (Figure 4) and also EC turbulence was detected in some of the

447 monitoring wells (Figure 4c, f and k), but the groundwater quickly recovered to its previous state (Figure

448 4).

4 Discussion

4.1 Mass retention mechanisms

4.1.1 Degassing process controlling the overall retention amount of released CO_2

452 If an inert tracer is continuously released into the groundwater system, the concentration will

453 gradually increase in monitoring wells and eventually become similar to the composition of injection

454 fluid. In this study, as the tracer-charged water was continuously released into the groundwater system,

455 the monitored concentration was expected to resemble the injection fluid's concentration by the final

456 stage. However, a notable difference in CO_2 and noble gas concentrations was observed between the

457 injection fluid and the plateau points (Figure 7). This phenomenon indicates that tracer mass was not

458 conserved in the groundwater system and suffered from mass-reducing processes. As the noble gas

459 tracer is biochemically inert in the groundwater system, the decrease is likely to be the result of physical

460 processes (Holland and Gilfillan, 2013). For instance, a similar noble gas deficit has been observed in

461 a natural CO_2-rich system, where CO_2 and CH_4 bubbles also stripped out the insoluble gases from the

462 groundwater system (Gilfillan et al., 2008, 2017; Brennwald et al., 2005; Zhou et al., 2005) and in

463 artificial CO_2 injection sites (Nimz and Hudson, 2005; Stalker et al., 2015). Hence, this deficit could be

464 explained by the degassing of unstable CO_2-rich plume.
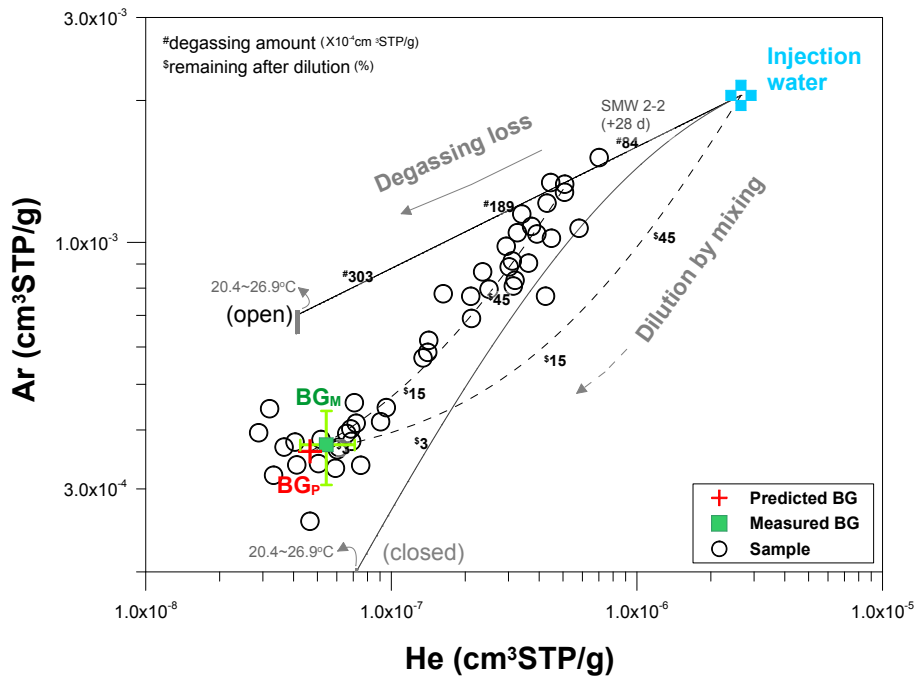
465

466 **Figure 8.** Mass balance of the CO_2 plume depicted with He and Ar tracer. The plume was expected to

467 follow the mixing line between the injection water (blue cross symbol) and the measured background

468 concentration (BG_M, green square symbol). Degassing loss of ~~the~~ CO_2 <u>from the dissolved CO_2</u> plume,

469 ~~however,~~<u>would</u> result~~ed~~ in a new mixing line starting from the SMW 2-2 (+28 days) toward the

470 background concentration (BG_P, red cross symbol). The BG_P was estimated based on the optimization

471 process of the degassing model (see the Appendix B Model optimization for detailed explanation). The

472 shaded zone on the degassing models indicates the uncertainty arising from the injection water

473 temperature (20.4–26.9°C).

474   A diagram was constructed using noble gas tracers to determine the major processes

475 influencing the CO_2 plume migration (Figure 8). In Figure 8, the concentrations of He and Ar at the

476 well SMW 2-2 (on 25 July 2017) decreased gradually to their background concentration (BG_p),

477 indicating mixing of the plume with the local groundwater. The mass distribution of observed samples

478 was the function of two distinct processes over the testing period: mass reduction of the CO_2 plume

479 occurred through the degassing process (black line), followed by the dilution of the plume by the local

groundwater (black dotted line). The observed data clearly indicated the mixing process was preceded

481 by the degassing process.

482 **Table 1** Mass balance of the leaked CO_2 plume in shallow aquifer system.

| Open system	Injection		After degassing loss			Solubility† (mM/atm)
	Amount (kg)	partial pressure (atm)	ΔAmount (kg)	Δpartial pressure (atm)	Remaining (%)	
He	7.04×10^{-5}	3.07×10^{-0}	5.64×10^{-0}	2.46×10^{-0}	~~80.1~~19.9	0.386
Ar	5.43×10^{-0}	6.11×10^{-0}	1.85×10^{-0}	2.08×10^{-0}	~~34.0~~66.0	1.50
Kr	2.50×10^{-0}	7.41×10^{-0}	5.13×10^{-0}	1.52×10^{-0}	~~20.5~~79.5	2.71
$CO_{2\,p.}$‡	1.70×10^{2}	6.62×10^{-0}	$2.72 \underline{\times\ 10^{0}}$	1.07×10^{-0}	~~1.6~~98.4	38.7

483 †NIST chemistry webbook of Sander (2017) at temperature of 21.8°C.

484 ‡~~the~~ The predicted value from model optimization (see the Appendix B Model optimization for detailed

485 explanation).

486 　　Elemental fractionation of noble gases is controlled by their differing solubilities and the

487 ambient reservoir conditions (Figure 8) (Ballentine et al., 2002; Ma et al., 2009). In a closed system,

488 the dissolved air remains in the groundwater, and equilibrium is achieved between the bubbles and the

489 surrounding groundwater. In an open system, the air bubbles are mobile after the phase transition and

490 escape from the aquifer system continuously until the end of the degassing process. In Figure 8, the

491 mixing line (black dotted line) intersects a degassing line (black line) explaining the loss of air bubbles

492 by 1.40×10^{-2} cm³/g_{H2O} through the degassing process in an open system. The analytical technique for

493 this calculation is shown in Appendix A Mass balance model. In the experiment, CO_2 degassing was

494 detected just above the water table at the IW reconfirming the initial loss happened into the vadose zone

495 (Supplementary Figure S2).

496 　　Unlike noble gases, CO_2 is involved in diverse chemical and biological processes in the

497 groundwater. To identify the major controls on the CO_2 distribution, the pCO_2 was plotted against

498 measured noble gas tracer concentrations in Figure 9. As expected, the total mass of CO_2 in the plume

499 was decreased by degassing and mixing processes. Our data designate a clear mixing line stretching

500 from SMW 1-2 (25 July 2017) to BGp, indicating that mixing process mainly controlled the mass

501 distribution of CO_2 in the plume after the initial degassing event. The minor variations from the mixing

502 trend mostly fall in the ranges of the initial composition of injected CO_2-infused water (Figure 9). The

503 solubility-controlled process is shown as the black arrow stretching from the blue-cross symbol to red-

504 cross symbol (Figure 9). The abrupt change in He/Ar ratio stands in strong contrast to the minimal

505 change observed in the pCO_2 during the degassing event (ca. 1.6% overall loss of CO_2). Losses of noble

506 gases (20.5% for Kr, 34.0% for Ar, and 80.1% for He) are much greater than for CO_2 (Table 1).
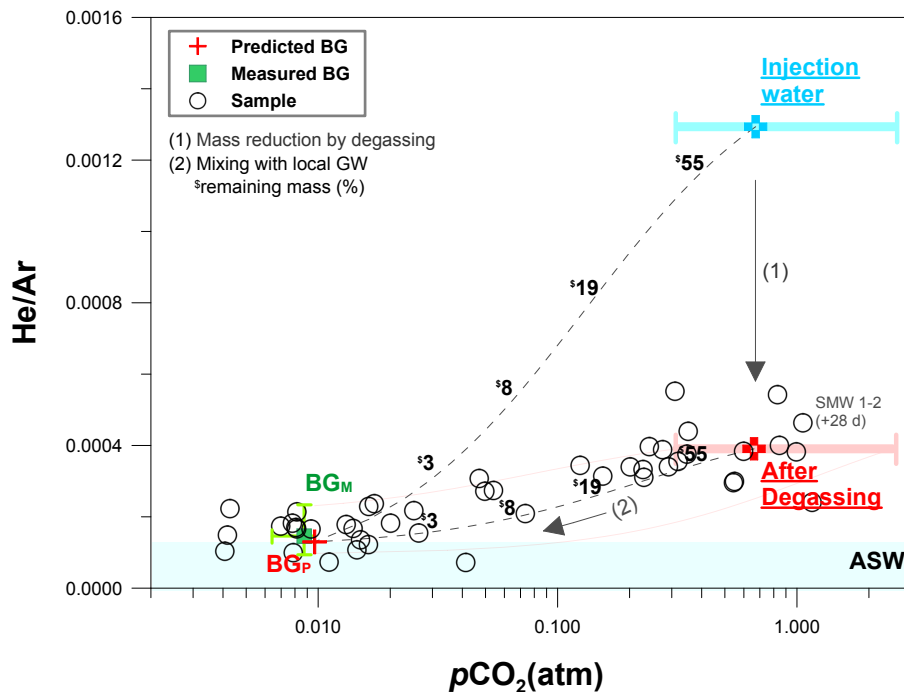
507

508 **Figure 9.** Plot of pCO_2 against He/Ar showing the concentration changes of CO_2 and noble gas tracers

509 during CO_2 plume evolution. The BG_M (green square symbol) is the measured background level, and

510 the BG_P (red cross symbol) is an estimated value from the optimization process of the degassing model

511 (see the Appendix B Model optimization for detailed explanation). The CO_2 plume firstly reduces total

512 mass by the degassing process (Arrow 1) and then gradually gets diluted by mixing with local

513 groundwater (Arrow 2).

514 **4.1.2 Diffusion process controlling the efficiency of noble gas tracing**

515   The different noble gas species cover a wide mass range and thus may provide a chance to

516   constrain the mass-dependent processes occurring in the groundwater system. A comparison was made

517   to scrutinize the behavioral difference for noble gases, as observed from the He/Ar (Figure. 8) and

518   He/Kr (Figure 10) relationships. The mixing line in Figure 10, represented by a black dotted line

519   stretching from the degassing line to BGp, corresponds to the mixing line estimated in Figure 8.

520   However, it is noteworthy that the He and Kr pair did not exhibit a singular trend with many variations

521   scattering from the estimated mixing line. It is also noteworthy that samples from the plume's center

522   tend to converge on the estimated mixing line, while the samples from both the plume's front and tail

523   display a large scatter pattern over the estimated line (Figure 10). Such discordance was also observable

524   in the pCO_2 versus He/Kr diagram (Figure 11) in which many samples, especially those from the

525   plume's front and tail had significantly lower He/Kr ratios (around 0.10) than the ratio describing the

526   estimated mixing line (0.24). This difference indicates that another mass-dependent process was

527   affecting the tracer distribution in addition to the solubility-controlled process.
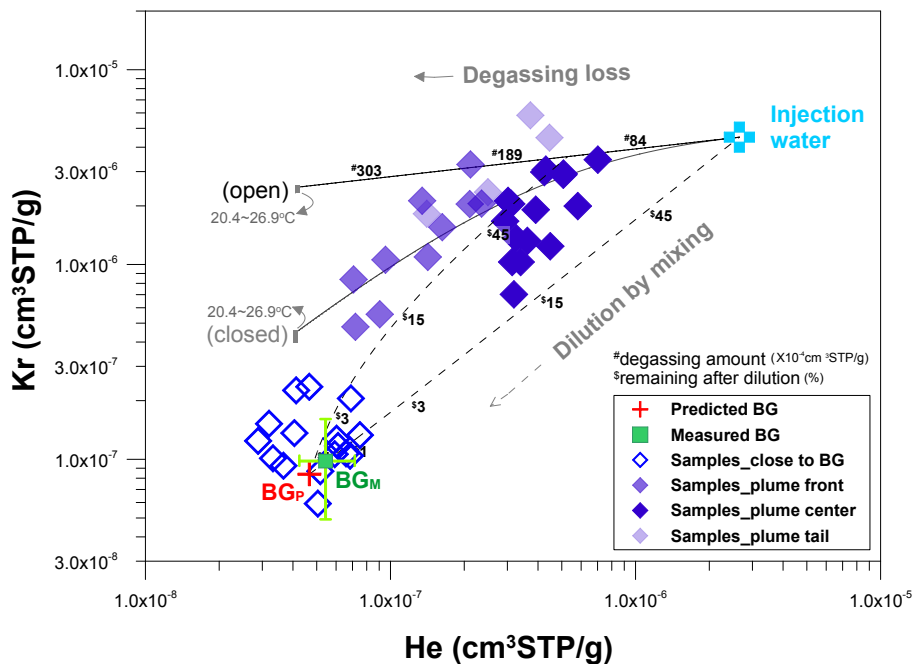
528

Figure 10. Mass balance of the CO_2 plume depicted with He and Kr tracers. To see the plume evolution

in detail, the samples were sorted by the breakthrough positions. Note that many samples, especially on

the plume front and tail, are scattered over the estimated mixing line, contrary to the He–Ar pair mixing

532   trend in Figure 8.
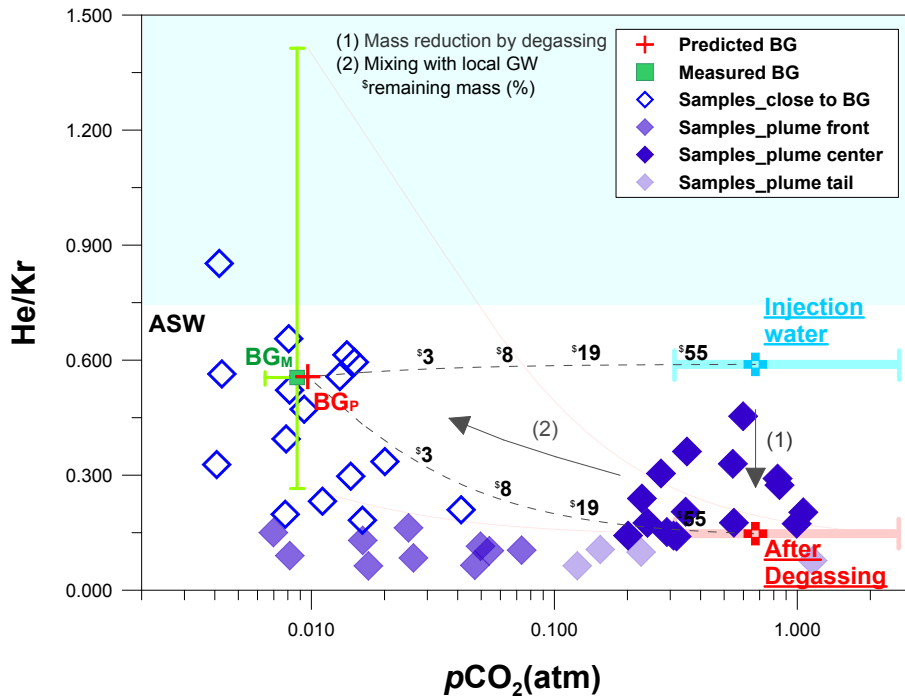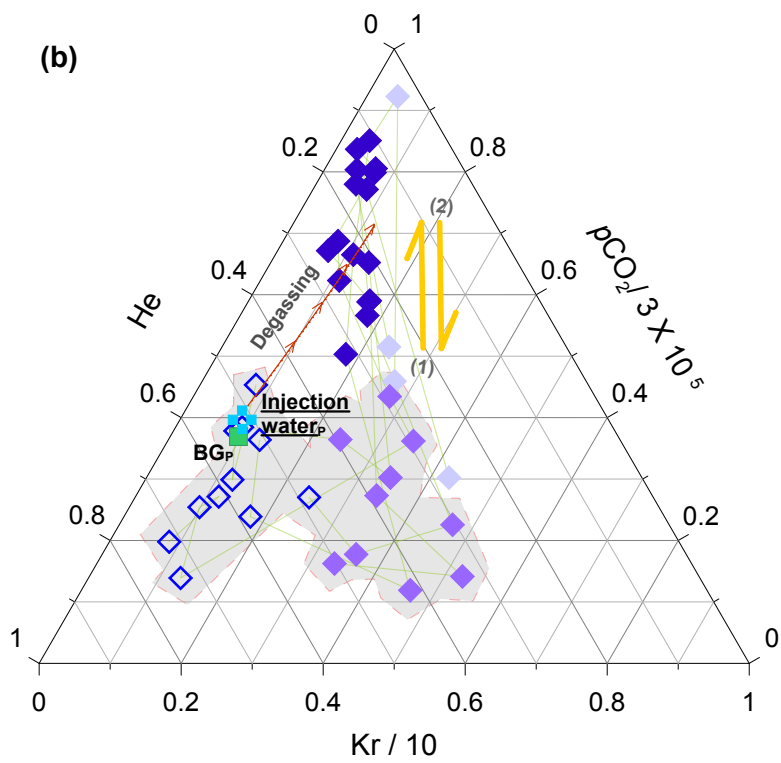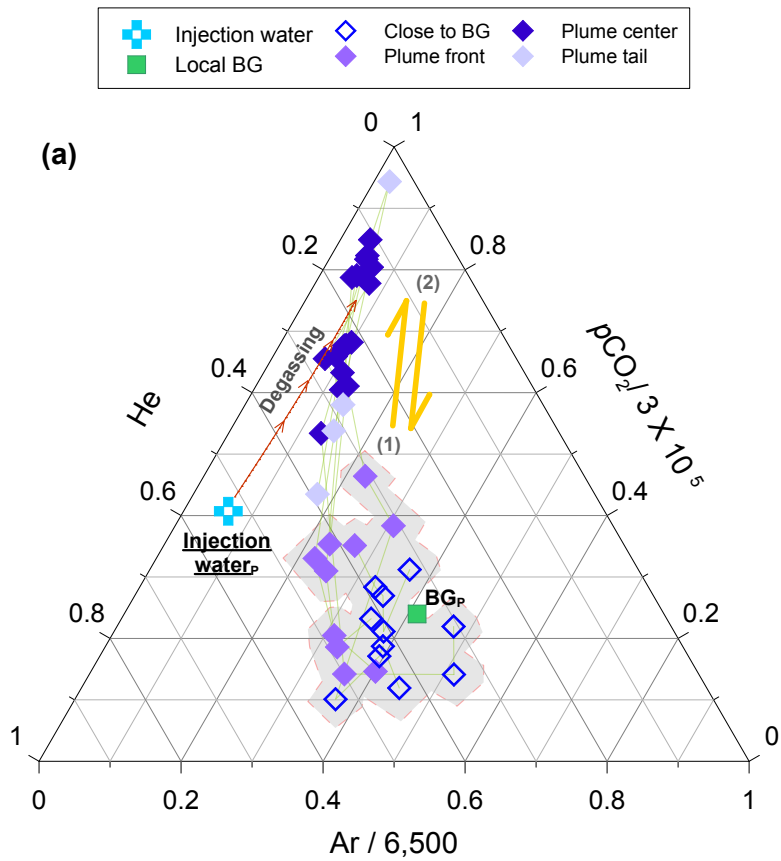

533

Figure 11. Diagrams showing the concentration changes of CO_2 and noble gas tracers during CO_2

plume evolution. To see the plume evolution in detail, the samples were sorted by the breakthrough

positions. Note that, many samples, especially on the plume's front and tail, are scattered from the

estimated mixing line, as compared to the observations in the pCO_2 versus He/Ar relationship in Figure

9.

To further examine the temporal progression of the CO_2 plume, ternary plots ~~among~~ of pCO_2

He, and Ar or Kr were composed according to the locations of samples in the plume (i.e., front, center,

and tail) (Figure 12). In the He/Ar/pCO_2 diagram, the samples have a small variation near BG_P in the

initial period, while as the plume center approached the monitoring points, it showed an upward shift

toward the degassing point in the Figure 12a. In the He/Kr/pCO_2 diagram, the samples show a much

wider variation during the initial stage of the CO_2 plume arrival than the observed change in the

He/Ar/pCO_2 diagram (Figure 12b). This difference indicated that another physical process was involved

in the mass distribution at the CO_2 plume's front. Note that the initial composition of the plume was

characterized by the high concentration of Kr as it appeared firstly in the observation wells (see also

548   Figure 7).

Figure 12. Ternary diagram showing the compositions of pCO_2, He, and Ar (a) or Kr (b) tracers. To scrutinize the plume evolution, the samples were sorted according to the breakthrough positions. In the initial period of plume evolution, the relative compositional change among pCO_2, He and Kr (b) showed a much wider variation near the background levels (BG_P, green square symbol) than that observed among pCO_2, He and Ar (a), which attributed to the diffusion process (see the text for details). This diffusion-dominant movement was followed by the upward shift toward the degassing point (see Arrow 1), as also shown by the intersection point in Figure 8. In the final stage, the samples return to the composition similar to the plume's front (see Arrow 2), after cessation of injection.

In open water, diffusion is capable of elemental fractionation depending on the molecular mass (Zheng and Bennett, 2002). According to Fick's law, the mass distribution of a solute in a groundwater system is restricted by molecular diffusion along the concentration gradient. In our experimental design, the artificial injection formed a CO_2- and tracer-rich plume in the groundwater system, setting a steep concentration gradient at the plume boundary. Consequently, the plume boundary was actively subjected to the diffusion process facing with the local groundwater of low concentration level of noble gases. As the diffusion rate is inversely proportional to the elemental mass of the solute, the tracer composition at the plume boundary was regulated by the mass-dependent fractionation. This phenomenon also has been observed in a coal bed methane field, where the free CO_2 and CH_4 gases stripped off the insoluble noble gases from groundwater and this action set the concentration gradient at interfaces with the un-degassed local groundwater, at which diffusion process resulting in a mass dependent fractionation of noble gas tracers (Zhou et al., 2005). Overall, the fact that the diffusion allocates the mass distribution at plume boundary (i.e., plume's front and tail) suggests that the early detection of the migrated CO_2 plume is dependent on this process. This further implies that the early-stage degassing loss is of primary importance in terms of the noble gas tracing efficiency because the degassing process is associated with the overall plume composition including the feature of the concentration gradient at plume front.

5   **Conclusions**

576   A portion of CO_2 stored within the deep subsurface may unintentionally migrate upward to

577   reach overlying shallow aquifers. Whilst noble gas tracers have proved to be useful in monitoring CO_2

578   leakage, they have been rarely adopted for monitoring purposes in the shallow aquifer system. This

579   study utilized the noble gas tracers to indicate the CO_2 leakage and also to elucidate the mass balance

580   of the leaked plume after injection of 1.70×10^2 kg of CO_2 into a shallow aquifer system. The CO_2- and

581   tracer-enhanced groundwater was released into the induced gradient field and subsequent monitoring

582   works have been conducted. The noble gas tracers produced a strong signal ~~with~~of the ~~the~~migrated

583   CO_2 ~~leakage~~, with Kr consistently exhibiting the first arrival time, ahead of the ~~CO_2~~ plume and ~~than~~ the

584   other noble gas tracers throughout all of the monitoring points.

585   The mass distribution of the CO_2 plume was controlled by three different physical processes:~~,~~

586   solubility-controlled (degassing), physical groundwater mixing and diffusion. The degassing process

587   reduced the overall mass of the CO_2 plume and caused noble gas tracers to be mass-dependently

588   fractionated, which occurred at the initial stage of CO_2 leakage before plume migration. The diffusion

589   process was also involved during the plume migration, but only influenced the noble gas distributions

590   in the leaked plume and did not act as a primary control for the CO_2 distribution within the monitoring

591   period. This phenomenon, however, can accelerate the dilution of artificial tracers at the plume front,

592   especially for the lighter elements, suggesting this process has an important control on the monitoring

593   efficiency of the artificial tracers in terms of early detection of CO_2 leakage. Most importantly, as the

594   noble gas tracers display more apparent changes according to the retention mechanisms than CO_2 itself,

595   ~~noble gas tracers~~they can provide a robust system for precisely monitoring both the fate and pathway

596   taken by the migrating CO_2.

597   Noble gas tracers were used to ~~explain~~ constrain the physical retention mechanisms of the

598   injected CO_2 ~~of~~ within a shallow aquifer ~~for the leaked CO_2~~. Our findings indicate that ~~A~~around the

599   ~~injection~~leak point, CO_2 degassing dominantly ~~occurred~~ occurs from ~~a~~ the dissolved plume ~~of~~due to the

600   ~~high~~the high gas pressure, suggesting a near-surface monitoring network is necessary for capturing the

601   active "vertical" movement of degassed budget in this area. This can be accomplished by performing a

602   continuous monitoring of CO_2 at the vadose zone, for example by a soil flux measure, soil gas sampling

603   and borehole head space sampling around a potential leak point. The monitoring regime can be

604   performed cost-effectively with limiting a "degassing boundary" around a suspected leak point. In this

605   study, only a few meters away from the leak point (>2.6 m), the degassing behavior was greatly

606   diminished as a gas pressure of CO_2 plume reduced significantly. From this point, the CO_2 plume was

607   stabilized as a dissolved phase and dominantly diluted by mixing with a local groundwater along a flow

608   direction. Therefore, from this stage, sparse monitoring of saturated zone is recommended for tracing

609   down a horizontal migration of a dissolved CO_2 plume, rather than an intensive gas monitoring for a

610   degassed component. Hence, the key aspect to establish an effective monitoring network is how well

611   constrained the "CO_2 degassing boundary" around a potential leak point is, and how well the

612   groundwater flow regime is understood.

613   Monitoring of degassed CO_2 might not be easily achieved in a real CCS field using direct

614   measurements. In this study, the degassing boundary was just a few meters ~~apart~~ from ~~a~~ the leak point

615   (< 2.6 m), whilst a strong artificial gradient (~0.18) was enforced for the plume migration. This suggests

616   that a degassing boundary would be even narrower in a natural gradient system, making a direct

617   detection of this extremely difficult. Furthermore, heterogeneity in the vadose zone can put an additional

618   uncertainty in monitoring of the vertical flux, as ~~gasesous~~gaseous CO_2 can take various pathways in the

619   vadose zone depending on ~~a~~ the soil permeability distribution (Cohen et al., 2013). Hence, identification

620   of a point source of CO_2 leakage using a direct measurement technique in the vadose zone would be

621   very difficult, unless an intensive monitoring is undertaken around the exact point source. However,

622   noble gas monitoring of groundwater is able to record the migration of a CO_2 plume from the leak point

623   along the groundwater flow pathway, as highlighted in this study. Our findings are similar to previous

624   work (Mackintosh and Ballentine, 2012) that showed monitoring of noble gases in groundwater is an

625   order of magnitude more sensitive for detecting migrated gases than vadose zone gas monitoring.

626   Therefore, we recommend that monitoring of noble gases in groundwaters should be used in addition

627   to direct vadose zone methods, in order to increase the sensitivity of the monitoring regime and improve

628   the protection of the shallow groundwater aquifer above a storage site.

Acknowledgements

Appendix A. Mass balance model

At least, two noble gases of different solubility are necessary to determine the degassed mass as outlined in Ju et al. (2019). The closed system is a one-step phase-partitioning process, and therefore, the degassed amount can be determined just by repeatedly adjusting the gas/liquid ratio until the result $\left(\left(\frac{A}{B}\right)_{(l)}\right)$ fits into the measured data:

$$\left(\frac{A}{B}\right)_{(g)} = \left(\frac{A}{B}\right)_{(l)} \times \alpha$$

$$\alpha = \frac{\frac{r_A}{\phi_A} K_A}{\frac{r_B}{\phi_B} K_B}$$

Here:

$\left(\frac{A}{B}\right)_{(g)}$ = A and B ratio in exsolved bubbles, where A and B are different noble gases

$\left(\frac{A}{B}\right)_{(l)}$ = the composition of A and B remaining in the dissolved phase

α = partitioning coefficient for gas/liquid system

K_A, K_B = Henry's constant for A and B, from Sander et al., (2017)

r_A, r_B = dissolved-phase activity coefficients for A and B and

ϕ_A, ϕ_B = gas-phase fugacity coefficients for A and B.

In open system, the CO_2 bubble ($V_{(g)}$) is continuously lost into vadose zone carrying the noble gas tracers with it from the groundwater system until the plume is stabilized. An iteration calculation can be undertaken to account for the continuous loss and which terminates when the resultant mass ($m_{(l)}^i$) fits the observed noble gas data:

$$m_A{}^i_{(l)} = m_A{}^{i-1}_{(l)} - m_A{}^{i-1}_{(g)}$$

$$m_B{}^i_{(l)} = m_B{}^{i-1}_{(l)} - m_B{}^{i-1}_{(g)}$$

659   Here:

660   i = Iteration step

661    $m^{i-1}{}_{(l)}$ = mass in dissolved phase before $i - 1^{th}$ degassing loss (g)

662    $m^{i}{}_{(l)}$ = mass in dissolved phase after $i - 1^{th}$ degassing loss (g)

663    $m^{i-1}{}_{(g)}$ = degassed mass during $i - 1^{th}$ degassing process (g)

664   and degassed mass was determined from the degassed volume, such that:

665    $m^{i-1}{}_{(g)} = C(V_{(g)} \times p^{i-1})$

666    $C = M/R \cdot T$

667    $p^{i-1} = \gamma\, K\, x^{i-1}/\Phi$

668    $x^{i-1} = 18\,[NG]^{i-1}\,(\rho_{(l)}\,V_{(l)})^{-1}$

669   Here:

670    $V_{(g)}$ = degassed volume during $i - 1^{th}$ degassing process (cc)

671   C = conversion factor from volume to mass

672   M = molar mass (g/mol)

673   R = gas constant (8.314 cc $\cdot$ atm/K/mol)

674   T = temperature (K)

675   p^{i-1} = partial pressure of removed noble gas during $i - 1^{th}$ degassing process

676   K = Henry's constant in units of pressure (atm)

677   γ = liquid-phase activity coefficient

678   Φ = gas-phase fugacity coefficient

679   x^{i-1} = molar fraction of noble gas in dissolved phase at $i - 1^{th}$ degassing moment ($mol_{NG}/mol_{(l)}$)

680    $[NG]^{i-1}$ = number of moles in dissolved phase at $i - 1^{th}$ degassing moment (mol)

681    $\rho_{(l)}$ = density of dissolved phase (g/cm^3)

682    $V_{(l)}$ = volume of dissolved phase (cm^3)

683   For an open system, an iterative model was used with a fixed $V_{(g)}$ value which should be small enough

684   to finally achieve convergence with the measured noble gas composition. The noble gas concentration

685   in the groundwater was gradually decreased in iterative steps. In the final stage (i = n), $\frac{m_A{}^n_{(l)}}{m_B{}^n_{(l)}}$ was

686   matched against the monitored composition, and then the total degassed volume was calculated by

687   multiplication of the bubble size ($V_{(g)}$) and the number of iteration steps (i) in the open system model.

688   **Appendix B. Model optimization**

689   Model optimization can be achieved in a similar manner to that used by Ballentine (1997) and

690   Castro et al. (2009). The optimization aims to replicate the monitored noble gas data into a calculated

691   mixing line with the smallest misfit to the observed data. As the monitored concentration is defined by

692   mixing between two end-members, therefore, to achieve the minimum misfit, the end-members

693   constituting the predicted mixing line were repeatedly updated. There are two end-members for the

694   mixing line such as: 1) the noble gas concentration after the degassing event; and 2) the noble gas

695   concentration of the background concentration (Supplementary Figure S3). The first end-member is the

696   function of the initial amount and total degassed budget ($V_{(g)}$) of a species as discussed in the previous

697   section. The second end-member is the function of excess air intrusion level (A) to the Air Saturated

698   Water (ASW) (Mazor and Bosch, 1987; Kipfer et al., 2002). Hence, this optimization process allows

699   quantification of the degassing amount and the background level of leaked plume within the

700   groundwater system. The optimization process is given by:

701

702 $$\chi^2 = \Sigma_{i=1}^{N} \left[\left(\frac{NG1_i^m - NG1_i^p}{\sigma_{NG_{1,i}}} \right)^2 + \left(\frac{NG2_i^m - NG2_i^p}{\sigma_{NG_{2,i}}} \right)^2 \right]$$

703 Here:

704 $i = i^{\text{th}}$ sample

705 N = the number of sample

706 σ = error of the observed data

707 $NG1^m$ = measured value of noble gas sample

708 $NG1^p$ = predicted value of noble gas sample from the arbitrary mixing line

709 This optimization process was conducted using a code compatible with the Matlab program.

710

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711

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Highlights

- Shallow aquifers are the last trapping zone for a CO_2 migrated from a storage site.

- CO_2 and noble gas tracers were co-injected into a shallow groundwater aquifer.

- ~~Noble gas~~The tracers showed a clear relationship to the~~with~~ CO_2 species ~~during CO₂~~after the injection ~~in shallow aquifer~~.

- ~~Most of~~The released CO_2 was mostly retained in the ~~shallow~~ aquifer rather than lost ~~in~~to the vadose~~atmosphere~~.

- Physical mixing and solubility trapping controls ~~primarily determine~~ the mass retention of ~~migrated~~ released CO_2.

- ~~Shallow aquifer is the last trapping zone for mobile CO₂ that migrates from the deep CO₂ storage.~~

1 **Application of noble gas tracers to identify the retention mechanisms of CO$_2$ migrated from a**

2 **deep reservoir into shallow groundwater**

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17

18   **Abstract**

19   Carbon Capture and Storage (CCS) is a valuable climate-mitigation technology, which offers

20   the potential to cost-effectively reduce the emissions associated with the burning of fossil fuels.

21   However, there is a potential risk of a small portion of the stored CO_2 unintentionally migrating from a

22   storage site to a shallow groundwater aquifer which is the final retaining zone for any migrated CO_2

23   before it escapes to the atmosphere. Hence, it is imperative to identify the physical retention

24   mechanisms of CO_2 within a shallow aquifer. In this study 1.70×10^2 kg of CO_2 and noble gas tracers

25   (He, Ar and Kr) were continuously injected into a groundwater aquifer over 28 days with the aim of

26   identifying the mechanisms and amount of CO_2 retention. Among the tracers, Kr was found to be the

27   earliest indicator of CO_2 migration. The other tracers – He and Ar – arrived later and exhibited diluted

28   signals. The diluted signals were attributed to degassing of the plume mass (1.6% of CO_2) during the

29   early stages of CO_2 migration. Diffusion accelerated the dilution of the lighter elements at the plume

30   boundaries. Consequently, the clear relation of the noble gases with the CO_2 proved that degassing and

31   mixing primarily control the mass retention of CO_2 in shallow groundwater, and the relative importance

32   of these processes varies along the evolving path of migrating CO_2.

33   **Keywords**: CCS; monitoring; CO_2 leakage; noble gas tracing; artificial tracer; geochemical monitoring

1. Introduction

Carbon Capture and Storage (CCS) is a climate change mitigation technology that comprises the capture of CO_2 from an industrial point source, such as a power plant or refinery, transport of the captured CO_2 to a storage site followed by the injection of the captured CO_2 into deep geological strata for permanent disposal (IPCC, 2005). However, there is a potential risk that a small portion of the mobile CO_2 in a storage site could accidently migrate out of the subsurface reservoir and inadvertently reach shallower levels of the subsurface (Alcalde et al., 2018). This CO_2 could potentially migrate through geological conduits such as permeable faults and/or abandoned wells resulting in the deterioration of fresh water resources above the CO_2 reservoir (Harvey et al., 2012; IEAGHG, 2011; Lemieux, 2011; Lion et al., 2014) and leakage of a small portion of the CO_2 into the atmosphere (Ide et al., 2006; IPCC, 2005). Recently, the Weyburn-Midale (Canada) CO_2 monitoring and storage project faced allegations that leakage of CO_2 injected into the Weyburn-Midale oil field for Enhanced Oil Recovery (EOR) and storage was causing a deterioration of the groundwater quality on a farm located above the field (Beaubien et al., 2013; Gilfillan et al., 2017).

A variety of geochemical tools have been used to verify CO_2 storage security and track the fate of CO_2 injected for storage. These include CO_2 soil gas and groundwater concentrations, stable C and O isotopes within the CO_2, on-site monitoring parameters (pH, alkalinity, ORP, EC, temperature and DO), inert gas tracers, major and trace ions and radiocarbon (^{14}C) (Flude et al., 2016; Lee et al., 2016). Soil gas and dissolved CO_2 concentrations in groundwater can provide a direct tracer of CO_2 migration, allowing discrimination of different CO_2 origins and providing a means to establish the mass balance of CO_2 present in the groundwater system (Ballentine et al., 2001; Beaubien et al., 2014; Gilfillan et al., 2011; Lollar et al., 1997; Sathaye et al., 2016). Recent developments in on-site monitoring technologies now allow the continuous measurement of a number of parameters (e.g. alkalinity, T, EC, pH) which can be used to establish the overall distribution and temporal evolution of a small CO_2 plume within a shallow groundwater aquifer (Lee et al., 2016). Noble gases are characterized by their inert behavior, which makes them ideal tracers within a subsurface system. This inertness means that noble gases are

60   conservative tracers and do not partake in the chemical reactions that dilute the CO_2 leakage signals and

61   hence are capable of providing a robust means to distinguish between natural and stored CO_2 (Risk et

62   al., 2015).

63   Noble gas tracing techniques have been used to track both the fate and migration pathways of

64   injected CO_2 in reservoirs. Within a typical porous CO_2 storage reservoir, CO_2 is retained by a

65   combination of structural, residual and solubility trapping mechanisms (Alcalde et al., 2018; Holland

66   and Gilfillan, 2013; IPCC, 2005). Recent experiments at the CO2CRC Otway Demonstration site for

67   CO_2 storage in Australia have used Kr and Xe as conservative tracers to determine the degree of residual

68   trapping within a porous saline formation, using a numerical mass balance approach (LaForce et al.,

69   2014). The degree of solubility trapping has also been determined using noble gases, through

70   identification of the degree of partitioning of the noble gases into groundwater present within the

71   reservoir formations (Ballentine et al., 1991; Brennwald et al., 2005; Gilfillan et al., 2008, 2009; 2014;

72   Pinti and Marty, 1995; Zhou et al., 2005).

73   Noble gas tracers are also suitable for monitoring the vertical migration of the reservoir CO_2,

74   thanks to the compositional difference of natural noble gas tracers between storage reservoir and the

75   near surface environment (Mackintosh and Ballentine, 2012). Gilfillan et al. (2011) applied noble gas

76   tracing tools to constrain the nature of CO_2 leakage into shallow groundwater and surface water bodies.

77   Further work by Gilfillan et al., (2017) used inherent tracers residing in the Weyburn-Midale injection

78   and storage project reservoir to show that CO_2 migration from the deep reservoir into the shallow aquifer

79   system had not occurred. This work found that the noble gas composition in the groundwater samples

80   above the CO_2 injection and storage project did not vary over a typical background level of a shallow

81   aquifer, of Air Saturated Water (ASW) with an excess air component of up to 45% (Gilfillan et al.,

82   2017). Recent work by Flude et al. (2016) and Flude et al. (2017) evaluated the inherent tracing ability

83   of noble gases focusing on the compositional difference of them between captured CO_2, the subsurface

84   storage reservoir, air and ASW. Differences in the noble gas contents of these samples stemmed from

85   the different CO_2 capturing processes and what controls the composition of noble gas tracer in a stored

86   fluid (e.g. gas stripping of reservoir water and/or interaction with radiogenic components).

87   The concept of inert tracers was extended to artificial enhancement studies, involving the

88   addition of inert gas tracers such as SF_6 and noble gases to the injected CO_2 in CCS storage. This aimed

89   to provide a much clearer distinction between the injected CO_2 and that naturally present in the

90   subsurface and so improving the monitoring efficiency (Myers et al., 2013; Nimz and Hudson, 2005).

91   For example, noble gases have been previously used as artificial tracers to indicate CO_2 leakage

92   pathways in the vadose zone (Cohen et al., 2013; Rillard et al., 2015) and in the aquifer system (Lu et

93   al., 2012; Nimz and Hudson, 2005; Stalker et al., 2009). In the CO_2-Vadose project, undertaken at a test

94   CO_2 release site in France, the lighter noble gases (He and Ne) were found to have the fastest arrival

95   time in monitoring wells due to their higher diffusion coefficient and low solubility within the soil water

96   compared to the CO_2 and other tracers (Cohen et al., 2013). In contrast, the heavier noble gas tracers

97   (Kr and Xe) exhibited the fastest arrival in the aquifer system due to their solubility in groundwater

98   compared to other noble gases following the artificial injection into a deep reservoir (~2 km) (Stalker

99   et al., 2015). In a recent test, a small amount of CO_2 (16.9 kg) spiked with noble gas was released into

100   a shallow aquifer at Korea CO_2 Storage Environmental Management (K-COSEM) study site, in order

101   to understand the behavior of the leaked plume in the shallow groundwater system. This study identified

102   that the mass distribution of the leaked CO_2 is predominantly controlled by the solubility of the

103   individual noble gases and mixing processes during the limited time of monitoring work (i.e. 4 months)

104   (Ju et al., 2019).

105   The shallow groundwater is the final zone encountered by migrating CO_2 before it is lost into

106   the vadose zone and atmosphere. Furthermore, this reservoir is directly linked into the human activity,

107   hence, should be protected from a potential leakage of stored CO_2 (Lee et al., 2016). While noble gas

108   tracers have proven useful to monitor leaked CO_2 plume in shallow aquifer systems (Flude et al., 2016;

109   2017), this has only been demonstrated on a few occasions, for example, in a natural CO_2 production

110   site using inherent noble gases (Gilfillan et al., 2011), in a CO_2 injection test site using artificially

111   enhanced noble gases (Ju et al., 2019) and to rule out CO_2 migration in a shallow aquifer above an

112 actual CO_2 storage reservoir using inherent noble gases (Gilfillan et al., 2017), as described above. In

113 this study, we present the results of applying noble gases to a CO_2 injection test into a near-surface

114 aquifer. This artificial CO_2 migration test aims to mimic a situation where a measurable amount of CO_2

115 $(1.70 \times 10^2$ kg) has migrated from a deep CO_2 storage reservoir into a shallow groundwater aquifer. This

116 study focuses on determining the amount of CO_2 retained in the groundwater and the mechanisms

117 controlling the migration of the CO_2 plume using noble gas tracers. A mass balance model was

118 constructed based on the partitioning coefficients of noble gas tracers in a gas-water system, to

119 understand and to quantify the final retention of the injected CO_2 within the shallow aquifer system.

120 **2. Materials and methods**

121 **2.1 Site description**

122 The Korea CO_2 Storage Environmental Management (K-COSEM) Research Center has

123 installed a controlled CO_2 release experiment at Eumseong gun (county) of South Korea (Figure 1). The

124 geology at the field experimental site includes three different subsurface media, firstly consisting of a

125 weathered soil layer composed of medium to coarse grained silty sand (0–30 m below ground surface

126 (bgs)), followed by weathered biotite granite (30–70 m bgs), and finally consolidated biotite granite

127 (starting at 70 m bgs) (Lee et al., 2017; Ju et al., 2018a). The water level was located at the 16.0–18.4

128 m bgs and the hydraulic conductivity of the aquifer was estimated from pumping tests, ranging from

129 1.7×10^{-5} cm/s for the consolidated bedrock to 2.0×10^{-4} cm/s for the weathered layer. Prior to the

130 commencement of the experiment, the groundwater was flowing from the northwest toward the

131 southeast following a hydraulic gradient of 0.003 (i.e., the regional flow in Figure 1a).

132 At the K-COSEM site, a total of 24 monitoring wells had been installed in the shallow aquifer

133 (i.e. < 15 m below the water table) including the injection well (IW), partially screened (PS), boreholes

134 (BH), borehole screened (BS) and saturated zone monitoring wells (SMWs) (Figure 1a). Each saturated

135 zone monitoring well (SMW) contained several screened multi-depth monitoring wells for groundwater

136 monitoring at different depths (Figure 1f). In this CO_2 injection study, the IW and six monitoring wells

137 (PS-04, SMW1 to 4, BS-04, -09 and -10) were employed for the CO_2 injection experiment (Figure 1b).

The wells BS-04 and BS-10 located at both ends of the monitoring range were used to create an induced pressure gradient field by pumping out groundwater at a down-gradient location (BS-10) and successive injection in at an up-gradient location (BS-4) (Figure 1c). The SMWs are located along the created groundwater flow pathway, while PS-04 was up-gradient relative to the CO_2 injection point. The well BS-09 was intended to capture the preferential movement of the released CO_2 along a high connectivity zone between injection well and BS-09, identified in the work of Ju et al. (2019). Details on the study site and monitoring network can also be found in previous works (Lee et al., 2017; Lee et al., 2018; Ju et al., 2018b; Ju et al., 2019).
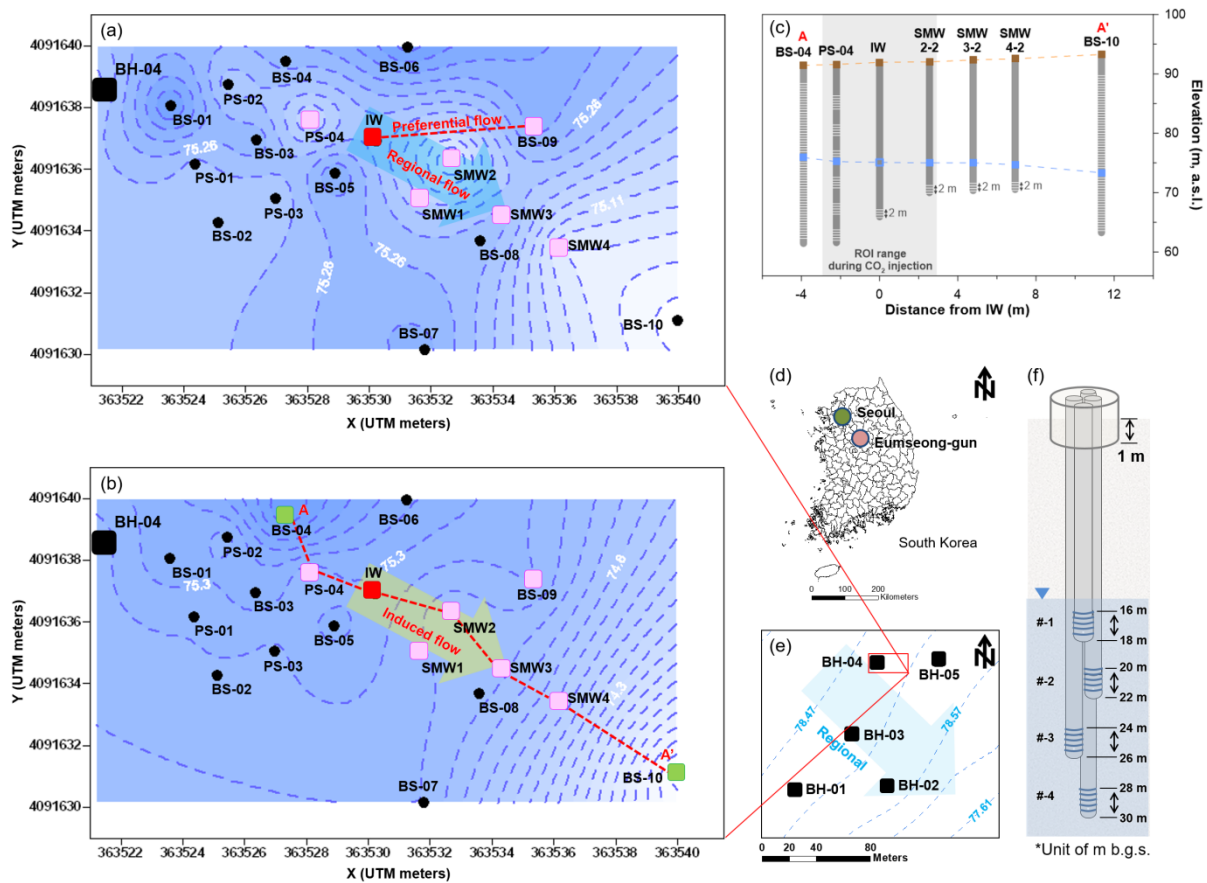
Figure 1. Maps of the study site. Figures on the left show (a) natural regional groundwater flow (shown as a blue-colored arrow) before enhanced groundwater circulation using the wells BS-04 and BS-10, where a preferential path exists in this field due to local hydrogeological heterogeneity (16 May 2016), (b) induced pressure gradient field (shown as a green-colored arrow) after the pumping out and pumping

151   in using the two wells (see green squares) (4 July 2016). Note that the induced flow was intended to

152   speed up the plume migration along the groundwater flow (i.e., regional flow in [a]). Pink squares

153   represent the wells used for monitoring; a red square represents the injection well (IW). Figures on the

154   right show (c) a cross-section view along the induced pressure gradient (4 July 2016), (d) the location

155   map of the study area, (e) the contours of groundwater levels obtained by kriging using 17 wells

156   surrounding the study site (7 March 2015), and (f) the structure of each saturated zone monitoring well

157   (SMW) containing a bundle of four screened pipes with different lengths.

158   **2.2   Artificial injection**

159   **2.2.1 Induced pressure gradient field**

160   The CO_2 injection was undertaken in the induced pressure gradient field to reinforce the

161   groundwater flow, therefore, to speed up the CO_2 plume migration (Figure 2c). The hydraulic pressure

162   gradient was achieved by enhancing groundwater circulation, consisting of water production and

163   reinjection using the BS-04 and BS-10 wells located at both ends of the monitoring network (Figure

164   2c). A total of 24.0 m³/d of groundwater was pumped from BS-10 and reinjected into BS-04 (Figure

165   2c). A period of 1 month was required to stabilize the pressure gradient (22 May 2017 to 27 June 2017).

166   The pressure gradient was steeper near the injection site and production points (i.e. the BS-04 and BS-

167   10), with the average gradient being 0.18 (Figure 2c). The circulation was maintained until 17

168   September 2017.

169

Figure 2. Injection systems for the artificial CO_2 release experiment. (a) tracer-infused groundwater was prepared in a 1 m^3 tank and (b) CO_2-infused groundwater was prepared in a 5 m^3 tank. (c) gas-charged groundwater was continuously released into the induced pressure gradient field through the IW.
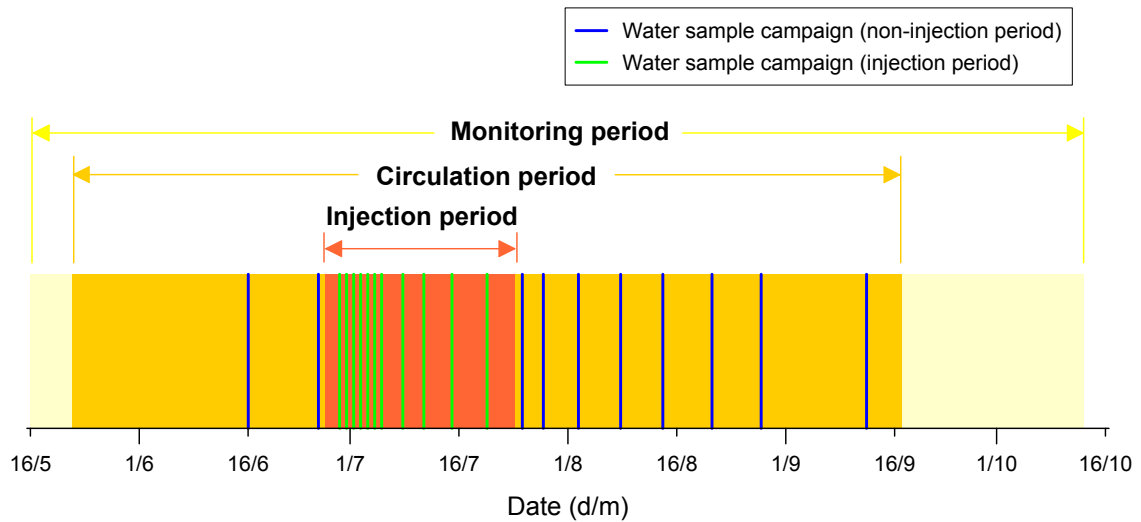
2.2.2 Injection

To prepare the injection water, the water flux sent to BS-04 (24.0 m^3/d) was reduced to 18.5 m^3/d and 5.5 m^3/d of groundwater was sent into the injection tank (Figure 2c). 5.0 m^3/d of groundwater was sent into the CO_2 dissolver tank (Figure 2b) and 0.5 m^3/d of tracer–enhanced water was prepared in the other tank (Figure 2a). The CO_2-infused groundwater was prepared in the 5 m^3 tank equipped with the circulation pump, CO_2 dissolver, water sampling port and flow meter (Figure 2b). Injection was initiated when the CO_2 concentration reached the equilibrium state (termed C_0). To ensure that the equilibrium concentration was maintained, alkalinity, pH, EC, DO, ORP, temperature, salinity, TDS

182   was continuously monitored with real time measurement devices such as YSI (YSI Inc./Xylem Inc.,

183   USA), LTC Levelogger Junior (Solinist, Canada) and SH-300-DS (SOHA TECH, Inc., Korea) while

184   circulating water within the tank using a pump (Figure 2b). These measurements showed that it took

185   approximately 24 hours to achieve the equilibrium state. The noble gas infused groundwater was also

186   prepared one day ahead of the injection test. Approximately 0.5 m^3/d of groundwater was pumped into

187   the 1 m^3 of closed tank equipped with the circulation pump, tracer tank, water sampling port and flow

188   meter (Figure 2a). The injected tracers were a mixture of He (0.2 vol. %), Ar (99.4 vol. %), and Kr (0.4

189   vol. %) and were injected through a flowmeter and diffuser (AS-10 3/8) into the 1 m^3 dissolver tank.

190   The infused liquids were first injected into the subsurface on 27 June 2017 and continued to be injected

191   for 27 days until 24 July 2017. Samples for initial concentration analyses (i.e. C_0) were collected during

192   the injection event and through the sampling ports (Figures 2a and b). Injection took place at 4.5–7.5 m

193   below the water table (corresponding to 21–24 m bgs) in an isolated zone below a packer (Figure 2c).

194   The ambient surface weather conditions during the injection event were 20.4–26.9°C without

195   precipitation. The injection rate was controlled by a submersible and controllable quantitative pump

196   (model MP1, Grundfos, Denmark) at a constant rate of 5.5 m^3/d (Figure 2c).

197   ## 2.3   Real-time monitoring

198   Real-time monitoring data was collected from 17 May 2017 to 13 October 2017 (Figure 3).

199   Over this period, hydraulic pressure (P), temperature (T) and electrical conductivity (EC) were

200   measured in-situ using the LTC Levelogger Junior (Solinist, Canada) and the barometric state was

201   monitored at the same time using the Barologger Edge (Solinist, Canada) at 10 minute intervals.

202

Figure 3. Schedule for water sample collection during the CO_2 injection test.

2.4   Water sampling campaign

2.4.1 Baseline survey period

Water samples were collected using a Waterra Inertial Pump with PowerPack PP-1 (Wattera, Canada) to obtain baseline data before the CO_2 injection. The local baseline of the pCO_2 was obtained on two occasions through water sampling between 16 June 2017 and 26 June 2017 (Figure 3). The baseline for the noble gas tracers was determined by a single water-sampling operation on 26 June 2017 (Figure 3). Alkalinity was determined in the field site by acid titration method with 0.05 N HNO_3. The pH and temperature were also measured in-situ using a portable water quality meter (YSI ProDSS, YSI Inc./Xylem Inc., USA). The noble gas samples were collected using a standard copper tube of 28 cm^3 and a pinch-off clamp set.

2.4.2 Injection and post-injection period

Data acquisition after the CO_2 injection was conducted in the same manner as the baseline data collection. Water samples were collected on 19 occasions following the injection event, over 76 days from 27 June 2017 to 12 September 2017 (Figure 3).

2.5   Laboratory analyses

2.5.1 Noble gas

220   The noble gas samples were analyzed in the noble gas analysis laboratory at the Korea Polar

221   Research Institute (KOPRI) using an automated system as outlined in Stanley et al. (2009) and Kim et

222   al. (2016). Gases were first extracted from a groundwater sample under high vacuum condition ($\sim 10^{-7}$

223   mbar) and stored in an aluminosilicate glass ampoule (Lott and Jenkins, 1998). Excessive water vapor,

224   active gases, and condensable gases were then removed using cryogenic traps and a series of hot and

225   cold Zr-Al alloy getters (St 101, SAES Getters S.p.A., Italy) before sample injection into the RGA200

226   mass spectrometer (Stanford Research Systems, California, USA) for analysis. The noble gases, He,

227   Ne, Ar, and Kr were calibrated against air standards of 0.9 and 2.7 cm^3 STP, to cover the wide range of

228   the tracer enhanced injection water. The discrepancy between duplicate samples was less than 5% (Ju

229   et al., 2019).

230   **2.6   Analytical methods**

231   **2.6.1 pCO$_2$ calculation**

232   pCO$_2$ values for the sampled waters were calculated using the monitored parameters of

233   alkalinity, pH, and temperature. Alkalinity, pH and temperature were measured in-situ. Using these data

234   a robust calculation for pCO$_2$ value was made using the program PHREEQC Version 3 (Parkhurst and

235   Appelo, 2013).

236   **2.6.2 Mass balance model**

237   At the early stage of the CO_2 injection, the CO_2 plume is unstable with a high partial pressure,

238   resulting in a degree of CO_2 degassing. Hence, CO_2 bubbles rise freely from the brine with a proportion

239   of the CO_2 remaining in the dissolved phase. During the degassing period, the free-phase CO_2 strips out

240   the dissolved, relatively insoluble noble gases, especially the lighter elements (He and Ne), leaving the

241   system relatively enriched in the heavier noble gases (Ar, Kr, Xe) (Ballentine et al., 2002; Holland and

242   Gilfillan, 2013). Based on the degree of this enrichment, we can inversely constrain the mass balance

243   of the CO_2 plume in terms of the degassing process (see the Appendix A mass balance model for detailed

244   explanation).

245   **3   Results**

246 **3.1 Prior to CO$_2$ injection**

247   Pressure and temperature changes result in the degassing of insoluble substances from the

248 groundwater system. At the K-COSEM test site, the groundwater level shows a clear decreasing trend

249 due to large-scale water consumption from nearby industrial complexes (Figure 4) (Ju et al., 2019).

250 However, prior to the experiment the hydrostatic pressure data showed a stable correlation with

251 atmospheric pressure changes and no irregular turbulence (Supplementary Figure S1). Groundwater

252 temperatures corresponded to normal seasonal values ranging between 12.7 to 13.6°C (Figure 4).

253   The induced pressure gradient commenced on the 22 May 2017 as a result of the onset of water

254 circulation (Figure 3c). Perturbations were detected in the water level (WL), temperature (T), and

255 electrical conductivity (EC) values during the initiation of water circulation (see the start points of dark

256 grey zone in Figure 4). The pressure turbulence was most noticeable within the monitoring wells located

257 inside the radius of influence (ROI) area both of the pumping (BS-10) and injection wells (BS-04). For

258 example, PS-04, SMW 1 series and SMW 2 series wells showed an instant pressure increase after the

259 circulation commenced, as they are located near the injection well (BS-04) (Figure 4d–j). In contrast,

260 wells SMW 3-2 and 4-3 showed an abrupt decrease in pressure, as a result of their location near to well

261 BS-10 where water was extracted (Figure 4k and l). Well BS-09 also displayed a modest increase in

262 pressure 9 days after water circulation commenced (specifically on 31 May 2017) (Figure 4c).

263 Temperature within all monitoring wells showed an overall increase after the water circulation regime

264 started (see the start points of dark grey zone in Figure 4). This is most likely linked to the groundwater

265 for injection having resided in the surface tank at temperatures warmer (i.e., 17.1 to 28.6°C) than those

266 of the subsurface groundwaters (i.e., 13.3°C) for the day prior to re-injection into the subsurface. The

267 EC showed the overall decreasing trend in the initial circulation period as the re-injected water (BS-10)

268 has a relatively low EC background compared to the other wells, with the exception of well SMW 2-1

269 (Figure 4).

Figure 4. Water level (WL), temperature (T) and electrical conductivity (EC) data. Measurements were completed in the monitoring wells continuously using a LTC data logger. The groundwater circulation was initiated at 22 May 2017 (dark grey shaded zone) and the CO_2 injection started at 27 June 2017 and kept going till 24 July 2017 (light grey shaded zone).

275   As outlined previously, two water sampling campaigns were conducted during the circulation

276   period and prior to CO_2 injection commenced, in order to establish the groundwater baseline

277   composition (16 June 2017 and 26 June 2017) (Figure 3). The baseline alkalinity values were relatively

278   low (27.5–64.1 mg/L), DO exhibited a wide variation (3.6–8.0), pH was weakly acidic (6.5–7.1) and

279   pCO_2 was relatively low (0.0–0.01 atm) prior to CO_2 injection (Figure 5). All of the parameters were

280   close to the baseline values of low carbonate levels in the biotite granite protolith (Ju et al., 2019).

Figure 5. pCO_2, pH, alkalinity and DO values. The grey vertical lines represent the injection period.

283   During the water circulation period, pH exhibited an overall decreasing trend as the low-pH

284   water was pumped out from the down-gradient well (BS-10) and reinjected into the up-gradient well

285   (BS-04) (Figure 5c). DO also exhibited a decreasing trend as groundwater was re-equilibrated in the

286   warm surface temperature (17.1–28.6°C) before being injected into the well BS-04 (Figure 4d). pCO_2

287   and alkalinity showed minor variation across the monitored region depending on the groundwater flow

288   direction and the initial C parameter distributions (Figure 4a and b).

289   Mean He, Ar and Kr concentrations measured before the injection commenced were 5.43×10^{-8}

290 cm^3 STP/g_{H2O}, 3.72×10^{-4} cm^3 STP/g_{H2O} and 9.80×10^{-8} cm^3 STP/g_{H2O}, respectively. These are close

291 to the Air Saturated Water (ASW) value at the temperature condition (i.e. 13.3^{o}C) of study site—such

292 as 4.58×10^{-8} cm^3 STP/g_{H2O}, 3.58×10^{-4} cm^3 STP/g_{H2O} and 8.30×10^{-8} cm^3 STP/g_{H2O} for He, Ar and

293 Kr values, respectively (Kipfer et al., 2002).

294 **3.2 Injection fluid**

295   The gas-infused groundwater was released into the IW from 27 June 2017 to 24 July 2017

296 (Figure 3). The CO_2–infused groundwater (C_0) collected from the 5 m^3 tank (Figure 2b) was initially

297 below the saturation point (0.40 atm) for 11 days after the injection (29 June 2017 to 8 July 2017), and

298 reached to the over-saturation state (> 2.3 atm) about 18 days after the injection on 15 July 2017 (Figure

299 5a). This CO_2 variation can be attributed to an accidentally reduced water flux going into the CO_2 tank,

300 causing a decrease of the water level, resulting in altering of the C system balance in CO_2 tank. For the

301 same reason, the pH and DO initially maintained 5.0 and 3.9 mg/L but showed a sudden decrease to 4.2

302 and 0.5 mg/L on the 15 July 2017. Water samples collected from the 1 m^3 tank (C_0) (Figure 2a) were

303 analyzed for their He, Ar and Kr concentrations, and reported at 2.92×10^{-5} cm^3 STP/g_{H2O}, 2.26×10^{-2}

304 cm^3 STP/g_{H2O} and 4.95×10^{-5} cm^3 STP/g_{H2O}, respectively. The noble gas concentrations lie between

305 fully saturated and Air Saturated Water (ASW) levels, and thus they will remain dissolved in the

306 groundwater system unless being exposed to low partial pressure conditions such as air bubbles or the

307 vadose zone interface (i.e. water table) (Ju et al., 2019).

308 **3.3 Post injection**

309   **3.3.1   P, T and EC**

310   Pressure turbulence was observed in all monitoring wells prior to the initiation of CO_2 injection

311 (Figure 4), which can be attributed to the change in water volume from 24.0 m^3/d to 18.5 m^3/d for

312 preparing the gas-infused water of 5.5 m^3 (C_0) before CO_2 injection within the circulation system (see

313 the section 2.2.2 Injection for detailed explanation). Minor changes in temperature were observed inside

314 the Radius of Influence (ROI) zone of IW such as PS-04, BS-09, SMW 1 and SMW 2 (Figure 4c~j).

315   The temperature showed a gradual increase since the groundwater circulation initiated in which the

316   SMW 2-2 showed the highest increase of up to +7.0°C and followed by SMW1-2 (+5.5°C), SMW 3-2

317   (+4.0°C), BS-09 (+3.8°C) and the others (< +2.8°C) (Figure 4). The higher increase in the temperature

318   of BS-09 indicates a preferential flow gradient still exists in the study site even after the formation of

319   the induced pressure gradient (Figure 1a). In EC data, the most prominent signals were recorded at

320   SMW 1-2 (+464 µS/cm, +472%), SMW 2-2 (+447 µS/cm, +368%), SMW 2-3 (+531 µS/cm , +301%),

321   SMW 3-2 (+383 µS/cm, +250%) with the others showing a less pronounced change (< +129%). These

322   observations were consistent with temperature data, exhibiting the greatest change in the SMW #-2

323   wells. This indicated that the CO_2 plume moved horizontally from the injection depth of 21–24 m to the

324   screen depth of SMW #-2 (i.e., 20–22 m) (Figure 1c). The response in EC is clearly different to that of

325   temperature as a notable increase in EC was only observed after CO_2 injection occurred. This is because

326   EC is the function of geochemical interaction between the CO_2 water and the rock materials (Vialle et

327   al., 2014). In the groundwater flow regime, the SMW series wells, BS-09 and BS-10 are located ahead

328   of the migration direction of the IW, which is illustrated by the clearly increasing EC trend (Figure 1b).

329   Alternatively, well PS-04 is located upgradient from the CO_2 injection point, resulting in a gradual

330   lowering of the EC trend after the CO_2 injection was initiated as there is no communication between

331   this well and the CO_2 rich-water (Figure 1b).

332   **3.3.2 pCO_2, pH, alkalinity and DO**

333   As expected, the chemical elements exhibited strong signals correlating with the CO_2 plume

334   arrival. The parameters are presented as breakthrough curves (BTCs) (Figure 5). Note that for the

335   SMWs, the parameters represent the data from the injection depth (i.e., SMW #-2) only, as this

336   generated the largest signals among all depths. The pCO_2 produced the strongest signal at SMW 1-2

337   (+1.15 atm, +25,385%) which was followed by SMW 2-2 (+1.05 atm, +18,067%), BS-09 (+0.82 atm,

338   +12,631%), SWM 4-2 (+0.35 atm, +3,746%) and the other wells (< +2,923%) (Figure 5a). The

339   pronounced response of pCO_2 compared to other parameters is attributed to its low baseline

340   concentration (0.0–0.01 atm) (Risk et al., 2015). Alkalinity also showed significant increases with the

341   arrival of the injected CO_2, particularly in wells SMW 1-2 (+326.4 mg/L, +1,189%), SMW 2-2 (+318.0

342   mg/L, +1,017%), BS-09 (+269.2 mg/L, +821%), SMW 4-2 (+270.0 mg/L, +478%) with other wells

343   showing smaller, but measureable changes (< +286%) (Figure 5b). Alkalinity gradually increases with

344   the chemical interactions between the CO_2 plume and the aquifer materials similar to the EC. The small

345   differences in response to CO_2 injection between EC and alkalinity can be attributed to the geochemical

346   variation of the study site resulting in different CO_2 related buffering capacities (Sechriest, 1960).

347   The pH also decreased noticeably, changing by -1.5 units at SMW 2-2, which was followed by

348   -1.5 units at SMW 1-2, -1.4 units at SMW 2-3, -1.3 units at BS-09 and > -0.96 units at the others (Figure

349   5c). The DO showed relatively modest change by up to -4.0 mg/L (-78%) at SMW 1-2 which was

350   followed by BS-09 (-4.9 mg/L, -72%), SMW 2-2 (-3.7 mg/L, -72%), SMW 3-2 (-2.8 mg/L, -60%) and

351   the others (< -58%) (Figure 5d). In this experimental setting, the DO evolves with the three-component

352   groundwater mixing between low-DO water volumes (re-injection water at BS-04 and injection water

353   at IW) and high-DO water volume (local groundwater) (Figure 2).

354   ### 3.3.3   Noble gas tracers

355   The measured concentrations of He, Ar and Kr tracers are presented in BTCs (Figure 6). The

356   concentration was normalized to the injection amount (C_0) after the background portion (i.e.

357   atmospheric origin) was subtracted from both monitored (C) and initial concentration (C_0), to simply

358   define the CO_2 arrival as a positive signal. Note that for the SMWs, the parameters present the data

359   from the injection depth (i.e., SMW #-2) only, as this exhibited the largest signals of all depths. As a

360   result, the tracers successfully produced the strong positive signals with the CO_2 plume arrival in the

361   BTCs (Figure 6). The tracer concentrations exhibited variable arrival times and concentrations due to

362   the CO_2 plume following different flow paths within the heterogeneous groundwater system at the site,

363   similar to the findings of Kilgallon et al. (2018), Lee et al. (2017), Lu et al. (2012) and Stalker et al.

364   (2015). Most importantly, Kr showed the earliest arrivals through all monitoring wells compared to the

365   He and Ar tracer. This was attributed to the Kr taking a less distributed pathway through the subsurface

366   than the other tracers, and a result of the dilution of CO_2 plume along the concentration gradient (see

367   the discussion section 4.1.2 Diffusion process controlling the efficiency of noble gas tracing).

368   The tracers associated with the CO_2 plume were firstly detected in SMW 2-2 (+4 d) followed

369   by BS-09 (+4 d), SMW 1-2 (+5 d), SMW 3-2 (+18 d) and SMW 4-2 (+23 d) (Figure 6a, c, d, e and f).

370   The strongest signal was recorded at SMW 2-2 (+1,430% for He, +322% for Ar and +6,904% for Kr)

371   suggesting the majority of the CO_2 plume moved along the induced groundwater pressure gradient

372   (Figure 6). A portion of the tracers also moved toward BS-09 and produced a strong signal in spite of

373   being a greater distance away from the injection point (5.2 m) than that of SWM 1-1 and SMW 2-2 (2.6

374   m). This can be attributed to the preferential flow pathway present in the study site (Figure 1a) (Ju et

375   al., 2019; Lu et al., 2012). Well PS-04 did not record the presence of any tracers during the injection

376   period due to its location behind the IW in the groundwater flow direction (Figure 1b). It is worth noting

377   that SMW 4-2 exhibited a higher concentration of Kr once the tracers arrived than SWM 3-2 (Figure

378   6), implying that a low conductivity zone hinders well SMW 3-2 from capturing the full CO_2 plume.

379   This result was consistent with the observations made in alkalinity and pCO_2 (Figure 5).
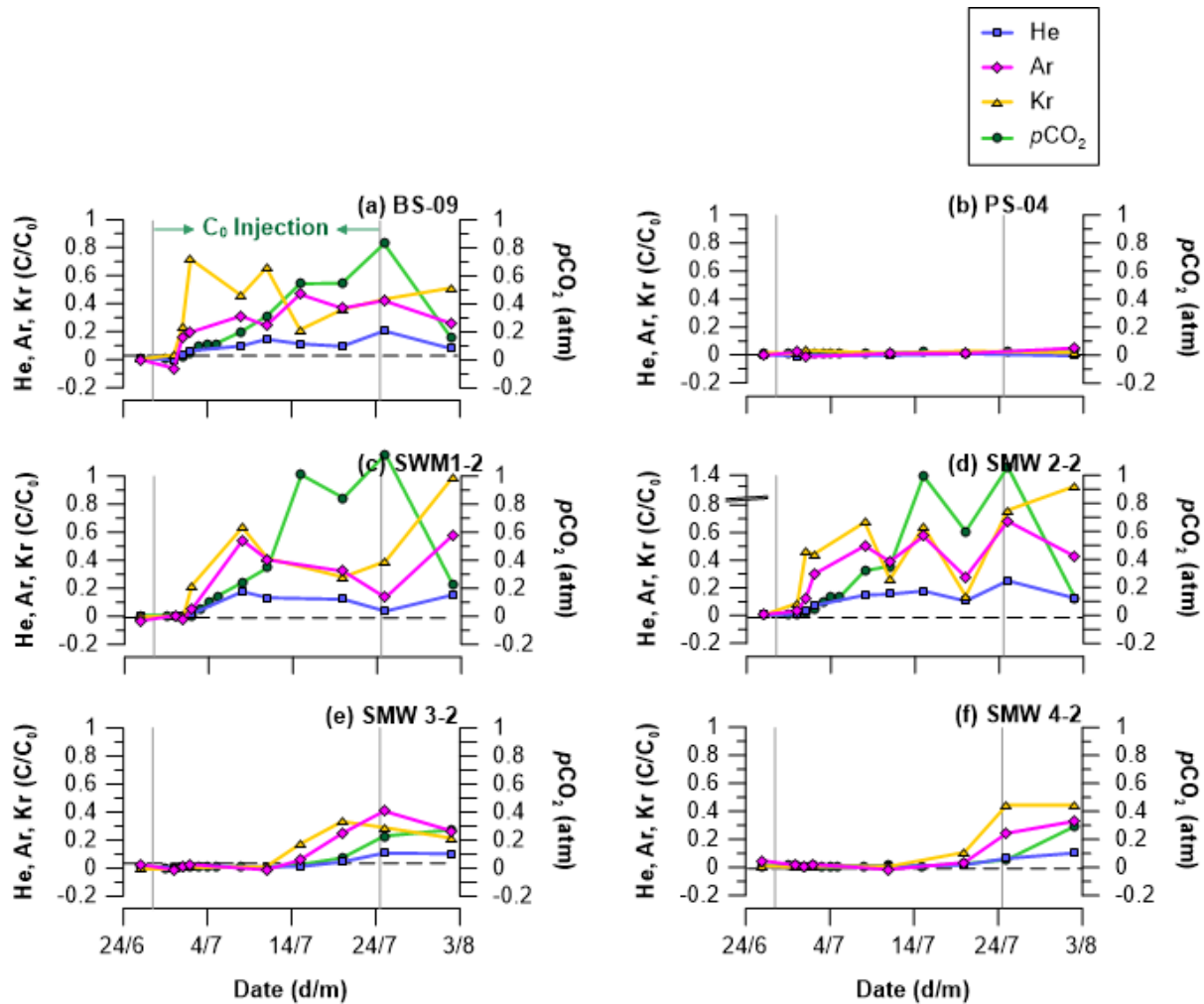
Figure 6. Gas tracer concentration during the experiment. Noble gas was presented as C/C_0 (see the text for details) with pCO_2. The grey vertical lines show the start and end of the injection period. The Air Saturated Water (ASW, black dotted horizontal line) was calculated according to Kipfer et al. (2002) to indicate the local background level of noble gas tracers.

As the injection water gradually approached the monitoring network, the observation wells captured the temporal evolution of the CO_2 plume. In the early stage of BTCs, Kr showed the fastest arrival time compared to the other tracers for all monitoring wells (Figure 6). This was followed by an increase in Ar and He concentrations, with both parameters soon reaching their peak concentration within a few days (Figure 6). In the final stage of BTCs, the plume tail is recorded in all of the monitoring wells through the decrease of noble gas concentrations after injection at the IW ceased. However, it can be observed that the concentration increased in the last stage of the BTCs for monitoring wells adjacent to IW (Figure 6c and d). This can be attributed to the circulation injection system of this

393   experiment. In the final stage of the injection period (4 days before the end of injection), the tracer-

394   charged plume had reached BS-10 (Figure 4b). As water was still being produced for the reinjection at

395   the IW, a portion of the CO_2 plume was returned back into the injection tank containing the artificial

396   noble gas tracers. Note that heavier components such as Ar and Kr acted as an early warning tracer for

397   CO_2 arrival in every monitoring well during the monitoring period. This was attributed to physical

398   mechanisms affecting the distribution of the dissolved gases (see the section 4.1.2 Diffusion process

399   controlling the efficiency of noble gas tracing).

Figure 7. Noble gas ternary diagram showing the two groups of wells categorized by their response. (a) monitoring wells which showed no concentration change from background level (i.e., PS-04) or only an early-stage evolution (i.e., SMW 3-2 and SMW 4-2). (b) monitoring wells that showed a three-step evolution as located close to the injection point (i.e., SMW 1-2 and SMW 2-2) and located in a preferential migration path (i.e., BS-09). The early-stage CO_2 plume is characterized by high Kr concentration (Arrow 1), the plume then gradually increases in He and Ar concentrations (Arrow 2). In the final stage, it becomes rich in Kr again, following the cessation of injection (Arrow 3). The peak composition was different from that of injection water due to initial degassing loss.

The consistent temporal evolution of the recorded noble gas concentrations within the six monitoring wells is depicted in the ternary diagram of Figure 7. The local BG (i.e., green star) represents the average of background level of individual monitoring wells. Prior to the CO_2 plume arrival, each monitoring well plots near to the Air Saturated Water (ASW) level. The initial arrival of the CO_2 plume was marked by a significant increase in Kr in all monitoring wells (see the arrow 1 in Figure 7) which corresponds to the early stage evolution in the BTCs (Figure 6). Note that PS-04 did not exhibit a response after injection. Following the arrival of the Kr tracer, the He and Ar concentrations within the monitoring wells increase as the plume center approached, converging at a single point (Figure 7). However, the concentrations of noble gas tracers at the peak concentrations were lower than those at the time of injection. They were 73.6–88.3% (He), 26.2–55.5% (Ar), and 0–65.5% (Kr) of the initial concentrations. The lower concentrations can be attributed to the degassing loss of the injection fluid (Sathaye et al., 2016), explained in more detail in the section 4.1.1. This degassing process controls the overall retention amount of the injected CO_2. The composition of the plume tail captured in the monitoring wells was similar to the composition of the plume front, characterized by a high Kr concentration (Figure 7).

3.4 Following injection

CO_2 injection ceased after 28 days (27 June 2017 to 24 July 2017) (Figure 3). This corresponds to the point where the monitoring parameters start to change at the BS-10 (Figure 4b and 5). In this

427   moment, the slight increase of EC was also observable in the CO_2 tank as CO_2 water re-entered the

428   injection tank (Figure 4a). Additionally, PS-04 also showed a minor increase in EC at the termination

429   period due to the re-circulation of CO_2 injected water (Figure 4d). From this point (24 July 2017), the

430   groundwater circulation system was modified to avoid the re-enhancement of the CO_2 plume. Another

431   local groundwater from BH-03 was prepared and from then onwards substituted the circulation portion

432   going to the BS-04 (Figure 1e and 2c).

433   **3.5 Following groundwater circulation**

434   The groundwater circulation ended on 17 September 2017, 56 days after CO_2 injection stopped

435   and 118 days after groundwater circulation commencement (Figure 3). The pressure turbulence was

436   observable in all monitoring wells (Figure 4) and also EC turbulence was detected in some of the

437   monitoring wells (Figure 4c, f and k), but the groundwater quickly recovered to its previous state (Figure

438   4).

439   **4   Discussion**

440   **4.1 Mass retention mechanisms**

441   **4.1.1   Degassing process controlling the overall retention amount of released CO_2**

442   If an inert tracer is continuously released into the groundwater system, the concentration will

443   gradually increase in monitoring wells and eventually become similar to the composition of injection

444   fluid. In this study, as the tracer-charged water was continuously released into the groundwater system,

445   the monitored concentration was expected to resemble the injection fluid's concentration by the final

446   stage. However, a notable difference in CO_2 and noble gas concentrations was observed between the

447   injection fluid and the plateau points (Figure 7). This phenomenon indicates that tracer mass was not

448   conserved in the groundwater system and suffered from mass-reducing processes. As the noble gas

449   tracer is biochemically inert in the groundwater system, the decrease is likely to be the result of physical

450   processes (Holland and Gilfillan, 2013). For instance, a similar noble gas deficit has been observed in

451   a natural CO_2-rich system, where CO_2 and CH_4 bubbles also stripped out the insoluble gases from the

452   groundwater system (Gilfillan et al., 2008, 2017; Brennwald et al., 2005; Zhou et al., 2005) and in

453   artificial CO_2 injection sites (Nimz and Hudson, 2005; Stalker et al., 2015). Hence, this deficit could be

454   explained by the degassing of unstable CO_2-rich plume.
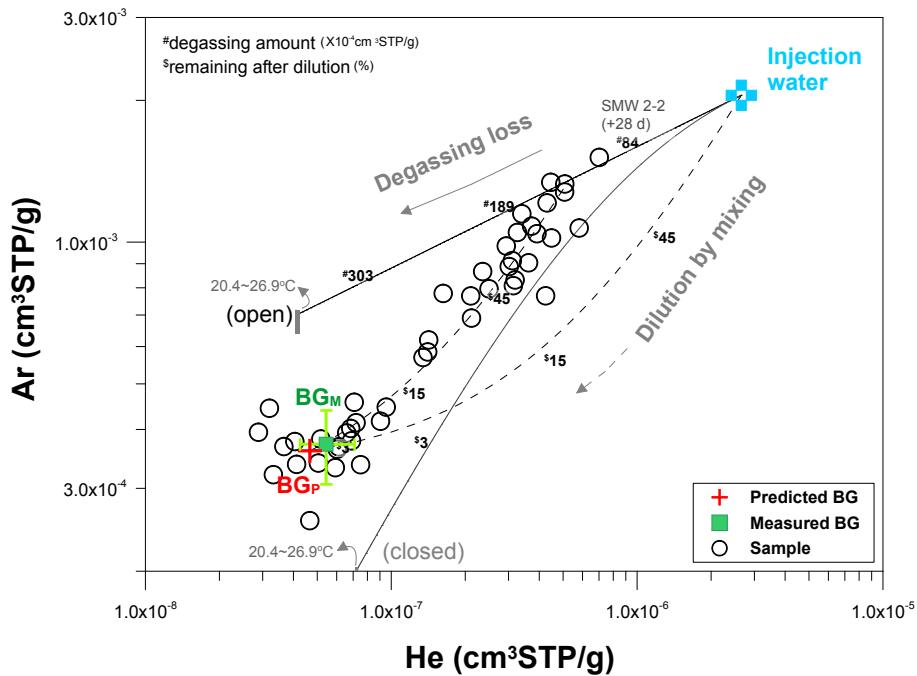
455

Figure 8. Mass balance of the CO_2 plume depicted with He and Ar tracer. The plume was expected to

457   follow the mixing line between the injection water (blue cross symbol) and the measured background

458   concentration (BG_M, green square symbol). Degassing loss of CO_2 from the dissolved CO_2 plume,

459   would result in a new mixing line starting from the SMW 2-2 (+28 days) toward the background

460   concentration (BG_P, red cross symbol). The BG_P was estimated based on the optimization process of

461   the degassing model (see the Appendix B Model optimization for detailed explanation). The shaded

462   zone on the degassing models indicates the uncertainty arising from the injection water temperature

463   (20.4–26.9°C).

464   A diagram was constructed using noble gas tracers to determine the major processes

465   influencing the CO_2 plume migration (Figure 8). In Figure 8, the concentrations of He and Ar at the

466   well SMW 2-2 (on 25 July 2017) decreased gradually to their background concentration (BG_p),

467   indicating mixing of the plume with the local groundwater. The mass distribution of observed samples

468   was the function of two distinct processes over the testing period: mass reduction of the CO_2 plume

469   occurred through the degassing process (black line), followed by the dilution of the plume by the local

470   groundwater (black dotted line). The observed data clearly indicated the mixing process was preceded

471   by the degassing process.

472   **Table 1** Mass balance of the leaked CO_2 plume in shallow aquifer system.

Open system	Injection		After degassing loss			Solubility †
	Amount (kg)	partial pressure (atm)	ΔAmount (kg)	Δpartial pressure (atm)	Remaining (%)	(mM/atm)
He	7.04×10^{-5}	3.07×10^0	5.64×10^0	2.46×10^0	19.9	0.386
Ar	5.43×10^0	6.11×10^0	1.85×10^0	2.08×10^0	66.0	1.50
Kr	2.50×10^0	7.41×10^0	5.13×10^0	1.52×10^0	79.5	2.71
$CO_{2\,p.}$ ‡	1.70×10^2	6.62×10^0	2.72×10^0	1.07×10^0	98.4	38.7

473   †NIST chemistry webbook of Sander (2017) at temperature of 21.8°C.

474   ‡The predicted value from model optimization (see the Appendix B Model optimization for detailed

475   explanation).

476   Elemental fractionation of noble gases is controlled by their differing solubilities and the

477   ambient reservoir conditions (Figure 8) (Ballentine et al., 2002; Ma et al., 2009). In a closed system,

478   the dissolved air remains in the groundwater, and equilibrium is achieved between the bubbles and the

479   surrounding groundwater. In an open system, the air bubbles are mobile after the phase transition and

480   escape from the aquifer system continuously until the end of the degassing process. In Figure 8, the

481   mixing line (black dotted line) intersects a degassing line (black line) explaining the loss of air bubbles

482   by 1.40×10^{-2} cm³/g_{H2O} through the degassing process in an open system. The analytical technique for

483   this calculation is shown in Appendix A Mass balance model. In the experiment, CO_2 degassing was

484   detected just above the water table at the IW reconfirming the initial loss happened into the vadose zone

485   (Supplementary Figure S2).

486   Unlike noble gases, CO_2 is involved in diverse chemical and biological processes in the

487   groundwater. To identify the major controls on the CO_2 distribution, the pCO_2 was plotted against

488   measured noble gas tracer concentrations in Figure 9. As expected, the total mass of CO_2 in the plume

489   was decreased by degassing and mixing processes. Our data designate a clear mixing line stretching

490   from SMW 1-2 (25 July 2017) to BGp, indicating that mixing process mainly controlled the mass

491   distribution of CO_2 in the plume after the initial degassing event. The minor variations from the mixing

492   trend mostly fall in the ranges of the initial composition of injected CO_2-infused water (Figure 9). The

493   solubility-controlled process is shown as the black arrow stretching from the blue-cross symbol to red-

494   cross symbol (Figure 9). The abrupt change in He/Ar ratio stands in strong contrast to the minimal

495   change observed in the pCO_2 during the degassing event (ca. 1.6% overall loss of CO_2). Losses of noble

496   gases (20.5% for Kr, 34.0% for Ar, and 80.1% for He) are much greater than for CO_2 (Table 1).

497

Figure 9. Plot of pCO_2 against He/Ar showing the concentration changes of CO_2 and noble gas tracers

during CO_2 plume evolution. The BG_M (green square symbol) is the measured background level, and

the BG_P (red cross symbol) is an estimated value from the optimization process of the degassing model

(see the Appendix B Model optimization for detailed explanation). The CO_2 plume firstly reduces total

mass by the degassing process (Arrow 1) and then gradually gets diluted by mixing with local

groundwater (Arrow 2).

4.1.2   Diffusion process controlling the efficiency of noble gas tracing

The different noble gas species cover a wide mass range and thus may provide a chance to

constrain the mass-dependent processes occurring in the groundwater system. A comparison was made

to scrutinize the behavioral difference for noble gases, as observed from the He/Ar (Figure. 8) and

He/Kr (Figure 10) relationships. The mixing line in Figure 10, represented by a black dotted line

stretching from the degassing line to BGp, corresponds to the mixing line estimated in Figure 8.

However, it is noteworthy that the He and Kr pair did not exhibit a singular trend with many variations

scattering from the estimated mixing line. It is also noteworthy that samples from the plume's center

tend to converge on the estimated mixing line, while the samples from both the plume's front and tail

display a large scatter pattern over the estimated line (Figure 10). Such discordance was also observable

in the pCO_2 versus He/Kr diagram (Figure 11) in which many samples, especially those from the

plume's front and tail had significantly lower He/Kr ratios (around 0.10) than the ratio describing the

estimated mixing line (0.24). This difference indicates that another mass-dependent process was

affecting the tracer distribution in addition to the solubility-controlled process.

Figure 10. Mass balance of the CO_2 plume depicted with He and Kr tracers. To see the plume evolution

in detail, the samples were sorted by the breakthrough positions. Note that many samples, especially on

the plume front and tail, are scattered over the estimated mixing line, contrary to the He–Ar pair mixing

trend in Figure 8.

523

Figure 11. Diagrams showing the concentration changes of CO_2 and noble gas tracers during CO_2

plume evolution. To see the plume evolution in detail, the samples were sorted by the breakthrough

positions. Note that, many samples, especially on the plume's front and tail, are scattered from the

estimated mixing line, as compared to the observations in the pCO_2 versus He/Ar relationship in Figure

9.

To further examine the temporal progression of the CO_2 plume, ternary plots of pCO_2 He, and

Ar or Kr were composed according to the locations of samples in the plume (i.e., front, center, and tail)

(Figure 12). In the He/Ar/pCO_2 diagram, the samples have a small variation near BG_P in the initial

period, while as the plume center approached the monitoring points, it showed an upward shift toward

the degassing point in the Figure 12a. In the He/Kr/pCO_2 diagram, the samples show a much wider

variation during the initial stage of the CO_2 plume arrival than the observed change in the He/Ar/pCO_2

diagram (Figure 12b). This difference indicated that another physical process was involved in the mass

distribution at the CO_2 plume's front. Note that the initial composition of the plume was characterized

by the high concentration of Kr as it appeared firstly in the observation wells (see also Figure 7).

538

Figure 12. Ternary diagram showing the compositions of pCO_2, He, and Ar (a) or Kr (b) tracers. To scrutinize the plume evolution, the samples were sorted according to the breakthrough positions. In the initial period of plume evolution, the relative compositional change among pCO_2, He and Kr (b) showed a much wider variation near the background levels (BG_P, green square symbol) than that observed among pCO_2, He and Ar (a), which attributed to the diffusion process (see the text for details). This diffusion-dominant movement was followed by the upward shift toward the degassing point (see Arrow 1), as also shown by the intersection point in Figure 8. In the final stage, the samples return to the composition similar to the plume front (see Arrow 2), after cessation of injection.

In open water, diffusion is capable of elemental fractionation depending on the molecular mass (Zheng and Bennett, 2002). According to Fick's law, the mass distribution of a solute in a groundwater system is restricted by molecular diffusion along the concentration gradient. In our experimental design, the artificial injection formed a CO_2- and tracer-rich plume in the groundwater system, setting a steep concentration gradient at the plume boundary. Consequently, the plume boundary was actively subjected to the diffusion process facing with the local groundwater of low concentration level of noble gases. As the diffusion rate is inversely proportional to the elemental mass of the solute, the tracer composition at the plume boundary was regulated by the mass-dependent fractionation. This phenomenon also has been observed in a coal bed methane field, where the free CO_2 and CH_4 gases stripped off the insoluble noble gases from groundwater and this action set the concentration gradient at interfaces with the un-degassed local groundwater, at which diffusion process resulting in a mass dependent fractionation of noble gas tracers (Zhou et al., 2005). Overall, the fact that the diffusion allocates the mass distribution at plume boundary (i.e., plume's front and tail) suggests that the early detection of the migrated CO_2 plume is dependent on this process. This further implies that the early-stage degassing loss is of primary importance in terms of the noble gas tracing efficiency because the degassing process is associated with the overall plume composition including the feature of the concentration gradient at plume front.

5 **Conclusions**

565   A portion of CO_2 stored within the deep subsurface may unintentionally migrate upward to

566   reach overlying shallow aquifers. Whilst noble gas tracers have proved to be useful in monitoring CO_2

567   leakage, they have been rarely adopted for monitoring purposes in the shallow aquifer system. This

568   study utilized the noble gas tracers to indicate the CO_2 leakage and also to elucidate the mass balance

569   of the leaked plume after injection of 1.70×10^2 kg of CO_2 into a shallow aquifer system. The CO_2- and

570   tracer-enhanced groundwater was released into the induced gradient field and subsequent monitoring

571   works have been conducted. The noble gas tracers produced a strong signal of the migrated CO_2, with

572   Kr consistently exhibiting the first arrival time, ahead of the plume and the other noble gas tracers

573   throughout all of the monitoring points.

574   The mass distribution of the CO_2 plume was controlled by three different physical processes;

575   solubility-controlled (degassing), physical groundwater mixing and diffusion. The degassing process

576   reduced the overall mass of the CO_2 plume and caused noble gas tracers to be mass-dependently

577   fractionated, which occurred at the initial stage of CO_2 leakage before plume migration. The diffusion

578   process was also involved during the plume migration, but only influenced the noble gas distributions

579   in the leaked plume and did not act as a primary control for the CO_2 distribution within the monitoring

580   period. This phenomenon, however, can accelerate the dilution of artificial tracers at the plume front,

581   especially for the lighter elements, suggesting this process has an important control on the monitoring

582   efficiency of the artificial tracers in terms of early detection of CO_2 leakage. Most importantly, as the

583   noble gas tracers display more apparent changes according to the retention mechanisms than CO_2 itself,

584   they can provide a robust system for precisely monitoring both the fate and pathway taken by the

585   migrating CO_2.

586   Noble gas tracers were used to constrain the physical retention mechanisms of the injected CO_2

587   within a shallow aquifer. Our findings indicate that around the injection point, CO_2 degassing

588   dominantly occurs from the dissolved plume due to the high gas pressure, suggesting a near-surface

589   monitoring network is necessary for capturing the active "vertical" movement of degassed budget in

590   this area. This can be accomplished by performing a continuous monitoring of CO_2 at the vadose zone,

591 for example by a soil flux measure, soil gas sampling and borehole head space sampling around a

592 potential leak point. The monitoring regime can be performed cost-effectively with limiting a

593 "degassing boundary" around a suspected leak point. In this study, only a few meters away from the

594 leak point (>2.6 m), the degassing behavior was greatly diminished as a gas pressure of CO_2 plume

595 reduced significantly. From this point, the CO_2 plume was stabilized as a dissolved phase and

596 dominantly diluted by mixing with a local groundwater along a flow direction. Therefore, from this

597 stage, sparse monitoring of saturated zone is recommended for tracing down a horizontal migration of

598 a dissolved CO_2 plume, rather than an intensive gas monitoring for a degassed component. Hence, the

599 key aspect to establish an effective monitoring network is how well constrained the "CO_2 degassing

600 boundary" around a potential leak point is, and how well the groundwater flow regime is understood.

601 Monitoring of degassed CO_2 might not be easily achieved in a real CCS field using direct

602 measurements. In this study, the degassing boundary was just a few meters from the leak point (< 2.6

603 m), whilst a strong artificial gradient (~0.18) was enforced for the plume migration. This suggests that

604 a degassing boundary would be even narrower in a natural gradient system, making a direct detection

605 of this extremely difficult. Furthermore, heterogeneity in the vadose zone can put an additional

606 uncertainty in monitoring of the vertical flux, as gaseous CO_2 can take various pathways in the vadose

607 zone depending on the soil permeability distribution (Cohen et al., 2013). Hence, identification of a

608 point source of CO_2 leakage using a direct measurement technique in the vadose zone would be very

609 difficult, unless an intensive monitoring is undertaken around the exact point source. However, noble

610 gas monitoring of groundwater is able to record the migration of a CO_2 plume from the leak point along

611 the groundwater flow pathway, as highlighted in this study. Our findings are similar to previous work

612 (Mackintosh and Ballentine, 2012) that showed monitoring of noble gases in groundwater is an order

613 of magnitude more sensitive for detecting migrated gases than vadose zone gas monitoring. Therefore,

614 we recommend that monitoring of noble gases in groundwaters should be used in addition to direct

615 vadose zone methods, in order to increase the sensitivity of the monitoring regime and improve the

616 protection of the shallow groundwater aquifer above a storage site.

Acknowledgements

627 **Appendix A. Mass balance model**

628   At least, two noble gases of different solubility are necessary to determine the degassed mass

629 as outlined in Ju et al. (2019). The closed system is a one-step phase-partitioning process, and therefore,

630 the degassed amount can be determined just by repeatedly adjusting the gas/liquid ratio until the result

631 $\left(\left(\frac{A}{B}\right)_{(l)}\right)$ fits into the measured data:

632 $\left(\frac{A}{B}\right)_{(g)} = \left(\frac{A}{B}\right)_{(l)} \times \alpha$

633 $\alpha = \dfrac{\frac{r_A}{\phi_A} K_A}{\frac{r_B}{\phi_B} K_B}$

634 Here:

635 $\left(\frac{A}{B}\right)_{(g)}$ = A and B ratio in exsolved bubbles, where A and B are different noble gases

636 $\left(\frac{A}{B}\right)_{(l)}$ = the composition of A and B remaining in the dissolved phase

637 α = partitioning coefficient for gas/liquid system

638 K_A, K_B = Henry's constant for A and B, from Sander et al., (2017)

639 r_A, r_B = dissolved-phase activity coefficients for A and B and

640 ϕ_A, ϕ_B = gas-phase fugacity coefficients for A and B.

641   In open system, the CO_2 bubble ($V_{(g)}$) is continuously lost into vadose zone carrying the noble

642 gas tracers with it from the groundwater system until the plume is stabilized. An iteration calculation

643 can be undertaken to account for the continuous loss and which terminates when the resultant mass (

644 $m_{(l)}^i$) fits the observed noble gas data:

645 $m_A{}_{(l)}^i = m_A{}_{(l)}^{i-1} - m_A{}_{(g)}^{i-1}$

646 $m_B{}_{(l)}^i = m_B{}_{(l)}^{i-1} - m_B{}_{(g)}^{i-1}$

647   Here:

648   i = Iteration step

649      $m^{i-1}{}_{(l)}$ = mass in dissolved phase before $i-1^{th}$ degassing loss (g)

650      $m^{i}{}_{(l)}$ = mass in dissolved phase after $i-1^{th}$ degassing loss (g)

651      $m^{i-1}{}_{(g)}$ = degassed mass during $i-1^{th}$ degassing process (g)

652   and degassed mass was determined from the degassed volume, such that:

653      $m^{i-1}{}_{(g)} = C(V_{(g)} \times p^{i-1})$

654      $C = M/R \cdot T$

655      $p^{i-1} = \gamma\, K\, x^{i-1}/\Phi$

656      $x^{i-1} = 18\,[NG]^{i-1}\,(\rho_{(l)}\, V_{(l)})^{-1}$

657   Here:

658      $V_{(g)}$ = degassed volume during $i-1^{th}$ degassing process (cc)

659   C = conversion factor from volume to mass

660   M = molar mass (g/mol)

661   R = gas constant (8.314 cc $\cdot$ atm/K/mol)

662   T = temperature (K)

663   p^{i-1} = partial pressure of removed noble gas during $i-1^{th}$ degassing process

664   K = Henry's constant in units of pressure (atm)

665   γ = liquid-phase activity coefficient

666   Φ = gas-phase fugacity coefficient

667   x^{i-1} = molar fraction of noble gas in dissolved phase at $i-1^{th}$ degassing moment ($mol_{NG}/mol_{(l)}$)

668     $[NG]^{i-1}$ = number of moles in dissolved phase at $i-1^{th}$ degassing moment (mol)

669     $\rho_{(l)}$ = density of dissolved phase (g/cm^3)

670     $V_{(l)}$ = volume of dissolved phase (cm^3)

671   For an open system, an iterative model was used with a fixed $V_{(g)}$ value which should be small enough

672   to finally achieve convergence with the measured noble gas composition. The noble gas concentration

673   in the groundwater was gradually decreased in iterative steps. In the final stage (i = n), $\frac{m_A{}^n_{(l)}}{m_B{}^n_{(l)}}$ was

674   matched against the monitored composition, and then the total degassed volume was calculated by

675   multiplication of the bubble size ($V_{(g)}$) and the number of iteration steps (i) in the open system model.

676   **Appendix B. Model optimization**

677   Model optimization can be achieved in a similar manner to that used by Ballentine (1997) and

678   Castro et al. (2009). The optimization aims to replicate the monitored noble gas data into a calculated

679   mixing line with the smallest misfit to the observed data. As the monitored concentration is defined by

680   mixing between two end-members, therefore, to achieve the minimum misfit, the end-members

681   constituting the predicted mixing line were repeatedly updated. There are two end-members for the

682   mixing line such as: 1) the noble gas concentration after the degassing event; and 2) the noble gas

683   concentration of the background concentration (Supplementary Figure S3). The first end-member is the

684   function of the initial amount and total degassed budget ($V_{(g)}$) of a species as discussed in the previous

685   section. The second end-member is the function of excess air intrusion level (A) to the Air Saturated

686   Water (ASW) (Mazor and Bosch, 1987; Kipfer et al., 2002). Hence, this optimization process allows

687   quantification of the degassing amount and the background level of leaked plume within the

688   groundwater system. The optimization process is given by:

689

690 $$\chi^2 = \Sigma_{i=1}^{N} \left[\left(\frac{NG1_i^m - NG1_i^p}{\sigma_{NG_{1,i}}} \right)^2 + \left(\frac{NG2_i^m - NG2_i^p}{\sigma_{NG_{2,i}}} \right)^2 \right]$$

691   Here:

692   $i = i^{th}$ sample

693   N = the number of sample

694   σ = error of the observed data

695   $NG1^m$ = measured value of noble gas sample

696   $NG1^p$ = predicted value of noble gas sample from the arbitrary mixing line

697   This optimization process was conducted using a code compatible with the Matlab program.

698

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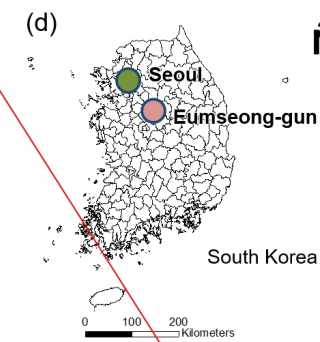849   acquisition. Energy Procedia 1(1), 2119–2125. https://doi.org/10.1016/j.egypro.2009.01.276.

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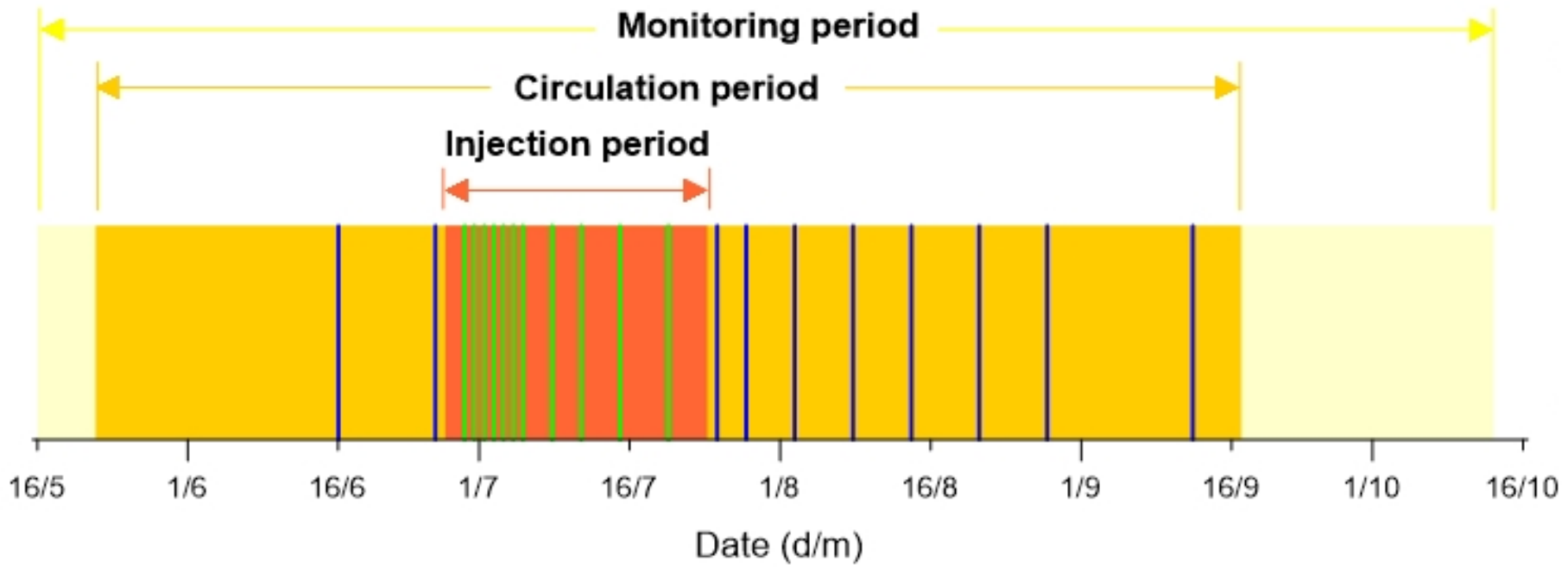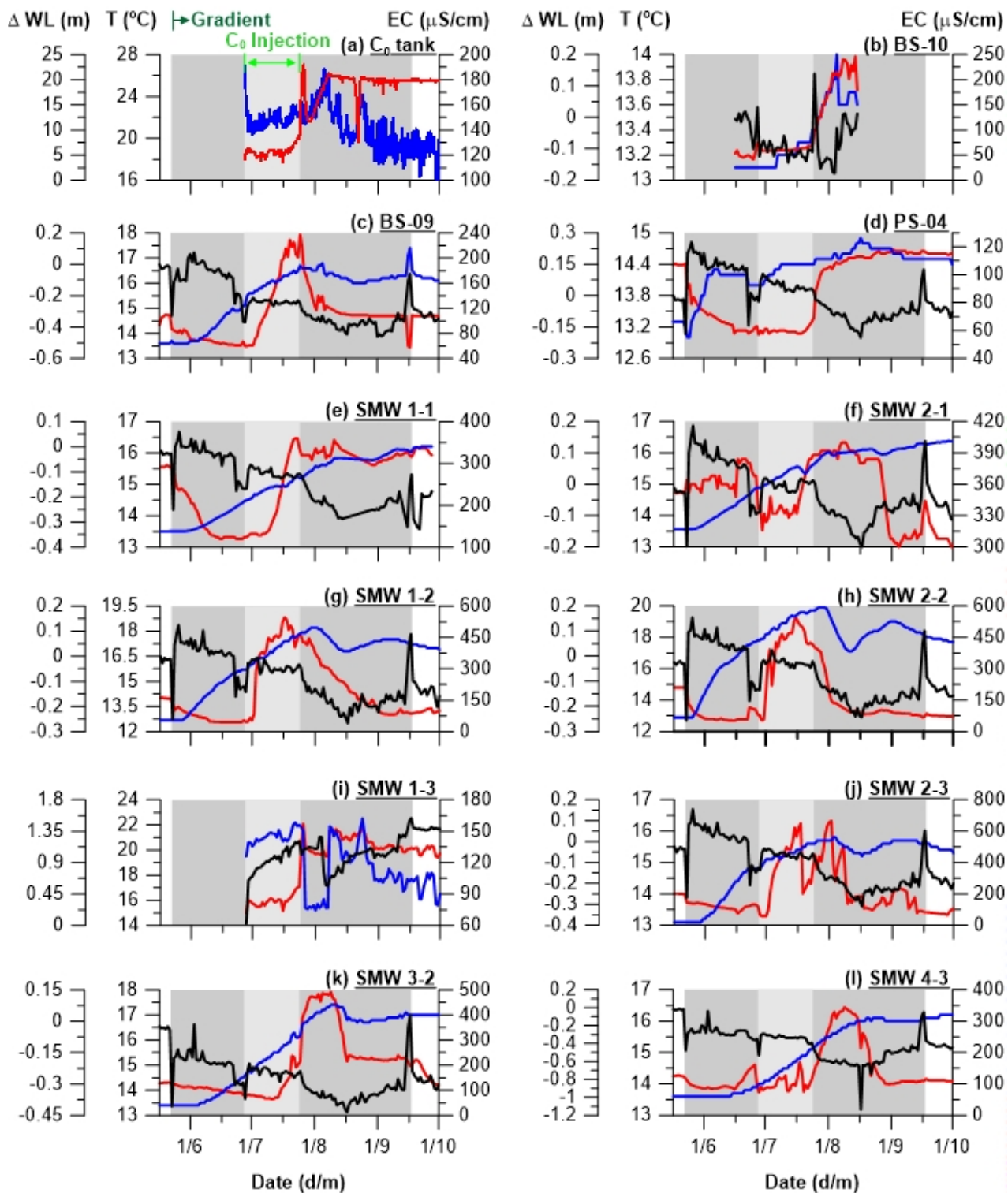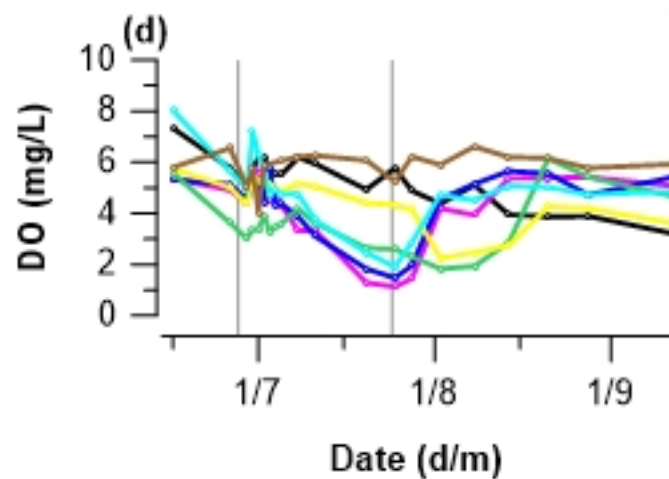
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(a)

(b)

(c)

(d) South Korea
Seoul
Eumseong-gun

(e)

(f) *Unit of m b.g.s.

(a)

FROM BS-10   TO IW

TRACER-FREE WATER (1 m³)

TRACER-INFUSED (1 m³)

TRACERS (He/Ar/Kr)

SAMPLING PORT (C_0)

(b)

⧖ : Hand valve

⧖ : Hand valve (closed off until injection start)

⧖ : Hand valve (closed off in normal state)

CO_2 INFUSED-WATER (5 m³)

CO_2 FREE-WATER (5 m³)

CO_2

Sensors (pH, EC, …)

DISSOLVER

FLOW METER

SAMPLING PORT (C_0)

FROM BS-10   TO IW

(c)

TRACER   0.5 m³/d   5 m³/d CO_2

0.5 m³/d   5 m³/d

18.5 m³/d   24 m³/d

BS-04   IW   BS-10

21 m

24 m

30 m   30 m

*Unit of m b.g.s.

Figure legend: He (blue square), Ar (magenta diamond), Kr (yellow triangle), pCO₂ (green circle)

(a) BS-09 — C₀ Injection

(b) PS-04

(c) SWM1-2

(d) SMW 2-2

(e) SMW 3-2

(f) SMW 4-2

He, Ar, Kr (C/C₀) — left y-axis

pCO₂ (atm) — right y-axis

Date (d/m)

#degassing amount (X10⁻⁴ cm³ STP/g)
$remaining after dilution (%)

(a)

Injection water ▢ Close to BG ◆ Plume center
Local BG   ◆ Plume front ◆ Plume tail

He

Degassing

$pCO_2 / 3 \times 10^5$

(2)

(1)

Injection water$_P$

BG$_P$

Ar / 6,500

(b)

He

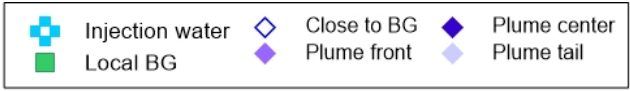Degassing

$pCO_2 / 3 \times 10^5$

(2)

(1)

Injection water$_P$

BG$_P$

Kr / 10

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

YeoJin Ju: Conceptualization, Methodology, Data Curation, Investigation, Writing - Original Draft

Stuart M. V. Gilfillan: Writing - Review & Editing

Seong-Sun Lee: Project administration, Investigation

Dugin Kaown: Data Curation

Doshik Hahm: Resources, Data Curation, Writing - Review & Editing

Sanghoon Lee: Data Curation

In-Woo Park: Data Curation

Seung-Wook Ha: Investigation

Keyhong Park: Resources, Data Curation

Hyun-Kwon Do: Investigation

Seong-Taek Yun: Funding acquisition, Project administration, Writing - Review & Editing

Kang-Kun Lee: Funding acquisition, Supervision, Writing - Review & Editing

Supplementary Material

Application of noble gas tracers to identify the retention mechanisms of CO_2 migrated from a deep reservoir into shallow groundwater

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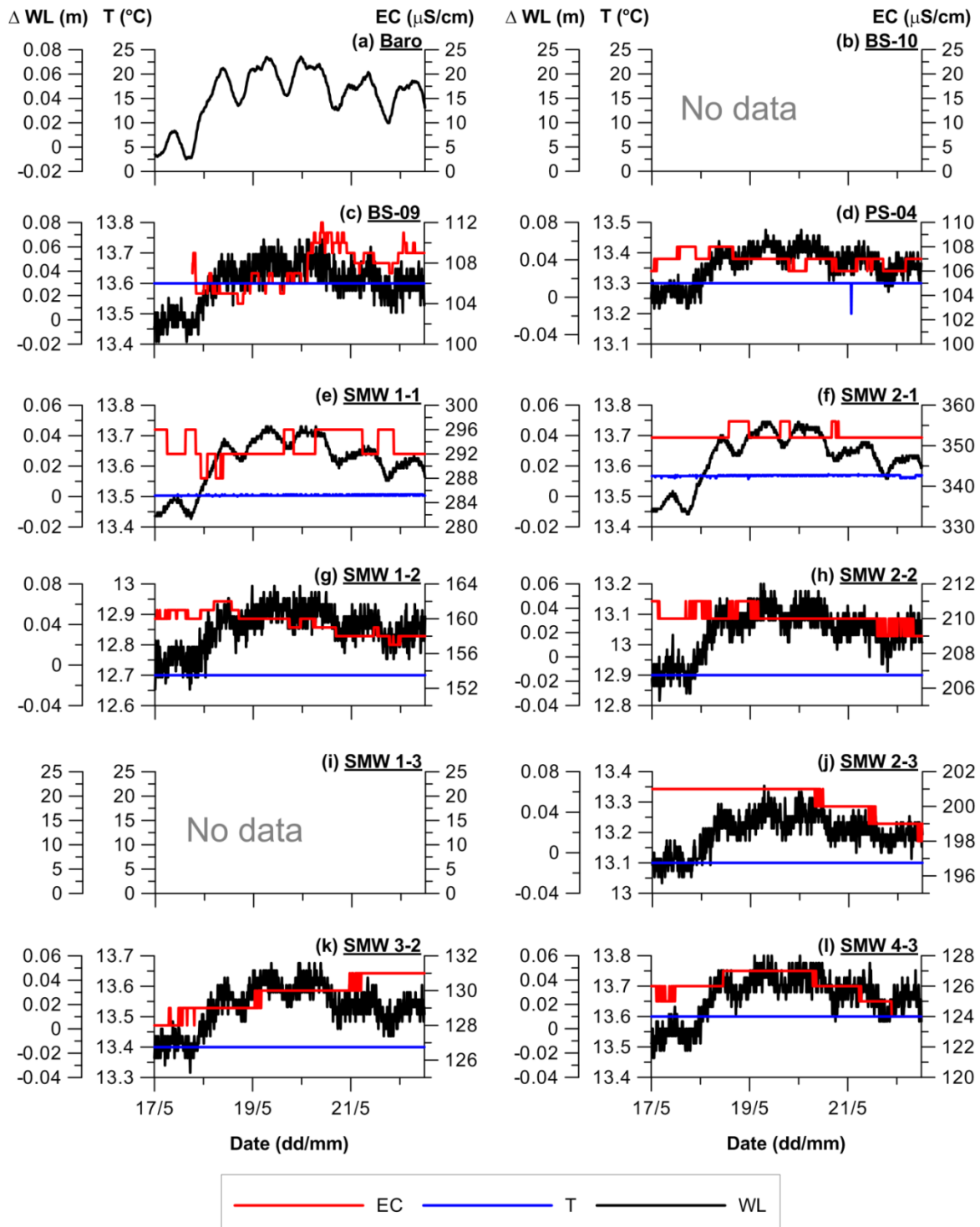
Supplementary Figure S1. Water level (WL), temperature (T) and electrical conductivity (EC) data. Measurement was completed in the monitoring wells continuously using LTC data logger before groundwater circulation (from 16 May 2017 to 22 May 2017). Note that the WL was corresponding to the atmospheric pressure chance before experiment initiation and, T and EC were consistent throughout this period.
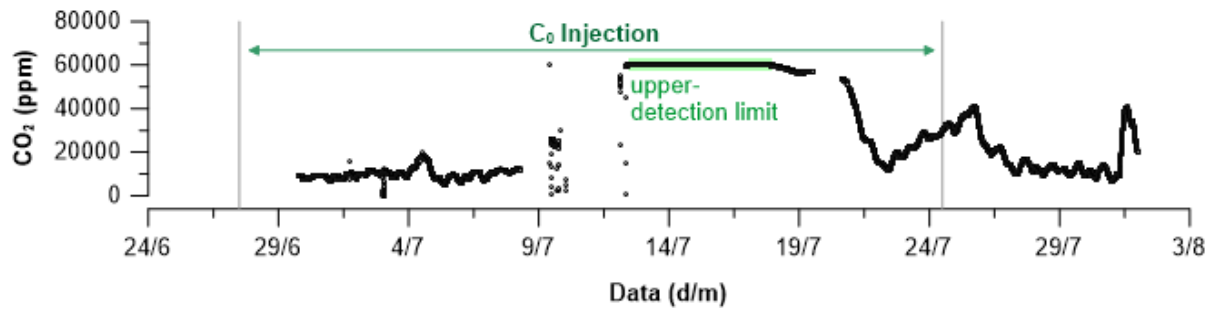
Supplementary Figure S2. CO_2 concentration monitored above the injection material inside the IW. The concentration was significantly elevated and reached to the maximum limit of the equipment suggesting the CO_2 leakage through the isolation materials occurred during injection period.
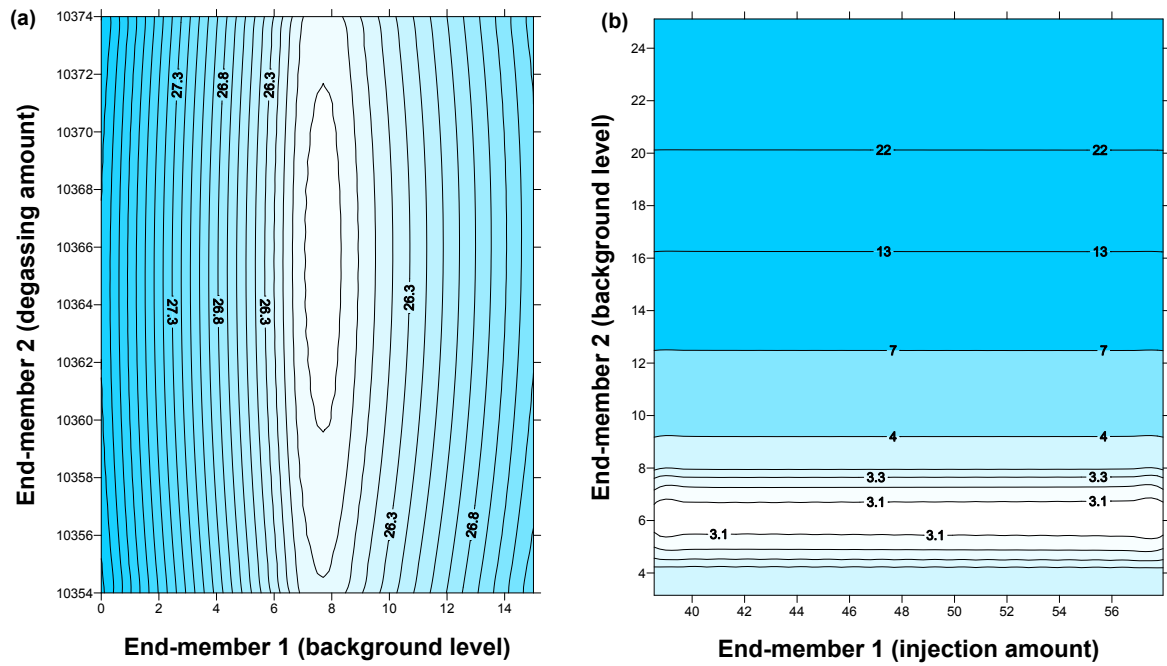
Supplementary Figure S3. Model optimization by χ^2 minimization method. In the left figure (a), the degassing amount (i.e. y-axis) and background level of noble gases (i.e. x-axis) were decided at the smallest χ^2 (i.e. center of the white-colored zone). In the right figure (b), the background level of CO_2 (i.e. y-axis) and injection amount of CO_2 (i.e. BG_P, x-axis) were decided at the smallest χ^2 (i.e. center of the white-colored zone).