Natural $^{222}$Rn as a tracer of mixing and volatilization in a shallow aquifer during a CO$_2$ injection experiment

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Funding information
Korea Environmental Industry Technology Institute, Grant/Award Number: 2018001810002; National Research Foundation of Korea, Grant/Award Number: 2017R1A2B3002119

Abstract
This study aims to evaluate the application of $^{222}$Rn in groundwater as a tracer for monitoring CO$_2$ plume migration in a shallow groundwater system, which is important to detect potential CO$_2$ leakage in the carbon capture and storage (CCS) project. For this research, an artificial CO$_2$-infused water injection experiment was performed in a shallow aquifer by monitoring hydrogeochemical parameters, including $^{222}$Rn. Radon in groundwater can be a useful tracer because of its sensitivity to sudden changes in subsurface environment. To monitor the CO$_2$ plume migration, the data were analysed based on (a) the influence of mixing processes on the distribution of $^{222}$Rn induced by the artificial injection experiment and (b) the influence of a carrier gas role by CO$_2$ on the variation of $^{222}$Rn. The spatio-temporal distributions of radon concentrations were successfully explained in association with horizontal and vertical mixing processes by the CO$_2$-infused water injection. Additionally, the mixing ratios of each monitoring well were calculated, quantitatively confirming the influence of these mixing processes on the distribution of radon concentrations. Moreover, one monitoring well showed a high positive relationship between $^{222}$Rn and Total dissolved inorganic carbon (TIC) by the carrier gas effect of CO$_2$ through volatilization from the CO$_2$ plume. It indicated the applicability of $^{222}$Rn as a sensitive tracer to directly monitor CO$_2$ leakage. When with a little effect of carrier gas, natural $^{222}$Rn in groundwater can be used to compute mixing ratio of CO$_2$-infused water indicative of CO$_2$ migration pathways. CO$_2$ carrier gas effect can possibly increase $^{222}$Rn concentration in groundwater and, if fully verified with more field tests, will pose a great potential to be used as a natural tracer for CO$_2$.

KEYWORDS
$^{222}$Rn, artificial CO$_2$-infused water injection experiment, carbon capture and storage (CCS), carrier gas, mixing ratio, shallow aquifer
1 | INTRODUCTION

Carbon Capture and Storage (CCS) is one of the most feasible greenhouse gas emission-reducing techniques (Metz, Davidson, De Coninck, Loos, & Meyer, 2005; Gielen, 2008). Massive CO2 gas emissions have triggered global climate changes, affecting the management of water resources and fossil energy. Carbon capture, storage, and sequestration techniques have been proposed to solve these environmental problems (Anwar et al., 2018; Shin, Ryu, Choi, Yun, & Lee, 2020; Öçtü, Ağralı, Arkan, & Avcioglu, 2014). However, despite various efforts to maintain stable and safe CO2 storage, this technology has some potential problems, such as the leakage of stored CO2. The fugitive CO2 can affect the groundwater system by leakage along the cracks before finally flowing to a near-surface ecosystem. This is especially important because shallow groundwater can be used for main potable water resources to people. When CO2 enters the aquifer, the pH decreases and harmful heavy metals in host rocks could be dissolved making the groundwater unsuitable for drinking. Thus, previous studies conducted groundwater quality monitoring related to the CO2 leakage (Bond et al., 2013; Humez, Lagneau, Lions, & Negrel, 2013; Jones et al., 2015; R. H. Patil, 2012; R. H. Patil, Colls, & Steven, 2010; Romanak et al., 2012; Smith et al., 2013; Spangler et al., 2010). However, few studies include experiments performed in shallow aquifers (Kharaka et al., 2010; Lions, Humez, Pauwels, Kloppmann, & Czemichowski-Lauriol, 2014; Spangler et al., 2010).

An artificial CO2 injection experiment was conducted in a shallow groundwater system at the Korea CO2 Storage Environmental Management (K-COSEM) field site in Eumseong, South Korea, which is designed to perform multidisciplinary research on environmental management induced by artificially injected CO2. The artificial injection experiment can determine the time, the location, and the amount of injection accurately. Thus, the range of CO2 concentration, which affects the groundwater environment, can be quantified. That is, this injection experiment would be useful to investigate the hydrogeological characteristics related to the migration and distribution of diffusive CO2 plumes induced by unexpected leakage.

Radon concentrations can generally be applied to explore groundwater flow characteristics, such as mixing processes, as concentrations are higher in groundwater than in surface or tap water (Banks, Rayset, Strand, & Skarphegen, 1995; Cook et al., 2008; Dimova, Burnett, Chanton, & Corbett, 2013; Ellins, Roman-Mas, & Lee, 1990). Radon is a naturally existing isotope in the subsurface system and is sensitive to sudden environmental changes such as the mixing between different concentration sources or seasonal effects, especially in groundwater. 222Rn belongs to the 238U decay series and has a relatively short half-life (3.8 days). The radon concentrations depend on rock microstructure, pore space, emanation coefficient, environmental decay conditions such as 224Ra activity, and dry density of the aquifer material. In addition, radon would be transported by advection with carrier gas, molecular diffusion, or dissolution from soil/bedrock. For the baseline, radon concentrations can be also obtained in any set of study site because the radon concentrations distributed by the bedrock characteristics. Consequently, many studies use the principal isotope of radon, 222Rn, as a tracer to identify mixing characteristics in the groundwater system (Bertin & Bourg, 1994; Burnett & Dulaiova, 2003; Burnett, Peterson, Moore, & de Oliveira, 2008; Genereux, Hemond, & Mulholland, 1993; Hoehn & Von Gunten, 1989; J. Kim, Choi, Kim, Ryu, & Lee, 2020; McCoy & Corbett, 2009). Radon concentrations in groundwater can especially be used as a tracer to characterize groundwater flow affected by other matter—such as artificially injected water—into the steady state groundwater system.

Moreover, radon activity in soil gases has been used as a tracer to monitor CO2 leakage, because CO2 is often regarded as the primary carrier gas for 222Rn in soil and/or groundwater (Elio et al., 2015a, 2015b; G. Etiope, Guerra, & Raschi, 2005; G. Etiope & Martinelli, 2002; Giammanco, Sims, & Neri, 2007; Huxol, Brennwald, Hoehn, & Kipfer, 2012; Voltattorni et al., 2009). CO2 gas leaks and/or release from deep sources (e.g., CO2 reservoir) can show anomalies in radon activity with peak patterns (Elio et al., 2015a; Giammanco et al., 2007). Thus, radon activity must be considered to monitor CO2 leakage at CCS sites. Moreover, radon measurements are easy, low-cost, and effective compared to other tracers, and have also less seasonal variations than CO2. The radon concentrations in groundwater can also provide the early warning signal as major water resources for people. However, previous studies related to the radon monitoring did not use radon concentrations in groundwater. Therefore, it is possible that there are potential relationships (e.g., positive correlations) between radon activity in groundwater and CO2 plumes.

This research describes and discusses the characterization of a groundwater flow system induced by CO2-infused water injection based on 222Rn monitoring data detected in groundwater. The primary goal of this study is to evaluate the application of 222Rn in groundwater as a natural tracer to monitor the CO2 plume distribution and migration in shallow aquifer system. For this research, the results were analysed focused on (a) investigating the spatio-temporal changes of radon concentration distribution with the mixing processes induced by CO2-infused water injection into a shallow aquifer and (b) tracing the carrier gas role of CO2-saturated water through volatilization from the CO2 plume on the variation of 222Rn in groundwater with artificial injection.

2 | SITE DESCRIPTION

The study site is located at the K-COSEM field site in Eumseong, South Korea, which has an approximate area of 10,000 m2 (Figure 1a, b). Seven wells (IW, MW1, MW2, PS, SW1, SW2, and SW3) were primarily used to monitor the radon concentration and other hydrological parameters (Figure 1c). MW1 and MW2 (multi-level groundwater monitoring wells) were installed as the bundle type with four specific depths at 2 m intervals. Information concerning the hydrostratigraphic layers and well depth is provided in Table 1. Downhole log data from monitoring wells (BH-1, BH-2, BH-3, and BH-4) indicate three distinct layers of weathered soils consisting of medium to coarse grained silty sand (0–30 m), weathered biotite granite (30–60 m), and unweathered biotite granite bedrock (>70 m). The depth of the water
The table is approximately 14–15 m below the surface. Groundwater generally flows from northwest to southeast based on equipotential groundwater level lines (Lee, Kim, Joun, & Lee, 2017). The results of push and pull tracer tests performed with multiple tracers (Chloride and SF$_6$) showed that hydraulic conductivity was from 4.0 $\times$ 10$^{-6}$ to 2.0 $\times$ 10$^{-5}$ m/s (H. H. Kim et al., 2015).

3 | MATERIAL AND METHODS

3.1 | Water sampling and analysis

Water samples were collected using 2-L polyethylene sampling bottles and an MP-1 pump (Grundfos, USA) from November 2016 to February 2017. The wells of IW, MW1, MW2, PS, and SW3 were used for water sampling in every sampling campaign conducted after the artificial CO$_2$-infused water injection. Groundwater level was measured in-situ using the LTC Levellogger Junior (Solinist, Canada) at 10-min intervals. Temperature, electrical conductivity (EC), dissolved oxygen (DO), and pH were detected using an YSI ProDSS digital sampling system (Xylem, USA). Stagnant water was removed by pumping for at least 15 min considering the well volume (IW well diameter: 100 mm, other monitoring wells diameter: 50 mm, and pumping rate: 4–6 L/min). Then, groundwater was collected when the parameters stabilized. The alkalinity was also determined in situ by titration with a 0.05-N HNO$_3$ solution to minimize degassing of CO$_2$ from the sampled waters.

Total dissolved inorganic carbon (TIC = [CO$_2$]$_g$ + [HCO$_3^-$] + [CO$_3^{2-}$]) was analysed at the Core Laboratory of Innovative
Marine and Atmospheric Technology (CLIMATE), Pohang University of Science and Technology (POSTECH). TIC was also measured in the five primary monitoring wells (IW, MW1, MW2, PS, and SW3) after the artificial CO2-infused water injection. These concentrations were determined via coulometric titration using the Versatile Instrument for the Determination of Total Alkalinity (VINDTA) system (Marianda, Kiel, Germany). The accuracy was checked daily against reference materials with known TIC values (certified by A. Dickson, Scripps Institution of Oceanography, San Diego, CA). The precision was ±2.0 μmol/kg (Park, Lee, & Tishchenko, 2008).

3.2 | CO2-infused water injection

The CO2-infused water injection experiment was conducted from 17:00 on November 29, 2016 to 00:40 on November 30, 2016 (total injection time: 459 min). The 5 m³ of CO2-infused water followed by 2.5 m³ of chaser fluid (Ar-infused water) was injected in IW at a rate of 16.34 L/min using a submersible and controllable quantitative pump (MP1, Grundfos). The schematic diagram of CO2-infused water injection method was drawn in Figure 2. This injection was performed at 21–24 m below ground surface in an interval isolated with a packer. The CO2-saturated solution was continuously bubbling pure CO2 gas into groundwater, which is pumped from the field site inside an unsealed tank. The injection system was at equilibrium with 1 atm of pure CO2.

3.3 | Radon measurement

The radon concentrations in the groundwater sample were measured for five sampling events (August 1, 2016, November 30, 2016, December 10, 2016, December 21, 2016, and January 5, 2017) using an RTM1688–2 radon monitor (SARAD, Germany). Sampled water was put in a 500-ml air-bubbling flask, which was connected to the monitor in a closed air loop. The radon concentration was determined from repeated measurements of the gas circulating inside the machine. Measurements were taken at 15 min intervals until equilibrium was reached. Then, an equilibrium value was obtained and adjusted for the short half-life of radon. This instrument offers sensitivity better than 3 cpm/(kBq/m³). Prior to the artificial injection test, the five monitoring wells (IW, MW2, PS, SW1, and SW2) were used to obtain background radon concentrations, and with the injection test, the other five monitoring wells (IW, MW1, MW2, PS, and SW3) were used for four sampling events.

4 | RESULTS

4.1 | Correlation analysis

A correlation analysis was conducted to interpret associations of hydrological indicators (DO, EC, pH, HCO3), TIC, and 222 Rn in the groundwater well used in this study. This analysis was performed by calculating the Pearson correlation coefficient (Table 2). There was not a strong correlation between two variables (correlation coefficients ≤0.6). Hence, the indicators should be analysed spatially and temporally, not just comparison in same sampling period. That is, the change patterns (e.g., increase after decrease or recovery after increase) of the indicators should be considered.

4.2 | Groundwater level monitoring

The groundwater level monitoring data in five monitoring wells (IW, MW1-2, MW2-2, PS, and SW3) had variations before, during, and after the artificial CO2-infused water injection (Figure 3). The data was taken at 10 min intervals. Figure 3 was drawn at 1 hr intervals. Before the injection, the water level differences between the groundwater wells were not high—less than 0.1 m. During the injection, from 17:00 on November 29, 2016 to 00:40 on November 30, 2016, all monitoring wells rapidly increased and then recovered to the original value range. Especially for the IW well, the background water level (78.0 m) in the interval before the injection is higher than that of other monitoring wells, because a single packer for interval isolation was installed. During injection, the water level in the IW well increased to 80.7 m and then decreased to 78.0 m at the end of the injection, showing two step curves. Sequentially, the first level drop was caused by the injection shutdown, and the second drop was induced by the removal of the packer installed for interval isolation in the IW well. The other monitoring wells showed maximum water level rises of 0.2–0.45 m. Generally, the water level differences were much higher than the data before the injection between the groundwater monitoring wells (maximum of 0.25 m).
4.3 | 222Rn and hydrogeochemical parameters (TIC, pH, HCO3, EC, DO, and temperature)

4.3.1 | Temporal variations

The temporal variations in the 222Rn data and the hydrogeochemical parameters (TIC, pH, HCO3, EC, DO, and temperature) were analysed during six sampling periods, including two pre-injection data (pre 1: August 1, 2016 and pre 2: November 22, 2016) (Figure 4). For radon concentrations, the injected water has a low value similar to that of general surface or tap water, as it was made by continuously dissolving pure CO2 gas into water. Thus, the four monitoring wells (IW, MW1-2, SW, and SW3) experienced a decrease immediately after the injection, followed by an increase—except in MW2-2, which showed a decrease after the first sampling period rather than immediately after the injection. During the second and third sampling periods, all the monitoring wells (except MW1-2, which showed an increase) maintained low concentrations and experienced an increase during the fourth sampling period.

Carbonate system components (TIC, pH, and HCO3) showed distinct patterns in the IW data. For the TIC data, the maximum IW values, rapid increases, slight decreases (by chaser fluid), and increases among the monitoring wells. Other wells had different peaks during different sampling periods. Although the TIC data was obtained only after the injection, other parameters, such as pH and HCO3, which were analysed considering the data before the injection, had similar patterns in accordance with the TIC data, especially in wells IW and SW3.

The other hydrologic parameters (EC, DO, Temperature) also had distinct characteristics in some wells. For EC data, MW 2–2 followed the patterns of IW at an early stage, and SW3 followed the patterns of MW 2–2 after the injection, suggesting preferential flow toward SW3. Total DO values showed a maximum drop of 66% compared to pre-injection values. Unlike most wells (IW, MW1-2, and PS), which recovered to the original value after the third sampling period, SW3 dropped to a low point in the fourth sampling period, indicating other influencing factors. For temperature data, all monitoring wells changed differently immediately after the injection and then maintained similar change patterns after the second sampling period.

4.3.2 | Vertical profile

The vertical profiles were analysed in MW1 and MW2, which were bundle type wells with four specific depths at 2 m intervals (Figure 4). The sampling depth was 17 m (below ground level) at the MW#-1,
21 m at the MW#-2, 25 m at the MW#-3, and 29 m at the MW#-4. Here, vertical mixing was originally caused by the influence of the injected water with the migration of a CO\textsubscript{2} plume near the injection depth. Thus, the dominant factor in mixing processes is the horizontal migration of the injected water; vertical mixing also occurs by physical processes, such as diffusion and dispersion between the injected water and the groundwater located in the upper and lower parts of injection point. If the influence of the lower groundwater is high, the pattern shows a curve similar to that of the pre-injection data and/or small differences between the injection depth and the deepest point.

For MW1, vertical mixing was observed during the second and third sampling periods. The \textsuperscript{222}Rn vertical profile showed the changing vertical mixing patterns, which is the decrease of radon concentration at 21 m after injection, and then recovery by vertical mixing. Especially during the third sampling period, radon concentrations were similarly high at depths of 21 and 29 m, suggesting vertical mixing with deep groundwater (29 m), which has high radon concentrations. Water level value differences were observed during the second, third, and fourth sampling periods. The upward flow could affect these patterns of change during the second sampling period (water level: 21 m > 17 m); downward flow could occur during the third and fourth sampling periods (water level: 17 m > 29 m). Depths of 17 and 21 m generally had higher radon concentrations than depths below 25 m in the background data.

MW2 showed vertical mixing during the first and fourth sampling periods, which had values similar to the original at a depth of 21 m. In contrast, data from the third sampling period had a lower value at 21 m and large differences with the 25 m data, suggesting the influence of vertical mixing during the first and fourth sampling periods. The water level data also supported this vertical mixing during the first and fourth sampling periods, showing large differences between 17 and 21 m. The high water level of 17 m could cause downward flow as vertical mixing. Additionally, the TIC data—the difference between 17 m and other depths (21 and 25 m)—showed that transport was located at depths of 21 and 25 m. A high TIC value was observed at 25 m with similar high radon concentrations between 21 and 25 m, especially during the fourth sampling period. This observation could suggest the influence of the CO\textsubscript{2} plume migration on the MW2-3 well during the fourth sampling period.

**FIGURE 4** Temporal variations of \textsuperscript{222}Rn, TIC, pH, HCO\textsubscript{3}, EC, DO, and temperature in five groundwater monitoring wells (IW, MW1-2, MW2-2, SW3, and PS) from August 1, 2016 to February 4, 2017. (Pre 1: August 1, 2016, Pre 2: November 22, 2016, first: November 30, 2016, second: December 10, 2016, third: December 21, 2016, and fourth: January 5, 2017)
4.4 | Mixing ratio calculation using $^{222}$Rn

For a quantitative interpretation of the study site, the mixing ratios were calculated for the four sampling periods using a radon tracer. Binary mixing ratios can also be calculated using a simple mass balance equation, as follows:

$$C_m = f \cdot C_{EM1} + (1-f) \cdot C_{EM2},$$

where $C_m$ is the concentration in the mixed groundwater well (Bq/m$^3$), $C_{EM1}$ and $C_{EM2}$ are the concentrations of first and second end-members (Bq/m$^3$), respectively, and the symbol $f$ represents the fraction of the first end-member. We assumed that the first end-member is from the background groundwater sample (the higher value from the sampling period is 35,287 Bq/m$^3$, and the second from the injection water (as 200 Bq/m$^3$). For this calculation, the basic assumptions were derived from J. Kim et al. (2020). The sampled water only consisted of two end members, with the same flow to the sampling well, constant velocity, and no chemical changes after mixing; the decrease in radon can be described using the law of radioactive decay; and the progenitors of radon are homogeneously distributed in the aquifer on a macroscopic scale. The calculation results were shown in Table 3 and Figure 5.

The average mixing ratio portions of the artificial injected water were relatively high (79.5%) compared to the background radon concentrations (20.5%) because of the end-member setting. These values were used to analyse temporal changes and the differences between the groundwater wells; therefore, the relative value is more important than the absolute value. Overall, the artificial injected water mixing ratios were high during the first sampling period (MW1-2 > IW > SW3 > PS > MW2-2), decreased slightly during the second (MW2-2 > PS > MW1-2 > IW > SW3) and third (MW2-2 > IW > SW3 > PS > MW1-2) sampling periods, and decreased during the fourth sampling period (MW1-2 > MW2-2 > IW > PS > SW3).

5 | DISCUSSIONS

The change patterns of spatio-temporal distributions in radon concentration induced by the artificial CO2-infused water injection could be attributed to two primary reasons: (a) the influence of local groundwater flow characteristics (e.g., mixing processes) by the water injection on $^{222}$Rn concentration distributions and (b) the influence of CO2 as a carrier gas by volatilization from the CO2 plume on the variation of $^{222}$Rn. To discuss the application of $^{222}$Rn in groundwater as a natural tracer to monitor CO2 plume migration, the spatio-temporal distributions of radon concentrations were analysed based on two reasons.

5.1 | Influence of artificially injected CO2-infused water on the distributions of $^{222}$Rn concentration by mixing processes

The first reason is that the spatio-temporal distributions of radon concentration are formed by the local groundwater flow induced by the artificial water injection. Radon concentrations are generally distributed by mixing processes between two or more different water types, such as surface water, river water, shallow aquifers, or groundwater from a deep source (Bertin & Bourg, 1994; Burnett & Dulaiova, 2003; Burnett et al., 2008; Genereux et al., 1993; Hoehn & Von Gunten, 1989; J. Kim et al., 2020). If the water mixing processes occurred by water injection, which has relatively low radon concentrations compared to the background level in the study site, the radon concentration distributions showed distinct mixing characteristics with the flow direction.

For the IW data, TIC values and radon concentrations do not have the same peak between the two parameters (Figure 6), showing that the mixing processes were dominant in the IW because of the injected CO2-infused water, which has low radon concentration despite the centre of CO2 plume staying near the IW well until the third sampling period. The active mixing between the injected water, which has very low concentrations, and background groundwater around the IW well induced the decrease of the radon concentrations in the monitoring wells. These mixing influences are more important than the role of CO2 as a carrier gas on $^{222}$Rn in groundwater. In accordance with the IW data, the PS and MW-2 wells showed similar patterns in early sampling periods, which is the opposite of the change patterns between TIC and radon concentration. That is, TIC values and radon concentrations had the peak pattern not in same sampling periods. In the PS well, the CO2 plume arrived during the first sampling period, as shown in the highest TIC value, and radon concentrations were low.

### TABLE 3

| November 30, 16 | December 10, 2016 | December 21, 2016 | January 5, 2017 |
|----------------|------------------|-----------------|----------------|
|                | B.G | IW | B.G | IW | B.G | IW | B.G | IW |
| MW1-2          | 2.15 | 97.85 | 9.45 | 90.55 | 30.74 | 69.26 | 26.04 | 73.96 |
| MW2-2          | 30.45 | 69.55 | 7.98 | 92.02 | 4.22 | 95.78 | 31.15 | 68.85 |
| IW             | 4.13 | 95.87 | 12.79 | 87.21 | 5.16 | 94.84 | 37.60 | 62.40 |
| PS             | 6.75 | 93.25 | 8.23 | 91.77 | 6.40 | 93.60 | 64.88 | 35.12 |
| SW3            | 5.03 | 94.97 | 21.91 | 78.09 | 6.02 | 93.98 | 89.87 | 10.13 |

Note: B.G refers the background radon concentration as the first end-member, and IW refers the artificial injected water as the second end-member.
FIGURE 5  The vertical profile data of $^{222}$Rn, TIC, and water level in wells (a) MW1 and (b) MW2.

FIGURE 6  The pie diagram graph for mixing ratios of the background groundwater sample (green colour) and the artificial injected water (pink colour). The background contour map is based on the radon concentrations data collected at each sampling date (Bq/m$^3$).
until the third sampling period. During the first sampling period, radon concentrations were low because of the active mixing with the injected water. During the third sampling periods after the second sampling period, the boundary of the CO₂ plume, which had higher TIC and lower radon concentrations, affected the distribution of radon concentrations. During the fourth sampling period, radon concentrations recovered to the background range.

The groundwater level monitoring data showed abrupt change patterns in IW during the injection (Figure 3). All other monitoring wells showed similar drastic water level change patterns within 1 hr after the start of the injection. These variations mean that the mixing between the injected water and background groundwater could be actively occurring around IW. Thus, during the first sampling period, the average mixing ratios of injected water reached a very high 90.3% (Figure 5). The low TIC value during the first sampling period in the IW well was attributed to the influence of chaser fluid. The abnormal pattern of MW2-2, which has a relatively high proportion of background groundwater, could be explained by the vertical mixing processes (Figure 4b). Moreover, the high TIC values in MW2-2 and PS could be affected by the momentary CO₂ plume migration by the chaser fluid.

During the second and third sampling periods, the average mixing ratio values of the injected water were high (88.0 and 89.5%, respectively). During the second sampling period, the high proportion of injected water in MW1-2 and MW2-2 could be attributed to the migration of the CO₂ plume (which has low radon concentrations) boundary, as shown by the high TIC values at these points (Figure 6). Additionally, SW3 had a high background radon concentration because of the late arrival of the CO₂ plume, which signified little influence of mixing at the CO₂ plume boundary. During the third sampling period, the high portion of background radon concentration in MW1-2 could be explained by vertical mixing, as proved in Section 4.3.2 (Figure 4a) or by the regional groundwater flow direction from northwest to southeast. This was also attributed to the preferential plume direction toward to SW3 and not to MW1.

At the last sampling period, 1 month after injection, radon concentrations of all the groundwater wells increased by more than 9,000 Bq/m³. In this period, average values for the injected water and the background radon concentration were 49.9 and 50.1%, respectively. These values meant that the high background radon concentration was caused by end-member setting. Most wells showed recovery toward the range of background radon concentrations before the injection. Comparatively, SW3 had radon concentrations higher than the pre-injection value, which could be attributed to the preferential flow path of the CO₂ plume migration. Horizontal mixing with longitudinal transport along a preferential flow path could occur at the study site because of heterogeneous permeability distributions (Ju et al., 2019; H. H. Kim et al., 2015; Lee et al., 2017).

5.2 Influence of CO₂ as a carrier gas on the variation of 222Rn

The second reason is that CO₂ is the primary carrier gas of 222Rn (Elio et al., 2015a, 2015b; Giammanco et al., 2007). Because there is no research on the application of CO₂ as a carrier gas for interpreting the data of 222Rn concentrations detected in groundwater samples rather
than in the soil, the analysis and interpretation of radon concentration variations with an artificial CO₂-infused water injection is necessary. Thus, the plots of TIC and radon concentrations in five monitoring groundwater wells were analysed (Figure 6). If CO₂ functions as a carrier gas by volatilization from the CO₂ plume on radon concentrations, the same peak can be observed in the same period, which means that the CO₂ leaked directly (Elio et al., 2015a; Giammanco et al., 2007). For this possibility, main hypothesis is that, by volatilization from the CO₂ plume, CO₂ goes upwards to main aquifer with carry on radon, so that the radon concentrations in soil gas increase. In general, the radon in soil can be dissolved in groundwater. That is, the increasing radon in soil by carrier gas effect can be dissolved in groundwater. Consequently, higher radon concentrations than background level can be observed at the CO₂ plume migration point.

Among the monitoring wells, only SW3 had a positive relationship between TIC and radon concentrations with the same peak in the TIC and radon concentration data during the fourth sampling period (Figure 6). This phenomenon can be attributed to the influence of CO₂ as a carrier gas by volatilization from the CO₂ plume on ²²²Rn. The other data (²²²Rn, pH, and HCO₃⁻) supported this phenomenon.

The highest radon concentration during the fourth sampling period, indicating a stronger influence of CO₂ on ²²²Rn in groundwater than of mixing processes by local groundwater flow (Figures 7 and 5). This specific variation during the fourth sampling period was also represented in pH and HCO₃ data (Figure 7) and agreed with the results of other research conducted at this study site, which showed the preferential movement of the CO₂ plume between IW and SW3 conditioned by local permeability anisotropy for a long-term monitoring basis (more than one month from the injection) (Ju et al., 2019; H. H. Kim et al., 2015; Lee et al., 2017) (Figure 7). Additionally, by the mixing ratio calculation results could also support the carrier gas effect. The background water ratios of SW3 using ²²²Rn were 5.03, 21.91, 6.02, and 89.87. Compared to these values, the background water ratios of SW3 using HCO₃⁻ were calculated with the same mass balance equation (end member as injected water: HCO₃⁻ value of IW at the first sampling period and end member as background water: HCO₃⁻ value of the lowest value before the injection) and had the values of 9.45, 7.07, 7.07, and 42.81 during sampling periods 1–4, respectively. The higher ratio of SW3 using ²²²Rn instead of HCO₃⁻ during the fourth sampling period indicated the concentration increase by the carrier gas effect.
gas effect in the SW3 well. Moreover, MW2-3 (sampling depth of 25 m) had high radon concentrations and TIC values during the last sampling period (Figure 4), indicating the arrival of the centre of the CO2 plume at a depth of 25 m in the MW2-3 well. Additionally, MW 1-2 experienced the possible influence of the carrier gas CO2 on 222Rn in groundwater. This well showed increased TIC after the fourth sampling period (Figure 7) and radon concentrations in the background concentrations range. If the radon concentrations increased beyond these values, this well would also support the carrier gas effect.

Finally, the CO2 plume migration can be conceptually illustrated as a schematic diagram (Figure 8). The CO2 plume mainly migrated toward SW3 and downwards. During the second period, the migration of the B-B’ section (from IW to MW2) was dominant because of the regional flow direction of the study site; after that period, the A-A’ section migration (from IW to SW3) was dominant because of the preferential flow path of the CO2 plume in this experiment. Therefore, although the mixing ratio portions of the artificially injected water were relatively higher than the background radon concentrations with the end-member setting, the mixing ratio distributions using radon concentrations clearly showed the influence of local groundwater flow characteristics, CO2 plume migration, and variations in radon concentrations in accordance with horizontal and vertical mixing in most monitoring wells. Moreover, some monitoring points had positive relationships between TIC and 222Rn, confirming the role of CO2 as a carrier gas for 222Rn. Therefore, results indicated that natural 222Rn can be applied as the tracer to monitor and generally interpret the distribution of CO2 plume migration.

6 | CONCLUSION

A CO2-infused water injection experiment was designed and conducted in a shallow aquifer to verify the application of 222Rn in groundwater as a natural tracer for monitoring the leakage of stored CO2. For a multilateral comparison, the 222Rn, TIC, pH, HCO3−, EC, DO, and temperature were monitored in several groundwater wells.

The data sufficiently explained that the spatio-temporal distribution of radon concentrations was formed by local groundwater flow induced by artificial water injection. Radon concentrations were distributed in accordance with the mixing processes by local groundwater flow. The calculated mixing ratio results quantitatively supported these assumptions. Abnormal patterns in some monitoring points could be explained by vertical mixing, regional groundwater flow, or the active lateral transport immediately after the injection. Additionally, the role of CO2 as the carrier gas for 222Rn, was established in well SW3. Unlike other wells that showed opposite change patterns between 222Rn and TIC, SW3 had the same peaks during the fourth sampling period in the 222Rn and TIC plot.

Thus, this study evaluated the application of radon concentrations in groundwater as a natural tracer to monitor CO2 plume migration with a CO2-infused artificial water injection into a shallow groundwater system. The spatio-temporal distributions of radon concentrations showed the deep influence of mixing processes and local groundwater flow characteristics induced by the injected water in the shallow aquifer system. Additionally, the high signal of the influence of CO2 as a carrier gas of 222Rn was detected in one monitoring well. Therefore, natural 222Rn in groundwater could be used as the tracer to broadly investigate the flow characteristics related to CO2 plume migration, by the interpretation of horizontal and vertical mixing processes with a little consideration of carrier gas effect. For directly leakage monitoring by carrier gas effect, it is necessary to conduct more field tests to apply 222Rn in groundwater as the high signal tracer completely.

ACKNOWLEDGMENTS
This research has supported by the “R&D Project on Environmental Management of Geologic CO2 storage” from the KEITI (Project number: 2018001810002). Tracer application test was partially supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIP) (No. 2017R1A2B3002119).

CONFLICT OF INTEREST
The authors declare no conflicts of interest.

DATA AVAILABILITY STATEMENT
The data that supports the findings of this study is available from the corresponding author upon reasonable request.

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**How to cite this article:** Kim, J; Lee S-S, Ha S-W, Jou W-T, Ju YJ, Lee K-K. Natural 222Rn as a tracer of mixing and volatilization in a shallow aquifer during a CO2 injection experiment. *Hydrological Processes*, 2020;34:5417–5428. https://doi.org/10.1002/hyp.13953