

Article

Changes in Geochemical Composition of Groundwater Due to CO₂ Leakage in Various Geological Media

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Abstract: This study evaluated the effects of CO₂ leakage on the geochemical composition of groundwater in various geological media through long-term column experiments. Four columns were set up with soil representing a silicate aquifer; clean sand; a sand and limestone mixture; and alluvium soil, respectively. The experiments were conducted under the same experimental conditions for approximately one year. As the CO₂-saturated synthetic groundwater was introduced into the columns, a decrease in pH and increases in electrical conductivity (EC), alkalinity, and concentrations of cations and trace elements were observed in all geological media. However, different patterns of changes were also observed depending on the mineralogical and physico-chemical characteristics of each material. As the column operation continued, while the pH decreased and low alkalinity values were more evident in the silicate soil and clean sand columns, the carbonate column continued to show high alkalinity and EC values in addition to high concentrations of most cations. The alluvium soil showed distinctive cation-exchange behaviors during the initial introduction of CO₂. The results indicate that changes in the geochemical composition of groundwater will depend on the characteristic of the geological medium such as pH buffering capacity and cation exchange capacity. This study can be useful for monitoring and managing the impacts of CO₂ leakage in various aquifer environments.

Keywords: carbon dioxide capture and storage (CCS); CO₂ leakage; groundwater composition; geological medium; column experiment

1. Introduction

Carbon dioxide capture and storage (CCS) is a technology that reduces CO₂ in the atmosphere by storing it in geologically stable areas consisting of rocks that are less likely to leak [1–6]. However, even if CO₂ is stored in stable sites, there is a risk of leakage due to unintended conditions such as corrosion in the injection pipe or defects caused by heterogeneity of the subsurface [7,8]. If the stored CO₂ is leaked into an aquifer, it will reduce the pH of the groundwater. Several ions can be dissolved and desorbed from geological media in a low pH condition, and this may affect groundwater composition [7,9–11]. This situation may be undetected for a long period of time if the CO₂ leakage is not identified early. It may thus have extensive environmental effects including deterioration of the quality of drinking, agricultural, or industrial water [8].

As the characteristics of the captured CO₂ leakage can be difficult to identify, it is necessary to develop methods for monitoring, quantifying, and predicting the leakage of CO₂ into aquifers. If early

identification of changes in the geochemical composition of groundwater is possible, this can reduce the impacts of leakage [9]. Studies on the effects of leaked CO₂ on groundwater composition have been conducted at laboratory and field scales in many regions of the world. A typical method to identify the factors influenced by the leakage is to artificially inject CO₂ directly into shallow groundwater systems to observe changes in the geochemical composition in the aquifers.

Previous studies have demonstrated that leakage of CO₂ can mainly be identified by a decrease in pH and increases in electrical conductivity (EC), alkalinity, and concentrations of cations and trace elements in groundwater [7,12]. Zheng et al. [13] showed that the main factors for these changing concentrations in groundwater include calcite dissolution, Ca-driven cation exchange reactions, and pH-driven adsorption or desorption reactions. These results imply that changes in groundwater composition can be different for different aquifer materials, and the identification of geochemical behaviors for different geological media is therefore necessary. In general, there are two classes of aquifer materials for aquifers surrounding geological storage areas where CCS technology is applied: silicate aquifers mainly consisting of silicate minerals and carbonate aquifers consisting of carbonate minerals such as calcite and dolomite. In addition, alluvial aquifers consisting of silt, clay, and gravel are often studied as a special case of geological setting (e.g., when a coastal area is considered as a potential CO₂ storage site), although they may not be classified as the third type of aquifer based on mineralogy.

Study sites evaluating silicate aquifers include the Plant Daniel field site and High Plains Aquifer [7,13–17]. In silicate aquifers, the pH buffer capacity is generally low, and thus pH greatly decreases upon contact with CO₂. CO₂ leakage experiments have demonstrated that cations can be detected in high concentrations resulting from cation exchange, surface complexation, and dissolution reactions [15,18].

Previous study sites of carbonate aquifers include the Edwards Aquifer and underground limestone quarry in Gironde [6,19–21]. Studies of carbonate aquifers have shown that as CO₂ leaks, carbonate minerals are dissolved by the lowered pH, but they prevent a further decrease in pH due to their high buffering capacity. Field-scale CO₂ injection projects in carbonate aquifers have shown that total dissolved solid (TDS), mainly Ca and Mg, can increase beyond regulatory limits.

Study sites for CO₂ leakage in alluvial aquifers include the Sanandaj-Sirjan Zone (SSZ), Montmiral area, Chimayó area, and Brackenridge field site [22–25]. In the case of the alluvial aquifers, the TDS values are typically high due to agricultural activities and vegetation. Some study sites showed characteristic features of high ratio of ¹³C [24], while most of sites showed low permeability and high cation exchange capacity due to the presence of clay or silt.

Through the studies on the effect of CO₂ leakage on various aquifer environments, geochemical parameters that can be used to indicate CO₂ leakage have been identified. Changes in alkalinity and EC values appear to be temporal in silicate aquifers, making them difficult to be used as leakage indicators. However, a large decrease in pH of around three units may indicate CO₂ leakage [15]. Carbonate aquifers are characterized by high alkalinity and EC values resulting from the dissolution of carbonate minerals. In addition, concentrations of cations such as Ca, Mg, Mn, Pb, and As are generally high, which could be used as indicators for CO₂ leakage detection [26–28]. For alluvial aquifers, no common indicators have been identified, although high TDS values are typically observed. Table 1 summarizes some important findings from recent studies that have evaluated the effects of CO₂ leakage on silicate, carbonate, and alluvium aquifers, which were conducted through laboratory batch and column experiments or with field studies.

Table 1. Previous studies conducted for monitoring the effects of CO₂ leakage on each type of aquifer geological material.

Aquifer Type	Study Site	Study Method	Major Findings	Reference
Silicate	High Plains (Texas)	Lab experiment	CO ₂ caused an increase in concentrations of various cations, such as Mn, Co, Ni, U, Ba, and Fe. Solid phase metal mobility, carbonate buffering capacity, and redox state in the shallow overlying aquifers influenced the impact of CO ₂ leakage.	Little and Jackson [7]
		Modeling	Calcite dissolution and Ca-driven cation exchange reactions were the major drivers for the concentration changes of Ca, Ba, Sr, and Cs. pH-driven adsorption/desorption reactions were the reason for concentration increases of As and Pb.	Zheng et al. [13]
	Plant Daniel (Mississippi)	Field test and lab experiment	CO ₂ leakage resulted in a sustained and easily detected decrease until pH 3. Major or minor elements (Ba, Ca, Cr, Sr, Mg, Mn, and Fe) showed initial high increase, and continued to be higher than the background levels even after stabilization. Trace constituents such as As and Pb remained at significant detection levels.	Trautz et al. [15]
		Lab experiment	The pH-driven process (e.g., carbonate dissolution and ion exchange) affected the groundwater content. The decrease in pH caused the mobilization of alkaline earth metals such as Ca, Mg, Ba, and Sr, indicating that the metallic elements could be controlled by carbonate ligand.	Varadharajan et al. [16]
	The Newark Basin (New Jersey)	Field test	Following the injection of CO ₂ , an increase in alkalinity was shown with a decrease in pH, and the concentration of major cations such as Ca, Mg, and Si, and trace elements including Fe, Mn, Cr, Co, Ni, Cu, and Zn were also confirmed to increase.	Yang et al. [17]
	Military airfield (Brandenburg)	Field test and modeling	As a result of CO ₂ injection, total inorganic carbon (TIC) concentration increased and pH decrease were confirmed, and also cations and trace elements were increased while anions tended to decrease. Carbon isotope (¹³ C/ ¹² C) analyses showed a clear deviation of more than 10.5‰.	Peter et al. [14]

Table 1. Cont.

Aquifer Type	Study Site	Study Method	Major Findings	Reference
Carbonate	Edward Aquifer (Texas)	Batch and column experiments	Calcite dissolution, ion exchange, and precipitation reactions triggered by calcite dissolution had a crucial role in controlling the cations concentration. Several cations such as Ca, Mg, Ba, Sr, Si, Na, and K were continuously released into aqueous phase and concentrations of trace elements such as Mo, Cs, and Sn were low.	Wang et al. [21]
		Modeling	Shallow groundwater resources may degrade locally around leakage points by reduced pH and increased TDS. pH and TDS were most sensitive to CO ₂ and brine leakage. The plume change in Cd was smallest, while plume volume distribution of As and Pb were similar to those of TDS.	Dai et al. [20]
		Modeling	Field simulations confirmed that CO ₂ leakage in the carbonate aquifer is caused by a decrease in pH and an increase in TDS beyond the regulatory limits. Trace elements such as Pb were shown not to exceed the maximum contaminant levels (MCLs).	Bacon et al. [6]
	Underground limestone quarry (Gironde)	Field experiment	It was confirmed that inert gases such as He and Kr can be applied as tracers, indicating a subsurface CO ₂ leakage.	Cohen et al. [19]
Alluvium ^a	Sanandaj-Sirjan Zone (SSZ) (Hamadan)	Field test and modeling	pH decreased due to CO ₂ leakage, and the concentrations of ions excluding sulfate and alkalinity increased. TDS increase in groundwater was caused by the dissolution of minerals by CO ₂ saline waters from deep source.	Delkhahi et al. [25]
	Montmiral reservoir area	Field test and modeling	$\delta^{13}\text{C}$ signature appeared to be due to the dissolution of Mg–calcite or dolomite, not from the effect of CO ₂ and did not show significant $\delta^{18}\text{O}$ change.	Lions et al. [24]
	Chimayó area (New Mexico)	Modeling	Lower pH increased the concentrations of Ca and U. The increase in U was not due to the geochemical reaction (e.g., calcite dissolution), but to the U advection with CO ₂ rising from the below.	Keating et al. [22]
	Brackenridge field site (Texas)	Field test and batch experiments	Ca, Mg, Sr, Ba, Mn, and U were controlled by carbonate dissolution and Si and K by silicate dissolution. Mo, V, Zn, Se, and Cd were controlled by pH. The concentration in the solution was reduced to the pre-test level by sorption.	Mickler et al. [23]

^a As a special case of geological setting, not classified based on the mineralogy of the aquifer.

Although numerous studies have been conducted to evaluate the effects of CO₂ leakage on groundwater composition in individual types of aquifer, systematic approaches to evaluate the effects across various types of aquifer materials are still rare. Considering that CCS projects can be applied in different types of aquifers and the effects can vary depending on the types of aquifer materials, a systematic approach to generalize the effects of CO₂ leakage can be useful to predict and manage the potential impacts of CO₂ leakage in any given site.

For a systematic approach, laboratory experiments are often more convenient than field tests because a field study is only applicable to a specific geological environment and may have cost and time constraints. Several batch experiments have been conducted to assess the impacts of CO₂ leakage [23,29–33]. In particular, Lu et al. [29] conducted a batch experiment using nine samples representing various aquifers throughout the Gulf Coast region. They identified two types of cation behaviors: type I showing rapid increase after the initial CO₂ flux and then stable concentrations for cations such as Ca, Mg, Si, K, Sr, Mn, Ba, Co, B, and Zn; and type II, showing increases and then decreases in concentrations for cations such as Fe, Al, Mo, U, V, As, Cr, Cs, Rb, Ni, and Cu. Cahill et al. [31] also conducted batch experiments using eight types of sediments obtained across Denmark. However, an issue with batch experiments is that they do not take into account geochemical reactive transport. To address this shortcoming, column experiments can be used since they are more economical compared to field tests and they can evaluate reactive transport. Moreover, column experiments can consistently evaluate the changes in different geological materials under the same experimental conditions for long-term observation.

In this study, we systematically tested the changes in the geochemical composition of groundwater produced by the reaction of CO₂ with various geological materials through column experiments, which were operated for approximately one year. Four columns were set up with soil from the Environmental Impact evaluation Test (EIT) facility of the Korea CO₂ Storage Environmental Management (K-COSEM) research center where (1) silicate minerals are dominant; (2) clean sand; (3) sand and limestone mixture; and (4) Quaternary alluvium (QA) soil from a coastal area of Korea.

Previous experimental studies of CO₂ leakage have mostly been short-term, and column experiments from the perspective of CO₂ leakage are still rare [34]. The objectives of this study were: (1) to compare the changes in geochemical composition for four different geological materials under the same experimental conditions, and (2) to observe differences in the early and late reaction time behaviors through long-term column experiments. The year-long column experiments in this study can be useful for identifying differences in geochemical changes in different geological materials and also dominant geochemical processes in early (e.g., cation-exchange and dissolution) and late (e.g., remobilization by desorption and dissolution-precipitation) stages of the reactions. Differences between more soluble minerals such as carbonate minerals, and less soluble minerals such as silicate minerals can also be identified.

2. Methods

2.1. Column Design and Characteristics of Geological Media

Different underground storage environments were simulated using columns packed with different geological materials. Temporal and spatial patterns of change in the geochemical composition for each material after the introduction of CO₂-saturated synthetic groundwater (SGW) were monitored by sampling at specific time intervals.

Each column was 7.62 cm in diameter and 40 cm in height, and it was made of an acrylic material. Ten sampling ports penetrating inside of the column were installed along the length of the column. Sampling ports 1 to 6 were installed at intervals of 2.5 cm, and sampling ports 6 to 10 were installed at intervals of 5 cm. Thus, along the 40 cm total length of each column, sampling ports were located at 2.5, 5, 7.5, 10, 12.5, 15, 20, 25, 30, and 35 cm from the influent end. Samplings were also conducted at the influent (0 cm) and the effluent (40 cm) ends of the column.

Each column was packed with four different geological materials, for which the characteristics of each column are shown in Table 2. Column 1 used soil the from EIT field site, which represents a silicate aquifer. The EIT site is a test site at which the K-COSEM research center is conducting a groundwater monitoring project by artificially injecting CO₂ to the aquifer and located in Eumseong-gun, Chungcheongbuk-do, Korea [35,36]. Detailed hydrogeological information can be found in Jun et al. [37] and Ha et al. [34]. Column 2 was packed with clean sand, which mainly consists of quartz (SiO₂), and was served as a control column in terms of geochemical behaviors. Column 3 was constructed by mixing the clean sand with limestone sieved in 2~95 mm (mass ratio of 9:1), and it represents a carbonate aquifer. Column 4 was constructed to represent a CO₂ storage site in a coastal area, and it was packed with Quaternary alluvium soil collected from Buan-gun, Jeollabuk-do, Korea. In order to make an even flow through the column, a 1 cm layer of silica was spread onto the top and bottom of each geological medium, thus, the layer of each geological material was approximately 38 cm. The columns were wrapped with aluminum foil to minimize the growth of algae during the long-term experiments.

In order to identify the characteristics and compositions of the geological media, various analyses were conducted prior to the column operation. Table 3 and Figure 1 show the soil composition and curve for grain size analysis, respectively. The grain size analysis for each geological material was performed using SediGraph at the Department of Geological Sciences at Pusan National University, Busan, Korea (SediGraph III 5100; Micromeritics Instruments Co., Norcross, GA, USA). Table 4 shows the Burnauer–Emmett–Teller (BET) surface area [38] and cation exchange capacity (CEC) values for each geological medium. The BET surface area was measured at the Regional Innovation Center for Industrialization of Advanced Chemical Materials (RIC) in Hanbat National University, Daejeon, Korea using a BET surface area analyzer (TriStar™ II 3020; Micromeritics Instruments Co., Norcross, GA, USA). CEC was measured at Cheillab, Seoul, Korea using inductively coupled plasma-optical emission spectrometry (ICP-OES) (ARCOS; SPECTRO, Kleve, Germany). To identify the elemental and mineralogical compositions of the geological media, X-ray fluorescence (XRF) analysis, and x-ray diffraction (XRD) analyses were conducted, and the results for each column are shown in Tables 5 and 6, respectively. XRF analysis was conducted at the Central Laboratory at Pukyong National University, Busan, Korea, using an x-ray fluorescence spectrometer (XRF-1800; SHIMADZU, Kyoto, Japan) and XRD analysis was conducted at the Center for University-wide Research Facilities (CURF) at Jeonbuk National University, Jeonju, Korea using a multi-purpose high performance x-ray diffractometer (X'PERT-PRO Powder; PANalytical; Malvern Panalytical Inc., Westborough, MA, USA).

Table 2. Characteristics of the four columns packed with different geological media.

Column	Column 1 (EIT Soil)	Column 2 (Sand)	Column 3 (Carbonate)	Column 4 (QA Soil)
Grain size (mm)	0.063~2	0.063~2	0.063~2 (Sand) + 2~95 (Limestone) (Mass ratio 9:1)	0.063~2 (QA Soil) + 3 (Glass beads ^a) (Mass ratio 3:7)
Mass of dry media (g)	2920	2805	2840 (Sand: 2556; Limestone: 284)	3095 (QA soil: 928; Glass beads: 2167)
Pore volume (PV; cm ³)	500	500	530	440
Porosity (-)	0.27	0.27	0.29	0.24
Bulk density (g cm ⁻³)	1.60	1.54	1.56	1.70
Operation period	265.46 PV (345 day)	244.27 PV (347 day)	241.83 PV (339 day)	281.70 PV (346 day)

^a Column 4 (Quaternary alluvium soil) was packed with the weight ratio of 3:7 for soil and glass beads to overcome low permeability and have consistent flow within the column.

Table 3. Soil composition and textural parameters for each geological medium.

Material ^a	Composition (wt.%)				Textural Parameter				Soil Type ^b
	Gravel	Sand	Silt	Clay	Mean	Sorting	Skewness	Kurtosis	
EIT soil	0.76	95.45	0.83	2.96	0.627	1.35	0.321	1.008	(vc)S
Sand	0	95.81	0.69	3.5	1.75	0.954	0.227	1.354	(vc)S
QA soil	1.49	9.87	49.35	39.29	7.208	2.931	0.045	0.766	(s)cSI

^a As limestone in column 3 was received as the form of a rock and was crushed for use in the column, grain size analysis was not carried out. ^b Soil type was classified based on sand, silt, and clay (SSC trigon) percentages, as suggested by Blott et al. [39]: (vc)S: very slightly clayey sand; (s)cSI: slightly sandy clayey silt.

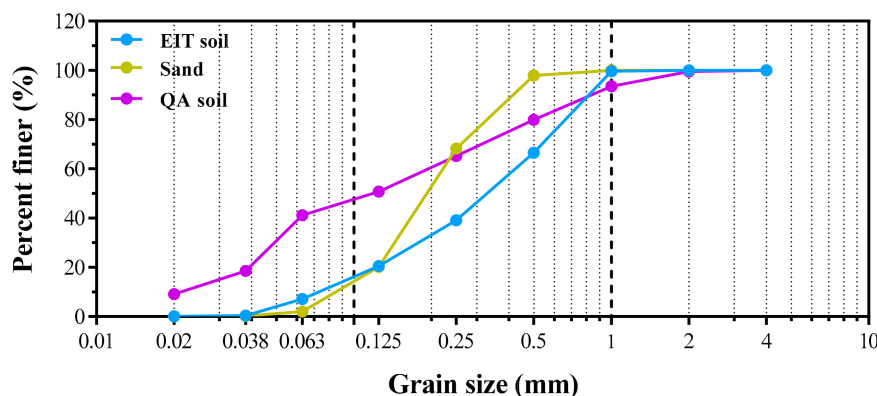


Figure 1. Percent finer curves according to the grain size distribution for each geological medium. Limestone, the packing material of column 3, was received as the form of a rock and was crushed for use in the column; it was thus excluded from the grain size analysis. The x-axis represents a log scale.

Table 4. Burnauer–Emmett–Teller (BET) surface area and cation exchange capacity (CEC) values for each geological medium.

Material	BET Surface Area (m ² g ^{−1})	CEC (cmol kg ^{−1})
EIT soil	5.11	14.39
Sand	2.63	1.33
Limestone	0.31	16.69
QA soil	21.10	12.97

Table 5. Elemental analysis of each geological medium using x-ray fluorescence (XRF).

Material	SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	LOI	Total (wt.%)
EIT soil	67.02	17.05	0.59	3.79	0.06	0.51	0.69	1.88	4.63	0.14	3.50	99.86
Sand	74.41	11.27	0.34	1.72	0.04	0.25	1.41	1.37	3.18	0.04	5.83	99.85
Limestone	32.29	0.10	0.01	0.10	0.01	0.23	38.84	0.00	0.04	0.02	28.16	99.80
QA soil	68.87	14.78	0.78	4.33	0.06	0.83	0.80	0.96	2.77	0.09	5.61	99.88

LOI = Loss on ignition.

Table 6. Major mineralogical composition for each geological material identified by x-ray diffraction (XRD) analysis.

Material	Minerals (Chemical Formula, Score ^a)
EIT soil	Quartz (SiO ₂ , 50), Plagioclase (Al ₃ Ca _{0.5} Si ₃ O ₁₁ , 39), K-feldspar (KAlSi ₃ O ₈ , 27)
Sand	α-quartz (SiO ₂ , 61), Hematite (Fe ₂ O ₃ , 36), High albite (Al ₁ Na ₁ O ₈ Si ₃ , 32)
Limestone	Calcite (CaCO ₃ , 84), Quartz (SiO ₂ , 44), Calcium peroxide (CaO ₂ , 15)
QA soil	β-quartz (SiO ₂ , 78), Anorthite (Al _{1.52} Ca _{0.52} Na _{0.48} O ₈ Si _{2.48} , 37)

α-quartz: quartz stabilized at temperatures below 573 °C (846 K); β-quartz: quartz stabilized at 573 °C to 870 °C (1143 K) temperatures; and high albite: albite produced at high temperatures above 750 °C (1023 K). ^a Score is a numerical representation of how close it is to the particular mineral phase, identified through peak position and x-ray intensity emitted from samples and accepted by the XRD detector (score value is up to 100, which indicates a perfect match).

2.2. Synthetic Groundwater (SGW)

Considering that the long-term experiments were operated for approximately one year, the input solution was artificially made to mimic groundwater at the EIT field site. The SGW was made based on the concentrations of major cations (i.e., Ca, Na, Mg, and K) at the EIT field site. Table 7 shows the composition of the on-site EIT field groundwater [34] and the SGW manufactured for this study.

Reagents of NaHCO_3 , NaSO_4 , $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, KNO_3 , and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ were used to manufacture the SGW to include the major cations. After the synthesis, the SGW was saturated with 100% CO_2 for approximately 2–3 h by purging with a gas sparger. The pH of the SGW was decreased from 7.7 to approximately 5.0 after CO_2 saturation. The input solution bottle containing the CO_2 -saturated SGW was connected to an aluminum foil balloon, which was filled with 100% CO_2 to compensate the head space in the input solution bottle as the influent water was introduced into the column (Figure 2). The input solution was introduced into the column at a flow rate of approximately 350 mL day^{-1} using a peristaltic pump (ISM834C; Ismatec; Cole-Parmer GmbH, Wertheim, Germany).

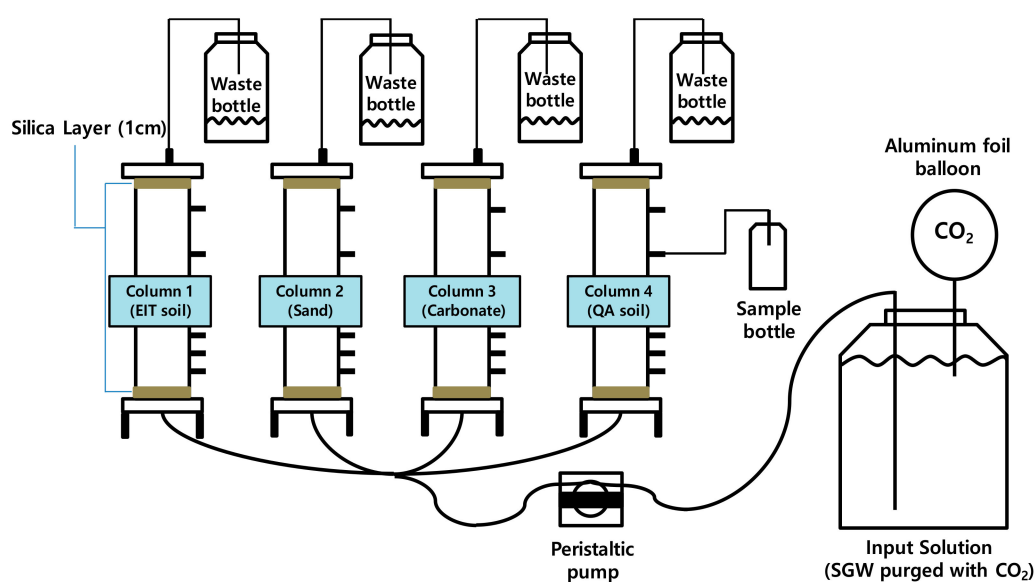


Figure 2. Schematics of the column experiments.

Table 7. Composition of the EIT groundwater [34] and synthetic groundwater (SGW) manufactured in this study.

Water Type	pH	Alkalinity (mg L^{-1} as CaCO_3)	Ca (mg L^{-1})	Mg (mg L^{-1})	Na (mg L^{-1})	K (mg L^{-1})
EIT groundwater	6.8	35	3.2	1.1	10.9	1.0
Synthetic groundwater (SGW)	7.7 ^a	20	3.4	1.1	11.5	1.2

^a After CO_2 saturation, the pH of the SGW decreased to approximately 5.0.

2.3. Operation and Sampling

Two types of sampling were conducted to evaluate the geochemical changes across time and space: time-series sampling and profile sampling. Time-series sampling was used to evaluate the temporal geochemical changes during the initial introduction of CO_2 -saturated SGW into the column. This time-series sampling was conducted at the column effluent through continuous sampling at certain time intervals. Profile sampling was used to evaluate spatial geochemical changes along the distance of the column. Profile sampling was conducted at 10 sampling ports in addition to the influent and effluent ends of the column. During the entire column operation, a total of seven profile sampling events were performed (i.e., after 2, 4, 8, 16, 24, 32, and 48 weeks of column operation). Total cumulative

pore volumes (PVs) for each column were 265, 244, 241, and 277 PVs for columns 1 to 4, respectively, which correspond to the elapsed day of 345, 347, 339, and 341 days, respectively. The average flow rates for all columns were maintained between 309 and 368 mL day⁻¹, having an average retention time of between 1.5 and 2.1 days. For each sampling event, the sampling bottles were purged using Ar gas for 15 min to prevent oxygen ingress into the bottle, and the outlet tubing from each sampling bottle was submersed under water to prevent oxygen ingress into the sampling bottle during the sampling procedure. For the sampling, a small quantity of stagnant water at the sampling port was removed and the outlet tubing from the sampling bottle was connected to the port, after which the sampled water flowed into the sampling bottle with the natural flow rate as designated by the peristaltic pump.

2.4. Analysis

All water samples were filtered using 0.45 µm cellulose acetate (CA) syringe filters and analyses were conducted for geochemical parameters (i.e., pH, EC, Eh, and alkalinity) and cations and trace elements.

pH was measured using an Orion VERSA STAR advanced electrochemistry meter and a ROSS Ultra pH/ATC Triode electrode from Thermo Orion (Thermo Fisher Scientific, Waltham, MA, USA). Calibration of pH was conducted using pH 4.00, 7.00, and 10.01 buffer solutions (Thermo Fisher Scientific). EC was measured using an Orion conductivity cell (013010MD; Thermo Fisher Scientific). Calibration was conducted using a standard solution of 1413 µS cm⁻¹ (Thermo Fisher Scientific). Oxidation–reduction potential (ORP) was measured using a STAR A215 pH/conductivity meter and sure-flow combination redox/ORP electrode (Thermo Fisher Scientific), and was converted to an Eh value. The electrode offset was checked with Zobell's solution (Hach Co., Loveland, CO, USA). Alkalinity was measured with a digital titrator (Hach Co.) by titration with 0.16 N H₂SO₄ and bromocresol green/methyl red indicator.

Cation concentrations were analyzed at the Center for University-wide Research Facilities (CURF) at Jeonbuk National University, Jeonju, Korea. The concentrations of Ca, Mg, Na, K, Mn, Sr, and Si were analyzed using ICP-OES (iCAP 7400 Duo; Thermo Fisher Scientific), whereas the concentrations of Al, Fe, Co, Zn, Ba, and Li were analyzed using inductively coupled plasma-mass spectrometry (ICP-MS) (iCAP RQ; Thermo Fisher Scientific). Additionally, the concentrations of trace elements such as Cr, As, Se, and Cd were analyzed using ICP-MS for the samples collected at 8, 24, and 48 weeks of column operation. Cu and Pb were analyzed only for the samples after eight weeks.

3. Results

3.1. Temporal Variation of Groundwater Composition during the Initial Introduction of CO₂-Saturated SGW

Figure 3 shows the temporal changes in geochemical parameters in the column effluents during the initial introduction of the CO₂-saturated SGW. All columns generally showed decreasing pH and increasing trends of EC, Eh, and alkalinity, while there were also differences in behaviors between the columns. Columns 1 and 2, representing silicate aquifers, showed relatively low EC and alkalinity, while column 3, representing a carbonate aquifer, showed the highest EC (close to 1500 µS cm⁻¹) and alkalinity values (around 750 mg L⁻¹ as CaCO₃). In column 4, reactions with CO₂-saturated SGW appeared to be faster than in the other columns; it showed a sharp decrease in pH and earlier increases and then decreases of EC and alkalinity after 1 PV. This may reflect that in the alluvium aquifer, minerals for pH buffering are consumed rapidly and cation-exchange may be an important process during the early stage of CO₂ leakage due to the large surface area of the aquifer material (Table 4).

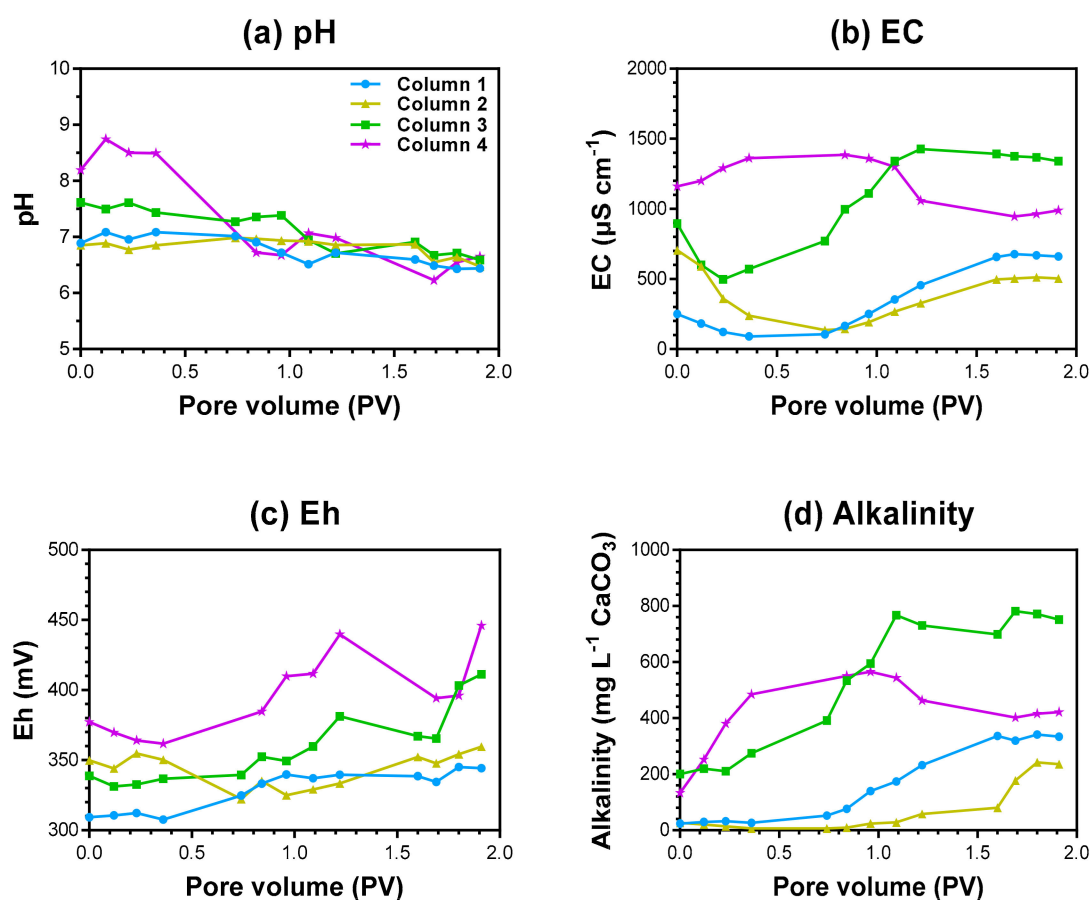


Figure 3. Initial changes of geochemical parameters up to 2 pore volumes (PVs) as the CO₂-saturated SGW was introduced into the column ((a) pH; (b) EC; (c) Eh; and (d) alkalinity) (time-series data at the column effluent). The legend is applied to all figures.

Figure 4 shows the temporal changes in cation concentrations in the column effluents as the CO₂-saturated SGW was initially introduced into each column. Most columns showed similar behaviors, in that cation concentrations increased with the reactions with CO₂; however, there were also differences in behaviors depending on the characteristics of geological media. Among all columns, the Si concentration in column 1 was the highest (12.5 mg L⁻¹ to 16.5 mg L⁻¹), presumably due to dissolution of silicate minerals such as quartz, plagioclase, and K-feldspar (Table 6), consisting of weathered granite. In the EIT site, there was a wide distribution of weathered soil on the thick coarse-grained gneissic granite bedrock, which would have been metamorphosed in the past [40]. On the other hand, K, Mn, and Ba showed lower concentrations in column 1 compared to the other columns. The cation concentrations in column 2 were generally lower than the other columns; however, K showed a relatively high concentration due to the relatively high K₂O content (3.18%). Mn also showed a relatively high concentration (around 1 mg L⁻¹).

In column 3, Ca showed a quite rapid increasing pattern, probably resulting from the dissolution of limestone. Mg also showed a similar tendency. Mn, Sr, Fe, and Ba concentrations were also highest in column 3, and these may be associated with the dissolution of carbonate minerals. The cation concentrations in column 4 generally showed faster increase patterns compared to the other columns during the initial introduction of CO₂-saturated SGW and then decreasing trends after 1 PV. Mg, Na, K, Si, and Li showed characteristic breakthrough behaviors, and these might be related to cation-exchange processes. Zn showed a delayed increasing behavior. The QA soil in column 4 had a relatively high CEC value of 12.97 cmol kg⁻¹ and also high BET value (21.10 m² g⁻¹) (Table 4), supporting the claim that cation-exchange reactions may occur rapidly during the initial introduction of CO₂-saturated

SGW with low pH. The initial concentration of Na in column 4 was highest among all columns and it showed a decreasing pattern, the opposite behavior to most of the cations. This may represent that the replacement of Na by other cations through cation-exchange reactions. Li concentration was also highest in column 4, probably due to dissolution of Li-bearing silicate minerals. Li can originate from the weathering and leaching of silicate rocks and minerals [41].

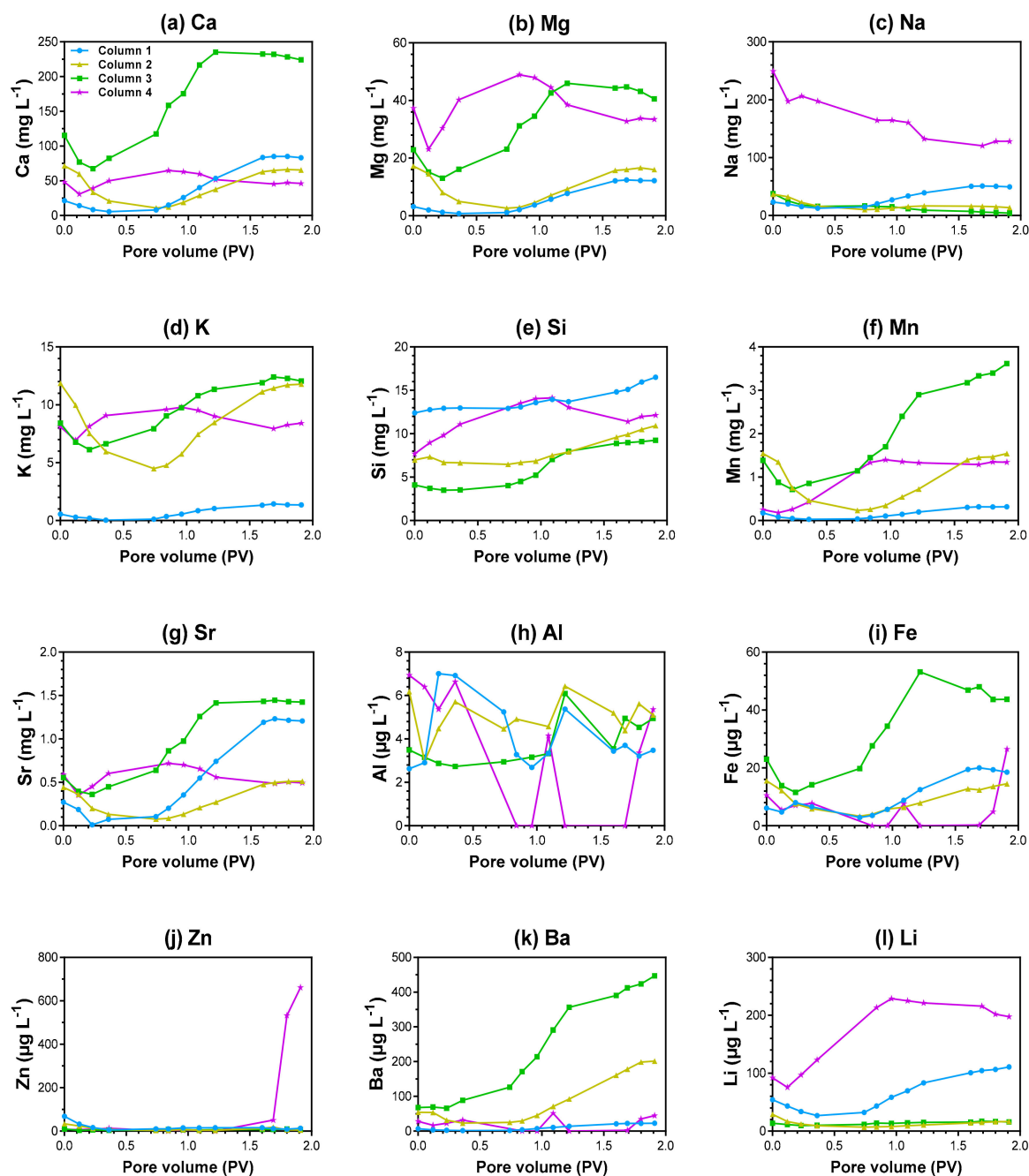


Figure 4. The initial changes in concentration ((a) Ca; (b) Mg; (c) Na; (d) K; (e) Si; (f) Mn; (g) Sr; (h) Al; (i) Fe; (j) Zn; (k) Ba; and (l) Li) up to two pore volumes (PVs) as the CO₂-saturated SGW was introduced into the column (time-series data at the column effluent).

3.2. Spatial Changes of Groundwater Composition

3.2.1. Early Time Changes (after Two Weeks of CO₂ Introduction)

Figure 5 shows the spatial changes in geochemical parameters along the distance of each column after two weeks of CO₂ introduction. It represents the early stage of reactions between the CO₂-saturated SGW and aquifer materials. The spatial changes caused by CO₂ introduction in each column showed that most of the geochemical parameters generally increased along the distance of the column, implying that dissolution of minerals results in increases in groundwater components as well as increases in pH.

The pH values along the distance of the columns generally increased, with the highest increase observed in column 3 (Figure 5). As pH increases, it shifts carbonate equilibria, causing an increase in bicarbonate (HCO₃[−]) concentration and thus increase in alkalinity. This increase in alkalinity may be one of the contributors to the increase in EC in addition to the dissolution of minerals. The Eh values had the opposite trends to those of pH.

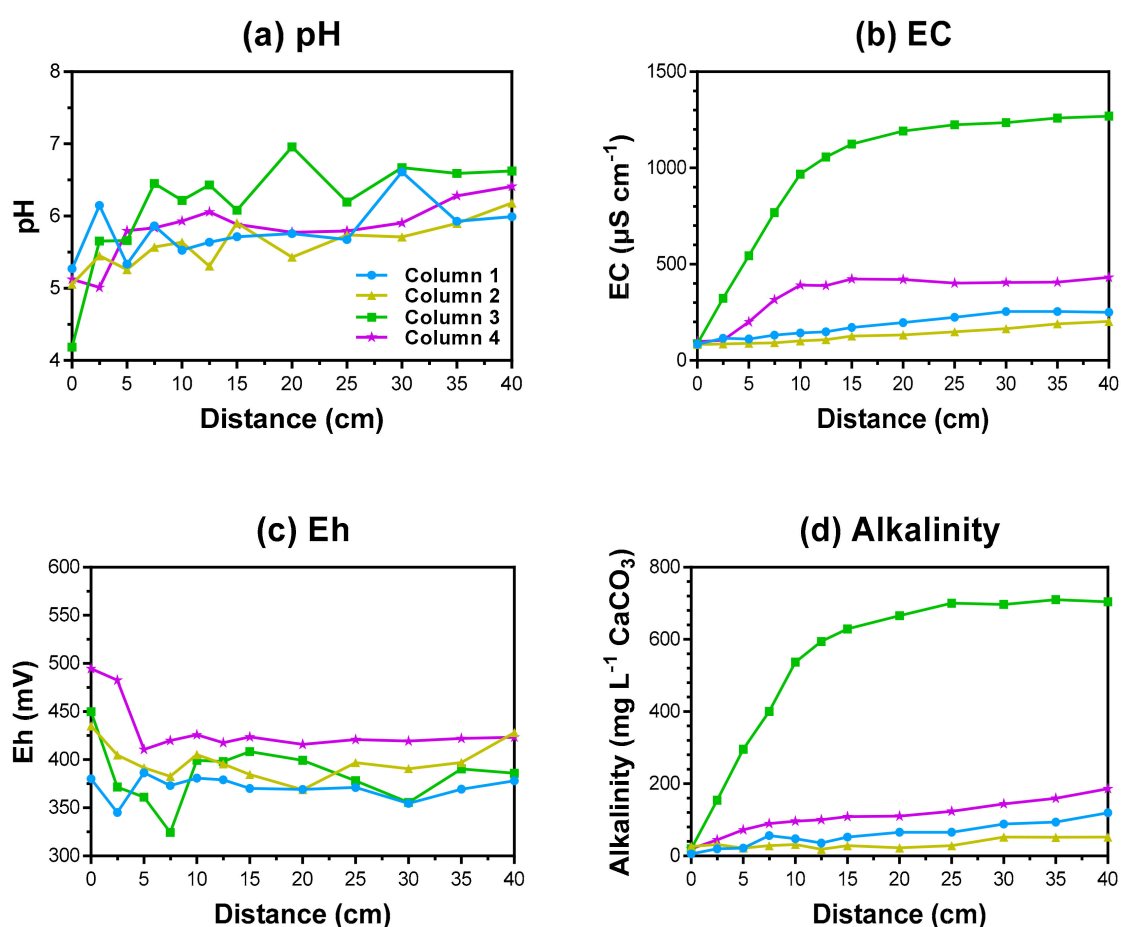


Figure 5. Spatial changes in geochemical parameters along the distance of each column after two weeks of CO₂ introduction ((a) pH; (b) EC; (c) Eh; and (d) alkalinity).

The two columns representing silicate aquifers, columns 1 and 2, showed similar trends for geochemical parameters; however, column 1 showed slightly higher values of EC and alkalinity. For both columns, pH had slightly increasing trends, while Eh had moderate decreasing trends. The lower EC value (Figure 5) and generally low cation concentrations (Figure 6) in column 2 appear to be related to the lowest CEC value (1.33 cmol kg^{−1}) of clean sand (Table 4). Specific surface area value (2.63 m² g^{−1}) was also lower than the EIT and QA soils. In column 3, which was composed of limestone, the pH, EC, and alkalinity showed the highest values among all columns. With the

introduction of the CO₂-saturated SGW, the pH increased up to 6.62 at the effluent of column 3 due to the high buffering capacity of limestone. As a result, alkalinity also increased up to around 700 mg L⁻¹ as CaCO₃ at the column effluent. Due to the properties of carbonate minerals with high solubility and high CEC (16.69 cmol kg⁻¹), the EC also showed a high value close to 1250 µS cm⁻¹. Column 4 showed higher levels of pH, EC, and alkalinity than those in the silicate columns, but lower than those in the carbonate column.

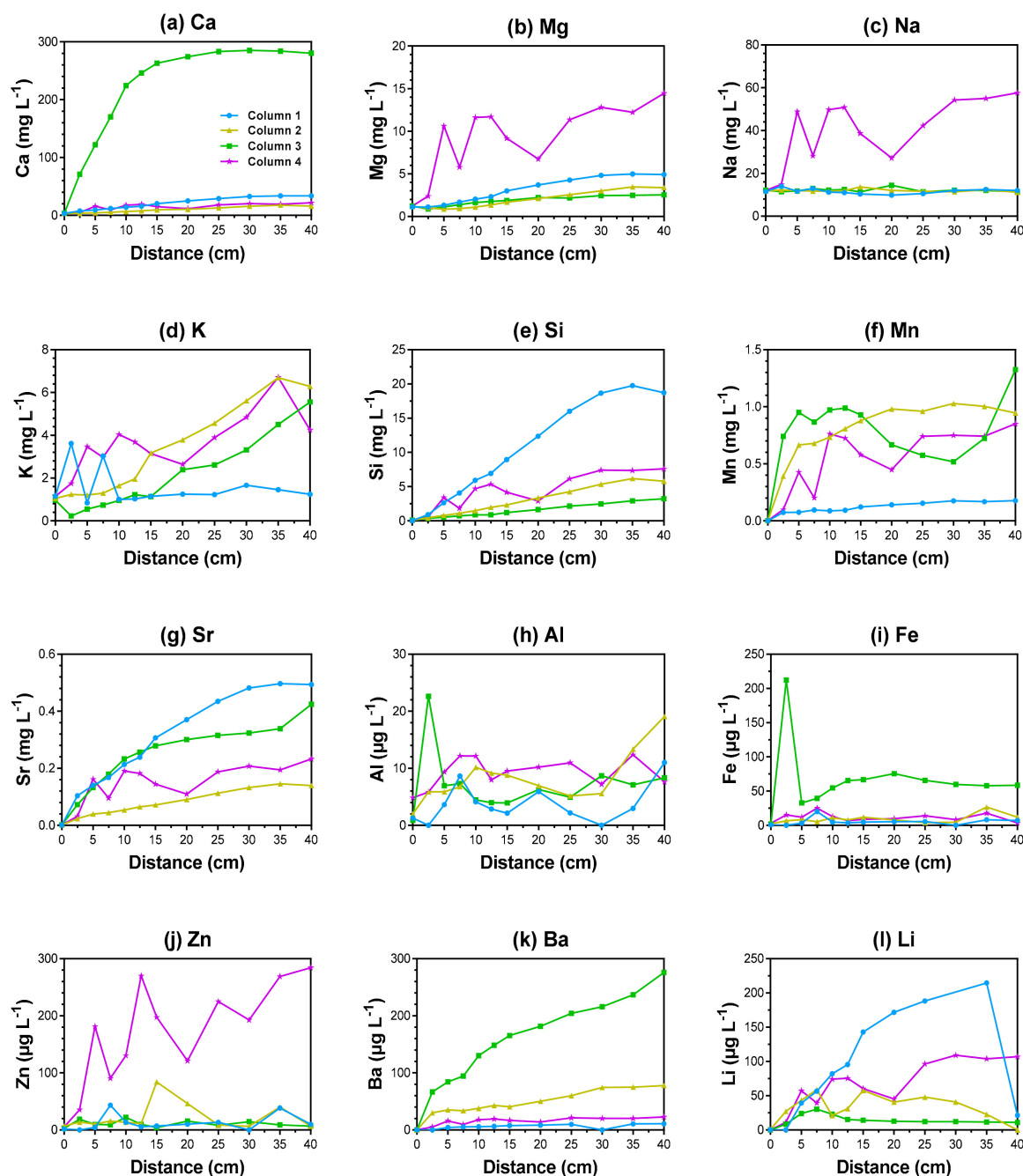


Figure 6. Spatial changes in cation concentrations along the distance of each column after two weeks of CO₂ introduction ((a) Ca; (b) Mg; (c) Na; (d) K; (e) Si; (f) Mn; (g) Sr; (h) Al; (i) Fe; (j) Zn; (k) Ba; and (l) Li).

Figure 6 shows the cation concentrations along the distance of each column. Cation concentrations had generally increasing trends with distance. This is because the dissolution of minerals caused by reactions with the CO₂-saturated SGW increases as the distance increases. The trends in cation concentrations were correlated with those of the EC (Figure 5). In the case of Ca, the concentrations increased in all columns, with the highest concentration observed in column 3. The XRD analysis showed that Ca was contained in all columns to some extent with the presence of plagioclase (Al₃Ca_{0.5}Si₃O₁₁), calcite (CaCO₃), calcium peroxide (CaO₂), and anorthite (Al_{1.52}Ca_{0.52}Na_{0.48}O₈Si_{2.48}) (Table 6). However, CaO weight percentages (wt.%) were only approximately 1% of the total mineral content in columns 1, 2, and 4 (Table 5). In contrast, column 3 showed a very high CaO content of 38.8% (Table 5), consistent with the highest Ca concentration detected: column 3 showed a Ca concentration of nearly 300 mg L⁻¹ compared to lower than 50 mg L⁻¹ in the other columns.

Mg and Na concentrations were highest in column 4, at around 10 mg L⁻¹ and 60 mg L⁻¹, respectively, and this might be affected by cation-exchange in addition to mineral dissolution. Due to the characteristics of the QA soil, which is alluvial soil, the elements such as Mg, Na, and K might be eluted from the soil. In column 1, representing a silicate aquifer, Si concentration was detected up to 20 mg L⁻¹, and the column showed the highest Si concentration among all columns. This is probably due to the high SiO₂ and aluminum silicate content of the EIT soils (Table 4). Mn, Sr, and Al were detected at similar concentrations in all columns, and showed increasing patterns along the distance of the columns. Fe showed the highest concentration in column 3. The abruptly high concentration of approximately 200 mg L⁻¹ at 2.5 cm from the influent end might be an experimental artifact. Zn was detected in the highest concentration at over 100 µg L⁻¹ in column 4. Ba was detected at a concentration over 200 µg L⁻¹ in column 3, which might be associated with carbonate minerals. Li concentration was highest in column 1, probably due to the dissolution of Li-bearing minerals.

3.2.2. Intermediate Time Changes (after 16 Weeks of CO₂ Introduction)

After 16 weeks of CO₂ introduction, the increase in pH in all columns slowed down, except for column 3, which had a high pH buffering capacity (Figure 7). The EC and alkalinity in column 3 were substantially higher than the other columns, although the degree of the increase slightly reduced after 16 weeks of operation. The EC and alkalinity in column 4 decreased to levels similar to those of silicate columns (i.e., columns 1 and 2), indicating that the more soluble minerals had already been substantially consumed or that cation-exchange capacity was exhausted by this stage of the experiment. The reduced generation of alkalinity appears to be caused by the continuous injection of CO₂ for columns 1, 2, and 4, which have low buffering capacities. The Eh values did not show significant trends in any column.

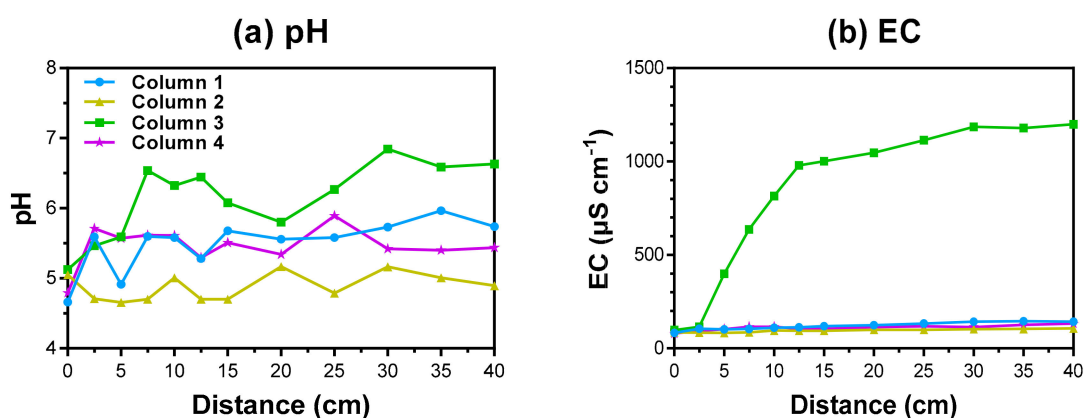


Figure 7. Cont.

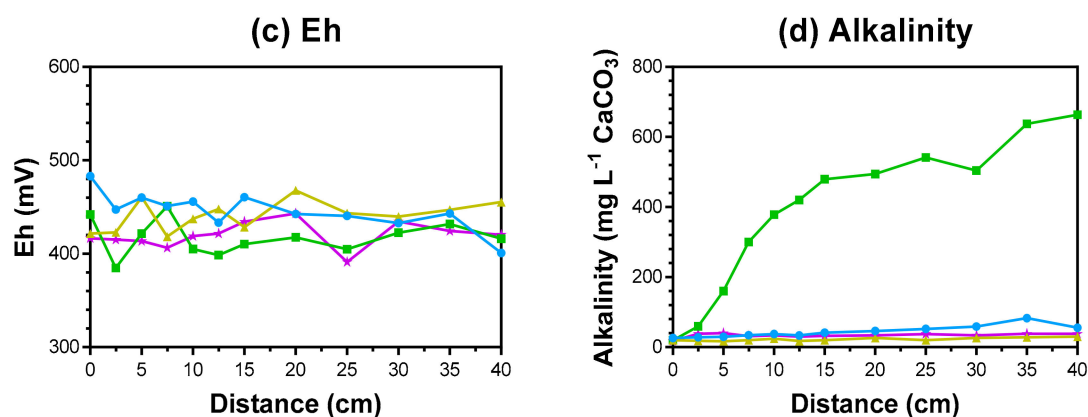


Figure 7. Spatial changes in geochemical parameters along the distance of each column after 16 weeks of CO₂ introduction ((a) pH; (b) EC; (c) Eh; and (d) alkalinity).

The trend of increasing cation concentrations continued for all columns, but the degree of the increase slowed after 16 weeks of CO₂ introduction (Figure 8). Among cations, Al did not show the same trends between the columns. Columns 1 and 2 showed the peak Al concentrations of 135 $\mu\text{g L}^{-1}$ and 50 $\mu\text{g L}^{-1}$, respectively, at 7.5 cm from the influent end and declining concentrations thereafter. The XRF analysis showed that the content of Al₂O₃ in the EIT soil and clean sand was 17.1% and 11.3% (Table 5), respectively, and the XRD analysis showed that plagioclase (Al₃Ca_{0.5}Si₃O₁₁), K-feldspar (KAlSi₃O₈), and high albite (Al₁Na₁O₈Si₃) were dominant minerals in these columns (Table 6). This suggested that concentrations of Al were increased due to the dissolution of alumino-silicate minerals. The decrease in Al concentration in the later part of columns 1 and 2 suggests the precipitation of secondary minerals such as gibbsite [Al(OH)₃] [12,34,42].

Fe was detected in a concentration of more than 200 $\mu\text{g L}^{-1}$ at the effluent of column 3, showing that Fe concentration increased even after 16 weeks of operation. Column 3 was packed with the limestone and sand mixture. The Fe content of fresh limestone was low (0.1%) (Table 5), indicating that the relatively high concentration of Fe was caused by the dissolution of sand containing Fe. The XRD analysis indicated the presence of hematite (Fe₂O₃) in sand (Table 6), supporting that Fe may be derived from the sand. The sudden drop of Fe concentration in the early portion of columns 2, 3, and 4 may indicate precipitation of secondary minerals such as iron oxides. Ba concentration in column 3 increased to 347 $\mu\text{g L}^{-1}$ and Li concentration in column 4 increased to 126 $\mu\text{g L}^{-1}$, suggesting that minor components in groundwater are highly dependent on the characteristics of aquifer materials.

3.2.3. Late Time Changes (after 48 Weeks of CO₂ Introduction)

The geochemical parameters after 48 weeks of column operation showed some differences compared to the behaviors in the early stage of the experiments (i.e., after two weeks of CO₂ introduction). In columns 1, 2 and 4, the EC and alkalinity fell below 100 $\mu\text{S cm}^{-1}$ and 50 mg L⁻¹ as CaCO₃, respectively, whereas in column 3, they decreased slightly but continued to have high concentrations (Figure 9). However, even in column 3, as the experiments proceeded, the increases in EC and alkalinity were reduced compared to the early and intermediate time periods, having maximum EC and alkalinity values of less than 1000 $\mu\text{S cm}^{-1}$ and 600 mg L⁻¹ as CaCO₃, respectively. In addition, decreasing concentrations after the mid-section of the column (20–25 cm) were also observed, indicating that the geochemical conditions now induced the precipitation of secondary minerals, perhaps secondary carbonate minerals, in the latter part of the column.

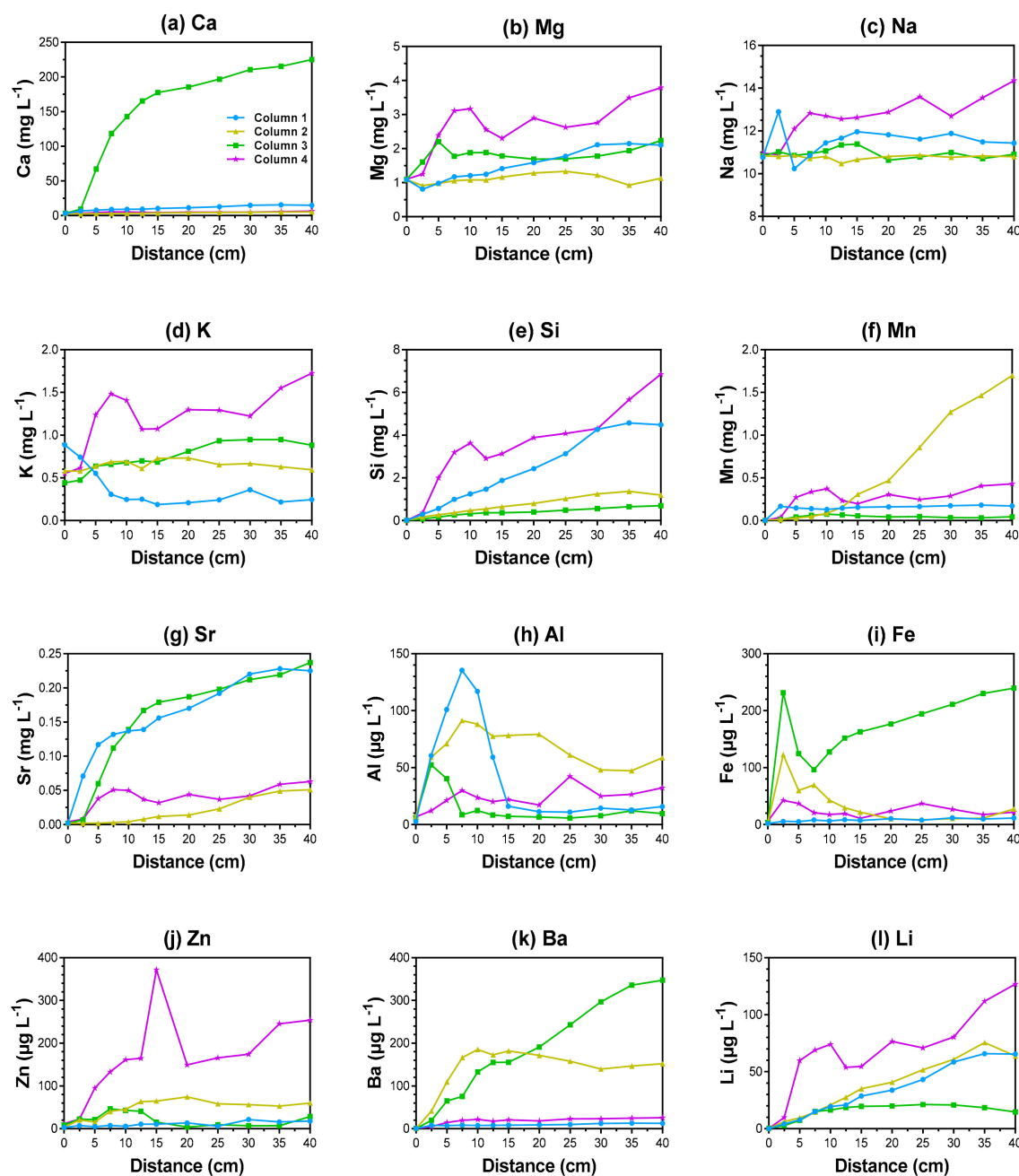


Figure 8. Spatial changes in cation concentrations along the distance of each column after 16 weeks of CO₂ introduction ((a) Ca; (b) Mg; (c) Na; (d) K; (e) Si; (f) Mn; (g) Sr; (h) Al; (i) Fe; (j) Zn; (k) Ba; and (l) Li).

At 48 weeks, columns 1 and 2 (representing silicate aquifers) showed pH values lower than those after two weeks of operation. In column 3 (carbonate column), the pH level was higher than the other columns; however, a pH increase was evident only in the later part of the column at this stage of the experiment. Among all columns, the Eh was lowest in column 3. On the other hand, column 4 showed a low pH of approximately 4.5 for most sections of the column, resulting in a high Eh value of approximately 550 mV. In general, as the experiments proceeded, the EC and alkalinity values in all columns showed lower values than those at early time periods.

For the samples collected after 48 weeks of operation, most cation concentrations had reduced due to the decrease in the quantity of dissolvable cations in the aquifer materials (Figure 10). The tendencies of concentration changes with distance were somewhat different for some cations. In column 3, Ca, K, Sr, Fe, and Ba showed the highest concentrations compared to the other columns. Sr and Ba continued to have increasing concentrations with distance, showing the characteristics of carbonate minerals, which may contain rather high contents of alkaline earth metals such as Ca, Ba, and Sr. In column 1, Al showed distinct characteristics such as the maximum occurred closer to the influent end at early times and moved further into the column as the experiment proceeded (Figures 8 and 10). This suggests that the dissolution front of Al-bearing minerals was moving forward as the pH buffering capacity was exhausted starting from the influent end. The precipitation front of secondary minerals such as gibbsite was thus moving forward accordingly. Zn concentration in column 4 continued to be higher than those in the other columns, suggesting the presence of Zn-bearing minerals such as smithsonite in the QA soil.

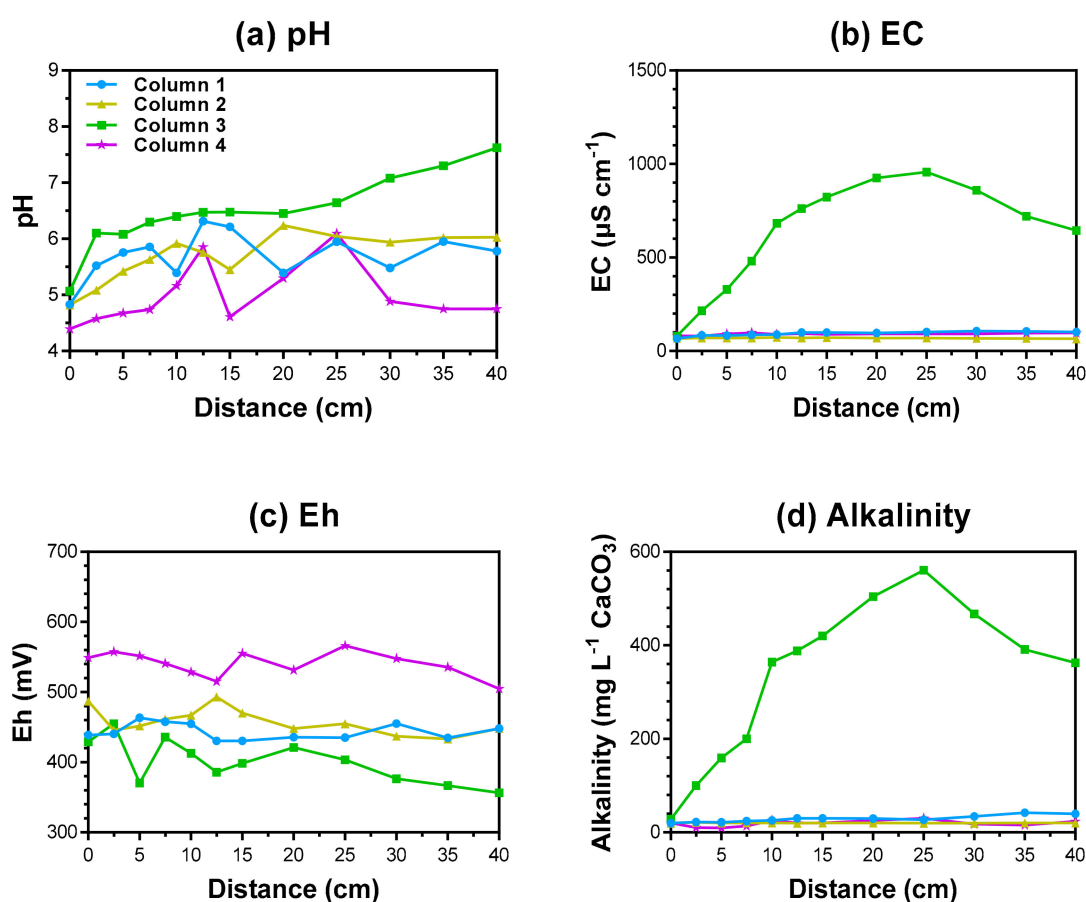


Figure 9. Spatial changes in geochemical parameters along the distance of each column after 48 weeks of CO₂ introduction ((a) pH; (b) EC; (c) Eh; and (d) alkalinity).

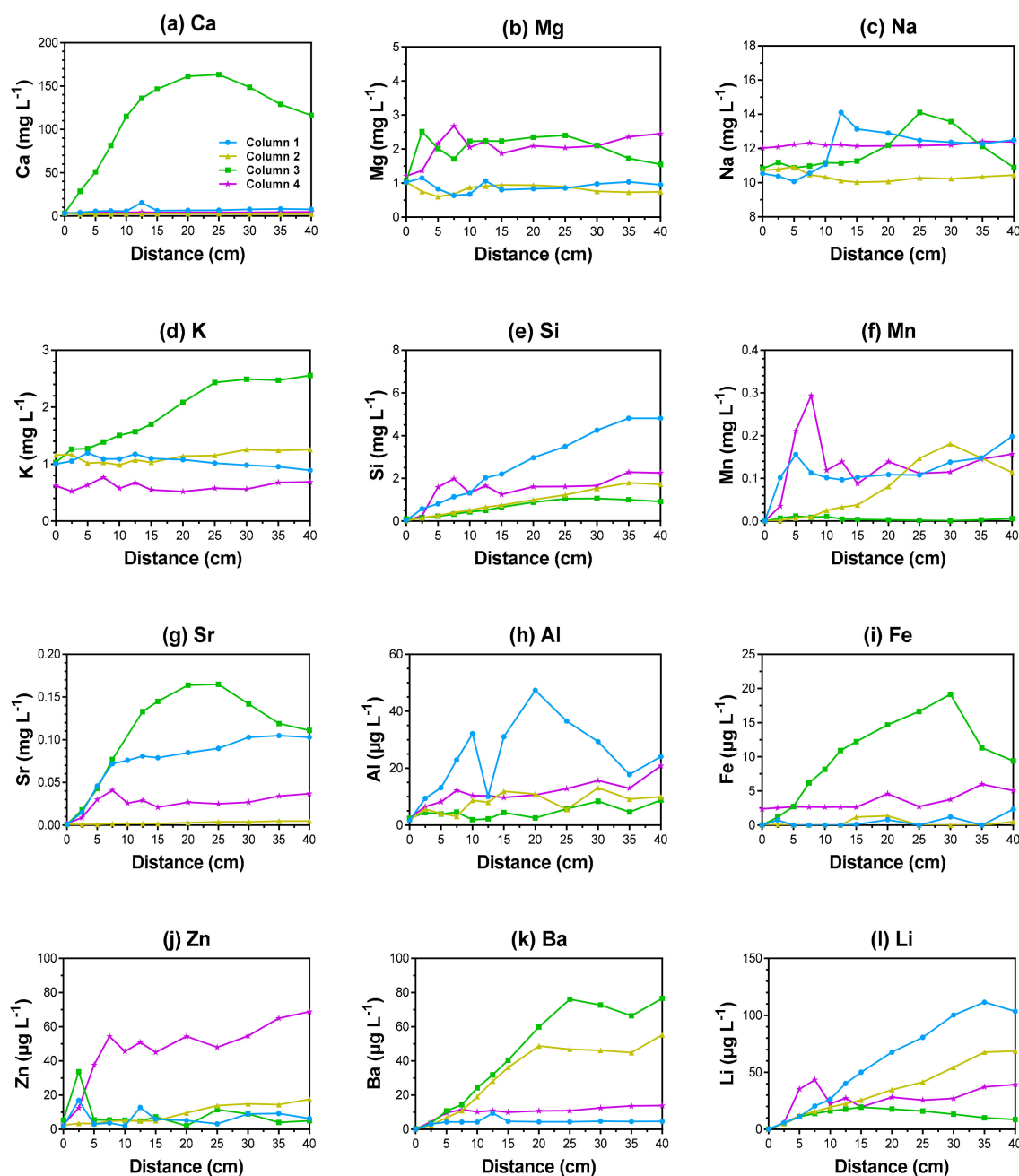


Figure 10. Spatial changes in cation concentrations along the distance of each column after 48 weeks of CO₂ introduction ((a) Ca; (b) Mg; (c) Na; (d) K; (e) Si; (f) Mn; (g) Sr; (h) Al; (i) Fe; (j) Zn; (k) Ba; and (l) Li).

3.3. Trace Elements

To identify specific indicators for the CO₂ leakage in a specific geological material, trace elements such as Cr, As, Se, and Cd were additionally analyzed for the samples at 8, 24, and 48 weeks, and the results for the 8 and 48 weeks are shown in Figures 11 and 12, respectively. Cu and Pb were analyzed only for the 8-week samples; however, the differences among the columns were not significant (not shown).

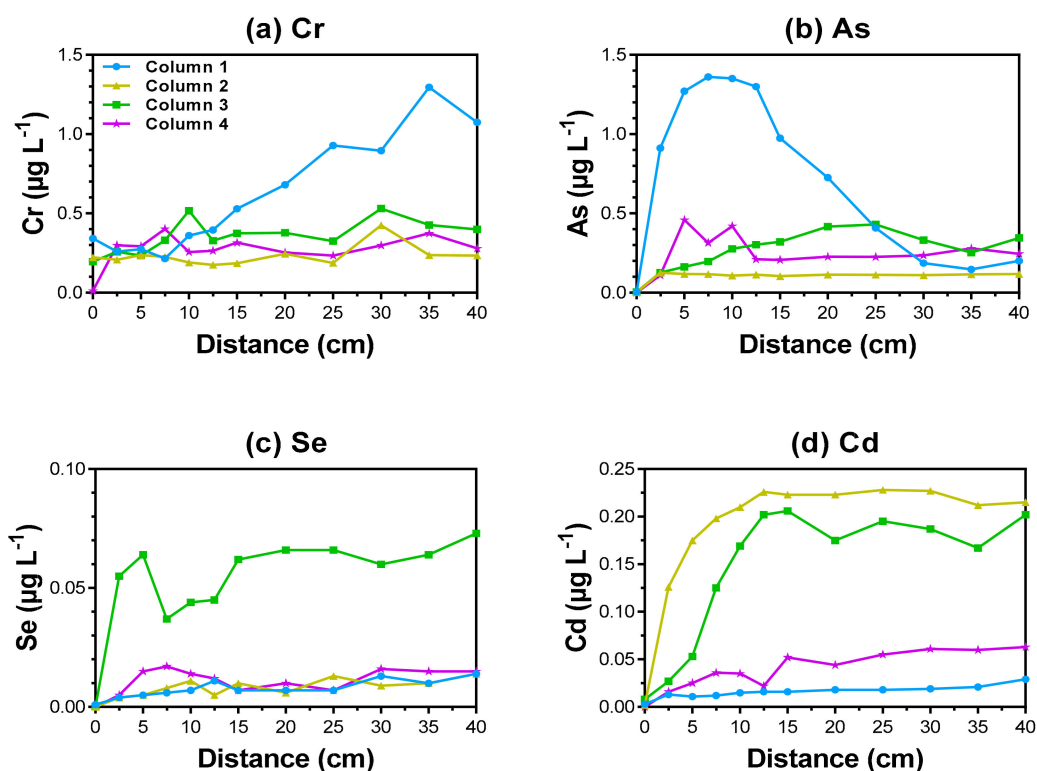


Figure 11. Spatial changes of trace element concentrations after eight weeks of CO_2 introduction ((a) Cr; (b) As; (c) Se; and (d) Cd).

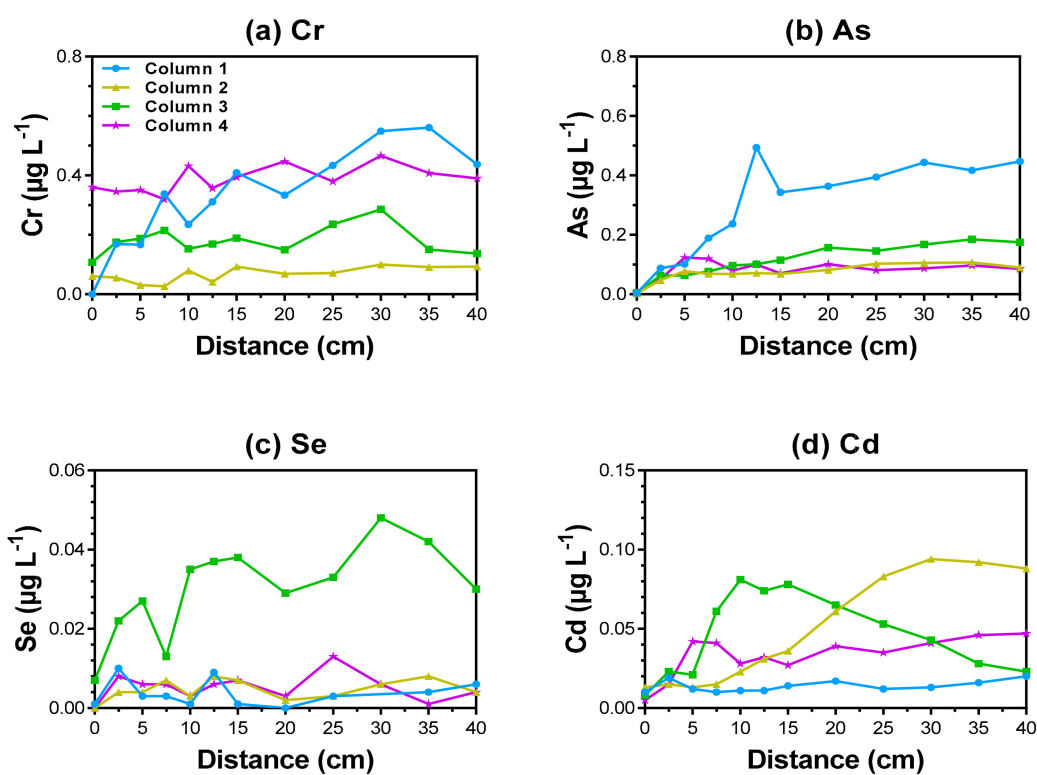


Figure 12. Spatial changes of trace element concentrations after 48 weeks of CO_2 introduction ((a) Cr; (b) As; (c) Se; and (d) Cd).

Cr was detected with a higher concentration in column 1 compared to the other columns, and showed an increasing trend along the distance of the column (Figure 11). As the column operation continued, Cr concentration decreased (Figure 12), but still showed an increase with distance. According to de Orte et al. [43], Cr concentration is generally affected by pH. Richard and Bourg [44] suggested that Cr concentration was high in the highly acidic conditions below pH 5. The pH conditions in column 1 were maintained at pH 5~6 throughout the experimental period, and the low pH conditions might have induced the dissolution of Cr-bearing minerals in the aquifer material. On the other hand, dissolved Cr has a strong adsorption tendency to the surface in a CO₂ saturated environment; the surface complexation of bicarbonate (HCO₃[−]) and Cr³⁺ in an aqueous solution can result in a reduction in Cr concentration [45,46]. These reactions may be controls for Cr concentration in this experimental condition.

The increase in As concentration was most noticeable in column 1. After eight weeks, the As concentration in column 1 showed a rapid increase close to the influent end and then a steep drop after 10 cm from the influent end (Figure 11). This suggested that dissolution and re-precipitation reactions occurred at this stage of the experiment. A control process for As concentration in this column may be the dissolution of As-bearing minerals. The changes in As concentration may also be related to desorption and remobilization processes associated with goethite [47]. The degree of increase in As slowed down as the operation continued (Figure 12).

Se showed the highest concentration in column 3. The Se concentrations in the other columns showed only slight increases along the distance of the columns. In the case of Se for column 1, similar concentrations of 0.05~0.06 µg L^{−1} were maintained throughout the experiment. Cd was detected at relatively higher concentrations in columns 2 and 3. Column 2 showed the increasing concentration patterns with distance, whereas column 3 showed increasing patterns to certain distances and then decreases, suggesting that there may be a sink process for Cd such as adsorption and/or precipitation of cadmium carbonate.

Montes-Hernandez et al. [47] evaluated the adsorption, desorption, and mobilization processes for the trace elements under the CO₂ leakage condition. They showed that, in the case of Se, the degree of desorption in calcite (carbonate) was stronger than goethite (oxide), indicating that the concentration of Se could be high in column 3, which is mainly composed of carbonates. They also suggested that Cd adsorption increases during the calcite dissolution reaction. In fact, column 3 showed a decreasing tendency in Cd concentration as the experiment proceeded, suggesting that adsorption may be a factor for controlling Cd concentration in column 3.

4. Discussion

This study evaluated the geochemical changes of groundwater composition resulting from reactions of leaked CO₂ with various geological media to simulate CO₂ leakage in various aquifer environments. The experiments were conducted systematically with the same experimental conditions, and thus, the results can be used to compare the geochemical behaviors of different geological materials. In general, aquifer materials are classified as silicate and carbonate. Alluvial aquifer materials can be considered as a particular case of geological setting, not based on mineralogical composition. Different geochemical behaviors were anticipated to result from different characteristics of the geological media [7,10,48].

In previous studies, the main characteristic of CO₂ leakage in silicate aquifers was a low pH value resulting from the low buffering capacity of the aquifer materials [15]. In this study, during the initial introduction of CO₂ (within 2 PVs) to the EIT soil and clean sand columns (columns 1 and 2 representing silicate aquifers), the pH value at the column effluent was approximately 6.4 for both columns. However, as the experiment progressed, the pH values at the effluent decreased to approximately 5.5 after 48 weeks. The generally low pH and moderate increase of EC and alkalinity in column 1 were consistent with the previous study of Ha et al. [34], which assessed the geochemical changes for the same EIT soil. In Ha et al. [34], a decrease in pH and increases of EC, alkalinity, and concentrations of Ca, Mg,

Na, K, Li, Mn, Fe, Ni, Co, Sr, and Ba were observed during the introduction of the CO₂-saturated EIT groundwater. They suggested that the dissolution of plagioclase, K-feldspar, K-mica, chlorite, vermiculite, and trace of carbonate minerals caused increases in cation concentrations. Column 2 showed lower EC and cation concentrations than those in column 1, and this is probably due to its much lower CEC and specific surface area. Among these cations, Si, Sr, and Li concentrations were highest in column 1, while K, Mn, and Ba concentrations were relatively high in column 2. For trace elements, Cr and As concentrations were highest in column 1, while Cd concentration was highest in column 2. In the previous studies, it has been shown that as pH was lowered by CO₂ leakage, As adsorption increased on the mineral surface, resulting in lower As concentration in the groundwater [7,49].

The carbonate column showed significant differences compared to the other columns. Previous studies on the effects of CO₂ leakage in carbonate aquifers demonstrated that they have sufficiently high buffering capacity for pH changes, and active reactions such as cation exchange, adsorption, desorption occur as carbonate minerals dissolve [6,18,50]. In fact, in this study, the pH in the carbonate column had the value of 7.8 after 48 weeks, indicating the significant buffering capacity of the carbonate aquifer. EC and alkalinity also showed high values, which is consistent with the characteristics of carbonate minerals [10]. The concentrations of cations such as Sr, Fe, and Ba were higher than those in the other columns, suggesting that these elements are associated with carbonate minerals. This is also consistent with the previous studies, demonstrating that as limestone is dissolved, elements such as Ba, Sr, and Mg may be released or Ca-driven cation exchange can occur due to the increase in Ca concentration, resulting in higher concentrations of additional elements [18]. For trace elements, Cd and Se showed significantly higher concentrations than those in the other columns.

The distinct feature for the alluvium column was the increasing EC, alkalinity, and most cation concentrations until 1 PV, and then a decreasing pattern afterward during the initial introduction of CO₂. The EC, alkalinity, and cation concentrations after two weeks showed increasing patterns with distance, although these tendencies declined over time. This indicates that concentrations of cations such as Mg, Na, K, Si, and Li increase primarily by cation exchange and dissolution reactions at the start of CO₂ introduction, and then decrease thereafter, probably due to adsorption onto the soil surfaces that have a large surface area [29]. This is supported by the fact that the QA soil has high specific surface area (21.10 m² g⁻¹) and relatively high CEC value (12.97 cmol kg⁻¹). Cation-exchange and surface complexation reactions have been recognized as important reaction mechanisms controlling cation concentrations for the reactions of aquifer materials with CO₂ [51,52]. In the alluvium column, Zn showed a considerably higher concentration compared to the other columns. There were no notable indicators among the trace elements in the alluvium column.

Comparing the geochemical behaviors between the early and late stages of the reactions with the CO₂-saturated SGW, rapid and active geochemical changes mostly occurred in the early time period, while some reactions such as carbonate mineral dissolution and resulting pH buffering reactions in column 3, remained consistent throughout the experimental period. It appears that more soluble minerals dissolve first, consuming the pH buffering capacity early and thus resulting in quite low pH conditions, as happened with the silicate and alluvium aquifers. The alluvium showed characteristic breakthrough behaviors for Mg, Na, K, Si, and Li during the initial introduction of CO₂-saturated SGW, and this might be related to the cation-exchange processes. In the later time period, most cation concentrations had declined due to the exhaustion of more soluble mineral contents and it appears that re-precipitation and/or precipitation of secondary minerals may also control the concentrations of cations and trace elements. The major findings for the changes in geochemical parameters and concentrations of major cations and trace elements in each geological medium in early and late reaction stages with the CO₂-saturated SGW are summarized in Table 8.

Table 8. Summary of the major findings for the changes in geochemical parameters and concentrations of major cations and trace elements in each geological medium in early and late reaction stages with the CO₂-saturated SGW.

Column	Reaction Stage	Geochemical Parameters	Major Cations	Trace Elements
Column 1 (EIT soil)	Early stage	pH was lowest (6.4~6.8) during the initial inflow of CO ₂ until 2 PVs. EC and alkalinity were also low. After 2 weeks, pH increased slightly with distance. EC and alkalinity showed the increasing trends with distance, but remained low (below 250 $\mu\text{S cm}^{-1}$ and 120 mg L^{-1} as CaCO ₃ , respectively).	Si concentration was detected up to 20 mg L^{-1} due to the high SiO ₂ content. Ca showed a typical increasing curve with distance, probably due to the dissolution of plagioclase (Al ₃ Ca _{0.5} Si ₃ O ₁₁). Sr and Li also showed the highest concentrations.	Cr concentration was highest among all columns (1.0 $\mu\text{g L}^{-1}$ at the column effluent) and tended to increase as water moved with distance. As concentration was highest among all columns; it showed the peak concentration in the early section of the column, while the concentration dropped sharply thereafter probably due to re-precipitation reaction.
	Late stage	pH dropped to 5.5 at the effluent end. Eh increased by around 50~100 mV. EC and alkalinity were lower than 100 $\mu\text{S cm}^{-1}$ and 50 mg L^{-1} as CaCO ₃ , respectively.	Overall cation concentrations decreased. Si concentrations were still highest among all columns. The location of the peak Al concentration moved towards the effluent end, indicating the advance of the dissolution and precipitation fronts.	Cr and As concentration continued to show the increasing trends with distance, but the maximum concentrations decreased as the experiment proceeded.
Column 2 (Sand)	Early stage	pH was low and similar to that of the EIT column. EC and alkalinity were lowest, probably due to the low CEC (1.33 cmol kg^{-1}) and specific surface area (2.63 $\text{m}^2 \text{g}^{-1}$) of the sand.	The cation concentrations were generally lower than those in the other columns; however, K showed a relatively high concentration due to the relatively high K ₂ O content (3.2%). Mn showed a relatively high concentration (around 1 mg L^{-1}).	Cd concentration was highest (0.2 $\mu\text{g L}^{-1}$) among all column and showed an increasing trend with distance.
	Late stage	pH remained low below 6.0. Eh slightly increased. EC and alkalinity decreased and were still lowest among all columns.	The concentrations of K and Mn, which were highest at 2 weeks, have decreased considerably. However, Ba was still found to be relatively high, close to 50 $\mu\text{g L}^{-1}$ and similar to that of column 3.	As the experiment proceeded, the maximum concentration of Cd decreased, but it still showed the increasing trend with distance. The increasing front moved further towards the effluent end.
Column 3 (Carbonate)	Early stage	During the initial CO ₂ inflow, limestone dissolution resulted in an EC value above 1000 $\mu\text{S cm}^{-1}$. Alkalinity also showed the highest concentration. After 2 weeks, the column continued to show a high EC of around 1250 $\mu\text{S cm}^{-1}$ and an alkalinity close to 700 mg L^{-1} as CaCO ₃ .	High content of carbonate minerals (e.g., calcite) (CaO content of 38.8%) resulted in a Ca concentration of nearly 300 mg L^{-1} . Higher levels of Fe and Mn were detected. Ba was detected at a concentration over 200 $\mu\text{g L}^{-1}$.	Cd was detected at high concentration. Se showed a significantly higher concentration (over 0.06 $\mu\text{g L}^{-1}$) than those of the other columns.
	Late stage	Due to the high buffering capacity, pH still maintained a value higher than 6.0 and increased up to 7.6 in the effluent end. Eh was lowest among all columns, showing below 400 mV. EC and alkalinity were still high, although somewhat decreased as the experiment proceeded.	Ca, K, Sr, Fe, and Ba showed higher concentrations compared to those in the other columns. They were mostly related to the characteristics of carbonate minerals, which have high contents of alkaline earth metals such as Ca, Ba, and Sr.	The Cd concentration showed an increasing pattern in the early section of the column, but a decreasing trend after 15 cm from the influent end due to cadmium sink processes. Se concentration did not show much change as time progressed, and maintained the highest concentration among all columns.

Table 8. Cont.

Column	Reaction Stage	Geochemical Parameters	Major Cations	Trace Elements
Column 4 (QA soil)	Early stage	During the initial CO ₂ inflow, cation-exchange reactions related to the high specific surface area (21.10 m ² g ^{−1}) and CEC (12.97 cmol kg ^{−1}) appeared to be rapid. The pH dropped sharply. EC and alkalinity increased to 1 PV and then decreased thereafter. After 2 weeks, pH, EC, and alkalinity were higher than those in the silicate columns and lower than those in the carbonate column.	During the initial CO ₂ inflow, Mg, Na, K, Si, and Li showed characteristic behaviors, which might be related to cation-exchange processes. Zn showed a delayed increasing behavior. After 2 weeks, concentrations of Mg, Na, and K increased with distance and showed the highest concentrations. Zn was detected at the highest concentration over 100 µg L ^{−1} .	Most of trace elements were detected at low concentrations, with no notable indicators detected. The trends for concentrations with distance were not significant, except for the slight increase for Cd.
	Late stage	The pH fell to below 5. The EC and alkalinity levels were also low, similar to those of the silicate columns.	The concentrations of most cations decreased and showed little trends with distance. However, Zn showed a pattern of increase with distance and consistently higher concentrations compared to those in the other columns.	The concentration of Cr was shown to be similar to that of the early stage, and was relatively higher than those in the other columns.

5. Conclusions

In this study, geochemical changes in groundwater composition resulting from reactions of CO₂-saturated groundwater with various aquifer materials were evaluated. Four different geological materials were packed into columns: EIT soil; clean sand; sand and limestone mixture; and QA soil. Temporal and spatial geochemical changes were systematically analyzed and compared through the long-term column experiment, which was operated for close to one year. Indicators for CO₂ leakage in specific aquifer materials were monitored and identified to be used for assessing and managing the potential impacts of CO₂ leakage in a given CCS site. In particular, this study evaluated the geochemical changes at early and late reaction times, and thus can compensate for the limited findings of short-term studies.

The EIT and sand columns representing silicate aquifers showed a typical decrease in pH, and increases of EC and alkalinity upon the initial contact with CO₂-saturated groundwater. The increases in EC and alkalinity were relatively low compared to those in the carbonate and alluvium columns. Most cation concentrations had similar tendencies, while Si, Sr, and Li showed the highest concentrations in the EIT column. For trace elements, Cr and As concentrations were highest in the EIT column, while Cd concentration was highest in the sand column. As the columns were continuously exposed to CO₂, pH further reduced, and decreasing EC and alkalinity values were observed due to the low pH buffering capacity that is characteristics of silicate minerals.

In the carbonate column, while pH slightly decreased during the initial inflow of CO₂-saturated groundwater, very high EC and alkalinity values and high cation concentrations were observed due to the dissolution of carbonate minerals. The increases in concentration were relatively rapid compared to those of the silicate columns. After the long-term operation of the column, the carbonate column continued to show a high pH value due to its sufficiently high pH buffering capacity. EC and alkalinity also maintained at high values. The alkaline earth metals such as Ca, Mg, Ba, and Sr were also detected at high concentrations, and this is considered to be associated with the dissolution of carbonate minerals. Among the trace elements, Cd and Se concentrations were high in the carbonate column.

During the initial introduction of the CO₂-saturated groundwater, the QA column showed distinctive breakthrough patterns for the changes in the concentrations of cations such as Mg, Na, K, Si, and Li, indicating that cation-exchange reactions may be important processes during the early reaction stage. This is supported by the high specific surface area and relatively high CEC value in the alluvium. The spatial distributions of EC, alkalinity, and cation concentrations showed increasing patterns with a distance similar to those in the other columns. As the column operation continued, the increases in concentration declined, and this pattern was similar to the other columns.

Through the long-term column experiments of this study, it was shown that changes in geochemical parameters and cation concentrations are most pronounced during the initial stage of the CO₂ leakage due to the dissolution of more soluble mineral contents and cation-exchange processes. Later, the rates of increase with distance declined considerably due to the exhaustion of the more soluble minerals and cation-exchange capacity. The carbonate aquifer maintained a high buffering capacity for a considerably long time due to the presence of carbonate minerals. The behaviors for geochemical parameters and concentrations of cations and trace elements were thus quite different than for the other types of aquifer materials. The results of this study emphasize that mineralogical composition of an aquifer is very important in response to the leaked CO₂ from a geological storage site. This study provides a general guideline for assessing potential impacts of CO₂ leakage in various aquifer materials, and thus will be useful for developing management strategies suitable for each geological repository.

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