Appl Biol Chem (2018) 61(6):617–623
https://doi.org/10.1007/s13765-018-0398-9

Online ISSN 2468-0842
Print ISSN 2468-0834

ARTICLE

Effect of CO_2 exposure on the mobility of heavy metals in submerged soils

Eun Hea Jho[1] · **Youngho Youn**[1] · **Seong Ho Yun**[1]

Received: 17 August 2018 / Accepted: 12 September 2018 / Published online: 20 September 2018

Abstract Increasing atmospheric carbon dioxide (CO_2) concentration can affect CO_2 level in soil, and this, in turn, may cause changes in soil chemical properties. This study investigated the effect of CO_2 exposure on pH and heavy metal mobility in submerged soils. Laboratory-scale batch tests were carried out using two soil samples with different initial pH conditions (A: 5.3; B: 6.3). The changes in the pH values of the soil solutions (i.e., water layer above soil) of the CO_2-affected soil samples and controls with time were not significant (p value > 0.05) with the both soil samples, and this may be attributed to the formation of bicarbonate, which may provide a buffering capacity. The effect on heavy metal mobility was different in the soil samples A and B. With the soil sample A, the soil heavy metal concentrations were generally lower in the CO_2-affected soil than in the controls. Accordingly, the soil solution heavy metal concentrations were changed. With the soil sample B, the soil heavy metal concentrations of the CO_2-affected soil and control did not show a significant difference (p value > 0.05). This can be partially attributed to the dissolution of carbonates that generate bicarbonates, and this is supported by the lower soil Ca concentration in the CO_2-affected soil. Overall, the results suggest that the elevated CO_2 level in submerged soils may have different effects on the soil chemical properties, and this necessitates continuous research efforts in order to manage and conserve soil environment under conditions of increasing atmospheric CO_2 concentration.

Keywords Carbon dioxide · Heavy metal · pH · Submerged soil

Introduction

The concentration of greenhouse gases in the atmosphere has been increasing, and the CO_2 concentration measured by the National Oceanic and Atmospheric Administration is now higher than 400 ppm (http://www.esrl.noaa.gov/gmd/ccgg/trends/full.html retrieved in June 2018). Atmospheric carbon accumulates in soil through plant photosynthesis, and soil carbon is released to atmosphere through microbial respiration. Soil is considered to be the largest pool of terrestrial organic carbon; thus, a small increase in soil carbon storage may bring a substantial increase in carbon storage potential [1]. A previous study reported that the increase in atmospheric CO_2 increases soil carbon input by stimulating plant growth and, at the same time, increases microbial decomposition of old and new soil carbon [2]. This means that, with increasing atmospheric CO_2 level, the possible role of soil as a carbon storage may not be significant due to the counteracting microbial response [2].

In order to determine the effect of increasing atmospheric CO_2 concentration on the terrestrial environment, previous studies largely focused on the carbon balance in the terrestrial environment [3–5]. So, the studies on the effect of soil CO_2 level increase on the soil environment are limited to the changes in the soil carbon cycle (i.e., flux) and plant growth, which is related to food production [6, 7]. For example, under the increased atmospheric CO_2 level, root production of pine seedlings and carbon losses through the root system were increased [7]. Also, climate change has possibility to increase risks of mycotoxins in crops and food [8]. However,

---

✉ Eun Hea Jho
ehjho@hufs.ac.kr

[1] Department of Environmental Science, Hankuk University of Foreign Studies, 81 Oedae-ro, Mohyeon-eup, Cheoin-gu, Yongin-si, Gyeonggi 17035, Republic of Korea

there are only limited studies investigating the effect of increasing atmospheric CO_2 level on soil chemical properties. One study observed that the changes in chemical properties such as pH and organic matter of the submerged soil due to elevated CO_2 were significantly greater than the changes in the un-submerged soil, suggesting that increasing atmospheric CO_2 level can be of more concern in paddy soils [9]. Also, the increased atmospheric CO_2 level may change the fate and bioavailability of heavy metals in soil [10, 11]. For example, the increase in the marine sediment CO_2 level due to CO_2 leakage from marine carbon capture and storage system resulted in the sediment acidification, and consequently, heavy metals such as cobalt (Co), copper (Cu), zinc (Zn), lead (Pb), and iron (Fe) were released, which, in turn, inhibited diatom growth [10, 12]. Thus, increasing bioavailability of heavy metals in soil may increase toxic effects on crops grown in soil. Furthermore, microbial activities, particularly carbonic anhydrase activities involved in hydration and dehydration of CO_2, can be affected by the increased atmospheric CO_2 level, and this, in turn, can affect mineral dissolution and carbonate formation in soil environment [13]. Dissolution of minerals and metals into soil solution due to increased CO_2 levels in soil may have adverse effects on groundwater quality, particularly on groundwater used as drinking water [14].

Previous studies showed that the increase in soil CO_2 level can change soil physicochemical properties, and the soil solution concentrations of heavy metals can be affected. The changes may be more significant with rice paddies as soil in rice paddies is often flooded with water. The importance of soil conservation is getting more attention with progressing climate change, as soil environment is directly related to food security. One study looked at the effect of increasing atmospheric CO_2 concentration on the availability of mineral nutrients in soil under both submerged and un-submerged conditions [9]. However, the effect of soil CO_2 level increase on the fate of heavy metals in submerged soil has not been studied yet. Therefore, it is necessary to investigate the effect of the increased soil CO_2 level on the mobility of heavy metals in submerged soil. Laboratory-scale batch tests were carried out to simulate the submerged soil environment that is continuously exposed to CO_2. Soil samples with different initial pH conditions were used to investigate the effect of initial soil pH on soil response to the increased soil CO_2 level.

Materials and methods

Soil samples

Soil samples with different pH conditions were collected, and the soil samples were air-dried and then sieved through a 2-mm mesh [15]. The soil sample A texture was loamy sand, and the pH and organic matter content were 5.3 and 2.7%, respectively. The cation-exchange capacity (CEC) was 18 cmol kg^{-1}. The background concentrations of Cu, Pb, arsenic (As), Zn, and cadmium (Cd) were 58, 26, 9.5, 110, and 3.5 mg kg^{-1}, respectively. The soil sample B texture was loamy sand, and the pH and organic matter content were 6.3 and 10%, respectively. The CEC was 19 cmol kg^{-1}. The background concentrations of Cu, Pb, As, Zn, and Cd were 13, 42, < detection limit, 94, and < detection limit mg kg^{-1}, respectively.

Experimental setup

The soil sample (1000 g) was placed in a rectangular reactor (22 cm wide, 15 cm long, 12 cm high), and deionized water (1000 mL) was added to simulate a submerged soil environment. Carbon dioxide was injected from the bottom of the reactor at 35 mL min^{-1} for 25 days to the soil sample A. Based on the changes in the soil solution pH with the soil sample A, the CO_2 exposure period was increased to 40 days for the soil sample B to see whether a longer exposure has a different result. The reactor without CO_2 injection was used as a control. With the soil sample A, the CO_2-affected soil samples were prepared in triplicate, while a single sample was prepared for the controls. Single sample was used for the soil sample B. Changes in the soil metal concentrations and soil solution pH and metal concentrations were monitored. In this study, the soil solution indicates the water above the soil layer.

Analytical methods

The soil solutions were sampled and filtered through 0.45-μm syringe filters. The soil solution pH was measured using a pH meter (Mettler-Toledo GmbH S603, Switzerland). The inorganic carbon (IC) concentrations of the soil solutions were measured using TOC (TOC-L, Shimadzu, Kyoto, Japan). The changes in the soil metal concentrations [Cu, Zn, Pb, Fe, Cd, and As] and calcium (Ca) concentrations were determined by using ICP-OES (ICAP 7400 Duo, Thermo Scientific, Waltham, MA, the USA) after extraction following the Korea Standard Test Method for Soil [16]. The detection limits of Cu, Zn, Cd, Pb, Fe, As, and Ca were 0.002, 0.002, 0.001, 0.045, 0.001, 0.004, and 0.016 mg L^{-1}, respectively. The statistical analysis (i.e., *t* test, one-way ANOVA) was done using SPSS (v 21).

Results and Discussion

Effect of CO_2 increase on soil solution pH

Figure 1 shows the changes in the soil solution pH with continuous exposure to CO_2 in the soil samples A and B.

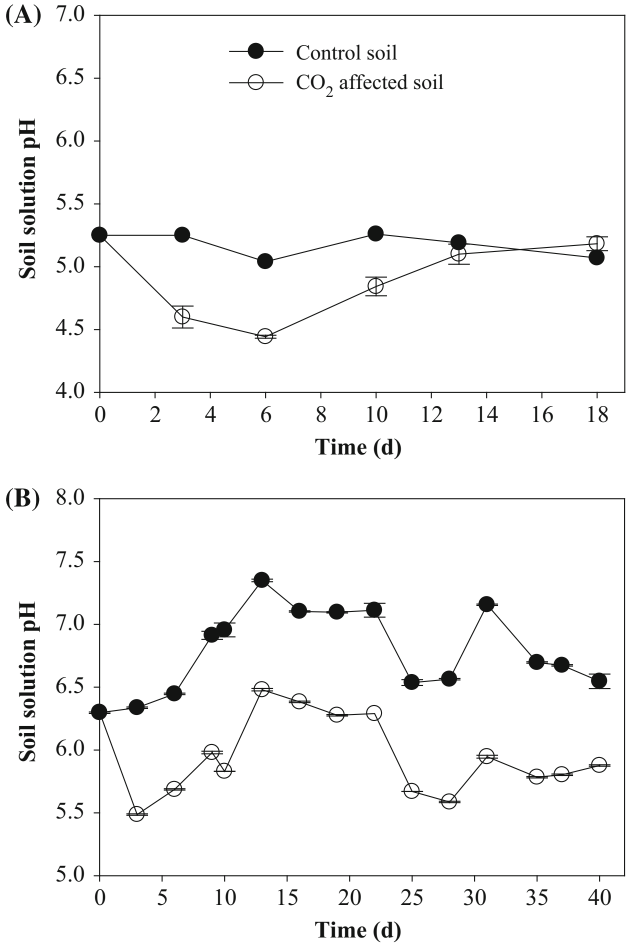

Fig. 1 Changes in the soil solution pH in (**A**) the soil sample A over 18 days of the 25-day CO_2 exposure period and (**B**) the soil sample B over the 40-day CO_2 exposure period. The control soil data are a single sample measurement for the soil sample A, while the others are average values of triplicate samples

The initial soil solution pH of the soil sample A was slightly acidic (i.e., 5.3), which was dropped by 0.8 pH unit to 4.4 after 6 days, but the solution pH gradually retrieved its initial pH level of 5.2 after 18 days (Fig. 1A). The control soil solution pH was almost constant over 18 days. The changes in the soil solution pH of both the control and CO_2-affected soil samples were not significant (p value > 0.05). On the other hand, the control soil solution pH of the soil sample B gradually increased from 6.3 to 7.4 in the first 13 days and then decreased slowly to reach the initial pH level (Fig. 1B), and the overall change was not statistically significant (p value > 0.05). The CO_2-affected soil solution pH was dropped to 5.5 after 3 days, and then, it retrieved its initial pH level after 13 days (Fig. 1B). The soil solution pH then gradually decreased to 5.9 over the rest of the reaction period (Fig. 1B). But the overall changes in the soil solution pH with time were not statistically significant (p value > 0.05). Thus, it can be assumed that the short-term changes in the soil solution pH can be expected with exposure to CO_2; however, the soil solution pH changes were not significant after a relatively long-term exposure to CO_2. However, the pH values of the CO_2-affected soil solution were lower than that of the control on the 40th day (i.e., the end of exposure period; Fig. 1B).

The initial lower solution pH values of the CO_2-affected soil than the control soil can be explained by the generation of H^+ from the HCO_3^{2-} generated due to CO_2 injection, and this suggests possibility of soil acidification with the presence of additional CO_2 in the soil environment. This may bring changes in mobility of metals and ions in soil [11]. Previous studies reported different observations regarding soil pH changes with CO_2 injection. For example, a slight increase in pH (0.5 pH units, p value < 0.05) [17] or an insignificant change in pH [18] has been reported, while other researchers observed a decrease in soil pH [9, 19, 20].

The negligible overall change in the soil solution pH of the soil samples A and B over the CO_2 exposure period may be attributed to the dissolution of carbonates and/or

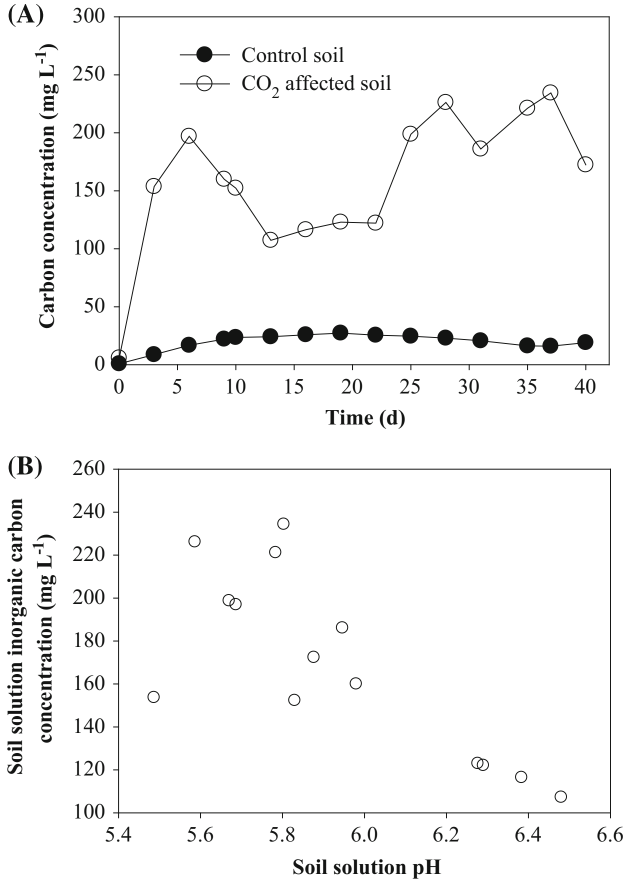

Fig. 2 (**A**) Changes in the soil solution inorganic carbon (IC) concentration over the 40-day CO_2 exposure period and (**B**) correlation between the soil solution pH and soil solution IC concentration for the soil sample B

organic matter [21]. Furthermore, the CO_2 injection may promote the formation of bicarbonate in the soil solution, which may provide a buffering capacity. This is supported by the changes in the IC concentrations of the soil B solution (Fig. 2A). The IC concentrations of the control soil (i.e., without CO_2 injection) gradually increased to 27 mg L^{-1} over 9 days and were kept at a similar level (21 mg L^{-1}, on average) for the rest of the exposure period (Fig. 2A). On the other hand, the IC concentration of the CO_2-affected soil solution rapidly increased to 200 mg L^{-1} in 6 days, suggesting the contribution of the added CO_2. The IC concentration had another peak after 28 days (Fig. 2A). The changes in the TOC concentration of the soil sample B were not significant (p value > 0.05). This suggests that the injected CO_2 was involved in the formation of carbonic acid that is in equilibrium with bicarbonate in the soil solution. The formation of bicarbonate, in turn, may result in an increase in the IC concentration of the soil solution. Also, the buffering capacity of the soil solution increases with the bicarbonate formation. As can be seen in Fig. 2B, the soil solution IC concentration decreased as the CO_2-affected soil solution pH increased, and they showed a negative correlation ($R^2 = 0.90$, p value = 0.000). This agrees with the increasing fraction of bicarbonate with increasing pH in the carbonic acid-bicarbonate equilibrium system. Also, these results support the formation of bicarbonate in the CO_2-injected reactors.

Effect of CO_2 injection on soil metal concentrations

Figure 3A shows the concentrations of the major heavy metals in the soil sample A with and without the 25-day CO_2 exposure period. When compared to the control soil (i.e., without CO_2 exposure), the heavy metal concentrations of the CO_2-affected soil were generally lower, except for Cd and Zn where negligible changes were observed (Fig. 3A). The decreases in Pb, As, Cu, and Fe concentrations were 32, 18, 20, and 14%, respectively (Fig. 3A). This indicates that heavy metals in the soil sample seem to be released with CO_2 exposure. This may be supported by the soil solution heavy metal concentrations (Fig. 3B–D). The soil solution Pb concentration increased in the first

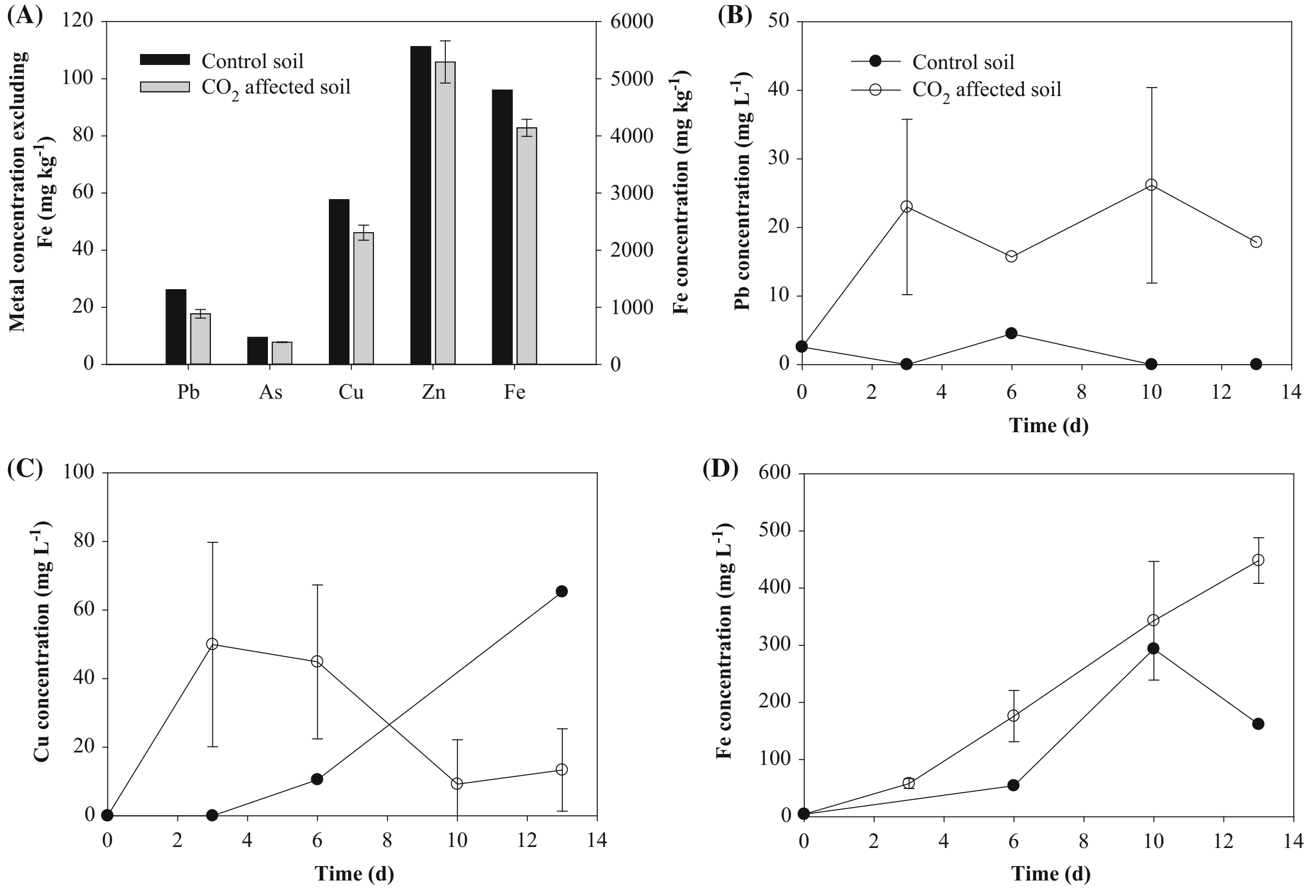

Fig. 3 Changes in (**A**) the heavy metal concentrations of the soil sample A after 25-day exposure to CO_2, (**B**) the soil solution Pb concentration, (**C**) the soil solution Cu concentration, and (D) the soil solution Fe concentration in the first 13 days of the 25-day CO_2 exposure period. The control soil data are a single sample measurement, and the CO_2-affected soil data are an average of triplicate samples

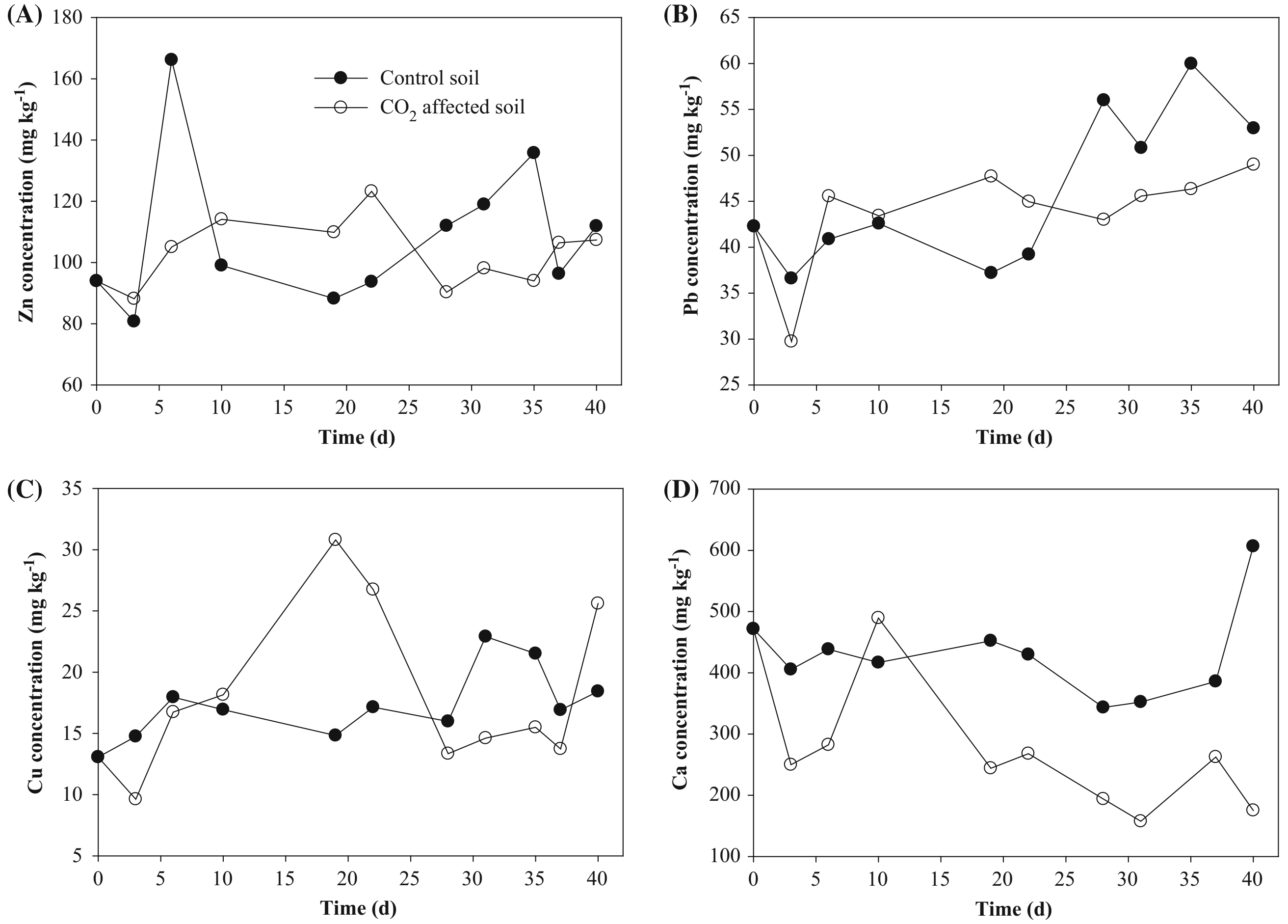

Fig. 4 Changes in the (**A**) Zn, (**B**) Pb, (**C**) Cu, and (**D**) Ca concentrations in the soil sample B over the 40-day CO_2 exposure period. The data are a single sample measurement

3 days and then was maintained at a similar level for the CO_2-affected soil sample, while the change in the Pb concentration of the control soil solution was negligible (Fig. 3B). The average soil solution As concentrations were similar in the control and the CO_2-affected soil samples (data not shown). The soil solution Cu concentration in the CO_2-affected soil sample was increased initially and then decreased (Fig. 3C). On the other hand, the solution Cu concentration of the control soil sample kept increasing with time (Fig. 3C). The initial increase in the soil solution Cu concentration in the CO_2-affected soil sample may be attributed to the initial decrease in pH (Fig. 1B) promoting the release of Cu, and the subsequent decrease in the Cu concentration may be due to the formation of $CuCO_3$, which is stable under high CO_2 pressure and pH between 4 and 8 [22]. The soil solution Fe concentration of the CO_2-affected soil samples and the control sample kept increasing with time, but the Fe concentrations were lower in the control sample (Fig. 3D). Overall, the lower soil metal concentrations in the CO_2-affected soil sample could be related to the higher soil solution metal concentrations, suggesting potential changes in heavy metal fate in soils exposed to CO_2. The soil solution metal concentrations generally increased in the early stage of the CO_2 exposure period, and during this period, the soil solution pH was lower in the CO_2-affected soil sample (Fig. 1A). Thus, the decrease in the soil metal concentrations (Fig. 3A) can be attributed to the lower pH conditions. In addition, although the changes in the Zn concentration were not statistically significant, the average Zn concentration was decreased with CO_2 exposure (Fig. 3A). The decrease in the soil Zn level is likely to suggest an increase in the soil solution Zn level. Previous study showed that the available Zn increased with exposure to the elevated CO_2 level [9].

Figure 4 shows the changes in the concentrations of Zn, Pb, Cu, and Ca in the soil sample B. Unlike the soil sample A, the heavy metal concentrations in the control soil and the CO_2-affected soil samples did not show a significant difference (p value > 0.05; Fig. 4). Also, the changes in the concentrations with time were not significant (p value > 0.05), except for Pb, which showed a weak positive linear relationship ($R^2 = 0.20$, p value = 0.016; Fig. 4B). Given that the average pH values were lower in the CO_2-affected soil sample (Fig. 1B), lower soil metal concentrations can be expected due to the dissolution of heavy metals at lower pH conditions. However, this was not the case with the soil sample B. The CO_2 injection to the soil sample B did not have a significant effect on the heavy metal mobilization (Fig. 4). This can be partially attributed to the negligible overall change in the pH during the 40-day CO_2 exposure period (Fig. 1B). Previous study used the Ca concentrations to detect CO_2 leakages of CCS [23], so the changes in the soil Ca concentrations were compared (Fig. 4D). In the CO_2-affected soil, the Ca concentration was decreased in the first 3 days and then maintained at a similar level (Fig. 4D). Although the changes with time were not significant, the Ca concentration in the CO_2-affected soil sample showed a decreasing trend over the 40-day CO_2 exposure period. Similarly, a decrease in Ca was observed in the soil exposed to elevated CO_2 levels [9]. On the 40th day, the Ca concentration was lower in the CO_2-affected soil than in the control soil (Fig. 4D). This may suggest the dissolution of Ca-bearing carbonates, which might provide a buffering capacity [21]. The buffering capacity provided by the bicarbonates generated may explain the similar heavy metal concentrations in the CO_2-affected and control soil samples (Fig. 4).

The results show that the soil solution pH values seem to decrease initially when soil is exposed to CO_2; however, after a relatively long-term CO_2 exposure, the soil solution pH changes with time were not significant under the studied conditions. This may largely be attributed to the bicarbonate formation due to the CO_2 injection and/or dissolution of carbonates that can either provide a buffering capacity or form metal complexes. Because different soils have different chemical properties, the fate of heavy metals in different soils in response to the exposure to elevated CO_2 levels can be different as observed in this study. With the soil sample A, the soil metal concentrations were generally lower in the CO_2-affected soil than in the control soil, although the final soil solution pH values were similar. On the other hand, with the soil sample B, the final soil pH value was lower in the CO_2-affected soil than in the control soil, but the studied soil metal concentrations were similar, except for Ca. Thus, further research is needed to better understand the effect of CO_2 increase in soil environment with increasing atmospheric CO_2 concentration in order to manage and conserve soil environment in the era of climate change.

Acknowledgments This research was supported by National Research Foundation of Korea (NRF-2018R1C1B6002702). This work was also supported by the Hankuk University of Foreign Studies Research Fund (2018).

References

1. Paustian K, Lehmann J, Ogle S, Reay D, Robertson GP, Smith P (2016) Climate-smart soils. Nature 532:49–57
2. van Groenigen KJ, Qi X, Osenberg CW, Luo Y, Hungate BA (2014) Faster decomposition under increased atmospheric CO_2 limits soil carbon storage. Science 344:508–509
3. Sleeter BM, Liu J, Daniel C, Rayfield B, Sherba J, Hawbaker TJ, Zhu Z, Selmants PC, Loveland TR (2018) Effects of contemporary land-use and land-cover change on the carbon balance of terrestrial ecosystems in the United States. Environ Res Lett 13:045006
4. Owusu PA, Asumadu-Sarkodie S (2017) Is there a causal effect between agricultural production and carbon dioxide emissions in Ghana? Environ Eng Res 22:40–54
5. Shin J, Hong SG, Lee S, Hong S, Lee J (2017) Estimation of soil carbon sequestration and profit analysis on mitigation of CO_2-eq. emission in cropland cooperated with compost and biochar. Appl Biol Chem 60:467–472
6. Brevik CE (2013) The potential impact of climate change on soil properties and processes and corresponding influence on food security. Agric 3:398–417
7. Janssens IA, Crookshanks M, Taylor G, Ceulemans R (2002) Elevated atmospheric CO_2 increases fine root production, respiration, rhizosphere respiration and soil CO_2 efflux in Scots pine seedlings. Glob Change Biol 4:871–878
8. Lee HS, Nam JK, Kim Y, Lee H (2018) Prediction of mycotoxin risks due to climate change in Korea. Appl Biol Chem 61:389–396
9. Kumeleh AS, Sharmila P, Uprety DC, Saradhi PP (2009) Effects of elevated CO_2 on soil physicochemical characteristics under Free Air CO_2 Enrichment (FACE) technology. In: IOP conference series: earth and environmental science, vol 6, No. 29. IOP Publishing, UK, p 292045
10. De Orte MR, Lombardi AT, Sarmiento AM, Basallote MD, Rodriguez-Romero A, Riba I, Del Valls A (2014) Metal mobility and toxicity to microalgae associated with acidification of sediments: CO_2 and acid comparison. Mar Environ Res 96:136–144
11. Millero FJ, Woosley R, Ditrolio B, Waters J (2009) Effect of ocean acidification on the speciation of metals in seawater. Oceanogr 22:72–85
12. De Orte MR, Sarmiento AM, Basallote MD, RodrÃ−guez-Romero A, Riba I, DelValls A (2014) Effects on the mobility of metals from acidification caused by possible CO_2 leakage from sub-seabed geological formations. Sci Total Environ 470–471:356–363
13. Xiao L, Lian B, Hao J, Liu C, Wang S (2015) Effect of carbonic anhydrase on silicate weathering and carbonate formation at present day CO_2 concentrations compared to primordial values. Sci Rep 5:7733
14. Siirila ER, Navarre-Sitchler AK, Maxwell RM, McCray JE (2012) A quantitative methodology to assess the risks to human health from CO_2 leakage into groundwater. Adv Water Resour 36:146–164
15. Hur JR, Jho EH (2017) Effect of hemoglobin on the growth and Cd accumulation of pea plants (*Pisum sativum* L.). Appl Biol Chem 60:673–678
16. KMOE (2009) Official standard methods of soil quality—metal. Korean Ministry of Environment, Korea
17. Biose E, Amaechi CF, Nnaji GU, Biose O, Erhunmwunse NO (2016) Effects of elevated soil carbon dioxide (CO_2) concentrations on spring wheat (*Triticum aestivum* L.) and soil chemical properties in Sutton Bonington Campus of the University of Nottingham, UK. J Appl Sci Environ Manage 20:293–301

18. Patil RH, Colls JJ, Steven MD (2010) Effects of CO_2 gas as leaks from geological storage sites on agro-ecosystems. Energy 35:4587–4591
19. Smith KL, Colls JJ, Steven MD (2005) A facility to investigate effects of elevated soil gas concentration on vegetation. Water Air Soil Pollut 161:75–96
20. Zhao X, Deng H, Wang W, Han F, Li C, Zhang H, Dai Z (2017) Impact of naturally leaking carbon dioxide on soil properties and ecosystems in the Qinghai-Tibet plateau. Sci Rep 7:3001
21. West JM, Pearce JM, Coombs P, Ford JR, Scheib C, Colls JJ, Smith KL, Steven MD (2009) The impact of controlled injection of CO_2 on the soil ecosystem and chemistry of an English lowland pasture. Energy Procedia 1:1863–1870
22. Gamsjager H, Preis W (1999) Copper content in synthetic copper carbonate. J Chem Educ 76:1339
23. Lee K-K, Lee SH, Yun S-T, Jeen S-W (2016) Shallow groundwater system monitoring on controlled CO_2 release sites: a review on field experimental methods and efforts for CO_2 leakage detection. Geosci J 20:569–583