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Assessment of CO_2 discharge in a spring using time-variant stable carbon isotope data as a natural analogue study of CO_2 leakage

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CO_2-rich springs have been studied as a natural analogue of CO_2 leakage through shallow subsurface environment, as they provide information on the behaviors of CO_2 during the leakage from geologic CO_2 storage sites. For this study, we monitored the δ^{13}C values as well as temperature, pH, EC, DO, and alkalinity for a CO_2-rich spring for 48 hours. The water samples (N=47) were collected every hour in stopper bottles without headspace to avoid the interaction with air and the CO_2 degassing. The δ^{13}C values of total dissolved inorganic carbon (TDIC) in the water samples were analyzed using a cavity ring-down spectroscopy (CRDS) system (Picarro). The values of $\delta^{13}C_{TDIC}$, temperature, pH, EC, DO, and alkalinity were in the range of -9.43 $\sim$ -8.91 ‰ 12.3 $\sim$ 13.2^{o}C, 4.86 $\sim$ 5.02, 186 $\sim$ 189 μS/cm, 1.8 $\sim$ 3.4 mg/L, and 0.74 $\sim$ 0.95 meq/L, respectively. The concentrations of TDIC calculated using pH and alkalinity values were between 22.5 and 34.8 mmol/L. The $\delta^{13}C_{TDIC}$ data imply that dissolved carbon in the spring was derived from a deep-seated source (i.e., magmatic) that was slightly intermixed with soil CO_2. Careful examination of the time-series variation of measured parameters shows the following characteristics: 1) the $\delta^{13}C_{TDIC}$ values are negatively correlated with pH (r = -0.59) and positively correlated with TDIC (r = 0.58), and 2) delay times of the change of pH and alkalinity following the change of $\delta^{13}C_{TDIC}$ values are 0 and -3 hours, respectively; the pH change occurs simultaneously with the change of $\delta^{13}C_{TDIC}$, while the alkalinity change happens before 3 hours. Our results indicate that the studied CO_2-rich spring is influenced by the intermittent supply of deep-seated CO_2. [Acknowledgment] This work was financially supported by the fundamental research project of KIGAM and partially by the "Geo-Advanced Innovative Action (GAIA) Project (2014000530003)" from Korea Ministry of Environment (MOE).