

Dissolved inorganic carbon export from carbonate and silicate catchments estimated from carbonate chemistry and $\delta^{13}\text{C}_{\text{DIC}}$

W. J. Shin^{1,2}, G. S. Chung¹, D. Lee², and K. S. Lee^{2,3}

¹Department of Geology and Earth Environmental Sciences, Chungnam National University, Daejeon, 305-764, Republic of Korea

²Division of Earth and Environmental Science, Korea Basic Science Institute, Ochang, 363-883, Republic of Korea

³Graduate School of Analytical Science and Technology, Chungnam National University, Daejeon, 305-764, Republic of Korea

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Abstract. This work presents a study of the dissolved inorganic carbon (DIC) exchange associated with groundwater discharge and stream flow from two upstream catchments with distinct basement lithologies (silicate vs. carbonate). The effects of catchment lithology were evident in the spring waters showing lower $\delta^{13}\text{C}_{\text{DIC}}$ and alkalinity ($-16.2 \pm 2.7\%$ and $0.09 \pm 0.03 \text{ meq l}^{-1}$, respectively) in the silicate and higher values ($-9.7 \pm 1.5\%$ and $2.0 \pm 0.2 \text{ meq l}^{-1}$) in the carbonate catchment. The streams exhibited relatively high $\delta^{13}\text{C}_{\text{DIC}}$, $-6.9 \pm 1.6\%$ and $-7.8 \pm 1.5\%$, in silicate and carbonate catchments, respectively, indicating CO_2 degassing during groundwater discharge and stream flow. The catchment lithology affected the pattern of DIC export. The CO_2 degassing from stream and groundwater could be responsible for 8–55 % of the total DIC export in the silicate catchment, whereas the proportion is comparatively low (0.4–5.6 %) in the carbonate catchment. Therefore, the dynamic carbon exchange occurring at headwater regions and its possible variability with catchment lithology need to be examined for a more reliable carbon budget in river systems.

an important role in global carbon cycling by transporting carbon from terrestrial to marine realms. The global flux of carbon transported by rivers in the form of dissolved inorganic carbon (DIC) is estimated to be $0.43 \times 10^{15} \text{ gC yr}^{-1}$, representing $\sim 50\%$ of the total carbon flux (Meybeck, 1987; Cole et al., 2007). Moreover, the evasion of CO_2 from rivers during DIC transport is an important component of the atmospheric CO_2 budget (Richey et al., 2002). Thus, considerable effort has been directed toward quantifying both vertical (evasion of CO_2) and lateral (discharge) exports of DIC via rivers (Dubois et al., 2010).

In upstream regions (e.g. headwater catchments) where the stream flow is mainly due to groundwater discharge, groundwater acts as a conduit of subsurface DIC transport across the interface between terrestrial (e.g. soils) and aquatic reservoirs (e.g. streams). The onset of carbon exchange at the headwater regions is characterized by enhanced CO_2 evasion due to strong CO_2 over-saturation of the groundwater. Because the effect of groundwater DIC is transient and is only observed near the immediate source at the first order stream, carbon exchange at this interface has been largely unexplored (Johnson et al., 2008; Öquist et al., 2009). Therefore, a more quantitative understanding of carbon exchange in headwater systems is essential to derive a reliable carbon budget of river systems.

An isotope tracer, $\delta^{13}\text{C}_{\text{DIC}}$, is especially useful because it reveals reaction pathways and transport processes that may otherwise be difficult to discern with normative carbonate systems (Tan and Edmond, 1993; Taylor and Fox, 1996; Yang et al., 1996). The DIC in river water originates from several sources, including influx of soil CO_2 via groundwater, CO_2 exchange with the atmosphere, in-river respiration, and dissolution of carbonate rocks. About 67 % of the DIC

1 Introduction

The current increase of atmospheric carbon dioxide, a greenhouse gas, and associated climate changes necessitate a more in-depth understanding of the global carbon cycle (Friedlingstein et al., 2003; Govindasamy et al., 2005). Rivers play



Correspondence to: K. S. Lee
(kslee@kbsi.re.kr)

in the world's rivers is known to originate from soil CO₂ (Meybeck, 1987; Ludwig et al., 1997). Based on simple stoichiometric considerations, the proportion of soil CO₂ in rivers ranges from ~50 % in carbonate catchments (another 50 % is from the carbonate minerals) to ~100 % in silicate catchments (e.g. Spence and Telmer, 2005). In upstream regions where groundwater contributes largely to stream flow, the input of groundwater containing DIC from soil CO₂ lowers the ¹³C/¹²C ratio of DIC in river water because soil CO₂ is largely derived from the microbial degradation of soil organic matter (Amiotte-Suchet et al., 1999; Finlay, 2003). In contrast, atmospheric exchange and dissolution of carbonate minerals increase the ¹³C/¹²C ratio of DIC because these sources are enriched in ¹³C relative to ¹²C (Amiotte-Suchet et al., 1999). In addition to the strong over-saturation with CO₂ in groundwater components, stream water in upstream regions may also be more turbulent, causing rapid degassing of CO₂ into the atmosphere and remarkable ¹³C enrichment in DIC (Doctor et al., 2008).

The uppermost tributaries of the South Han River (SHR), South Korea, provide an ideal hydro-geological setting to investigate the effect of catchment lithology on δ¹³C_{DIC} and carbonate chemistry because they drain catchments with contrasting bedrock lithologies: silicate vs. carbonate. Moreover, their drainage system that consists of the first to fifth order streams provides an adequate condition for studies on carbon exchanges from the headwater regions to the main channels. In this study, the stable carbon isotopic composition of DIC and carbonate chemistry were determined from springs and streams draining upstream catchments with silicate and carbonate basements. The objectives were to (1) determine factors controlling carbonate chemistry and δ¹³C_{DIC} in catchments with different lithologies and (2) quantify lateral and vertical transport of DIC at the studied catchments and their possible variation with the catchment lithology.

2 Materials and methods

2.1 Description of the study sites

The study sites were two upstream tributaries of the SHR in the middle part of the Korean peninsula (Fig. 1). Both catchments were located at the headwater regions of the SHR basin. The Odae drains a basin (452 km²) dominated exclusively by silicate rocks, consisting of Precambrian metamorphic crystalline rocks, Permian to Triassic sandstone and shale, and Jurassic to Cretaceous granite. In contrast, the Jijang drains a basin (225 km²) dominated by Cambro-Ordovician carbonate rocks with some sandstone at its upper reach (Kim et al., 2001). The lower reach of the carbonate catchment consists of Ordovician limestone and both spring and stream water samples were collected from the same rock formation. The sedimentary rocks that constitute silicate catchment and part of carbonate catchment unconformably

Table 1. Comparison of the physical characteristics and mean discharge for the Odae and Jijang catchments (Water Management Information System: <http://www.wamis.go.kr>).

Tributary	Odae (silicate)	Jijang (carbonate)
Catchment area (km ²)	452	225
Total stream length (km)	521	464
1st order stream length (km)	272	230
Main channel* length (km)	44	37
Mean width (m)	8.2	5.6
Mean discharge (m ³ s ⁻¹)	7	3

* Main channel corresponds to 5th order stream in both catchments.

overlie the Ordovician limestone. In the silicate catchment, the thickness of sedimentary rocks is known to be greater than ~500 m and both spring and stream water samples were collected on this sedimentary formation. The elevation of the study sites ranges from 340 to 1560 m for the Odae and from 260 to 1570 m for the Jijang catchment. The vegetation in the study area consisted mainly of C3 plants (mixed deciduous broadleaf and conifer forests) with seasonally cultivated crops such as rice, barley, corn, and cabbages. Table 1 presents information of the two streams (Water Management Information System: <http://www.wamis.go.kr>).

2.2 Sampling and analytical procedures

Water sampling and in-situ measurements of geochemical parameters were conducted at four locations on a biweekly basis for 18 months (July 2004 to December 2005). Water was collected from the two perennial springs and the outlet of the main channel (fifth-order stream) in both catchments. In the silicate catchment (Odae), samples were collected from a spring located at the bottom of a sandstone cliff from which water was discharging at ~37 m³ day⁻¹. In the carbonate catchment (Jijang), a perennial spring flowing from the base of a carbonate cliff was chosen. Although sampling began in July 2004, this study focused on the data from 2005 because a more complete dataset was available in terms of measured parameters and seasonal coverage. An independent isotope survey was conducted on soil organic materials and leaf litter at the studied catchments in summer, 2011. Samples were collected near the spring waters, and from the deposits near the river outlets (close to the stream sample locations) to obtain representative soil organic materials for the entire catchments.

Temperature, pH, dissolved oxygen (DO), and electrical conductivity (EC) were measured on site during water sampling using a YK-2001PH portable meter (Lutron Electronic CO., Taiwan). Alkalinity was measured on site by titration with 0.05 N HCl according to the Gran method (Rounds and Wilde, 2001). To fully characterize the carbonate system,

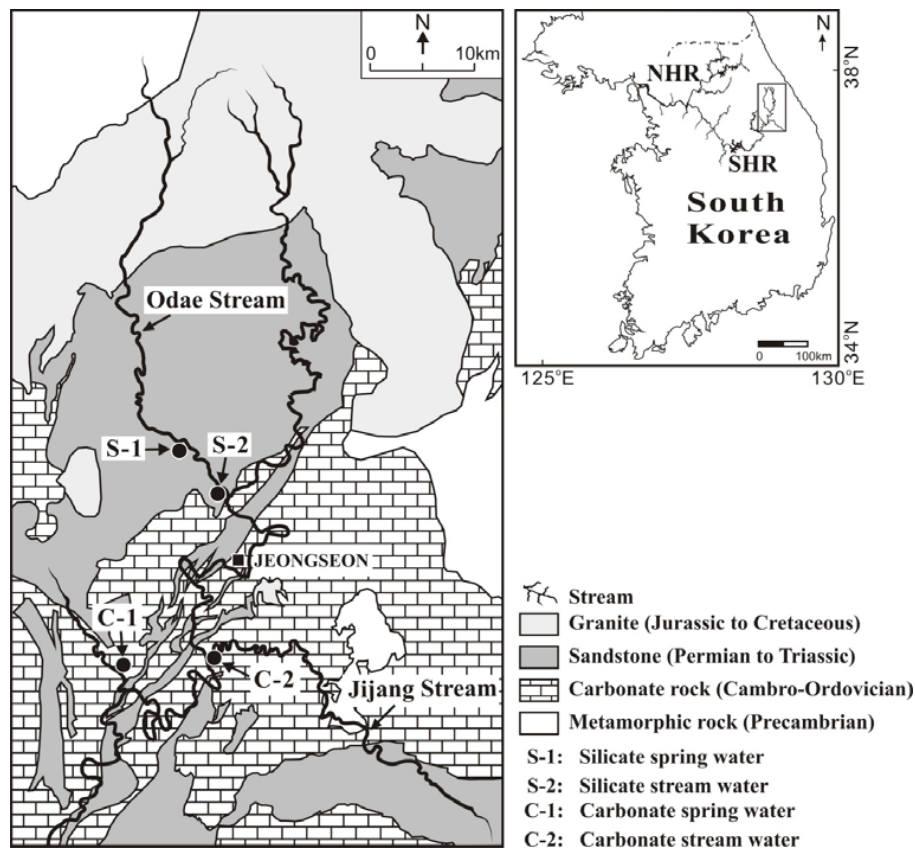


Fig. 1. Map showing the basement lithology and sampling locations of the studied catchments, two uppermost tributaries of the South Han River. Spring and stream waters in the silicate catchment were collected at S-1 and S-2, respectively; spring and stream waters in the carbonate catchment were collected at C-1 and C-2. NHR and SHR represent the North Han River and the South Han River, respectively.

ion activities were evaluated by PHREEQC (Parkhurst and Appelo, 1999). The partial pressure of CO_2 ($p\text{CO}_2$) was calculated by the speciation outputs from PHREEQC. The temperature-dependent equilibrium constants for the three species (H_2CO_3 , HCO_3^- , and CO_3^{2-}) of the DIC summarized by Langmuir (1997) were used to calculate the activities of the three species.

For $\delta^{13}\text{C}_{\text{DIC}}$ analysis, water samples were collected using two evacuated glass bottles (150 ml) pre-loaded with 85 % phosphoric acid and a magnetic stir bar, as reported by Atekwana and Krishnamurthy (1998). Water sampling was carried out in the field using a syringe with a 0.45- μm Millipore membrane filter. Samples were kept refrigerated until analysis. The DIC in water samples was converted into CO_2 gas by a gas-evolution technique (Atekwana and Krishnamurthy, 1998). The CO_2 gas was then extracted and cryogenically purified. Next, the $\delta^{13}\text{C}_{\text{DIC}}$ of the evolved CO_2 was measured using an Optima isotope-ratio mass spectrometer (GV Instruments, UK) at Chungnam National University. Soil organic materials and leaf litters were dried at 50 °C for 24 h and powdered. The mixtures of organic materials and soils were treated with dilute

HCl to remove carbonates, then rinsed with deionized water, and dried. The carbon isotope compositions of soil organic materials and leaf litters were determined using an isotope ratio mass spectrometer (GV IsoPrime, UK) interfaced with elemental analyzer (EuroVector EuroEA3000 series, Italy) at the Korea Basic Science Institute. Carbon isotopic ratios are reported using standard δ notation, in per mil (‰) differences relative to the Vienna Pee Dee belemnite (VPDB) standard, i.e. δ (‰) = $(R_{\text{sample}}/R_{\text{standard}} - 1) \times 1000$, where R represents $^{13}\text{C}/^{12}\text{C}$. The analytical reproducibility was ± 0.2 ‰ based on repeated analyses of laboratory and NBS standards.

3 Results

Figure 2 shows the precipitation, $\delta^{13}\text{C}_{\text{DIC}}$, and $p\text{CO}_2$ of the four water types. Ranges and averages of the measured parameters are shown in Table 2. The pH and alkalinities were consistently higher in the carbonate spring. Remarkable seasonal variations in $\delta^{13}\text{C}_{\text{DIC}}$ were observed especially in the silicate spring waters. $\delta^{13}\text{C}_{\text{DIC}}$ of the silicate spring (average

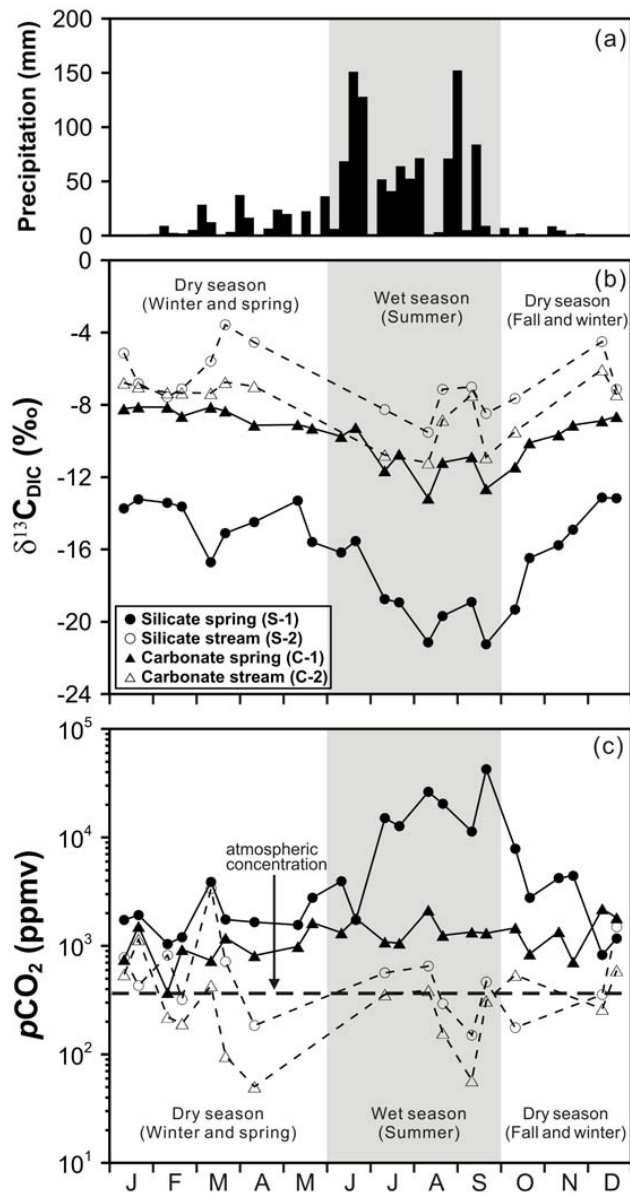


Fig. 2. Figures showing (a) monthly precipitation, (b) $\delta^{13}\text{C}_{\text{DIC}}$, and (c) $p\text{CO}_2$ of waters from the silicate and carbonate catchments during 2005.

of -16.2 ± 2.7 ‰) was much lower than the carbonate spring (average of -9.7 ± 1.5 ‰). The $p\text{CO}_2$ in the silicate spring was higher than that of the carbonate spring water (Fig. 2c). The $\delta^{13}\text{C}_{\text{DIC}}$, alkalinity, and pH were the major parameters used to distinguish silicate and carbonate spring waters. The two spring waters were distinguished by a pH of 7, and the silicate spring had a wider range than the carbonate spring (Fig. 3). The carbonate spring water had greater alkalinity with larger variability, whereas the variability of the silicate spring was limited.

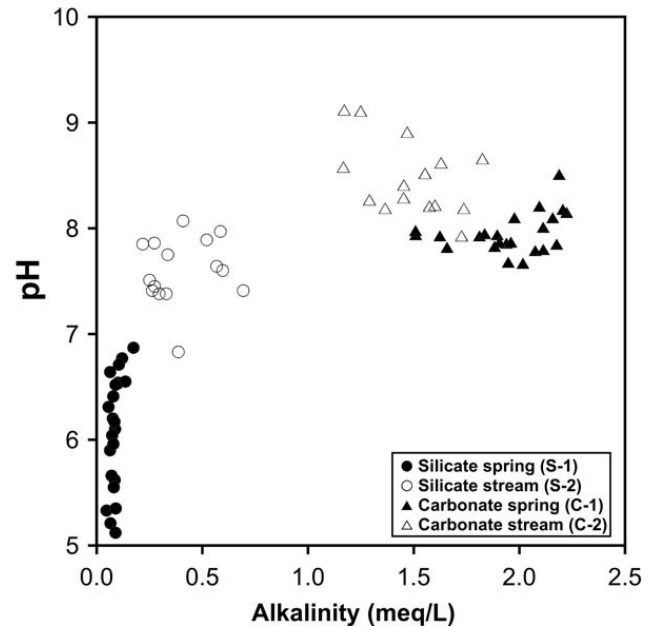


Fig. 3. Cross plot of alkalinity vs. pH in spring and stream waters. Note that the four different types of water are clearly distinguished in this figure.

The pH, alkalinity, and EC were higher in the carbonate stream. $\delta^{13}\text{C}_{\text{DIC}}$ was slightly higher in the silicate stream (-6.9 ± 1.6 ‰) than the carbonate stream (-7.8 ± 1.5 ‰). The $p\text{CO}_2$ was higher in the silicate stream than in the carbonate stream. DO was mostly supersaturated with respect to atmospheric O_2 , showing the average dissolved O_2 saturation (DO_{sat}) of ~ 1.2 in both streams. Alkalinity was the parameter that differentiated stream waters (Fig. 3). Both stream waters had higher pH than the respective spring water in each catchment. Compared to the respective spring water, alkalinity was higher in the silicate stream, but was lower in the carbonate stream. Notably, in the carbonate catchment, alkalinity in the stream decreased with simultaneous increase in EC compared to the spring waters. Alkalinity and EC generally correlate positively if mineral weathering is the major control. However, Hill and Neal (1997) reported a negative correlation between alkalinity and EC in stream waters of small headwater catchments, i.e. EC increases were associated with alkalinity decreases when soil- and surface-derived components (nutrients and organic acids) increased in the stream waters.

$\delta^{13}\text{C}$ of soil organic carbon was from -27.1 to -22.1 ‰. $\delta^{13}\text{C}$ tends to increase with the soil depth and no distinction in $\delta^{13}\text{C}$ of soil organic carbon was observed between two catchments. The leaf litters (relatively recent organic components) have the similar $\delta^{13}\text{C}$ in both catchments ranging from -31.1 to -29.3 ‰.

Table 2. Statistical summary of geochemical parameters measured from springs and streams in the study area.

Parameters	Silicate catchment								Carbonate catchment							
	Spring water				Stream water				Spring water				Stream water			
	Min*	Max*	Aver*	SD*	Min*	Max*	Aver*	SD*	Min*	Max*	Aver*	SD*	Min*	Max*	Aver*	SD*
$\delta^{13}\text{C}_{\text{DIC}}$ (‰)	-21.2	-13.1	-16.2	2.7	-10.0	-3.6	-6.9	1.6	-13.2	-8.1	-9.7	1.5	-11.2	-6.1	-7.8	1.5
Temp. (°C)	8.8	12.7	10.7	1.3	0.4	28.0	11.0	8.9	8.9	14.3	11.6	1.9	0.3	28.0	13	8.4
pH	5.1	6.9	6.1	0.5	6.8	8.1	7.9	0.3	7.7	8.5	8.0	0.2	7.9	9.1	8.5	0.4
DO _{sat}	ND**	ND**	ND**		1.0	1.6	1.2	0.1	ND**	ND**	ND**		1.0	1.7	1.2	0.2
EC ($\mu\text{S cm}^{-1}$)	ND**	ND**	ND**		11	122	64	31	171	389	254	62	222	433	301	60
Alk (meq l^{-1})	0.05	0.17	0.09	0.0	0.22	0.74	0.44	0.15	1.50	2.21	1.96	0.21	1.18	1.83	1.46	0.16
DIC (mg l^{-1})	5.6	103.3	22.7	23.3	13.7	45.5	26.0	10.0	93.1	137.9	121.8	12.8	71.3	110.2	91.0	12.0
$p\text{CO}_2$ (ppmv)	827	42546	7520	10239	150	3380	720	813	372	2197	1245	466	50.3	1150	357	282

* Min, Max, Aver, and SD represent minimum, maximum, average, and standard deviation, respectively. ** ND: not determined.

4 Discussion

4.1 Sources of spring water DIC

The clear distinction in geochemical and carbon isotope characteristics between the two spring waters indicated that the springs may represent the characteristics of the groundwater in each catchment. To examine this, the expected carbon isotopic composition was calculated for the groundwater DIC originating exclusively from soil CO_2 (silicate catchment) and from a 1:1 mixture of soil CO_2 and carbonate minerals (carbonate catchment). The calculation was made using the measured $\delta^{13}\text{C}$ of soil organic matter in both catchments ranging from -27 to -22 ‰ and the temperature dependence of carbon isotope fractionation between CO_2 and $\text{H}_2\text{CO}_3/\text{HCO}_3^-$ (Zhang et al., 1995). The ratio between H_2CO_3 and HCO_3^- was calculated using K_1/a_{H^+} , where K_1 is the first dissociation constant of H_2CO_3 , and a_{H^+} was calculated from the measured pH. The expected $\delta^{13}\text{C}_{\text{DIC}}$ in the silicate spring (with 31 % HCO_3^- and 69 % H_2CO_3 at the average pH of 6.1) derived from soil CO_2 was $-25.1 \sim -20.1$ ‰, which was lower than the measured average value of -16.2 ± 2.7 ‰. For the carbonate spring, the expected $\delta^{13}\text{C}_{\text{DIC}}$ (97 % HCO_3^- at the average pH of 8.0) derived from 1:1 mixture of soil CO_2 and carbonate minerals was $-9.1 \sim -6.6$ ‰, which was closer to or higher than the measured average value (-9.7 ± 1.5 ‰).

The discrepancy between measured and expected $\delta^{13}\text{C}_{\text{DIC}}$ may be related to degassing of CO_2 from the water. While diffusive efflux of soil CO_2 may impart ^{13}C enrichment (e.g. Chap. 5 of Clark and Fritz, 1997), the major ^{13}C enrichment likely occurred during CO_2 degassing associated with the groundwater discharge (e.g. Johnson et al., 2008).

Degassing can explain the greater discrepancy observed in the silicate catchment. Because the proportion of dissolved CO_2 (H_2CO_3) in the total DIC was large in the silicate spring due to relatively low pH, the effect of CO_2 degassing was more significant. To verify the effect of CO_2 degassing on $\delta^{13}\text{C}_{\text{DIC}}$ of the silicate spring, the method from Doctor et al. (2008) was applied. They reported that the increase in $\delta^{13}\text{C}_{\text{DIC}}$ per natural log-unit decrease of excess $p\text{CO}_2$ was 2.4 ‰, where excess $p\text{CO}_2$ is the measured $p\text{CO}_2$ normalized to the expected $p\text{CO}_2$ at atmospheric equilibrium. In this study, the relationship was calculated as a 2.3 ± 0.2 ‰ increase per unit decrease of excess $p\text{CO}_2$, indicating that the variability in silicate spring $\delta^{13}\text{C}_{\text{DIC}}$ closely followed the reported change associated with the CO_2 degassing. DIC in the carbonate spring water consisted primarily of HCO_3^- ; therefore, the effect of CO_2 degassing and associated enrichment of ^{13}C was not clearly observed. Unlike the silicate spring, the expected $\delta^{13}\text{C}_{\text{DIC}}$ in the carbonate spring was higher than the measured, which may indicate that the assumed stoichiometric proportion of carbonate-derived DIC (~ 50 %) could be an over-estimation. In summary, the spring waters may well represent the groundwater component modified by CO_2 degassing in the silicate catchment and variable carbonate input in the carbonate catchment.

4.2 The evolution of $\delta^{13}\text{C}_{\text{DIC}}$ in stream waters

Because the spring waters likely represent the source groundwater composition, it is informative to compare spring and stream waters to understand processes occurring along the hydrological pathways. Although the variability in $\delta^{13}\text{C}_{\text{DIC}}$ between stream and spring waters was generally correlated in each catchment (with $r^2 = 0.62$ in the carbonate and $r^2 = 0.31$

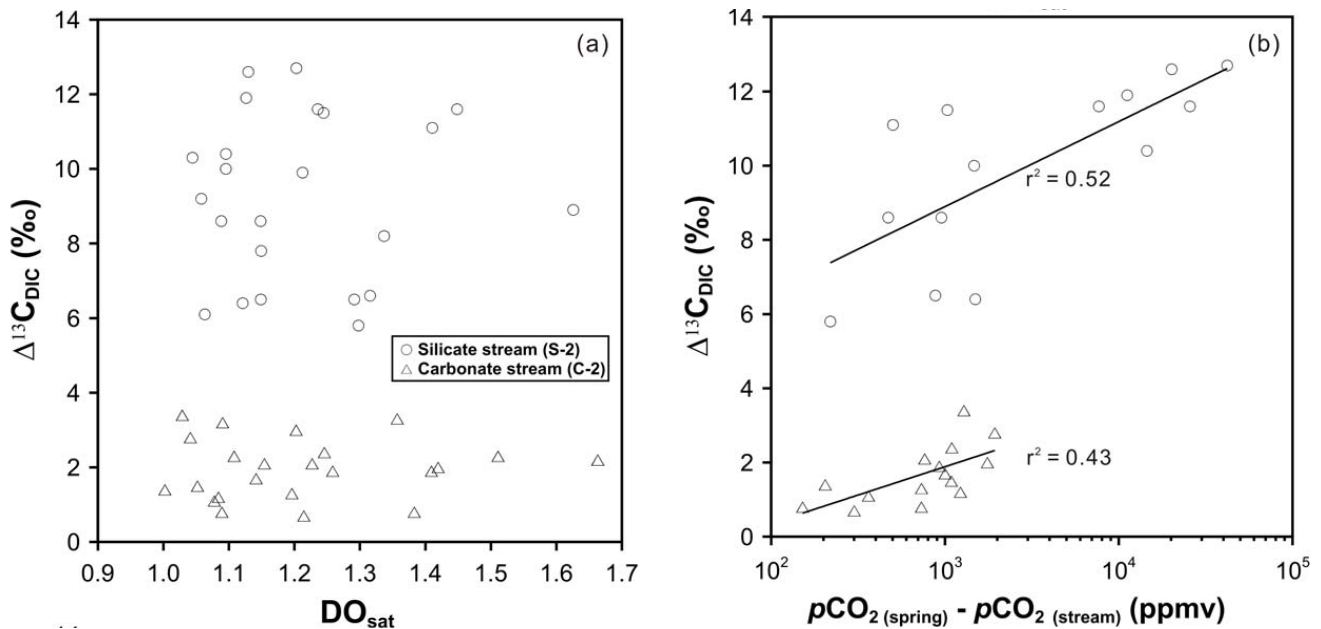


Fig. 4. Cross plots of (a) DO_{sat} vs. $\Delta^{13}\text{C}_{\text{DIC}}$ [$\delta^{13}\text{C}_{\text{DIC}}$ (stream water) – $\delta^{13}\text{C}_{\text{DIC}}$ (spring water)], and (b) [$p\text{CO}_2$ (spring water) – $p\text{CO}_2$ (stream water)] vs. $\Delta^{13}\text{C}_{\text{DIC}}$.

in the silicate catchment), the difference between catchments was reduced ($\sim 0.9\text{‰}$ between streams compared to $\sim 6.5\text{‰}$ between springs) and DIC was more enriched in ^{13}C in stream waters. The increase in $\delta^{13}\text{C}_{\text{DIC}}$ was likely related to aquatic photosynthesis and CO_2 degassing.

To examine the relative importance of aquatic photosynthesis and CO_2 degassing, the difference in $\delta^{13}\text{C}_{\text{DIC}}$ between the spring and stream waters ($\Delta^{13}\text{C}_{\text{DIC}}$) was plotted against the DO_{sat} in stream waters (Fig. 4a) and the difference in $p\text{CO}_2$ between the spring and stream waters ($\Delta p\text{CO}_2$) (Fig. 4b). Because the stream waters were mostly over-saturated with O_2 relative to atmospheric equilibrium, photosynthesis was assumed to be prevalent, and associated ^{13}C enrichment was expected. However, the correlation between $\Delta^{13}\text{C}_{\text{DIC}}$ and DO_{sat} was low ($r^2 < 0.1$), indicating that aquatic photosynthesis may not have been the major process for ^{13}C enrichment. In addition, if photosynthesis resulted in ^{13}C enrichment, there would have been a seasonal difference in $\delta^{13}\text{C}_{\text{DIC}}$ because photosynthesis is more intense in summer than in winter. However, the magnitude of ^{13}C enrichment was similar regardless of the season.

In contrast, $\Delta^{13}\text{C}_{\text{DIC}}$ exhibited a higher correlation ($r^2 = 0.52$ and 0.43) with $\Delta p\text{CO}_2$ in both catchments. Therefore, a simplified interpretation regarding the enrichment of ^{13}C in stream water DIC is that it was caused mainly due to CO_2 degassing along the pathways from the groundwater reservoirs to the stream. In the carbonate catchment, $\Delta^{13}\text{C}_{\text{DIC}}$ was comparatively small because of the minor proportion of dissolved CO_2 in the total DIC; thus, the effect of CO_2 degassing from the groundwater was smaller than that

in the silicate catchment. Moreover, due to the slight under-saturation with CO_2 in the carbonate stream, CO_2 dissolution may also have occurred that led to a different degree of ^{13}C enrichment compared to that expected from CO_2 degassing.

4.3 Seasonal variation in $\delta^{13}\text{C}_{\text{DIC}}$ and carbonate chemistry

The spring and stream samples exhibited well-defined seasonal variations characterized by low $\delta^{13}\text{C}_{\text{DIC}}$ during summer (June to September) and high $\delta^{13}\text{C}_{\text{DIC}}$ during winter (November to February) (Fig. 2b). In addition, $p\text{CO}_2$ showed a seasonal dependence, with higher values during June–October and lower values during November–March, especially in the silicate spring water (Fig. 2c). In the study area, the observed seasonality could have been due to (1) the seasonal change in metabolic activity related to changes in temperature and (2) changes in the water regime related to precipitation patterns.

Because both stream waters were assumed to be dominantly photosynthetic, the higher $p\text{CO}_2$ during summer does not support in-situ production, but likely reflects CO_2 transport from soils via groundwater discharge associated with the enhanced microbial and root respiration during the season (Barth and Veizer, 1999; Hope et al., 2004; Yao et al., 2007). The addition of soil CO_2 via soil/groundwater resulted in low $\delta^{13}\text{C}_{\text{DIC}}$ of the water. A negative correlation ($r^2 = 0.92$) between $\delta^{13}\text{C}_{\text{DIC}}$ and $p\text{CO}_2$ in the spring samples in the silicate catchment indicates that the changes in the amount of soil-derived CO_2 were the main cause of seasonality in $\delta^{13}\text{C}_{\text{DIC}}$

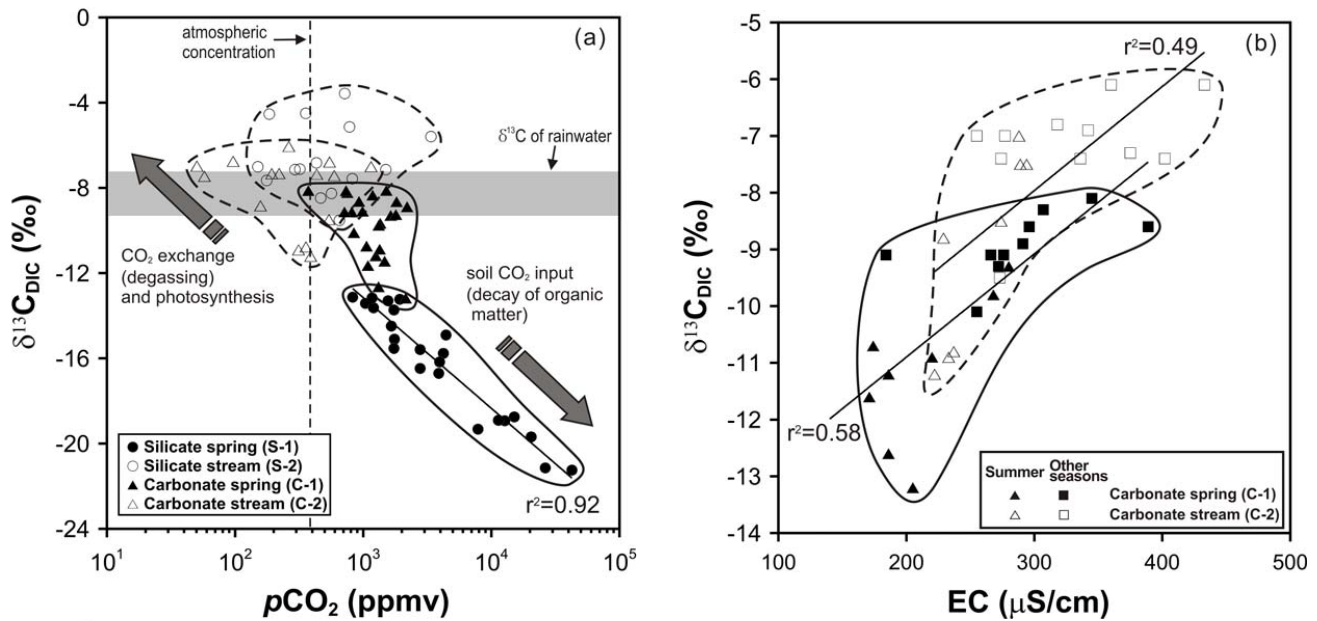


Fig. 5. Cross plots of (a) $p\text{CO}_2$ vs. $\delta^{13}\text{C}_{\text{DIC}}$, and (b) EC vs. $\delta^{13}\text{C}_{\text{DIC}}$. Summer: June through September. The $\delta^{13}\text{C}_{\text{DIC}}$ value of rainwater is from Zhang et al. (1995).

(Fig. 5a). The correlation between $\delta^{13}\text{C}_{\text{DIC}}$ and $p\text{CO}_2$ in other types of water was not as obvious as in the spring samples in the silicate catchment. In the carbonate catchment, the changes in $\delta^{13}\text{C}_{\text{DIC}}$ were positively correlated with EC in the spring ($r^2 = 0.58$) and stream ($r^2 = 0.49$) waters (Fig. 5b), and waters with low EC occurred during the summer when $\delta^{13}\text{C}_{\text{DIC}}$ was also low. EC increased as the residence time of water in soil and groundwater reservoirs increased; thus, during summer, EC decreased due to the higher precipitation and rapid turnover of subsurface water (Clark and Fritz, 1997). This indicates that the seasonality of $\delta^{13}\text{C}_{\text{DIC}}$ in the carbonate catchment was related to the change of the water regime due to seasonal precipitation patterns.

Precipitation, which was measured at the Yeongweol meteorological station about 40 km from the study area (data from Korea Meteorological Administration, KMA: <http://www.kma.go.kr>), varied throughout the study period (Fig. 2a). The average monthly precipitation during summer and early fall (June to September) was 249 mm, but for the rest of the year (October to May) it was only 32 mm. The seasonal variation of precipitation roughly coincided with the fluctuations in $\delta^{13}\text{C}_{\text{DIC}}$ (Fig. 2b) of all water samples and in EC of the carbonate catchment. During the dry season, pore water has a long residence time in the soil horizon, allowing for an extended exchange of CO_2 with the atmosphere through the soil zone, thereby increasing $\delta^{13}\text{C}_{\text{DIC}}$ and EC of the soil water. In contrast, during the wet season, the frequent infiltration of rainwater into the soil and the outflow of interstitial soil waters from the vadose zone result in a shorter residence time for soil water and limit CO_2 exchange with the atmosphere. Therefore, soil water in the wet season displays

lower $\delta^{13}\text{C}_{\text{DIC}}$ and EC than does soil water during the dry season (Amiotte-Suchet et al., 1999). The transport of CO_2 produced by increased soil respiration via soil/groundwater with distinct EC is facilitated by the concentrated precipitation in summer. The effect of $p\text{CO}_2$ was not clearly observed in the waters from the carbonate catchment due to lower $\text{CO}_2/\text{HCO}_3^-$ ratios, but the analogous effect associated with seasonal changes in soil respiration and water regime can be expressed by EC vs. $\delta^{13}\text{C}_{\text{DIC}}$ plots (Fig. 5b).

4.4 DIC export from the river system

The importance of CO_2 degassing was suggested from the previous discussion on the changes in $\delta^{13}\text{C}_{\text{DIC}}$ of spring and stream waters. The calculated excess $p\text{CO}_2$ was 19.8 in the silicate spring, 3.3 in the carbonate spring, 1.9 in the silicate stream, and 0.9 in the carbonate stream (all as annual averages in 2005). Except for the carbonate stream, the studied waters were over-saturated with CO_2 and assumed to act as the source of atmospheric CO_2 (Yao et al., 2007). Although the excess $p\text{CO}_2$ in the carbonate stream was lower than 1, indicating possible invasion of atmospheric CO_2 , its DIC was still depleted in ^{13}C compared with atmosphere-derived DIC ($\sim 0\text{‰}$, assuming $\delta^{13}\text{C}$ of atmospheric CO_2 to be -7.8‰ from Brunet et al., 2005).

To quantitatively determine the amount of CO_2 degassing, the following flux equation was applied:

$$F = k_{\text{CO}_2} (C_{\text{eq}} - C),$$

where F is the diffusive flux of CO_2 to the atmosphere, k_{CO_2} is the gas transfer coefficient, and C_{eq} and C are the dissolved

CO₂ concentrations in equilibrium with the atmosphere and as measured, respectively. Because k_{CO_2} was not determined in this study, F was calculated for all possible ranges of k_{CO_2} using various relationships between wind speed and k_{CO_2} . The estimated k_{CO_2} ranged from 0.14 m d⁻¹ (based on Wanninkhof, 1992) to 1.92 m d⁻¹ (based on Borges et al., 2004) at the mean wind speed of 1.54 m s⁻¹ during the study period (from KMA). The carbon flux to the atmosphere was estimated at 220 to 3000 gC m⁻² yr⁻¹ for the silicate spring water and 30 to 430 gC m⁻² yr⁻¹ for the carbonate spring water. The silicate stream water had a carbon flux of 10 to 150 gC m⁻² yr⁻¹, whereas the carbonate stream water may have incorporated atmospheric CO₂ at rates of 2 to 30 gC m⁻² yr⁻¹. Although the estimated carbon flux was within the range reported in other studies (Richey et al., 2002; Yao et al., 2007; Brunet et al., 2009; Dubois et al., 2010), it is notable that the effect varied depending on the catchment lithology. In terms of the atmospheric CO₂ budget, the silicate catchments were assumed to act as stronger sources than the carbonate catchments, and carbonate stream waters may even act as a minor sink.

Table 3 presents a comprehensive carbon budget for the studied river systems. A few assumptions were made to derive the catchment-scale carbon budget. First, the data measured at the mouth of the stream collectively represent the carbon exchange characteristics of the stream waters, except for the first-order streams in the catchment. The first-order streams likely retained characteristics of the groundwater, which diminish in the higher-order streams (Johnson et al., 2008). Second, the spring waters represent the subsurface waters in each catchment, as discussed in Sect. 4.1. Third, the stream waters consisted primarily of discharged groundwater, although the hydrograph separation of the studied streams was not available.

The DIC discharge via the stream was the largest component, ranging from 12.7 gC m⁻² yr⁻¹ in the silicate catchment to 38.3 gC m⁻² yr⁻¹ in the carbonate catchment. CO₂ degassing from the stream (higher than second order) was 0.05 to 0.68 gC m⁻² yr⁻¹ in the silicate catchment, whereas CO₂ dissolution of -0.01 to -0.17 gC m⁻² yr⁻¹ occurred in the carbonate stream. Notably, the estimated CO₂ degassing associated with the groundwater discharge was significant, 1.1 to 14.9 gC m⁻² yr⁻¹ in the silicate catchment and 0.17 to 2.4 gC m⁻² yr⁻¹ in the carbonate catchment. Depending on the adopted k_{CO_2} , the CO₂ degassing (from both stream and groundwater) may have been responsible for 8–55 % of the total DIC export from the silicate catchment, whereas it took up only 0.4–5.6 % in the carbonate catchment. The results clearly indicate that CO₂ degassing at the interface between groundwater and streams in headwater regions needs to be considered to derive a reliable carbon budget in river systems, especially in silicate-dominant catchments.

The carbon budget estimates obtained in this study are different from those in other studies because the CO₂ degassing during groundwater discharge into the stream was

Table 3. Estimated annual carbon budget of the studied catchments. All units are gC m⁻² yr⁻¹.

Stream	Odae (silicate)	Jijang (carbonate)
DIC discharge via streams	12.7	38.3
CO ₂ degassing from streams*	0.05 ~ 0.68	-0.01 ~ -0.17
CO ₂ degassing from groundwater*	1.1 ~ 14.9	0.17 ~ 2.4

* Fluxes were calculated for the range of gas transfer coefficient.

considered. However, uncertainties may exist in the estimation of CO₂ evasion from groundwater. For example, there is uncertainty related to the characterization of the interface between groundwater and the stream because the quantity of CO₂ degassing depends on the dimension of the water surface. The interface was assumed to be the first-order stream where the immediate confluence of groundwater occurs. Previous studies (Johnson et al., 2008; Öquist et al., 2009) reported that the evasion of CO₂, accompanied by subsurface water input, was concentrated along a short distance (~200 m) of stream water from the confluence, which may substantiate this assumption. Another uncertainty is related to the proportion of groundwater components in the stream. Stream waters may contain variable amounts of surface runoff and direct precipitation. Hydrograph separation using various tracers can give quantitative estimates of these water components (Genereux and Hooper, 1998). Because it is assumed that the stream water was mostly derived from groundwater, the CO₂ degassing estimates in this study likely represent the highest possible amount. Moreover, the bi-weekly sampling adopted in this study possibly induce uncertainty in that rapid changes in water regimes associated with storm events may not be properly captured. A continuous monitoring of key variables (that can be used as surrogate for important water properties) of river waters is suggested for a more comprehensive and reliable understanding of river dynamics and associated carbon exchanges (e.g. Waldron et al., 2007).

5 Conclusions

The uppermost tributaries of the SHR, South Korea, provided an ideal natural setting to examine the effects of catchment lithology, seasonality in metabolic activities and water regimes, and atmospheric exchange on $\delta^{13}\text{C}_{\text{DIC}}$ and carbonate chemistry. $\delta^{13}\text{C}_{\text{DIC}}$ of the groundwater, represented by that of spring waters, clearly exhibited the effects of catchment lithologies, i.e. silicate vs. carbonate, on soil carbon dynamics. Seasonal variations were obvious in relation to the temperature-induced changes in metabolic activities in soils and the precipitation-induced changes in hydrologic regimes. Both stream waters were enriched with ¹³C compared to the

respective spring waters. This was in part due to aquatic photosynthesis, but was primarily caused by CO₂ degassing, which occurred during groundwater discharge and stream flow, but the magnitude was far greater from the groundwater. The estimated carbon budget depended on the catchment lithology. In the silicate catchment, CO₂ degassing associated with the groundwater discharge could be as high as the DIC discharge via the rivers. In contrast, DIC discharge via stream waters far exceeded CO₂ degassing from groundwater in the carbonate catchment, with possible CO₂ uptake by the stream. The results of this study emphasize the importance of CO₂ export associated with groundwater discharge at the headwater regions and the evaluation of its variability with the catchment lithology for a more comprehensive carbon budget of river systems.

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