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

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Abstract

We investigated dissolved inorganic carbon (DIC) exchange associated with groundwater discharge and stream flow from two upstream catchments with distinct basement lithology (silicate vs. carbonate). The effects of catchment lithology were evident in the spring waters showing lower $\delta^{13}C_{\text{DIC}}$ 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 $\delta^{13}C_{\text{DIC}}$ values, $-6.9 \pm 1.6\%$ 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. We emphasize the importance of dynamic carbon exchange occurring at headwater regions and its variability with catchment lithology for a more reliable carbon budget in river systems.

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 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 $0.43 \times 10^{15} \text{ g C yr}^{-1}$, representing about 40% of the total global carbon flux (Meybeck, 1987). 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, $\delta^{13}$C$_{DIC}$, 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 in the world’s rivers is known to originate from soil CO$_2$ (Meybeck, 1987; Ludwig et al., 1997). Based on stoichiometric considerations, the proportion of soil CO$_2$ in rivers ranges from $\sim$50% in carbonate catchments (another 50% is from the carbonate minerals) to $\sim$100% in silicate catchments. In upstream regions where groundwater contributes largely to stream flow, the input of groundwater containing DIC from soil CO$_2$ lowers the $^{13}$C/$^{12}$C ratio of DIC in river water because soil CO$_2$ 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 $^{13}$C/$^{12}$C ratio of DIC because these sources are enriched in $^{13}$C relative to $^{12}$C (Amiotte-Suchet et al., 1999). In addition to the strong over-saturation with CO$_2$ in groundwater components, stream water in upstream regions may also be more turbulent, causing rapid degassing of CO$_2$ into the atmosphere and remarkable $^{13}$C enrichment in DIC (Doctor et al., 2007).
The uppermost tributaries of the South Han River (SHR), South Korea, provide an ideal hydro-geological setting to investigate factors controlling 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, we measured the stable carbon isotopic composition of DIC and carbonate chemistry 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 upstream 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 are 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 rock, 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 rock with some sandstone at its upper reach. 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 largely of C₃ plants (mixed deciduous broadleaf and conifer forests) with seasonally cultivated C₄ (e.g., corn) crops. Table 1 presents information on the two streams (Water Management Information System: 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), we chose a perennial spring located at the bottom of a sandstone cliff from which water was discharging at ~37 m$^3$ day$^{-1}$. In the carbonate catchment (Jijang), we also chose a perennial spring flowing from the base of a carbonate cliff. 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.

Temperature, pH, dissolved oxygen (DO), and electrical conductivity (EC) were measured on site during water sampling using a YK-2001PH portable meter. Alkalinity was measured by titration with 0.05N HCl according to the Gran method (Rounds and Wilde, 2001). To fully characterize the carbonate system, ion activities were evaluated by PHREEQC (Parkhurst and Appelo, 1999). The partial pressure of CO$_2$ ($p$CO$_2$) was calculated by the speciation outputs from PHREEQC. The temperature-dependent equilibrium constants for the three species (H$_2$CO$_3$, HCO$_3^-$, and CO$_3^{2-}$) of the DIC summarized by Langmuir (1997) were used to calculate the activities of the three species.

For $\delta^{13}$C$_{DIC}$ 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-$\mu$m Millipore membrane filter. Samples were stored in a refrigerator prior to analysis. The DIC in water samples was converted into CO$_2$ gas by a gas-evolution technique (Atekwana and Krishnamuthy, 1998). The CO$_2$ gas was then extracted and cryogenically purified. Next, the $\delta^{13}$C values of the evolved CO$_2$ were measured using an Optima isotope-ratio mass spectrometer (GV Instruments, UK) at Chungnam National University. Carbon isotopic ratios are reported using standard $\delta$ notation, in per mil (‰) differences relative to the Vienna Pee Dee belemnite (VPDB).
standard, i.e., \( \delta (\%) = (R_{\text{sample}}/R_{\text{standard}} - 1) \times 1000 \), where \( R \) represents \(^{13}\text{C}/^{12}\text{C} \). The analytical reproducibility was \( \pm 0.2\% \).

3 Results

3.1 Spring waters

Figure 2 shows the precipitation, \( \delta^{13}\text{C}_{\text{DIC}} \) values, and \( p\text{CO}_2 \) of the four water types. Ranges and averages of the measured parameters are shown in Table 2. The pH values in silicate and carbonate springs were between 5.1 and 6.9 (average of 6.1, \( n = 23 \)) and between 7.7 and 8.5 (average of 8.0, \( n = 23 \)), respectively. Alkalinites were between 0.05 and 0.17 meq L\(^{-1}\) (average of 0.09 meq L\(^{-1}\)) in the silicate spring and between 1.50 and 2.21 meq L\(^{-1}\) (average of 1.96 meq L\(^{-1}\)) in the carbonate spring. Figure 2b shows seasonal variations in \( \delta^{13}\text{C}_{\text{DIC}} \) values of the spring waters. The silicate spring had \( \delta^{13}\text{C}_{\text{DIC}} \) values ranging from \(-21.2\) to \(-13.1\)\(\%\) (average of \(-16.2 \pm 2.7\)\(\%\)), and the carbonate spring had values from \(-13.2\) to \(-8.1\)\(\%\) (average of \(-9.7 \pm 1.5\)\(\%\)). The \( p\text{CO}_2 \) showed contrasting values between silicate and carbonate waters (Fig. 2c). The silicate spring waters had \( p\text{CO}_2 \) values ranging from 827 to 42,546 ppmv (average of 7520 ppmv), and the carbonate spring waters had \( p\text{CO}_2 \) values from 372 to 2196 ppmv (average of 1245 ppmv).

The \( \delta^{13}\text{C}_{\text{DIC}} \), alkalinity, and pH were the major parameters used to distinguish water derived from silicate and carbonate catchments. 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.
3.2 Stream waters

The pH ranged from 6.8 to 8.1 (average of 7.6, \( n = 15 \)) in the silicate stream and from 7.9 to 9.1 (average of 8.5, \( n = 15 \)) in the carbonate stream. EC (from 11 to 122 \( \mu \text{S cm}^{-1} \), average of 64, \( n = 20 \)) and alkalinity (from 0.22 to 0.74 meq L\(^{-1} \), average of 0.44, \( n = 23 \)) were lower in the silicate stream than in the carbonate stream, where EC ranged from 222 to 433 \( \mu \text{S cm}^{-1} \) (average of 301, \( n = 19 \)), and alkalinity ranged from 1.18 to 1.83 meq L\(^{-1} \) (average of 1.46, \( n = 23 \)). As shown in Fig. 2b, the silicate stream had \( \delta^{13} \text{C}_{\text{DIC}} \) values from –10 to –3.6‰, with an average of –6.9 ± 1.6‰ (\( n = 23 \)), whereas values from the carbonate stream ranged from –11.2 to –6.1‰, with an average of –7.8 ± 1.5‰ (\( n = 23 \)). The \( p\text{CO}_2 \) was higher in the silicate stream, ranging from 150 to 3380 ppmv (average of 720, \( n = 15 \)), than in the carbonate stream (50 to 1150 ppmv, average of 357). DO was mostly supersaturated with respect to atmospheric \( \text{O}_2 \), showing average DO\(_{\text{sat}}\) of 1.21 and 1.22 in the streams in the silicate and carbonate catchments, respectively.

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 with the respective spring water, alkalinity was higher in the silicate stream, but was lower in the carbonate stream.

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 have retained pristine characteristics of the groundwater in each catchment. To examine this, we calculated expected carbon isotopic composition of groundwater DIC originating exclusively from soil \( \text{CO}_2 \) (silicate catchment) and from a 1:1 mixture of soil \( \text{CO}_2 \) and carbonate minerals (carbonate catchment) and from 1:1 mixture of soil \( \text{CO}_2 \) and carbonate minerals (carbonate catchment).
catchment) (Clark and Fritz, 1997). We assumed that soil organic matter was from C3 plants with a mean $\delta^{13}C$ of $-27\%$ (O’Leary, 1988) and used the temperature dependence of carbon isotope fractionation between CO$_2$ and H$_2$CO$_3$/HCO$_3^-$ (Zhang et al., 1995). The ratio between H$_2$CO$_3$ and HCO$_3^-$ was calculated using $K_1/a^{H^+}$, where $K_1$ is the first dissociation constant of H$_2$CO$_3$, and $a^{H^+}$ was calculated from the measured pH. The expected average $\delta^{13}C_{DIC}$ in the silicate spring (with 35% HCO$_3^-$ and 65% H$_2$CO$_3$ at the average pH of 6.1) derived from soil CO$_2$ was $-24.7\%$, which was significantly lower than the measured average value of $-16.2 \pm 2.7\%$. For the carbonate spring, the expected $\delta^{13}C_{DIC}$ (over 99.9% HCO$_3^-$ at the average pH of 8.0) derived from 1:1 mixture of soil CO$_2$ and carbonate minerals was $-9.0\%$, which was close to the measured average value ($-9.7 \pm 1.5\%)$.

The discrepancy between measured and expected $\delta^{13}C_{DIC}$ values may be related to the presence of C4 plants (mostly corn) in the catchment area and/or degassing of CO$_2$ during the residence of water in the soil and groundwater reservoirs. The effect of C4 plant material cannot be quantitatively examined due to the lack of carbon isotope data of soil organic matter. The second possibility can explain the greater discrepancy observed in the silicate catchment. Because the proportion of dissolved CO$_2$ (H$_2$CO$_3$) in the total DIC was large in the silicate spring due to relatively low pH, the effect of CO$_2$ degassing was more significant. This interpretation is validated by the negative correlation ($r^2 = 0.92$) between $pCO_2$ and $\delta^{13}C_{DIC}$ and by the fact that water samples with higher $pCO_2$ showed $\delta^{13}C_{DIC}$ values closer to those of expected groundwater DIC (Fig. 4a) verify the effect of CO$_2$ degassing on $\delta^{13}C_{DIC}$ of the silicate spring, we referred to the study by Doctor et al. (2007). They reported that the increase in $\delta^{13}C_{DIC}$ per natural log-unit decrease of excess $pCO_2$ was 2.4\%, where excess $pCO_2$ is the measured $pCO_2$ normalized to the expected $pCO_2$ at atmospheric equilibrium. In our study, the relationship was calculated as a $2.3 \pm 0.2\%$ increase per unit decrease of excess $pCO_2$, indicating that the variability in silicate spring $\delta^{13}C_{DIC}$ 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 as remarkable as were those effects in the silicate spring. In summary, the spring waters may well represent the groundwater component modified by the CO$_2$ degassing to a variable degree.

4.2 The evolution of $\delta^{13}$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 $\delta^{13}$C$_{\text{DIC}}$ values between stream and spring waters was generally correlated in each catchment (with $r^2 = 0.62$ in the carbonate and $r^2 = 0.31$ in the silicate catchment), the difference between catchments was reduced (~0.9‰ between streams compared to ~6.5‰ between springs) and DIC was more enriched in $^{13}$C in stream waters. The increase in $\delta^{13}$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, we plotted the difference in $\delta^{13}$C$_{\text{DIC}}$ between the spring and stream waters ($\Delta \delta^{13}$C$_{\text{DIC}}$) against the dissolved O$_2$ saturation (DO$_{\text{sat}}$) in stream waters (Fig. 5a) and the difference in pCO$_2$ between the spring and stream waters ($\Delta$ pCO$_2$) (Fig. 5b). 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 $\Delta \delta^{13}$C$_{\text{DIC}}$ and DO$_{\text{sat}}$ was low ($r^2 < 0.1$), indicating that aquatic photosynthesis may not have been a major process for $^{13}$C enrichment. In addition, if photosynthesis resulted in $^{13}$C enrichment, there would have been a seasonal difference in $\delta^{13}$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, $\Delta \delta^{13}$C$_{\text{DIC}}$ exhibited a higher correlation ($r^2 = 0.52$ and 0.43) with $\Delta$ pCO$_2$ in both catchments. Therefore, a simplified interpretation regarding the enrichment of
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4.3 Seasonal variation in $\delta^{13}$C$_{DIC}$ and carbonate chemistry

The spring and stream samples exhibited well-defined seasonal variations characterized by low $\delta^{13}$C$_{DIC}$ values during summer (June to September) and high $\delta^{13}$C$_{DIC}$ values during winter (November to February) (Fig. 2b). In addition, $p$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 $p$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; Hamada and Tanaka, 2001; Hope et al., 2004; Xie et al., 2005; Yao et al., 2007; Jin et al., 2008). The addition of soil CO$_2$ via soil/groundwater resulted in low $\delta^{13}$C$_{DIC}$ values of the water. A negative correlation between $\delta^{13}$C$_{DIC}$ and $p$CO$_2$ in the spring samples in the silicate catchment indicates that soil-derived CO$_2$ was the main cause of seasonality in $\delta^{13}$C$_{DIC}$ values (Fig. 4a). The correlation between $\delta^{13}$C$_{DIC}$ and $p$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 $\delta^{13}$C$_{DIC}$ were positively correlated with EC.
in the spring ($r^2 = 0.58$) and stream ($r^2 = 0.49$) waters (Fig. 4b), and waters with low EC occurred during the summer when $\delta^{13}C_{DIC}$ values were 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 $\delta^{13}C_{DIC}$ 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: www.kma.go.kr), varied throughout the study period (Fig. 2a). The average monthly precipitation during summer and early fall (June to October) was 202.8 mm, but for the rest of the year (November to May) it was only 39.3 mm. The seasonal variation of precipitation roughly coincided with the fluctuations in $\delta^{13}C_{DIC}$ (Fig. 2b) of all water samples and in EC (Fig. 4b) of the carbonate catchment. During the dry season (October to May), 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 $\delta^{13}C_{DIC}$ and EC of the soil water. In contrast, during the wet season (June to September), 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 summer and early fall displays lower $\delta^{13}C_{DIC}$ values and EC than does soil water during the winter season (Amiotte-Suchet et al., 1999). The transport of $CO_2$ produced by soil respiration via soil/groundwaters with distinct EC is facilitated by the concentrated precipitation in summer. The effect of $CO_2$ was not clearly observed in the waters from the carbonate catchment due to lower $CO_2/HCO_3^-$ ratios, but the analogous effect associated with seasonal changes in soil respiration and water regime can be expressed by EC vs. $\delta^{13}C_{DIC}$ plots (Fig. 4b).
4.4 DIC export from the river system

The importance of CO₂ degassing was suggested from the previous discussion on the changes in δ¹³C_DIC values of spring and stream waters. The calculated excess pCO₂ 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 CO₂ and assumed to act as the source of atmospheric CO₂ (Yao et al., 2007). Although the excess pCO₂ in the carbonate stream was lower than 1, indicating possible invasion of atmospheric CO₂, its DIC was still depleted in ^{13}C compared with atmosphere-derived DIC (∼0‰, assuming δ^{13}C of atmospheric CO₂ to be −7.8‰ from Brunet et al., 2005). 

To quantitatively determine the amount of CO₂ degassing, we applied the following flux equation:

\[ F = k_{CO_2} (C_{eq} - C) \]

where \( F \) is the diffusive flux of CO₂ 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, we calculated \( F \) 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 g C m⁻² y⁻¹ for the silicate spring water and 30 to 430 g C m⁻² y⁻¹ for the carbonate spring water. The silicate stream water had a carbon flux of 10 to 150 g C m⁻² y⁻¹, whereas the carbonate stream water may have incorporated atmospheric CO₂ at rates of 2 to 30 g C m⁻² y⁻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 g C m$^{-2}$ y$^{-1}$ in the silicate catchment to 38.3 g C m$^{-2}$ y$^{-1}$ in the carbonate catchment (data are normalized to the catchment area). CO$_2$ degassing from the stream (higher than second order) was 0.05 to 0.68 g C m$^{-2}$ y$^{-1}$ in the silicate catchment, whereas CO$_2$ dissolution of $-0.01$ to $-0.17$ g C m$^{-2}$ y$^{-1}$ occurred in the carbonate stream. Notably, the estimated CO$_2$ degassing associated with the groundwater discharge was significant, 1.1 to 14.9 g C m$^{-2}$ y$^{-1}$ in the silicate catchment and 0.17 to 2.4 g C m$^{-2}$ y$^{-1}$ in the carbonate catchment. Depending on the adopted $k_{CO_2}$, the CO$_2$ 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 CO$_2$ 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.

Our carbon budget estimates are different from those in other studies because we considered the CO$_2$ degassing during groundwater discharge into the stream. However, uncertainties may exist in our estimation of CO$_2$ evasion from groundwater. For example, there is uncertainty related to the characterization of the interface between
groundwater and the stream because the quantity of CO$_2$ degassing depends on the dimension of the water surface. We assumed that the interface was 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 CO$_2$, accompanied by subsurface water input, was concentrated along a short distance (∼200 m) of stream water from the confluence, which may substantiate our 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 (Genereaux and Hooper, 1998). Because we assumed that the stream water was mostly derived from groundwater, the CO$_2$ degassing estimates in this study likely represent the highest possible amount.

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 δ$_{13}$C$_{DIC}$ values and carbonate chemistry. The relatively pristine DIC sources can be represented by spring waters, which clearly exhibited the effects of catchment lithology, i.e., silicate vs. carbonate, on δ$_{13}$C$_{DIC}$ values. Seasonal variations were obvious in relation to the temperature-induced changes in metabolic activities and the precipitation-induced changes in hydrologic regimes. Both stream waters were enriched with $^{13}$C compared to the respective spring waters. This was in part due to aquatic photosynthesis, but was primarily caused by CO$_2$ degassing, which occurred from the groundwater and streams, but the magnitude was far greater from the groundwater. The estimated carbon budget depended on the catchment lithology. In the silicate catchment, CO$_2$ 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 CO$_2$ degassing from groundwater.
in the carbonate catchment, with possible CO$_2$ uptake by the stream. We emphasize the importance of CO$_2$ export associated with groundwater discharge at the headwater regions and its variability with the catchment lithology for a more comprehensive carbon budget of river systems.

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Taylor, C. B. and Fox, V. J.: An isotopic study of dissolved inorganic carbon in the catchment of the Waimakariri River and deep ground water of the North Canterbury Plains, New Zealand,
**Table 1.** Comparison of the physical characteristics and mean discharge for the Odae and Jijang catchments (Water Management Information System: www.wamis.go.kr).

<table>
<thead>
<tr>
<th>Tributary</th>
<th>Odae (silicate)</th>
<th>Jijang (carbonate)</th>
</tr>
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<tbody>
<tr>
<td>Catchment area (km²)</td>
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<td>225</td>
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<tr>
<td>Total stream length (km)</td>
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<td>1st order stream length (km)</td>
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<td>Mean width (m)</td>
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<td>5.6</td>
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<tr>
<td>Mean discharge (m³ s⁻¹)</td>
<td>7</td>
<td>3</td>
</tr>
</tbody>
</table>

* Main channel corresponds to 5th order stream in both catchments.
### Table 2. Statistical summary of geochemical parameters measured from springs and streams in the study area.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Min</th>
<th>Max</th>
<th>Aver</th>
<th>SD</th>
<th>Min</th>
<th>Max</th>
<th>Aver</th>
<th>SD</th>
<th>Min</th>
<th>Max</th>
<th>Aver</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta^{13}$C$_{DIC}$ (‰)</td>
<td>$-21.2$</td>
<td>$-13.1$</td>
<td>$-16.2$</td>
<td>$2.7$</td>
<td>$-10.0$</td>
<td>$-3.6$</td>
<td>$-6.9$</td>
<td>$1.6$</td>
<td>$-13.2$</td>
<td>$-8.1$</td>
<td>$-9.7$</td>
<td>$1.5$</td>
</tr>
<tr>
<td>Temp. (°C)</td>
<td>$8.8$</td>
<td>$12.7$</td>
<td>$10.7$</td>
<td>$1.3$</td>
<td>$0.4$</td>
<td>$28.0$</td>
<td>$11.0$</td>
<td>$8.9$</td>
<td>$8.9$</td>
<td>$14.3$</td>
<td>$11.6$</td>
<td>$1.9$</td>
</tr>
<tr>
<td>pH</td>
<td>$5.1$</td>
<td>$6.9$</td>
<td>$6.1$</td>
<td>$0.5$</td>
<td>$6.8$</td>
<td>$8.1$</td>
<td>$7.9$</td>
<td>$0.3$</td>
<td>$7.7$</td>
<td>$8.5$</td>
<td>$8.0$</td>
<td>$0.2$</td>
</tr>
<tr>
<td>DO (mg L$^{-1}$)</td>
<td>$9.7$</td>
<td>$18.8$</td>
<td>$12.2$</td>
<td>$2.0$</td>
<td>$10.0$</td>
<td>$19.6$</td>
<td>$13.4$</td>
<td>$2.8$</td>
<td>$8.6$</td>
<td>$15.6$</td>
<td>$11.6$</td>
<td>$1.6$</td>
</tr>
<tr>
<td>EC (µS cm$^{-1}$)</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>11</td>
<td>122</td>
<td>64</td>
<td>31</td>
<td>171</td>
<td>389</td>
<td>254</td>
<td>62</td>
<td>222</td>
</tr>
<tr>
<td>Alk (meq L$^{-1}$)</td>
<td>$0.05$</td>
<td>$0.17$</td>
<td>$0.09$</td>
<td>$0.0$</td>
<td>$0.22$</td>
<td>$0.74$</td>
<td>$0.44$</td>
<td>$0.15$</td>
<td>$1.50$</td>
<td>$2.21$</td>
<td>$1.96$</td>
<td>$0.21$</td>
</tr>
<tr>
<td>DIC (mg L$^{-1}$)</td>
<td>$5.6$</td>
<td>$103.3$</td>
<td>$22.7$</td>
<td>$23.3$</td>
<td>$13.7$</td>
<td>$45.5$</td>
<td>$26.0$</td>
<td>$10.0$</td>
<td>$93.1$</td>
<td>$137.9$</td>
<td>$121.8$</td>
<td>$12.8$</td>
</tr>
<tr>
<td>$p$CO$_{2}$ (ppmv)</td>
<td>$827$</td>
<td>$42.546$</td>
<td>$7520$</td>
<td>$10.239$</td>
<td>$150$</td>
<td>$3380$</td>
<td>$720$</td>
<td>$81.9$</td>
<td>$372$</td>
<td>$2197$</td>
<td>$1245$</td>
<td>$466$</td>
</tr>
</tbody>
</table>

ND: not determined.
Min, Max, Aver, and SD represent minimum, maximum, average, and standard deviation, respectively.
Table 3. Estimated annual carbon budget of the studied catchments. All units are g C m\(^{-2}\) y\(^{-1}\) and normalized to the catchment area.

<table>
<thead>
<tr>
<th>Tributary</th>
<th>Odae (silicate)</th>
<th>Jijang (carbonate)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DIC discharge via streams</td>
<td>12.7</td>
<td>38.3</td>
</tr>
<tr>
<td>CO(_2) degassing from streams(^*)</td>
<td>0.05 ~ 0.68</td>
<td>−0.01 ~ −0.17</td>
</tr>
<tr>
<td>CO(_2) degassing from groundwater(^*)</td>
<td>1.1 ~ 14.9</td>
<td>0.17 ~ 2.4</td>
</tr>
</tbody>
</table>

\(^*\) Fluxes were calculated for the range of gas transfer coefficient.
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.
Fig. 2. Amount of precipitation (a), $\delta^{13}$C$_{\text{DIC}}$ values (b), and $p$CO$_2$ (c) of waters from the silicate and carbonate catchments during 2005.
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.
**Fig. 4.** Cross plots of $p$CO$_2$ vs. $\delta^{13}$C$_{DIC}$ (a), and EC vs. $\delta^{13}$C$_{DIC}$ (b). Summer = June through September. The $\delta^{13}$C$_{DIC}$ value of rainwater is from Zhang et al. (1995).
Fig. 4. Cross plots of $pCO_2$ vs. $\delta^{13}C_{DIC}$ (a), and EC vs. $\delta^{13}C_{DIC}$ (b). Summer = June through September. The $\delta^{13}C_{DIC}$ value of rainwater is from Zhang et al. (1995).

Fig. 5. Cross plots of (a) $DO_{sat}$ vs. $\Delta\delta^{13}C_{DIC}$ [$\delta^{13}C_{DIC}$ (stream water) – $\delta^{13}C_{DIC}$ (spring water)], and (b) $\Delta pCO_2$ [$pCO_2$ (spring water) – $pCO_2$ (stream water)] vs. $\Delta\delta^{13}C_{DIC}$.

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