Variation Pattern of $\delta^{13}C_{DIC}$ of the Odaecheon Stream Water

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ABSTRACT

Carbon isotopic composition of a stream (Odaecheon Stream) monitored over 7 months from July 2004 to January 2005 in Gangweon Province ranges from −9.24 to −4.69‰. Strong negative correlation between $\delta^{13}C_{DIC}$ and water temperature suggests that temperature is a dominant factor controlling $\delta^{13}C_{DIC}$ in the Odaecheon Stream. The variation pattern of $\delta^{13}C_{DIC}$ was thought to be caused by fractionation of C isotope between stream water and atmosphere and more fractionation at reduced temperature. More fractionation of C isotope between stream water and atmosphere at reduced temperature resulted in increase of $\delta^{13}C_{DIC}$ of stream water in winter compared to summer. Photosynthesis and respiration of aqueous biota seem to affect little in $\delta^{13}C_{DIC}$ as indicated by little variation of dissolved oxygen and reverse variation pattern of Eh in the stream and scarce aqueous biota in stream water. pH seems to be controlled by CO_2 exchange between stream water and atmosphere. During summer more CO_2 exchange between stream water and atmosphere resulted in decrease in pH value.

Keywords : stream water, $\delta^{13}C$, dissolved inorganic carbon (DIC), fractionation.

Introduction

Measurements of the $\delta^{13}C_{DIC}$ in water samples are generally used in studies of carbon geochemistry of natural waters (Atekwana and Krishnamuthy, 1998). $\delta^{13}C_{DIC}$ has widely been used as an effective tool in distinguishing carbon originating from a variety of sources (Mook et al., 1974; Rau, 1978; Mook and Tan, 1991; Pawellek and Veizer, 1995). The $\delta^{13}C$ value of atmospheric CO_2 is about -7 to -8‰ and plant organic matter shows -24 to -34‰ for plant organic matter. Because the soil CO_2 is derived mostly from decomposed organic matter, it has similar $\delta^{13}C$ values to those of the plant organic matter (Wang and Veizer., 2000). The dissolution of soil CO_2 into water results in the fractionation of about +7‰ (Wigley et al., 1978), giving a $\delta^{13}C$ value for DIC of about -17 to -21‰ (Wang & Veizer, 2000). Photosynthesis of aqueous biota leads enrichment of $\delta^{13}C_{DIC}$ in water whereas respiration leads depletion of $\delta^{13}C_{DIC}$ (Wang & Veizer, 2000). Exchange of CO_2 between water and atmosphere results in the fractionation of C isotope. Photosynthesis and respiration of aqueous biota affects $\delta^{13}C_{DIC}$, pH and Eh. The purpose of this paper is to reveal the variation pattern of $\delta^{13}C_{DIC}$ of a stream (Odaecheon) and its controlling factors.

Fig. 1. Map showing the Odaecheon Stream and locality where water samles were collected and geochemical parameters were measured.

Material and method

Water samples were collected from the Odaecheon Stream located at Pyongchang and Jeongseon area, Gangwon Province (Fig. 1). The stream flows on the sandstone drainage area which is covered by thick forest. Relatively steep slope of drainage area allows relatively thin soil cover. Water samples were collected almost every two weeks from July 2004 to January 2005. Occasionally, water sample was collected once in three to four weeks. Two vacutainer glass bottles (150ml) were used for sampling, which include pre-loaded 85% phosphoric acid (5ml) and magnetic stir bar as used by Atekwana and Krishnamuthy (1998). The water samples were collected using the syringe in the field and it was filtered through the 0.45㎛ millipore membrane during sampling (Telmer and Veizer, 1999). The samples were stored in refrigerator before analysis. Temperature, redox potential, total dissolved solid, pH, electrical conductivity and dissolved oxygen were measured during water sampling using a YK-2001PH meter. The pH meter was calibrated using the buffer solution of which pH is both 7.00 and 4.00. Electrical conductivity was measured after calibrating pH meter with 1.413mS calibration solution. The water sample was reacted with 5ml of 85% phosphoric acid (H_3PO_4) then DIC was converted into gaseous CO_2. Water vapour was eliminated by double trapping device (first a liquid N_2-trap of nearly -200℃, second a alcohol trap of nearly -85℃) (Hélie et al., 2002), and then gaseous CO_2 was only collected in glass tube. $\delta^{13}C$ of collected gaseous CO_2 was measured using a stable isotope ratio mass spectrometer (VG-Optima) at the Chungnam National University.

Results

The values of $\delta^{13}C$ and other geochemical parameters are presented in Table 1. $\delta^{13}C_{DIC}$ ranges from -9.24 to -4.69‰ with a mean value of -7.22‰. Water temperature in the study area ranges from 0.8 to 24.8℃. Redox potential value varies from 58 to 255mV. The mean redox potential value from July ninth to October eighth record 206.6mV thereafter its mean value is 89.2mV. Electrical conductivity value is between 24 to 88μS and it had no characteristic pattern throughout the investigation period. Total dissolved solid demonstrates the same pattern with electrical conductivity. Dissolved oxygen ranges from 9.6 to 15.8mg/l and tends to be increased toward the winter months.

Table 1. values of $\delta^{13}C$ and other geochemical parameters of the Odaecheon Stream.

Date	$\delta^{13}C_{DIC}$(‰)	T(℃)	pH	Eh(mV)	EC(μS)	DO(mg/l)	TDS(mg/l)
7/9/04		16.1	7.55	249	24	12.3	16
7/27/04	-9.24	21.9	7.8	232	72	10.6	48
8/6/04	-8.57	24.8	8.23	188	86	9.6	43
9/3/04	-8.16	20.7	8.92	155	88	10.9	58
9/16/04	-8.37	18.7	7.81	256	38	11.8	25
9/24/04	-7.95	17.2	8.28	193	43	12.1	29
10/1/04	-7.93	18.1	8.49	204	63	10.8	42
10/8/04	-7.67	15.8	8.34	176	71	12.4	47
10/15/04	-6.90	13.3	8.42	83	72	12.2	49
11/5/04	-6.58	9.9	8.56	93	73	13.1	48
12/3/04	-4.69	4.7	8.63	80	63	15.4	42
12/22/04	-5.10	1.1	8.45	58	56	15.6	37
1/7/05	-5.50	0.8	7.64	132	87	15.8	58
average	-7.22	14.1	8.24	161	64	12.5	42

Discussion

$\delta^{13}C_{DIC}$ of riverine system was controlled by exchange of CO_2 between stream water and atmosphere, photosynthesis and respiration of aqueous biota, and groundwater CO_2 (Atekwana and Krishnamuthy, 1998). These processes isotopically imprinted on DIC (Hélie et al., 2002). In general, the enrichment in $\delta^{13}C_{DIC}$ is caused by evasion of isotopically light aqueous CO_2 into atmosphere and exchange of CO_2 between atmosphere and water results in equilibrium state between aqueous and atmospheric CO_2 (Amiette-Suchet et al., 1999). Photosynthesis causes $\delta^{13}C_{DIC}$ enrichment whereas respiration causes $\delta^{13}C_{DIC}$ depletion (Mook et al., 1974; Mook and Tan, 1991; Pawellek and Veizer, 1995).

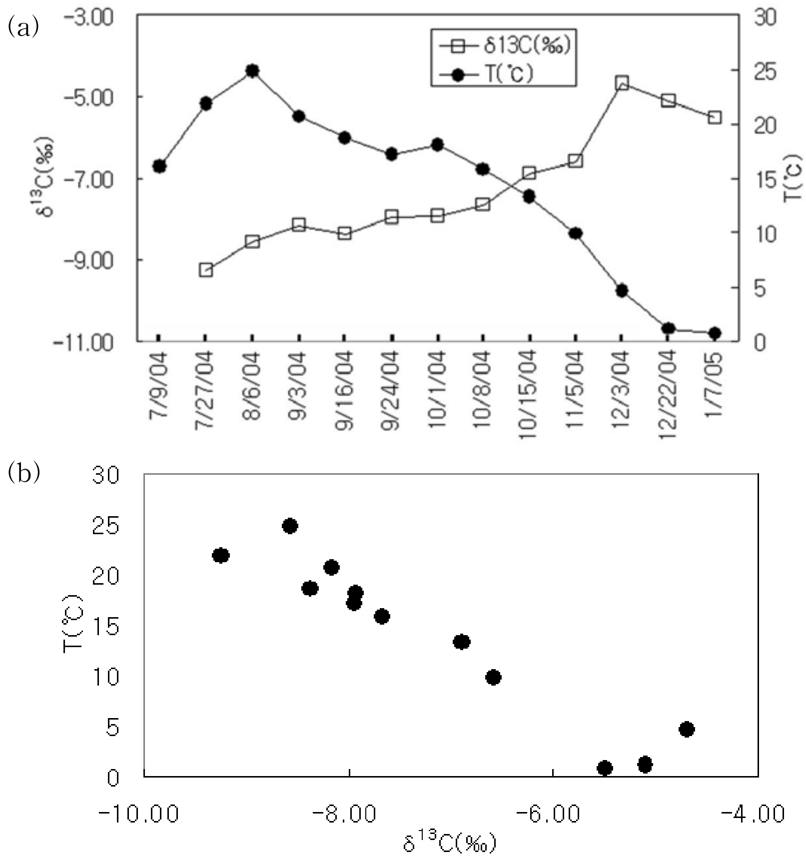

Fig. 2. Seasonal variation of the $\delta^{13}C_{DIC}$ and T for the Odaecheon Stream. (a) shows the $\delta^{13}C_{DIC}$ value and T variation with time and (b) shows the cross plot of the $\delta^{13}C$ and T.

$\delta^{13}C_{DIC}$ vs. water temperature shows a strong correlation (Fig. 2) which suggests that water temperature is a dominant factor controlling $\delta^{13}C_{DIC}$. As CO_2 gas dissolves into water, some of it hydrates and dissociates into HCO_3^- and CO_3^{2-} depending on pH of water. Exchange of CO_2 between air and water and phase change of CO_2 into HCO_3^- and CO_3^{2-} result in fractionation of C isotope. Dissolution of CO_2 gas into water results in 1.1‰ depletion of $\delta^{13}C$ value whereas phase change of aqueous CO_2 into HCO_3^- results in 9.0‰ enrichment (Clark and Fritz, 1997). As the pH value of the Odaecheon Stream is 8.24 in average, most of carbonate species in water is HCO_3^- and phase change of CO_2 into $CO_{2\,3}^{-}$ is negligible. Fractionation of ^{13}C between $CO_{2(g)}$, $CO_{2(aq)}$ and HCO_3^- is temperature dependent; more fractionation occurs at lower temperature (Mook et al., 1974; Vogel et al., 1970).

A strong negative correlation between temperature and $\delta^{13}C_{DIC}$ of the Odaecheon Stream water is interpreted to be caused by the following reasons. Firstly fractionation factor between $CO_{2(aq)}$ and HCO_3^- is 9.0‰ which surpasses the fractionation factor of -1.1‰ between $CO_{2(g)}$ and $CO_{2(aq)}$. Secondly fraction of ^{13}C between $CO_{2(g)}$ and $CO_{2(aq)}$ as well as $CO_{2(aq)}$ and HCO_3^- is temperature dependent; more fractionation occurs at lower temperature. Therefore more fractionation of ^{13}C toward enrichment occurs in winter stream CO_2 which resulted in a negative

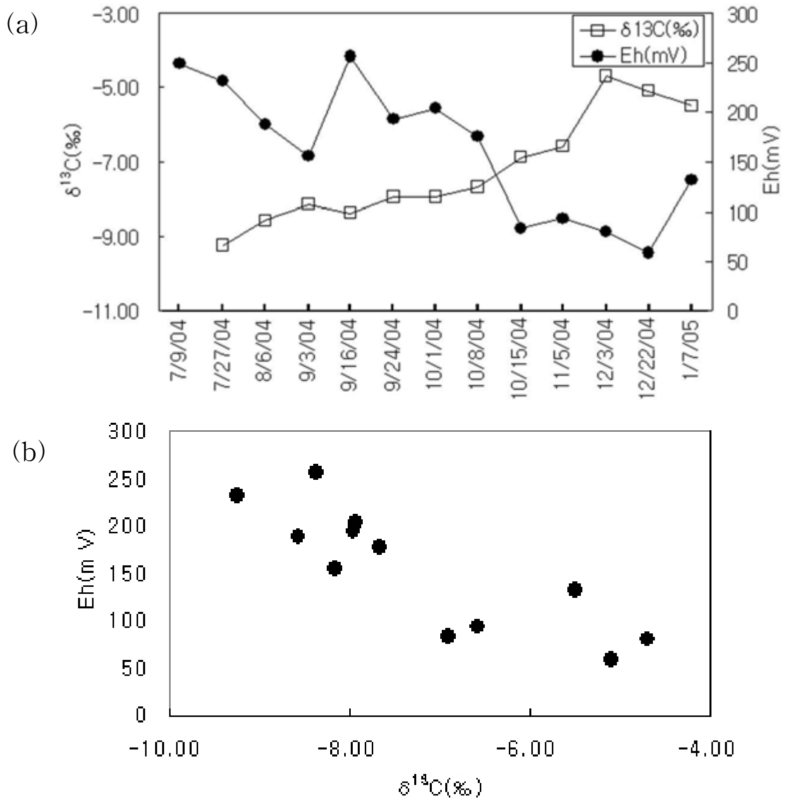

Fig. 3. Seasonal variation of Eh and $\delta^{13}C$ for the Odaecheon Stream. (a) is the $\delta^{13}C$ and Eh relation. (b) is the cross plot of the $\delta^{13}C$ and Eh relation.

correlation between $\delta^{13}C_{DIC}$ vs. temperature. On the other hand $\delta^{13}C$ values in December and January water sample shows a decreasing pattern as temperature decreases (Fig. 2). This pattern of decreasing value of $\delta^{13}C_{DIC}$ seems to be resulted from ice cover of the stream which prevents evasion of light C isotope from the water surface.

Eh value varies with dissolved oxygen; high Eh value is expected at high DO value in water. The redox potential values from July ninth to October eighth shows high compared to those from October fifteenth to January seventh (Fig. 3). This pattern of Eh value seems to be resulted from photosynthesis (Brownlow, 1979). Active photosynthesis in summer and early autumn tends to produce disequilibrium and high oxidation potential which reflects high Eh value (Fig. 3).

pH value varies with CO_2 exchange between air and water, and photosynthesis and respiration. Lowering of pH occurs as more CO_2 gas invades into water. Dissolution of air CO_2 into water and respiration result in the lowering of pH whereas evasion of water CO_2 and photosynthesis result in increasing of pH of water. pH with time shows no distinct variation pattern (Fig. 4). This suggest that amount of CO_2 exchange and metabolism of aqueous biota in the Odaecheon Stream did not affect significantly the variation of $\delta^{13}C_{DIC}$ value.

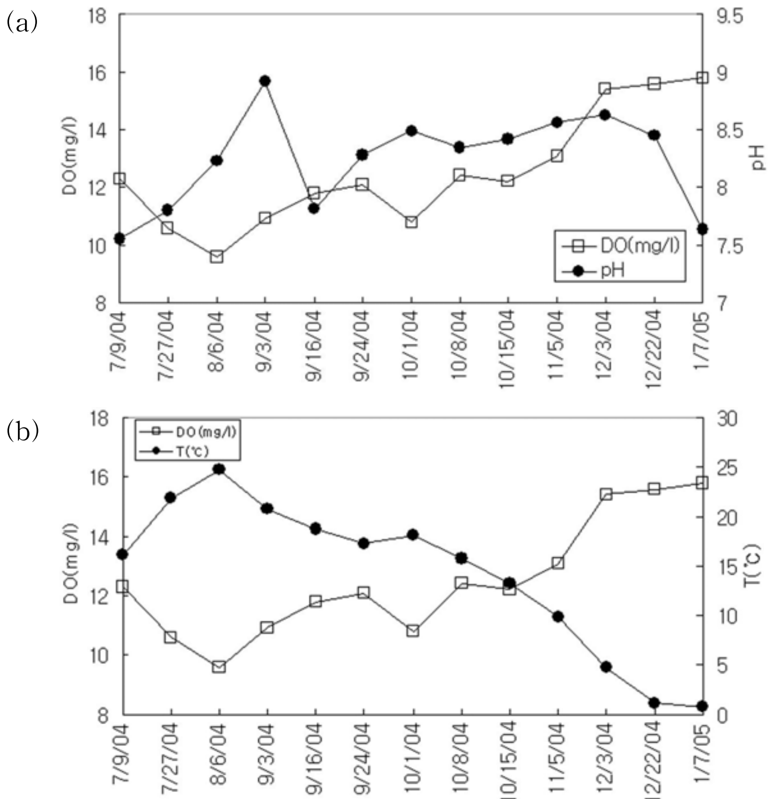

Fig. 4. Seasonal variation of the DO, pH and T for the Odaecheon Stream. (a) shows the DO and pH variation, and (b) shows the DO and T variation.

Total ion concentration and temperature influence electrical conductivity. Electrical conductivity increases with temperature increase and total dissolved solid is in proportional to electrical conductivity in the fresh water system (Kim, 1995). Composition of the surface water generally depends on the type of rock and soil. In general, groundwater contains more solutes than water from surface runoff (Brownlow, 1979). EC value of the Odaecheon Stream is thought to reflect the input of base flow.

Dissolved oxygen value depends on photosynthetic activities of aquatic plants and invasion of oxygen into water from the atmosphere (Wilde and Radtke, 1998). Dissolved oxygen will be undersaturated when respiration exceeds photosynthesis (Kiddon et al., 1993). The opposite case will result in saturating dissolved oxygen (Wang and Veizer, 2000). Dissolved oxygen in the study area appeared to increasing trend in winter (Fig. 4). This pattern of DO variation suggests that DO from metabolism of aquatic biota is overwhelmed by DO increase by lowering of temperature.

Conclusion

A strong negative correlation between $\delta^{13}C_{DIC}$ and water temperature in the Odaecheon Stream suggests that water temperature is a main factor controlling $\delta^{13}C_{DIC}$ of stream water. Higher $\delta^{13}C_{DIC}$ value during winter than summer resulted from the facts that (1) temperature dependent fractionation of ^{13}C during exchange of CO_2 between air and water, (2) phase change of carbonate between aqueous CO_2 and HCO_3^-, (3) ^{13}C tends to be enriched in water during phase change of carbonate species, and (4) metabolism of aquatic biota little affects $\delta^{13}C_{DIC}$ of the Odaecheon Stream water as indicated by an indistinct seasonal variation pattern of pH with $\delta^{13}C_{DIC}$ and reverse variation pattern of DO against temperature. Total ion concentration and temperature influence electrical conductivity. No characteristic pattern of electrical conductivity and intermediate value of electrical conductivity suggest that some portion of the Odaecheon Stream water comes from groundwater. High Eh values in summer resulted from active aquatic photosynthetic activity.

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