

# Identification of sources affecting water chemistry in the Nakdong River, South Korea

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**Abstract** The sources impacting the water chemistry of the Nakdong River (NR) in South Korea were investigated in order to examine the pollution mechanism including the fate and transport of the contaminants and how much such sources may affect its main channel of water resource. Water samples were collected between 2007 and 2008 from 8 sites along a 510 km downstream transect of the NR, and chemical and isotopic compositions of the water samples were evaluated to identify natural and anthropogenic sources contributing to the water chemistry of the NR. The results showed that the major ion concentrations were mainly controlled by chemical weathering that occurred in the watershed, in which a silicate weathering is more dominant than a carbonate weathering. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the water samples were in a range from 0.71043 to 0.71520 within those of the Mesozoic volcanogenic sedimentary rocks long developed in the watershed, thereby supporting the fact that the water chemistry is governed by a chemical weathering. The  $\delta^{34}\text{S}$  values varied in a narrow range of 1.8–3.1‰, regardless of spatial and seasonal variations. Mass balance calculations indicated that the contributions of chemical weathering and anthropogenic sources during summer time increased along a downstream transect, from  $67.3 \pm 1.3$  to  $73.6 \pm 0.5\%$  and from 6.0 to 15.7%, respectively. In contrast, the contribution of chemical weathering during winter time decreased from

$82.7 \pm 0.8$  to  $72.5 \pm 0.3\%$ , while anthropogenic contribution increased up to 22.2%. These results indicated that the water chemistry of the NR was mainly caused by a chemical weathering, followed by anthropogenic inputs and rainwater. This study will provide baseline information for comparing the water quality issue before and after the implementation of the Four Rivers Restoration Project of South Korea.

**Keywords** Chemical weathering · Anthropogenic source · Sulfur isotope · The Nakdong River · Four Rivers Restoration Project

## Introduction

It has been a big issue in numerous studies to quantify mineralogical sources of Ca and Mg in rivers because the release of Ca and Mg from minerals during chemical weathering is closely related to biogeochemical processes and global carbon cycle (e.g., Berner et al. 1983; Likens et al. 1996; White et al. 2005). However, this is quite difficult to explain how the chemical weathering is related to various type of rocks that contain multiple Ca- and Mg-bearing minerals, and therefore, most studies have indirectly constrained source apportionment using major ion balances or strontium isotope ratios ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) (Gaillardet et al. 1999; Miller et al. 1993; Négrelet et al. 1993; Spence and Telmer 2005; Wu et al. 2008). Elemental and isotope tracers are useful because they reveal reaction pathways, transport processes, and source apportionments that may otherwise be difficult to discern with normative mineral calculations and other bulk elemental accounting methods.

The sulfate ( $\text{SO}_4$ ) in rivers is generally derived from soil sulfur (Balík et al. 2007; Mayer et al. 1995; Stevenson and

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Cole 1999; Yu and Park 2004); total S  $\approx$  10–2500 mg/L, atmospheric inputs,  $[\text{SO}_4] \approx$  0.3–16 mg/L, sulfide oxidation, and anthropogenic sources from chemical fertilizers, domestic wastewater, and detergents,  $[\text{SO}_4] \approx$  1.0–130 mg/L. Their relative proportions can determine the riverine sulfur isotopic composition ( $\delta^{34}\text{S}$ ) (Krouse and Mayer 2000; Mayer et al. 1995; Yu and Park 2004); soil has  $\delta^{34}\text{S}$  values of  $-1.0$  to  $8.0\%$ , precipitation of  $-3.9$  to  $8.2\%$  ( $n = 23$ ), sulfide oxidation of  $-35$  to  $8.0\%$ , detergents of  $18.0$  to  $31.3\%$  ( $n = 5$ ), domestic wastewater of  $15.1$  to  $24.2\%$  ( $n = 2$ ), and fertilizers of  $-7.6$  to  $-2.6\%$  ( $n = 5$ ), respectively. Thus,  $\delta^{34}\text{S}$  value combined with  $\text{SO}_4$  concentration can be a powerful tracer to identify the riverine  $\text{SO}_4$  sources (Grasby et al. 1997; Mayer 2005).

Likewise, boron (B), which is abundant in coal,  $[\text{B}] \approx$  5–400 mg/L (Swaine 1994; Swaine and Goodarzi 1995) and man-made materials such as detergents and chemical fertilizers, 0.5–100% as a form of various boron compounds (Ghavanloughajar 2015), can be used to apportion their sources in river waters because it is not affected by adsorption or microbial activity in rivers, and is not even removed by traditional wastewater treatment process (Chetelat and Gaillardet 2005; Petelet-Giraud et al. 2009; Sakata et al. 2010). Although numerous studies have suggested an excess of B in surface/subsurface waters due to anthropogenic inputs including sewage, urban irrigation, and industrial effluent (Chetelat and Gaillardet 2005; Hasenmueller and Criss 2013; Lee et al. 2005), chemical weathering of basalts and carbonate rocks was a major contributor (Stefánsson and Gíslason 2001; You et al. 1993).

The Nakdong River (NR) is the longest river in South Korea and flows through various land areas such as national industrial districts, a great number of wastewater treatment plants, agricultural areas, and metropolitan areas, and eventually reaches to the South Sea, Korea. In spite of the socioeconomic importance of the NR as a major source of drinking water supply to over 6.5 million populations in the South-East Korean Peninsula, however, no up-to-date watershed-scale information is available on the chemical and isotopic characteristics of the rivers. Only a few studies investigated regional water contaminations focusing on tributaries draining industrial districts and agricultural areas (Chung et al. 1997, 1998; Lee et al. 2005; Seo et al. 2003). In a recent event, the Four Rivers Restoration Project, a part of the “Green New Deal” policy that launched in 2009, was commenced and finished at the Korean major rivers including the NR until 2013. During this mega civil project, many weirs were constructed in a number of locations of the four rivers, and many tributaries were subject to restoration.

The study was conducted on a watershed scale, quantifying the seasonal and spatial variations of chemical and

isotopic compositions of the NR waters, and identifying various sources affecting the river water chemistry. This study will provide baseline information on the overall characteristics of the NR water chemistry and further comparison with the water quality in NR after the implementation of the ongoing controversial Four Rivers Restoration Project. Furthermore, it will provide a basis for future biogeochemical watershed-scale investigations in the NR.

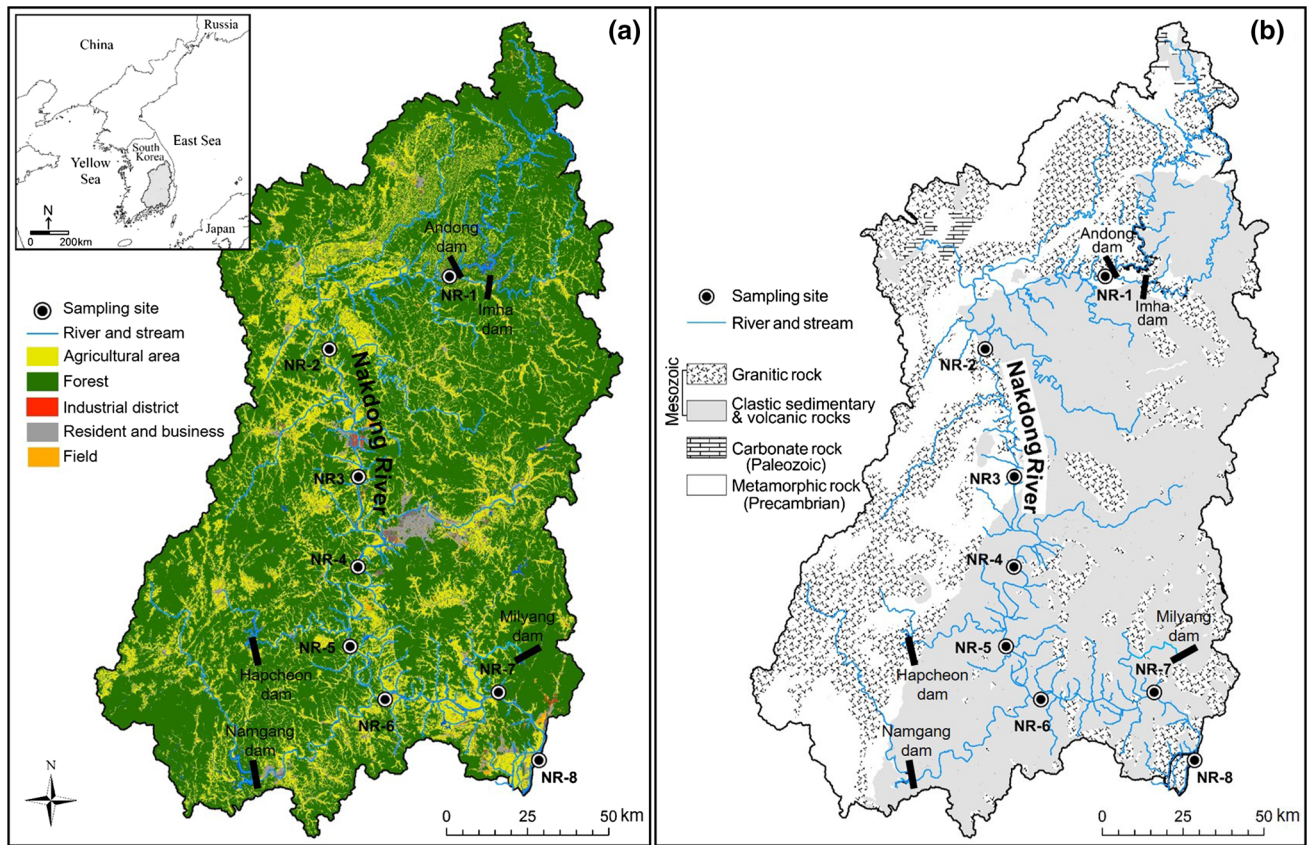
## Materials and methods

### Description of the study area

The NR, with a length of 510 km, is the longest river in South Korea and has the second-largest drainage area of 23,384 km<sup>2</sup> (Nakdong River Flood Control Office 2016). The discharge rates during the sampling activities between August 2007 and February 2008 were 1248 and 611 m<sup>3</sup>/s, respectively (Water Resources Management Information System 2016). The NR flows from the northeastern to southeastern area of South Korea. There are two dam structures such as Andong and Imha in the upstream reaches and three dams such as Hapcheon, Namgang, and Milyang at the main tributaries in the upper to lower reaches (Fig. 1). The NR land cover was estimated using ArcGIS 10 (Esri, Redlands, CA, USA), which mainly consists of areas including forest (69%), agricultural (23%), river water (5%), and residential/business and industrial (4%) zones (Fig. 1a). The proportion of agricultural area increases from 14% in the upper reach to 23% in the lower reach, whereas that of forest decreases from 81 to 69%. Two national industrial complex towns (Gumi and Daegu) are located near the main channel in the middle reaches, and scores of small industrial and agricultural areas are included near the Nakdong watershed (Korea Industrial Complex Corp. 2016) (Fig. 1a).

The NR basin is mainly composed of Precambrian metamorphic rocks, Mesozoic granitic rocks, and Mesozoic clastic sedimentary and volcanic rocks (e.g., conglomerate, sandstone, mudstone, andesite, rhyolite, tuff, tuffaceous sandstone/conglomerate) (Fig. 1b) (The Geological Society of Korea 1999). The proportion of Mesozoic sedimentary and volcanic rocks is over 60% of the outcrop area and greatly increases in the mid- and lower reaches. Paleozoic carbonate rock is barely distributed in the upper reaches of the NR watershed (Fig. 1b).

South Korea has a temperate climate with four seasons, and approximately 70% of the annual precipitation is concentrated from July through September during the summer season (Korea Meteorological Administration 2015). The winter season is typically from late November through early March.



**Fig. 1** A simplified map showing land-use patterns (a), lithologies (b) and sampling locations in the Nakdong River watershed, South Korea

**Sampling and analysis**

Water samples were collected at the eight sites along a downstream transect during sampling activities in Fig. 1. The sampling periods, characterized with high- and low-water stages, were likely to show water chemistry indicative of the river. All sampling sites were carefully selected to reflect impact from the dominant land use in order to avoid anthropogenic contamination and direct influences from small tributaries. Water temperature, pH, and electrical conductivity were measured in situ, using an Orion 5-star meter equipped with an Orion combination epoxy pH electrode and DuraProbe 4-electrode conductivity cells; uncertainties were  $\pm 0.1$  °C,  $\pm 0.02$  pH, and  $\pm 0.01$   $\mu\text{S}/\text{cm}$ , respectively. Water samples were introduced through 0.45- $\mu\text{m}$  mixed cellulose ester membrane filters and collected in acid-cleaned Nalgene LDPE bottles. When analyzing cations, the  $^{87}\text{Sr}/^{86}\text{Sr}$  were acidified to  $\text{pH} < 2$  in the field, using ultrapure  $\text{HNO}_3$  solution. To analyze the  $\delta^{34}\text{S}$  of  $\text{SO}_4$ , the samples were filtered with 0.45- $\mu\text{m}$  membrane filters and transferred to a 4-L sterilized container. All of the water samples were stored at 4 °C until the analysis was finished up to a week.

Alkalinity was determined in a laboratory with 0.01 N HCl using the Gran titration method (Gran 1952). Anions and cations were analyzed with ion chromatography (IC) system (Dionex ICS-1500 IC, Sunnyvale, CA, USA) at the Korea Institute of Geoscience and Mineral Resources (KIGAM) and with inductively coupled plasma–optical spectrometer (ICP-OES) (PerkinElmer Optima 4300DU ICP-OES, Akron, OH, USA) at the Korea Basic Science Institute (KBSI). Repeat analyses of two international standards (SLRS-4 and TMDW-A) yielded external reproducibility values  $< \pm 5\%$ . Most of the water samples showed a percent charge balance error [CBE (%) =  $(\text{TZ}^+ - \text{TZ}^-)/(\text{TZ}^+ + \text{TZ}^-) \times 100$ ] within the range of  $\pm 8\%$ , where  $\text{TZ}^+ = \text{Na}^+ + \text{K}^+ + 2\text{Ca}^{2+} + 2\text{Mg}^{2+}$  and  $\text{TZ}^- = \text{Cl}^- + 2\text{SO}_4^{2-} + \text{NO}_3^- + \text{HCO}_3^-$ . The ratio of  $^{87}\text{Sr}/^{86}\text{Sr}$  was determined using multicollector inductively coupled plasma–mass spectrometry (VG Elemental Axiom MC-ICP-MS, Winsford, UK) at the KBSI. The analytical reproducibility of the ratios of  $^{87}\text{Sr}/^{86}\text{Sr}$  by multiple repeating analyses of NBS987 was  $0.710247 \pm 0.000020$  ( $2\sigma$ ,  $n = 24$ ), and the total blank of the Sr was negligible. To analyze the  $\delta^{34}\text{S}$  of  $\text{SO}_4$ , the content of  $\text{SO}_4$  in the water samples was precipitated as a

form of BaSO<sub>4</sub> using 10% BaCl<sub>2</sub> solution. The precipitate was recovered by passing the treated samples through a 0.45- $\mu$ m membrane filter, being washed with hot distilled water, and thoroughly dried at room temperature. Following the method reported by Yanagisawa and Sakai (1983), SO<sub>2</sub> gas was extracted by the thermal decomposition of the precipitate. The  $\delta^{34}\text{S}$  was determined, using an isotope ratio mass spectrometer (IRMS) (Micromass Optima, Ringoes, NJ, USA) at the KBSI, and is expressed in delta ( $\delta$ ) notation relative to Canyon Diablo Troilite (CDT), where  $\delta^{34}\text{S}$  (‰) =  $[(^{34}\text{S}/^{32}\text{S})_{\text{sample}}/(^{34}\text{S}/^{32}\text{S})_{\text{standard}} - 1] \times 1000$ . The analytical reproducibility for the  $\delta^{34}\text{S}$  was  $\pm 0.2\%$ .

### Correction of atmospheric inputs

The major ions in rivers stem from atmospheric inputs, chemical weathering, and anthropogenic inputs, and numerous studies have quantitatively calculated the contributions of such three sources to river water chemistry (Fan et al. 2014; Gaillardet et al. 1999; Shin et al. 2011). The previous studies have used Mg/Na and Ca/Na ratios for carbonate, silicate, and evaporite mineral end members, as suggested by Gaillardet et al. (1999), and suggested that the water chemistry was mainly characterized by the representative rock types in their respective drainage areas; anthropogenic input was ignored or was not a main source. The contribution of chemical weathering can be estimated after extracting the contribution of atmospheric input.

Assuming that the lowest Cl concentration measured in this study was entirely derived from precipitation, the contribution of an element derived from atmospheric input to river water (R) could be determined as follows:

$$R = \text{lowest Cl}_{\text{river}} \times (E_{\text{precipitation}}/\text{Cl}_{\text{precipitation}}), \quad (1)$$

where  $E$  represents elemental concentration measured in the precipitation. The lowest Cl<sub>river</sub> was 55  $\mu\text{M}$ , and the annual average Cl<sub>precipitation</sub> value used was 43.5  $\mu\text{M}$  for 1999 through 2006 in South Korea [Ministry of Environment (MOE) 2006]. The lowest Cl<sub>river</sub> concentration in this study was much lower than that of water samples collected from six major rivers in South Korea during the similar sampling period, which was 88  $\mu\text{M}$  (Shin et al. 2011). Therefore, the lowest Cl<sub>river</sub> concentration in this study could be regarded as representative of precipitation, which was derived Cl in the NR, and the ratio of each element to Cl in precipitation is as follows: Ca/Cl = 0.57, K/Cl = 0.26, Mg/Cl = 0.22, Na/Cl = 0.69, SO<sub>4</sub>/Cl = 1.07. Corrected concentrations are shown in Table 1 and are denoted using an asterisk (e.g., Ca\*, Mg\*, Na\*, Cl\*, and SO<sub>4</sub>\*).

### Results and discussion

The chemical compositions and isotopic ratios ( $\delta^{34}\text{S}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$ ) of the water samples and the variables measured in the field are represented in Table 1. On average, pH was somewhat lower in the summer time (average of  $6.4 \pm 0.1$ ) than in the winter time (average of  $7.0 \pm 0.7$ ), showing little notable variation. Its range was from 6.3 to 6.5 in the summer time. In the winter time, the pH gradually increased from 6.4 up to 8.4 in accordance with the distance of downstream. The total dissolved solids (TDS = Na<sup>+</sup> + K<sup>+</sup> + Ca<sup>2+</sup> + Mg<sup>2+</sup> + Cl<sup>-</sup> + SO<sub>4</sub><sup>2-</sup> + NO<sub>3</sub><sup>-</sup> + HCO<sub>3</sub><sup>-</sup>) for the water samples ranged from 28.4 to 60.7 mg/L (average of  $44.3 \pm 9.0$  mg/L) in the summer time and from 53.7 to 76.7 mg/L (average of  $70.6 \pm 7.6$  mg/L) in the winter time.

Figure 2 shows the spatial and seasonal variations in major ion concentrations with the distance from the upper reaches. The confluence of water flowing from the two dams in the most upper reaches is hereafter considered pristine water, and the distance shown represents the distance from the confluence. Most of the water samples showed higher ion concentrations in winter than in summer. Overall, the ion concentrations tended to increase along a downstream, except for the NO<sub>3</sub> concentration in summer. It was found that a water sample collected in winter at the middle reaches (NR-4) included markedly high ion concentrations compared to those of other samples in the same season. Water types were mainly Ca–HCO<sub>3</sub>–(Cl, SO<sub>4</sub>) in summer, regardless of spatial variations, but those in winter changed from Ca–HCO<sub>3</sub> at the most upper reaches to Na–(Cl, SO<sub>4</sub>) at the lower reaches (not shown).

The  $\delta^{34}\text{S}$  of the water samples ranged from 0.9 to 4.0‰, with an average of  $2.5 \pm 0.7\%$ . On average, the  $\delta^{34}\text{S}$  was slightly higher in summer with  $2.9 \pm 0.5\%$  than in winter with  $2.2 \pm 0.6\%$ . In summer, the  $\delta^{34}\text{S}$  tended to be lowered in accordance with the distance of downstream, while in winter, the trend oppositely occurred (Fig. 2g). The  $\delta^{34}\text{S}$  values of both seasons were similar at the middle and the lower reaches of the river. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio, which was only determined for water samples collected in summer, ranged from 0.71043 to 0.71520 ( $0.71307 \pm 0.00177$  in average). The ratio exhibited obvious spatial variation. Specifically, the ratio was the lowest at the most upper reaches, with the highest value occurring at ca. 100 km from pristine water, and then gradually decreased toward the lower reaches. Nonetheless, the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios were within the range of those of Cenozoic volcanic-derived sedimentary and volcanic rocks and Mesozoic silicate rock reported in South Korea, 0.70402–0.75594 (Kim et al. 2013).

**Table 1** Chemical and isotopic compositions of water samples collected in the Nakdong River (NR) in summer and winter

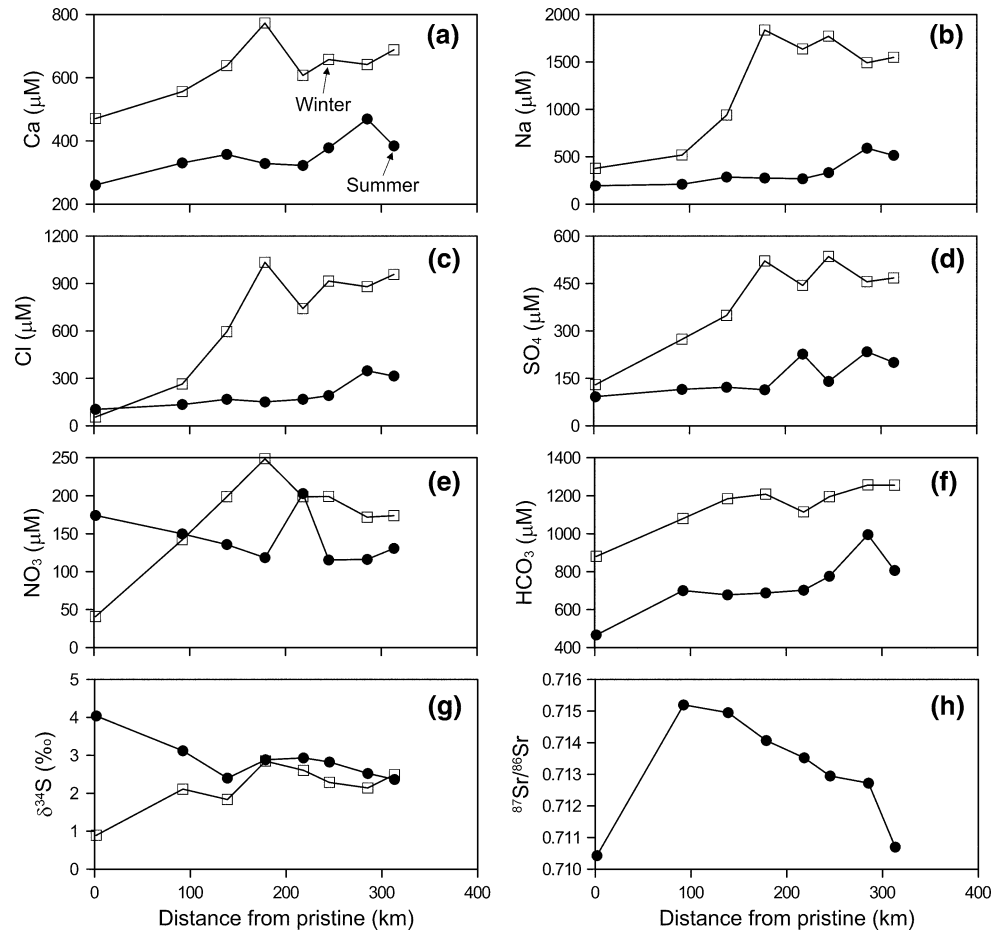
Sample	Distance (km) <sup>a</sup>	T (°C)	pH	EC (µS/cm)	B (µM)	Ca (µM)	K (µM)	Mg (µM)	Na (µM)	Cl (µM)	SO <sub>4</sub> (µM)	NO <sub>3</sub> (µM)	HCO <sub>3</sub> (µM)	TDS (mg/L)	CBE (%)	<sup>87</sup> Sr/ <sup>86</sup> Sr	δ <sup>34</sup> S (‰)	
<i>August 2007 (summer)</i>																		
NR-1	2	20	6.4	103	1.52	261 (229)	32.0 (17.4)	93.6 (81.3)	194 (156)	103 (48.0)	92.1 (32.5)	174	466	28.4	0.40	0.71043	4.0	
NR-2	92	21	6.4	128	1.67	330 (299)	42.2 (27.6)	118 (106)	210 (171)	134 (78.5)	115 (55.6)	150	700	42.7	-2.78	0.71520	3.1	
NR-3	139	21	6.5	130	2.27	357 (325)	53.6 (39.0)	124 (111)	285 (247)	168 (112)	122 (62.3)	136	678	41.4	2.98	0.71495	2.4	
NR-4	179	22	6.4	122	1.98	329 (297)	57.0 (42.4)	119 (107)	275 (237)	151 (95.6)	114 (54.4)	118	688	42.0	1.77	0.71407	2.9	
NR-5	218	22	6.4	125	2.12	322 (291)	33.5 (18.9)	117 (105)	268 (229)	167 (112)	227 (167)	203	703	42.9	-12.7	0.71352	2.9	
NR-6	245	23	6.4	143	2.91	378 (346)	33.7 (19.1)	140 (127)	332 (293)	191 (135)	140 (80.5)	115	776	47.4	1.38	0.71295	2.8	
NR-7	285	25	6.5	198	3.25	469 (438)	82.0 (67.4)	172 (160)	590 (551)	348 (293)	234 (174)	116	995	60.7	0.71	0.71272	2.5	
NR-8	313	26	6.5	175	2.99	384 (352)	74.4 (59.8)	146 (134)	514 (476)	314 (259)	201 (141)	131	806	49.2	-0.07	0.71070	2.4	
<i>February 2008 (winter)</i>																		
NR-1	2	4.0	6.4	187	1.37	471 (439)	33.6 (19.0)	149 (136)	378 (340)	55.5 (0)	130 (70.1)	40.9	880	53.7	14.4	-	0.9	
NR-2	92	3.4	6.4	243	1.69	556 (524)	50.4 (35.9)	199 (187)	518 (479)	264 (209)	274 (214)	142	1080	65.9	1.11	-	2.1	
NR-3	139	3.3	6.5	331	8.80	638 (606)	85.4 (70.8)	241 (229)	938 (900)	596 (540)	349 (289)	199	1185	72.3	1.91	-	1.8	
NR-4	179	4.1	6.6	470	7.51	772 (741)	139 (125)	292 (280)	1836 (1797)	1034 (979)	521 (462)	249	1209	73.7	7.47	-	2.8	
NR-5	218	3.7	7.1	382	5.32	607 (576)	97.8 (83.2)	233 (220)	1635 (1596)	741 (686)	444 (384)	199	1114	68.0	7.40	-	2.6	
NR-6	245	2.9	7.0	426	5.94	657 (626)	109 (94.2)	253 (241)	1770 (1731)	915 (860)	535 (476)	199	1196	73.0	4.51	-	2.3	
NR-7	285	3.0	7.8	401	5.07	642 (610)	94.9 (80.4)	282 (269)	1491 (1452)	880 (824)	455 (396)	172	1257	76.7	3.21	-	2.1	
NR-8	313	5.4	8.4	408	5.43	688 (656)	96.8 (82.2)	293 (281)	1548 (1509)	957 (902)	468 (408)	174	1256	76.6	4.11	-	2.5	

The numbers in parenthesis represent the dissolved ion concentrations after being corrected with atmospheric inputs

<sup>a</sup> Distance from confluence of water flowing from the two dams in the most upper reaches

“-” Not collected

**Fig. 2** Diagrams showing variations of major ions (a–f),  $\delta^{34}\text{S}$  value (g) and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio (h) from the upper to lower reaches in the Nakdong River in summer and winter seasons



## Chemical weathering as a main source of dissolved ions

### Correlation between major ions

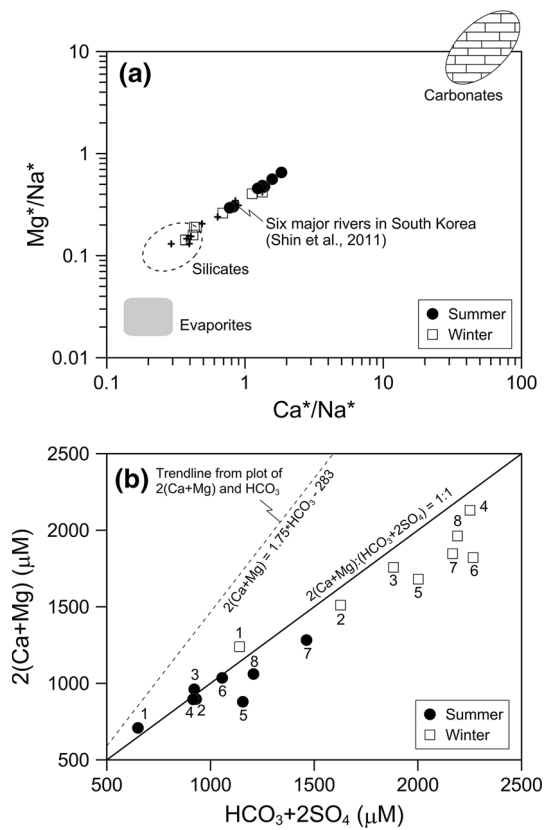
After the correction on the atmospheric input,  $\text{Ca}^*/\text{Na}^*$  ranged from 0.74 to 1.74 in summer and from 0.36 to 1.29 in winter, and  $\text{Mg}^*/\text{Na}^*$  ranged from 0.28 to 0.62 in summer and from 0.14 to 0.40 in winter. On a plot of  $\text{Mg}^*/\text{Na}^*$  and  $\text{Ca}^*/\text{Na}^*$ , the water samples fell between the silicate and carbonate end members supported by Gaillardet et al. (1999), and most samples were plotted toward silicates (Fig. 3a). This occurrence was observed more evidently in winter than in summer when rainwater contributed more substantially to water chemistry. The  $\text{Ca}^*/\text{Na}^*$  and  $\text{Mg}^*/\text{Na}^*$  ratios of the water samples are between 0.29 and 1.42, and between 0.13 and 0.48, respectively, which are consistent with the previous study (Shin et al. 2011). It indicates that water chemistry is mainly controlled by both the weathering of silicates and carbonates and that silicate weathering is more dominant in the NR.

Theoretically, carbonic acid in the soil zone reacts with carbonate minerals in the watershed, resulting in 2 mol of

$\text{HCO}_3^-$  for each mole of Ca and Mg (Appelo and Postma 2005) as follows:  $\text{H}_2\text{O} + \text{CO}_2 + \text{CaMg}(\text{CO}_3)_2 \rightarrow \text{Ca}^{2+} + \text{Mg}^{2+} + 4\text{HCO}_3^-$ . Furthermore, the oxidation of sulfide minerals in the presence of oxygen and water generates sulfuric acid, which participates in chemical weathering (Calmels et al. 2007). In this study, the water samples had 1.75 of  $(\text{Ca} + \text{Mg})/\text{HCO}_3^-$  ratio. Overall, the water samples were near, but plotted below, the binary line of  $2(\text{Ca} + \text{Mg})$  and  $\text{HCO}_3^- + 2\text{SO}_4^{2-}$  (Fig. 3b). Thus, it appeared that the water chemistry was mainly determined by chemical weathering arising from a combination of carbonic and sulfuric acid generated in the watershed, attributing to an additional source (e.g., anthropogenic source).

### Variation in $^{87}\text{Sr}/^{86}\text{Sr}$ ratio with the distance of downstream

The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios for water samples in the river ranged from 0.7104 to 0.7152, which are similar to those for stream and groundwater within this watershed (0.70690–0.71332; Song et al. 2014). Although the Nakdong River drains Precambrian metamorphic rocks,



**Fig. 3** Plots of  $Mg^*/Na^*$  versus  $Ca^*/Na^*$  (a) and  $2(Ca + Mg)$  versus  $HCO_3 + 2SO_4$  (b) for the water samples [the three end members in a are from Gaillardet et al. (1999)]. Each sample name was simplified as the numbers near the symbol in b without prefix (NR-)

Mesozoic granitic rocks, and Mesozoic clastic sedimentary and volcanic rocks, most of the  $^{87}Sr/^{86}Sr$  ratios for water samples in this study are within those of the Cenozoic and Mesozoic granites (0.70514–0.73359; Cheong and Chang 1996; Kim and Kim 1997; Na et al. 1997) but higher than those of the Cenozoic volcanic-derived sedimentary and volcanic rocks (0.70402–0.70623; Kim et al. 1999). Because precipitation has a significantly low Sr concentration ( $<0.88 \mu\text{g/L}$ ; Miller et al. 1993) and the lowest Sr concentration in the NR-1 sample is approximately 90 times higher than that of precipitation, riverine Sr concentrations from the upper to the lower reaches, even prior to NR-1, are attributed to chemical weathering and/or anthropogenic inputs. That is,  $^{87}Sr/^{86}Sr$  ratios of the water samples can be explained by weathering of the Mesozoic volcanogenic sedimentary rocks and the granitic rocks. Given that potential anthropogenic sources in South Korea have  $^{87}Sr/^{86}Sr$  ratios as follows: 0.71111–0.71260 for detergent ( $n = 5$ ), 0.71004–0.71455 for chemical fertilizer ( $n = 5$ ), and 0.71453–0.71629 for sewage (e.g., Lee et al. 2014), the  $^{87}Sr/^{86}Sr$  ratios of water samples indicates that

the Nakdong River would be also affected by those anthropogenic sources.

### Effects of anthropogenic inputs on water chemistry

#### Increase of anion in accordance with the distance of downstream

Given that the water chemistry of surface water is entirely influenced by rainwater input, the elemental ratios in surface water should be the same as those of seawater (Sarin et al. 1989; Stallard and Edmond 1983). The Na/Cl ratio of seawater reported by Zhang et al. (1995) was 0.85, and the precipitation monitored in South Korea from 1999 to 2006 was Cl and Na of 43.5 and 30.2  $\mu\text{M}$  in average, respectively (MOE 2006), which yielded a correlation of  $Na = (0.60 \times Cl) + 4.09$ . In this study, the water samples could be expressed by the equation;  $Na = (1.75 \times Cl) + 33.0$  ( $R^2 = 0.96$ ). With the fact that relatively high Na/Cl ratio of the water samples compared to both seawater and local precipitation, and high Na and Cl concentrations in the water samples with 439 and 799  $\mu\text{M}$ , respectively, it seemed like that the water chemistry was influenced by some anthropogenic factors in the watershed because there were no evaporites in South Korea (Chough et al. 2000).

In winter, concentrations of Cl,  $NO_3$ , and  $SO_4$  increased rapidly from the upper reaches through the middle (NR-1 to NR-4) and then increased slightly or decreased to the lower (NR-4 to NR-8). However, for water samples collected in summer having relatively lower ion concentrations, this trend was not obvious, probably due to the dilution by heavy rain. The overall  $NO_3$  concentration became lower with passage through the watershed, except for NR-5. Because atmospheric inputs and chemical weathering were not accountable for spatial and seasonal variations in ion concentrations, particularly elevated Cl concentration toward the downstream region, it could be induced that anthropogenic inputs related to land-use patterns might impact the river water chemistry. As earlier discussed, the relationship between land-use patterns and the water chemistry would be of help in precisely identifying the sources contributing to the water chemistry, and its spatial and seasonal variations.

#### Contribution of land covers to each sampling site

The proportions of agricultural area, forest, industrial district, and residential/business areas drained into each sampling site were estimated using ArcGIS software (RockWare, Ver. 2015). The NR-1 site was occupied with 13.8% of agricultural area and 80.9% of forest, whereas the NR-2 was with 22.0% of agricultural area and 71.9% of

forest. The percentages of agricultural area and forest of the NR-2 and the NR-8 were similar. At the downstream, the percentages of industrial district and residential/business areas were interestingly small, compared to agricultural area and forest.

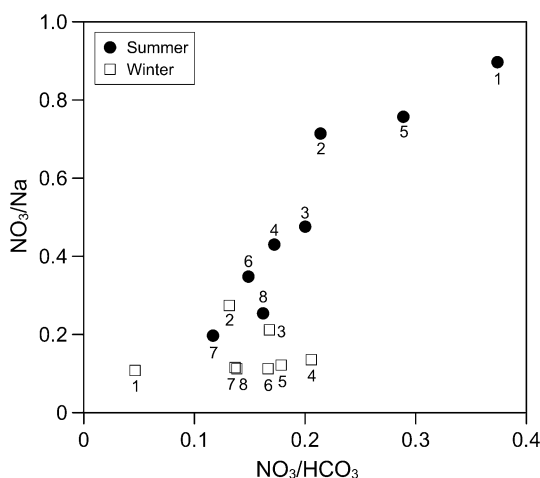
On the plot of  $\text{NO}_3/\text{HCO}_3$  versus  $\text{NO}_3/\text{Na}$  (Fig. 4), the summer water samples were positively correlated and the NR-1 was characterized by the highest  $\text{NO}_3/\text{HCO}_3$  and  $\text{NO}_3/\text{Na}$  ratios. In contrast, such ratios of the winter samples were drawn scattered. The NR-1 was completely opposite to the summer samples. A study showed that the  $\text{NO}_3$  concentration in river water was negatively correlated with a percentage of forest cover in watershed (Herlihy et al. 1998). Considering the results and land-use pattern in the NR, it can be inferred that the highest ratios of  $\text{NO}_3/\text{HCO}_3$  and  $\text{NO}_3/\text{Na}$  of the NR-1 during summer were due to agricultural activities at the upper reaches. However, the ratios of  $\text{NO}_3/\text{HCO}_3$  and  $\text{NO}_3/\text{Na}$  became lower even with the increased activity from agricultural areas because of the enhanced chemical weathering. In addition, the ratios of  $\text{NO}_3/\text{Na}$  of most winter samples were lower than those of the summer samples. The results imply that land-use pattern greatly affects the water chemistry at the upstream, but its effect on the water chemistry at the downstream becomes minimal because of the enhanced weathering inputs.

#### Sulfur isotopic composition

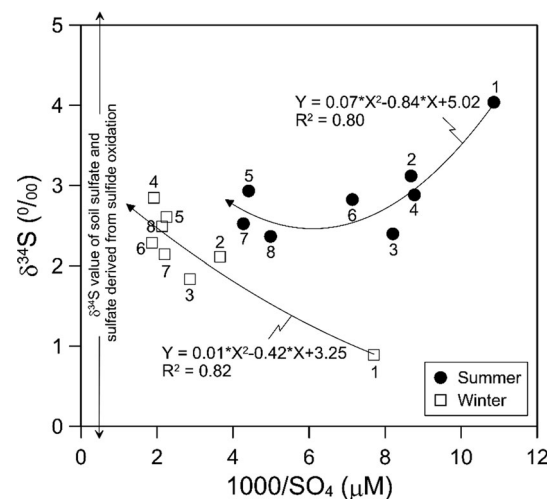
Typically, the transformation processes during the sulfur cycle, including sulfide oxidation, mineralization, leaching, and assimilation, result in little or no sulfur isotope fractionation (Krouse 1980; Tuttle et al. 2009; Van Stempvoort and Krouse 1994). Although large sulfur isotope fractionation often occurs during the reduction by bacterial dissimilatory sulfate reduction (BDSR) processes, it is not the

case in riverine environment. Therefore, sulfur isotopic composition in river water can be an effective tracer to apportion various sources in associated with the water chemistry in river. In the study, the  $\text{SO}_4$  concentration of water samples ranged from 92.1 to 234  $\mu\text{M}$  in summer and from 130 to 535  $\mu\text{M}$  in winter (Table 1). The lower  $\text{SO}_4$  concentration of 156  $\mu\text{M}$  in average in summer than 397  $\mu\text{M}$  in average in winter was typically due to dilution from the intensified rainfall that occurred in the summer season. Although water samples from the middle and lower reaches generally had relatively higher  $\text{SO}_4$  concentrations because of anthropogenic inputs derived from agricultural areas and industrial districts, the  $\delta^{34}\text{S}$  values of the water samples varied within a substantially narrow range (1.8–3.1‰) without seasonal variations. This result indicates that both sulfide oxidation and soil  $\text{SO}_4$  had an impact with negligible effect of anthropogenic input on  $\delta^{34}\text{S}$  of the NR (Fig. 5).

For the NR-1, the higher  $\delta^{34}\text{S}$  value in summer (4.0‰) than in winter (0.9‰) might be attributed to  $\text{SO}_4$  contents flushed from the soil zone by intensified rain for a certain short time during summer. However, this phenomenon was gradually masked up as river flows. The small  $\delta^{34}\text{S}$  variation with big variation of the  $\text{SO}_4$  concentration indicated that  $\text{SO}_4$  was possibly derived from sources that do not depend on seasonal change. The  $\delta^{34}\text{S}$  values of anthropogenic inputs, ranging from  $-7.1$  to 31.3‰, were much bigger than those of the water samples. If anthropogenic inputs were not dominant in river water, chemical weathering would control a riverine  $\delta^{34}\text{S}$  value (Yang et al. 1996). Based on the fact that the soil water in the vicinity of a refinery located at the most upper reaches of the NR watershed had the  $\delta^{34}\text{S}$  values of 3–5‰, thus the sulfur content in the soil water was not derived directly from the refinery (National Institute of Environmental Research;



**Fig. 4** Plot of  $\text{NO}_3/\text{Na}$  versus  $\text{NO}_3/\text{HCO}_3$  for water samples



**Fig. 5** Relationship between  $\delta^{34}\text{S}$  and  $1000/\text{SO}_4$



NIER 2013), and the main source of SO<sub>4</sub> was likely due to sulfide oxidation rather than anthropogenic inputs.

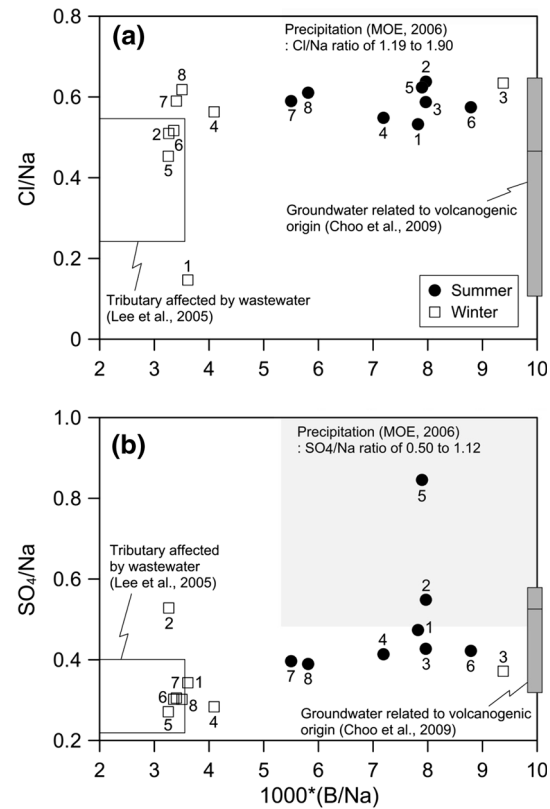
### Use of boron (B) for identifying sources

#### Potential sources of boron

The boron (B) concentration of samples collected during summer exhibited an increasing trend with the distance from 1.52 to 3.25 μM with relatively high amplitude in the NR-3 (Table 1). In comparison, that of winter samples increased from 1.37 μM at NR-1 to 8.80 μM at NR-3 and then tended to gradually decrease with the distance. It was figured that a tributary affected by effluent from an industrial district had a high B concentration of 12.2 μM (Lee et al. 2005). Therefore, the national industrial districts were located in the near upper part of NR-3, and the tributary between NR-3 and NR-4 played a role in being a point source of B in river water. If consistent with the assumptions above, the NR-3 displayed the highest B concentration. Nonetheless, anthropogenic inputs should be identified with a caution because groundwater developed within Mesozoic volcanogenic sedimentary rocks displayed extremely high B concentrations of 37.9 up to 427 μM (Choo et al. 2009). Also, it was reported that B-bearing minerals (e.g., tourmaline, dumortierite) existed within the NR watershed (Koh et al. 2000; Woo et al. 2014). For example, tourmaline obtained from the watershed had a B content of 269–309 μmol (9.38–10.8 wt% as B<sub>2</sub>O<sub>3</sub>). Thus, further studies using B isotopes can be useful to identify the B source.

#### Main source of boron (B) affecting the water chemistry

The B concentrations at the upper reaches are between 1.37 and 1.69 μM, regardless of season, which are within the range reported in rainwater (Chetelat et al. 2005, 2009; Hasenmueller and Criss 2013; Park and Schlesinger 2002; Rose et al. 2000). Therefore, the B concentrations of the upper reaches can be a representative of rainwater. Figure 6 shows the relationship between major elements such as Cl and SO<sub>4</sub> and B for the water samples. To efficiently identify B sources from the watershed, the ions were normalized by Na to minimize the effects of factors such as dilution and evaporation on the water chemistry. The ratios of precipitation in South Korea, and surface water affected mainly by wastewater, and groundwater associated with volcanic rock (e.g., volcanic breccia, tuffaceous conglomerate, and basaltic rocks) developed in the watershed were illustrated together with the water samples on a plot of 1000 × (B/Na) versus Cl/Na and versus SO<sub>4</sub>/Na (Fig. 6a, b). Because there were few data on available B concentration in the precipitation in South Korea, the ratio of



**Fig. 6** 1000 × (B/Na) ratio versus Cl/Na (a) and versus SO<sub>4</sub>/Na (b)

1000 × (B/Na) was calculated using data from the studies (Chetelat et al. 2005, 2009; Rose et al. 2000); the ratios corresponding from the 25th through 75th quartiles were 5.33–27.2.

The molar ratios of 1000 × (B/Na) of summer samples were from 5.50 to 8.79, plotted within precipitation region, while the ratios of winter samples were from 3.25 to 4.09 (except for NR-3), plotted within tributary region affected by wastewater with a ratio of 0.86–3.48. Interestingly, the Cl/Na and SO<sub>4</sub>/Na molar ratios of the samples did not stay in a remarkable spatial variation, and most were lower than those of precipitation and/or within the range of groundwater related to the volcanogenic source. Although more than 50% of winter samples were plotted within the ranges of the tributary mainly affected by wastewater, it was not entirely dependent on wastewater input. Firstly, the sample NR-3 expecting the largest contribution of wastewater was far from the cluster of tributaries contaminated by wastewater (Fig. 6). Secondly, the low 1000 × (B/Na) ratio in winter could be due to groundwater input experiencing the enhanced chemical weathering of sodium-rich rock (e.g., granite) in the watershed, because granitic rocks (e.g., leucogranite, diorite, granodiorite, granite) had 1000 × (B/Na) values of 0.23–1.38 (n = 8) (Hu and Gao 2008). Furthermore, the contribution of agricultural activities to the water chemistry could be ignored in this study

because intensive agricultural practice caused high molar ratios of  $\text{NO}_3/\text{Na}$  (more than 6) and  $\text{Cl}/\text{Na}$  (more than 4) along with relatively high B concentrations (Chetelat et al. 2005). In this study, the  $\text{NO}_3/\text{Na}$  molar ratios in summer decreased overall from  $\sim 0.90$  to  $\sim 0.20$  with the distance (except for NR-5), and those in winter were all below 0.3. Therefore, the results suggest that rainfall in summer was a potential main source of B at the upper reaches, but its effect decreased gradually with the distance as chemical weathering was dominant. Still, chemical weathering was likely to be the main source of B concentration in winter.

### Contributions of natural and anthropogenic sources to the water chemistry

Considering no evaporites in South Korea, rain-corrected  $\text{Cl}^*$  in river water should be entirely derived from anthropogenic inputs. Assuming that  $\text{SO}_4$  in river water is mainly derived from the oxidation of sulfide minerals,  $\text{Cl}_{\text{river}}^*$  and  $\text{SO}_{4\text{river}}^*$  can be expressed as follows:

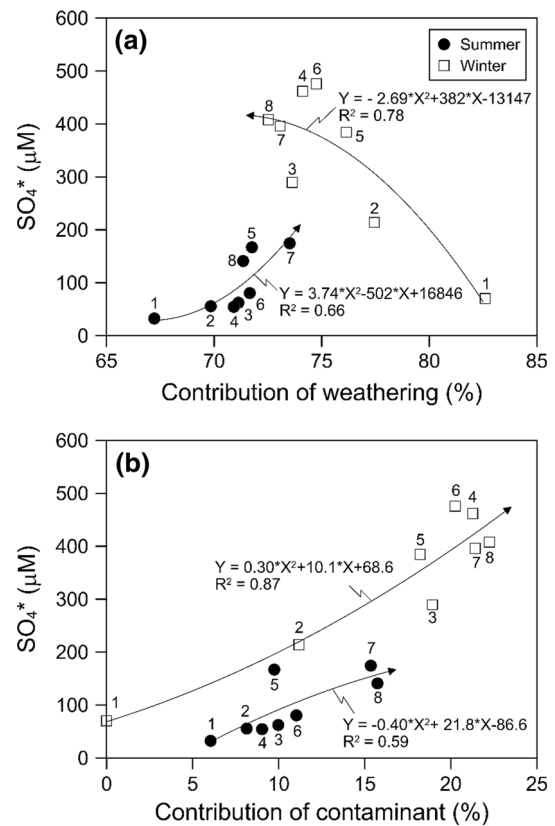
$$[\text{Cl}]_{\text{river}}^* = [\text{Cl}]_{\text{anthropogenic}} \quad (2)$$

$$[\text{SO}_4]_{\text{river}}^* = [\text{SO}_4]_{\text{sulfide minerals}} \quad (3)$$

It can be possible to estimate the relative contributions of rain, chemical weathering, and anthropogenic sources to the water chemistry. Variation in  $[\text{SO}_4]_{\text{river}}^*$  concentration corresponds to the proportions of chemical weathering and anthropogenic sources (Fig. 7a, b); here, sulfate derived from chemical weathering was entirely triggered by the hydrolysis of sulfide minerals because there is no evaporite in this study area. In summer, the contributions of chemical weathering and anthropogenic sources increased as river flows downstream, from 67.2 to 73.5%, and from 6.0 to 15.7%, respectively. In contrast, the contribution of chemical weathering in winter decreased from 82.6% in the upstream to 72.5% in the downstream, while that of anthropogenic inputs increased by up to 22.2% toward the middle and lower reaches. The fact that summer  $[\text{SO}_4]_{\text{river}}^*$  was more correlated with the contribution of chemical weathering ( $R^2 = 0.66$ ) than that of anthropogenic sources ( $R^2 = 0.59$ ), but winter had the opposite ( $R^2 = 0.87$ ) which indicates that high discharge in summer makes the effect of anthropogenic inputs diluted. Therefore, the use of  $[\text{SO}_4]_{\text{river}}^*$  should be carefully considered when for estimating chemical weathering.

### Chemical weathering rates and $\text{CO}_2$ consumption rates

Based on the results and assumptions above, chemical weathering rates and associated  $\text{CO}_2$  consumption rates can be estimated. Using hydrological information and rain-



**Fig. 7** Variations of  $\text{SO}_4^*$  with contribution of chemical weathering and contaminant to the water chemistry: the asterisk represents  $\text{SO}_4$  concentration after correcting atmospheric input

corrected chemical compositions of river water, the chemical weathering rate of silicates and carbonates in the NR can be calculated as follows:

$$\text{SSWR} = \Phi \cdot (\text{Na}^+ + \text{K}^+ + \text{Ca}^{2+} + \text{Mg}^{2+})_{\text{SSW}} \quad (4)$$

$$\text{CSWR} = \Phi \cdot (\text{Na}^+ + \text{K}^+ + \text{Ca}^{2+} + \text{Mg}^{2+})_{\text{CSW}} \quad (5)$$

$$\begin{aligned} \text{TSWR} &= \text{SSWR} + \text{CSWR} \\ &= \Phi \cdot (\text{Na}^+ + \text{K}^+ + \text{Ca}^{2+} + \text{Mg}^{2+})_{\text{SW}}, \end{aligned} \quad (6)$$

where SSW, CSW, and SW represent silicate weathering by sulfuric acid, by carbonic acid, and by both acids, respectively. SSWR, CSWR, and TSWR represent silicate weathering rate corresponding to each of them, and  $\Phi$  indicates yield ( $\text{t}/\text{km}^2/\text{year}$ ). Similarly, carbonate weathering rate can be calculated as follows:

$$\text{SCWR} = \Phi \cdot (\text{Ca}^{2+} + \text{Mg}^{2+})_{\text{SCW}} \quad (7)$$

$$\text{CCWR} = \Phi \cdot (\text{Ca}^{2+} + \text{Mg}^{2+})_{\text{CCW}} \quad (8)$$

$$\text{TCWR} = \text{SCWR} + \text{CCWR} = \Phi \cdot (\text{Ca}^{2+} + \text{Mg}^{2+})_{\text{CW}}, \quad (9)$$

where SCW, CCW, and CW represent carbonate weathering by sulfuric acid, by carbonic acid, and by both acids,

**Table 2** Chemical weathering rates and associated CO<sub>2</sub> consumption rates estimated for the NR watershed

Sampling time	Discharge (m <sup>3</sup> /s) <sup>a</sup>	Chemical weathering rate (t/km <sup>2</sup> /year)						CO <sub>2</sub> consumption rate (10 <sup>3</sup> mol/km <sup>2</sup> /year)	
		SSWR	CSWR	TSWR	SCWR	CCWR	TCWR	SW	CW
August 2007 (summer)	1755	12.4	19.3	31.7	9.88	29.5	39.4	1428	1113
February 2008 (winter)	643	9.84	15.5	25.3	8.22	9.04	17.3	1197	488

<sup>a</sup> Discharge represents the average of discharge rates reported in summer season (July through September) and winter season (December through February)

respectively. SCWR, CCWR, and TCWR represent carbonate weathering rate corresponding to each of them. The calculated chemical weathering rates are given in Table 2. In short, chemical weathering rates were higher in summer than those in winter, specifying that chemical weathering rates were much more related to discharge rates than elemental concentrations.

Assuming that bicarbonate and cations derived from chemical weathering are in charge-balanced state (Roy et al. 1999), related CO<sub>2</sub> consumption rates can be calculated as follows:

$$\begin{aligned} \Phi \cdot [\text{CO}_2]_{\text{SW}} &= \Phi \cdot [\text{HCO}_3^-]_{\text{SW}} \\ &= \Phi \cdot (\text{Na}^+ + \text{K}^+ + 2\text{Ca}^{2+} + 2\text{Mg}^{2+})_{\text{CSW}} \end{aligned} \tag{10}$$

$$\Phi \cdot [\text{CO}_2]_{\text{CW}} = \Phi \cdot [\text{HCO}_3^-]_{\text{CW}} = \Phi \cdot (\text{Ca}^{2+} + \text{Mg}^{2+})_{\text{CCW}}, \tag{11}$$

where SW and CW represent silicate and carbonate weathering by only carbonic acid, respectively. The calculated CO<sub>2</sub> consumption rates by SW and CW was 2062 × 10<sup>3</sup> and 1282 × 10<sup>3</sup> mol/km<sup>2</sup>/year in summer, and 1930 × 10<sup>3</sup> and 559 × 10<sup>3</sup> mol/km<sup>2</sup>/year in winter, respectively. The findings were that the CO<sub>2</sub> consumption rate by SW was relatively consistent regardless of a season, while the rate by CW was higher in summer than in winter. Such difference may explain that the CO<sub>2</sub> consumption rates were also discharge dependent, so elemental concentrations in winter were likely influenced by groundwater input developed in a silicate-dominant basin.

### Conclusions

Water samples were collected from sampling activities along a downstream transect in the NR in order to identify and estimate the sources impacting the water chemistry with the help of elemental and isotope geochemistry. The concentrations of most dissolved ions were lower in summer than in winter because of the dilution effect arising from intensified rainfall in summer. The δ<sup>34</sup>S

values of water samples were plotted within the ranges of sulfide oxidation and soil SO<sub>4</sub>, and there was no distinct spatio-seasonal variation for the δ<sup>34</sup>S values with the exception of the most upper samples. The <sup>87</sup>Sr/<sup>86</sup>Sr ratios varied from 0.71043 to 0.71520, being consistent with the range of the Mesozoic volcanogenic sedimentary rocks in the catchment. These results indicated that chemical weathering was a major controlling factor over the water chemistry in the NR, although the effect of anthropogenic inputs existed. As for combined boron with major elements, the findings were that rainfall in summer was a main source of B concentration at the upper reaches, but its effect decreased gradually with the distance as chemical weathering became dominant. Still, chemical weathering was likely to be linked with B concentrations in winter. The calculated chemical weathering rates and CO<sub>2</sub> consumption rates were more discharge dependent, and elemental concentrations in winter were likely influenced by groundwater input developed in a silicate-dominant basin. One another finding was that the influence of many potential anthropogenic inputs in the watershed on the water chemistry could be masked up, which resulted from the large buffering capacity of the NR, and will eventually provide baseline data and actual information when comparing the water quality of before and after implementation of the a mega-size civil and environmental infrastructure project such as the Four Rivers Restoration Project of South Korea.

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