



Hydrogeochemical and isotopic features of the groundwater flow systems in the central-northern part of Jeju Island (Republic of Korea)



Woo-Jin Shin ^{a,*}, Youngyun Park ^{a,1}, Dong-Chan Koh ^{b,c}, Kwang-Sik Lee ^{a,*}, Yongcheol Kim ^b, Yongje Kim ^b

^a Division of Earth and Environmental Sciences, Ochang Center, Korea Basic Science Institute, 162 Yeongudanji-ro, Ochang-eup, Cheongwon-gu, Cheongju-si 28119, Chungbuk, Republic of Korea

^b Groundwater & Ecohydrology Research Center, Korea Institute of Geoscience and Mineral Resources, 124 Gwahang-no, Yuseong-gu, Daejeon 34132, Republic of Korea

^c University of Science and Technology, 217 Gajeong-ro, Yuseong-gu, Daejeon 34113, Republic of Korea

ARTICLE INFO

Article history:

Received 8 May 2016

Revised 21 November 2016

Accepted 6 January 2017

Available online 7 January 2017

Keywords:

Jeju Island

Stable isotope

Flow path

Aquifer system

Regional flow system

Water poverty

ABSTRACT

Groundwater from 10 production wells located in lowlands to highlands was investigated from July 2008 to February 2010 for chemical and isotopic compositions ($\delta^{18}\text{O}$, $\delta^2\text{H}$, and $\delta^{13}\text{C}_{\text{DIC}}$) to understand groundwater recharge processes and to assess geochemical conditions of groundwater in the volcanic aquifers. The groundwater in lowlands had elevated concentrations of Cl and NO_3 with greater seasonality when compared with those from higher areas, indicating that groundwater in the lowlands is affected by contamination. Based on $\delta^{18}\text{O}$ values and altitudinal variations, groundwater was classified into two regional flow systems with different flow paths. The regional flow systems are likely connected from highland to lowland areas, considering consistent $\delta^{18}\text{O}$ values and major ion contents throughout the seasons. Of the two regional flow systems, the wells clustered in one regional flow system showed low $\delta^{13}\text{C}_{\text{DIC}}$ values (average -14.3‰) and high P_{CO_2} (average 2.04 in $-\log\text{P}_{\text{CO}_2}$), reflecting relatively high contribution of soil CO_2 to groundwater. The other regional flow system with low P_{CO_2} (average 2.39 in $-\log\text{P}_{\text{CO}_2}$), however, consisted of two highland wells with enriched $\delta^{13}\text{C}_{\text{DIC}}$ value, -9.3‰ and two lowland wells with relatively depleted $\delta^{13}\text{C}_{\text{DIC}}$ value, -13.7‰ . These findings indicate that the two regional flow systems were mixed with local recharge from soil layers during recharge. The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values in groundwater from the regional flow systems were not clearly consistent with the local meteoric water line due to mixing of summer and dry season precipitation. The isotopic variations showed a phase lag and cyclic temporal patterns, suggesting that a considerable portion of groundwater was derived from fast recharge with short residence times on monthly time scales. This study suggests that groundwater in lowland areas in Jeju Island can be significantly contributed from highland areas, which was revealed by chemical and isotopic compositions, especially, altitude effect and seasonal variation of $\delta^{18}\text{O}$ value. We expect that the knowledge on the volcanic aquifer system can be useful for management of groundwater resources including projects (e.g. artificial recharge technology) which has been carried out to mitigate water poverty over the world.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

The water resources shortage has drawn worldwide concern. Recently, Lawrence et al. (2002) reported a water poverty index (WPI) for 140 countries based on factors such as the total amount of water, water management by humans, and evaluation of the environment for water reserves. South Korea ranked as 59th, with a relatively high WPI, suggesting a less severe shortage of water resources. Moreover, the Oxford Centre for Water Research, using a world map classified by WPI (<http://ocwr.ouce.ox.ac.uk>), determined that South Korea provides water to its residents without severe problems. Nevertheless, these data

are not applicable to Jeju Island in South Korea due to regional characteristics of climate, topography, geology, and continuously increasing tourism.

The amount of precipitation on Jeju Island is generally more than that in any other area of South Korea; during the last thirty years (1981–2010), the average annual precipitation on Jeju Island was 1633 mm, whereas that in continental areas was 1333 mm (Korea Meteorological Administration [KMA], www.kma.go.kr). Despite higher amount of precipitation, the water resources have not been efficiently managed due to both the absence of proper structures for a good storage of the water resources and the concentration of precipitation in the summer season. That is, according to precipitation reported in 2000 to 2010, >56% of precipitation on Jeju Island is concentrated in the summer season, i.e., June to September, and perennial streams are lacking because of extensively distributed permeable basaltic rocks. As a result, only 46% of total precipitation infiltrates into groundwater, and 19% is

* Corresponding authors.

E-mail addresses: sirms4@kbsi.re.kr (W.-J. Shin), kslee@kbsi.re.kr (K.-S. Lee).

¹ Present Address: Department of Geology, Kangwon National University, Chuncheon 200–701, Republic of Korea.

washed away to oceans by runoff (KOWACO, 2003). The great increase in Jeju Island's total population (settled and tourist populations), from 4.7 million in 2000 to 8.3 million in 2010 (Jeju Synthesis Data Center [http://jejudb.jeju.go.kr/content/stat/stat_02_5.php]; Jeju Special Self-Governing Province [<http://www.seogwipo.go.kr/contents/index.php?page=4&mid=033112>]), demands more sustainable water resources and also underscores the necessity for efficient water management. In similar, many arid and semiarid countries suffer from water resources shortage and thus have interested in how to mitigate water poverty and efficiently manage them, with consideration for a lack of water storage infrastructure. For example, artificial recharge technology, which directly divert precipitation collected into injection wells, was carried out in several countries (Asano and Cotruvo, 2004; Dillon, 2005; Sheng, 2005; Bouri and Dhia, 2010). To do the state-of-the art technique, it is prerequisite to understand aquifer properties (e.g., thickness, linkage of aquifers, flow direction) and to determine whether anthropogenic sources contribute to groundwater chemistry in production well.

In terms of geochemical processes occurring in volcanic aquifer, silica (Si) is regarded as a main constituent to understand recharge and flow system of groundwater. Si is not involved significantly in the reaction such as ion exchange and biological exploitation (Drever and Clow, 1995). Thus, Si concentration becomes higher with increasing residence time and as flowing through bedrock than above it (Mandal et al., 2011). Numerous studies have deciphered groundwater system in volcanic aquifer using the variation of Si concentration and Si related to ions (Koh et al., 2009). According to companion studies of Koh et al. (2006a, 2009), Si concentration rapidly increased in the early stage of reaction and thereafter constant later due to formation of secondary silicate mineral, with comparison of groundwater age and mineralization. In addition, Mandal et al. (2011) inferred, depending on the level of Si concentration, that spring water, groundwater and submarine groundwater discharge would undergo a different flow path, and this was supported by environmental tracers such as CFC-12 and SF₆ and ³H reported by Asai et al. (2008).

On Jeju Island, high- and low-permeability layers alternate and there is very thick unsaturated zone, approximately 50% of the elevation on which it is (Kim and Kim, 2009). Additionally, pahoehoe, generally including lava tunnels and lava tubes, is widely distributed (Won et al., 2005). The total amount of precipitation per year declines from ca. 3400 mm in the most upland to ca. 1200 mm in coastal regions (Korean Water Resources Corporation [KOWACO] 2003). The geological and meteorological characteristics suggest the possibility that aquifers with high storage capacity at high altitudes would be connected to wells at low altitudes as a form of regional flow. The island can be divided into two regions of coastal area, <200 m above sea level (asl), and high-altitude area, >200 m asl based on topography and land use patterns (Koh et al., 2007b). The high-altitude area contributes 69% of total recharge of the island (Park et al., 2014).

The aim of this study was to determine whether wells at relatively high altitudes, >200 m above sea level (asl), are connected to groundwater at the lower altitudes, <200 m asl, and then to decipher how groundwater in the wells is recharged. For these purposes, groundwater samples were collected from five wells located at low altitude, ca. 150 to 200 m asl, and from the other five wells at high altitude, ca. 200 to 400 m asl, from 2008 to 2010. Chemical and isotopic compositions of the groundwater were determined to understand the geochemical conditions of each groundwater for purposes of classifying groundwater pathways and groundwater recharge processes.

2. Site description

2.1. Description of Jeju Island and study area

Jeju Island, a typical volcano shield with gentle topography and an elliptical shape, is located in southwestern South Korea; it is the largest

island in the country, with an area of 1845 km² (Fig. 1). Jeju Island is naturally mountainous area dominated by Halla Mountain (1950 m asl), and consists of lowlands in the coastal areas (<200 m asl) and mountainous areas from 200 to 600 m asl. Most residents live in the coastal areas of Seogwipo and Jeju. These cities offer various facilities for tourists such as hotels, restaurants, and rental car service centers in addition to an airport, buildings, orange orchards, and agricultural areas. The mountainous areas are mainly used for agricultural purposes, pastures, forests, and golf courses, whereas the Halla Mountain areas are dominated by forests. Compared with the high areas, the thicker soil layers are developed widely in the lowland areas on Jeju Island (Water Management Information System, WAMIS: www.wamis.go.kr) (Fig. 1).

Jeju Island has a humid subtropical climate that is warmer than that of the rest of South Korea and has clear seasonal variation. The monthly mean air temperature reported by the Korea Meteorological Administration (KMA, www.kma.go.kr) during 1981–2010 ranged from 5.7 to 26.8 °C.

2.2. Geological and hydrological properties of Jeju Island

Jeju Island was formed by volcanism from the Pliocene to Quaternary, and >90% of the island is covered by basaltic rocks (Koh et al., 2006a). The basaltic rocks overlie a hydro-volcanic sedimentary formation, the Seogwipo Formation, which consist of sand, tuffaceous material, and basaltic rock fragments (Sohn et al., 2003). The U Formation, mainly composed of unconsolidated sand and silt, underlies the Seogwipo Formation (Sohn, 1996; Won et al., 2006). The Seogwipo Formation in the northern part of Jeju Island occurs mostly at an altitude of — 100 to 50 m asl (Won et al., 2006). The basaltic rocks contain numerous interflow structures that are not filled and are significantly permeable with high storage capacity (Koh et al., 2006a, 2009). The lithology of the Jeju Island aquifers is characterized by thick unsaturated zones, and high- and low-permeable vertically alternated layers (Kim and Kim, 2009). Hydrological properties such as hydraulic conductivity, specific capacity, and groundwater flow were summarized in previous studies (Hagedorn et al., 2011, and references therein). Vertical hydraulic conductivity (K) values for the basaltic aquifers overlying the Seogwipo Formation were estimated to range from 3 to 28 m/d (Kim et al., 2003). According to previous studies, basaltic aquifers distinctly include the higher specific capacities from ca. 1290 to ca. 2410 m²/day and younger groundwater with ca. 10 to ca. 30 years. These data are comparable to those of sedimentary aquifers with relatively low specific capacity (average 1010 m²/day) and older groundwater, i.e., 20 to 60 years (Won et al., 2005; Koh et al., 2006a). Groundwater elevations are roughly dependent on topography, and the amount of rainfall increases with altitude (KOWACO, 2003). Water table elevation varies from 180 m asl in high-lying areas to 2 m asl in low-lying areas (Hagedorn et al., 2011), and the N-S-oriented horizontal hydraulic gradient was greater than that of E-W (Koh et al., 2006b). The amount of groundwater use in Jeju city was approximately 73×10^6 m³/year ($n = 1898$ wells) in 2010, and of the total amount, 62% was for domestic use ($n = 858$ wells) and 36% for agricultural practices ($n = 842$ wells) (WAMIS: www.wamis.go.kr).

2.3. The studied wells: water level and flow direction

10 wells distributed throughout highland to lowland areas were shown in Fig. 1. For all wells, it was hard to obtain the simple information such as the pumping rates, depth to water and screen length during the study period because they were in private. Alternatively, the information on the wells was summarized on the basis of the report written during pumping test period (Table 1). In brief, the length of the wells ranges from 190 m to 350 m. Natural groundwater level (NWL) was measured from 95 m to 185 m in terms of depth to water. By comparison, stable groundwater level (SWL) measured after pumping out approximately 700–800 m³/d was slightly lowered, 102 m to 190 m. The length and number of screens in each well are dependent on lithological

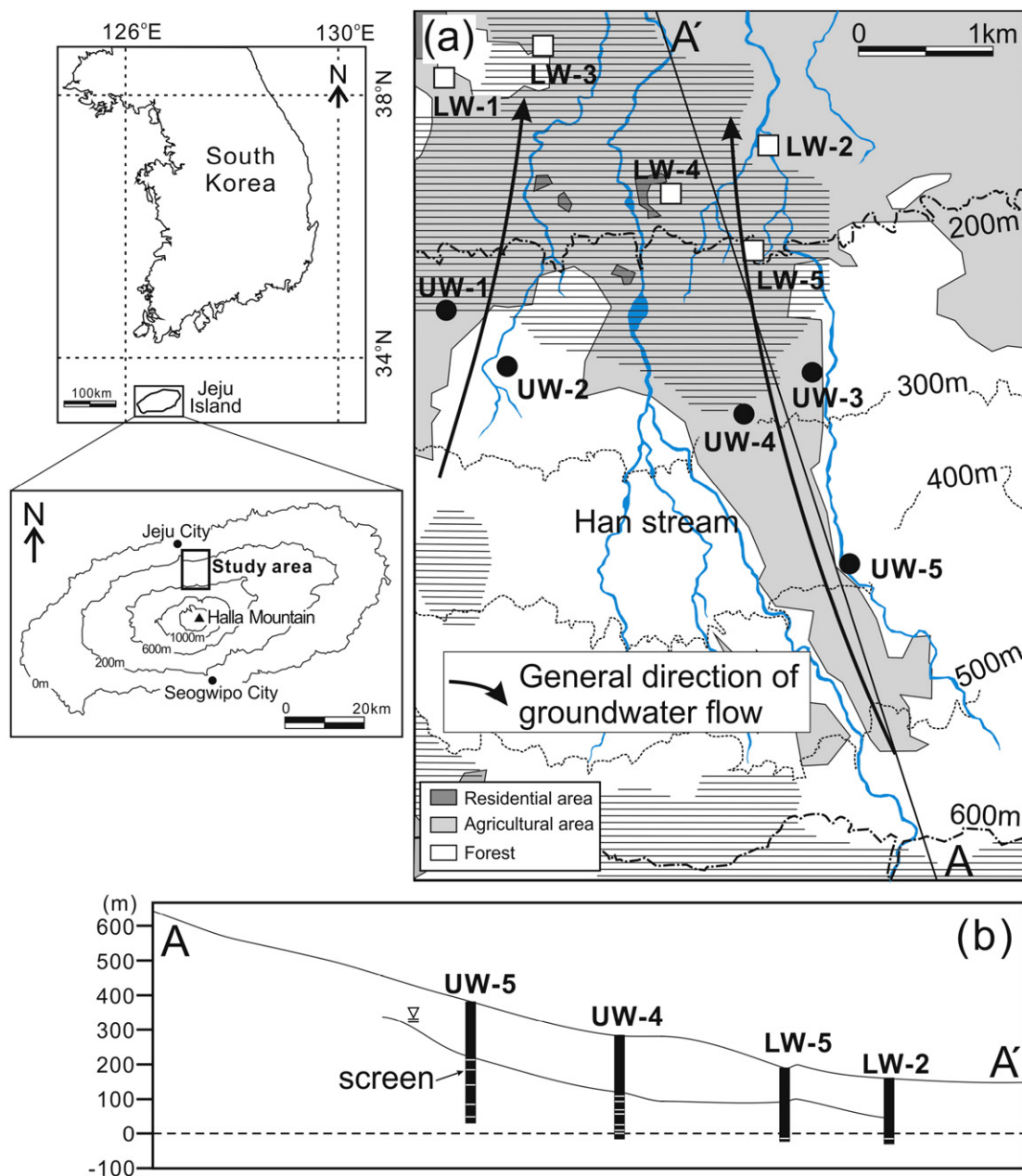


Fig. 1. Location map of the study area including 10 wells to collect groundwater samples (a) and cross-section of the study area for A-A' (b). In Fig. 1a, the hatched areas have thick soil layers compared to other areas (WAMIS: www.wamis.go.kr). LW and UW represented wells in lowland and highland areas, respectively.

Table 1

The simple information on the wells studied.

Well	Altitude (m asl)	Depth (m)	NWL ^a (m)	SWL ^b (m)	Pumping rate (m ³ /d)	Screen length (m)
LW-1	152	192	120	122	720	24
LW-2	160	190	115	129	800	24
LW-3	165	190	135	140	810	30
LW-4	189	214	n.a.	n.a.	n.a.	n.a.
LW-5	200	212	95	102	800	24
UW-1	247	270	138	170	700	52
UW-2	253	272	127	138	800	20
UW-3	281	300	185	190	700	40
UW-4	286	300	162	168	838	40
UW-5	380	350	156	163	800	32

^a NWL: natural groundwater level.

^b SWL: stable groundwater level.

properties. Groundwater pumped out from the wells has been mainly used for agricultural practices. As mentioned above, unfortunately, the information on pumping rate during the study period was not available. Alternatively, we assumed that groundwater use at each well could be roughly estimated at average 85 m³/d, with consideration for the number of wells and the amount of groundwater used for agricultural practices. Thus, considering groundwater level did not largely vary when groundwater was even pumped out from each well at >700 m³/d during pumping test, the groundwater level during the study period would be constant. In addition, from the information above and altitude of each well site, groundwater in the study area, in general, would be separated into two main flow directions (Fig. 1).

2.4. Sampling and methods

To understand the spatial evolution and temporal variations in chemical and isotopic compositions of the groundwater system in Jeju Island,

water samples were collected from 10 selected wells at increasing altitudes (Fig. 1). The sampling campaigns were conducted six times from July 2008 to February 2010 which includes the four seasons (Fig. 2). Precipitation was concentrated in the summer season (June to September) but appeared throughout the seasons. Temperature ranges from 18 to 30.2 °C (average 25.0 ± 2.6 °C) in summer season and from -0.1 to 22.7 °C (average 11.4 ± 5.8 °C) in dry seasons. After sufficient groundwater was pumped from the wells, the water samples were filtered through a 0.45- μ m membrane filter and collected in Nalgene bottles for the analysis of anions, cations, and oxygen and hydrogen isotopic compositions. The water samples for cation analysis were acidified to pH < 2 with 6 N HNO₃ on site. For analyzing the carbon isotopic compositions of dissolved inorganic carbon ($\delta^{13}\text{C}_{\text{DIC}}$), the water samples were injected into two pre-evacuated glass bottles (150 mL) preloaded with 85% H₃PO₄ (5 mL) using a 60-mL syringe equipped with a 0.45- μ m membrane filter according to the procedure reported by Atekwana and Krishnamurthy (1998). Temperature, pH, and electrical conductivity (EC) were measured with an Orion portable meter calibrated in the field. All water samples were kept at 4 °C until analysis.

Alkalinity was calculated in the laboratory according to the Gran method, in which 0.01N HCl was progressively added to the water samples. Major cations and anions were analyzed using inductively coupled plasma–atomic emission spectrometry (ICP–AES; Optima 4300DU, PerkinElmer) at the Korea Basic Science Institute (KBSI) and ion chromatography (IC; DX-500, Dionex) at the Korea Institute of Geoscience and Mineral Resources (KIGAM), respectively. Water samples for oxygen isotope analysis were prepared by obtaining equilibration between the water sample and CO₂ gas (Epstein and Mayeda, 1953), and oxygen isotopic ratios were measured using an isotope ratio mass spectrometer (IRMS; Optima, VG Isotech, UK) at the KBSI. Hydrogen isotope ratios were analyzed by an IRMS (Isoprime, GV Instrument, UK) linked online with an elemental analyzer (EA; EuroEA3000 Series, EuroVector, Italy); metallic chromium was used as a catalyst to produce hydrogen gas. With CO₂ gas stripped from water samples by gas evolution and a cryogenic method (Atekwana and Krishnamurthy, 1998), carbon isotopic ratios were determined by IRMS (Optima, VG Isotech, UK) at the KBSI. The isotopic values were expressed using the δ notation relative to the international standards of Vienna Standard Mean Ocean Water (VSMOW) for oxygen and hydrogen isotopes and Vienna Pee Dee Belemnite (VPDB) for carbon isotopes as follows:

$$\delta (\text{‰}) = (R_{\text{sample}}/R_{\text{standard}} - 1) \times 1000,$$

where R represents $^{18}\text{O}/^{16}\text{O}$, $^2\text{H}/^1\text{H}$, or $^{13}\text{C}/^{12}\text{C}$ isotopic ratios. The analytical reproducibility was $\pm 0.1\text{‰}$ for $\delta^{18}\text{O}$, $\pm 1\text{‰}$ for $\delta^2\text{H}$, and $\pm 0.2\text{‰}$ for $\delta^{13}\text{C}$.

3. Results and discussion

Table 2 shows the physiochemical and isotopic compositions of the groundwater samples collected from five wells at altitudes below approximately 200 m asl (LW-1 to LW-5; LW group) and from five other wells at approximately 250 m to 400 m asl (UW-1 to UW-5; UW group) on Jeju Island from July 2008 to February 2010. The total dissolved solids (TDS), including the sum of the major elements (Ca + Mg + Na + K + SiO₂ + HCO₃ + Cl + SO₄ + NO₃), ranged from 52.0 to 123 mg/L throughout the seasons; bicarbonate ion was divided by 2.03366 to account for CO₂ loss and its transformation to carbonate (Hubert and Wolkersdorfer, 2015). Higher values were observed in groundwater samples collected from the LW group than those from the UW group, except for relatively low TDS in LW-2 and LW-5 and higher TDS in UW-1 and UW-2. The TDS generally decreased with an increase in altitude (Fig. 3). Additionally, the LW groundwater samples clearly showed seasonal variation, particularly in January 2009 (the lowest level) and in July 2008 and August 2009 (the highest levels), compared with those in UW (Table 2). As in TDS, altitudinal and temporal variations were observed in dissolved ions (Ca, Na, Cl, SO₄, NO₃, and HCO₃) as well (Fig. 3). The contributions of Cl, NO₃, and SO₄ to groundwater chemistry were higher in the LW group (27.6–52.6%; average 38.7%), than in the UW group (23.9–46.3%; average 32.2%). The proportion of HCO₃ was higher in the UW group (53.7–76.1%; average 67.8%), than in the LW group (47.4–72.4%; average 61.3%).

Oxygen and hydrogen isotopic compositions ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) of groundwater ranged from -8.2‰ to -7.3‰ and from -53‰ to -48‰ , respectively. Overall, $\delta^{18}\text{O}$ values were progressively depleted with increased altitude (Table 2; Fig. 3), with LW-2 and LW-5 representing the most depleted $\delta^{18}\text{O}$ values relative to other wells in the LW group. Of wells in the UW group, UW-3 showed the most enriched $\delta^{18}\text{O}$ value and the largest variation in $\delta^{18}\text{O}$ value throughout the seasons. Carbon isotopic compositions of dissolved inorganic carbon for groundwater ($\delta^{13}\text{C}_{\text{DIC}}$) ranged from -15.9 to -8.8‰ . Of the groundwater samples, UW-4 and UW-5, both located at the relatively high altitudes, were clearly distinguishable from the others by their high $\delta^{13}\text{C}_{\text{DIC}}$ values.

3.1. Groundwater chemistry related to altitudinal variations

Dissolved ion concentrations in the LW group largely fluctuated relative to those in the UW group (Fig. 3). Of the dissolved ions, Cl, NO₃,

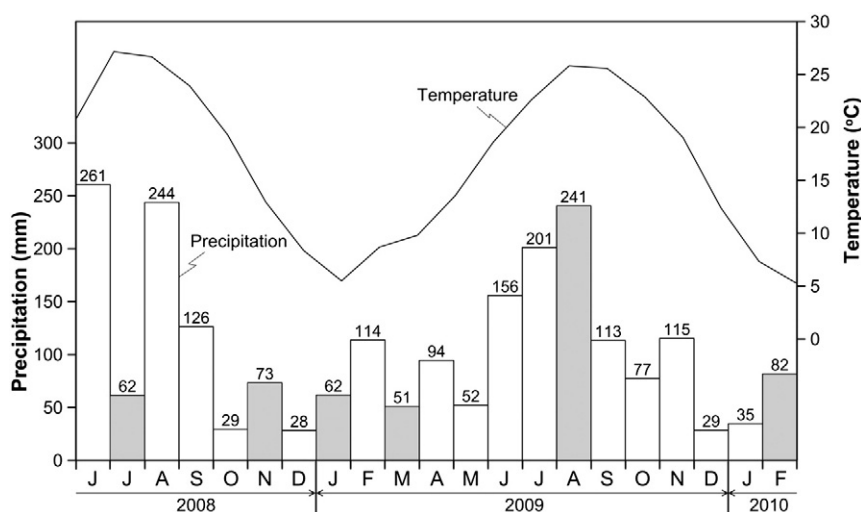


Fig. 2. Variation of the amount of precipitation and air temperature reported from June 2008 to February 2010 on Jeju Island, South Korea. The gray bars highlighted months when the sampling campaigns were carried out and the numbers on top of the bars represent the amount of precipitation (in mm) during each month.

Table 2

Physiochemical and isotopic compositions of groundwater taken from wells in upper to lower lands on Jeju Island, South Korea during July 2008 to February 2010.

Date	Temp. (°C)	EC (μS/cm)	pH	Ca	K	Mg	Na	Cl	SO ₄	NO ₃	HCO ₃	TDS (mg/L)	δ ¹⁸ O	δ ² H	δ ¹³ C _{DIC}	d-Value ^a	-logP _{CO2}
(meq/L)													(‰)				
LW-1																	
July 2008	17.6	109	6.27	0.29	0.06	0.40	0.31	0.24	0.06	0.10	0.70	79.9	−7.5	−49	−13.9	11.9	1.69
November 2008	14.9	108	6.16	0.32	0.06	0.45	0.33	0.24	0.07	0.09	0.73	83.3	−7.7	−51	−13.8	10.5	1.56
January 2009	13.9	97.5	6.34	0.26	0.05	0.38	0.31	0.19	0.05	0.06	0.65	71.4	−7.8	−48	−14.4	14.2	1.79
March 2009	14.1	102	6.89	0.26	0.05	0.36	0.30	0.22	0.06	0.08	0.67	74.9	−7.6	−49	−14.4	12.1	2.33
August 2009	15.5	108	6.78	0.30	0.03	0.42	0.32	0.30	0.10	0.07	0.65	78.8	−7.6	−49	−14.3	11.7	2.23
February 2010	15.7	103	7.10	0.29	0.06	0.39	0.31	0.24	0.07	0.07	0.79	84.9	−7.8	−51	−14.3	11.1	2.46
LW-2																	
July 2008	15.0	99.7	6.29	0.25	0.09	0.27	0.36	0.16	0.03	0.08	0.74	77.4	−7.9	−52	−11.3	11.3	1.68
November 2008	14.3	67.2	6.89	0.19	0.05	0.22	0.26	0.16	0.03	0.06	0.49	55.4	−8.0	−52	−13.3	11.7	2.46
January 2009	13.4	65.5	6.89	0.17	0.04	0.19	0.25	0.15	0.03	0.05	0.40	47.5	−8.0	−50	−13.8	13.7	2.55
March 2009	14.2	80.3	7.15	0.20	0.05	0.22	0.25	0.19	0.04	0.12	0.50	60.6	−7.8	−50	−13.8	12.5	2.72
August 2009	15.6	82.1	6.65	0.23	0.06	0.26	0.29	0.16	0.03	0.09	0.57	63.7	−7.8	−50	−13.6	12.7	2.16
February 2010	15.2	67.1	7.06	0.18	0.05	0.19	0.23	0.16	0.04	0.06	0.48	53.8	−8.0	−52	−13.7	11.4	2.64
LW-3																	
July 2008	15.3	108	6.37	0.30	0.06	0.41	0.31	0.25	0.06	0.13	0.67	81.0	−7.7	−48	−14.3	13.3	1.80
November 2008	14.9	106	6.84	0.31	0.06	0.42	0.34	0.24	0.06	0.11	0.69	82.3	−7.7	−51	−14.4	10.7	2.26
January 2009	14.0	108	6.43	0.30	0.03	0.41	0.34	0.22	0.06	0.11	0.67	78.9	−7.9	−49	−14.8	13.8	1.86
March 2009	14.0	112	6.00	0.30	0.06	0.38	0.31	0.25	0.07	0.14	0.64	79.7	−7.6	−49	−14.9	11.9	1.45
August 2009	15.8	117	6.91	0.33	0.06	0.44	0.35	0.32	0.09	0.20	0.73	94.7	−7.7	−49	−14.9	12.4	2.31
February 2010	14.9	109	6.85	0.31	0.06	0.40	0.32	0.26	0.07	0.11	0.79	88.6	−7.7	−52	−14.8	10.3	2.21
LW-4																	
July 2008	16.1	161	6.07	0.46	0.08	0.48	0.42	0.33	0.10	0.32	0.79	113	−7.4	−48	−15.9	11.2	1.43
November 2008	14.8	104	6.70	0.31	0.06	0.35	0.35	0.24	0.06	0.18	0.62	81.4	−7.7	−51	−14.4	10.6	2.17
January 2009	14.1	102	6.58	0.30	0.03	0.33	0.35	0.22	0.05	0.15	0.62	76.8	−7.7	−49	−14.9	12.2	2.05
March 2009	15.1	160	6.75	0.48	0.07	0.49	0.45	0.36	0.10	0.37	0.75	116	−7.3	−48	−15.6	10.9	2.13
August 2009	16.6	156	6.76	0.51	0.07	0.54	0.46	0.33	0.11	0.30	0.79	114	−7.4	−48	−15.2	11.0	2.13
February 2010	15.3	147	7.20	0.47	0.08	0.47	0.44	0.41	0.00	0.38	0.77	113	−7.5	−51	−14.9	9.1	2.58
LW-5																	
July 2008	14.8	76.1	6.29	0.18	0.05	0.20	0.24	0.16	0.03	0.09	0.46	54.6	−7.9	−52	−14.8	11.4	1.89
November 2008	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
January 2009	14.2	64.8	6.91	0.17	0.05	0.21	0.24	0.15	0.03	0.05	0.43	49.0	−8.0	−52	−13.4	11.7	2.54
March 2009	13.0	64.6	6.75	0.18	0.04	0.20	0.24	0.15	0.03	0.04	0.42	48.1	−8.1	−50	−13.4	14.3	2.39
August 2009	14.2	71.7	7.25	0.18	0.05	0.21	0.26	0.17	0.03	0.08	0.42	52.6	−7.9	−50	−13.5	12.9	2.89
February 2010	14.9	64.9	7.05	0.17	0.05	0.19	0.23	0.20	0.03	0.04	0.47	52.8	−8.0	−53	−13.5	11.5	2.64
UW-1																	
July 2008	15.2	99.5	6.10	0.26	0.05	0.36	0.29	0.21	0.06	0.06	0.74	77.7	−7.7	−49	−13.7	12.3	1.49
November 2008	14.8	97.9	6.32	0.28	0.05	0.40	0.30	0.21	0.06	0.06	0.71	76.5	−7.8	−51	−13.9	11.5	1.73
January 2009	13.6	99.6	6.54	0.28	0.03	0.39	0.30	0.20	0.05	0.06	0.65	71.3	−7.6	−50	−14.0	11.3	1.99
March 2009	14.4	103	6.96	0.31	0.05	0.41	0.32	0.22	0.07	0.07	0.69	78.2	−7.6	−49	−14.1	11.8	2.38
August 2009	15.5	96.4	7.18	0.28	0.03	0.38	0.30	0.24	0.07	0.06	0.81	83.6	−7.7	−49	−14.0	12.4	2.53
February 2010	14.7	97.1	7.22	0.27	0.05	0.37	0.29	0.17	0.03	0.04	0.77	75.5	−7.7	−50	−13.9	11.8	2.60
UW-2																	
July 2008	15.0	81.3	6.29	0.21	0.05	0.30	0.26	0.17	0.04	0.04	0.62	64.0	−7.9	−50	−14.0	13.6	1.76
November 2008	14.5	79.2	7.27	0.21	0.06	0.32	0.27	0.17	0.04	0.04	0.64	65.9	−7.8	−51	−14.1	11.1	2.73
January 2009	13.2	77.4	6.25	0.20	0.05	0.29	0.26	0.15	0.03	0.04	0.57	59.3	−7.9	−50	−14.5	13.0	1.76
March 2009	14.3	79.8	7.10	0.21	0.05	0.29	0.28	0.23	0.04	0.04	0.62	66.6	−7.7	−50	−14.2	12.3	2.57
August 2009	15.8	81.3	6.74	0.23	0.05	0.31	0.27	0.21	0.05	0.06	0.69	72.0	−7.9	−50	−14.3	12.7	2.16
February 2010	14.0	79.3	7.27	0.21	0.06	0.28	0.25	0.16	0.03	0.05	0.64	65.1	−8.0	−51	−14.5	13.0	2.73
UW-3																	
July 2008	14.5	68.7	6.24	0.17	0.05	0.18	0.22	0.15	0.03	0.07	0.43	49.7	−7.8	−49	−12.5	13.7	1.87
November 2008	14.3	61.2	7.29	0.17	0.05	0.19	0.23	0.15	0.03	0.04	0.41	47.2	−7.9	−52	−15.5	11.2	2.94
January 2009	13.0	60.8	7.62	0.16	0.04	0.18	0.23	0.15	0.03	0.04	0.40	45.8	−7.9	−50	−11.7	13.2	3.28
March 2009	14.5	87.1	6.62	0.25	0.04	0.26	0.29	0.20	0.04	0.17	0.48	65.5	−7.6	−48	−13.4	12.1	2.20
August 2009	15.3	66.9	6.38	0.18	0.03	0.20	0.24	0.15	0.03	0.06	0.47	52.0	−7.8	−49	−12.3	13.4	1.97
February 2010	13.9	60.5	6.78	0.16	0.05	0.17	0.22	0.16	0.04	0.04	0.42	47.6	−7.9	−51	−11.8	11.9	2.42
UW-4																	
July 2008	14.1	60.9	6.43	0.15	0.05	0.17	0.21	0.12	0.03	0.02	0.45	45.8	−8.1	−50	−9.1	14.1	2.04
November 2008	13.8	60.5	6.88	0.16	0.05	0.19	0.23	0.14	0.03	0.02	0.47	49.3	−8.1	−52	−9.3	12.6	2.47
January 2009	13.0	60.2	7.01	0.16	0.04	0.18	0.22	0.13	0.03	0.02	0.52	51.0	−8.0	−51	−9.9	13.8	2.56
March 2009	14.1	62.3	6.74	0.17	0.05	0.19	0.23	0.14	0.03	0.02	0.48	50.2	−8.0	−50	−9.3	13.9	2.32
August 2009	14.7	60.7	6.34	0.17	0.05	0.18	0.22	0.17	0.04	0.03	0.44	48.9	−8.0	−50	−9.4	14.6	1.96
February 2010	13.2	59.5	6.77	0.16	0.05	0.17	0.21	0.14	0.03	0.02	0.47	48.9	−8.1	−52	−8.8	12.6	2.36

(continued on next page)

Table 2 (continued)

Date	Temp. (°C)	EC (μS/cm)	pH	Ca	K	Mg	Na	Cl	SO ₄	NO ₃	HCO ₃	TDS (mg/L)	δ ¹⁸ O	δ ² H	δ ¹³ C _{DIC}	d-Value ^a	-logP _{CO2}
(meq/L)													(‰)				
UW-5																	
July 2008	13.4	48.5	6.37	0.11	0.04	0.11	0.17	0.11	0.03	0.01	0.31	34.0	−8.1	−51	−9.3	13.7	2.14
November 2008	13.4	49.5	6.84	0.12	0.05	0.13	0.19	0.12	0.03	0.01	0.41	41.7	−8.2	−53	−8.9	12.9	2.49
January 2009	13.2	50.4	7.12	0.13	0.04	0.13	0.20	0.12	0.03	0.01	0.32	36.6	−8.2	−51	−9.0	14.1	2.87
March 2009	13.0	50.6	6.55	0.12	0.04	0.11	0.19	0.13	0.03	0.01	0.33	36.7	−8.1	−51	−9.1	13.7	2.30
August 2009	13.6	48.9	6.84	0.13	0.04	0.13	0.19	0.17	0.04	0.02	0.38	42.8	−8.1	−50	−10.2	15.1	2.52
February 2010	12.9	50.6	6.76	0.13	0.05	0.12	0.18	0.12	0.03	0.00	0.47	45.0	−8.2	−53	−9.4	12.4	2.35

n.a.: not analyzed.

LW and UW represent wells located at below and over ca. 200 m asl, respectively.

^a d = δD - 8 + δ¹⁸O (Dansgaard, 1964).

and SO₄ are known to be associated with anthropogenic sources and have been widely used as indicators of anthropogenic contamination in many watersheds (e.g., Grasby and Hutcheon, 1997; Mayer et al., 2002; Lee et al., 2008). The proportions of Cl, SO₄, and NO₃ to their sum (in equivalent unit) were 58.0, 13.6, and 28.4% in the LW group and 69.0, 15.8, and 15.3% in the UW group, respectively. That is, Cl and NO₃ distinguished the LW and UW groups.

The variations of electrical conductivity (EC) and alkalinity and their relationships were used to explain hydrological processes occurring in groundwater (Fig. 4). EC was positively correlated with alkalinity as a whole, and most of the UW group, including LW-2 and LW-5, were

below the regression line of EC and alkalinity for uncontaminated groundwater (Koh et al., 2009). The EC values (approximately 50 μS/cm) of precipitation-dominated spring water at high altitudes (561 to 1307 m) on Jeju Island (Koh et al., 2009) were similar to that for groundwater at the highest altitude (e.g. UW-5). The results indicate that the UW group was likely to be rapidly recharged by precipitation, and natural mineralization predominated in its chemical composition. In contrast, the LW group, plotted above the regression line, indicating that the groundwater was progressively affected by contamination sources in residential and agricultural areas of downgradient regions. Similarly, Yoon and Park (1998) reported that the TDS values of spring waters in

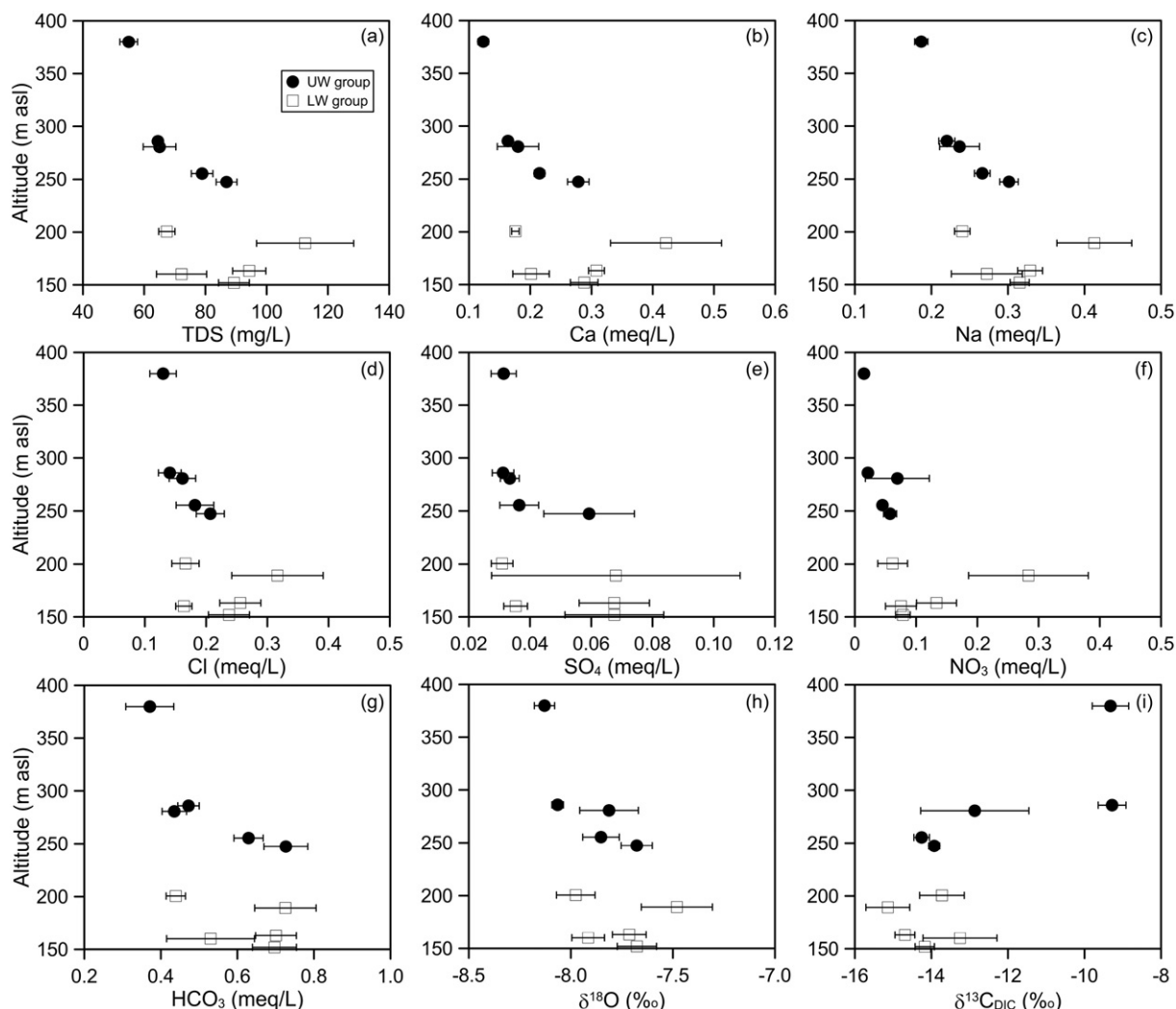


Fig. 3. Diagram showing altitudinal and temporal variations of TDS, dissolved ions and isotopic compositions for groundwater collected in Jeju Island, South Korea.

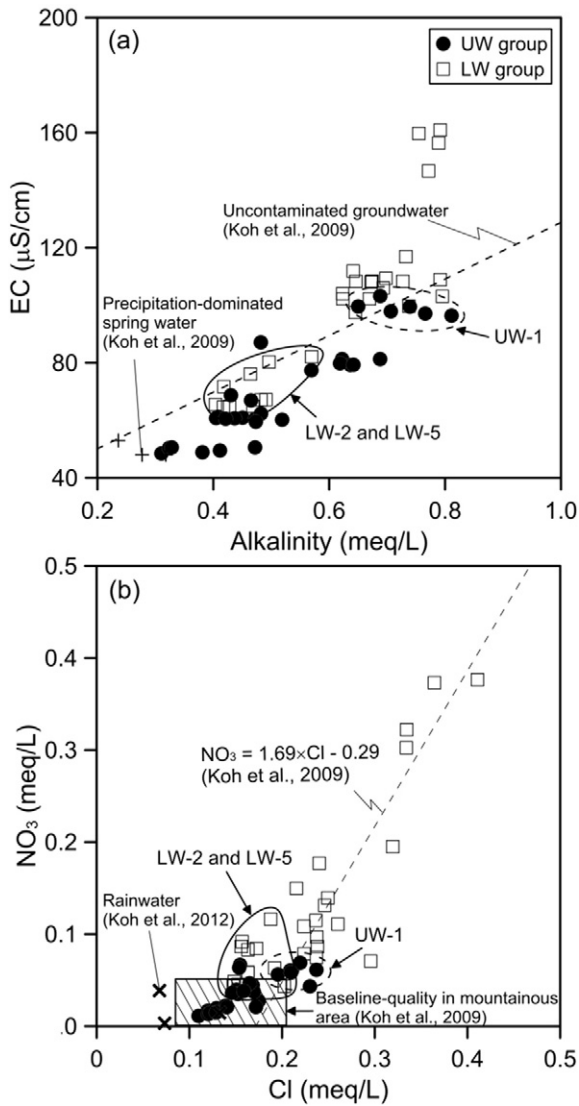


Fig. 4. Plot of EC vs. alkalinity (a) and Cl vs. NO₃ (b) for groundwater in Jeju Island. LW and UW represented wells in low- and high-lying areas, respectively.

lower lands increased because of penetration of anthropogenic substances accompanying precipitation.

The relationship between Cl and NO₃ in groundwater on Jeju Island was employed as an important proxy in determining whether groundwater quality was affected by anthropogenic sources (Koh et al., 2007b). Based on the relationship between Cl and NO₃ for groundwater, most of the UW group mainly plotted close to the baseline level for a mountainous area (Koh et al., 2009), whereas the LW group plotted along with the regression line for Cl and NO₃ affected by anthropogenic sources (NO₃ = 1.69 × Cl - 0.29), as suggested by Koh et al. (2007b); Fig. 4b). The regression line was established based on the data of groundwater from domestic wells throughout Jeju Island, which removed the effect of seawater on groundwater chemistry by excluding samples below 200 m asl. Furthermore, Cl and NO₃ concentrations for rainwater collected at 5 m asl in Jeju Island showed significantly low values (0.07–0.13 meq/L and 0.003–0.04 meq/L, respectively) (Koh et al., 2012), when compared to those of groundwater. Thus, it appears that large proportions of Cl and NO₃ in the LW group were derived from anthropogenic sources, whereas those in the UW group were from natural sources such as precipitation. This suggestion was supported by land-use distributions estimated quantitatively on Jeju Island (Ha et al., 2009); that is, urban and agricultural areas versus forests comprise 40% and 7% of the area below 200 m asl and 9% and 20% of that 200–

600 m asl, respectively. Additionally, LW-2 and LW-5 plotted away from the regression line, but UW-1 was close to the line, indicating notable differences in groundwater recharge processes.

3.2. Altitude effect of δ¹⁸O value and existence of regional flows

Thin soil layers with an average depth of 0.6 m (Jejudo, 1997) and the prevailing distribution of permeable basaltic rocks in Jeju Island readily lead to infiltration of precipitation without remarkable evaporation. Additionally, perched aquifers resulting from the presence of low-permeability layers composed of tuffaceous rocks or dense lava flow below permeable basaltic rocks, can be rapidly recharged by precipitation (Koh et al., 2012). Furthermore, infiltrated water in hilly areas is linked to groundwater in lower lands where low-permeability layers have formed. If groundwater in this study were recharged by infiltration related to distinct lithology, as mentioned above, the groundwater could be classified by the altitude effect of the δ¹⁸O value.

δ¹⁸O values of precipitation below 1000 m asl for the northern slope on Jeju Island were depleted by 0.2‰ per 100 m (Lee et al., 1999), and the isotopic depletion trend was consistent with those of samples collected throughout continental Italy (Longinelli and Selmo, 2003). With the regression line constructed from the variation in δ¹⁸O values as a function of altitude reported in previous studies, the δ¹⁸O values for groundwater were shown to correspond to each altitude in this area (Fig. 5). Based on flow paths inferred from the relationship of the δ¹⁸O value and altitude and from groundwater elevations depending on topography on Jeju Island (KOWACO, 2003), groundwater was classified into two groups: (1) UW-1, LW-1, and LW-3 and (2) UW-5, UW-4, LW-5, and LW-2. For the group (1), UW-1 is likely recharged primarily by precipitation at altitudes between 200 and 300 m, which could reach LW-1 and LW-3 as a regional flow. As shown in Fig. 3, dissolved ions in UW-1, LW-1, and LW-3 all showed similar seasonal variations. For those from group (2), UW-5 could depend on groundwater recharged by precipitation at a higher altitude, such as that estimated at approximately 559 m using the regression equation line. Thereafter, UW-5 water could reach UW-4, LW-5, and LW-2. In LW-2 and LW-5, the low Cl and NO₃ concentrations were comparable to those from other LW groundwater. This result supports the hypothesis that LW-2 and LW-5, mainly derived from regional flow, were linked to UW-4 and UW-5. It is noteworthy that the δ¹⁸O values and dissolved ion concentrations, such as Cl and NO₃, in LW-2 and LW-5 were slightly higher than those in UW-4 and UW-5 (see below).

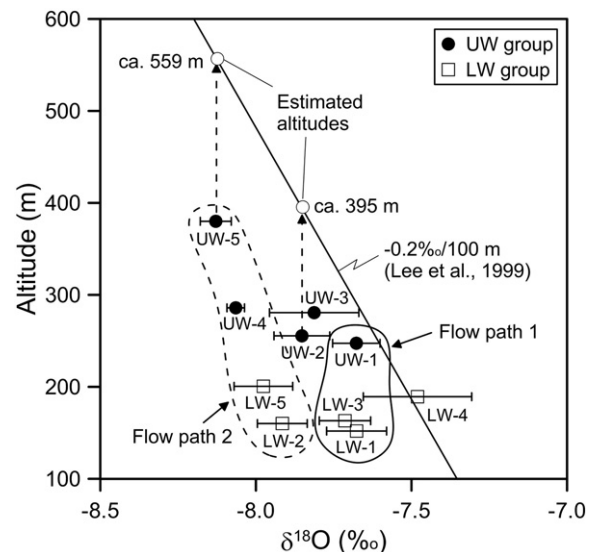


Fig. 5. δ¹⁸O values of groundwater varied with altitude increase on Jeju Island. The dashed line was yielded by reflecting the altitude effect of δ¹⁸O value reported by Lee et al. (1999).

Besides the regional flow, stream waters may rapidly infiltrate into the groundwater system due to the distinct lithology of Jeju Island. If this were the case, other water bodies with $\delta^{18}\text{O}$ values reflecting altitude effects and seasonal variations could be introduced into the stream during downward movement. Subsequently, the groundwater classified by the regional flow systems would show a different $\delta^{18}\text{O}$ value. However, in this study, such occurrences caused by streamwater infiltration were not observed in groundwater involved in the regional flow systems. Furthermore, most streams in Jeju Island are ephemeral. Therefore, the portion of stream water could be considered negligible with regard to forming the regional flow throughout the seasons.

The remaining groundwater, LW-4, UW-2, and UW-3, was independent from the two regional flow systems mentioned above in terms of the recharge process. From the regression line in Fig. 5, LW-4 and UW-3 are expected to be directly recharged by local precipitation, and UW-2 would be linked to groundwater fed at a high altitude of approximately 395 m. However, these hypotheses are not examined in this study due to a lack of data.

3.3. Verifying the evolution of regional flows

Generally, the CO_2 exchange between atmosphere and water, weathering of carbonate rocks, and soil CO_2 produced from the decay of soil organic material were major contributors to the carbon isotopic composition of natural water (Yang et al., 1996). Most C3 plants have $\delta^{13}\text{C}$ values between -30 and -24‰ (Vogel, 1993). Assuming the contribution of C3 plant-based soil CO_2 as a dissolved inorganic carbon (DIC) source, the $\delta^{13}\text{C}_{\text{DIC}}$ value in non-carbonate regions could theoretically represent a main range of approximately -17 to -11‰ (Fig. 6) due to enrichment by diffusion of soil CO_2 (approximately 4.4‰ ; Cerling et al., 1991) and carbon isotope fractionation between CO_2 and HCO_3^- (approximately 9‰ ; Zhang et al., 1995). Indeed, the $\delta^{13}\text{C}_{\text{DIC}}$ value of soil water obtained in South Korea ranged from -21.2 to -13.1‰ (average -16.7‰) with seasonality, and its CO_2 concentration during the summer season, which supplies abundant soil organic carbon, was substantially high; $-\log P_{\text{CO}_2}$ ranged from 1.4 to 2.8 (average 1.9 ; Shin et al., 2011).

For most groundwater samples, with exception for UW-4/UW-5, the $\delta^{13}\text{C}_{\text{DIC}}$ values were within the range of the estimated $\delta^{13}\text{C}_{\text{DIC}}$ value for soil water, i.e., -17 to -11‰ (Fig. 6). Additionally, as shown in soil water throughout the seasons (Shin et al., 2011), the $\delta^{13}\text{C}_{\text{DIC}}$ value decreased gradually with an increase in soil CO_2 from highland to lowland areas (e.g., from UW-4/UW-5 to LW-1/LW-3), with the exception of

LW-2 and LW-5, which were classified by the same flow path to UW-4/UW-5. This result indicates that soil-derived CO_2 contributes to groundwater as the main carbon source with decreasing altitude. LW-1, LW-3, and UW-1 were distinguished from others by showing relatively low $\delta^{13}\text{C}_{\text{DIC}}$ and $-\log P_{\text{CO}_2}$ values, thus representing a regional flow (flow path 1; Fig. 6).

Atmospheric CO_2 ($-\log P_{\text{CO}_2} = 3.5$; Ali and Atekwana, 2011) is characterized by $\delta^{13}\text{C}$ values between -8 and -6‰ (Cerling et al., 1991), and rainwater $\delta^{13}\text{C}_{\text{DIC}}$ values are from -9.2 to -7.2‰ due to 1.2‰ depletion when atmospheric CO_2 is converted into H_2CO_3 (Zhang et al., 1995). Additionally, the distribution of DIC species depends on pH and results in distinct ^{13}C fractionation. For example, HCO_3^- of DIC is the major species in pH within the range of 6 – 10 , and the $\delta^{13}\text{C}_{\text{DIC}}$ value would be approximately 0‰ due to the enrichment by ^{13}C fractionation between HCO_3^- and atmospheric CO_2 of approximately 8‰ (Clark and Fritz, 1997). For UW-4 and UW-5, which had pH values of 6.34 to 7.12 (Table 2), the $\delta^{13}\text{C}_{\text{DIC}}$ values (-10.2 to -8.8‰) were not established by CO_2 exchange alone between precipitation DIC and atmospheric CO_2 . In addition to the $\delta^{13}\text{C}_{\text{DIC}}$ values, the P_{CO_2} was >10 times higher than that of atmospheric CO_2 . Weathering of non-carbonate bedrock does not provide an additional carbon source to groundwater. For these reasons, $\delta^{13}\text{C}_{\text{DIC}}$ values for UW-4 and UW-5 were governed by a limited contribution of soil CO_2 from poorly developed soil layers at high altitudes. By comparison, either the similar or the slightly low P_{CO_2} in LW-2 and LW-5 could result from CO_2 consumption by weathering. Because soil CO_2 accompanied with recharge water infiltrating soil layers was partially involved in the weathering during downward movement, $\delta^{13}\text{C}_{\text{DIC}}$ values would be depleted (flow path 2).

The existence of flow path 1 and flow path 2, which were characterized by altitude effect and $\delta^{13}\text{C}_{\text{DIC}}$ values combined with P_{CO_2} , were verified on the basis of HCO_3^- and carbon isotopic composition related to Si concentration as well. In general, silicate weathering supplies both HCO_3^- and Si to groundwater, and the ratio of Si to HCO_3^- would be dependent on silicate mineralogy developed along flow paths (e.g. Das et al., 2005). Samples for flow path 1 and flow path 2 were illustrated on plot of Si and HCO_3^- (Fig. 7) and Si concentration showed a trend to increase together with HCO_3^- . In addition to the trend, the samples were roughly separated into two clusters; i.e., flow path 1 and flow path 2. The results indicate that the two groups of groundwater were variably affected by distinct silicate weathering processes along the two different flow paths.

Although there are no available chemical and isotopic properties of volcanic CO_2 on Jeju Island, contribution of volcanic CO_2 to groundwater

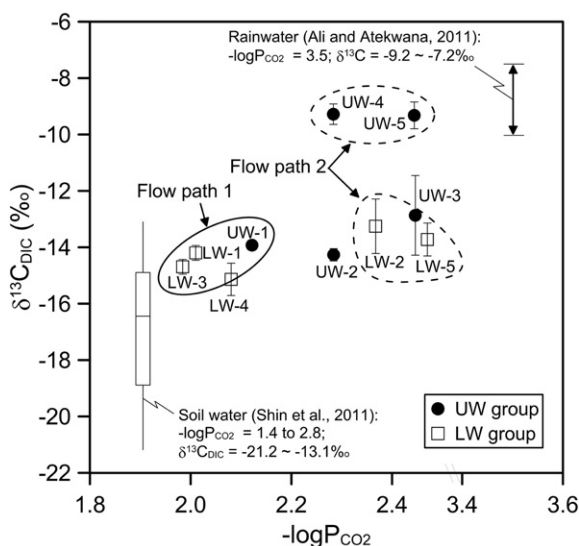


Fig. 6. Plot of $\delta^{13}\text{C}_{\text{DIC}}$ value and $-\log P_{\text{CO}_2}$ for groundwater collected in Jeju Island. Please see the text for $\delta^{13}\text{C}_{\text{DIC}}$ values of the end-members.

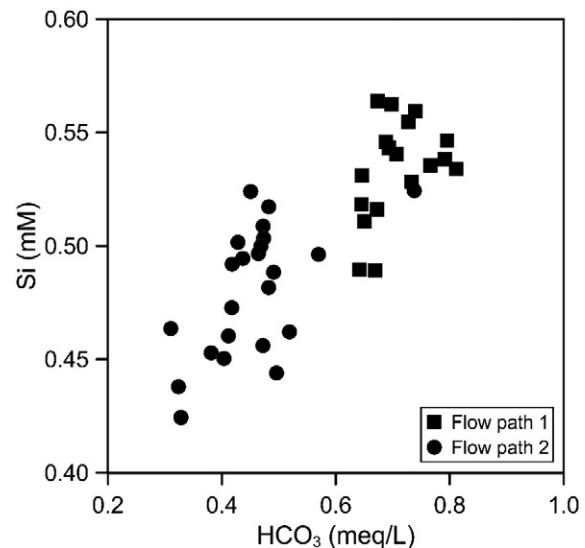


Fig. 7. Plot of Si and HCO_3^- for groundwater samples characterized by flow path 1 and flow path 2.

DIC would not be important. The $\delta^{13}\text{C}$ values of CO_2 released from fumarolic areas and of fumarolic CO_2 were around -4% (Kita et al., 1993; Ohsawa et al., 2002). Furthermore, according to mixing curves between air samples (CO_2 concentration of 357–380 ppmv; $\delta^{13}\text{C}$ of -9.3 to -8.3%) and atmospheric plumes of three Italian volcanoes, the higher contribution of volcanic CO_2 (up to 36,900 ppmv) led to the more enriched $\delta^{13}\text{C}$ value, i.e., up to -1.8% (Chiodini et al., 2011). If volcanic CO_2 played a critical role as a DIC source in the groundwater studied, the groundwater would include the enriched $\delta^{13}\text{C}_{\text{DIC}}$ values with increasing P_{CO_2} and, furthermore, much higher $\delta^{13}\text{C}_{\text{DIC}}$ values than those of volcanic CO_2 due to the enrichment by ^{13}C fractionation between HCO_3 and CO_2 gas.

3.4. Contribution of precipitation to two regional groundwater flows

The LMWL on Jeju Island yielded a different slope and an intercept with seasonality: $\delta^2\text{H} = 8.0 * \delta^{18}\text{O} - 9.6$ for summer season precipitation (June to September) and $\delta^2\text{H} = 8.1 * \delta^{18}\text{O} + 20.3$ for dry season precipitation (October to May; Lee et al., 2002, 2003; Fig. 8). The isotopic data of the precipitation in Jeju included significantly wide ranges between -13.5 and -1% for $\delta^{18}\text{O}$ and between -105 and 20% for $\delta^2\text{H}$. For the two regional flow systems with different flow paths in this study, the comparison with $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values was not significant because of the remarkably narrow range of the isotopic data. Nonetheless, in the plot of $\delta^2\text{H}$ and $\delta^{18}\text{O}$, groundwater samples collected during the following winter (i.e., in November 2008 and February 2010) were distinguished from those in other seasons (July 2008 and January to August 2009). The former, expressed by $\delta^2\text{H} = 4.3 * \delta^{18}\text{O} - 17.6$, was distinguished from the latter, with $\delta^2\text{H} = 3.5 * \delta^{18}\text{O} - 22.5$ (Fig. 8).

Assuming that groundwater was recharged by both precipitations infiltrated in summer and dry seasons, interceptions obtained from the regression lines of the two equations above and two LMWLs for summer and dry seasons would be representative for groundwater recharged only in the summer season and in the dry season, respectively (Fig. 8). Based on the interceptions, the contributions of precipitation in the summer and dry seasons to groundwater could be quantitatively calculated. That is, summer season precipitation was one portion of between ca. 65 and ca. 85% of groundwater collected in November 2008 and February 2010, and between ca. 45 and ca. 80% in July 2008 and January to August 2009. It is notable that the higher proportion of

precipitation in summer season was observed for groundwater corresponding to the following winter.

3.5. Residence time of groundwater fed by two regional flow systems

Precipitation in Jeju Island showed seasonality in the deuterium excess or d-value ($d = \delta^2\text{H} - 8 * \delta^{18}\text{O}$), which was defined by Dansgaard (1964), with the higher value ($d > \sim 15\%$) in dry season (October to May) and the lower value ($d < \sim 10\%$) in summer season (June to September; Lee et al., 2007). In this study, all d-values for the two regional flow systems were within a relatively narrow range: 10 to 15‰ (Table 2; Fig. 9a), when compared with that of the precipitation. This also resulted from mixing of precipitation in the summer and dry seasons. It is noteworthy that the d-values in November 2008 and February 2010, i.e., 10.3 to 12.9‰ (average $11.6 \pm 0.8\%$), were lower than those in the other seasons: 11.3 to 15.1‰ (average $12.9 \pm 1.1\%$; Fig. 9a). As shown earlier, groundwater in November 2008 and February 2010 included the higher portion of summer season precipitation, and the d-value was the opposite of that for seasonality. Additionally, on average, the isotopic signals were depleted after July 2008 and were enriched after November 2008, and this occurred repeatedly from August 2009 to February 2010 (Fig. 9b). These results indicated that groundwater lagged approximately 6 months during the study period. Temperature of groundwater characterized by two regional flow systems decreased with the altitude increase (Temperature = $-0.007 * \text{Altitude} + 16.04$, $R^2 = 0.80$) suggesting the shallow depth of groundwater circulation.

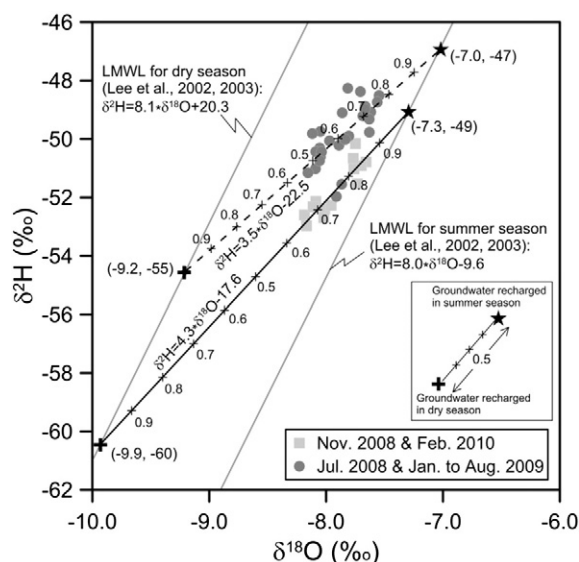


Fig. 8. Plot of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values for groundwater derived from two regional flow systems during July 2008 to February 2010. The two interceptions from LMWL for summer season and the others from LMWL for dry season indicated groundwater recharged completely by summer season precipitation and by dry season precipitation, respectively.

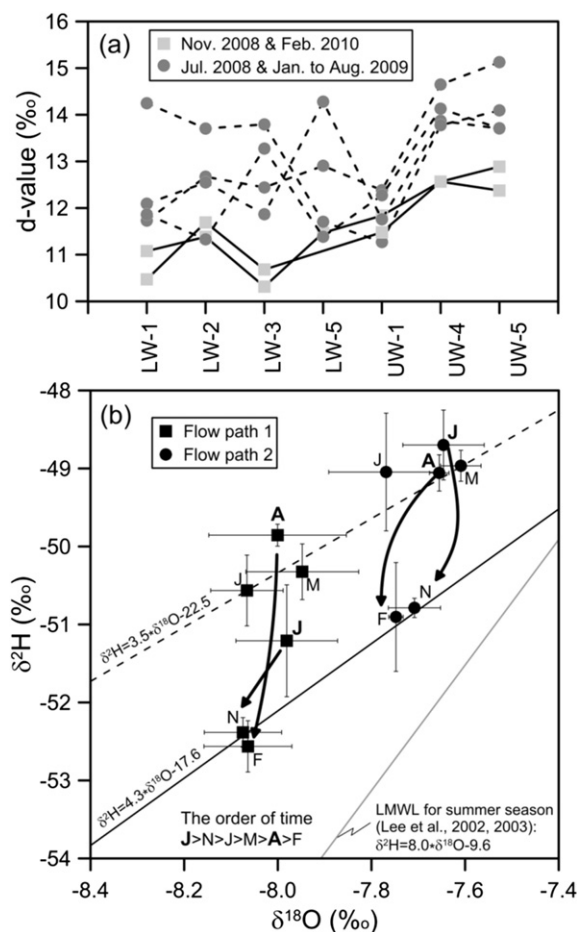


Fig. 9. Variation of deuterium excess or d-values for the groundwaters during July 2008 to February 2010 (a). Plot of the average of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values for groundwater fed by two regional flows (flow path 1 and 2) during July 2008 to February 2010 (b). The alphabet (J, N, J, M, A, F) represented months when collecting samples. The sampling campaign was carried out as following order: J > N > J > M > A > F; the bold represented mid-summer.

This can also be associated with high transmissivity of the aquifer and short residence time of groundwater. Similarly, Koh et al. (2007a) reported a short residence time of groundwater in Jeju Island using chlorofluorocarbons (CFCs). According to this study, groundwater age became temporarily younger in October and recovered in December, suggesting that groundwater recharge by heavy rain in mid-summer (August) lagged by up to 2 months.

4. Conclusions

Groundwater samples were collected from 10 wells distributed in low to highland areas and classified as LW and UW groups, respectively, in a volcanic island to understand the seasonal geochemical characteristics of groundwater and to reveal the groundwater recharge processes. Two groups of groundwater were characterized by Cl and NO₃ concentrations and the relationship between them. The LW group with relatively high concentrations of Cl and NO₃ was in agreement with the regression line for Cl and NO₃ previously established in agricultural areas, indicating contamination of groundwater by agricultural activities. In contrast, most of the UW group was within the domain representing groundwater derived from mountainous areas with natural cover. The altitude effect of the $\delta^{18}\text{O}$ values suggested that the two groups were mostly fed by distinct recharge pathways, or two regional flow systems, with hydrologic connection between highland and lowland areas. In addition to contribution from these two regional flow systems, the aquifer is recharged locally by precipitation along the slope. Overall, $\delta^{13}\text{C}_{\text{DIC}}$ values were negatively correlated with P_{CO_2} , indicating that the regional flows were influenced by local recharge penetrating soil layers during evolution from high to low altitudes. In addition, the relationship between $\delta^{13}\text{C}_{\text{DIC}}$ value and P_{CO_2} indicated that the two regional flow systems were differently by geochemical processes in soil layers and volcanic rocks.

$\delta^2\text{H}$ and $\delta^{18}\text{O}$ values for groundwater derived from two regional flow systems were between LMWLs in summer and dry seasons, indicating that the groundwater was recharged by mixing summer and dry season precipitation. With mixing processes, contribution of summer season precipitation to groundwater recharge was higher in groundwater collected in the following winter rather than that of in seasons including summer. Deuterium excess (d-value) was also lower in groundwater collected in the following winter. These results suggested that the groundwater recharge lagged on monthly basis compared to precipitation. Stable isotopes of groundwater varied cyclically with a period of one year, indicating a considerable portion of the groundwater is recharged by precipitation with a timescale less than one year. An isotopic composition combined with groundwater chemistry is useful for understanding hydrologic connections between groundwater flow systems in the two topographic areas in that high altitude areas mainly contributed to recharge in the island. It is expected that the production wells in this study can effectively supply groundwater to residents because of the linkage of groundwater from highland to lowland areas as a form of regional flow and its short residence time.

Acknowledgements

This work was supported by a national agenda program (NAP) of the National Research Council of Science and Technology and partly by a KBSI grant (C37701). We would like to thank H.S. Shin and Y.S. Bong for their help in chemical and isotopic analyses, and S.H. Lee and Y.Y. Jung for supplying more information on wells.

References

Ali, H.N., Atekwana, E.A., 2011. The effect of sulfuric acid neutralization on carbonate and stable carbon isotope evolution of shallow groundwater. *Chem. Geol.* 284, 217–228.

Asai, K., Zhang, J., Asai, K., Mandal, A.K., Mogi, K., Hasegawa, K., 2008. Residence time of submarine fresh groundwater discharge in Rishiri Island, North Japan: application of groundwater age tracers of tritium, CFCs and SF₆. AGU Fall Meeting Suppl (Abstract (H53E-1134A)).

Asano, T., Cotruvo, J.A., 2004. Groundwater recharge with reclaimed municipal wastewater: health and regulatory considerations. *Water Res.* 38, 1941–1951.

Atekwana, E.A., Krishnamurthy, R.V., 1998. Seasonal variations of dissolved inorganic carbon and $\delta^{13}\text{C}$ of surface waters: application of a modified gas evolution technique. *J. Hydrol.* 205, 265–278.

Bouri, S., Dhia, H.B., 2010. A thirty-year artificial recharge experiment in a coastal aquifer in an arid zone: the Teboulba aquifer system (Tunisian Sahel). *Compt. Rendus Geosci.* 342, 60–74.

Cerling, T.E., Solomon, D.K., Quade, J., Bowman, J.R., 1991. On isotopic composition of carbon in soil carbon dioxide. *Geochim. Cosmochim. Acta* 55, 3403–3405.

Chiodini, G., Caliro, S., Aiuppa, A., Avino, R., Granieri, D., Moretti, R., Parello, F., 2011. First $^{13}\text{C}/^{12}\text{C}$ isotopic characterisation of volcanic plume CO₂. *Bull. Volcanol.* 73, 531–542.

Clark, I.D., Fritz, P., 1997. *Environmental Isotope Hydrogeology*. Lewis Publishers.

Dansgaard, W., 1964. Stable isotopes in precipitation. *Tellus* 16, 436–468.

Das, A., Krishnaswami, S., Bhattacharya, S.K., 2005. Carbon isotope ratio of dissolved inorganic carbon (DIC) in rivers draining the Deccan Traps, India: sources of DIC and their magnitudes. *Earth Planet. Sci. Lett.* 236, 419–429.

Dillon, P., 2005. Future management of aquifer recharge. *Hydrogeol. J.* 13, 313–316.

Drever, J.I., Clow, D.W., 1995. Weathering rates in catchment. In: White, A.F., Brantley, S.L. (Eds.), *Chemical Weathering Rates of Silicate Minerals*. Mineralogical Society of America, Washington, DC, pp. 463–483.

Epstein, S., Mayeda, T., 1953. Variation of O^{18} content of waters from natural sources. *Geochim. Cosmochim. Acta* 4, 213–224.

Grasby, S.E., Hutcheon, I., 1997. Application of the stable isotope composition of SO₄ to tracing anomalous TDS in Nose Creek, southern Alberta, Canada. *Appl. Geochem.* 12, 567–575.

Ha, K., Park, W.B., Moon, D., 2009. Estimation of direct runoff variation according to land use changes in Jeju Island. *Econ. Environ. Geol.* 42, 343–356 (in Korean with English abstract).

Hagedorn, B., El-Kadi, A.I., Mair, A., Whittier, R.B., Ha, K., 2011. Estimating recharge in fractured aquifers of a temperate humid to semiarid volcanic island (Jeju, Korea) from water table fluctuations, and Cl, CFC-12 and ^3H chemistry. *J. Hydrol.* 409, 650–662.

Hubert, E., Woltersdorfer, C., 2015. Establishing a conversion factor between electrical conductivity and total dissolved solids in South African mine waters. *Water SA* 41, 490–500.

Jeju, 1997. Report on the General Investigation of the Mountainous Area in Jeju Island. Jeju Provincial Government (in Korean).

Kim, Y., Kim, Y., 2009. Artificial recharge technology of groundwater preparing for climate change. *Mag. Korea Water Resour. Assoc.* 42, 58–65 (in Korean).

Kim, Y., Lee, K.S., Koh, D.C., Lee, D.H., Lee, S.G., Park, W.B., Koh, G.W., Woo, N.C., 2003. Hydrogeochemical and isotopic evidence of groundwater salinization in a coastal aquifer: a case study in Jeju volcanic island, Korea. *J. Hydrol.* 270, 282–294.

Kita, I., Nagao, K., Taguchi, S., Nitta, K., Hasegawa, H., 1993. Emission of magmatic He with different $^3\text{He}/^4\text{He}$ ratios from the Unzen volcanic area, Japan. *Geochim. J.* 27, 251–259.

Koh, D.C., Chae, G.T., Yoon, Y.Y., Kang, B.R., Koh, G.W., Park, K.H., 2009. Baseline geochemical characteristics of groundwater in the mountainous area of Jeju Island, South Korea: implications for degree of mineralization and nitrate contamination. *J. Hydrol.* 376, 81–93.

Koh, D.C., Ha, K., Lee, K.S., Yoon, Y.Y., Ko, K.S., 2012. Flow paths and mixing properties of groundwater using hydrogeochemistry and environmental tracers in the southwestern area of Jeju volcanic island. *J. Hydrol.* 432–433, 61–74.

Koh, D.-C., Cheon, S.-H., Park, K.-H., 2007a. Characterization of groundwater quality and recharge using periodic measurements of hydrogeochemical parameters and environmental tracers in basaltic aquifers of Jeju Island. *J. Korean Soc. Soil Groundwater Environ.* 12, 57–68.

Koh, D.C., Ko, K.S., Kim, Y., Lee, S.G., Chang, H.W., 2007b. Effect of agricultural land use on the chemistry of groundwater from basaltic aquifers, Jeju Island, South Korea. *Hydrogeol. J.* 15, 727–743.

Koh, D.C., Plummer, L.N., Solomon, D.K., Busenberg, E., Kim, Y.J., Chang, H.W., 2006a. Application of environmental tracers to mixing, evolution, and nitrate contamination of ground water in Jeju Island, Korea. *J. Hydrol.* 327, 258–275.

Koh, G.W., Park, Y.S., Kim, G.P., 2006b. Fluctuation factors and changes of groundwater levels on Jeju Island. *Proceedings of the Jeju Hawaii Water Forum*, pp. 378–409.

KOWACO, 2003. Meteorology, Hydrology, and Water Budget Analysis, Technical Report. Korea Water Resources Corporation, Jeju Province.

Lawrence, P., Meigh, J., Sullivan, C., 2002. The Water Poverty Index: an International Comparison. *Keele Economics Research Papers KERP 2002/19*, Keele University, UK, p. 16.

Lee, K.S., Bong, Y.S., Lee, D., Kim, Y., Kim, K., 2008. Tracing the sources of nitrate in the Han River watershed in Korea, using $\delta^{15}\text{N}\text{-NO}_3^-$ and $\delta^{18}\text{O}\text{-NO}_3^-$ values. *Sci. Total Environ.* 395, 117–124.

Lee, K.S., Grundstein, A.J., Wenner, D.B., Choi, M.S., Woo, N.C., Lee, D.H., 2003. Climatic controls on the stable isotopic composition of precipitation in Northeast Asia. *Clim. Res.* 23, 137–148.

Lee, K.S., Kim, J.M., Lee, D.R., Kim, Y., 2007. Analysis of water movement through an unsaturated soil zone in Jeju Island, Korea using stable oxygen and hydrogen isotopes. *J. Hydrol.* 345, 199–211.

Lee, K.S., Koh, D.C., Lee, D., Park, W.B., 2002. The temporal and spatial distribution of stable isotope compositions of precipitation in Jeju Island: application to groundwater recharge study. *J. Geol. Soc. Korea* 38, 151–161 (in Korean with English abstract).

Lee, S., Shimada, J., Kayane, I., 1999. Stable isotopes in precipitation in the volcanic island of Cheju, Korea. *Hydrol. Process.* 13, 113–121.

Longinelli, A., Selmo, E., 2003. Isotopic composition of precipitation in Italy: a first overall map. *J. Hydrol.* 270, 75–88.

Mandal, A.K., Zhang, J., Asai, K., 2011. Stable isotopic and geochemical data for inferring sources of recharge and groundwater flow on the volcanic island of Rishiri, Japan. *Appl. Geochem.* 26, 1741–1751.

- Mayer, B., Boyer, E.W., Goodale, C., Jaworski, N.A., Breemen, N.V., Howarth, R.W., Seitzinger, S., Billen, G., Lajtha, K., Nadelhoffer, K., Dam, D.V., Hetling, L.J., Nosal, M., Paustian, K., 2002. Sources of nitrate in rivers draining sixteen watersheds in the northeastern U.S.: isotopic constraints. *Biogeochemistry* 57 (58), 171–197.
- Ohsawa, S., Kazahaya, K., Yasuhara, M., Kono, T., Kitaoka, K., Yusa, Y., Yamaguchi, K., 2002. Escape of volcanic gas into shallow groundwater systems at Unzen Volcano (Japan): evidence from chemical and stable carbon isotope compositions of dissolved inorganic carbon. *Limnology* 3, 169–173.
- Park, C., Seo, J., Lee, J., Ha, K., Koo, M.H., 2014. A distributed water balance approach to groundwater recharge estimation for Jeju volcanic island, Korea. *Geosci. J.* 18, 193–207.
- Sheng, Z., 2005. An aquifer storage and recovery system with reclaimed wastewater to preserve native groundwater resources in El Paso Texas. *J. Environ. Manag.* 75, 367–377.
- Shin, W.J., Chung, G.S., Lee, D., Lee, K.S., 2011. Dissolved inorganic carbon export from carbonate and silicate catchments estimated from carbonate chemistry and $\delta^{13}\text{C}_{\text{DIC}}$. *Hydrol. Earth Syst. Sci.* 15, 2551–2560.
- Sohn, Y.K., 1996. Hydrovolcanic processes forming basaltic tuff rings and cones on Cheju Island, Korea. *Geol. Soc. Am. Bull.* 108, 1199–1211.
- Sohn, Y.K., Park, J.B., Khim, B.K., Park, K.H., Koh, G.W., 2003. Stratigraphy, petrochemistry and quaternary depositional record of the Songaksan tuff ring, Jeju Island, Korea. *J. Volcanol. Geotherm. Res.* 119, 1–20.
- Vogel, J.C., 1993. Variability of carbon isotope fractionation during photosynthesis. In: Ehleringer, J.R., Hall, A.E., Farquhar, G.D. (Eds.), *Stable Isotopes and Plant Carbon-water Relations*. Academic Press, San Diego, pp. 29–38.
- Won, J.H., Kim, J.W., Koh, G.W., Lee, J.Y., 2005. Evaluation of hydrogeological characteristics in Jeju Island, Korea. *Geosci. J.* 9, 33–46.
- Won, J.H., Lee, J.Y., Kim, J.W., Koh, G.W., 2006. Groundwater occurrence on Jeju Island, Korea. *Hydrogeol. J.* 14, 532–547.
- Yang, C., Telmer, K., Veizer, J., 1996. Chemical dynamics of the “St. Lawrence” riverine system: $\delta\text{D}_{\text{H}_2\text{O}}$, $\delta^{18}\text{O}_{\text{H}_2\text{O}}$, $\delta^{13}\text{C}_{\text{DIC}}$, $\delta^{34}\text{S}_{\text{sulfate}}$, and dissolved $^{87}\text{Sr}/^{86}\text{Sr}$. *Geochim. Cosmochim. Acta* 60, 851–866.
- Youn, J.S., Park, S.W., 1998. Hydrochemical characteristics of spring water in Cheju Island. *J. Korean Soc. Groundwater Environ.* 5, 66–79.
- Zhang, J., Quay, O.D., Wilbur, D.O., 1995. Carbon isotope fractionation during gas–water exchange and dissolution of CO_2 . *Geochim. Cosmochim. Acta* 59, 107–114.