

Sulfur and oxygen isotopic compositions of the dissolved sulphate in the meteoric water in Chuncheon, Korea

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ABSTRACT: The meteoric water deposited in the Chuncheon area was collected from July 2002 to May 2004 and its chemical and isotopic compositions were analyzed to examine if the isotopic data can help trace the sources of the sulfur pollutant and understand the details of acid formation processes in the air. The chemical compositions of the meteoric water indicate that the sulfate mostly comes from anthropogenic sources. The sulfur isotopic compositions of the dissolved sulfate in the meteoric water ($\delta^{34}\text{S}_{\text{SO}_4}$) vary from 2.6 to 7.5‰ with little seasonal differences, which are significantly different from those of the sulfur in the coal being locally consumed (–4.5 to –0.7‰). This difference indicates that the local coal consumption gives insignificant contribution to the pollutant sulfur in the acid deposition of the area. The relationship between $\delta^{34}\text{S}_{\text{SO}_4}$ and the concentration of sulfate suggests that the sources of pollutant sulfur are variable and inhomogeneous. The oxygen isotopic compositions of the dissolved sulfate in the meteoric water ($\delta^{18}\text{O}_{\text{SO}_4}$) range from 9.0 to 17.2‰, which are generally lower in winter than in spring. Comparison between the measured and calculated values of $\delta^{18}\text{O}_{\text{SO}_4}$ suggests that the oxygen isotopic exchange between sulfite and water occurs before its oxidation to sulfate. The extent of isotopic exchange seems to be not controlled by equilibrium but by kinetic fractionation. The poor correlation between $\delta^{18}\text{O}_{\text{SO}_4}$ and the oxygen isotopic composition of the meteoric water confirms the disequilibrium nature of the isotopic exchange.

Key words: sulfur and oxygen isotope, meteoric water, pollutant sulfur sources, acid forming processes

1. INTRODUCTION

The rapid industrial growth of East Asia forces the countries in the region, including Korea, Japan, and China, to face a number of serious environmental problems. One of the environmental problems more concerned is the acid deposition caused by the anthropogenic sulfur and nitrogen emission into the air. Sulfur has been considered to be a greater contributor to the acid deposition than nitrogen, although the importance of nitrogen is increasing as the controls on sulfur emission have been tightened in recent years (Han et al., 2006). The chemical compositions of the

precipitation from Yu and Park (2004) and Jeon and Chung (2005) indicated that pollutant sulfur plays bigger role in forming acid deposition than nitrogen in the southern Korean peninsular.

Like most of the other air pollutants, sulfur can travel a fairly long distance and make a transboundary pollution. Since there has been dispute on the estimation on the amount of transboundary pollution of sulfur, especially in East Asia (Huang et al., 1995; Ichikawa and Fujita, 1995; Streets et al., 2000; Carmichael et al., 2002), the sulfur pollution may raise a delicate conflict among neighboring countries in the region. An appropriate estimation of the transboundary pollution may first require tracing the sources of the acid and understanding the principles of the acid formation. Tracing the sources of the pollutant sulfur has mostly relied on the physical models (e.g. Dastoor and Pudykiewicz, 1996). An addition of another tracer, e.g. a chemical or an isotopic tracer, to the physical models can enhance the efficiency and accuracy of the source tracking.

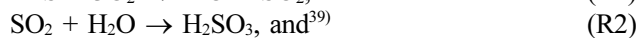
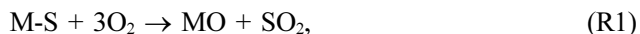
Isotopic compositions of the acids in the precipitation can be used as an effective tool for tracing the acid sources and elucidate the details of the acid formation processes. The sulfur isotopic compositions ($\delta^{34}\text{S}$) of atmospheric sulfur dioxide (SO_2) or sulfate (SO_4) have been investigated to trace the sulfur sources, as summarized by Krouse (1980) for the researches before 1980. Recently, Na et al. (1995), Ohizumi et al. (1997), McArdle et al. (1998) Pichlmayer et al. (1998), Panettiére et al. (2000), and Yu and Park (2004) studied $\delta^{34}\text{S}$ of sulfate ($\delta^{34}\text{S}_{\text{SO}_4}$) in the atmospheric precipitation. The results from these previous investigations show that the $\delta^{34}\text{S}$ values of atmospheric pollutant sulfur are generally lower than that of sea sulfate and could be indicative of the pollution sources. In many cases, however, the sources not only produce variable amount of sulfur but also have inhomogeneous $\delta^{34}\text{S}$ values (Krouse, 1980), which may be partly responsible for the disagreements in identifying the sources of sulfur pollutants among investigations.

Sulfur is mainly emitted as SO_2 , most of which is probably an oxidation product of sulfide in the fossil fuels during combustion. SO_2 is hydrated to sulfite (SO_3) and then

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further oxidized to SO_4 which forms sulfuric acid causing acid rain:



As shown in the above reactions, the oxygen in the sulfur oxides comes from two sources; water and free oxygen whose isotopic compositions are remarkably different. The oxygen isotopic composition of meteoric water ($\delta^{18}\text{O}_w$) is commonly less than 0‰ (Epstein and Mayeda, 1953; Torran and Harris, 1989), while that of free oxygen ($\delta^{18}\text{O}_a$) is 23.5‰ (Kroopnick and Craig, 1972). This big difference in $\delta^{18}\text{O}$ between the two sources may enable to estimate the relative contribution of each source to the sulfate oxygen with the oxygen isotopic composition of sulfate ($\delta^{18}\text{O}_{\text{SO}_4}$) and to check if the estimated contribution is pertinent to that expected from the stoichiometry given by the above reactions. The investigations on $\delta^{18}\text{O}_{\text{SO}_4}$, however, have been relatively rare. A few studies on $\delta^{18}\text{O}_{\text{SO}_4}$ showed that the oxygen in sulfate mainly originates from water (Lloyd, 1968; Mizutani and Rafter, 1969; Cortecchi and Longinelli, 1970; Holt et al., 1981), which is quite contrary to what the stoichiometry of the above reactions suggest, that is, most of the sulfate oxygen should come from free oxygen.

The purposes of this study are to examine $\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^{18}\text{O}_{\text{SO}_4}$ in the meteoric water in Chuncheon, Korea, and to see if the combination of these two isotopes helps trace the sources of the sulfur pollutant and understand the acid formation processes further. As mentioned earlier, $\delta^{18}\text{O}_{\text{SO}_4}$ is rarely investigated and this study is probably one of the few combining sulfur and oxygen isotopes for the investigation on pollutant sulfur.

2. METHODS

Samples of meteoric water (rain + snow) were collected at each precipitation event with a homemade sampler placed at the top of Natural Science building 3 of Kangwon National University in Chuncheon from July 2002 to May 2004. The collected water samples were filtered through a 0.2 μm micropore membrane and an aliquot of 250 ml of each filtered sample was acidified with approximately 0.2 ml HNO_3 . The filtered and acidified samples were refrigerated at 4 °C for later analysis. The samples of the coal and petroleum being locally consumed for heating and automobiles were also collected.

The pH, Eh, conductivity (K_{25}) and temperature (T) of water samples were measured when the samples were being collected at the site. The alkalinities of the water samples were determined using Gran method (Wetzel and Likens, 1991) on a 50 ml aliquot of the filtered sample on the same day of sample collection. The carbonate concentrations were calculated from the measured alkalinities assuming that

only carbonates significantly contribute to the alkalinity (Stumm and Morgan, 1981). The chemical compositions of the water samples were analyzed with an inductively coupled plasma atomic emission spectrometer (ICP-AES; for Si, Al, Ca, Mg, K, and Na) at the Seoul Branch of the Korean Basic Science Institute (KBSI) and an ion chromatograph (IC; for NH_4 , Cl, NO_3 , and SO_4) at the Department of Geology, Kangwon National University.

$\delta^{18}\text{O}_w$ and hydrogen isotopic compositions of water (δD_w) were obtained from the analysis of CO_2 equilibrated with the water (Epstein and Mayeda, 1953) and H_2 released from the water by Zn-reduction (Coleman et al., 1982), respectively. The dissolved sulfate in the water samples was precipitated as BaSO_4 (Kolthoff et al., 1969), which was then analyzed for sulfur and oxygen isotopic compositions. $\delta^{34}\text{S}_{\text{SO}_4}$ was determined by analyzing SO_2 released from the BaSO_4 mixed with V_2O_5 and quartz glass at 1120°C (Yanagisawa and Sakai, 1983). $\delta^{18}\text{O}_{\text{SO}_4}$ was measured with CO generated from the mixtures of BaSO_4 and Ag_2S in the presence of graphite and glassy carbon in the Finnigan Thermal Combustion/Elemental Analyzer (TC/EA) at 1450 °C. Sulfur in the petroleum samples were attempted to extract with combustion in an oxygen bomb (Na et al., 1995) and in a furnace while the exhaustion gas was being bubbled through 1% H_2O_2 solution (Lodge, 1990). None of these methods gave enough sulfur for isotopic analyses of petroleum. Sulfur in the coal samples were extracted by igniting coal with CuO in an electric furnace, from which the evolved SO_2 was directly trapped and analyzed.

The standards for reporting the isotopic compositions are Standard Mean Oceanic Water (SMOW) for $\delta^{18}\text{O}$ and δD and the troilite from Cañon Diablo meteorite (CDT) for $\delta^{34}\text{S}$. All the isotopic analyses except $\delta^{18}\text{O}_{\text{SO}_4}$ were performed with a mass spectrometer, model PRISM II of Micromass UK Ltd. at KBSI in Daejeon, Korea. $\delta^{18}\text{O}_{\text{SO}_4}$ were measured with Finnigan Conflo III and Finnigan MAT 253 SIR-MS in Jet Propulsion Laboratory (JPL) in Pasadena, USA. The reference materials used in the analyses were: SMOW ($\delta D=0.0\text{‰}$) and SLAP ($\delta D=428\text{‰}$) from International Atomic Energy Agency (IAEA) for δD_w ; KBSI Lab standard KBSI-27 ($\delta^{18}\text{O}=9.6\text{‰}$) and SMOW ($\delta^{18}\text{O}=0.0\text{‰}$) for $\delta^{18}\text{O}_w$, NBS-127 BaSO_4 ($\delta^{34}\text{S}=20.3\text{‰}$) for $\delta^{34}\text{S}_{\text{SO}_4}$, NBS-127 BaSO_4 ($\delta^{18}\text{O}=8.6\text{‰}$) and JPL Lab standard BaSO_4 ($\delta^{18}\text{O}=11.6\text{‰}$) for $\delta^{18}\text{O}_{\text{SO}_4}$, and NBS-123 sphalerite ($\delta^{34}\text{S}=17.4\text{‰}$) for $\delta^{34}\text{S}$ of coal. The standard errors of the measurements were estimated to be less than 2‰ for δD_w , 0.1‰ for $\delta^{18}\text{O}_w$, 0.2‰ for $\delta^{34}\text{S}$, and 0.3‰ for $\delta^{18}\text{O}_{\text{SO}_4}$.

3. RESULTS AND DISCUSSION

Appendix I lists the chemical and isotopic compositions of the collected meteoric water samples. The chemical compositions of the meteoric water in the study area indicate that Ca-(Mg)- SO_4 rather than Na- CO_3 is the dominant cat-

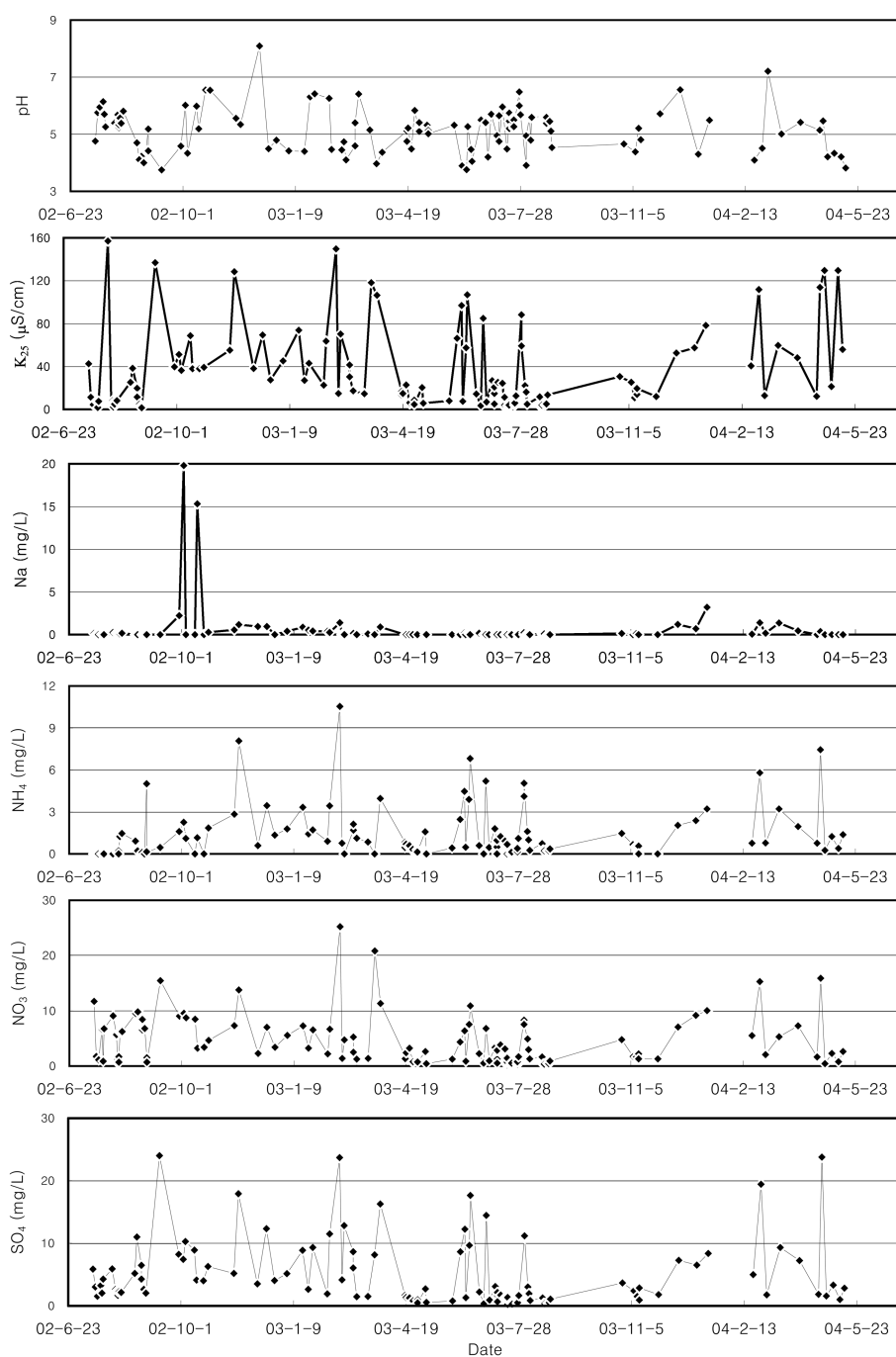


Fig. 1. Temporal variations of some of the dissolved components in the meteoric water.

ion-anion couple. The sources of Ca, Mg and SO_4 in the meteoric water could be the natural mineral dust, artificial gases and airborne particles, or the sea salt spray. Park et al. (2006) described detailed chemistries and the possible sources of the dissolved components in the meteoric water in the Chuncheon area.

Fig. 1 compares the concentration variations of some of the major dissolved components in the meteoric water. The variation patterns of the conductivity (K_{25}), and three major air pollutants (NH_4 , NO_3 , and SO_4) are similar to one another, but significantly different from those of the rest.

The correlation coefficients are fairly high among the three pollutants (Fig. 2), but those among other dissolved components are generally very low. It implies that the extent of air pollution is the key factor in controlling the chemistry of the meteoric water.

δD_w and $\delta^{18}O_w$ show good correlation to each other, but both of them are poorly correlated with the air temperature (Fig. 3). Fig. 4 shows that the meteoric water aligns along a line parallel to the global meteoric water line, indicating that the water vapor formed at various locations and transported to Chuncheon with little fractionation before deposition.

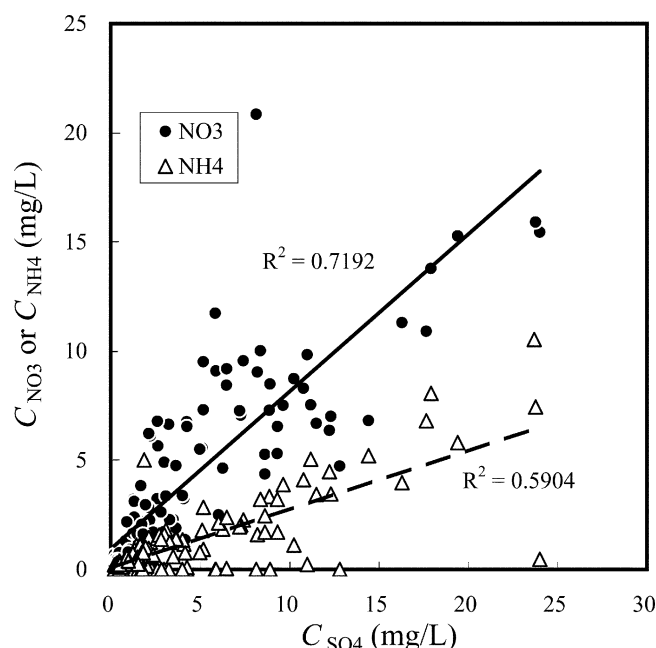


Fig. 2. Variations of the concentrations of NH_4 and NO_3 as a function of the concentration of SO_4 in the meteoric water.

$\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^{18}\text{O}_{\text{SO}_4}$ were measured only for the meteoric water samples having enough amount of the dissolved SO_4 to produce recoverable BaSO_4 precipitate. Fig. 5 shows that $\delta^{34}\text{S}_{\text{SO}_4}$ varies from 2.6 to 7.5‰ and its variation is independent of the concentration of the sulfate (C_{SO_4}), suggesting that the sources are not only variable but also inhomogeneous (Krouse, 1980). Seasonal difference in $\delta^{34}\text{S}_{\text{SO}_4}$ is not distinct. $\delta^{34}\text{S}$ of the coal being locally consumed has the values ranging from -4.5 to -0.7‰ with an average of -2.7‰ ($n=7$), which is significantly different from $\delta^{34}\text{S}_{\text{SO}_4}$ of the local meteoric water. Thus, the local sulfur emission from the coal combustion may insignificantly contribute to the local acid deposition.

One of the sources of SO_4 in the meteoric water is the sea salt spray, whose fraction, A , in the total dissolved SO_4 can be calculated from

$$A = \frac{C_{\text{Cl}}}{7.1 C_{\text{SO}_4}} \quad (1)$$

where C_{Cl} is the concentration of the dissolved Cl in the meteoric water (Mizutani and Rafter, 1969). The rest of the dissolved sulfate may originate primarily from pollution sources. The calculated A values range from 0.006 to 0.15, but only a few are greater than 0.1. The isotopic compositions of non-sea-salt-spray SO_4 (nss SO_4) can be calculated from $\delta^{34}\text{S}_{\text{SO}_4}$ of meteoric water and sea salt spray together with the A values obtained from equation (1) (Yu and Park, 2004). The calculated $\delta^{34}\text{S}_{\text{SO}_4}$ of nss SO_4 are little different from that of total SO_4 in the meteoric water.

$\delta^{18}\text{O}_{\text{SO}_4}$ values range from 9.0 to 17.2‰ and show a little seasonal difference; the values in winter (from December to

February) are generally lower than those in spring (from March to May) (Fig. 6). $\delta^{18}\text{O}_{\text{SO}_4}$ values are considerably scattered, especially at low C_{SO_4} , but tend to increase with increasing C_{SO_4} .

If there is little oxygen isotope fractionation or exchange during the oxidation and hydration of sulfide to form SO_4 (from reactions (R1) to (R3)), $\delta^{18}\text{O}_{\text{SO}_4}$ should be determined by 3:1 mixing of free oxygen and water oxygen, that is,

$$\delta^{18}\text{O}_{\text{SO}_4} = 0.75 \delta^{18}\text{O}_a + 0.25 \delta^{18}\text{O}_w \quad (2)$$

$\delta^{18}\text{O}_a$ has been known to have a fairly constant value of 23.5‰ (Kroopnick and Craig, 1972). $\delta^{18}\text{O}_w$ values from this study vary from -16.1 to 0.5‰. With these oxygen isotopic data, equation (2) gives $\delta^{18}\text{O}_{\text{SO}_4}$ values between 13.6 and 17.5‰.

Fig. 6 indicates many of the measured $\delta^{18}\text{O}_{\text{SO}_4}$ falls below the range defined by equation (2) (window A in Fig. 6), especially when C_{SO_4} is low. This discrepancy is probably due to the isotope exchange between sulfite and water. Lloyd (1968) compared the oxygen isotope exchange rate of sulfate-water with sulfite-water pair. The former is a function of pH and extremely slow at ambient pH. The latter is approximately 10^5 times faster than the former. Stempfroot and Krouse (1980) confirmed that $\delta^{18}\text{O}_{\text{SO}_4}$ was little affected by $\text{SO}_4\text{-H}_2\text{O}$ exchange reaction. Holt et al. (1981) showed that $\delta^{18}\text{O}$ of sulfite was completely controlled by $\delta^{18}\text{O}_w$ and enriched by 24‰ with respect to $\delta^{18}\text{O}_w$ in an equilibrium condition. Recently, Brunner et al. (2006) reported that the equilibrium fractionation at 23°C produced the sulfite enriched by 11.5 and 7.9‰ with respect to the water at pH=7 and 8, respectively. The enrichment factor of Brunner et al. (2006) becomes fairly close to that of Holt et al. (1981), if the values of Brunner et al (2006) are extrapolated to the pH of 4.5 corresponding to that of acid rain.

If SO_2 is hydrated to form sulfite (reaction R2) and have enough time to be in equilibrium with water before further oxidation to sulfate (reaction R3), $\delta^{18}\text{O}$ of sulfite would be determined totally by the equilibrium fractionation between sulfite and water regardless of the amount of free oxygen constituting the sulfite. Then, if there is little oxygen isotope fractionation during the oxidation of sulfite, the resultant $\delta^{18}\text{O}_{\text{SO}_4}$ should be given by

$$\delta^{18}\text{O}_{\text{SO}_4} = 0.75(\delta^{18}\text{O}_w + \epsilon_w) + 0.25\delta^{18}\text{O}_a \quad (3)$$

where ϵ_w is the enrichment factor between sulfite and water given by Holt et al. (1981). Putting $\delta^{18}\text{O}_w = -16.1$ to 0.5‰, $\epsilon_w = 24$ ‰, and $\delta^{18}\text{O}_a = 23.5$ ‰ into equation (3) gives $\delta^{18}\text{O}_{\text{SO}_4}$ values ranging from 11.8 to 23.5‰. Fig. 6 shows that $\delta^{18}\text{O}_{\text{SO}_4}$ limits calculated with equation (3) (window B in Fig. 6) enclose most of the measured $\delta^{18}\text{O}_{\text{SO}_4}$ values of the samples, but there are still a few samples below the lower limit. Moreover, the distribution of the $\delta^{18}\text{O}_{\text{SO}_4}$ values are biased

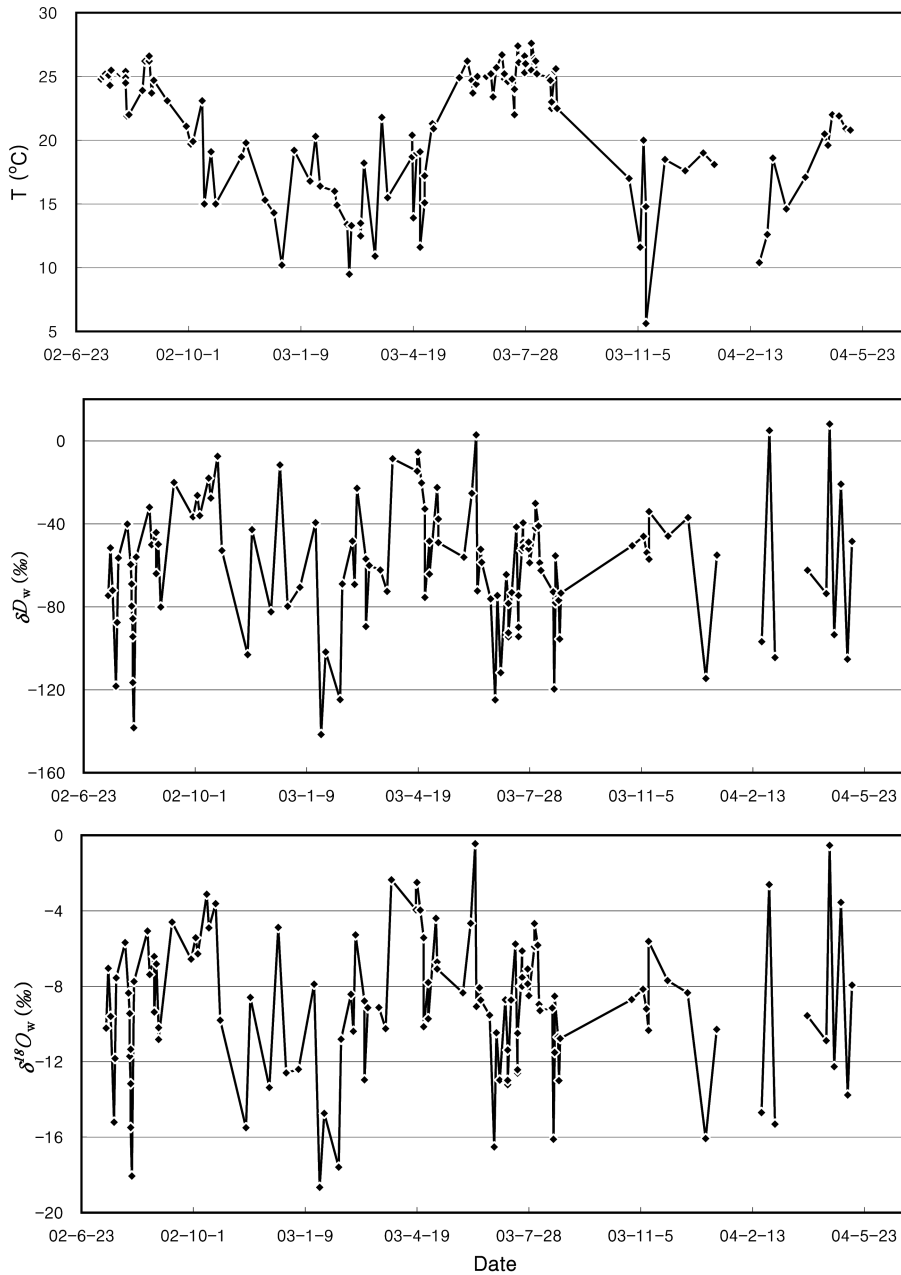


Fig. 3. Temporal variations of the air temperature and hydrogen and oxygen isotopic compositions. The hydrogen and oxygen isotopic compositions are from Park et al. (2006).

towards the lower part of window B.

The biased distribution and the presence of outliers of $\delta^{18}O_{SO_4}$ are possibly caused by the disequilibrium between sulfite and water, the non-zero oxygen isotopic fractionation during the sulfite oxidation, or the combination of the above two. Holt et al. (1981) performed numerous experiments of abiotic oxidation of sulfite and summarized the results with the following equation;

$$\delta^{18}O_{SO_4} = 0.75\delta^{18}O_w + K. \quad (4)$$

where K varies depending on the experimental conditions. From equations (3) and (4), the parameter K becomes

$$K = 0.75\epsilon_w + 0.25\delta^{18}O_a. \quad (5)$$

Thus, the experiments by Holt et al. (1981) confirm that $\delta^{18}O_{SO_4}$ is primarily determined by $\delta^{18}O_w$ and the fractionation of the oxygen isotopes between sulfite and water, where the fractionation occurs not necessarily under equilibrium condition.

It is worth noting that the lower C_{SO_4} the meteoric water shows, the lower $\delta^{18}O_{SO_4}$ values and the wider concentration range the dissolved SO_4 has. The low C_{SO_4} often results from the dilution by water. The longer the sulfur stays in the air, the more water it would be diluted with and exchange oxygen isotopes with. Thus, C_{SO_4} may inversely proportional to the residence time or the travel distance of sulfur in the air and proportional to $\delta^{18}O_{SO_4}$. The wide variation of $\delta^{18}O_{SO_4}$ may result from isotopic inhomogeneity of the

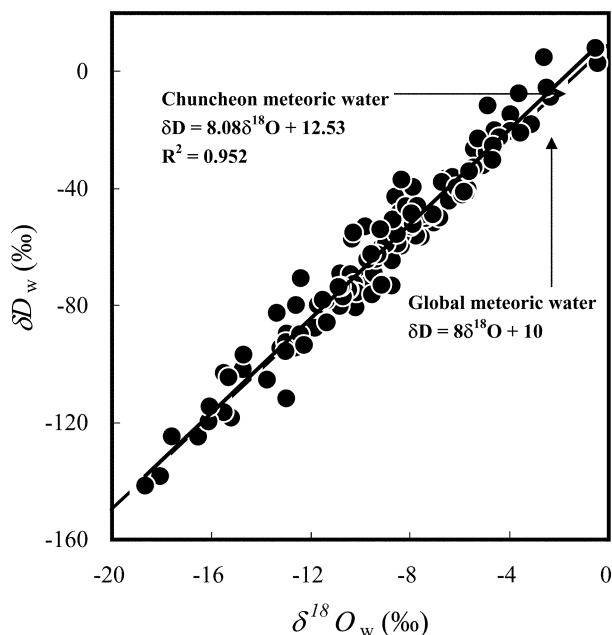


Fig. 4. Variations of hydrogen isotopic composition as a function of oxygen isotopic composition of the meteoric water.

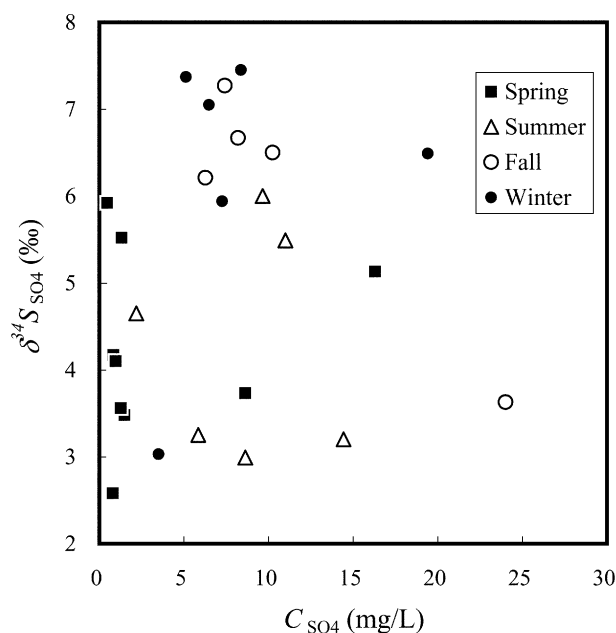


Fig. 5. Sulfur isotopic compositions ($\delta^{34}S_{SO_4}$) plotted against the concentrations (C_{SO_4}) of the dissolved sulfate in the meteoric water. The spring, summer, fall and winter samples include those samples collected in March to May, June to August, September to November, and December to February, respectively.

remote water sources or variation in the extent of isotopic exchange depending on the physicochemical conditions of air mass. Fig. 7 shows that $\delta^{18}O_{SO_4}$ has little correlation with $\delta^{18}O_w$, which indicates that the variation not only in oxygen isotopic composition of the meteoric water but also in the extent of the isotopic exchange is responsible for the vari-

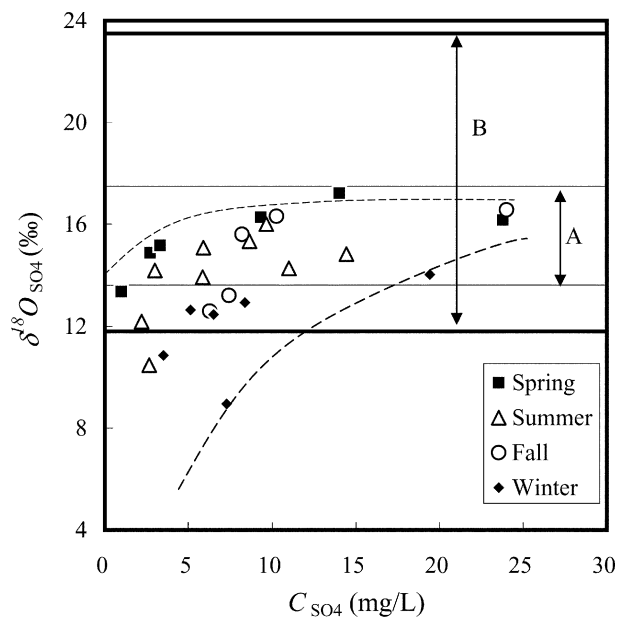


Fig. 6. Variation of the oxygen isotopic compositions ($\delta^{18}O_{SO_4}$) as a function of the concentrations (C_{SO_4}) of the dissolved sulfate in the meteoric water. Windows A and B are the oxygen isotopic compositional limits calculated by equation (2) and (3), respectively.

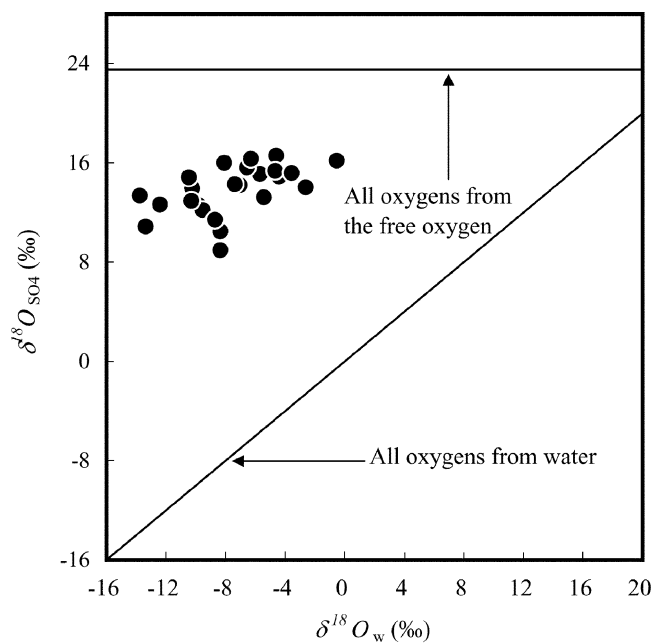


Fig. 7. Oxygen isotopic compositions of the dissolved sulfate ($\delta^{18}O_{SO_4}$) plotted against those of water of the precipitation ($\delta^{18}O_w$).

ation in $\delta^{18}O_{SO_4}$.

4. SUMMARY AND CONCLUSIONS

The sulfate in the meteoric water in Chuncheon, Korea comes primarily from anthropogenic sources. $\delta^{34}S_{SO_4}$ of the

meteoric water collected from July 2002 to May 2004 varies from 2.6 to 7.5‰ without a significant seasonal variation. $\delta^{34}\text{S}$ of the sulfur in the coal being locally consumed has the values ranging from -4.5 to -0.7‰, indicating that the local coal consumption gives a minor contribution to the pollutant sulfur in the acid deposition of the area. The plot of $\delta^{34}\text{S}_{\text{SO}_4}$ against C_{SO_4} reveals that the sources of pollutant sulfur are not only variable but also inhomogeneous.

$^{114})\delta^{18}\text{O}_{\text{SO}_4}$ of the meteoric water ranges from 9.0 to 17.2‰ and are generally lower in winter than in spring. The reason for this seasonal variation needs further investigation. Comparison of the measured with the calculated $\delta^{18}\text{O}_{\text{SO}_4}$ values suggests that oxygen isotopic exchange between sulfite and water occurs during the acid forming processes, especially before the oxidation of sulfite. The lower C_{SO_4} the meteoric water shows, the lower $\delta^{18}\text{O}_{\text{SO}_4}$ the dissolved sulfate has. C_{SO_4} may inversely proportional to the residence time of the sulfur in the air. Then, the decrease of C_{SO_4} means an increase in the isotopic exchange between the sulfite and water, which resulted a decrease in $\delta^{18}\text{O}_{\text{SO}_4}$. The poor cor-

relation between $\delta^{18}\text{O}_{\text{SO}_4}$ and $\delta^{18}\text{O}_a$ indicates a disequilibrium nature of the isotopic exchange.

This study demonstrates that utilizing isotopic data can help understand the characteristics of the sources of the pollutant sulfur as well as the acid forming processes between sulfur and water. However, it is inappropriate to trace the pollution sources or to elucidate the acid generation mechanisms based on the isotopic fingerprints only. Combining the isotopic data with other physical models such as a back trajectory modeling may provide a powerful tool for studying the atmospheric pollutant sulfur.

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Appendix I. The chemical and isotopic compositions and other water quality parameters of the meteoric water.

Sampling date* type**	pH	T (°C)	Eh (mV)	K ₂₅ (mS/cm)	Chemical compositions (mg/L)													Isotopic compositions (‰)				
					Fe	Si	Mg	Ca	Al	Na	NH ₄	K	F	Cl	NO ₃	SO ₄	CO ₃	δ ¹⁸ O _w	δ ¹⁸ D _w	δ ³⁴ S _{SO4}	δ ³⁴ O _{SO4}	
02/7/15-7/17	R	4.8	24.8	557	42.6	-	-	0.1	1.4	-	0.1	-	0.3	0.4	1.6	11.7	5.8	2.3	-10.2	-74.5	3.3	13.9
02/7/17-7/19	R	5.8	25.0	518	11.2	-	-	-	0.5	-	0.0	-	0.0	0.1	0.8	1.7	3.0	-	-7.0	-51.6	-	14.2
02/7/19	R	6.0	25.2	506	4.3	-	-	-	0.2	-	-	-	0.0	0.1	0.5	1.1	1.5	1.0	-9.6	-72.2	-	-
02/7/22	R	6.1	25.1	518	7.8	-	-	-	0.2	0.5	0.0	-	0.0	0.4	1.2	6.6	3.2	0.7	-15.2	-118.3	-	-
02/7/22-7/23	R	5.7	24.3	526	1.9	-	-	-	0.1	-	-	-	0.0	0.5	0.9	2.0	0.5	-	-11.8	-87.6	-	-
02/7/23-7/24	R	5.3	25.5	469	7.5	-	-	-	0.3	0.5	-	-	-	0.4	1.3	6.8	4.3	0.1	-7.6	-56.5	-	-
02/8/1-8/3	R	5.4	25.2	450	157	-	-	0.1	1.1	0.5	0.3	-	0.3	0.4	1.7	9.1	5.9	1.0	-5.7	-40.1	-	15.1
02/8/4-8/5	R	5.7	25.3	446	6.6	-	-	-	-	0.5	0.2	0.2	-	0.1	1.8	5.7	2.6	0.1	-8.4	-59.6	-	10.5
02/8/5	R	5.2	25.3	459	8.0	-	-	-	-	-	0.1	0.2	-	0.0	0.8	1.2	2.3	-	-9.5	-69.0	-	-
02/8/5-8/6	R	5.3	25.4	455	5.3	-	-	-	-	-	0.1	0.1	-	0.0	0.6	0.6	2.0	-	-11.7	-79.7	-	-
02/8/6	R	5.5	25.4	459	1.9	-	-	-	-	-	-	-	-	0.0	0.2	0.8	1.7	-	-13.2	-94.4	-	-
02/8/6	R	5.5	24.9	469	5.2	-	-	-	-	-	-	0.2	-	0.0	0.2	1.7	1.7	-	-11.3	-85.7	-	-
02/8/6-8/7	R	5.6	24.5	468	2.3	-	-	-	-	-	-	-	-	0.0	0.4	0.7	2.3	0.7	-15.5	-116.5	-	-
02/8/7	R	5.4	21.9	463	4.8	-	-	-	0.8	0.5	0.1	1.2	-	-	1.3	6.1	2.2	0.6	-18.1	-138.3	-	-
02/8/9-8/10	R	5.8	22.0	455	8.1	-	-	-	0.5	0.5	0.2	1.5	-	-	1.3	6.2	2.1	1.8	-7.8	-56.1	-	-
02/8/21	R	4.7	23.9	574	25.2	-	-	-	0.5	0.5	-	0.9	-	0.4	1.5	9.5	5.2	-	-5.1	-32.1	-	-
02/8/23	R	4.1	26.2	527	38.3	-	-	-	-	0.5	-	0.2	-	0.5	2.2	9.8	11.0	-	-7.4	-50.1	5.5	14.3
02/8/27	R	4.3	26.2	539	19.7	-	-	-	0.3	0.5	-	0.0	-	0.4	1.4	8.4	6.5	-	-6.4	-44.2	-	-
02/8/27	R	4.0	26.6	370	11.5	-	-	-	0.3	0.5	-	0.1	-	0.1	1.4	6.5	4.3	-	-9.4	-64.1	-	-
02/8/29	R	4.4	23.7	485	4.8	-	-	-	-	0.5	-	-	-	0.1	1.5	6.8	2.6	-	-6.8	-49.9	-	-
02/8/31	R	5.2	24.8	463	3.8	-	-	-	1.2	-	-	5.0	-	0.0	0.5	1.5	1.9	1.0	-10.2	-80.6	-	-
02/8/31-9/1	R	4.4	24.7	477	1.6	-	-	-	-	-	-	0.2	-	0.0	0.4	0.7	2.0	-	-10.8	-80.2	-	-
02/9/12-9/13	R	3.8	23.1	644	137	-	-	-	0.3	0.5	-	0.5	-	0.5	2.3	15.4	24.0	-	-4.6	-20.1	3.6	16.6
02/9/29	R	4.6	21.1	506	39.7	-	-	0.2	1.6	0.5	2.2	1.6	-	0.5	1.4	9.0	8.2	-	-6.6	-36.6	6.7	15.6
02/10/3	R	6.0	19.7	452	51.3	-	-	0.4	2.4	0.5	19.8	2.3	-	0.5	5.5	9.6	7.4	2.4	-5.4	-26.4	7.3	13.2
02/10/5-10/6	R	4.3	19.9	523	36.3	-	-	-	0.6	0.5	-	1.1	-	-	1.4	8.7	10.2	-	-6.3	-36.1	6.5	16.3

Appendix I. (continued).

Sampling date* type**	pH	T (°C)	Eh (mV)	K ₂₅ (mS/cm)	Chemical compositions (mg/L)													Isotopic compositions (‰)				
					Fe	Si	Mg	Ca	Al	Na	NH ₄	K	F	Cl	NO ₃	SO ₄	CO ₃	δ ¹⁸ O _w	δ ¹⁸ D _w	δ ³⁴ S _{SO4}	δ ³⁴ O _{SO4}	
02/10/13	R	6.0	23.1	444	68.7	-	0.14	-	-	-	-	-	-	0.1	2.3	8.5	8.9	∞	-3.1	-18.0	-	-
02/10/15	R	5.2	15.0	485	38.0	0.02	0.04	0.3	1.3	-	15.3	1.2	-	0.0	3.5	3.2	4.1	0.1	-4.9	-27.7	-	-
02/10/21	R	6.6	19.1	452	37.9	-	0.11	-	-	-	-	-	-	0.0	1.5	3.4	4.0	3.4	-3.6	-7.4	-	-
02/10/25	R	6.5	15.0	467	39.2	-	0.02	0.3	2.3	-	0.3	1.8	-	0.0	1.3	4.6	6.3	1.1	-9.8	-52.9	6.2	12.6
02/11/17	S	5.6	18.7	429	55.2	-	0.07	0.3	3.2	-	0.6	2.8	-	0.1	1.5	7.3	5.2	1.8	-15.5	-103.1	-	-
02/11/21	R	5.3	19.8	420	128	0.13	0.17	0.5	5.7	0.2	1.2	8.1	0.8	0.2	2.7	13.8	17.9	3.3	-8.6	-42.8	-	-
02/12/8	S	8.1	15.3	429	38.1	-	0.06	0.2	4.1	-	1.0	0.6	-	0.0	1.1	2.3	3.5	15.9	-13.4	-82.5	3.0	10.9
02/12/16	R	4.5	14.3	513	69.5	0.07	0.08	0.2	4.2	0.1	1.0	3.5	-	0.1	1.5	7.0	12.3	-	-4.9	-11.6	-	-
02/12/23-12/24	R+S	4.8	10.2	527	27.5	-	-	-	0.8	-	-	1.3	-	0.0	0.3	3.4	4.0	-	-12.6	-79.8	-	-
03/1/3	S	4.4	19.2	487	45.2	0.05	0.04	0.2	1.3	0.1	0.4	1.8	-	0.0	2.2	5.6	5.1	-	-12.4	-70.6	7.4	12.6
03/1/17	S	4.4	16.8	462	73.8	0.06	0.02	0.2	2.2	0.1	0.9	3.3	0.2	0.1	2.0	7.3	8.9	-	-7.9	-39.5	-	-
03/1/22	S	6.3	20.3	450	27.1	-	0.04	-	1.7	-	0.5	1.4	-	0.1	0.8	3.2	2.6	1.9	-18.7	-141.6	-	-
03/1/26-1/27	S	6.4	16.4	480	43.0	-	0.05	-	3.5	-	0.4	1.7	-	0.1	2.2	6.6	9.3	4.7	-14.7	-101.8	-	-
03/2/8	R+S	6.3	16.0	445	22.7	-	0.04	-	1.3	-	0.4	0.9	-	0.0	1.0	2.2	1.9	1.4	-17.6	-124.8	-	-
03/2/10-2/11	R+S	4.5	14.9	525	63.7	0.02	0.03	0.1	1.8	0.0	0.2	3.4	-	0.1	0.9	6.7	11.5	-	-10.8	-69.0	-	-
03/2/19	R+S	4.5	13.4	499	150	0.28	0.18	0.6	6.1	0.3	1.4	10.5	1.3	0.2	3.8	25.2	23.7	-	-8.4	-48.3	-	-
03/2/21-2/22	R+S	4.7	9.5	525	14.8	-	0.00	-	0.2	-	-	0.8	-	0.0	0.3	1.4	4.2	-	-10.4	-69.3	-	-
03/2/23	R+S	4.1	13.3	562	70.3	0.03	0.05	-	-	0.0	-	-	-	0.1	0.8	4.7	12.8	-	-5.3	-22.9	-	-
03/3/3	R	4.6	13.5	538	41.4	0.03	0.04	0.1	1.6	0.0	0.2	1.7	-	0.1	0.8	5.3	8.6	-	-8.8	-57.0	-	-
03/3/3	S	5.4	12.5	477	30.3	0.01	0.03	-	1.0	0.0	0.1	2.1	-	0.0	0.9	2.5	6.0	0.4	-13.0	-89.5	-	-
03/3/6-3/8	R	6.4	18.2	474	17.3	-	0.02	-	1.0	-	-	1.1	-	0.0	0.4	1.2	1.4	3.0	-9.1	-60.1	-	-
03/3/16-3/17	R	5.2	10.9	489	14.7	-	0.01	-	0.7	0.0	0.1	0.9	-	0.0	0.2	1.4	1.5	0.4	-9.1	-62.3	-	-
03/3/22	R	4.0	21.8	467	118	0.12	0.15	-	-	0.2	-	-	-	0.0	1.5	20.9	8.1	-	-10.3	-72.6	-	-
03/3/27	R	4.4	15.5	285	107	0.08	0.12	0.5	6.6	0.2	0.9	4.0	-	0.1	1.2	11.3	16.3	-	-2.4	-8.6	-	-
03/4/18	R	5.1	18.7	513	16.8	0.01	-	-	-	-	-	0.8	-	0.3	0.4	1.8	1.7	1.8	-4.0	-14.6	-	-
03/4/18	R	4.8	20.4	499	13.4	-	-	-	-	-	-	0.5	-	0.3	0.3	1.3	1.1	-	-2.5	-5.6	-	-
03/4/19-4/20	R	5.2	13.9	520	14.8	-	-	-	-	-	-	0.7	-	0.3	0.3	2.4	1.3	-	-2.5	-5.5	-	-
03/4/22-4/23	R	4.5	19	541	22.9	0.01	-	-	-	-	-	0.6	-	0.3	0.4	3.2	1.3	-	-4.0	-20.3	-	-
03/4/25	R	5.9	19.1	507	5.4	0.01	-	-	-	-	-	0.2	-	0.3	0.3	0.7	0.8	2.5	-5.4	-32.8	-	-
03/4/25	R	5.8	11.6	507	6.3	0.01	-	-	-	-	-	0.3	-	0.3	0.3	0.8	0.8	1.6	-10.2	-75.5	-	-
4/29/03	R	5.1	15.1	541	8.6	0.01	-	-	0.2	-	-	0.3	-	0.3	0.4	1.0	1.0	-	-7.8	-48.3	-	-
4/29/03	R	5.4	17.2	493	4.6	0.01	-	-	-	-	-	0.1	-	0.2	0.2	0.7	0.5	-	-9.7	-64.2	-	-
03/5/6	R	5.3	21.3	475	20.4	0.01	-	-	0.4	-	-	1.6	-	0.3	0.4	2.6	2.7	8.6	-4.4	-22.5	3.7	14.9
03/5/7	R	5.1	20.9	489	5.6	0.01	-	-	-	-	-	0.1	-	0.2	0.3	0.6	0.7	-	-6.7	-37.7	-	-
03/5/7	R	5.0	20.9	505	5.7	0.01	-	-	-	-	-	-	-	0.2	0.3	0.4	0.5	-	-7.1	-49.1	-	-
03/5/30	R	5.3	24.9	466	8.0	0.01	-	-	-	-	-	0.4	-	0.3	0.4	1.2	0.8	-	-8.4	-56.1	3.5	-
03/6/6	R	3.9	26.2	491	66.4	0.04	0.04	-	0.6	0.1	-	2.5	-	0.3	0.7	4.4	8.6	-	-4.7	-25.3	3.0	15.3
03/6/10	R	3.8	24.7	526	97.0	0.09	0.07	0.1	1.0	0.1	0.2	4.5	-	0.2	0.8	6.4	12.2	-	-0.4	2.8	-	-
03/6/11-6/12	R	5.3	23.7	479	7.5	0.01	-	-	-	-	-	0.5	-	0.2	0.3	0.9	1.3	14.4	-9.1	-72.4	-	-
03/6/14	R	4.5	24.4	411	57.5	0.02	0.05	0.1	1.5	0.1	0.1	3.9	-	0.3	1.1	7.5	9.6	-	-8.1	-52.3	6.0	16.0
03/6/15	R	4.1	25.0	506	107	0.04	0.07	-	2.1	0.1	-	6.8	0.4	0.3	1.3	10.9	17.7	-	-8.7	-58.6	-	-
03/6/23-6/25	R	5.5	25.0	477	14.5	-	0.06	-	0.8	-	0.2	0.6	-	0.2	0.4	2.3	2.2	9.9	-9.5	-76.2	4.7	12.2
03/6/27	R	5.4	25.2	464	3.5	-	-	-	-	-	-	-	-	0.2	0.2	0.5	0.3	2.4	-16.5	-124.8	-	-

Appendix I. (continued).

Sampling date* type**	pH	T (°C)	Eh (mV)	K ₂₅ (mS/cm)	Chemical compositions (mg/L)													Isotopic compositions (‰)				
					Fe	Si	Mg	Ca	Al	Na	NH ₄	K	F	Cl	NO ₃	SO ₄	CO ₃	δ ¹⁸ O _w	δ ¹⁸ D _w	δ ³⁴ S _{SO4}	δ ³⁴ O _{SO4}	
03/6/29	R	4.2	23.4	518	85.0	0.02	0.04	-	-	0.1	-	5.2	-	0.3	0.6	6.8	14.4	-	-10.5	-74.6	3.2	14.8
03/7/2-7/3	R	5.7	25.7	464	6.9	-	-	-	-	-	-	0.5	-	0.2	0.2	0.9	0.9	4.0	-13.0	-111.8	-	-
03/7/7	R	5.0	26.7	496	26.9	0.01	0.03	-	-	-	-	1.8	-	0.2	0.3	3.4	3.1	12.8	-8.7	-64.5	-	-
03/7/9	R	4.7	25.1	503	14.8	-	-	-	-	-	-	0.5	-	0.2	0.3	1.3	1.6	-	-11.4	-78.4	-	-
03/7/9	R	5.7	24.8	495	5.0	-	-	-	-	-	-	-	-	0.2	0.2	0.5	0.7	-	-13.2	-94.5	-	-
03/7/9	R	4.8	25.2	512	20.9	0.01	-	-	-	-	-	1.0	-	0.2	0.2	2.8	2.1	-	-13.0	-92.5	-	-
03/7/12-7/13	R	6.0	24.6	442	25.2	-	-	-	1.8	-	-	1.2	-	0.2	0.4	3.8	1.7	19.4	-8.7	-73.2	-	-
03/7/16	R	4.5	24.8	516	24.5	0.01	-	-	-	-	-	0.9	-	0.2	0.3	3.1	1.3	-	-5.8	-41.5	-	-
03/7/18	R	5.5	22.0	507	2.7	-	-	-	-	-	-	-	-	0.2	0.2	0.2	0.3	-	-12.6	-94.4	-	-
03/7/18	R	5.2	23.9	486	3.9	-	-	-	-	-	-	-	-	-	0.2	0.7	0.2	-	-12.4	-89.9	-	-
03/7/18-7/19	R	5.7	24.0	484	11.4	-	-	-	-	-	-	0.7	-	0.2	0.3	1.4	1.3	-	-10.5	-74.6	-	-
03/7/21-7/22	R	5.6	27.4	517	3.6	-	-	-	-	-	-	-	-	0.2	0.2	0.2	0.5	-	-8.0	-52.9	-	-
03/7/22	R	5.2	26.3	481	6.4	-	-	-	-	-	-	0.1	-	0.2	0.2	0.7	0.6	-	-6.1	-39.6	-	-
03/7/22	R	5.5	26.2	476	2.1	-	-	-	-	-	-	0.2	-	-	-	0.1	0.2	-	-7.5	-48.9	-	-
03/7/22-7/23	R	5.3	26.1	486	3.9	-	-	-	-	-	-	0.1	-	-	-	0.5	0.3	-	-8.0	-51.5	-	-
03/7/27	R	6.5	26.6	296	3.9	-	-	-	-	-	-	0.2	-	0.2	0.2	0.3	0.3	-	-7.9	-52.1	-	-
03/7/27	R	6.0	25.3	403	6.1	-	-	-	-	-	-	0.4	-	0.2	0.2	0.8	0.5	2.0	-7.1	-48.8	-	-
03/7/28-7/29	R	5.7	26.0	456	12.7	-	-	0.4	-	-	-	1.1	-	0.2	0.3	1.7	1.7	-	-8.5	-58.8	-	-
03/8/2	R	3.9	25.5	524	88.3	0.04	0.05	0.6	-	0.1	-	4.1	-	0.2	0.6	8.3	10.8	-	-5.9	-42.0	-	-
03/8/2-8/3	R	4.9	27.6	463	59.2	0.01	0.07	1.0	-	-	0.2	5.0	-	0.2	0.8	7.5	11.2	-	-4.7	-30.2	-	-
03/8/5	R	5.6	26.4	442	22.1	-	0.08	1.0	-	-	0.1	1.6	-	0.2	0.5	4.9	3.0	4.9	-5.8	-41.1	-	-
03/8/6	R	4.8	26.2	502	16.3	-	-	0.3	-	-	-	1.0	-	0.2	0.4	3.0	2.0	-	-9.0	-58.9	-	-
03/8/7	R	5.6	25.2	497	4.8	-	-	-	-	-	-	0.2	-	-	0.3	1.3	0.8	-	-9.3	-62.5	-	-
03/8/18	R	5.6	24.9	462	11.8	-	0.06	0.9	-	-	0.1	0.7	-	0.2	0.5	1.7	1.2	13.0	-9.2	-72.9	-	-
03/8/19	R	5.6	24.7	466	2.7	-	-	-	-	-	-	0.3	-	-	0.2	0.3	0.4	-	-16.1	-119.6	-	-
03/8/19-8/20	R	5.4	22.5	475	2.8	-	-	-	-	-	-	0.2	-	-	0.3	0.4	0.3	-	-11.5	-78.0	-	-
03/8/20	R	5.6	23.0	483	3.9	-	-	-	-	-	0.1	0.2	-	0.2	0.4	0.4	0.4	-	-8.5	-55.5	-	-
03/8/23	R	5.5	25.4	493	4.2	-	-	-	-	-	-	0.2	-	-	0.2	0.5	0.4	-	-10.7	-76.9	-	-
03/8/24	R	5.1	25.6	490	5.2	-	-	-	-	-	-	0.2	-	-	0.2	0.4	0.5	-	-13.0	-95.6	-	-
03/8/25	R	4.5	22.5	511	13.5	-	-	-	-	-	-	0.4	-	-	0.2	0.9	1.1	-	-10.8	-73.5	-	-
03/10/28	R	4.7	17.0	502	30.6	0.01	0.05	0.9	0.1	-	0.1	1.5	0.0	0.2	0.6	4.8	3.7	-	-8.7	-50.6	6.9	11.4
03/11/7	R	4.4	11.6	528	25.3	0.01	-	0.2	-	-	-	0.7	0.3	0.2	0.3	1.7	2.4	-	-8.2	-46.1	-	-
03/11/10-11/11	R	5.2	20.0	510	10.8	-	-	0.5	-	-	0.1	0.6	0.6	0.2	0.4	1.6	1.5	-	-9.2	-54.0	-	-
03/11/12	R	4.8	14.8	511	14.0	-	-	0.3	-	-	-	0.6	-	0.2	0.3	2.2	0.9	-	-10.3	-57.1	-	-
03/11/13	R	5.62	464	19.5	-	-	-	-	-	-	-	-	-	0.2	0.4	1.3	2.8	-	-5.6	-34.1	-	-
03/11/29	R	5.7	18.5	447	12.0	-	-	-	-	-	-	-	-	0.2	0.4	1.3	1.8	8.4	-7.7	-46.0	-	-
03/12/17	S	6.6	17.6	427	52.5	0.01	0.12	4.4	0.3	-	1.2	2.0	-	0.2	2.3	7.1	7.3	8.0	-8.4	-37.0	5.9	9.0
04/1/2	S	4.3	19.0	495	57.4	0.03	0.05	1.9	0.2	0.1	0.7	2.4	0.3	0.2	1.1	9.2	6.5	-	-16.1	-114.5	7.1	12.5
04/1/12-1/13	S	5.5	18.1	397	78.3	0.02	0.12	3.3	0.5	-	3.2	3.2	-	0.2	6.5	10.0	8.4	21.2	-10.3	-55.1	7.5	12.9
04/2/21	R	4.1	10.4	517	40.7	-	-	0.8	-	-	0.1	0.8	-	0.2	2.0	5.5	5.0	-	-14.7	-96.8	-	-
04/2/28	R	4.5	12.6	412	112	0.09	0.12	5.7	0.5	0.2	1.4	5.8	-	0.3	2.3	15.3	19.4	-	-2.6	4.9	6.5	14.0
04/3/4	S	7.2	18.6	480	12.8	-	-	0.6	-	-	0.2	0.8	0.5	0.2	0.5	2.1	1.7	0.7	-15.3	-104.5	-	-
04/3/16-3/17	R	5.0	14.6	471	59.6	0.02	0.04	2.4	0.4	-	1.4	3.2	-	0.2	2.8	5.3	9.3	-	-	5.1	16.3	-

Appendix I. (continued).

Sampling date* type**	pH	T (°C)	Eh (mV)	K ₂₅ (mS/cm)	Chemical compositions (mg/L)													Isotopic compositions (‰)				
					Fe	Si	Mg	Ca	Al	Na	NH ₄	K	F	Cl	NO ₃	SO ₄	CO ₃	δ ¹⁸ O _w	δ ¹⁸ D _w	δ ³⁴ S _{SO4}	δ ³⁴ O _{SO4}	
04/4/2	R	5.4	17.1	486	48.1	0.01	0.07	4.2	0.2	-	0.4	2.0	-	0.2	1.0	7.3	7.2	39.6	-9.6	-62.4	-	-
04/4/19	R	5.1	20.5	495	12.3	-	-	0.6	-	-	-	0.8	-	0.2	0.3	1.6	1.8	21.1	-10.9	-73.7	-	-
04/4/22	R	5.5	19.6	507	114	-	0.23	6.2	0.5	-	0.4	7.4	-	0.4	1.5	15.9	23.8	14.7	-0.5	8.1	5.5	16.2
04/4/26-4/27	R	4.2	22.0	514	130	-	-	0.6	-	-	-	0.2	-	0.2	0.2	0.4	1.5	-	-12.3	-93.5	3.6	-
04/5/2-5/4	R	4.3	21.9	538	21.3	-	0.04	0.8	-	-	-	1.2	-	0.2	0.4	2.3	3.3	-	-3.6	-20.9	4.2	15.2
04/5/8-5/10	R	4.2	20.9	514	129.6	-	-	0.5	-	-	-	0.4	-	0.2	0.2	0.8	1.0	-	-13.8	-105.3	2.6	13.4
04/5/12	R	3.8	20.8	515	56.0	-	-	0.6	-	-	-	1.4	-	0.2	0.3	2.6	2.8	-	-7.9	-48.5	4.1	-

*: R=rain, S=snow.

**: Date format=year/month/day

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