



## Sulfur isotope and chemical compositions of the wet precipitation in two major urban areas, Seoul and Busan, Korea



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### ABSTRACT

The seasonal variations of  $\delta^{34}\text{S}$  together with major ions in snow and rainwater samples were measured in urban areas. Precipitation samples were collected from metropolitan city, Seoul and large port city, Busan, Korea, for about one year from June 2002 to June 2003. The  $\delta^{34}\text{S}$  values of sulfate in precipitation ranged from  $-4.3\text{‰}$  to  $+6.6\text{‰}$  (mean:  $3.72\text{‰}$ ) and  $+1.0\text{‰}$  to  $+18.6\text{‰}$  (mean:  $5.55\text{‰}$ ) in Seoul and Busan, respectively. Even though both of the study areas have large populations and transportation infrastructure,  $\delta^{34}\text{S}$  values of sulfate in Seoul precipitation originate more from anthropogenic sources relative to that of Busan. The elevated anthropogenic sources in Seoul might be influenced by human activities from surrounding industrial cities, while the scatter of  $\delta^{34}\text{S}$  values in Busan may be influenced by marine air. During the study,  $\delta^{34}\text{S}$  values are high in the fall season and low in the spring season. It may be inferred from this data that spring time  $\delta^{34}\text{S}$  values are affected more by biogenic sources compared to the fall season. As such, Seoul and Busan showed significant differences in chemical compositions, such as  $\delta^{34}\text{S}$  and  $\text{nss-SO}_4^{2-}$ . Especially,  $\delta^{34}\text{S}$  values in the Seoul show very good relationship with anthropogenic emissions (e.g., emission from coal combustion) and  $\delta^{34}\text{S}$  values in the Busan may be influenced by sea spray from the oceanic surface micro-layer. This correlation and the  $\delta^{34}\text{S}$  values indicate that the major source in this region is likely to be anthropogenic source in Seoul and sea spray in Busan, rather than traditionally suggested sources such as soil resuspension, stratospheric air intrusion, volcanic emissions, and biogenic emissions.

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### 1. Introduction

Fast growing industry-based economic development has caused many environmental problems over the world. Industrial belts emit many types of contaminating gases into the atmosphere, causing acid rain and excess ozone. Acid rain has been one of the major issues in the studies of atmospheric environment in the twenty-first century and recently has troubled East Asia. To understand this problem, scientists have been studying the origins and composition of acidic precipitation. The major element and isotopic composition analyses of precipitation have provided useful information on sources and aerial transport processes of atmospheric pollutants. In this study, chemical composition and sulfur isotopes in urban precipitation were used to understand atmospheric transportation and origin.

Major sources of element in rainwater are marine (sea spray), terrestrial (soils, biological emissions), and anthropogenic (indus-

trial, biomass burning) (Junge, 1963; Mason, 1971; Granat et al., 1976; Stallard and Edmond, 1981). The importance of marine source varies with distance from the coast. A “hierarchy of ions” can be established (after Means et al., 1981 and Stallard and Edmond, 1981) based on relative importance of marine sea-salt sources and continental (terrestrial or pollutive) sources. Major ions of rainwater are from both natural (marine, terrestrial and biogenic emission) and anthropogenic (industries, vehicle emission and others) sources. In general, the chemical composition of atmosphere has the following patterns. The “hierarchy of ions”,  $\text{Cl}^- = \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+ > \text{Ca}^{2+} > \text{SO}_4^{2-} > \text{NO}_3^- = \text{NH}_4^+$ , was established by Means et al. (1981) and Stallard and Edmond (1981), illustrating from left to right the decreasing importance of the marine source relative to the terrestrial or pollutant sources (Panettiere et al., 2000).

Among principal cations,  $\text{Na}^+$  is the major cation in marine-influenced rain, while  $\text{Ca}^{2+}$  is dominant in inland rain due to  $\text{NaCl}$  solution in the ocean and  $\text{CaSO}_4$  solution in the continent. In the coastal area, precipitation has generally similar sea-salt ratios as  $\text{Na}^+$ ,  $\text{Cl}^-$  and  $\text{Mg}^{2+}$ , but  $\text{Ca}^{2+}$  and  $\text{K}^+$  ratios may be different

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depending on continental inputs (Bernier and Bernier, 2012). A majority of sodium might be derived from marine source but it sometimes comes from particularly an arid, dusty area of igneous rocks (over most sedimentary rocks), saline dry lake beds, and soil dust from agriculturally developed areas (Munger, 1982). Chlorine also is mainly from a marine source. The decrease of chlorine content inland is explained by rapid deposition of sea salt in precipitation and air mixing (Junge, 1963). However, all  $\text{Cl}^-$  in rainfall is not originated from sea salt; some come from chlorine-containing gases from automobiles, coal combustion, and burning of polyvinyl chloride in incinerators (Paciga and Jervis, 1976).

The contribution of sea salt to  $\text{Ca}^{2+}$  in inland rain is very trivial. Instead,  $\text{Ca}^{2+}$  comes dominantly from the dissolution of calcium carbonate ( $\text{CaCO}_3$ ) in soil dust.  $\text{HCO}_3^-$  and  $\text{Ca}^{2+}$  are formed by dissolving  $\text{CaCO}_3$  in the rain.  $\text{Ca}^{2+}$  in rain is also derived  $\text{CaSO}_4$  (gypsum) soil dust and occasionally from  $\text{CaCl}_2$  (road salt) (Butler et al., 1984). In addition,  $\text{Ca}^{2+}$  can be produced by pollution from coal burning and from cement manufacture (Pearson and Fisher, 1971). Magnesium is correlated with calcium, presumably due to a similar soil source (Munger and Eisenreich, 1983). Except for coastal areas or areas of strong marine influence such as the Amazon, Mg is not an importance source for sea salt (Stallard and Edmond, 1981). Non-marine sources of potassium are soil dust, K-bearing fertilizers, biogenic aerosol, pollen seed, and forest burning, particularly in tropical areas (Junge, 1963; Gillette et al., 1992; Munger, 1982). From the partial reaction between ammonia gas ( $\text{NH}_3$ ) and water, ammonium can be formed. This reaction raises the pH of rainwater. Atmospheric ammonia can be produced

from the bacterial decomposition of animal and human excreta, fertilizer release, burning coal, and biomass burning (Bernier and Bernier, 2012). Agricultural sources are seasonal, being at a maximum in the spring and summer. Ammonia is a very minor product of coal combustion. In fact, well-burned coal releases no  $\text{NH}_3$  at all (Stedman and Shetter, 1983), with all of the nitrogen appearing as  $\text{N}_2$  instead as  $\text{NO}_x$ . However, some data show little areal correlation with other fuel combustion products such as  $\text{SO}_2$  (Healy et al., 1970; Junge, 1963). Nitrate in atmosphere originates from natural sources (lightning, photochemical oxidation in the stratosphere, chemical oxidation of ammonia to  $\text{NO}_x$  and soil production of  $\text{NO}$ ) and anthropogenic sources (fossil fuel combustion and biomass burning).

Sulfur in the atmosphere originate from sea spray, organic compounds from sulfur reducing bacteria, volcanic gases, combustion of fossil fuels, and other human activities (Newman et al., 1991). The ratio of  $^{34}\text{S}$  to  $^{32}\text{S}$  in the rainwater is used to identify and trace the source of sulfur in atmospheric fallout. Generally, sea spray sulfate contributes to only a minor fraction of the total atmospheric sulfate content, especially in urban conditions (Na et al., 1995; Lim et al., 2012). The sources of NSS (Non-Sea Salt) sulfate are either anthropogenic sulfur dioxide originating from oil and fossil fuel combustion, or natural biogenic reduced sulfur gases (Junge, 1963; Bonsang et al., 1980; Bernier and Bernier, 1987; Gammon and Charlson, 1993; Herut et al., 1995).

The purpose of this study is to examine and compare the S isotope and chemical compositions of the wet precipitation in Seoul and Busan to determine the possibility of using sulfur as a tracer in evaluating the sources of atmospheric pollution in these areas.

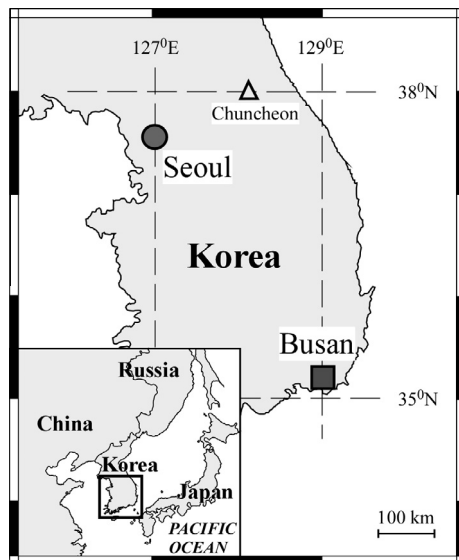


Fig. 1. Map of the sampling location of study area in Seoul (black circle) and Busan (black square) and reference area in Chuncheon (open triangle; Yu et al., 2007).

## 2. Study area

The two largest cities in Korea, Seoul and Busan, were selected for this study because the effects of pollution from anthropogenic sources in these areas are expected to be maximized within the Korean peninsula in recent years compared to reference rural site Chuncheon (Yu et al., 2007) during rain and snow events from June, 2002 to June, 2003 (Fig. 1).

Seoul accommodates around ten million people with about three million vehicles and numerous industrial belts. The sampling site is located at Seoul National University in the southern part of the Seoul metropolitan area. The locations of the sampling site are presented in Fig. 1. The Gwanaksan granite is a stock -size pluton which belongs to the Jurassic Daebo granite series, and placed in the southern Seoul granitic batholith (Kwon et al., 1995).

Busan is the second largest city in Korea with nearly four million people and about one million vehicles. Busan is located on the southeastern end of the peninsula and is a harbor city. Samples were collected in Pukyong National University. Both of the sampling areas are in the metropolitan city and samples were acquired from a roof of a school building. The Busan region, located

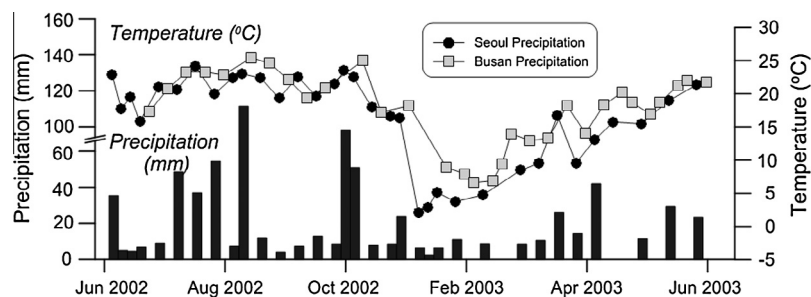


Fig. 2. Seasonal variations of precipitation and air temperature in Seoul and Busan.

southeast of Yucheon basin, mainly consists of volcanic and plutonic rocks of the Cretaceous in age (Kim, 1988).

As a reference rural site, Chuncheon is the capital city of Kangwon-Do Province, which occupies the eastern central part of the Korean peninsula (Fig. 1) (Yu et al., 2007). The city, with a population less than 200,000, mainly consists of residential and commercial areas surrounded by agricultural and forested areas. The majority of Chuncheon city is sited on Jurassic Chuncheon Granite which intrudes the pre-Cambrian Gubongsan Group and the underlying Yongduri metamorphic complexes which consist of gneiss, schist, amphibolite, marble, and quartzite (Yu et al., 1994).

### 3. Methodology

Wet deposition samples were collected at Seoul National University in Seoul and Pukyong National University in Busan. Both cities are the most crowded and industrial areas in Korea. The samplers were equipped with stainless steel funnels ( $\varnothing$ 650 mm), large enough for the collection of high volume precipitation samples. It was designed to get rain sample directly without contacting sampler's walls and plastic boxes ( $60 \times 40 \times 15$  cm) on the roof of building at E 126°90' N 37°40' from June 2002 to June 2003 and E 129°00' N 35°10', in Seoul and Busan respectively. The samplers were set just before raining and were carried to the laboratory immediately after each rain event. Collected samples from Busan were delivered to Seoul as soon as possible and pretreated in the laboratory before being kept in the cold storage.

Climatic data of rainwater were obtained from KMA (Korea Meteorological Administration) weather stations, located at Seoul and Busan near sampling sites. Analyses of the major chemical composition of rainwater were carried out using the Inductively Coupled Plasma-Atomic Emission Spectrometer (located at National Center for Inter-University Research Facilities, Seoul National University: SHIMADZU/ICPS-1000IV) for  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , S and the Ion Chromatography system (located at Institute of Environmental Protection and Safety, Seoul National University) for  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{NH}_4^+$ . For sulfur isotopic analysis, large volume (>20 l) precipitation samples were collected and filtered through a 0.45  $\mu\text{m}$  Millipore filter, and then 1 ml of conc.  $\text{HNO}_3$  was added. Dissolved  $\text{SO}_4$  in the sample was precipitated as  $\text{BaSO}_4$  by adding 10%  $\text{BaCl}_2$  and was heated for more than 24 h at a temperature lower than the boiling point. The  $\text{BaSO}_4$  precipitates were collected through a centrifuging, drying, and weighing process. About 3 mg of  $\text{BaSO}_4$  powder was mixed with  $\text{V}_2\text{O}_5$  and quartz glass, and the prepared sample was heated at 1150 °C to reduce to  $\text{SO}_2$  following the method given by Yanagisawa and Sakai (1983). Then the prepared  $\text{SO}_2$  was analyzed for the  $\delta^{34}\text{S}$  of sulfate ions dissolved in water using the gas source mass spectrometer at KBSI (Korea Basic Science Institute). The  $\delta^{34}\text{S}$  ( $\text{SO}_4^{2-}$ ) values are given in per mil [‰] units, with reference to the international standard CDT. To deduce the probable source regions of the air masses from which our water samples derived, the backward trajectories were modified based on the Hybrid Single-Particle Lagrangian Intergrated Trajectories (HYSPPLIT) ARL trajectory tool database of the National Oceanic and Atmospheric Administration (NOAA, <http://www.arl.noaa.gov/ready/hysplit4.html>). Administration Trajectories for time periods of 120 h were computed for 1500 m above ground level (m.a.g.l.), because rainfall and snowfall are expected to originate from these altitudes. However, backward trajectory analysis indicates only the synoptic situation, and is only an approximation of the general origin of an air mass. Minor local moisture sources cannot be excluded. The trajectories were calculated for every rainwater-sampling day. Additionally, we calculated weekly backward trajectories for the summer (June, July and August) in 2002 and (June) in 2003 and for winter in

(November, and December) in 2002 and (January and February) in 2003. This procedure helped to identify changes of sulfur isotopic and chemical data in the source regions for rainfall over our study site.

### 4. Results

The pH values of Seoul and Busan precipitation are in the ranges of 4.4–7.1 and 2.6–6.2, averaging 5.3 and 4.0, respectively (Fig. 2) (Table 1). Similar mean pH values of 5.7–7.0 for Seoul and 5.0–7.0 for Seoul area were also obtained by Lee et al. (2000) and Lim et al. (2012). Here, the pH value of Busan area (pH: 4.0) is comparable to pH value of Tokyo (pH: 3.9), reported by Fujita et al. (2000). However, the pH value during the Asia Dust season (Yellow sand), 2003, was 6.4 for Seoul and 5.4–6.24 for Busan (Table 1), respectively.

The average concentration of individual ions in Seoul and Busan are presented in Fig. 3. Among cations, concentrations of  $\text{NH}_4^+$ ,  $\text{Na}^+$  and  $\text{Ca}^{2+}$  were dominant and were followed by  $\text{Mg}^{2+}$  in Seoul and Busan (Table 3, Fig. 3). The average concentration of ammonia, a dominant major ion, in Seoul's precipitation was 1.66 mg/L except for an abnormal datum of 15.9 mg/L in June 2002. The source of abnormal ammonia (15.9 mg/L) might be affected from the Chinese air mass during summer because of the backward trajectory from china and enriched continental ions ratio in Table 2. Lee et al. (1999) reported that the ammonia content of air samples was also dominant; these values were 2.94 and 6.52 mg/L for summer and winter in Seoul, respectively. Generally ammonia can originate from biomass burning as well as biological sources especially in rural areas (Berner and Berner, 2012). In cities, however, ammonia is related to population and traffic density (Suh et al., 1994). Therefore Fraser and Cass (1998) reported that ammonia can come from vehicles operating under rich air–fuel ratio. However, in this study during winter, calcium is a predominant ion (Table 3, Fig. 3). The enrichment factor of calcium which is a predominant ion in this research is 61.4 in Seoul (Table 3). Contribution of sea salt to  $\text{Ca}^{2+}$  in Seoul rainwater is very small relative to weight ratios ( $\text{Ca}^{2+}/\text{Na}^+$ ) of sea water (Table 2, Fig. 4-a). The following are data for Busan. Among cations,  $\text{Na}^+$  is the most dominant followed by  $\text{Ca}^{2+}$  in Busan. Most of the sodium might come from seawater, which is continuously contributed from eastern coast. Therefore ammonia was a predominant ion in the summer and fall season in Seoul, while on the contrary, the higher ammonia concentrations in Busan occurred in winter season (Table 3, Fig. 4).

Among anions,  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  are dominant ions in Seoul and Busan. Average values of  $\text{SO}_4^{2-}$  concentrations in Seoul and Busan are 3.3 mg/L and 2.08 mg/L and of  $\text{Cl}^-$  are 0.84 mg/L and 12.6 mg/L (Table 3, Fig. 4-b). These species which are quickly absorbed to aerosols are washed out from the atmosphere by initial rain or snow. Therefore initial rain or snow can effectively remove  $\text{SO}_4^{2-}$  from the atmosphere. For individual precipitation samples, enrichment factors and the mean contributions from sea spray can be calculated by using the weight mean ratios of sea water (Berner and Berner, 2012) and the results are presented Table 3. Individual  $\text{SO}_4^{2-}$  enrichment factor does not clearly show seasonal variation but does indicate the characteristic weather condition. In Seoul, enrichment factors of ions relative to seawater are the highest for  $\text{Ca}^{2+}$  with a factor of 61.4, followed by  $\text{SO}_4^{2-}$  (33.0),  $\text{K}^+$  (14.5),  $\text{Mg}^{2+}$  (1.5),  $\text{Cl}^-$  (1.2). On the other hand, in Busan,  $\text{Ca}^{2+}$  (10.9) is the highest, followed by  $\text{SO}_4^{2-}$  (4.1),  $\text{Cl}^-$  (3.37), and  $\text{Mg}^{2+}$  (1.1) (Table 3).

The chemical composition between the concentration of  $\text{Na}^+$  and  $\text{Cl}^-$  can be considered to be components of sea salt. The relation between the concentrations of  $\text{Na}^+$  and  $\text{Cl}^-$  in Seoul and Busan are shown in Fig. 5. The regression line between  $\text{Na}^+$  and  $\text{Cl}^-$  are

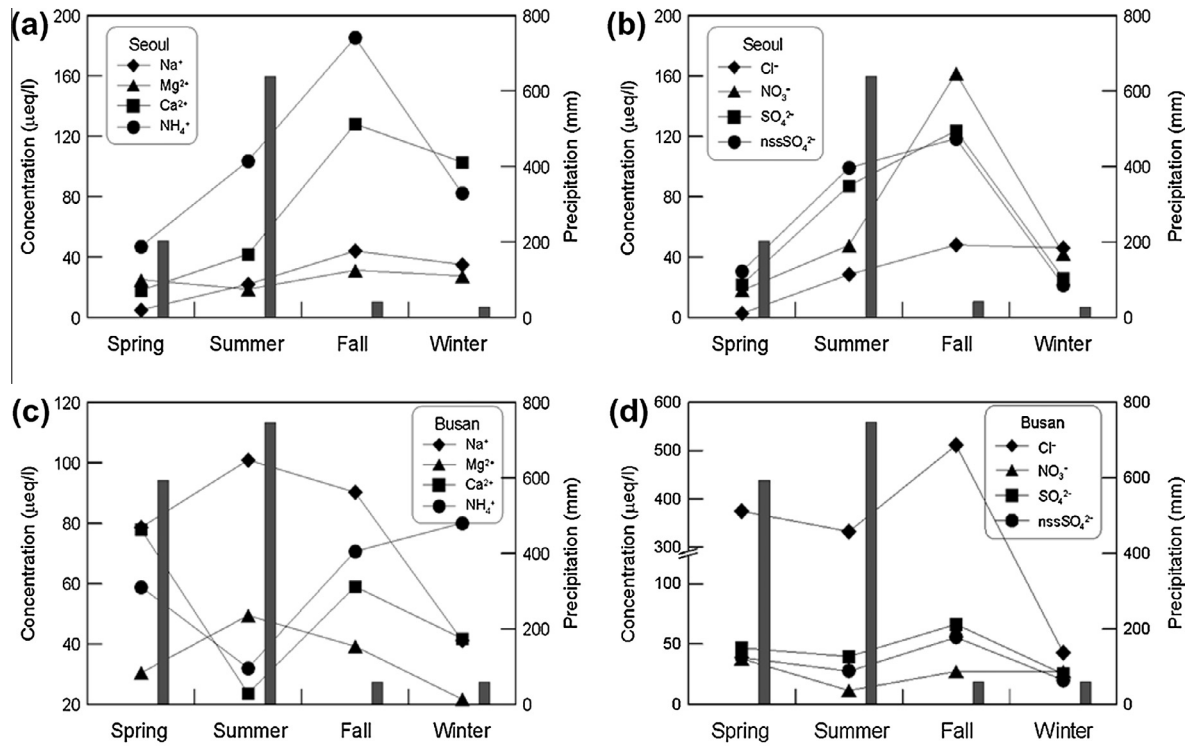
**Table 1**  
The general weather information of precipitation in Seoul (urban area) and Busan (coastal area), Korea.

Date	Wind		Precipitation				Condition
	Direction	Velocity (m/s)	mm	Temp.	pH	EC (s/cm)	
<i>Seoul</i>							
10-June-2002	SW	2.7	35.5	23.0	5.81	12.9	
12-June-2002	WNW	1.0	5.0	17.5	6.28	153	
20-June-2002	NE	0.0	4.5	19.4	5.06	45.7	
24-June-2002	ENE	1.4	7.0	15.4	6.52	14.0	
02/July/2002	WSW	1.3	9.0	21.0	4.46	32.7	
05/July/2002	NE	2.9	48.5	20.6	5.83	4.9	Typhoon
14/July/2002	SW	1.6	37.0	24.4	4.55	35.9	
19/July/2002	NE	3.5	54.5	19.9	4.62	11.4	
03/August/2002	W	2.0	7.5	22.5	4.76	28.7	
04/August/2002	SW	0.4	112	23.2	4.95	7.6	
06/August/2002	NE	3.9	12.0	22.5	5.47	5.1	
11/August/2002	ENE	1.3	4.0	19.2	5.73	8.1	
17/August/2002	NNE	1.2	7.5	22.7	5.62	16.1	
18/August/2002	NNE	2.7	13.0	19.5	4.64	17.3	
22/August/2002	W	3.2	8.5	21.5	5.33	11.6	
27/August/2002	WSW	1.8	98.0	23.7	4.50	14.1	
31/August/2002	NE	3.2	51.0	22.6	5.70	2.5	
28/September/2002	S	3.1	8.0	17.7	5.67	107	
06/October/2002	SW	1.8	8.5	16.2	5.66	47.3	
13/October/2002	SSW	1.2	24.0	15.9	5.06	17.0	
08/December/2002	NE	2.8	6.5	0.5	6.19	19.7	Snow
03/January/2003	SW	1.1	2.5	1.3	6.40	68.6	Snow
08/February/2003	NE	1.8	6.5	3.8	5.48	10.7	
21/February/2003	E	2.5	11.0	2.3	4.40	17.7	
06/March/2003	NE	1.0	8.7	3.4	7.10	18.6	Yellowsand
07/April/2003	ENE	1.3	8.5	7.4	5.16	11.0	
11/April/2003	WNW	1.0	10.5	8.6	5.00	13.5	
18/April/2003	NNE	2.0	26.0	16.3	5.00	11.6	
22/April/2003	SSW	1.9	14.5	8.6	4.94	14.4	
29/April/2003	ENE	3.3	42.0	12.4	5.33	6.4	
06/May/2003	NE	0.1	80.0	15.3	4.90	9.8	
24/May/2003	NNE	2.6	11.5	15.0	5.03	19.8	
11/June/2003	SSW	3.8	29.5	18.8	4.97	22.9	Rainy season
23/June/2003	SE	1.9	23.5	21.4	4.73	31.8	Rainy season
27/June/2003	NE	2.0	82.5	19.7	4.95	12.2	Rainy season
<i>Busan</i>							
24/June/2002	NNW	6.6	45.0	17.1	4.80	29.8	
01/July/2002	WNW	1.0	28.0	20.7	nd	nd	
05/July/2002	NE	4.3	68.5	23.5	3.50	118	Typhoon
13/July/2002	SW	5.0	9.0	23.5	3.50	148	
19/July/2002	NE	4.1	50.5	22.6	3.80	66.1	
05/August/2002	SW	5.3	48.0	25.8	5.20	15.5	
08/August/2002	SW	1.7	45.0	24.9	4.00	33.3	
10/Aug/2002	ESE	2.8	35.5	22.2	4.30	17.9	
12/August/2002	NE	3.1	26.5	19.2	3.10	396	
14/August/2002	NNE	1.7	20.0	20.9	3.40	191	
30/August/2002	NNE	4.0	12.0	25.3	3.00	736	
15/September/2002	NNE	4.8	18.0	16.9	3.39	174	
19/October/2002	NE	4.9	40.0	18.0	3.62	126	
08/February/2003	NE	4.7	43.0	7.9	4.74	18.3	
22/February/2003	NNE	3.8	15.5	6.8	4.60	43.2	
01/March/2003	N	3.1	15.0	5.4	5.40	33.2	
06/March/2003	NE	6.7	32.0	5.7	4.28	32.8	
14/March/2003	NE	3.3	6.0	8.4	5.44	72.6	Snow
31/March/2003	ENE	4.8	8.0	13.4	3.10	697	Snow
07/April/2003	E	4.0	14.5	12.3	3.58	264	
11/April/2003	SE	0.8	16.5	12.6	3.93	286	
18/April/2003	SW	5.5	50.5	18.0	6.24	83.0	Yellowsand
23/April/2003	NNE	0.1	40.5	13.5	4.12	59.4	
29/April/2003	SW	4.5	27.5	18.1	2.61	872	
06/May/2003	SW	2.9	119	20.2	4.08	24.0	
14/May/2003	NE	1.6	8.0	18.5	4.06	43.7	
24/May/2003	NNE	6.3	98.5	16.6	4.15	65.5	
30/May/2003	NNE	3.4	168	18.5	3.84	181	
12/June/2003	NE	2.5	93.5	21.3	3.74	131	
16/June/2003	NNE	9.6	127	22.1	3.94	61.1	Rainy season
23/June/2003	ENE	1.5	48.5	21.8	4.09	116	Rainy season
27/June/2003	ENE	1.5	89.0	20.5	3.45	120	Rainy season

indicated by the broken line. The regression solid line shows the ratio of the concentrations of  $\text{Na}^+$  and  $\text{Cl}^-$  in sea water (Fig. 5), respectively (Nozaki, 1992). The plot shows a linear relation to

the ratio of sea salt in Seoul, indicating that most of  $\text{Na}^+$  and  $\text{Cl}^-$  in wet depositions originated from sea salt. However, the plot of Busan shows a linear relation to the ratio in sea salt, surplus chlo-





**Fig. 3.** The seasonal dominant ion (broken line graphs) and precipitation (bar graphs) in study area; spring (March–May), summer (June–August), autumn (September–November), and winter (December–February).

rides were also observed in Busan. The combustion of industrial and domestic waste involving organic chloride is a possible source of the surplus chlorides, since combustion is a common method of waste disposal in Busan.

The pH values in both study areas are typical except during the so-called “Asian Dust” season (Fig. 6). During the study period, although its pH values were lower than that of a normal year, the pH was little higher than average. The Korean atmospheric environment may also be affected from China. Neutralizing acid rain by reaction with alkali ion of  $\text{Ca}^{2+}$ , in yellow sand season may be derived from calcite and dolomite in limestone which mainly originates from China. “Asian Dust” phenomenon is increasing with increasing industrial activities in China which causes desertification. The Korea peninsula is located in eastern China and therefore is always influenced by yellow sand phenomenon. It also carries soil dust with pollution from the China industrial belt to the Korea peninsula (Fig. 7).

The major group of samples show the positive  $\delta^{34}\text{S}$  values with the range  $+1.7\text{‰} \sim +6.6\text{‰}$  for Seoul and  $+1.0\text{‰} \sim +18.6\text{‰}$  for Busan except for one sample ( $-4.3\text{‰}$  for Seoul). The average values of  $\delta^{34}\text{S}$  are  $3.7\text{‰}$  in Seoul and  $5.5\text{‰}$  in Busan (Table 2, Fig. 8).

The isotopic composition of NSS sulfate ( $\delta^{34}\text{S}_{\text{NSS}}$ ) was calculated from the isotopic composition of the sample's total sulfate ( $\delta^{34}\text{S}_{\text{measured}}$ ) using the equation,

$$\delta^{34}\text{S}_{\text{NSS}} = \frac{(\delta^{34}\text{S}_{\text{sample}} - \delta^{34}\text{S}_{\text{ss}}f)}{(1 - f)}$$

where  $f$  is a fraction of sea-salt sulfate in a sample as evaluated from the following relationship:

$$f = (\text{Na}^+)_{\text{measured}} \times \frac{(\text{SO}_4^{2-}/\text{Na}^+)_{\text{ss}}}{(\text{SO}_4^{2-})_{\text{measured}}}$$

$(\text{Na}^+)_{\text{measured}}$  and  $(\text{SO}_4^{2-})_{\text{measured}}$  stand for the measured concentration of  $\text{Na}^+$  and  $\text{SO}_4^{2-}$  of samples and  $(\text{SO}_4^{2-}/\text{Na}^+)_{\text{ss}}$  indicate the  $\text{SO}_4^{2-}/\text{Na}^+$  ratio of seawater of 0.252 (Ohizumi et al., 1991). The sulfur isotope composition of the sulfate which is derived from NSS (pollution) sources is presented Table 2 and Fig. 8. Most of samples show  $\delta^{34}\text{S}_{\text{NSS}}$  values with the range  $-4.6\text{‰} \sim +5.9\text{‰}$  for Seoul and  $0.3\text{‰} \sim +12.2\text{‰}$  for Busan.

Negative value of  $\delta^{34}\text{S}$  in Seoul can be attributed to high proportion of sulfur gas concentration from a biogenic source. Sulfur compounds, in both gaseous and aerosol phases, are ubiquitous in the background atmosphere and are generally conceded to result from natural processes, i.e. marine, volcanic, and biospheric system. The biospheric source is the result of biological action in soils, water, or vegetation and thus includes land, water, and oceanic sources. The Korean peninsula is geographically included in Seoul that is surrounded by China, Russia, Japan and the Pacific Ocean. The biosphere from land and oceanic sulfur gas is considered to be the major source of non-anthropogenic sulfur compounds in Seoul. Plots of  $\delta^{34}\text{S}$  value versus  $\text{SO}_4^{2-}$ , estimated from seawater are presented in Fig. 8. These data are very useful to trace sources and to observe the origin of sulfur compounds. Generally the  $\delta^{34}\text{S}$  value shows variation depending on how much sulfate is from sea salt; the three  $\delta^{34}\text{S}$  values of Busan are higher than that of other samples relative to the sea salt percentage in winter (Fig. 8). Busan during the winter season may include much sulfate in atmosphere.

On the other hand,  $\delta^{34}\text{S}$  values of Busan samples trend to show wide spread nature in comparison to values of Seoul samples, in terms of sea salt proportion and biogenic activity. Generally,  $\text{Na}/\text{Mg}$  in seawater is approximately 8.34 based on dissolved components of seawater with 35‰ salinity. It may also indicate that most of nss  $\text{SO}_4^{2-}$  in Busan is derived from the ocean. The dominant values of  $\delta^{34}\text{S}$  in Seoul and Busan are, respectively,  $+3.5\text{‰} \sim +6.6\text{‰}$  and  $+1.9\text{‰} \sim +7.6\text{‰}$  within  $0\text{‰} \sim +10\text{‰}$ , corresponding to the values of natural oil and coal (Newman et al., 1991). Therefore,

**Table 2**  
Chemical compositions and isotopic data of precipitation both cities, Korea.

Date	Na <sup>+</sup>	Mg <sup>2+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	NH <sub>4</sub> <sup>+</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	nss-SO <sub>4</sub> <sup>2-</sup>	%SO <sub>4</sub> <sup>2-</sup> seawater	δ <sup>34</sup> S(‰) measured	nss-δ <sup>34</sup> S(‰)
<i>Seoul</i>												
10-June-2002	0.20	nd	nd	0.30	1.21	nd	nd	nd	-	-	-	-
12-June-2002	2.56	0.57	4.16	6.65	15.9	6.67	19.4	27.4	26.8	2.35	-	-
20-June-2002	0.29	0.13	nd	1.24	3.47	nd	5.19	7.25	7.18	1.01	5.3	5.1
24-June-2002	0.50	0.17	nd	1.19	1.06	0.97	2.08	1.75	1.63	7.13	5.4	3.7
02/02	0.39	nd	nd	0.36	2.11	0.64	4.30	3.18	3.08	3.10	2.3	1.6
05/July/2002	nd	nd	nd	0.17	nd	0.45	0.53	nd	-	-	-	-
14/July/2002	0.26	nd	nd	0.73	3.29	0.77	3.19	6.71	6.64	1.00	6.1	5.8
19/July/2002	nd	nd	nd	nd	nd	0.50	0.67	nd	-	-	-	-
03/August/2002	1.08	0.15	nd	0.90	2.16	1.61	2.20	5.32	5.05	5.12	5.0	3.8
04/August/2002	0.20	nd	nd	nd	nd	0.49	0.63	1.10	1.05	4.65	-	-
06/August/2002	0.34	nd	nd	0.11	nd	0.67	0.46	0.61	0.53	13.9	-	-
11/August/2002	0.12	nd	nd	0.19	1.57	0.27	1.12	0.73	0.72	4.20	-	-
17/August/2002	0.25	nd	nd	0.74	1.86	0.51	2.66	2.11	2.05	2.97	2.9	2.2
18/August/2002	0.10	nd	nd	0.20	2.00	0.31	3.54	1.01	0.98	2.60	-	-
22/August/2002	0.64	0.10	nd	0.43	1.99	1.89	3.58	5.19	5.03	3.08	5.5	4.7
27/August/2002	0.21	nd	nd	0.12	1.10	0.34	0.89	1.85	1.80	2.83	-	-
31/August/2002	nd	nd	nd	0.12	0.78	0.25	0.23	0.19	-	-	-	-
28/September/2002	1.56	0.42	2.17	4.35	8.83	2.19	22.6	19.7	19.3	2.00	-	-
06/October/2002	1.13	0.33	1.24	2.75	3.53	1.63	5.76	10.3	10.0	2.77	6.6	5.9
13/October/2002	0.35	nd	nd	0.59	1.15	1.29	1.71	2.24	2.15	3.92	-	-
08/December/2002	0.29	0.10	nd	1.17	2.00	0.21	2.32	2.05	1.93	3.65	-	-
03/January/2003	2.62	0.56	nd	6.34	2.00	6.16	6.38	2.00	1.34	32.9	4	4.4
08/February/2003	0.18	nd	nd	0.51	0.54	0.08	0.89	0.54	0.49	8.39	6.1	4.1
21/February/2003	0.13	nd	nd	0.21	0.39	0.09	0.86	0.39	0.36	8.45	3.4	1.6
06/March/2003	0.13	nd	nd	0.91	1.56	0.11	1.76	1.56	1.53	2.10	-4.3	-4.6
07/April/2003	nd	nd	nd	0.35	0.70	0.19	1.17	0.7	-	-	-	-
11/April/2003	0.10	nd	nd	0.31	0.79	0.11	1.28	1.43	1.40	1.76	2.4	2.1
18/April/2003	nd	nd	nd	0.24	0.58	0.10	0.82	0.83	-	-	3.8	-
22/April/2003	nd	nd	nd	0.44	0.54	0.09	1.14	1.37	-	-	1.7	-
29/April/2003	nd	nd	nd	0.14	0.31	0.03	0.42	0.78	-	-	4.5	-
06/May/2003	nd	nd	nd	0.19	0.33	0.04	0.69	0.86	-	-	3.3	-
24/May/2003	nd	nd	nd	0.29	0.84	0.09	1.57	0.82	-	-	3.9	-
11/June/2003	nd	nd	nd	0.51	1.01	0.13	2.54	2.31	-	-	2.9	-
23/June/2003	0.44	nd	nd	0.29	1.86	0.65	2.47	4.22	4.11	2.63	3.5	2.9
27/June/2003	nd	nd	nd	nd	0.29	nd	0.59	0.32	-	-	-	-
<i>Busan</i>												
24/June/2002	3.06	0.38	nd	0.53	nd	6.41	0.67	1.64	0.87	46.99	7.6	4.3
01/July/2002	0.29	nd	nd	0.27	nd	11.11	1.14	1.42	1.35	5.09	1.8	0.7
05/July/2002	1.88	0.22	nd	0.22	nd	12.96	0.67	1.24	0.77	38.22	-	-
13/July/2002	1.02	0.16	nd	0.68	nd	15.37	0.74	1.82	1.56	14.11	5.5	2.3
19/July/2002	0.93	0.12	nd	0.23	nd	6.28	1.03	1.84	1.61	12.73	5.4	2.5
05/August/2002	1.33	0.21	nd	0.73	nd	2.97	0.6	1.29	0.95	25.97	-	-
08/August/2002	0.36	nd	nd	nd	nd	3.12	0.39	0.79	0.7	11.56	-	-
10/August/2002	0.47	nd	nd	0.11	nd	1.60	0.49	0.83	0.71	14.22	-	-
12/August/2002	0.16	nd	nd	nd	nd	24.42	0.35	1.02	0.98	3.83	-	-
14/August/2002	0.35	2.86	nd	nd	nd	18.53	0.65	1.35	1.26	6.45	-	-
30/August/2002	23.56	0.2	1.09	1.94	nd	43.24	0.92	8.16	2.23	72.71	18.6	12.2
15/September/2002	1.15	0.47	nd	1.00	0.7	20.34	0.7	1.73	1.44	16.72	8.4	4.2
19/October/2002	3	nd	nd	1.36	1.42	15.96	2.68	4.64	3.89	16.26	7.5	3.6
08/February/2003	0.53	0.26	nd	0.22	0.62	1.13	0.43	0.62	0.49	21.53	-	-
22/February/2003	1.36	0.26	nd	1.45	1.78	1.91	2.97	1.78	1.44	19.24	-	-
01/March/2003	1.14	0.48	nd	2.26	1.3	3.80	2.03	1.3	1.01	22.08	-	-
06/March/2003	3.36	0.78	nd	1.44	0.73	5.64	0.58	0.73	0.12	115.9	-	-
14/March/2003	3.2	0.43	nd	5.16	2.91	5.56	10.32	2.91	2.1	27.69	-	-
31/March/2003	2.12	0.59	nd	1.79	1.41	31.30	4.87	1.41	0.88	37.86	-	-
07/April/2003	3.91	0.22	nd	0.83	0.62	32.76	2.19	0.62	0.36	158.8	7.6	4.7
11/April/2003	1.66	0.09	nd	0.49	0.75	20.41	1.37	4.22	3.8	9.91	-	-
18/April/2003	0.81	0.01	nd	0.26	0.28	13.41	0.72	1.81	1.61	11.27	2.9	0.6
23/April/2003	0.21	0.7	nd	0.11	0.27	2.02	0.56	1.48	1.43	3.57	1	0.3
29/April/2003	4.01	nd	nd	2.84	0.63	33.86	1.93	5.41	4.4	18.66	-	-
06/May/2003	0.24	0.21	nd	nd	0.36	1.03	0.77	1.63	1.57	3.71	1.3	0.5
14/May/2003	1.19	0.14	nd	1.8	1.71	3.99	4.24	5.27	4.97	5.69	-	-
24/May/2003	1.28	nd	nd	0.17	0.47	5.72	0.66	1.71	1.39	18.85	7.2	2.8
30/May/2003	0.36	nd	nd	nd	0.04	13.40	0.19	0.61	0.52	14.86	-	-
12/June/2003	0.17	nd	nd	0.14	0.21	10.53	0.48	1.11	1.07	3.86	3.9	3.0
16/June/2003	0.53	nd	nd	0.21	nd	4.85	0.19	0.54	0.41	24.71	-	-
23/June/2003	0.28	nd	nd	0.32	0.62	7.28	1.25	3.03	2.96	2.33	2.6	2.1
27/June/2003	0.42	nd	nd	0.29	0.61	8.28	1.07	2.46	2.35	4.3	1.9	1.0

**Table 3**

Weighted average concentration values of ions individual study areas for rain water and snow water, along with concentration to Na<sup>+</sup> ratio and enrichment factors relative seawater.

	Na <sup>+</sup>	Mg <sup>2+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>
<i>Seoul</i>						
Average	0.40	0.07	0.22	0.94	0.84	3.34
Ion/Na <sup>+</sup>	1.00	0.18	0.54	2.35	2.10	8.30
(Ion/Na <sup>+</sup> ) <sup>a</sup> <sub>sw</sub>	1.00	0.12	0.04	0.04	1.80	0.25
E.F. <sup>b</sup>	1.00	1.49	14.5	61.4	1.17	32.9
<i>Busan</i>						
Average	2.01	0.27	0.03	0.84	12.6	2.08
Ion/Na <sup>+</sup>	1.00	0.14	0.02	0.42	6.05	1.03
(Ion/Na <sup>+</sup> ) <sup>a</sup> <sub>sw</sub>	1.00	0.12	0.04	0.04	1.80	0.25
E.F. <sup>b</sup>	1.00	1.14	0.46	10.8	3.37	4.10

<sup>a</sup> Ion to sodium ratios in seawater are from Berner and Berner (2012).

<sup>b</sup> Enrichment factor relative to seawater.

the relationship between nss-SO<sub>4</sub><sup>2-</sup> and δ<sup>34</sup>S has relatively low correlation for Seoul's precipitation (Table 2, Fig. 8).

## 5. Discussion

### 5.1. Chemical composition of wet precipitation

The major dissolved elements of composition and sulfur isotopic data in urban (Seoul, Busan) rainwater are presented in Table 2. Rainwater is formed by condensing vapor in the ocean which has been purified by natural dilution (Berner and Berner, 2012). However, rain is not perfectly pure. It dissolves solid particles and gases in the atmosphere which results in a wide range in chemical composition and variations of pH. Generally, major dissolved ions in

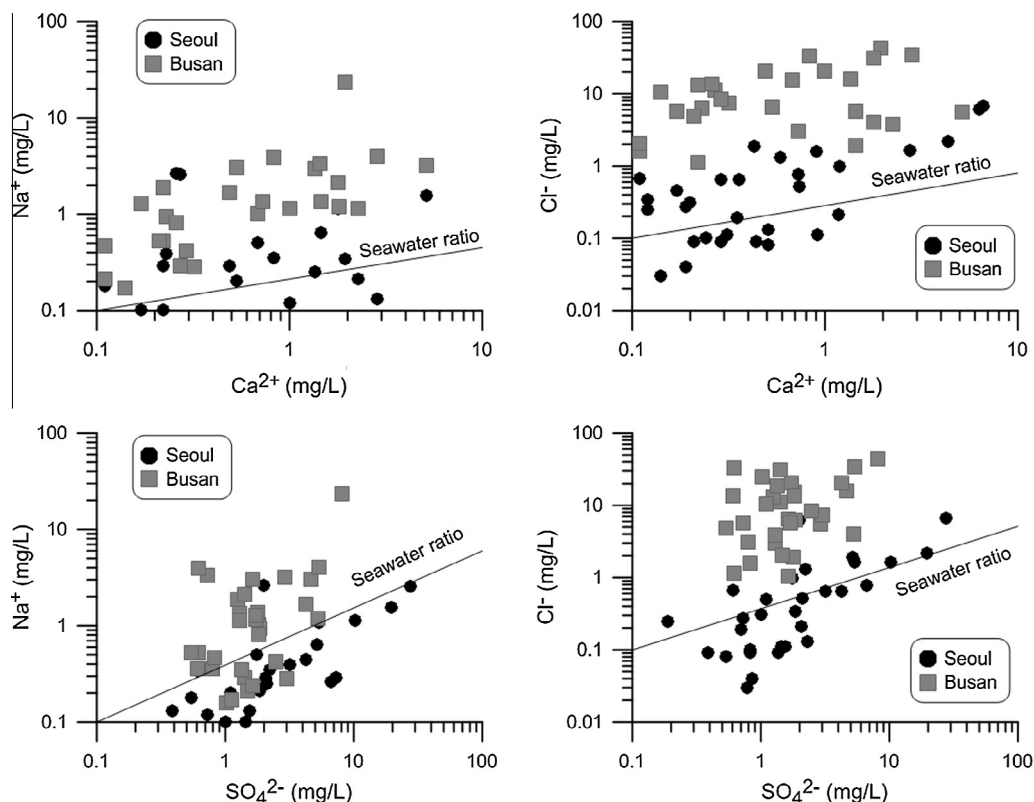
rainfall can be separated by two groups: those originating from (1) air particles (grains of dust, plant pollen, or ash from fires) and (2) atmospheric gases (nitrogen, oxygen, argon, carbon dioxide and other gases) (Junge, 1963).

Non-sea salt ion (or excess ion) can be expressed as the ratio of dissolved elements of rainwater, and reference is either dissolved Na<sup>+</sup> or Cl<sup>-</sup>. These references can be chosen depending on observation site. Generally, Na<sup>+</sup> is better choice in polluted sites such as urban area, because Cl<sup>-</sup> can be produced from pollutive HCl in industrial areas (Keene and Galloway, 1986). In this study, Na<sup>+</sup> was also used as a reference for the NSS ion value (Table 2). The NSS value of dissolved rainwater can be used to compare rainfall composition with sea salt composition. Using known sodium and chlorine weight ratio in sea water and assuming no fractionation during aerosol formation from sea water, the contribution from sea salt can be determined (Berner and Berner, 2012). The concentration of ions which are larger than sea water in proportion is referred to as *non-sea salt ion* or *excess ion* (e.g., nss-SO<sub>4</sub><sup>2-</sup>).

$$\text{nss}[\text{ion}] = [\text{ion}]_{\text{sample}} - \left( \frac{[\text{ion}]}{[\text{Na}^+]}\right)_{\text{seawater}} \times [\text{Na}^+]_{\text{sample}}$$

Calcium may primarily originate from the dissolution of calcium carbonate (CaCO<sub>3</sub>) or dolomite (CaMg[CO<sub>3</sub>]<sub>2</sub>) in soil dust and partly derived from road salt (CaCl<sub>2</sub>) in winter.

The sources of atmospheric ammonia are mainly biological decomposition of animal and human excreta, use of fertilizer and biomass burning. The collected ammonium ion in the sampling area, Seoul, is dominant in major ions. The Seoul is largest city and has ten millions population and three million motor vehicles. It suggests that most of ammonia is excreted from vehicle operation which is generally separated by a minor source. The sampling area is geographically included in Seoul but located around a



**Fig. 4.** Relationship between Ca<sup>2+</sup> versus Na<sup>+</sup>, Ca<sup>2+</sup> versus Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> versus Na<sup>+</sup>, and SO<sub>4</sub><sup>2-</sup> versus Cl<sup>-</sup> concentration, respectively, for the precipitation in Seoul (black circles) and Busan (gray squares). The solid line denotes 1:1 of ion concentration.

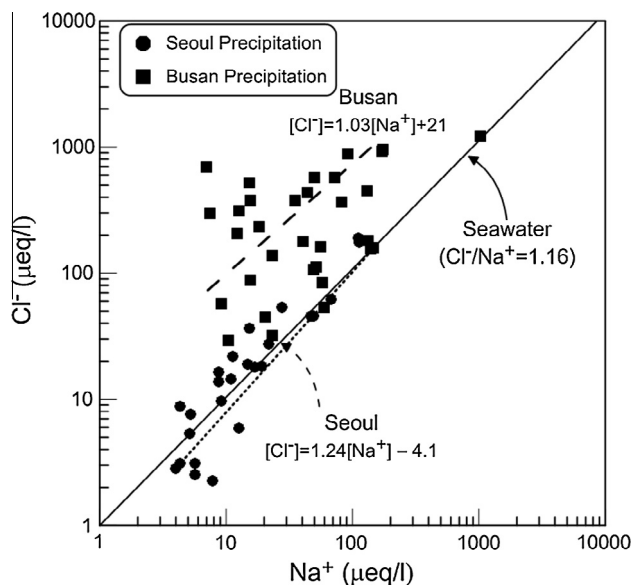


Fig. 5. Relationship between the concentration of  $\text{Na}^+$  and  $\text{Cl}^-$ . The regression line between  $\text{Na}^+$  and  $\text{Cl}^-$  in Seoul and Busan are indicated by broken line. The solid line shows the ratio of the concentration of  $\text{Na}^+$  and  $\text{Cl}^-$  in sea water (Nozaki, 1992).

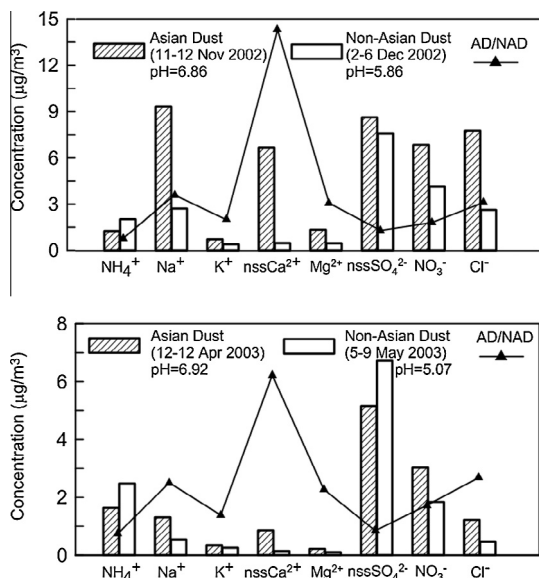


Fig. 6. Diagram for chemical composition of Asian dust and Non-Asian dust observed in Fall, 2002 and March, 2003 in Seoul, Korea.

mountain. Therefore ammonium contributions from biological activity cannot be ignored in that sampling area. Ammonium in summer was a predominant due to more biological activity than other seasons in Seoul (Fig. 3).

The two largest sources of sulfate in rain are sea-salt aerosol and sulfur dioxide from fossil fuel combustion. Other important sources include biogenic reduced sulfur gas such as  $\text{H}_2\text{S}$  and volcanic emission of sulfur dioxide. The value of non-sea salt (NSS) ion and sulfate ions in Seoul's precipitation may originate from fossil fuel combustion. It is also the principal indicator of worldwide atmospheric pollution. The  $\text{SO}_2$  forms during combustion from the oxidation of sulfur contaminants such as pyrite ( $\text{FeS}_2$ ) in coal and organic sulfur compounds in both coal and oil. It is effectively removed from the atmospheric sulfur through the formation of precipitation, or it may be injected into the gas phase through

evaporation processes. A representative pollution,  $\text{SO}_4^{2-}$  in the atmosphere in urban area also shows a similar relationship with  $\text{Na}^+$  and  $\text{Cl}^-$  concentrations in Seoul (Fig. 4). In Busan, sodium and chlorine were mainly derived from marine sources. Relationships between  $\text{Na}^+$  and  $\text{Cl}^-$  concentration in both sampling areas are positive in both cities due to dilution effects when washed out by rainfall (Fig. 5). Even though Busan is mainly influenced by marine source, the contribution from anthropogenic source cannot be ignored.

## 5.2. Chemical composition of Asian dust

The pH of Seoul's precipitation samples are in a range of 4.4–7.1 averaging 5.3. It is also found to be higher than pH value given by ( $4.7 \pm 1.4$ ) (Lee et al., 2000) due to different methods of getting samples and the yellow sand dust phenomenon in early spring (Table 1).

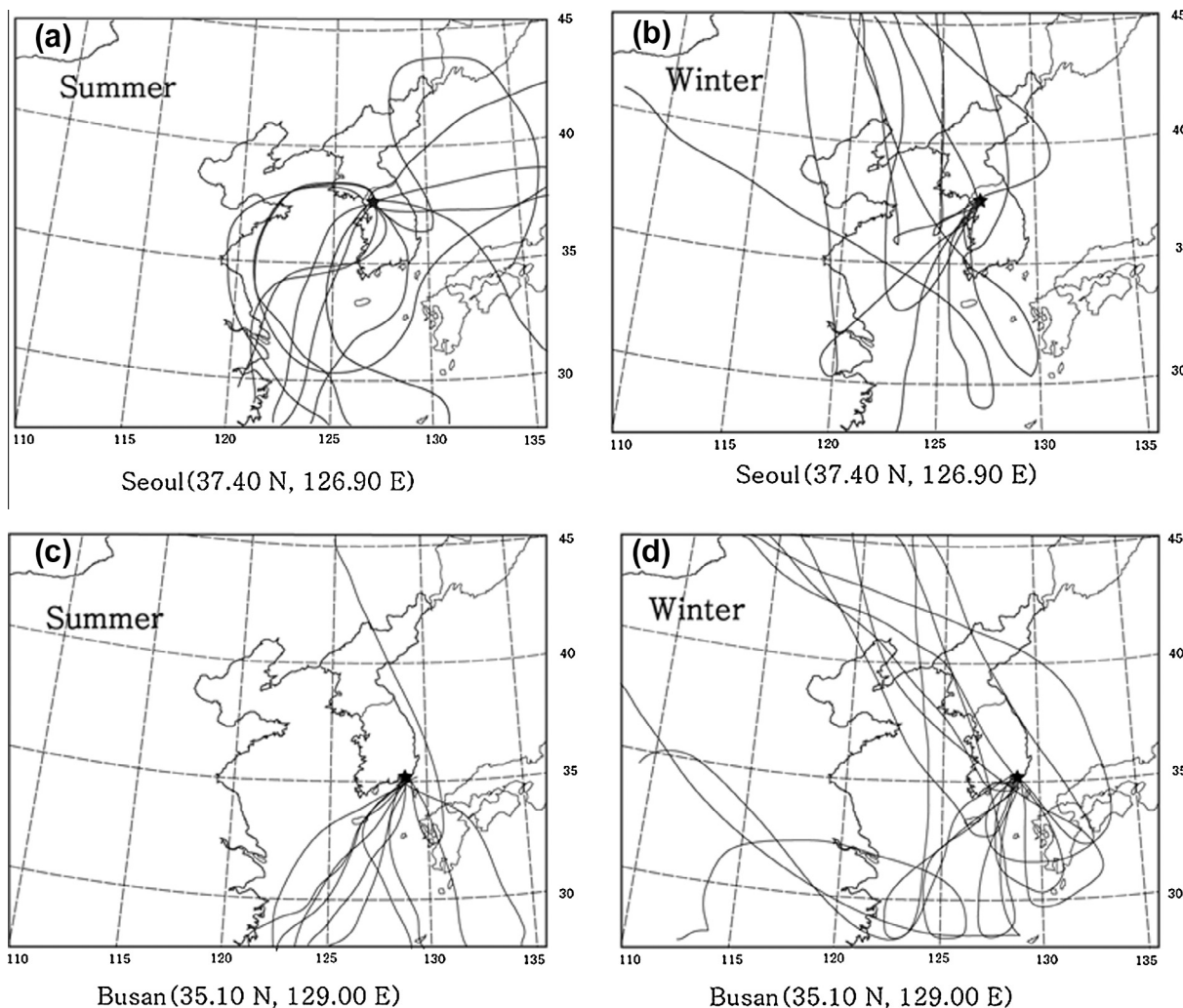
The rain collected on 21th February 2003 is slightly acidic (pH 4.4) whereas spring season precipitation indicates a pH of about 6.5 (see Table 1). This variation in the pH values is attributed to the intensity of rainfall received and the yellow sand phenomenon prevailing in spring time. The dust-rich environment due to yellow sand dust and congested traffic might have the lower levels of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in the precipitation in spring in Seoul (Fig. 3).

Spring time of this year is a remarkable season to observe the yellow sand phenomenon in the Seoul area. In particular, most of the phenomenon tends to occur in spring. However, the yellow sand phenomenon was observed from almost in whole county of Korea in early spring of May, 2002. The result showed the characteristic feature of the synoptic system associated with yellow sand phenomena, that is, the wind was remarkably intensified in the source region. A trajectory analysis showed that the yellow sand particle could reach Seoul within 2 days from the source region, Gobi desert, through Loess plateau and Loess deposition region (Fig. 7). The pH and alkali ion concentration of Seoul abruptly increased above the mean concentration during the yellow sand phenomenon (Table 1). After yellow sand phenomenon, there was heavy snow and rain-water in Seoul. By the analysis of XRF in aerosol collected during that time, it was observed that amount of  $\text{K}_2\text{O}$ ,  $\text{Na}_2\text{O}$ ,  $\text{CaO}$ ,  $\text{Al}_2\text{O}_3$  were over 90% very close to the reported values (Fujita et al., 2000).

## 5.3. Change in air mass travel distance

The history of the air mass trajectories for all 68 of our samples in Seoul and Busan are evaluated using modified backward trajectories before reaching the sampling site depend on seasonal variation (Fig. 7). To control whether our samples are representative for the time of the year, we calculated trajectories for every week during the summer and winter both cities. By comparing the different seasons we find a change in moisture source just before the onset of the air-mass. Two major source regions in Seoul and Busan are found, one over the continent (central Asia and Northern China) during the summer (Fig. 7(a and c)), and one over the southern China and Pacific Ocean during the winter in Seoul and Busan (Fig. 7(b and d)). These two sources have distinct trajectories between summer and winter. The winter air is likely characterized by being directed from "continental" moisture, while the maritime airs from the ocean come during the summer (Fig. 7(b and d)). Pre-monsoon and early-winter rain stems largely from the northern china, while later in the winter season the transport pathway moves to the Pacific Ocean (Fig. 7(a and c)).





**Fig. 7.** Modified Backward trajectories at NOAA HYSPLIT MODEL for air masses ([www.arl.noaa.gov/ready/hysplit4.html](http://www.arl.noaa.gov/ready/hysplit4.html)). (a) summer, 2002 in Seoul; (b) winter, 2002–2003 in Seoul; (c) summer, 2002 in Busan; (d) winter, 2002–2003 in Busan.

#### 5.4. Seasonal characteristic and sources of sulfur

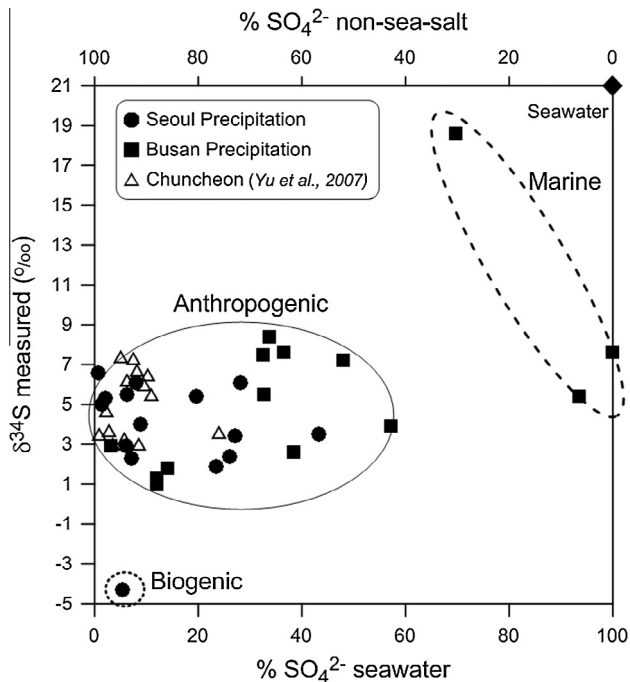
Sulfur isotopic composition of precipitation in other countries and this study is presented in Fig. 9. Isotopic composition of  $\text{SO}_4^{2-}$  may not depend on wind provenance (Fig. 8). The precipitation shows negative correlations between  $\text{SO}_4^{2-}$ ,  $\delta^{34}\text{S}$  and rainfall amount due to a dilution effect during increasing rainfall intensity in both of study areas.

The measurements point to a primary anthropogenic sulfate in the precipitation at urban areas. Based on  $\delta^{34}\text{S}$  in both study areas, most sources of sulfate in precipitation are from anthropogenic sources. Even though both cities are in heavily urban areas, Busan is affected more by sea salt than Seoul. The observed isotopic composition in Seoul is similar to  $+0.5\text{‰} \sim +5.5\text{‰}$ , reported by Ohizumi et al. (1991) in Tokyo and Nagoya, which were very industrial and urbanized cities.

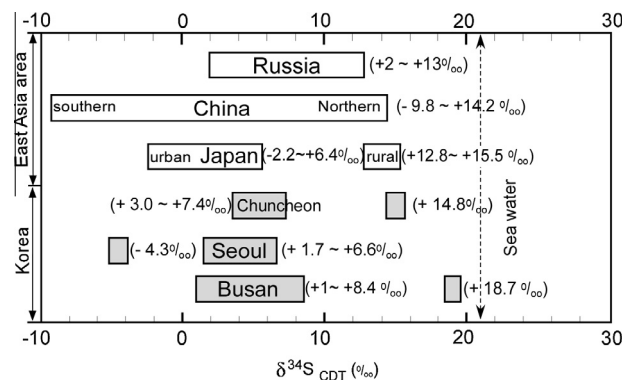
The isotopic values and sources of sulfur in precipitation consist of diverse sources such as 21‰ from sulfates of seawater, 3.4‰ from  $\text{H}_2\text{S}$  of land and seawater, 2.5‰ from volcano gas and 0–10‰ from anthropogenic  $\text{SO}_4^{2-}$  of fossil fuel combustion (Sasaki et al., 1979). During the period of this study, no volcanic activities are reported around the study areas, so this parameter can be removed. The  $\delta^{34}\text{S}$  values of organic S in coal from Gangwon province, Korea is known to contain less than 1% total sulfur with a

value of  $-2.4\text{‰}$ , which falls within the range ( $-10.0 \sim +1.6\text{‰}$ ) of pyrite from oal mines in Korea (Yu and Coleman 2000). The  $\delta^{34}\text{S}$  value of Bunker C crude oil (one representative oil sample used in Korea: measured in this study) which contains less than 4% total sulfur has a low value of about  $-6\text{‰}$ . For fossil fuels in China and Japan, the concentrations of organically bound S in petroleum vary within limits of 0.1–10%. The  $\delta^{34}\text{S}$  values of petroleum span a range from 7.2‰ to 24.2‰ in northern China, and from 13.7‰ to 20.6‰ in southern China (Ohizumi et al., 1991; Maruyama et al., 2000). The isotopic composition of S in coal varies widely from  $-27.3\text{‰}$  to 28.9‰ in northern China, from  $-3.1\text{‰}$  to 10.3‰ in southern China, and from  $\delta^{34}\text{S} = -2.2\text{‰}$  to 9.4‰ in Russia (Hong et al., 1993; Maruyama et al., 2000). In general,  $\delta^{34}\text{S}$  of petroleum gas indicates a lower value than coal.  $\delta^{34}\text{S}$  value of  $\text{SO}_2$  when burning petroleum gas was  $+4.4\text{‰}$  (Kajiwara and Sasaki, 1987) whereas coal shows various values of  $\delta^{34}\text{S}$  depending on the areas. In this study, both of the study areas show that sources of sulfur in precipitation are derived from anthropogenic fossil fuel combustion while the range of isotopic sulfur values in Seoul is narrower than that of Busan (Fig. 8).

It may be considered to derive from DMPo (dimethyl polonide) of sea spray which belongs to sulfur group like DMS (dimethyl sulfide) (Kim et al., 2005). It suggests that Busan area is more affected by marine source compared to Seoul area. On the other hand, the



**Fig. 8.** Plot of  $\delta^{34}\text{S}$  against the concentration of the  $\text{SO}_4^{2-}$  in precipitation from Seoul and Busan. The broken circles show the sources of sulfur isotopic values on 21‰ from sulfates of seawater, -5‰ from biogenic sources. And the solid circle ranges shows 0–10‰ from anthropogenic  $\text{SO}_4^{2-}$  of fossil fuel combustion (Sasaki et al., 1979).



**Fig. 9.** Sulfur isotopic compositions of the wet precipitation in Seoul and Busan and reference area in Chuncheon (Yu et al., 2007), Korea and compare to other East Asia (Maruyama et al., 2000).

range of sulfur isotopic value in Seoul area is very narrowly correlated with NSS sulfate concentration which mainly originates from human activity. It suggests that Seoul area is affected by anthropogenic source. The variation of isotopic sulfur value depends by season slightly in both of the study areas. In the spring season of biologically large production, the isotopic sulfur value is a little lower than other seasons. Anthropogenic sulfur source which is mostly derived from fossil fuel combustion can be identified to analyze each sulfur-bearing of fossil fuel which is combusted into the atmosphere such as coal and petroleum. The resource dependence of Korea on foreign countries is very high; most of its fossil fuels is imported from other countries. For example, the isotopic composition of sulfur values can change depending on countries of origin and their refining techniques.

In this study, plots between prevailing wind direction and sulfur isotope value of  $\text{SO}_4^{2-}$  in precipitation were not perfectly

correlated. Our neighboring country, China, is accelerating its development of industry in the East Asia. Even though this relationship is not obvious to trace the origins, sources of dissolved total sulfate in precipitation is not interpreted only to come from local source (Fig. 9). In addition to this kind of study, basic data through neighboring countries and systematic monitoring will be able to trace contaminant sources.

## 6. Conclusions

Experiments to trace and evaluate air pollution in urban precipitation were carried out in Seoul and Busan for 13 months from June 2002 to June 2003. The isotopic sulfur values of dissolved sulfate in precipitation range from -4.3‰ to +6.6‰ in Seoul and from +1.0‰ to +18.6‰ in Busan. Most of sulfur isotopic values of both of study areas show the evidence of anthropogenic sulfur values; however  $\delta^{34}\text{S}$  value of Busan signifies the wide spread trend likely due to influence of seawater sulfate. The total sulfur of dissolved sulfate in precipitation in both study areas cannot be interpreted only to come from local sources because the atmospheric pollutants are able to transport ions hundreds of kilometers in aerosol form in the atmosphere. Precipitation shows negative correlations between  $\text{SO}_4^{2-}$ ,  $\delta^{34}\text{S}$  and rainfall amount due to dilution effect in both of study areas. It suggests that small precipitation can remove most of the pollutants from the atmosphere and initial rain events are much important in the elimination of air pollution. The sulfur isotopic value of precipitation is a very useful tracer for air pollution in the atmosphere, while measurements of each sulfur-bearing source should be preceded effectively.

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