Studies on Pollution Characteristics and Sources of Precipitation in Jeju Island

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Abstract

The pH, electric conductivity, and the major ionic components were analyzed for the precipitation samples collected at 1100 Site of Mt. Halla and Jeju city. The quality of analytical data was verified by the comparison of ion balances, conductivities and acid fractions, all of which correlation coefficients were over 0.952. The ionic strengths lower than 10^{-4} M were found in 57 and 28% at 1100 Site and Jeju city respectively. The precipitation in Jeju city was influenced more by the oceanic effect than those in 1100 Site. The acidification of precipitation was caused mostly by SO_4^{2-} and NO_3^- in both areas, and the organic acids have contributed to the acidity with only 7~8%. The neutralization factors by NH_3 were about 44 and 47% at the 1100 site and the Jeju city, respectively, whereas those by $CaCO_3$ were 21 and 24%, and the free acidity were about 38 and 28% at two sites. From the investigation of seawater and soil enrichment factors, the SO_4^{2-}, NO_3^- and NH_4^+ were immigrated by other sources rather than from the seawater or soil origins, but not in the case of Mg^{2+}, Cl^-, Na^+, and K^+. Factor analysis has shown that the precipitation at the 1100 site had been influenced mostly by anthropogenic sources, followed by soil and seawater sources. On the other hand, the precipitation at the Jeju city was mainly influenced by oceanic sources, followed by anthropogenic and soil sources.

Key words : Precipitation, Ionic strength, Acid fraction, Neutralization factor, Factor analysis, Jeju Island

1. INTRODUCTION

The sulfur species and the oxides of nitrogen emitted mostly from combustion of fossil fuels are changed to strong acids with the reactions of ozone, hydrogen peroxide, peroxides and hydrocarbons, and they act as a great part of pollutants in precipitation. Besides, MSA (methanesulfonic acid) as well as organic acids causes the precipitation to be acidic, but its contribution to acidification is relatively low compared to the

sulfur species and the oxides of nitrogen. On the other hand, it has been reported that the contribution of organic acids, existed in ambient air mostly with gas phase, has grown higher at the remote and clean areas in tropical regions (Galloway *et al.*, 1989; Keene *et al.*, 1988). Also it has been found that MSA originated from oceanic DMS (dimethyl sulfide) usually exists in fine particles lower than 2.0 μm, and cause acidic precipitation partially after being dissolved in rainwater (Hansen and Eatough, 1991).

The recent increases of fossil fuel consumption and fast industrialization cause the acid precipitation to a serious level as well as emission of various air pollu-

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tants. Especially the extreme amount of air pollutants has been produced in the East Asia region due to high population growth and increase of energy consumption. By Bhatti *et al.* (1992), it has been reported that SO_2 emitted from the East Asia region in 1990 was 2.9 million tons but it would be about 7.5 million tons in 2010, which is much larger than the estimated sum of SO_2 production in Europe (3.9 million tons) and the United States (1.6 million tons). In the East Asia region, China is spotted to be the country that produces the largest amount of air pollutants due to the rapid industrial development. The China's SO_2 emissions have grown by about three times over the past two decades, and it is anticipated that in 2020 it will be three times more than that in 1990 (An *et al.*, 2002; Arndt *et al.*, 1998; Carmichael *et al.*, 1997). It is because about 76% of the total fuel usage is coal, and the coals in China are mostly high sulfur coal. Especially, the large amount of SO_2 emitted from industrial complexes residing at the eastern region of China could be delivered by long−range transportation in prevailing westerlies (Carmichael *et al.*, 2002; Moon *et al.*, 1999), so that it is expected to cause the serious acidic precipitation rapidly in Korean peninsula. In order to study the transportation and their effects of air pollutants originated from nearby countries, the air pollutants should be monitored at a background site with few pollution sources in itself. Jeju island is a remote and clean area in Korea, and is located at the middle of China and Japan, so that it is very suitable for monitoring long−range transported air pollutants from nearby countries and studying their effects (Arimoto *et al.*, 1996; Carmichael *et al.*, 1995). Therefore, consistent measurement of various air pollutants in Jeju area should be necessary (Ro *et al.*, 2001; Kim *et al.*, 1998a, b, 2000; Chen *et al.*, 1997), and the precise characteristic analysis of precipitation must also be performed in this area.

In this study, the precipitation samples were collected at the 1100 site in Mt. Halla and the Jeju city, then the pH and electric conductivity were measured, and the major ionic components were chemically analyzed.

Finally the pollution characteristics and its some source origins of the precipitation have been discussed (Kang *et al.*, 1999).

2. EXPERIMENTAL METHODS

2. 1 Collection of precipitation samples

The precipitation samples were collected at the 1100 site in Mt. Halla (33° 21′N, 126° 27′E) and the Jeju city (Cheju National University building, 33° 26′N, 126° 33′E) simultaneously. An automated rain sampler (Shinil Science, model SL−4−001, wet−only) equipped with a rain sensor was used at the 1100 site, which had a funnel of 253 mm in diameter and its cover was open automatically when rain starts. The funnel of sampler was rinsed with ultra−pure water each time after collecting sample bottles. Total of 145 precipitation samples were collected from the 1100 site in every week−base or each rain event base; 34 samples in (1997, 38 in 1998, 37 in 1999, and 36 in 2001. A manual type rain sampler (337 mm diameter, polyethylene material) was used for the Jeju city samples from October 1996 to May 1997, and the automated rain sampler same as in the 1100 site was used. Total of 263 precipitation samples were collected from the Jeju city site; 9 samples in 1996, 62 in 1997, 51 in 1998, 51 in 1999, 43 in 2000, and 47 in 2001. The collected precipitation samples were moved to the laboratory, and then the pH and electric conductivity were measured immediately from a portion of samples. The remaining precipitation samples were divided into two fraction parts. One aliquot was stored in a deep freezer at −20°C without pre−treatment to be analyzed for major eight ions, and the other aliquot was stored at the same temperature after adding a drop of chloroform for the analysis of organic acids and MSA. They were melted and warmed up to 20°C just before the chemical analyses have been performed (Keene *et al.*, 1988, 2002).

2. 2 Chemical analysis of precipitation samples

The pH and electric conductivity were measured at

Table 1. Instrumental conditions of ion chromatographic analysis.

Components	SO_4^{2-}, NO_3^-, Cl^-	$HCOO^-$, CH_3COO^-, $CH_3SO_3^-$, F^-	NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}
Instrument	Dionex DX-500, Metrohm Modula IC	Dionex DX-500	Metrohm Modula IC
Column	IonPac AG4A-SC/AS4A-SC, Metrohm Metrosep A-SUPP-4	IonPac AG11/AS11	Metrohm Metrosep Cation 1-2-6
Eluent	2.4 mM Na_2CO_3/2.25 mM $NaHCO_3$, 1.8 mM $NaHCO_3$/1.7 mM Na_2CO_3	0.25 mM NaOH/ 5 mM NaOH	4.0 mM tartaricacid/ 1.0 mM pyridine-2,6- dicarboxylic acid
Injection Volume	50 μL, 100 μL	25 μL	20 μL
Flow Rate	1.0 mL/min	2.5 mL/min	1.0 mL/min

the constant temperature of 20~25°C using the pH meter (ORION, model 720A with model 81-02 electrode) and conductivity meter (TOA, model CM-11P with CVP-101P electrode or ORION, model 105 with 011050 electrode). The atomic absorption spectrophotometer (GBC, model Avanta-P) has been used for the analysis of Na^+, K^+, Ca^{2+}, Mg^{2+} cations, and the indophenol method was applied for NH_4^+ analysis. The SO_4^{2-}, NO_3^- and Cl^- anions were analyzed by the ion chromatographic method (Dionex, model DX-500 IC with IonPac AG4A-SC/IonPac AS4A-SC column), and the analytical conditions were described in Table 1. The micro-components of F^-, $HCOO^-$, CH_3COO^- and $CH_3SO_3^-$ in precipitation were also analyzed by IC (Dionex, model DX-500 IC with IonPac AG11/IonPac AS11 column), and the analytical conditions were described in Table 1 (Kieber et al., 2002; Andreae et al., 1987; Jaffrezo et al., 1998; Hofmann et al., 1997). While, all ionic components of total 84 samples collected in 2001 have been analyzed simultaneously by the ion chromatographic method, which was the system combined two sets of Metrohm Modula IC with one autosampler. This system makes it possible to analyze all cations and anions at the same time with one time injection of samples. For the analysis of NH_4^+, Na^+, K^+, Ca^{2+}, and Mg^{2+} cations, the Metrohm Modula IC with Metrohm Metrosep Cation 1-2-6 column was applied. For the analysis of SO_4^{2-}, NO_3^- and Cl^- anions, same type IC with Metrohm Metrosep A-SUPP-4 column was used, and the con-

ditions were showed in Table 1.

3. RESULTS AND DISCUSSION

3. 1 Quality control of analytical data

3. 1. 1 Ion balance comparison

The precipitation samples generally have similar matrices and corresponding components, so that their analytical data are in good confidence when the ion balance (i.e., the correlation coefficient between the sum of cation equivalent concentrations and the sum of anion equivalent concentrations) is high within a reasonable degree. From the analytical data of precipitation samples collected in the 1100 site and the Jeju city, the sum of cation equivalent concentrations and the sum of anion equivalent concentrations were calculated, and their correlation as well as the imbalance (%) (Shim et al., 1994; Miles et al., 1982) were shown in Table 2. The correlation coefficient (r) showed good linearity with the value of 0.979 and 0.982 at the 1100 site and the Jeju city respectively. The imbalance showed 74% of total data below 20%-imbalance, and the analytical data were confirmed to be in good confidence.

3. 1. 2 Conductivity comparison

The electric conductivity of precipitation depends on the concentrations of ionic components, when the concentrations of ionic components in solution are very

Table 2. Data quality control parameters and % imbalance.

Regression results		% imbalance[1]	
1100 Site			
Number of points	145	<10% imbalance	64
Slope	0.972	10–20% imbalance	34
Intercept	2.984	20–50% imbalance	39
Correlationcoefficient (r)	0.979	>50% imbalance	8
Jeju City			
Number of points	263	<10% imbalance	110
Slope	0.897	10–20% imbalance	93
Intercept	10.747	20–50% imbalance	53
Correlationcoefficient (r)	0.982	>50% imbalance	7

[1] % imbalance = $(T_{Cation} - T_{Anion}) \times 100 / (T_{Cation} + T_{Anion}) \times 0.5$

low so that the ionic interactions are ignored. That is, in the solution with ionic strength lower than 10^{-4} M, the electric conductivity of precipitation can be calculated using the analytical ion concentrations and the each ionic component (Sequeira et al., 1995). This method can be applied to the theoretical conductivity calculation within a relatively small error limit, because its ionic concentrations are quite low in a great part of precipitation samples. Also the confidence of analytical data can be evaluated indirectly comparing the above calculated conductivity to the experimentally measured one. From the correlation comparison between the calculated and measured conductivities of our analytical data, the correlation coefficient showed 0.993 and 0.989 at the 1100 site and the Jeju city, respectively.

3. 1. 3 Acid fraction comparison

The theoretical calculation for the acid fraction (AF) of ions dissolved in precipitation is possible by the equation (1) with knowledge of the concentrations of cations and anions as well as hydrogen ion. Also the measurements of conductivity and pH are used to calculate the acid fraction by the equation (2) with concentration–weighted mean equivalent conductivity (Kramer et al., 1996; Peters and Klemm, 1989). Therefore, the confidence of analytical data can be evaluated by comparison between the AF values calculated from two different methods.

$$AF = \frac{[H^+]}{[Cat] + [H^+]} = \frac{[H^+]}{[An]} \tag{1}$$

$$AF = \frac{\overline{\Lambda}_{eq_{Cat}} + \overline{\Lambda}_{eq_{An}}}{\left(\dfrac{\sigma}{[H^+]}\right) - \Lambda_{eq_{H^+}} + \overline{\Lambda}_{eq_{Cat}}} \tag{2}$$

In equation (2), $\overline{\Lambda}_{eq_{Cat}}$ and $\overline{\Lambda}_{eq_{An}}$ are the concentration –weighted mean equivalent conductivity of cations and anions respectively, and $\Lambda_{eq_{H^+}}$ is the equivalent conductivity of H^+. The correlation between two acid fractions calculated from each different method has shown that the correlation coefficients were 0.952 and 0.969 at the 1100 site and the Jeju city respectively, so that the confidence of analytical data in this study represented a good result.

3. 2 Analytical results of precipitation

The electric conductivities and pH for total 408 precipitation samples collected at the 1100 site and the Jeju city have been measured, and the analytical results of major ions were compared with those from other areas as shown in Table 3 (Lee et al., 2000; Seto et al., 2000; Tanner, 1999). The H^+ concentration was obtained from pH measurement and also the HCO_3^- concentration was also calculated from the relation $[HCO_3^-] = 10^{(pH-11.3)}$ (Avila, 1996; Stumm et al., 1981). The volume–weighted mean pH value was 4.93 and 4.85 at the 1100 site and the Jeju city, respectively, showing relatively week acidic precipitation during the period of this study, and the volume–weighted mean conductivity was (12.6 µS/cm and 21.1 µS/cm at two sites, respectively. From the measurement of ionic strengths of precipitation as shown in Fig. 1 and Fig. 2, the mean ionic strength was 0.15 ± 0.17 mM and 0.23 ± 0.23 mM at two sites, respectively, showing that 57% of the 1100 site precipitation and 28% of the Jeju city were below 10^{-4} M which is considered as a criterion of pure rainwater (Sequeira et al., 1995). The equivalent concentrations of major ionic components were in the order of $Cl^- > Na^+ > SO_4^{2-} > NH_4^+ > H^+ > NO_3^- > Mg^{2+} > Ca^{2+} > K^+ > HCOO^- > CH_3COO^- > F^- > HCO_3^- > CH_3SO_3^-$ at the 1100 site, and $Cl^- > Na^+ >$

Table 3. The pH, conductivity (μS/cm) and volume-weighted mean concentrations (μeq/L) of rainwater ions.

Components	1100 Site	Jeju City	Seoul[1]	Chunchon[1]	Anmyon[1]	Hong-Kong[2]	Hiroshma[3]
pH	4.93	4.85	4.7	4.7	4.6	4.24	5.0
Conduct.	12.6	21.1	–	–	–	–	–
H+	11.9	14.3	21.3	20.7	26.0	57.7	9.8
NH4+	13.1	18.3	66.4	37.4	34.6	–	29.9
Na+	27.5	63.8	10.5	7.0	31.0	44.0	17.7
K+	2.5	5.0	3.5	3.4	3.4	3.5	1.2
nss-Ca2+	4.1	7.5	34.4	22.5	19.7	11.2	10.0
Mg2+	6.6	15.1	6.9	5.0	10.7	9.7	5.7
nss-SO4^2-	21.5	27.4	69.6	44.9	41.5	82.8	40.2
NO3-	8.9	16.0	29.9	23.6	17.9	30.6	15.5
Cl-	28.3	66.2	18.2	12.9	43.9	47.3	29.7
F-	0.6	0.8	–	–	–	–	–
HCO3-	0.4	0.4	–	–	–	–	–
HCOO-	1.6	2.0	–	–	–	–	–
CH3COO-	1.2	1.3	–	–	–	–	–
CH3SO3-	0.03	0.04	–	–	–	–	–

[1] Precipitation in Seoul, Chunchon and Anmyon Island during the period from May 1996 to April 1998 (Lee et al., 2000).
[2] Precipitation in Hong Kong during the period from March 1994 to April 1995 (Tanner, 1999).
[3] Precipitation in Hiroshima during the period from April 1984 to March 1988 (Seto et al., 2000).
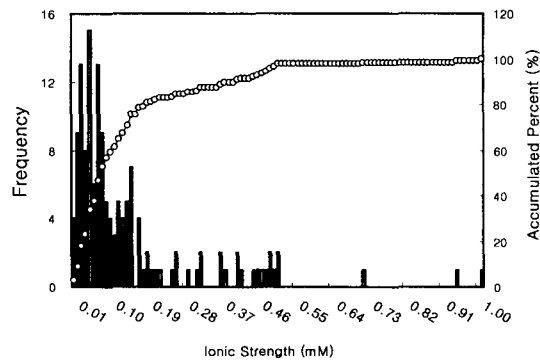

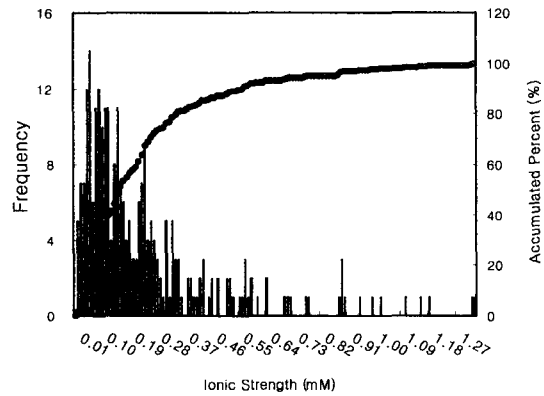Fig. 1. Frequency distributions of the ionic strength in precipitation at 1100 Site of Mt. Halla.

Fig. 2. Frequency distributions of the ionic strength in precipitation at Jeju city.

$SO_4^{2-} > NH_4^+ > NO_3^- > Mg^{2+} > H^+ > Ca^{2+} > K^+ >$ $HCOO^- > CH_3COO^- > F^- \approx HCO_3^- > CH_3SO_3^-$ at the Jeju city, indicating a similar pattern except only the reverse order of H^+ and NO_3^-. On the basis of ionic composition, Na^+, Cl^- and Mg^{2+} occupied 47% of all the precipitation components at the 1100 site, but 59% of those at the Jeju city, so it implied that the precipitation at the Jeju city was more influenced by the ocean. On the other hand, it was found that NH_4^+, SO_4^{2-} and NO_3^- occupied 10%, 19% and 7% of all the precipita-

tion components at the 1100 site, and 7%, 14% and 6% at the Jeju city. In general, it has been known that NH_4^+ and Ca^{2+} have the highest concentrations among the precipitation components at most large cities or high altitude areas, however this was not the same case in Jeju island.

3. 3 Seasonal variations of ionic concentrations

The seasonal variations of major ionic concentra-

tions in precipitation were investigated as shown in Figs. 3 and 4. The concentrations of H^+, NO_3^- and $nss-SO_4^{2-}$(non-sea-salt SO_4^{2-}), which are the components originated from various human activities, were in the order of winter > spring > fall > summer at both sites. The concentrations of NH_4^+ were in the same order as the above ions at the Jeju city, but the highest in fall season as in the order of fall > spring > winter > summer at the 1100 site. On the other hand, the concentrations of $nss-Ca^{2+}$ originated from soil sources, were the highest in spring, followed by winter season at the both sites. The concentrations of sea salt com-

Fig. 3. Seasonal comparisons of H^+, NH_4^+, $nss-SO_4^{2-}$, NO_3^- and K^+ concentrations between 1100 Site and Jeju city.

Fig. 4. Seasonal comparisons of Na^+, Cl^-, Mg^{2+} and nss $-Ca^{2+}$ concentrations between 1100 Site and Jeju city.

ponents Na^+, Cl^-, Mg^{2+} were in the order of winter > spring > fall > summer at the 1100 site and winter > fall > spring > summer at the Jeju city. Usually the wind directions in Jeju island are monitored as northwest in spring, southeast in summer, northeast in fall, and north in winter season (Carmichael et al., 1997). The concentration increase of most ionic components usually in winter and spring seasons could be reasoned from the possibility that the pollutants delivered by long-range transport from the Asia continent have affected the atmosphere in Jeju area, rather than by local emission of air pollutants. Especially, it may be reasonably supported by the fact about the increase of H^+, NO_3^-, SO_4^{2-} concentrations in winter and spring, and the increase of Ca^{2+} concentration in spring at the background area of the 1100 site in Mt. Halla.
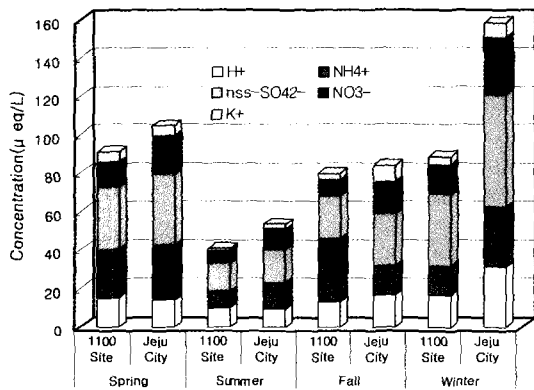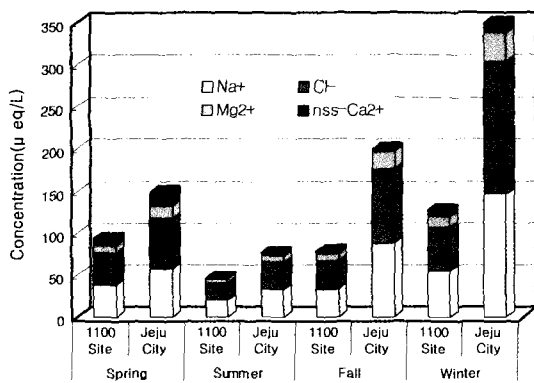
3. 4 Acidification of precipitation

The sums of cation and anion equivalent concentrations in the 1100 site and the Jeju city precipitation were compared in Table 4. The sum of cationic concentrations and the sum of anionic concentrations should be the same if the acidification of precipitation occurred only by the components shown in Table 4. However the sum of anionic concentrations was higher than those of cations at both sites. It might be explained because there was an error from the pH measurement or the analysis of basic cations and otherwise any other components would have contributed to the neutralization (Legrand et al., 1996, 1998). Especially, other sea salt basic components could have affected to the neutralization in precipitation (Galloway et al., 1989), since the Jeju island is very much influenced by the ocean. The relative composition ratios of major five acidic anions showed that the inorganic acid ions (i.e., $nss-SO_4^{2-}$ and NO_3^-) have contributed to the acidification of precipitation by 90% at the 1100 site and 91% at the Jeju city. It suggests that H_2SO_4 and HNO_3 are the most possible contributors to the acidification of precipitation in Jeju area. On the other hand, HCOOH and CH_3COOH have contributed by 7~8% each, so it was confirmed that the contribution of organic acids to

Table 4. Volume-weighted mean concentrations (μeq/L) of protons, possible proton donors and neutralizing substances in rainwater.

1100 Site				Jeju City			
Cations		Anions		Cations		Anions	
H^+	11.9	$nss-SO_4^{2-}$	21.5	H^+	14.3	$nss-SO_4^{2-}$	27.4
$nss-Ca^{2+}$	4.1	NO_3	8.9	$nss-Ca^{2+}$	7.5	NO_3^-	16.0
NH_4^+	13.1	F^-	0.6	NH_4^+	18.3	F^-	0.8
Total	29.1	$HCOO^-$	1.6	Total	40.1	$HCOO^-$	2.0
		CH_3COO^-	1.2			CH_3COO^-	1.3
		Total	33.8			Total	47.5

the acidification of precipitation was not so significant in this area (Khare et al., 1997).

3. 5 Neutralization of precipitation

The neutralization factors among major acidic and basic components were calculated from the following equations (Galloway et al., 1989), where [nss-SO$_4^{2-}$], [NO$_3^-$], [NH$_4^+$], and [nss-Ca^{2+}] were the equivalent concentrations of each component. And the calculated neutralization factors are shown in Table 5.

$$NF_{NH_4^-} = \frac{[NH_4^+]}{[nss-SO_4^{2-}] + [NO_3^-]}$$

$$NF_{Ca^{2+}} = \frac{[nss-Ca^{2+}]}{[nss-SO_4^{2-}] + [NO_3^-]}$$

It has been shown that NH$_3$ has more contributed to the neutralization of precipitation than CaCO$_3$, such that the neutralization factors by NH$_3$ were 44% and 47%, and those by CaCO$_3$ were 21% and 24% at the 1100 site and the Jeju city, respectively. Based on the seasonal comparison, it was found that the neutralization by NH$_3$ occurred mostly in spring and summer seasons. The free acidity which is actually related to the precipitation acidity was in the range of average 38% and 28% at the 1100 site and the Jeju city, respectively. The correlation study between major acidic anions and basic cations, i.e., (nss-SO$_4^{2-}$ + NO$_3^-$) and (H$^+$ + nss-Ca^{2+} + NH$_4^+$), which had great contributions to the neutralization as well as acidification, showed quite high correlation coefficients (0.861 and 0.912, respectively). This indicates that those com-

Table 5. The comparison of neutralization factors by NH$_4^+$ and Ca^{2+}.

Site	NF_{NH_4}.	$NF_{Ca^{2}}$,	Freeacidity (%)[1]
1100 Site	0.44	0.21	38
Jeju City	0.47	0.24	28

[1] Free acidity (%) : $[H^+]_{eq} / \Sigma$ (acidic anions)

ponents are the major ones for the neutralization as well as acidification in precipitation at Jeju area (Kaya et al., 1997).

3. 6 Seawater and soil enrichment factor

The airborne suspended particles are generally composed of sea salt, fly ash, soot, soil, etc., and they are introduced into precipitation by wash-out effect. In general, the composition ratio of soil components at a remote unpolluted area is relatively higher than that at an urban area. It has been reported that the concentrations of sea salt as well as soil components are relatively higher in the airborne particles at Jeju island because of the oceanic influence (Kang et al., 1999). Therefore it might be predicted that the precipitation in Jeju could contain those components with a considerable amount by the wash-out effect, so the investigation has been necessarily performed by a method with seawater and soil enrichment factors (EF). The enrichment factor can be obtained from the ratios of typical immigrant components to atmospheric aerosols, generally based on Na$^+$ for seawater effect and Ca^{2+}, Al, and Fe for soil effect. In this study, these effects were investigated using the enrichment factors in terms of

Table 6. Seawater and soil enrichment factors calculated from the analytical data.

Site	Seawater enrichment factors						
	SO_4^{2-}/Na^+	Cl^-/Na^+	Mg^{2+}/Na^+	Ca^{2+}/Na^+	K^+/Na^+	–	–
1100 Site	17.6	0.9	1.6	11.9	6.1	–	–
Jeju City	17.9	0.9	1.8	16.9	9.1	–	–

Site	Soil enrichment factors						
	SO_4^{2-}/Ca^{2+}	Cl^-/Ca^{2+}	NO_3^-/Ca^{2+}	NH_4^+/Ca^{2+}	Na^+/Ca^{2+}	Mg^{2+}/Ca^{2+}	K^+/Ca^{2+}
1100 Site	4574.8	2820.2	2232.6	861.5	9.7	2.9	1.7
Jeju City	3836.1	3183.3	2666.5	885.6	10.6	3.0	2.1

Na^+ and Ca^{2+} from the following equations (Carmi-chael *et al.*, 1997),

$$EF = (C_X/C_{Na^\cdot})_{Rainwater} / (C_X/C_{Na^+})_{Seawater}$$

$$EF = (C_X/C_{Ca^{2-}})_{Rainwater} / (C_X/C_{Ca^{2+}})_{Crust}$$

where $(C_X/C_{Na^\cdot})$ and $(C_X/C_{Ca^{2+}})$ are ratios of seawater and soil components, respectively. The calculated results of these two enrichment factors at the 1100 site and the Jeju city are shown in Table 6. The average seawater and soil enrichment factors of SO_4^{2-} have shown quite high values (17.6 and 4574.8, respectively, at the 1100 site, and 17.9 and 3836.1, respectively, at the Jeju city) which indicated a possible influx by other sources rather than seawater or soil influence. The soil enrichment factors of NO_3^- and NH_4^+ were 2232.6 and 861.5 at the 1100 site, and 2666.5 and 885.6 at the Jeju city, respectively, so these components were rarely influenced by soil. On the other hand, the seawater enrichment factors of Mg^{2+} and Cl^-, and the soil enrichment factors of Na^+, K^+ and Mg^{2+} showed values quite close to 1, so it could be said that these components were affected mostly by seawater and soil.

3. 7 Factor analysis

The factor analysis has been performed in order to investigate major influencing sources on the precipitation components using a varimax rotation of principal component by SPSS program, and its results are listed in Tables 7 and 8. The three factors extracted by considering an eigenvalue showed 79.7% and 69.9% of cumulative factor loadings at the 1100 site and the Jeju city, respectively (Lee *et al.*, 2000; Seto *et al.*, 2000;

Table 7. Rotated varimax factor matrix of factor analysis for the precipitation components at 1100 Site.

Components	Factor 1	Factor 2	Factor 3
H^+	0.780	−0.109	0.267
NH_4^+	0.564	0.621	0.216
Na^+	0.388	0.193	0.883
K^+	0.156	0.541	0.730
$nss-Ca^{2+}$	0.421	0.577	0.095
Mg^{2+}	0.364	0.194	0.858
$nss-SO_4^{2-}$	0.894	0.267	0.230
NO_3^-	0.907	0.198	0.230
Cl^-	0.275	0.295	0.889
$HCOO^-$	−0.238	0.854	0.372
CH_3COO^-	−0.264	0.821	0.417
$CH_3SO_3^-$	0.482	−0.078	0.127
F^-	0.201	0.854	0.123
Eigenvalue	6.6	2.5	1.2
Variance (%)	50.7	19.6	9.4
Cummulated (%)	50.7	70.3	79.7

Table 8. Rotated varimax factor matrix of factor analysis for the precipitation components at Jeju city.

Components	Factor 1	Factor 2	Factor 3
H^+	0.055	0.591	−0.091
NH_4^+	0.184	0.825	0.296
Na^+	0.972	0.046	0.075
K^+	0.648	0.472	0.047
$nss-Ca^{2+}$	0.287	0.222	0.666
Mg^{2+}	0.960	0.123	0.170
$nss-SO_4^{2-}$	0.305	0.793	0.408
NO_3^-	0.299	0.822	0.286
Cl^-	0.967	0.015	0.057
$HCOO^-$	−0.014	−0.013	0.905
CH_3COO^-	−0.014	0.054	0.885
$CH_3SO_3^-$	−0.113	0.461	0.012
F^-	0.128	0.305	0.417
Eigenvalue	5.2	2.3	1.6
Variance (%)	39.8	17.7	12.4
Cummulated (%)	39.8	57.5	69.9

Olsen *et al.*, 1990; Crawley *et al.*, 1986). For the case of the 1100 site as shown in Table 7, the first factor showing 50.7% of explanation could be regarded as anthropogenic sources mostly due to H^+, NH_4^+, nss–SO_4^{2-} and NO_3^- components. The second factor largely containing nss–Ca^{2+}, NH_4^+, $HCOO^-$ and CH_3COO^- showed 19.6% of explanation, among which nss–Ca^{2+} is usually originated from soil, but the other components generally from plants (Chebbi *et al.*, 1996; Likene *et al.*, 1987). The third factor, on the other hand, mainly containing Na^+, Mg^{2+} and Cl^- could be regarded as seawater sources, and its effect was relatively as low as less than 10%. In precipitation at the Jeju city as shown in Table 8, the first factor indicated 39.8% of explanation due to high values of Na^+, Mg^{2+} and Cl^- which are mostly seawater components. The second factor containing H^+, NH_4^+, nss –SO_4^{2-} and NO_3^- showed 17.7% of explanation, and it could be explained as an effect by anthropogenic pollution sources. The third factor mostly with nss–Ca^{2+}, $HCOO^-$ and CH_3COO^- could be originated from soil and plant sources. In consequence of this factor analysis, it can be concluded that the anthropogenic sources may influence the most into the precipitation at the 1100 site, followed by soil and seawater sources. However, at the Jeju city, the main source might be said as seawater, and followed by anthropogenic and soil sources.

4. CONCLUSIONS

The precipitation samples have been collected at the 1100 site and the Jeju city, and chemically analyzed for major ionic components. The pollution characteristics and sources of precipitation have been investigated after verifying the confidence of analytical data. From this study, the following conclusions have been found.

1) The reliability investigation of analytical data has been performed by ion balance, conductivity, and acid fraction comparison methods. And the correlation coefficients were confirmed to show reasonably good

relations by over 0.952.

2) The precipitation at the Jeju city has shown to have relatively high concentrations of Cl^-, Na^+, SO_4^{2-}, and NH_4^+ compared to those at the 1100 site, having meant that more influenced by the ocean. And the measurement for ionic strength of precipitation has proven that 57% and 28% of precipitation at the 1100 site and the Jeju city respectively showed the ionic strength well below 10^{-4} M which is the criterion of pure rainwater.

3) The acidification by both nss–SO_4^{2-} and NO_3^- was 90–91% at the 1100 site and the Jeju city, but CH_3COO^- and $HCOO^-$ have contributed only 7~8% to the acidification in precipitation, so it is confirmed that the organic acids would not have a significant contribution to the acidification.

4) It has been investigated that the neutralization factor by NH_3 was 44% and 47% to the precipitation at the 1100 site and the Jeju city respectively, and that of $CaCO_3$ was 21% and 24%. And the free acidity of precipitation was in average 38% and 28% at two sites.

5) The investigation of seawater and soil enrichment factors has indicated that NO_3^- and NH_4^+ as well as SO_4^{2-} might be possibly immigrated by other sources rather than from the regional seawater or soil origin. But it was confirmed that Mg^{2+}, Cl^-, Na^+, and K^+ would be from seawater and soil sources.

6) The factor analysis study has shown that the precipitation at the 1100 site had been influenced mostly by anthropogenic sources, and followed by soil and seawater sources. On the other hand, the precipitation at the Jeju city were mainly influenced by oceanic sources, followed by the factors from anthropogenic and soil sources.

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