Chemical Composition Characteristics of Precipitation at Two Sites in Jeju Island

Chang-Hee Kang,* Won-Hyung Kim, and Won Lee†

Research Institute for Basic Sciences and Department of Chemistry, Cheju National University, Jeju 690-756, Korea
†Research Institute for Basic Sciences and Department of Chemistry, Kyunghee University, Seoul 130-701, Korea
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The major ionic components of precipitation collected at the 1100 Site of Mt. Halla and Jeju city have been determined. The reliability of the analytical data was verified by the comparison of ion balances, electric conductivities and acid fractions; all of their correlation coefficients were above 0.94. Ionic strengths lower than 10^{-4} M were found in 53% of the 1100 Site samples and 28% of the Jeju city samples. Compared with other inland areas, the wet deposition of Na^+, Cl^- and Mg^{2+} was relatively larger, but that of NH_4^+, nss-SO_4^{2-} (non-sea salt sulfate) and NO_3^- was lower. Especially the wet deposition increase of Ca^{2+} in the spring season supports the possibility of the Asian Dust effect. The acidification of precipitation was caused mostly by SO_4^{2-} and NO_3^- in the Jeju area, and the organic acids have contributed only about 7% to the acidity. The neutralization factors by NH_3 were 0.47 and 0.48, and that of $CaCO_3$ was 0.31 and 0.25 at the 1100 Site and Jeju city, respectively. Investigation into major influencing sources on precipitation components by factor analysis showed that the precipitation at the 1100 Site had been influenced mostly by an anthropogenic source, followed by soil and seawater sources. The precipitation at Jeju city was mainly influenced by oceanic sources, followed by anthropogenic and soil sources.

Key Words : Chemical composition, Wet deposition, Acid precipitation, Neutralization factor, Factor analysis

Introduction

An extreme amount of air pollutants has been produced in the East Asia region due to high population growth and an increase in energy consumption. Bhatti *et al.* reported that SO_2 emitted in the East Asia region in 1990 totaled 2.9 million tons and projected the amount 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).[1] China's SO_2 emissions have grown by about three-fold over the last two decades, and it is anticipated that in 2020 it will be three times as high as that in 1990.[2-5] The large amount of SO_2 emitted from industrial complexes in the eastern region of China can be delivered by the prevailing westerlies,[6,7] so it is expected to cause serious acidic precipitation rapidly on the Korean peninsula. Therefore, it is important to understand the effects of the emissions and transport of ambient trace species from East Asia, especially China, to the regional and global environment. Jeju Island is located at about 100 km south of the Korean Peninsula and surrounded by the Asia Continent, Korea, and Japan. Also, Jeju Island is considered one of the background areas in Korea, with low local emissions of air pollutants. Thus, Jeju Island is an excellent location to study the transport and transformation of ambient trace species in East Asia and to study the impact of continental outflow.[8-14] In the present study, the precipitation samples were collected at the 1100 Site on Mt. Halla, which is a remote high-elevation site, and Jeju city. The major precipitation components were analyzed.[15] Finally, the composition characteristics and wet deposition of the precipitation have been discussed.

*Corresponding Author. Fax: +82-64-756-3561; E-mail: changhee @cheju.ac.kr

Experimental Section

Collection of precipitation samples. The precipitation samples were collected at the 1100 Site on Mt. Halla (33º21'N, 126º27'E) and the Jeju city (Cheju National University building, 33º26'N, 126º33'E). The automated rain sampler (Shinil Science, model SL-4-001) equipped with a rain sensor was used at the 1100 Site, which had a funnel of 253 mm in diameter, and its cover opened automatically during rain. The 161 precipitation samples were collected from the 1100 Site between March 1997 and May 2002. And the 281 precipitation samples were collected from the Jeju city site using a manual type rain sampler (337 mm diameter) in the beginning and the automated rain sampler later, between October 1996 and May 2002. The collected precipitation samples were moved to the laboratory, and the pH and electric conductivity were measured immediately. The remaining samples were divided into two fraction parts. One aliquot was stored in a deep freezer at -20 ºC 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.[16,17]

Chemical analysis. pH and electric conductivity were measured using a 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), respectively. An atomic absorption spectrophotometer (GBC, model Avanta-P) was used for the

determination of Na^+, K^+, Ca^{2+}, Mg^{2+} cations, and the indophenol method was applied for NH_4^+ analysis. SO_4^{2-}, NO_3^- and Cl^- anions were determined using an ion chromatograph (Dionex, model DX-500 IC with IonPac AG4A-SC/IonPac AS4A-SC column), and the analytical conditions were as follow: flow rate = 1.0 mL/min, injection volume = 50 μL, eluent = 2.4 mM Na_2CO_3 / 2.25 mM $NaHCO_3$. 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 as follow: flow rate = 2.5 mL/min, injection volume = 25 μL, eluent = 0.25 mM NaOH/5 mM NaOH.[18-21] Since the beginning of 2001, all ionic components have been analyzed simultaneously by the ion chromatographic method, which 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 a 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, and its separation conditions were as follow: flow rate = 1.0 mL/min, injection volume = 20 μL, eluent = 4.0 mM tartaric acid / 1.0 mM pyridine-2,6-dicarboxylic acid. For the analysis of SO_4^{2-}, NO_3^- and Cl^- anions, the same type IC with Metrohm Metrosep A-SUPP-4 column was used, and the conditions were as follow: flow rate = 1.0 mL/min, injection volume = 100 μL, eluent = 1.8 mM $NaHCO_3$ / 1.7 mM Na_2CO_3, suppressor solution = 0.1% H_2SO_4.

Results and Discussion

Quality control of analytical data. The confidence of the analytical data was verified by comparison of the ion balance, electric conductivity, and acid fraction methods.

Table 1. Data quality control parameters by the comparisons of ion balances, electric conductivities and acid fractions

Parameter	Correlation Coefficient (r)	
	1100 Site	Jeju City
Ion Balance	0.979	0.983
Electric Conductivity	0.991	0.989
Acid Fraction	0.935	0.966

From the analytical data of precipitation samples collected at the 1100 Site and Jeju city, the sum of cation equivalent concentrations and the sum of anion equivalent concentrations were calculated, and their correlation is shown in Table 1.[22] The correlation coefficient (r) shows good linearity with the value of 0.979 and 0.983 at the 1100 Site and Jeju city, respectively.[23] Also the confidence of analytical data can be evaluated indirectly comparing the calculated conductivity with the experimentally measured conductivity. From the correlation comparison between the calculated and measured conductivities of our analytical data, the correlation coefficient was 0.991 and 0.989 at the 1100 Site and Jeju city, respectively, in good linear relationship. And also the confidence of the analytical data can be evaluated by comparing the AF values calculated from two different methods.[24,25] The two theoretical acid fractions (AF) of precipitation can be calculated from the results of all ion concentrations and the measured conductivity and pH. The correlation between two acid fractions calculated from each method shows that the correlation coefficients were 0.935 and 0.966 at the 1100 Site and Jeju city, respectively, so that the confidence of analytical data in this study represented a good result.

Analytical results of precipitation. The electric conductivities and pH for a total of 442 precipitation samples were measured, and the analytical results of major ions were

Table 2. The pH, conductivity (μS/cm) and volume-weighted mean concentrations (μeq/L) of rainwater ions

Components	1100 Site	Jeju City	Seoul[a]	Chunchon[a]	Anmyon[a]	Hong-Kong[b]	Hiroshma[c]	Patras[d]
pH	4.91	4.83	4.7	4.7	4.6	4.24	5.0	5.16
Conduct.	13.2	21.4	–	–	–	–	–	–
H^+	12.4	14.9	21.3	20.7	26.0	57.7	9.8	7.0
NH_4^+	13.8	18.7	66.4	37.4	34.6	–	29.9	16.3
Na^+	28.0	62.9	10.5	7.0	31.0	44.0	17.7	90.2
K^+	2.5	4.9	3.5	3.4	3.4	3.5	1.2	6.6
nss-Ca^{2+}	4.7	7.9	34.4	22.5	19.7	11.2	10.0	94.6
Mg^{2+}	6.7	14.9	6.9	5.0	10.7	9.7	5.7	30.4
nss-SO_4^{2-}	22.4	27.8	69.6	44.9	41.5	82.8	40.2	34.7
NO_3^-	9.5	16.7	29.9	23.6	17.9	30.6	15.5	19.4
Cl^-	28.8	65.4	18.2	12.9	43.9	47.3	29.7	114.3
F^-	0.7	0.8	–	–	–	–	–	–
HCO_3^-	0.4	0.3	–	–	–	–	–	–
$HCOO^-$	1.6	2.0	–	–	–	–	–	–
CH_3COO^-	1.2	1.3	–	–	–	–	–	–
$CH_3SO_3^-$	0.0_3	0.0_4	–	–	–	–	–	–

[a]Precipitation in Seoul, Chunchon and Anmyon Island during the period from May 1996 to April 1998.[26] [b]Precipitation in Hong Kong during the period from March 1994 to April 1995.[27] [c]Precipitation in Hiroshima during the period from April 1984 to March 1988.[28] [d]Precipitation in Patras, Greece during the period from January 2000 to May 2001.[29]

compared with those from other areas, as shown in Table 2.[26-28] The H^+ concentration was obtained from pH measurement and the HCO_3^- concentration was calculated from the relation of $[HCO_3^-] = 10^{(pH-11.3)}$.[29] The volume-weighted mean pH value was 4.91 and 4.83 at the 1100 Site and Jeju city, respectively, showing relatively week acidic precipitation during the period of this study. The volume-weighted mean conductivity was 13.2 μS/cm and 21.4 μS/cm at the two sites, respectively. From the measurement of ionic strengths of precipitation, the mean ionic strength was 0.15 ± 0.16 mM and 0.23 ± 0.23 mM at the two sites, respectively, showing that 53% of the 1100 Site precipitation and 28% of that of Jeju city were below 10^{-4} M, which is considered a criterion of pure rainwater.[23] The equivalent concentrations of major ionic components showed a similar pattern, except for only the difference of H^+. On the basis of ionic composition, Na^+, Cl^- and Mg^{2+} occupied 47.8% of all the precipitation components at the 1100 Site, but 60.0% of those at Jeju city, implying that the precipitation at Jeju city was more influenced by the oceanic sources. On the other hand, we found that NH_4^+, nss-SO_4^{2-} and NO_3^- regarded as typical anthropogenic ions, occupied 10.4%, 16.9% and 7.1% of all the precipitation components at the 1100 Site, and 7.8%, 11.7% and 7.0% at Jeju city. From the seasonal comparison, the variation of precipitation components shows that the concentrations of H^+, NO_3^- and nss-SO_4^{2-}, which are the components originating from various human activities, were higher in winter and spring at both sites. But the concentrations of NH_4^+ at the 1100 Site were higher in fall season. The concentrations of nss-Ca^{2+} originating from soil sources were the highest in spring, followed by winter season, at both sites. At the 1100 Site in Mt. Halla, the H^+, NO_3^- and SO_4^{2-} concentrations in winter and spring, and the Ca^{2+} concentration in the spring were noticeably higher. On the other hand, the concentrations of Na^+, Cl^-, and Mg^{2+} were at their highest levels in winter due to the oceanic influences by strong and prevailing northwest winds in the winter season.

The concentrations of major precipitation components were compared with other domestic areas and foreign countries, as shown in Table 2. The concentrations of H^+, NH_4^+, nss-SO_4^{2-} and NO_3^- in Jeju shows values mostly much lower than those from other domestic areas and foreign countries. Those components in general originated from the anthropogenic sources, implying that the air pollution level is not very serious in the Jeju area. Also, the concentration of nss-Ca^{2+}, originating mainly from soil sources, was lower than in other areas. However, the Na^+, Cl^- and Mg^{2+} components in Jeju city showed higher concentrations compared with other landward areas, indicating relatively high oceanic influence, although that is not the case at the 1100 Site. Consequently, this study shows that the air quality in the Jeju area is relatively good, and that the 1100 Site is appropriate to measure the background level of air pollution. So, the analytical results of precipitation at the 1100 Site may be useful as background data for precipitation in Korea and a basic reference for air quality management.

Table 3. Annual wet deposition of major precipitation components in 1100 site, Jeju city and other areas of Korea

Components	Amounts of wet deposition (g/m^2yr)				
	1100 Site	Jeju City	Seoul[a]	Chun-chon[a]	An-myon[a]
Precipitation (mm)	2920	1386	1585	1488	1001
H^+	0.035	0.020	0.028	0.023	0.021
NH_4^+	0.59	0.45	1.4	0.84	0.65
Na^+	1.77	2.06	0.26	0.17	0.59
K^+	0.27	0.27	0.14	0.20	0.12
Ca^{2+}	0.29	0.27	0.77	0.48	0.46
Mg^{2+}	0.22	0.25	0.08	0.06	0.11
nss-SO_4^{2-}	2.71	1.80	4.2	2.6	2.0
NO_3^-	1.45	1.39	2.3	1.8	1.1
Cl^-	2.80	3.31	0.69	0.48	1.2
F^-	0.03	0.02	–	–	–
$HCOO^-$	0.20	0.13	–	–	–
CH_3COO^-	0.21	0.11	–	–	–
$CH_3SO_3^-$	0.01	0.01	–	–	–

[a]Precipitation during the period from 1994 to 1998.[31]

Wet deposition of major precipitation components. In the present study, the annual average wet deposition of major precipitation components deposited from the wash-out effect of rain was investigated quantitatively, and the results are shown in Table 3. The amounts of wet depositions at the 1100 Site and Jeju city are the annual mean values between 1997 and 2001, but the data at the 1100 Site in 2000 are omitted. The values may include some errors because the calculation has been performed excluding a few suspicious precipitation samples due to instrument malfunction. The comparison of wet deposition in the Jeju area with other areas of Korea shows relatively larger deposits of Na^+, Cl^-, Mg^{2+}, which are typical sea salt components. However, the deposition of NH_4^+, nss-SO_4^{2-} and NO_3^-, anthropogenic pollutant components, in the Seoul and Chunchon areas were much larger than those at two sites in the Jeju area. The case in Anmyon-Do shows a level similar to that in Jeju.[26,31] The wet deposition of a soil component Ca^{2+} in the Jeju area was also relatively lower compared with other areas. The seasonal comparison of the wet deposition in Jeju shows that the deposition of most components is comparably related to the amounts of precipitation, especially in the spring and summer seasons, as shown in Table 4. The wet deposition of Ca^{2+} is notably larger in spring. The implication is that the precipitation in the spring season in the Jeju area is possibly affected significantly by Asian Dust.

Acidification and neutralization of precipitation. The sums of equivalent concentrations of cations (proton and neutralizing substances) and anions (proton donors) in the 1100 Site and Jeju precipitation are compared in Table 5. The sum of cation concentrations and the sum of anion concentrations should be the same if the acidification and neutralization of precipitation involved only the components shown in the table; however, the sum of anion concentrations was higher than that of cations at both sites. This might have

Table 4. Seasonal comparison of wet deposition (g/m^2) in 1100 Site and Jeju city

Components	1100 Site				Jeju City			
	Spring	Summer	Fall	Winter	Spring	Summer	Fall	Winter
Precipitation (mm)	696	1455	553	245	227	636	341	134
H^+	0.01_1	0.01_4	0.00_7	0.00_4	0.01_4	0.00_6	0.00_6	0.00_4
NH_4^+	0.31	0.22	0.33	0.07	0.12	0.16	0.09	0.08
Na^+	0.60	0.65	0.42	0.30	0.26	0.47	0.69	0.45
K^+	0.13	0.07	0.07	0.04	0.04	0.06	0.11	0.04
nss-Ca^{2+}	0.15	0.05	0.04	0.04	0.08	0.05	0.03	0.05
Mg^{2+}	0.08	0.08	0.05	0.04	0.03	0.06	0.09	0.05
nss-SO_4^{2-}	1.13	1.00	0.60	0.45	0.40	0.52	0.45	0.38
NO_3^-	0.60	0.59	0.29	0.23	0.30	0.43	0.35	0.26
Cl^-	0.14	1.07	0.67	0.45	0.43	0.74	1.07	0.75
F^-	0.01	0.02	0.00_3	0.00_3	0.00_3	0.01_1	0.00_4	0.00_2
$HCOO^-$	0.10	0.05	0.03	0.03	0.04	0.03	0.04	0.01
CH_3COO^-	0.09	0.04	0.03	0.05	0.03	0.03	0.02	0.02
$CH_3SO_3^-$	0.00_2	0.00_4	0.00_2	0.00_0	0.00_1	0.002	0.001	0.00_0

Table 5. Concentrations (μeq/L) of protons, possible proton donors and neutralizing substances, and neutralization factors (NF) by NH_4^+ and Ca^{2+}

1100 Site				Jeju City			
H^+	12.4	nss-SO_4^{2-}	22.4	H^+	14.9	nss-SO_4^{2-}	27.8
nss-Ca^{2+}	4.7	NO_3^-	9.5	nss-Ca^{2+}	7.9	NO_3^-	16.7
NH_4^+	13.8	F^-	0.7	NH_4^+	18.7	F^-	0.8
–	–	$HCOO^-$	1.6	–	–	$HCOO^-$	2.0
–	–	CH_3COO^-	1.2	–	–	CH_3COO^-	1.3
Total	30.9		35.4	Total	41.5		48.6
$NF_{NH_4^+}$		0.469		$NF_{NH_4^+}$		0.476	
$NF_{Ca^{2+}}$		0.309		$NF_{Ca^{2+}}$		0.246	
Free Acidity (%)[a]		37.6		Free Acidity (%)[a]		28.0	

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

Table 6. Rotated varimax factor matrix of factor analysis for the precipitation components at 1100 Site and Jeju city

Components	1100 Site			Jeju City		
	factor 1	factor 2	factor 3	factor 1	factor 2	factor 3
H^+	**0.767**	0.245	-0.092	0.056	**0.549**	-0.096
NH_4^+	**0.579**	0.173	**0.618**	0.164	**0.839**	0.249
Na^+	0.389	**0.885**	0.176	**0.974**	0.057	0.067
K^+	0.161	**0.736**	0.530	**0.625**	0.501	0.026
nss-Ca^{2+}	0.407	0.102	**0.577**	0.284	0.272	**0.640**
Mg^{2+}	0.368	**0.855**	0.184	**0.960**	0.141	0.158
nss-SO_4^{2-}	**0.895**	0.223	0.269	0.302	**0.808**	0.374
NO_3^-	**0.907**	0.205	0.211	0.293	**0.835**	0.242
Cl^-	0.279	**0.892**	0.277	**0.970**	0.026	0.051
$HCOO^-$	-0.243	0.388	**0.832**	-0.007	-0.004	**0.911**
CH_3COO^-	-0.269	0.435	**0.806**	-0.005	0.063	**0.889**
$CH_3SO_3^-$	0.453	0.192	-0.131	-0.104	0.427	0.012
F^-	0.184	0.097	0.823	0.112	0.365	0.362
Eigenvalue	6.4	2.5	1.3	5.1	2.3	1.6
Variance	49.4	19.2	9.8	39.4	17.5	12.3
Cummulated	49.4	68.6	78.4	39.4	56.9	69.2

been due to an error in the pH measurement or the analysis of precipitation components. The presence of any other components would have contributed to the neutralization. Other sea salt basic components could have affected to the neutralization in precipitation,[32] since Jeju, an island, is very much influenced by the ocean. The relative composition ratios of the five major acidic anions shows that the inorganic acid ions, *i.e.*, nss-SO_4^{2-} and NO_3^-, account for 91% of the acidification of precipitation at both sites. This means that H_2SO_4 and HNO_3 are the most likely contributors to the acidification of precipitation in the Jeju area. On the other hand, HCOOH and CH_3COOH each account for about 7% of the acidification of precipitation, confirming that the contribution of organic acids to the acidification of precipitation was not significant in this area.[33]

The neutralization factors among major acidic (nss-SO_4^{2-}, NO_3^-) and basic (NH_4^+, nss-Ca^{2+}) components were calculated,[32] and the results are shown in Table 5. It has been confirmed that NH_3 has contributed more to the neutralization of precipitation than $CaCO_3$, such that the neutralization factors by NH_3 were 0.469 and 0.476, and those by $CaCO_3$ were 0.309 and 0.246 at the 1100 Site and Jeju city, respectively. Based on the seasonal comparisons, we found that neutralization by NH_3 occurred mostly in spring and summer seasons. And the free acidity, which is actually related to the precipitation acidity, was in the range of 38% and 28% on average at the 1100 Site and 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 contributed greatly to the neutralization as well as acidification, shows the quite high correlation coefficients of 0.901 and 0.863. This indicates that those components are the major ones for the neutralization as well as acidification in precipitation in the Jeju area.[34]

Emission sources by factor analysis. Factor analysis was

performed to investigate the sources having the major influence on the precipitation components. We used a varimax rotation of principal components by SPSS program, and the results are listed in Table 6. The three factors extracted by considering an eigenvalue showed 78.4% and 69.2% of cumulative factor loadings at the 1100 Site and Jeju city, respectively.[26,28,35] For the case of the 1100 Site, the first factor, showing 49.4% of explanation, could be reasoned as anthropogenic sources mostly due to H^+, NH_4^+, nss-SO_4^{2-} and NO_3^- components. The second factor, largely containing Na^+, Mg^{2+} and Cl^-, which were originated from seawater, showed 19.2% of explanation. The third factor, on the other hand, had high factor loadings for nss-Ca^{2+}, NH_4^+, $HCOO^-$ and CH_3COO^-, among which nss-Ca^{2+} is usually generated from soil. But the other components were generally from plants,[36,37] and its effect was relatively at less than 10%. In precipitation at Jeju city, the first factor indicated 39.4% of explanation due to high factor loadings 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 17.5% of explanation, and it could be explained as an effect of anthropogenic pollution sources. The third factor, mostly with nss-Ca^{2+}, $HCOO^-$ and CH_3COO^-, might be from soil and plant sources. Through this factor analysis, it can be concluded that the anthropogenic sources may have their greatest influence through precipitation at the 1100 Site, followed by seawater and soil sources. However, at Jeju city, the main source might be said to be seawater, followed by anthropogenic and soil sources.

Summary

The composition characteristics of precipitation at the 1100 Site of Mt. Halla and Jeju city have been investigated, and the results are as follow:

1) The comparison of ion balance, electric conductivity and acid fraction gave correlations of good linearity, and the reliability of the analytical data was in good.

2) All major precipitation components at Jeju city show relatively higher concentrations than at the 1100 Site, and the ionic strength of precipitation has proven that 53% and 28% of precipitation at the 1100 Site and Jeju city, respectively, showed ionic strength well below 10^{-4} M, which is the criterion of pure rainwater.

3) The wet deposition in the Jeju area showed relatively large deposits of Na^+, Cl^- and Mg^{2+}, indicating more oceanic influence compared with other areas of Korea. Especially, the wet deposition increase of Ca^{2+} in the spring season supports the possibility of the Asian Dust effect.

4) The acidification by means of nss-SO_4^{2-} and NO_3^- concentrations was about 91% at both sites, but the contribution of the organic acids such as CH_3COOH and HCOOH was not very significant. The neutralization factor by NH_3 was 0.47-0.48, and that of $CaCO_3$ was 0.31 and 0.25 at the 1100 Site and Jeju city, respectively. And the free acidity of precipitation was on average 38% and 28% at the two respective sites.

5) On the basis of factor analysis, we have shown that the precipitation at the 1100 Site was influenced mostly by anthropogenic sources, followed by seawater and soil sources. On the other hand, the precipitation at Jeju city was mainly influenced by oceanic sources, followed by factors from anthropogenic and soil sources.

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