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Article

Chemical Composition of Water Soluble Inorganic Species in Precipitation at Shihwa Basin, Korea

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Abstract: Weekly rain samples were collected in coastal areas of the Shihwa Basin (Korea) from June 2000 to November 2007. The study region includes industrial, rural, and agricultural areas. Wet precipitation was analyzed for conductivity, pH, Cl^-, NO_3^-, SO_4^{2-}, Na^+, K^+, Mg^{2+}, NH_4^+, and Ca^{2+}. The major components of precipitation in the Shihwa Basin were NH_4^+, volume-weighted mean (VWM) of 44.6 μeq·L^{-1}, representing 43% of all cations, and SO_4^{2-}, with the highest concentration among the anions (55%) at all stations. The pH ranged from 3.4 to 7.7 with a VMM of 4.84. H^+ was weakly but positively correlated with SO_4^{2-} ($r = 0.39$, $p < 0.001$) and NO_3^- ($r = 0.38$, $p < 0.001$). About 66% of the acidity was neutralized by NH_4^+ and Ca^{2+}. The Cl^-/Na^+ ratio of the precipitation was 37% higher than seawater Cl^-/Na^+. The high SO_4^{2-}/NO_3^- ratio of 2.3 is attributed to the influence of the surrounding industrial sources. Results from positive matrix factorization showed that the precipitation chemistry in Shihwa Basin was influenced by secondary nitrate and sulfate (41% ± 1.1%), followed by sea salt and Asian dust, contributing 23% ± 3.9% and 17% ± 0.2%, respectively. In this study, the annual trends of SO_4^{2-} and NO_3^- ($p < 0.05$) increased, different from the trends in some locations, due to the influence of the expanding power generating facilities located in the upwind area. The increasing trends of SO_4^{2-} and NO_3^- in the study region have important implications for reducing air pollution in accordance with national energy policy.

Keywords: acid precipitation; nitrate; precipitation; sulfate; Korea; pH

1. Introduction

Rain is the most effective process transporting soluble gases and particles from the atmosphere to the ground [1,2]. Precipitation chemistry plays an important role in understanding the air quality in a study area, because the concentrations and distribution of chemical components in rain depend on a variety of emission sources including sea spray, soil particles, and industrial pollutants [3–7].

In coastal areas, the Na^+/Cl^- ratio, SO_4^{2-}, Mg^{2+}, and Ca^{2+} are useful for evaluating both anthropogenic and natural influences [8]. Soil particles in northern China, Africa, and the Middle East play an important role in neutralizing the acidic components of rain [9]. The concentrations of anthropogenic components are related to energy consumption and the use of fertilizers [10,11].

Some anthropogenic acidic ions may greatly contribute to acidification and eutrophication of aquatic ecosystems [12]. Numerous long-term observations of precipitation have been carried out in Europe, North America, and Asia [13–17]. These studies have reported that SO_4^{2-} concentrations have decreased commensurate with reductions in SO_2 emissions. NO_3^- concentrations have also shown decreasing trends in regions where NO_2 emissions have decreased [18–20].

In many regions of Asia, rapid economic growth has led to an increase in pollutant emissions and seriously compromised air quality [21]. In addition, air quality has also been affected by wind-blown soil particles originating from the deserts of Mongolia and northern China [22–24]. Several studies conducted in this region have found that the rain is acidic, with H^+ concentration ranges similar to that reported for Europe [25–28].

In Korea, previous studies have shown that most precipitation events are acidic and even in background areas of Korea precipitation pH is <4.9 [29–31]. Some studies have suggested that air masses from the Asian continent increase the concentration of anthropogenic components of rainwater in Korea [31,32]. Choi *et al.* (2015) [33] studied precipitation chemistry in the area near Shihwa Lake (located in the mid-western area of the Korean peninsula), using both urban and background stations to compare precipitation chemistry. To date, precipitation chemistry in the industrial area has not been studied yet.

This study aimed to provide a detailed evaluation of the chemical composition of precipitation in the Shihwa Basin and to evaluate the relative contributions of various sources. Because the Shihwa Basin includes areas with industrial, agricultural, and coastal land use, the study are has experienced serious problems with air pollution [34–37].

2. Material and Methods

2.1. Sampling Sites

The Shihwa Basin is located 60 km southwest of Seoul, the capital of South Korea. The basin of Shihwa Lake has an area of about 475 km^2 and a population of more than 0.8 million people. The Shihwa and Banwol industrial complexes are located in Shihwa Basin. Three sampling stations were selected for precipitation monitoring, covering the southern (Hwasung), northern (Banwol), and western (Daeboo) areas of the Shihwa Basin (Table 1). Hwasung station is located inland about 20 km east of Shihwa Lake, in a residential and rural area. Banwol station is located 5 km east of Shihwa Lake and is important because the Banwol industrial complex is located there. This complex is a site for intensive chemical, leather, and metal processing industries, which have led to air pollution episodes, including pollutants such as ammonia, amines, hydrogen sulfide (H_2S) and mercaptans. Daeboo station is located on an island, about 2 km west of Shihwa Lake. The locations of the Shihwa Basin and the three sampling stations are shown in Figure 1.

Table 1. Characteristics of sampling stations in the Shihwa Basin.

Shihwa Basin	Latitude	Longitude	Elevation (m)	Land Type
Hwasung	37.236	126.918	31	Rural and residential
Banwol	37.315	126.750	56	Industrial
Daeboo	37.268	126.568	25	Agricultural

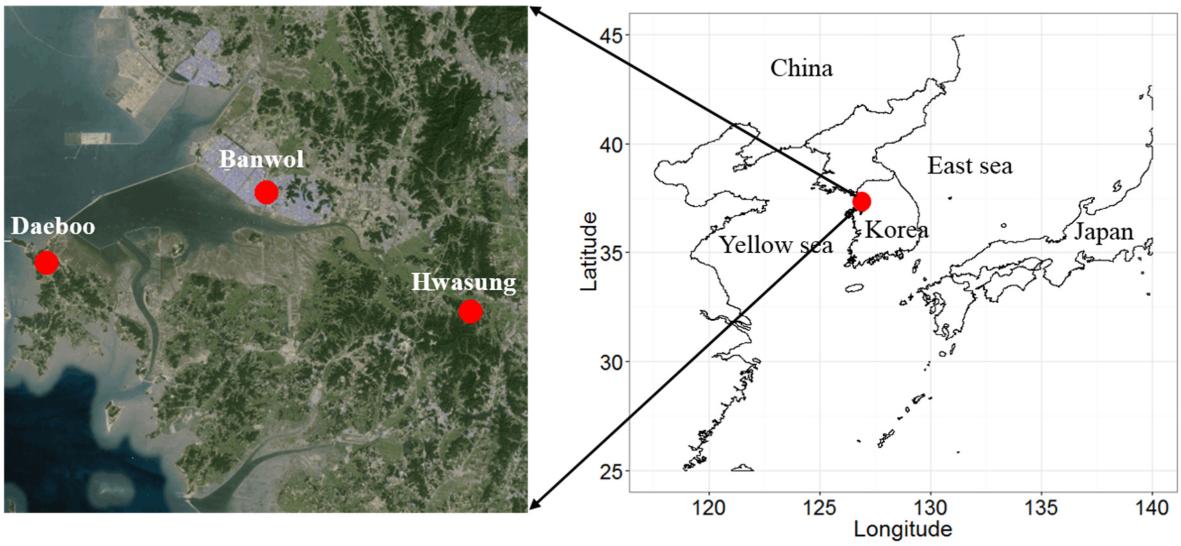

Figure 1. Locations of the study area and sampling stations.

The Shihwa Basin is strongly influenced by air masses driven by westerly winds. According to data from the Incheon meteorological administration (about 20 km north of Shihwa Lake), the average annual rainfall from June 2000 to November 2007 was 1187 mm·year^{-1}. The average temperature and wind speed were 15 °C and 2 m·s^{-1}, respectively. In the summer (June to August), the mean temperature was 24.5 °C and about 61% of the annual precipitation occurred during this season. In winter, the average temperature was 3.5 °C with only 5% of the annual precipitation occurring during winter. The spring season is characterized by the influence of Asian dust, with an average wind speed of 3.67 m·s^{-1}, 58% higher than that in winter. According to AWS data from Korea Meteorological Administration near the three sites, the prevailing wind directions were north and south at Hwasung station, east and west at Banwol station and northwest at Daeboo station. At Hwasung, the wind during spring and summer was north, but south during fall and winter. At Banwol and Daeboo stations, the prevailing wind was constant throughout the year.

2.2. Sample Collection

Precipitation samples were collected weekly using wet and dry collectors from June 2000 to November 2007. Butler and Likens (1998) [38] found that daily samples may provide a better estimate of actual rain chemistry than weekly samples. Gilliland *et al.* (2002) [39] also suggested that considerable monthly variation existed between daily and weekly data for H^+, NH_4^+ and SO_4^{2-}. All of the samplers were placed 1 m from the ground, and the wet sample collector was covered with a lid to prevent any contamination from dry deposition. The wet collector uses a conductivity sensor, which automatically opens at the onset of each precipitation event and closes again when a rain event stops. The automated samplers consisted of two Teflon buckets 28 cm in diameter. The average precipitation intensity for onset was 40 ± 59 mm/week during the study period. Before sampling, the buckets were carefully rinsed with deionized water several times until the conductivity of the water was <1.5 $\mu S \cdot cm^{-1}$. Precipitation samples were collected in a 30-mL high-density polyethylene bottle. The samples were unrefrigerated during sampling but stored in a freezer at −20 °C until chemical analysis. Prior to analysis, the precipitation samples were filtered using 0.45-μm membrane filters (Millipore).

2.3. Sample Analysis

After the precipitation samples were collected, the weight of the bucket was measured to calculate the volume-weighted mean (VWM) concentrations of the atmospheric components. The pH and conductivity of the unfiltered precipitation were also measured immediately with a pH and conductivity meters (Fisher Scientific) [40]. The pH meter was calibrated before each measurement using standard 4.00 and 7.01 buffer solutions. The conductivity meter was also calibrated with a standard solution. For this study, 528 rain samples were analyzed. Major anion and cation concentrations were determined using ion chromatography (Waters, USA). For anions (Cl^-, NO_3^-, and SO_4^{2-}), AS14 or AS11 columns were used; CS12A or CS14 columns were used to measure cations (Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}). The detection limits were 0.08 $\mu eq \cdot L^{-1}$ for Cl^-, 0.12 $\mu eq \cdot L^{-1}$ for NO_3^-, 0.11 $\mu eq \cdot L^{-1}$ for SO_4^{2-}, 0.54 for Na^+, 2.32 $\mu eq \cdot L^{-1}$ for NH_4^+, 0.2 $\mu eq \cdot L^{-1}$ for K^+, 0.44 $\mu eq \cdot L^{-1}$ for Mg^{2+} and 2.87 $\mu eq \cdot L^{-1}$ for Ca^{2+}. Detection limits were calculated by dividing the standard deviation of the response by the slope of the calibration and then multiplying by 3.3.

2.4. Quality Assurance

Of the 678 precipitation samples collected, about 7% were discarded because the amount of precipitation was insufficient to perform the chemical analyses. An additional 12% of the rain samples were discarded due to noticeable contamination by dry deposition (soil, leafs and insects) or because of sampler malfunction [41]. The remaining samples were subjected to a quality check based on ionic balance and conductivity balance. When the pH was above 5.6, the concentration of HCO_3^-

(in μeq·L^{-1}) was calculated using the formula (HCO_3^-) = $10^{(pH - 11.24)}$ [42–44]. According to Okuda *et al.* (2005) [15], the acceptable ion range (∑ cation/∑ anion) and conductivity (∑ measured conductivity/∑ anion conductivity) ratio for a rain sample is 0.67–1.5. Data points outside this range were excluded. The percentage of samples excluded at each sampling station was 38% at Hwasung, 21% at Banwol, and 32% at Daeboo, averaging 30% overall. Linear regression of the relationship between cation sum *vs.* the anion sum showed an r^2 = 0.95 and slope of 0.95 (Figure 2a,b). Edmonds *et al.* (1991) [45] suggested that anion deficit means of the amount of unmeasured organic acids. Kim *et al.* (2013) [32] found that the organic acids (CH_3COO^-, $HCOO^-$) contributed to 12.4% of the acidity in precipitation at Jeju Island in Korea. The relationship between the calculated and measured conductivity was also highly correlated with a r^2 = 0.96 and slope of 0.92.

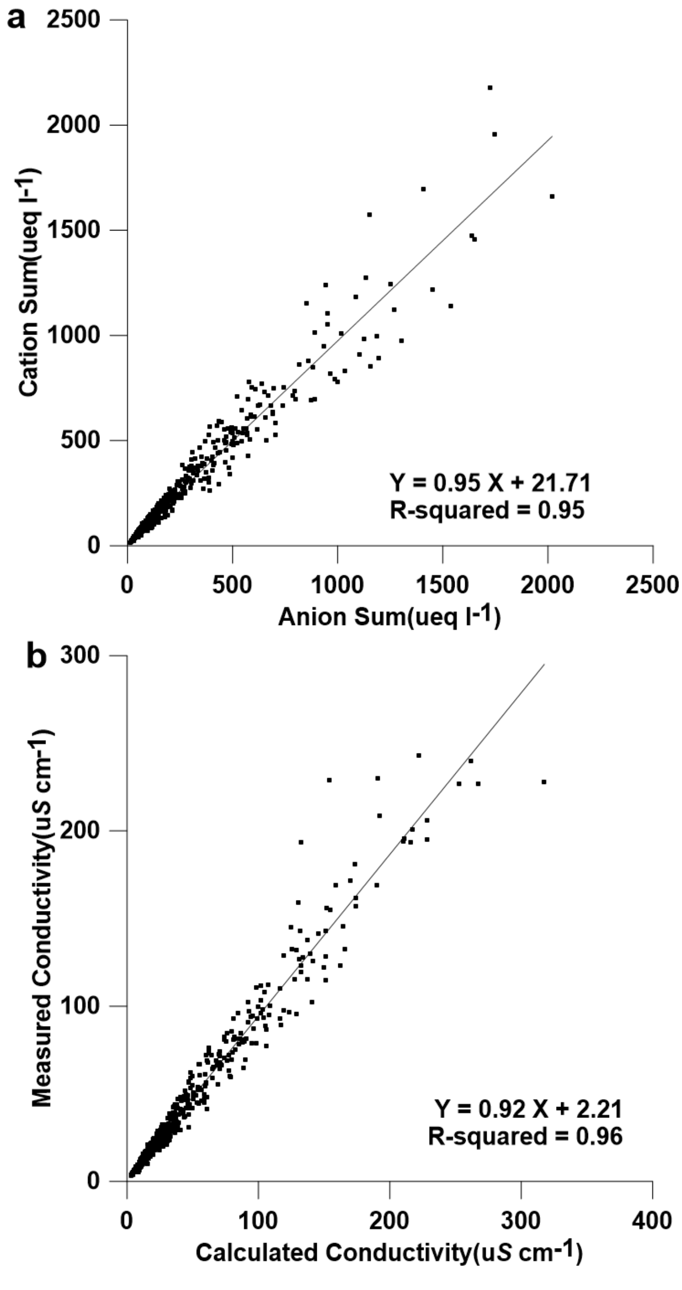

Figure 2. Linear regression (**a**) between the sum of cations and anions, and (**b**) between measured and calculated conductivity.

2.5. Positive Matrix Factorization (PMF)

Positive Matrix Factorization is a multivariable factor analysis tool to identify the contributions of various emission sources. PMF decomposes a speciated data matrix *X* of *n* by *m* dimensions (n number of samples and m chemical species) into factor profiles (*g*) and factor contributions (*f*) based on the correlation between the different components (Equation (1)). The objective of the PMF solution is to minimize the object function Q based on the uncertainties (*u*) as follows [46]:

$$Q = \sum_{i=1}^{n}\sum_{j=1}^{m}\left[\frac{X_{ij} - \sum_{k=1}^{p} g_{ik}f_{kj}}{u_{ij}}\right]^2 \quad (1)$$

where x_{ij} are the measured concentrations (in μeq·L^{-1}), u_{ij} are the estimated uncertainty values (in μeq·L^{-1}), n is the number of samples, m is the number of species and p is the number of factors included in the analysis [47].

PMF needs two input files: one for the measured concentrations of the species and the other for the estimated uncertainties of the concentrations. The uncertainty greater than the detection limit was calculated using the concentration and detection limit (Equation (2)). If the concentration was less than or equal to the detection limit, the uncertainty was calculated with a fixed fraction (Equation (3)). Missing data and their uncertainty value were replaced with the value of the species-species median and four times the median value, respectively [48].

$$uncertainty = \sqrt{(\text{Error fraction } \times \text{Concentration})^2 + (0.5 \ \times \text{Detection limit})^2} \quad (2)$$

$$uncertainty = \frac{5}{6} \times (Detection\ limit) \quad (3)$$

A variable was defined to be weak if its S/N was between 0.2 and 2.0. Most of the scaled residuals were between −3.0 and 3.0. Fpeak values between −1 and 1 (in steps of 0.1) were examined to find out the most appropriate solution. Error estimate with bootstrap results showed 100% mapping for five factors at three sites.

3. Results and Discussion

3.1. Acidity

SO_2 and NO_x are the major precursors of acidity in precipitation. Wind-blown soil particles and sea spray species atmosphere play an important role in neutralizing acidic constituents. In uncontaminated precipitation, the equilibrium concentration of $CO_{2(aq)}$ generates a pH of approximately 5.6, which serves as a reference value. Figure 3 shows the frequency distribution for pH in the Shihwa Basin. Among the samples, 84% of the pH values were <5.6. The pH of uncontaminated precipitation is considered to be 5.0–5.6; this acidity originates from natural levels of atmospheric CO_2, NOx, and SO_x [49]. About 66% of the rain samples had a pH < 5.0, indicating that the rain samples were affected by additional acidic components. At Banwol station in the center of two industrial complexes, 69% of the samples had a pH of <5.0 and 14% had a pH < 4.0. At Hwasung station, 59% of the samples had a pH of <5.0 and 7% had a pH < 4.0. At Daeboo, 78% of the samples had a pH lower than 5.0 and 15% of the samples had a pH < 4.0.

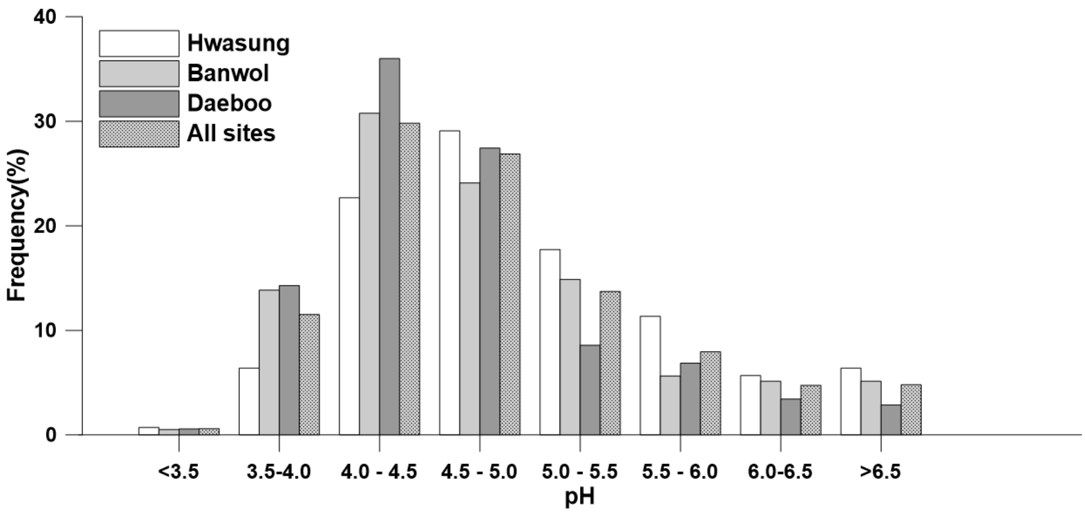

Figure 3. Frequency distribution for wet-only precipitation volume-weighted mean (VWM) pH.

Overall, the pH of the precipitation ranged from 3.4 to 7.7 (Table 2). The VWM pH was 4.84, indicating slight acidity in the study area. For Hwasung, located east of Banwol, the VWM pH was 4.96, higher than at the other sites (p < 0.001). At Banwol, the pH was 4.77, lowest among all the stations (p < 0.001), reflecting its proximity in the industrial complex. Daeboo had the highest VWM pH (4.81), similar to the VWM pH at Banwol.

Table 2. Major ionic compositions of precipitation in the Shihwa Basin (μeq·L^{-1} except pH).

Station	Parameter	Cl^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	pH
Hwasung	Min	0.5	3.8	6.8	0.6	5.9	0.02	0.3	0.7	7.5
	Max	472	482	1495	567	1758	163	297	781	3.4
	Mean	45	68	127	33	117	9	15	57	4.5
	Standard deviation	82	101	72	79	122	20	32	134	0.8
	VWM	13.9	19.6	45.2	9.3	43.6	3.6	4.5	13.5	4.7
Banwol	Min	1.4	2.0	4.7	0.5	5.7	0.03	0.4	0.6	7.7
	Max	683	598	839	506	539	308	144	639	3.5
	Mean	58	71.3	145	34.7	116	9	14	65	4.3
	Standard deviation	93	83	160	66	104	12	23	108	0.8
	VWM	20	23	56	10	51	4.4	4.6	15	4.6
Daeboo	Min	1.2	1.9	3.5	0.4	1.6	0.11	0.3	0.6	6.9
	Max	1505	594	753	1434	588	87	320	763	3.5
	Mean	70	73	118	59	88	8.5	20	61	4.4
	Standard deviation	119	89	134	88	89	20	33	115	0.7
	VWM	25	22	40	17	40	5.1	6.6	15	4.6

3.2. Concentration of Inorganic Species

The minimum and maximum concentrations of chemical components in the individual precipitation samples and their VWMs are shown in Table 2. SO_4^{2-} and NH_4^+ were the most abundant ions in precipitation at the three stations. At Hwasung, the concentrations of anthropogenic species were lower than those at the other stations. The VWM concentration of sea salts was also lowest in Hwasung, as it is located farthest from the seashore. The highest concentrations of SO_4^{2-}, NH_4^+ and NO_3^- were measured at Banwol, related to anthropogenic sources associated with two industrial complexes and motor vehicles. The VWM concentration of H^+ was also highest in Banwol. In Daeboo, the precipitation acidity was similar to that in Banwol due to the low concentration of NH_4^+. The VWM conductivities in Hwasung, Banwol, and Daeboo were 18, 24, and 23 μS·cm^{-1} with VWM total ions of 181, 253, and 235 μeq·L^{-1}, respectively.

For the combined data collected in the Shihwa Basin, the ion concentrations fell in the order $SO_4^{2-} > NH_4^+ > H^+ > NO_3^- > Cl^- > Ca^{2+} > Na^+ > Mg^{2+} > K^+$. Among the anions, SO_4^{2-} had the highest concentrations at all stations (54%). The next most abundant anion was NO_3^- at nearly 24%. The precipitation chemistry in the Shihwa Basin was mainly dominated by NH_4^+ with an average VWM of μeq·L^{-1}, representing 40% of all cations. Considering the sampling period, the concentration of NH_4^+ can be as high as 49.5 μeq·L^{-1} (10%). The next most abundant cations were H^+, Ca^{2+}, and Na^+, representing 24%, 15%, and 12% of the total, respectively. NH_4^+ in the Shihwa Basin is associated with agricultural activities and an industrial wastewater treatment facility. Ca^{2+} is related to resuspension of dust from the soil and Asian dust originating from China mainly in the spring. [50]. These alkali components neutralize and decrease the acidity of the rainwater [51,52]. The ratios of individual ions to Na^+ are higher than seawater ratios, which indicates that contributions from anthropogenic and soil sources are important, while the marine contribution is negligible [53,54]. The Cl^-/Na^+ ratio in the combined precipitation samples over six years was 45% higher than that of seawater Cl^-/Na^+ (1.165). This suggests that the Cl^- originated from industrial activities in the area such as coal combustion and incineration of polyvinyl chloride [55,56]. The SO_4^{2-}/Na^+, K^+/Na^+, Mg^2/Na^+, and Ca^{2+}/Na^+ ratios for precipitation in the Shihwa Basin were 4.02, 0.32, 0.45, and 1.25, respectively, higher than the seawater ratios (0.12, 0.23, 0.04, and 0.02, respectively). This suggests that anthropogenic influences were present from local (two industrial complexes) or regional (Asian continent) sources.

The SO_4^{2-}/NO_3^- ratio has been used as an index to evaluate anthropogenic characteristic sources in rainfall samples [54,57]. SO_4^{2-}/NO_3^- ratios are diverse globally and temporally: 0.67 in the southwestern United States during 1995~2010 [58], 1.5 in Belgium in 2003 [41], 1.6 in Turkey in 2002 [51], 2.3 in central Pennsylvania during 1993~2001 [59], 2.4 in Mexico from 1994 to 2000 [60], 8.7 in Brazil in 2002 [55] and 18.6 in Costa Rica in 2009 [61]. Kulshrestha *et al.* (2003) [62] reported that the SO_4^{2-}/NO_3^- ratio in India increased as the degree of urbanization or industrialization increased. In Korea, SO_4^{2-}/NO_3^- ratios ranging from 0.6 to 3.6 have been reported (1990 to 2013) [30,33,63,64]. The mean SO_4^{2-}/NO_3^- at three EANET sites located in the western area of Korea averaged 0.97 during 2001~2007 (EANET). The average SO_4^{2-}/NO_3^- ratio of 2.3 in this study was attributed to the close proximity to industrial areas in Korea [30]. The $H^+/(NO_3^- + SO_4^{2-})$ ratio can represent the relative contributions of H_2SO_4 and HNO_3 to the acidity of rain, and deviations from unity indicate the degree of neutralization [65]. Earlier studies in Korea showed that acidity due to H^+ was less than 7% in rural areas, while that in urban areas ranged from 18% to 34%. The combined contribution of H_2SO_4 and HNO_3 to acidity in the Shihwa Basin was 0.36 ± 0.26, indicating that about 64% of the acidity was neutralized by cations [66]. The $H^+/(NO_3^- + SO_4^{2-})$ ratios for China, Southeast Asia, Korea, and Japan are about 20%, 60%, 30%, and 37%, respectively. The mean pH for wet-only precipitation (4.84) in the Shihwa Basin is higher than or similar to the results from other major cities in Asia.

3.3. Temporal Variation

During the study period, there were 26 episodic events in which the total ion concentration precipitation was >2000 μeq·L^{-1}. There were 14 events in winter, 11 in spring, and one in autumn. In summer, there were no events when the total ion concentration was >2000 μeq·L^{-1}. Rastogi and Sarin (2007) [67] reported that low-solute events are associated with heavy amounts of rain or successive events. The concentrations of most of the chemical components in the wet-only samples were inversely related to precipitation amount. About 74% of the rain in the Shihwa Basin fell from June to September (Figure 4). Concentrations during the rainy period (June to August) were significantly lower ($p < 0.05$ for H^+ and $p < 0.01$ for other ions) than those in the dry period (September to May). The concentrations of the inorganic species decreased due to dilution during the rainy period, thus ion concentrations were lower during the rainy period than ion concentrations in the dry period. The concentrations of soil-derived species (Ca^{2+} and Mg^{2+}) in the dry season were about six times higher than those in the rainy season. In March, influenced by dust from Asian continental deserts such as the Taklamakan, Gobi, and Loess plateau, the concentrations of all chemical components were highest. The monthly VWM concentrations of SO_4^{2-} and NO_3^- in the wet-only samples were correlated with concentrations of SO_2 ($r = 0.466$, $p < 0.001$) and NO_2 ($r = 0.559$, $p < 0.001$) in atmosphere (Figure 5). The NO_2 and SO_2 data are available from the National Institute of Environmental Research (NIER) in the same administrative district (Ansan city). Tu *et al.* (2005) [19] also reported that the SO_4^{2-} concentration had a temporal trend corresponding to SO_2 in atmosphere in China. Similar results have been found in a number of studies [15,68].

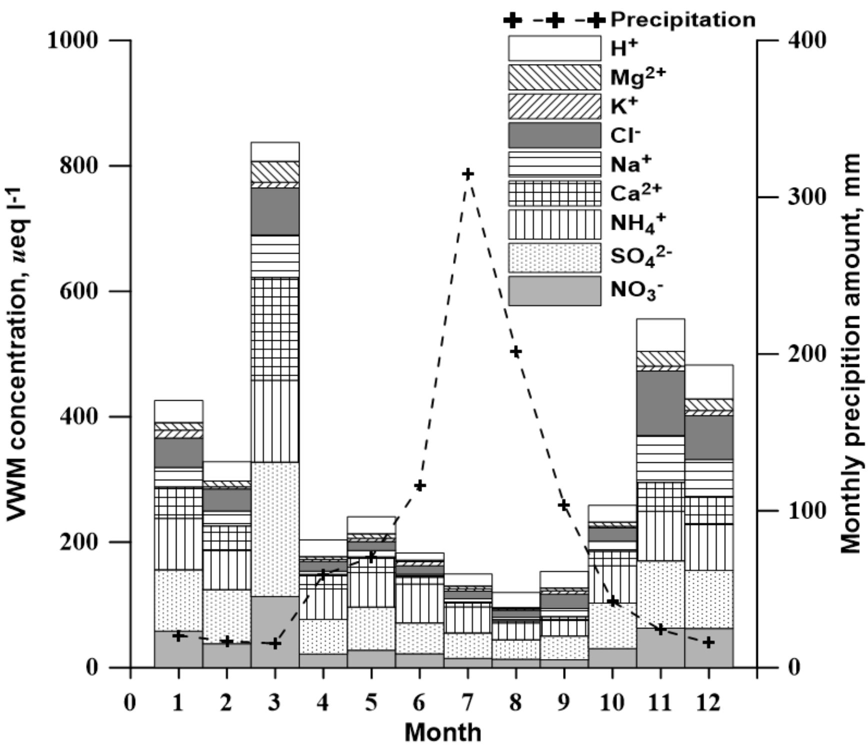

Figure 4. Monthly VWM concentrations of ions in rainfall and rainfall amount.

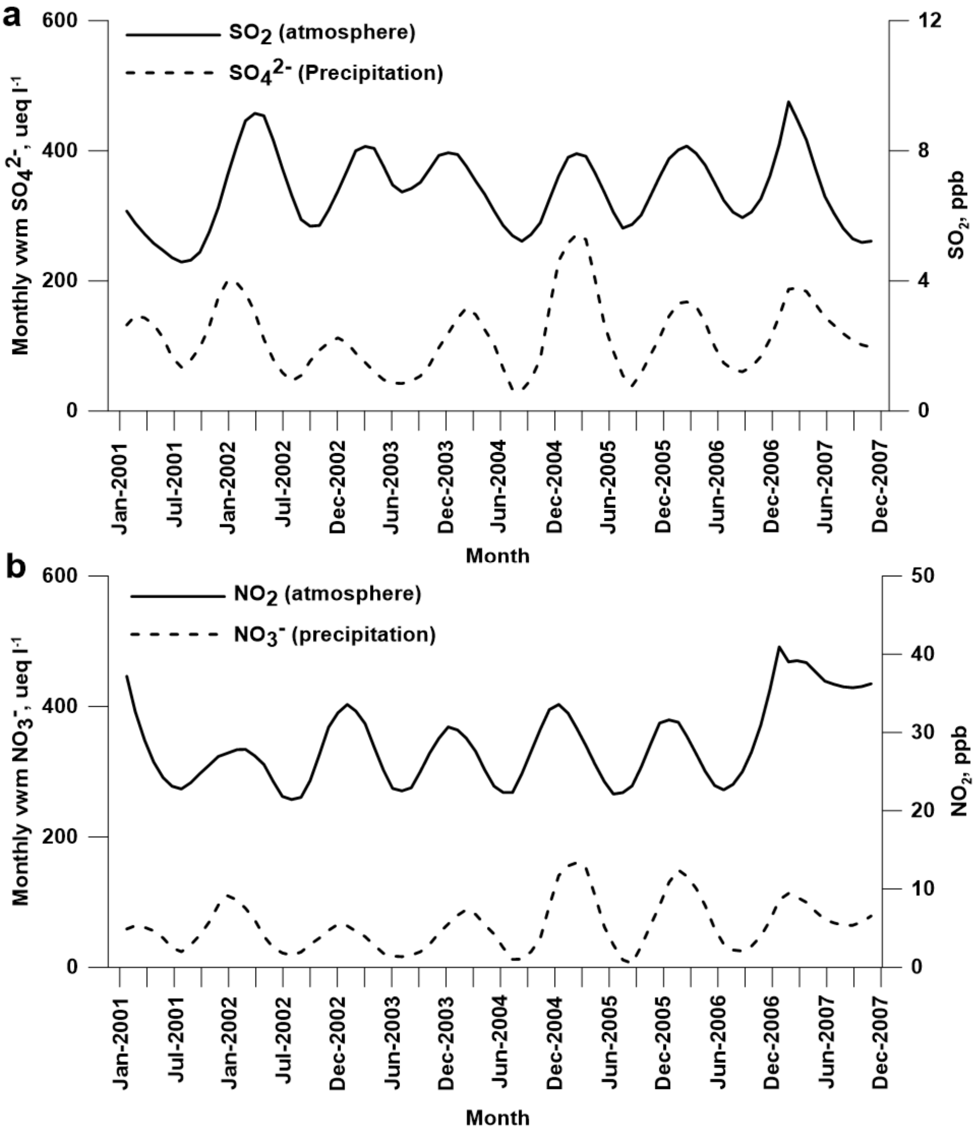

Figure 5. Trends with Lowess smoothing (span = 0.2): (**a**) monthly VWM SO_4^{2-} concentration in wet-only precipitation and the monthly mean atmospheric SO_2 concentration and (**b**) monthly VWM NO_3^- concentration in wet-only precipitation and the monthly mean atmospheric NO_2 concentration.

Figure 6 shows the annual VWM concentrations of the major components in precipitation. Anthropogenic SO_2 and NO_2 emitted from mobile and power plant sources contributed to the increasing of SO_4^{2-} and NO_3^- in the wet-only samples [69]. In 2002, power plants (450 MW) near the study area expanded to Boryeong thermal power plant located about 100 km south of Daebudo station. Thermal power facilities (1600 MW) were also added to the Yeungheung thermal power plant located 13 km west from Daebudo station in 2004. In 2005, the Incheon thermal power plants located 20 km north of the Banwol industrial complex expanded to a 342 MW power plant facility. Additional power generating capacity (5275 MW) has been added to these three power plants between 2008 and 2014. During the study period, the NH_4^+/SO_4^{2-} ratio decreased from 1.01 to 0.68. The NH_4^+/NO_3^- ratio also decreased from 2.39 to 1.20. Results from studies of wet-only precipitation in Austria, Brazil, Canada, USA, Japan, and China have shown significant decreasing trends in the concentrations of SO_4^{2-} and H^+

over long-term periods [15,16,70–72]. Table 3 shows VWM concentrations in recent precipitation studies in East Asia. The concentrations of water-soluble components in the Shihwa Basin were lower than those found in other Asian continental countries. The average concentrations of NO_3^- and SO_4^{2-} ranged from 1.8 to 2.0 and were 2.0 to 2.4 times higher than average concentrations in Seoul [33].

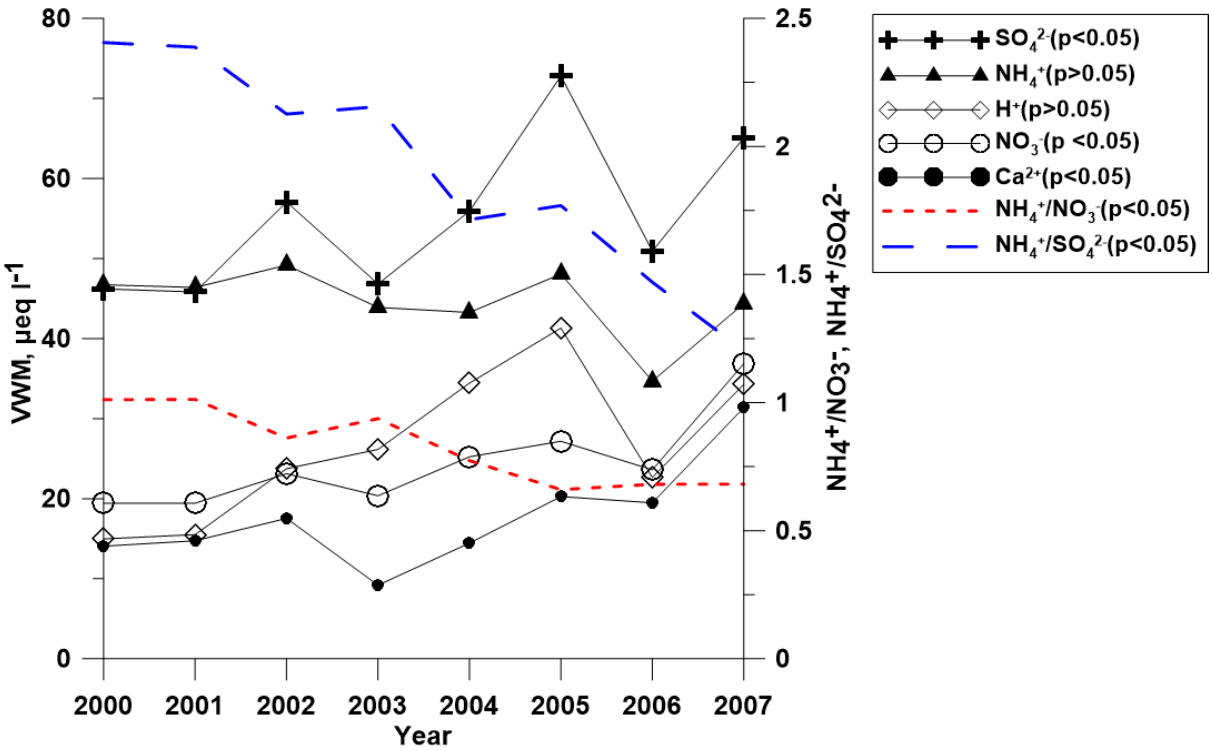

Figure 6. Annual variations of major inorganic VWM concentrations in the precipitation.

Table 3. Volume-weighted mean (VWM) concentrations of the chemical components in wet-only precipitation in East Asia (μeq·L^{-1} except pH).

East Asia	Year(s)	Cl^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	pH
Beijing [a] (N China)	2003	-	118	380	-	211	-	-	159	6.48
China [b] (SE China)	2004	9	31	95	6	81	5	3	48	4.54
Cai Jia Tang [c] (S China)	2003	11	60	155	7	112	10	10	60	4.33
Hong Kong [d]	1999–2000	43	27	74	37	22	4	7	16	4.20
Singapore [e]	1999–2000	34	22	84	33	19	7	7	16	4.20
Japan [f] (Tokyo)	1990–2002	55	31	50	37	40	3	12	25	4.52
Jeju [g] (Korea)	2000-2007	40	23	22	24	40	21	3	9	5.37
This study	2000–2007	23	23	54	13	44	4	6	17	4.84

[a] Tang *et al.* (2005); [b] Zhang *et al.* (2007b); [e] Hu *et al.* (2003); [f] Okuda *et al.* (2005); [g] EANET(2013).

3.4. Statistical Analysis

Table 4 shows the correlation coefficients among chemical species for this study. Significant and strong correlations were found among Na^+, Cl^-, Mg^{2+} and Ca^{2+}, indicating that this region is heavily affected by sea salts and soil. Ca^{2+} and Mg^{2+} correlations with Cl^-, NO_3^-, and SO_4^{2-} indicate that $CaCl_2$, $MgCl_2$, $Ca(NO_3)_2$, $Mg(NO_3)_2$, $CaSO_4$, and $MgSO_4$ were the primary soil-derived components in the wet-only precipitation [73]. The correlation among NH_4^+, NO_3^-, and SO_4^{2-} indicate that they originated from similar anthropogenic sources. The significant correlation between NH_4^+ and NO_3^- ($r = 0.76$, $p < 0.001$) and between NH_4^+ and SO_4^{2-} ($r = 0.83$, $p < 0.001$) indicate that NH_4NO_3, $(NH_4)HSO_4$, and $(NH_4)_2SO_4$ were the major forms of NH_4^+ in precipitation. Although positive correlations between acidic anions and H^+ were observed, their correlations were weaker due to neutralization effect by basic soils components [74].

Table 4. Correlations between ionic components in wet-only precipitation over seven years in the Shihwa Basin ($p < 0.001$ for all correlation).

	Cl^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Mg^{2+}
NO_3^-	0.56						
SO_4^{2-}	0.62	0.82					
Na^+	0.89	0.58	0.64				
NH_4^+	0.52	0.76	0.83	0.48			
K^+	0.66	0.43	0.54	0.61	0.55		
Mg^{2+}	0.74	0.67	0.69	0.82	0.49	0.47	
Ca^{2+}	0.63	0.71	0.82	0.68	0.60	0.49	0.80

Additional details on the patterns in the chemical constituents were analyzed using PMF. Similar studies have also used this technique to identify sources of air pollutants. Anttila *et al.* (1995) [75] determined the sources of bulk wet deposition in Finland using PMF analysis. Recently, Kitayama *et al.* (2010) [76] used PMF to identify the sources of SO_2 in Japan. The number of factors was determined by the optimized values. Five factors were chosen (Figure 7). The factors were identified as sea salts (Na^+, ss-Cl^-), Asian dust (Mg^{2+}, Ca^{2+}), sulfuric acid (H^+, SO_4^{2-}), ammonium salt with nitrate (NH_4NO_3), and ammonium salt with sulfate (NH_4HSO_4 and $(NH_4)_2SO_4$)components. The first factor was characterized by high concentrations of sea salts and its contribution to ions in precipitation was 18%–26%. At the Banwol site, some anthropogenic components (NO_3^-, NH_4^+, and SO_4^{2-}) were also included in this factor. The second factor, accounting for 17% of the total ions, was dominated by Asian dust at all three sites, indicated by high concentrations of Mg^{2+} and Ca^{2+}. This factor explained 70%–79% of the variation in Ca^{2+} and 42%–74% of that in Mg^{2+}. The average contribution of the Asian dust factor was especially high during the spring. The third factor represents H^+ and SO_4^{2-}, accounting for 16%–23% of the total. The acidity of the precipitation is largely affected by the dissolution of SO_2 and NO_2 as precursors of the acidic components. As noted above, the high SO_4^{2-}/NO_3^- ratio in the Shihwa basin indicates that emissions of SO_2 from the industrial complex were dominant sources for acidity. SO_4^{2-} accounted for 93%, 52%, and 57% of this acidity factor at Hwasung, Banwol, and Daeboo, respectively. The fourth factor was characterized by ammonium nitrate, which explained 17%–21% of the total and originated from either local industrial or farmland sources. The presence of nitrate with ammonium ions indicates dissolutions of ammonium nitrate from aerosols. The fifth factor represents high loadings of NH_4^+ and SO_4^{2-}. The highest NH_4^+ concentrations were found in Hwasung where sizeable NH_3 sources, such as farmland, exist. The relative contributions of five factors to measured components varied largely by the month of year (Figure 8). The acidity and secondary aerosol factors were mainly associated with the temperature and precipitation amount. Their contribution was highest in summer. However, Asian dust influences were dominant during the spring.

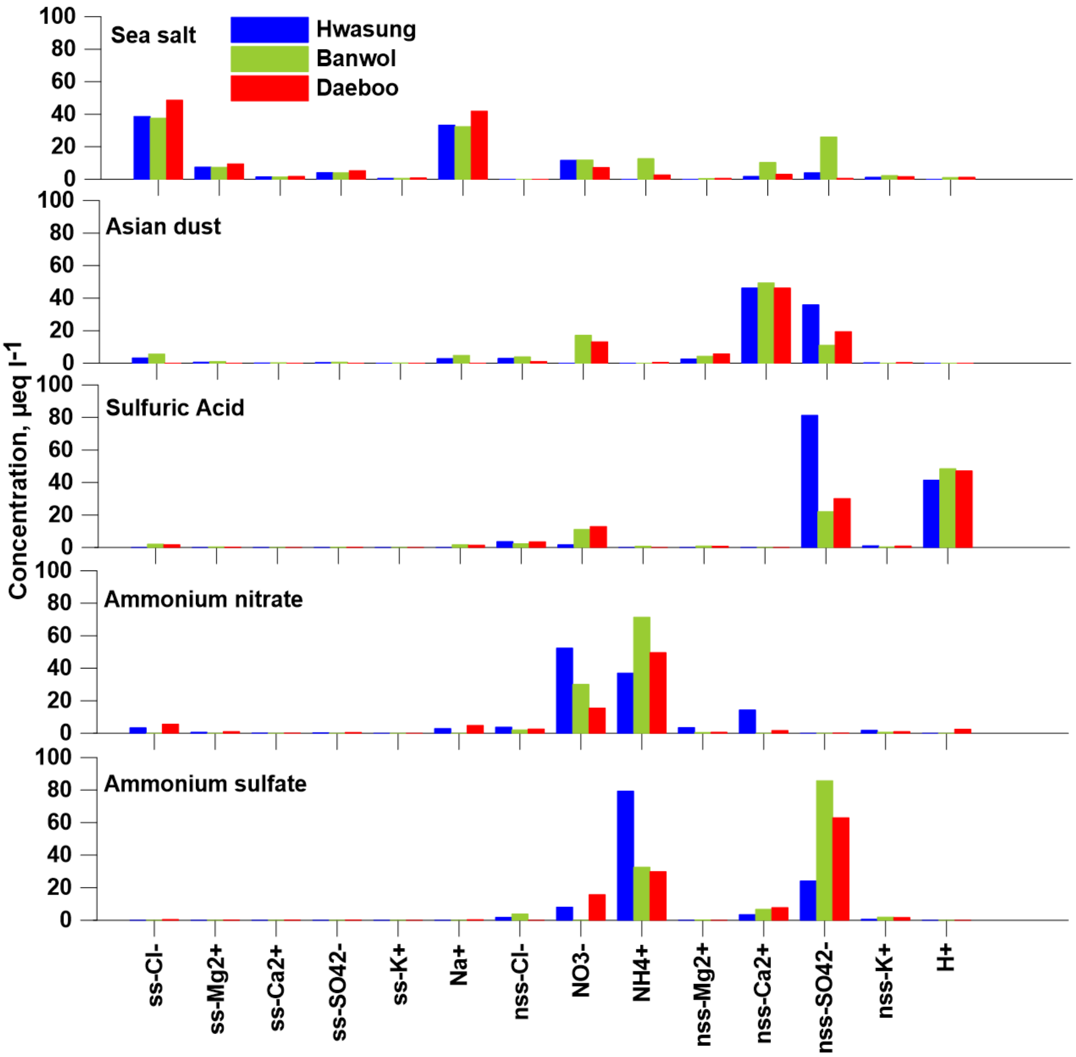

Figure 7. Source contributions of factors 1–5 at the three stations.

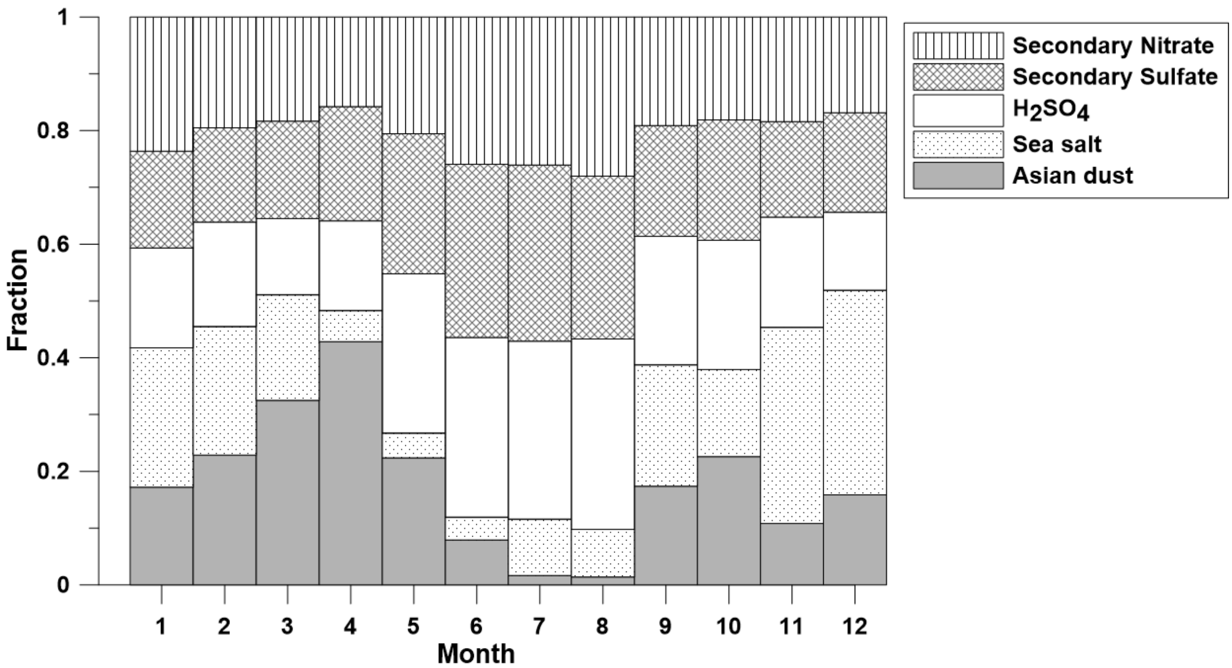

Figure 8. Temporal variations in the five source contributions.

4. Conclusions

The composition of precipitation at three sites in the Shihwa Basin was studied from June 2000 to November 2007. A total of 532 wet-only precipitation samples were used to characterize features of the precipitation and to evaluate the influence of anthropogenic sources.

The VWM for pH for all sites combined was 4.84, with pH < 5.0 in 66% of the precipitation samples, confirming that precipitation in the Shihwa Basin is acidic. The chemical composition of the precipitation was influenced by both natural (sea salt and soil components) and anthropogenic (acidic and alkali components) sources. SO_4^{2-} and NH_4^+ were the dominant ions, followed by NO_3^- and sea salts. Based on the $H^+/(NO_3^- + SO_4^{2-})$ ratio, 66% of the acidity in the Shihwa Basin was neutralized by alkaline particles. The SO_4^{2-}/NO_3^- ratio showed that the contribution of SO_4^{2-} to acidity was twice as high as that of NO_3^-. Seventy-four percent of the rain fell during the summer, when the concentrations of all of the ions were significantly lower than those in other seasons.

Although the mean concentrations of the anthropogenic components ($NO_3^- + SO_4^{2-} + NH_4^+$) in the Shihwa basin were 1.8~2.2 times higher than those in Seoul, the VWM concentrations of most of the chemical components were lower than those in other areas of East Asia. To identify the sources of the inorganic species in wet-only precipitation, the components were evaluated using statistical analysis. The moderate correlations of H^+ with NO_3^- and SO_4^{2-} and the strong correlations of NO_3^- and SO_4^{2-} with NH_4^+, Mg^{2+}, and Ca^{2+} suggest that neutralization reactions have a strong effect on acidity in the Shihwa Basin. Power generating facilities have expanded in the vicinity of the Shihwa basin from 2002 to 2013. This trend may have impacted the trend of increasing SO_4^{2-} concentrations during the study period. The results from PMF indicated that the main contributors to the wet-only precipitation chemical components in this study were secondary aerosols (40%–42%) followed by acidity (16%–23%), while sea salts and Asian dust contributed 19%–26% and 17%–18%, respectively.

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Author Contributions

Seung-Myung Park: Sampling, Data analysis, Drafting of Manuscript
Beom-Keun Seo: Sampling, Data analysis
Gangwoong Lee: Study conception and design, Research performance, Critical revision
Sung-Hyun Kahang: Study conception and design
Yu Woon Jang: Sampling, Data analysis, Drafting of Manuscript

Conflicts of Interest

The authors declare no conflict of interest.

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