

# 1 **Confirming anthropogenic influences on the major organic** 2 **and inorganic constituents of rainwater in an urban area**

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## 14 15 **Abstract**

16 **Recently, rainwater composition affected by atmospheric pollutants has been the topic of intense**  
17 **study in East Asia because of its adverse environmental and human health effects. In the present**  
18 **study**, the chemical composition and organic compounds of rainwater were investigated from June to  
19 December 2012 at Gwangju in Korea. **The aim of this study is to determine the seasonal variation**  
20 **of rainwater chemical composition, and to identify possible sources of inorganic and organic**  
21 **compounds.** The volume weighted mean of pH ranged from 3.83 to 8.90 with an average of  
22 5.78. 50% of rainwater samples had pH values below 5.6. The volume-weighted mean  
23 concentration (VWMC) of major ions followed the order:  $\text{Cl}^- > \text{SO}_4^{2-} > \text{NH}_4^+ > \text{Na}^+ > \text{NO}_3^-$   
24  $> \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$ . The VWMC of trace metals decreased in the order as follows  $\text{Zn} > \text{Al} >$   
25  $\text{Fe} > \text{Mn} > \text{Pb} > \text{Cu} > \text{Ni} > \text{Cd} > \text{Cr}$ . The VWMCs of major ions and trace metals were higher  
26 in winter than in summer. The high enrichment factors indicate that Zn, Pb, Cu, and Cd  
27 originated predominantly from anthropogenic sources. Factor analysis (principal component  
28 analysis) indicates the influence of anthropogenic pollutants, sea salt, and crustal materials on  
29 the chemical compositions of rainwater. Benzoic acids, 1H-Isoindole-1,3(2H)-dione, phthalic  
30 anhydride, benzene, acetic acids, 1,2-benzenedicarboxylic acids, benzonitrile, acetaldehyde,

1 and acetamide were the most prominent pyrolysis fragments for rainwater organic  
2 compounds identified by pyrolysis gas chromatography/mass spectrometry (Py-GC/MS). The  
3 results indicate that anthropogenic sources are the most important factors affecting the  
4 organic composition of rainwater in urban area.

## 6 **1 Introduction**

7 Rain is an efficient scavenging process for pollutants in the air and is becoming a source of  
8 pollution to the environment (Santos et al., 2011). The emission of SO<sub>2</sub> and NO<sub>x</sub> from fossil  
9 fuel combustion and industrial processes has rapidly increased in East Asia due to its fast  
10 growing economy. These gases are converted into sulfuric and nitric acids before  
11 precipitating as acid rain (Lee et al., 2000; Báez et al., 2006). Consequently, there have been  
12 adverse environmental effects on aquatic, biological, and terrestrial systems (Bard, 1999;  
13 Başak and Alagha, 2004). Thus, the chemical composition of precipitation has been  
14 investigated all around the world during the last decade (Lara et al., 2001; Mouli et al., 2010;  
15 Santos et al., 2011).

16 Coal combustion, automobile exhaust, and industrial emissions represent the dominant  
17 anthropogenic sources of heavy metals in rainwater (Kaya and Tuncel, 1997; Hu and  
18 Balasubramanian, 2003; Cheng et al., 2011). Heavy metals from precipitation accumulate in  
19 the biosphere and may cause adverse human health and environmental effects (Barrie et al.,  
20 1987; Báez et al., 2007). Thus, the studies of heavy metals in rainwater have increased in  
21 many countries (Pike and Moran, 2001; Al-Momani, 2003; Báez et al., 2007).

22 Dissolved organic carbon (DOC) is a major component of both continental (161 μM) and  
23 marine rain (23 μM) (Willey et al., 2000). DOC is a mixture of simple substances such as  
24 alkanes, carbohydrates, and fatty acids, and of complex polymeric molecules, such as  
25 aromatic, aliphatic, and carboxylic carbons (Muller et al., 2008). Rainwater DOC plays a  
26 significant role in the atmospheric carbon cycle, and the global rainwater flux of DOC is  
27  $430 \times 10^{12} \text{ g C yr}^{-1}$  (Willey et al., 2000). Sources of DOC compounds in rainwater are  
28 primary anthropogenic and biogenic emissions, and photochemical transformations of  
29 precursors (Klouda et al., 1996). While numerous studies have been conducted on the  
30 inorganic chemistry of rainwater, little attention has been paid to organic compounds.  
31 Kawamura et al. (1983) initiated the identification and distribution of organic compounds in

1 rainwater. The role of organic compounds in atmospheric processes has gained much  
2 attention in the last few years, and knowledge of organic compounds has improved with  
3 various analytical methods (Kieber et al., 2002; Seitzinger et al., 2003). However, the organic  
4 compounds in the atmosphere are very complicated and chemical characterization of organic  
5 matter in precipitation requires further work (Santos et al., 2009).

6 Several studies have examined chemical composition of rainwater in Korea. Although  
7 many studies have been conducted on the seasonal variation of all the major ions or heavy  
8 metals in rainwater (Lee et al., 2000; Kang et al., 2004; Kim et al., 2012; Moon et al., 2012),  
9 there are few on the organic compounds and the sources and variation of DOC in  
10 precipitation (Yan and Kim, 2012).

11 In this study, rainwater samples were collected from June to December 2012 in an urban  
12 area of Gwangju city, Korea. The objectives of this study are to investigate the seasonal  
13 variation of rainwater chemical composition, and to identify possible sources of inorganic  
14 and organic compounds in rainwater.

## 16 **2 Materials and Methods**

### 17 **2.1 Study site**

18 Rainwater samples were collected at the Gwangju Institute of Science and Technology  
19 campus (35°13'N, 126°50'E) in Gwangju city in Korea (Fig. 1) from June to December in  
20 2012. Gwangju has an area of 501.34 km<sup>2</sup> and a population of around 1,480,000. The annual  
21 average of temperature is 13.5 °C and the average precipitation is 1,368 mm per year.

### 22 **2.2 Sample collection and analysis**

23 Rainwater samples were collected per event using a Teflon-coated collector designed to  
24 manually take samples with time. Samples from initial precipitation events were collected  
25 with care not to be mixed with later precipitation samples. All the initial and later samples  
26 were transported to the laboratory, and pH and electrical conductivity (EC) measured. The  
27 remaining samples were filtered through 0.45 µm filters (mixed cellulose ester, Advantec,  
28 Japan) and then stored at 4 °C until further chemical analyses were performed within one

1 week. pH and EC were measured using a pH meter and an EC meter, respectively (Orion 3-Star, Thermo Scientific, USA).

3 Major ions were quantified using a suppressed type ion chromatograph (DX-120, ICS-90, 4 Dionex, Sunnyvale, CA, USA). Ion Pac AS14 and an Ion Pac CS12A column (Dionex, 5 Sunnyvale, CA, USA) were used for measurements of major anions ( $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{Cl}^-$ ) 6 and the cations ( $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ , and  $\text{K}^+$ ), respectively. The concentrations of trace 7 metals were measured using inductively coupled plasma mass spectrometry (ICP-MS) 8 (7500ce, Agilent, Santa Clara, CA, USA). All the samples were acidified to a final nitric acid 9 concentration of 2% using 70% nitric acid solution. The levels of DOC and total nitrogen 10 (TN) contents of rainwater samples were determined using a total organic carbon analyzer 11 (TOC-V CPH, Shimadzu, Japan) equipped with a TN analyzer (TNM-1, Shimadzu, Japan). 12 The UV absorbance of the samples at 254 nm ( $\text{UV}_{254}$ ) was measured using a UV-vis 13 spectrophotometer (UV-1601, Shimadzu, Japan). The specific UV absorbance (SUVA) value 14 (an indicator of aromaticity) was calculated from the ratio of  $\text{UV}_{254}$  to DOC concentration. 15 Rainwater samples were concentrated to a final DOC concentration of approximately 100 mg 16  $\text{C l}^{-1}$  with a rotary evaporator (Eyela, Japan). Approximately 20 ml of concentrated samples 17 was freeze-dried using a freeze dryer (Ilshin, Korea) prior to pyrolysis gas 18 chromatography/mass spectrometry (Py-GC/MS) analysis. Approximately 0.5–1.0 mg of 19 freeze-dried sample powders were pyrolyzed at 590 °C for 5 s in the pyrofoil (Pyrofoil F590, 20 Japan Analytical Industry, Tokyo, Japan) within a curie point pyrolyzer (JCI-22, Japan 21 Analytical Industry, Tokyo, Japan) coupled with an Agilent 7890A gas chromatograph 22 coupled to a 5975C quadrupole mass spectrometer (ion source temperature 220 °C, scanning 23 from 40 to 500 amu, electron energy 70 eV). Pyrolysis fragments were separated by GC 24 equipped with a DB-5MS (Agilent Technologies, USA) column and identified using a mass 25 spectrometer. Helium was used as the carrier gas. The temperature program of the GC oven 26 was initially maintained at 40 °C for 5 min, then increased at 7 °C  $\text{min}^{-1}$  to a final temperature 27 of 300 °C, and maintained there for 10 min, giving a total run time of 52.14 min. The 28 interpretation of the pyrochromatograms was conducted according to the methods described

1 in Bruchet et al. (1990).

2

### 3 **3 Results and Discussion**

#### 4 **3.1 Variation of pH value and precipitation amount**

5 The average monthly rainfall from June to December during 2012 was 195.4 mm and the  
6 highest amount of rain fall (473.5 mm) was observed in August in 2012 (Fig. 2). 79% of the  
7 total rainfall was concentrated during summer (July–September). The percent frequency  
8 distribution of pH for the rainwater samples is presented in Fig. 3. The volume weighted  
9 mean of pH was 5.78. The lowest pH value was observed on July 11 with a pH of 3.83, while  
10 the highest was on August 22, 2012 with a pH value of 8.90. Most pH values ranged between  
11 5.0 and 5.5 (23.9%), while about 2.6% of pH values were in the range of 3.5–4.5. 50% of the  
12 samples had pH values below 5.6, which is the value of unpolluted water equilibrated with  
13 atmospheric CO<sub>2</sub> (Charlson and Rodhe, 1982). On the other hand, approximately 12% of the  
14 samples had pH above 7.0, suggesting strong inputs of alkaline substances to rainwater in this  
15 area.

#### 16 **3.2 Ionic composition of rainwater**

17 The volume-weighted mean concentration (VWMC), standard deviation of the VWMC  
18 (SDVWMC), and minimum (Min) and maximum (Max) concentrations of the rainwater  
19 chemical components are summarized in Table 1. The VWMC of major ions in rainwater  
20 follows the order: Cl<sup>-</sup> > SO<sub>4</sub><sup>2-</sup> > NH<sub>4</sub><sup>+</sup> > Na<sup>+</sup> > NO<sub>3</sub><sup>-</sup> > Ca<sup>2+</sup> > Mg<sup>2+</sup> > K<sup>+</sup>. Among all the ions,  
21 Cl<sup>-</sup> was the most abundant with an average of 123.5 µeq l<sup>-1</sup>, accounting for 28.5% of the ionic  
22 concentration. SO<sub>4</sub><sup>2-</sup> was the second highest anion with an average of 91.9 µeq l<sup>-1</sup>, accounting  
23 for 21.2% of total ions. The contribution of NO<sub>3</sub> was 8.5% (concentration of 36.8 µeq l<sup>-1</sup>).  
24 The high value of SO<sub>4</sub><sup>2-</sup> and highest of Cl<sup>-</sup> can be attributed to emissions from fossil fuel  
25 combustion and typhoons and sea salts, respectively. As for cation species, NH<sub>4</sub><sup>+</sup> made the  
26 highest contribution at 63.0 µeq l<sup>-1</sup>, accounting for 14.5% of the total ions. Meanwhile, Na<sup>+</sup>  
27 was the second highest cation accounting for 13.5% of the total ions. The concentration of  
28 Ca<sup>2+</sup>, Mg<sup>2+</sup> and K<sup>+</sup> ions accounted for 8.5%, 3.5%, and 1.8%, respectively. The high level of

1  $\text{NH}_4^+$  in Gwangju city was comparable to Seoul (with a mean concentration of  $66.4 \mu\text{eq l}^{-1}$   
2 (Lee et al., 2000)). Wastes from agricultural and domestic activities as well as the use of  
3 fertilizers are believed to be the main sources of the emission of gaseous ammonia (Dianwu  
4 and Anpu, 1994; Panyakapo and Onchang, 2008).  $\text{Ca}^{2+}$  may originate from wind-blown dust  
5 and calcareous soil,  $\text{Mg}^{2+}$  from sea salts and dusts in the atmosphere, while  $\text{Na}^+$  from sea salts.  
6 EC of rainwater ranged from 0.87 to  $169.00 \mu\text{S cm}^{-1}$ , with a VWM value of  $27.82 \mu\text{S cm}^{-1}$ .  
7 The VWMs of UV and SUVA in rainwater were 0.0160 and 1.09, respectively. Organic  
8 matter in rainwaters exhibit relatively hydrophilic characteristic, with SUVA values less than  
9 two generally indicating a high fraction of hydrophilic non-humic matter with low UV  
10 absorbance.

11 The VWMC of major ions in rainwater at Gwangju were compared to those reported in  
12 other urban areas around the world (Table 2). The pH value measured in our study is lower  
13 than that in Tirupati, India, but higher than those reported for other sites. The concentration of  
14  $\text{Na}^+$  is comparable to that in Shanghai, but lower than Istanbul and higher than other areas.  
15 The  $\text{Cl}^-$  value is comparable to that in Istanbul and much higher than those reported for other  
16 sites. The high concentration of marine elements was likely due to typhoons during summer  
17 seasons. The value of  $\text{NO}_3^-$  is higher than that in Southeast Brazil and close to that in other  
18 sites. Regarding  $\text{SO}_4^{2-}$ , its concentration is higher than that in Seoul, Mexico and Brazil and  
19 lower than in other areas. Shanghai shows the highest value of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  indicating  
20 severe air pollution problems in China. Both of these ions were mainly derived from the high  
21 coal/fuel consumption and mobile sources. The concentration of  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  are higher  
22 than those in Seoul, Mexico, Brazil and lower than ones in other sites. The concentrations of  
23 these ions are comparatively higher in Istanbul than in other areas. The value of  $\text{NH}_4^+$  is  
24 comparable to that in Seoul and higher than that in India, Turkey, and Brazil.

### 25 3.3 Seasonal variation

26 Fig. 4 displays the monthly variation of VWM of pH, conductivity, TOC, TN, SUVA and UV  
27 of rainwater samples. pH values measured during summer seasons (June–September) with  
28 greater rainfall were higher than those during the winter season (October–December). This is  
29 consistent with previous studies (Cerón et al., 2013). Lee et al. (2000) also mentioned that the  
30 amount of rainfall influences pH. Conductivity values increased from summer to winter

1 seasons, in agreement with the seasonal trend of major ions. Less conductivity during  
2 summer was caused by the dilution effect of higher rainfall. The values of TOC show similar  
3 monthly trends to TN, increasing with decreasing rainfall amounts. Similar seasonal  
4 variations of TOC have been reported in other studies (Pan et al., 2010; Yan and Kim, 2012).  
5 DOC in the atmosphere is known to vary with the seasons due to biogenic emission from  
6 vegetation. Kieber et al. (2002) reported relatively higher levels of DOC in rainwater in  
7 warmer seasons. In contrast, Yan and Kim (2012) indicated that it was due to the prevailing  
8 anthropogenic contributions (mostly fossil fuel burning) and low precipitation in the  
9 relatively dry winter season. They also found that DOC in precipitation over Seoul was  
10 mainly produced by incomplete combustion of fossil fuel. The values of TN display similar  
11 monthly trends with TOC. It was higher in spring, fall, and winter, which are relatively dryer  
12 than summer. As expected, this is consistent with the monthly variation of  $\text{NO}_3^-$  and  $\text{NH}_4^+$ .  
13 The value of  $\text{UV}_{254}$  measured during winter season (November–December) is higher than in  
14 summer season (July–September). SUVA values higher than 1.4 were measured in September,  
15 November and December, but in the other months were lower than 1.0. The monthly VWMC  
16 of major ions in rainwater samples are depicted in Fig. 5. The mean concentration of major  
17 ions in samples during summer (July–September), typhoons, and winter (November–  
18 December) are illustrated in Fig. 6. More than half of the total rainfall is concentrated in  
19 summer, while in the winter, precipitation is less than 10% of the total in Korea (Lee et al.,  
20 2000). Thus, seasonal variations of ionic concentration in rainwater were mainly affected by  
21 precipitation patterns and monsoonal winds (Lee et al., 2000). The major ions had relatively  
22 higher concentrations in the winter, which is a pattern opposite to the trend in rainfall. The  
23 ionic concentrations showed decreasing trends with increasing rainfall amounts, suggesting a  
24 dilution effect of rainwater on precipitation chemistry. The lowest ion concentrations were  
25 observed during typhoon periods, except  $\text{Na}^+$  and  $\text{Cl}^-$ , which are typical marine components.

### 26 3.4 Correlation analysis

27 To investigate and identify potential correlation between major ions in rainwater samples,  
28 Pearson correlation analysis was applied (Table 3). A strong correlation was found between  
29  $\text{Na}^+$  and  $\text{Mg}^{2+}$  ( $R^2 = 0.99$ ), and between  $\text{Na}^+$  and  $\text{Cl}^-$  ( $R^2 = 1.00$ ) suggesting a marine source.  
30 The high correlation between  $\text{Mg}^{2+}$  and  $\text{Cl}^-$  ( $R^2 = 0.99$ ) also corresponds to salts of marine

1 origin. Relatively high correlations between  $\text{NO}_3^-$  and  $\text{NH}_4^+$  ( $R^2 = 0.86$ ), and between  $\text{SO}_4^{2-}$   
2 and  $\text{NH}_4^+$  ( $R^2 = 0.82$ ), may reveal co-occurrence of  $\text{NH}_4^+$  with  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  in rainwater.  
3 This was probably due to dissolution of secondary inorganic aerosols ( $(\text{NH}_4)_2\text{SO}_4$  and  
4  $\text{NH}_4\text{NO}_3$ ) in rainwater (Panyakapo and Onchang, 2008). Among the compounds of  
5 ammonium, ammonium sulfate is known to predominate in the atmosphere (Seinfeld, 1986).  
6 However, our study showed slightly higher correlation between  $\text{NH}_4^+$  and  $\text{NO}_3^-$  ( $R^2 = 0.86$ )  
7 than between  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  ( $R^2 = 0.82$ ), indicating that  $\text{NH}_4\text{NO}_3$  dominates over  
8  $(\text{NH}_4)_2\text{SO}_4$ . The dominance of  $\text{NH}_4\text{NO}_3$  has also been reported previously (Saxena et al.,  
9 1996). The high correlation between  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  suggests a common source origin, due  
10 to the co-emission of precursors ( $\text{SO}_2$  and  $\text{NO}_x$ ) from the same sources, such as fossil fuel  
11 burning, and the similarity of their behavior in precipitation. Correlations were also found  
12 between  $\text{NO}_3^-$  and  $\text{Ca}^{2+}$  ( $R^2 = 0.78$ ), and between  $\text{SO}_4^{2-}$  and  $\text{Ca}^{2+}$  ( $R^2 = 0.66$ ), suggesting that  
13  $\text{Ca}(\text{NO}_3)_2$  and  $\text{CaSO}_4$  are formed from the neutralization reactions of acidity in rainwater  
14 (Zhao et al., 2013). Moderate correlation was found between  $\text{K}^+$  and  $\text{Ca}^{2+}$ , indicating a  
15 common origin in marine aerosol.  $\text{K}^+$  and  $\text{SO}_4^{2-}$  were somewhat correlated ( $R^2 = 0.61$ ),  
16 suggesting the occurrence of reactions between the acid  $\text{H}_2\text{SO}_4$  and the alkaline compounds  
17 carried into the atmosphere by windblown sea salts/dusts (Huang et al., 2008).

### 18 3.5 Trace metals

19 The VWMCs of trace metals in rainwater samples are presented in Table 4. The concentration  
20 of trace metals decreased in the order as follows:  $\text{Zn} > \text{Al} > \text{Fe} > \text{Mn} > \text{Pb} > \text{Cu} > \text{Ni} > \text{Cd} >$   
21  $\text{Cr}$ . Table 5 provides the comparison of trace metal concentrations in precipitation from this  
22 study and with values obtained from other rural and urban regions of the world. This order of  
23 element abundance is similar to those obtained from precipitation in Chunchun, Suwan,  
24 Mexico, and Newcastle in USA. While Al and Fe were much higher in Ankara, the authors  
25 indicate that this is due to its location in the middle of the semi-arid Anatolia plateau. In  
26 general, the concentrations of trace metals in Gwangju are lower than those in other countries,  
27 due to the lack of industry in the city. With respect to Al, Fe, Ni, Cd, and Cr, concentrations  
28 in this study were the lowest of all the other countries. Most of the industries in Korea are  
29 located in and near Seoul and Kyonggi province, but Gwangju is a city of education, culture,



1 and universities with limited industrial activity. With respect to trace metals, values measured  
2 in Ankara, Turkey, were the highest of all of the other countries with the exception of Zn.

### 3 3.6 Variations in trace metal levels in rainwater

4 Monthly variations of VWMC of trace metals in rainwater are shown in Fig. 7. As expected,  
5 the lowest concentrations of trace metals were found during typhoon periods (July–  
6 September), caused by more frequent rain events and the consequent dilution effect. The  
7 samples collected in winter had higher concentrations of trace metals than the samples in  
8 summer (Fig. 8). Similar seasonal variations have been reported in other studies (Cheng et al.,  
9 2011; Kim et al., 2012).

### 10 3.7 Correlation analysis

11 Table 6 lists the matrix correlation between ions and trace metals (correlation coefficients  
12 greater than 0.5 are marked in bold letters). Moderate correlation was found among the trace  
13 metals and  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$ , with the exception of Cr and Zn, suggesting  
14 anthropogenic origin of the species. These correlations were also observed in previous studies  
15 (Garcia et al., 2006; Jung et al., 2011). Significant correlations between  $\text{SO}_4^{2-}$  and trace  
16 metals in rainwater were observed in Clarke and Radojevic (1987).

### 17 3.8 Enrichment factor analysis

18 An enrichment factor (EF) has been used to evaluate the contribution of non-crustal sources  
19 (Kaya and Tuncel, 1997; Kim et al., 2012). The EF values were calculated using the  
20 following relation:

$$21 \text{EF} = (\text{C}_X/\text{C}_{\text{Al sample}})/(\text{C}_X/\text{C}_{\text{Al crust}}),$$

22 where  $(\text{C}_X/\text{C}_{\text{Al sample}})$  is the ratio of the concentration of an element X and Al in the  
23 rainwater sample and  $(\text{C}_X/\text{C}_{\text{Al crust}})$  is the same ratio in crustal material, adapted from  
24 Wedepohl (1995).

25 EFs from 1 to 10 suggest crustal origin; EFs from 10 to 100 suggest moderate  
26 anthropogenic enrichment; and EFs > 100 indicate anthropogenic origin. Fig. 9 presents the  
27 bars of the EF of the trace elements. Fe and Cr with EF values of 1–10 were significantly

1 enriched by soil. Mn and Ni with EF values in the range of 10–100 were moderately enriched  
2 by anthropogenic sources, while Zn, Pb, Cu, and Cd with EF values exceeding 100 were  
3 highly enriched by human activities. Ni and Mn are mainly emitted from manufacture of  
4 ferro-alloys and from oil-fired furnaces (Báez et al., 2007). The primary sources of Zn, Pb,  
5 Cu, and Cd are industrial and traffic activities such as metal smelting and fuel combustion  
6 (Al-monani, 2003; Cheng et al., 2011). The variation of monthly EFs of trace metals in  
7 rainwater is depicted in Fig.10. The monthly EFs of trace metals were relatively high during  
8 summer (from June to September). Cd and Cr were not detected during the typhoon periods  
9 and September. The highest EF values of (Fe and Mn), (Pb, Cu, Cd, and Cr), and (Zn and Ni)  
10 were found during September, July, and June, respectively.

### 11 3.9 Comparison of chemical components in initial and subsequent rainfall

12 A comparison of the mean concentrations of major ions and trace metals in initial (n = 40)  
13 and subsequent (n = 73) rainfall samples is presented in Fig. 11. Greater amounts of major  
14 ions and trace metals appeared in initial rainfall samples than in subsequent samples as large  
15 amount of pollutants were dissolved in less water. Mean values of TOC, TN, UV, SUVA, pH  
16 and conductivity in initial (n = 40) and subsequent (n = 73) samples are shown in Table 7.  
17 Again, higher mean concentrations of TOC, TN, UV, SUVA, pH, and conductivity were  
18 observed in initial rainfall, with the values of TOC, TN, and UV in initial rainfall being twice  
19 as high as in subsequent rainfall.

### 20 3.10 Factor analysis

21 Factor analysis (principal component analysis) has been widely applied in previous studies to  
22 investigate the influence of different sources on the chemical components in precipitation  
23 (Báez et al., 2006; Garcia et al., 2006; Panyakapo and Onchang, 2008). A varimax-rotated  
24 principal component analysis (PCA) was performed using Minitab version 16 for Windows.  
25 Table 8 presents the result of the factor analysis that identified three factors that explained  
26 approximately 73.1% of the total variance. Factor 1 explained 27.1% of the total variance  
27 with high loadings for  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{NH}_4^+$ , and moderate loadings for  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and Cu.  
28 This factor indicates marine sources for  $\text{K}^+$  and  $\text{Ca}^{2+}$ , with an anthropogenic source for Cu, as  
29 is indicated by EF. Cu is a typical metal contaminant emitted from industrial processes (Wong

1 et al., 2003). The loadings of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{NH}_4^+$  suggest that these ions come from  
2 anthropogenic sources associated with precursor gases such as  $\text{SO}_2$  and  $\text{NO}_x$ . The co-  
3 occurrence of  $\text{NH}_4^+$  with  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  are caused by dissolution of aerosols and secondary  
4 pollutants containing  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NH}_4\text{NO}_3$  in rainwater. Factor 2 accounted for 22.4% of  
5 the total variance with high loading for  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Cl}^-$ , indicating the influence of sea  
6 spray. Factor 3, which explained 22.2% of the total variance, proposed moderate loadings of  
7 most of the trace metals. This factor indicates the contribution of anthropogenic sources and  
8 significant crustal contributions for Al, Cr, and Fe, as indicated by EF. Overall, the  
9 anthropogenic pollutants, sea salts, and crustal materials were the main sources of the  
10 chemical species in rainwater in Gwangju.

### 11 3.11 Organic compounds in rainwater

12 Table 9 lists dominant pyrolysis fragments for rainwater organic compounds collected from  
13 June to December 2012 as identified by Py-GC/MS based on peak area percent of pyro-  
14 chromatograms. Each sample could be fractionated and categorized into polysaccharides (PS),  
15 amino sugars (AS), proteins (PR), polyhydroxy aromatics (PHA), lignins (LG), and lipids (Lp)  
16 (Leenher and Croue, 2003). Benzoic acids were the most abundant compound during June,  
17 which originates from anthropogenic sources, such as fossil fuel combustion. Kawamura et al.  
18 (1986) identified benzoic acids in used engine oil and motor-exhausts. Benzoic acids have  
19 been found in rainfall in Los Angeles and Norway (Lunde et al., 1977; Kawamura and  
20 Kaplan, 1983). 2-fluoro-acetamide and acetic acids were the most abundant compounds in  
21 July and September. Acetamide was one of the major pyrolysis organic compounds with  
22 precipitation in Konigstein, Germany (Laniewski et al., 1998), which is a source of plasticizer  
23 and industrial solvents and normally found near industrial areas (Cho and Shin, 2013). Acetic  
24 acids originate from primary natural sources such as emissions from microbial activity and  
25 vegetation and from anthropogenic sources (biomass burning and traffic exhaust) (Avery et  
26 al., 1991). It has been found in rainwaters from both developed and remote areas (Galloway  
27 et al., 1982; Keene and Galloway, 1984). 1H-Isoindole-1,3(2H)-dione, phthalic anhydride,  
28 benzene, and acetic acids were the most abundant species during August. 1H-Isoindole-  
29 1,3(2H)-dione was one of the major pyrolysis organic compounds from precipitation in  
30 Konigstein, Germany (Laniewski et al., 1998) and found to be from tire derived aggregates.

1 Phthalic anhydride originates from agricultural crop burning and open burning of scrap tires  
2 (Lemieux et al., 2004). Benzene is an important aromatic compound from gasoline,  
3 automobile exhaust, and urban atmosphere (Sigsby et al., 1987). Benzene was generally  
4 found as the major compound of volatile organic carbons in rainwater from Yokohama, Japan  
5 (Sato et al., 2006). 1,2-benzenedicarboxylic acids were the most abundant compound in  
6 October, which have been identified to be from particulate automobile exhaust emissions,  
7 cigarette combustion, production of plastics degradation, and products of lignin-type material  
8 metabolized by microorganisms (Johnstone and Plimmer, 1959; Simoneit, 1985; Kawamura  
9 and Kaplan, 1987). Benzotrile was the most abundant species during November, which has  
10 been found in accidental vehicle fires (Estrellan and Lino, 2010) and biomass combustion in  
11 improved stoves in rural China (Wang et al., 2009). Acetaldehyde was the most abundant  
12 compound in December, probably derived from primary incomplete combustion of fossil fuel  
13 and secondary photochemical reactions of hydrocarbons emitted from anthropogenic sources  
14 (Sakugawa et al., 1993). Acetaldehyde was also detected in Los Angeles (Kawamura et al.,  
15 2001) and Spain (Peña et al., 2002). Among fatty acids, n-hexadecanoic acid (C<sub>16</sub>),  
16 octadecanoic acid (C<sub>18</sub>), and tetradecanoic acid (C<sub>14</sub>) were found in the top 10 organic  
17 compounds during June and July. This is in agreement with previous work (Kawamura and  
18 Kaplan, 1986), where lower molecular fatty acids (C<sub>12</sub>–C<sub>19</sub>) are major compounds while  
19 higher molecular weight fatty acids (C<sub>20</sub>–C<sub>30</sub>) are minor. A major source of fatty acids (C <  
20 20) is known to be from cooking and biomass combustion in urban areas (Xu et al., 2008).  
21 All results in the present study indicate that anthropogenic sources were significant  
22 contributors to the organic compounds present in rainwater.

23

#### 24 **4 Conclusion**

25 Rainwater samples collected from Gwangju, Korea during June to December 2012 were  
26 analyzed to determine the chemical composition and organic compounds present in rainwater.  
27 The VWM of pH was 5.78 (ranging from 3.83 to 8.90) and acid rain (pH < 5.6) frequency  
28 was 50%. The VWMC of major ions and trace metals followed the order: Cl<sup>-</sup> > SO<sub>4</sub><sup>2-</sup> > NH<sub>4</sub><sup>+</sup>  
29 > Na<sup>+</sup> > NO<sub>3</sub><sup>-</sup> > Ca<sup>2+</sup> > Mg<sup>2+</sup> > K<sup>+</sup> and Zn > Al > Fe > Mn > Pb > Cu > Ni > Cd > Cr. The  
30 higher VWM values of TOC, TN, UV, SUVA, pH, conductivity, major ions, and trace metals  
31 appeared in initial rainfall than in subsequent rainfalls. The VWMCs of major ions and trace

1 metals were relatively lower in summer due to the dilution effect. The lowest VWMCs of  
2 ions (except Na<sup>+</sup> and Cl<sup>-</sup>) and trace metals were observed during typhoons. Based on EF  
3 values, Zn, Pb, Cu, Ni, Cd, and Mn were emitted mainly from anthropogenic sources whereas  
4 Fe and Cr originated from crustal sources. The factor analysis (principal component analysis)  
5 revealed that the anthropogenic pollutants, sea salts, and crustal materials were the main  
6 sources of ionic species and trace metals in rainwaters. The most abundant pyrolysis  
7 fragments for rainwater organic compounds were benzoic acids, 1H-Isoindole-1,3(2H)-dione,  
8 phthalic anhydride, benzene, acetic acids, 1,2-benzenedicarboxylic acids, benzonitrile,  
9 acetaldehyde, and acetamide, indicating that anthropogenic pollutants are significant  
10 contributors to rainwater organic compounds.

11

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1 Table 1. Volume-weighted mean concentration (VWMC), standard deviation of the VWMC  
 2 (SDVWMC), and minimum (Min) and maximum (Max) concentrations of chemical  
 3 composition in rainwater collected from June to December during 2012.

N=113		VWMC	SDVWMC	Min	Max
	pH	5.78	1.66	3.83	8.90
	Conductivity $\mu\text{S}/\text{cm}$	27.82	11.13	0.87	169.00
	TOC $\text{mg C}/\text{l}$	1.49	0.53	0.15	6.90
	UV $\text{cm}^{-1}$	0.0160	0.0061	0.0006	0.0972
	SUVA	1.09	0.30	0.03	2.42
	TN $\text{mg N}/\text{l}$	1.13	0.40	N.D.	8.62
	$\text{Na}^+$ $\text{mg}/\text{l}$	1.4	0.7	0.0	19.65
	$\mu\text{eq}/\text{l}$	58.5	30.7	1.2	854.50
	$\text{NH}_4^+$ $\text{mg}/\text{l}$	1.1	0.4	0.0	5.9
	$\mu\text{eq}/\text{l}$	63.0	22.1	1.6	327.1
	$\text{K}^+$ $\text{mg}/\text{l}$	0.3	0.1	0.0	1.9
	$\mu\text{eq}/\text{l}$	7.7	4.1	0.3	53.0
	$\text{Mg}^{2+}$ $\text{mg}/\text{l}$	0.2	0.1	N.D.	2.5
	$\mu\text{eq}/\text{l}$	15.3	7.5	N.D.	208.6
	$\text{Ca}^{2+}$ $\text{mg}/\text{l}$	0.7	0.4	N.D.	6.7
	$\mu\text{eq}/\text{l}$	36.7	17.7	N.D.	337.1
	$\text{NO}_3^-$ $\text{mg}/\text{l}$	2.28	0.9	N.D.	12.4
	$\mu\text{eq}/\text{l}$	36.8	14.8	N.D.	199.2
	$\text{SO}_4^{2-}$ $\text{mg}/\text{l}$	4.4	2.1	0.0	19.5
	$\mu\text{eq}/\text{l}$	91.9	42.6	0.9	405.4
	$\text{Cl}^-$ $\text{mg}/\text{l}$	4.4	3.0	0.0	39.3
	$\mu\text{eq}/\text{l}$	123.5	83.7	1.0	1106.4

4 N=number of samples

5 WHO drinking water guidelines: pH: 6.5–8.5,  $\text{NH}_4^+$ : 1.5 mg/l,  $\text{NO}_3^-$ : 50 mg/l,  $\text{SO}_4^{2-}$ : 250  
 6 mg/l,  $\text{Cl}^-$ : 250 mg/l

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1 Table 2. Comparison of VWMC of major ions ( $\mu\text{eq/l}$ ) in precipitation in Gwangju with that at other sites.

Location	Period	pH	Na <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	References
This study	Jun. ~ Dec. 2012	5.78	58.5	63.0	7.7	15.3	36.7	36.8	91.9	123.5	
Seoul, Korea	May 1996 ~ Apr. 1998	4.7	10.5	66.4	3.5	6.9	10.5	29.9	70.9	18.2	Lee et al., 2000
Tirupati, India	Jul. 2000 ~ Jun. 2001	6.78	33.08	20.37	33.89	50.51	150.66	40.84	127.96	33.91	Mouli et al., 2005
Istanbul, Turkey	Oct. 2001 ~ Jul. 2002	4.81	75.2	12.8	57.4	99.6	285	33.4	115.2	124.8	Basak and Alagha, 2004
Mexico city, Mexico	(May to Oct.) 2001 ~ 2002	5.08	7	92.35	2.16	2.46	26.44	42.62	61.94	9.56	Baez et al., 2007
Shanghai, China	2005	4.49	50.11	80.68	14.89	29.64	203.98	49.8	199.59	58.34	Huang et al., 2008
Piracicaba, Southeast Brazil	Aug. 1997 ~ Jul. 1998	4.5	2.7	17.1	2.9	2.3	5.3	16.6	18.7	7	Lara et al., 2001

1 Table 3. Correlation matrix between ions in rainwater samples. The Pearson correlation  
 2 coefficient and the P-value are shown in cells

Variables	Na <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	NO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>
NH <sub>4</sub> <sup>+</sup>	0.19 0.04						
K <sup>+</sup>	0.50 0.00	0.50 0.00					
Mg <sup>2+</sup>	<b>0.99</b> 0.00	0.23 0.01	0.53 0.00				
Ca <sup>2+</sup>	0.41 0.00	0.55 0.00	<b>0.67</b> 0.00	0.48 0.00			
NO <sub>3</sub> <sup>-</sup>	0.39 0.00	<b>0.86</b> 0.00	0.59 0.00	0.44 0.00	<b>0.78</b> 0.00		
Cl <sup>-</sup>	<b>1.00</b> 0.00	0.19 0.04	0.49 0.00	<b>0.99</b> 0.00	0.39 0.00	0.38 0.00	
SO <sub>4</sub> <sup>2-</sup>	0.29 0.00	<b>0.82</b> 0.00	<b>0.61</b> 0.00	0.32 0.00	<b>0.66</b> 0.00	<b>0.81</b> 0.00	0.29 0.00

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1 Table 4. Concentrations of trace metals in rainwater samples (ppb).

Trace metals	VWMC	SDVWMC	Min	Max <sup>2</sup>
Zn	18.78	14.08	N.D.	567.29
Al	12.99	6.64	N.D.	104.60
Fe	11.00	6.55	N.D.	74.51 <sup>4</sup>
Mn	4.58	2.89	N.D.	33.45
Pb	3.10	1.77	N.D.	25.01
Cu	1.69	0.89	N.D.	14.70 <sup>6</sup>
Ni	0.28	0.18	N.D.	8.04 <sup>7</sup>
Cd	0.09	0.05	N.D.	1.14
Cr	0.06	0.03	N.D.	0.47 <sup>8</sup>

9 WHO drinking water guidelines: Zn: 3mg/l, Al: 0.2 mg/l, Fe: 0.3 mg/l, Mn: 0.5 mg/l, Pb:  
 10 0.01 mg/l, Cu: 2 mg/l, Ni: 0.07 mg/l, Cd: 0.03 mg/l, Cr: 0.05 mg/l



1 Table 5. Comparison of VWMC of trace metals in precipitation between Gwangju and that at other locations.

Location	Zn	Al	Fe	Mn	Pb	Cu	Ni	Cd	Cr	References
This study	18.78	12.99	11.00	4.58	3.10	1.69	0.28	0.09	0.06	
Chunchun, Korea	9.9	13.85		3.23	1.51	1.73	0.52	0.07		Kim et al., 2012
Suwon, Korea	13.06				9.98	6.08	0.66	0.2	0.43	Jung et al., 2007
Mexico		50.7		9.64	2.48		3.37	0.41	0.52	Baez et al., 2007
Ankara, Turkey	0.03	980	750		19.1	6.1	4.1	9.5	3	Kaya and Tuncel, 1997
Singapore	7.23	18.44	23.91	2.78	3.37	5.58	3.86	0.33	1.62	Hu and Balasubramanian, 2003
Jordan	6.52	382	92	2.11	2.57	3.08	2.62	0.42	0.77	Al-Momani et al., 2003
New Castle, NH, USA	25.5	24.4	22.8		1.31	1.33	0.85	0.24	0.14	Pike and Moran, 2001

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1 Table 6. Correlation coefficients and P-value between ions and trace metals in rainwater  
 2 samples from Gwangju (n=113).

	Na <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	NO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>
Al	0.32	<b>0.60</b>	0.44	0.36	<b>0.51</b>	<b>0.66</b>	0.33	<b>0.59</b>
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cr	0.17	0.41	0.19	0.20	0.30	0.41	0.18	0.42
	0.07	0.00	0.04	0.03	0.00	0.00	0.06	0.00
Mn	0.36	0.35	0.29	0.40	<b>0.52</b>	<b>0.57</b>	0.36	0.38
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe	0.36	<b>0.53</b>	0.39	0.41	0.49	<b>0.64</b>	0.37	<b>0.53</b>
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ni	0.02	<b>0.53</b>	0.32	0.05	0.23	0.39	0.03	0.37
	0.82	0.00	0.00	0.63	0.01	0.00	0.79	0.00
Cu	0.05	<b>0.67</b>	0.35	0.07	0.35	<b>0.58</b>	0.06	<b>0.58</b>
	0.59	0.00	0.00	0.43	0.00	0.00	0.54	0.00
Zn	0.08	0.24	0.32	0.12	0.33	0.22	0.08	0.20
	0.39	0.01	0.00	0.19	0.00	0.02	0.38	0.03
Cd	0.31	<b>0.59</b>	0.42	0.36	<b>0.50</b>	<b>0.61</b>	0.33	<b>0.64</b>
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Pb	<b>0.50</b>	<b>0.56</b>	0.44	<b>0.54</b>	0.39	<b>0.63</b>	<b>0.51</b>	<b>0.63</b>
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

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1 Table 7. Mean values of TOC, TN, UV, SUVA, and pH and conductivity in initial (n=40) and  
 2 subsequent (n=73) rainfall during 2012.

	Initial rainfall		Subsequent rainfall	
	Mean	SD	Mean	SD
TOC (mg C/l)	2.18	1.41	1.11	0.68
TN (mg N/l)	1.95	1.19	0.79	0.47
UV (cm <sup>-1</sup> )	0.0244	0.0135	0.0111	0.0073
SUVA	1.19	0.39	1.06	0.33
pH	5.97	0.52	5.55	0.64
Conductivity (μS/cm)	38.17	25.67	25.72	19.07

3 SD: standard deviation

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1 Table 8. Factor analysis of chemical constituents in rainwater.

Variable	Factor 1	Factor 2	Factor 3
Na <sup>+</sup>	0.12	<b>0.97</b>	0.10
NH <sub>4</sub> <sup>+</sup>	<b>0.88</b>	0.03	0.27
K <sup>+</sup>	<b>0.61</b>	0.46	0.11
Mg <sup>2+</sup>	0.15	<b>0.96</b>	0.15
Ca <sup>2+</sup>	<b>0.67</b>	0.39	0.19
NO <sub>3</sub> <sup>-</sup>	<b>0.85</b>	0.29	0.28
Cl <sup>-</sup>	0.11	<b>0.96</b>	0.12
SO <sub>4</sub> <sup>2-</sup>	<b>0.85</b>	0.18	0.23
Al	0.51	0.20	<b>0.71</b>
Cr	0.14	0.08	<b>0.79</b>
Fe	0.41	0.28	<b>0.76</b>
Ni	0.44	-0.18	<b>0.50</b>
Zn	0.04	0.02	<b>0.62</b>
Cd	0.47	0.24	<b>0.63</b>
Pb	0.44	0.42	<b>0.59</b>
Mn	0.36	0.35	<b>0.50</b>
Cu	<b>0.75</b>	-0.14	0.41
% Total variance	28.5	22.4	22.2

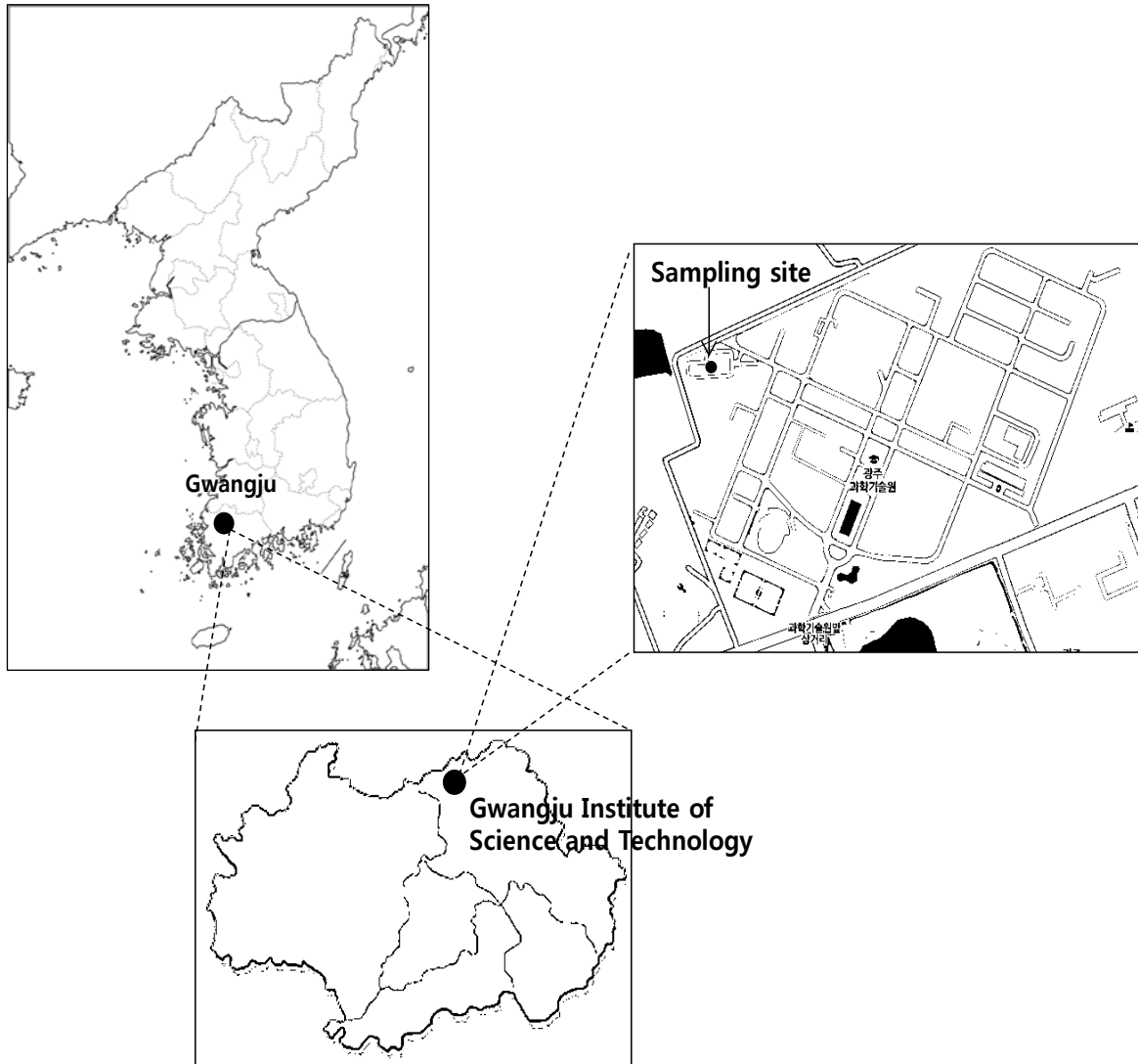
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1 Table 9. Dominant pyrolysis fragments for rainwater samples as identified by Py-GC/MS.

Ranking	Pyrolysis fragments									
	June 02	June 08	June 18	June 19	June 29	June 30	July 12	July 18 (Typhoon-Khanun)	Aug 06	Aug 10–15
1	Benzoic acid, 2,4-dichloro-(PHA)	Benzoic acid, 2,6-dichloro- (PHA)	Benzoic acid, 2,6-dichloro-(PHA)	Benzoic acid, 2,6-dichloro-(PHA)	Benzoic acid, 2,6-dichloro-(PHA)	Benzoic acid, 2,6-dichloro-(PHA)	Acetic acid (PS,AS)	Acetamide, 2-fluoro-(PS,AS)	1H-Isoindole-1,3(2H)-dione (Pr)	1H-Isoindole-1,3(2H)-dione (Pr)
2	1H-Isoindole-1,3(2H)-dione (Pr)	Benzoic acid, 4-chloro-(PHA)	Acetic acid (PS,AS)	Benzoic acid, 4-chloro-(PHA)	Acetic acid (PS,AS)	Phthalic anhydride (PHA)	1H-Isoindole-1,3(2H)-dione (Pr)	1,3-Benzenedicarbonitrile (Pr,PHA)	Phthalic anhydride (PHA)	Phthalic anhydride (PHA)
3	2,5-Pyrrolidinedione (Pr)	2,4-Dichlorobenzamide (PHA)	Benzenecarboxylic acid (PHA)	2,4-Dichlorobenzamide (PHA)	Benzoic acid, 4-chloro-(PHA)	1H-Isoindole-1,3(2H)-dione (Pr)	Furan, 2-methyl-(PS)	1H-Isoindole-1,3(2H)-dione (Pr)	Furan, 2-methyl-(PS)	Furan, 3-methyl-(PS)
4	Benzenecarboxylic acid (PHA)	Benzenecarboxylic acid (PHA)	Benzonitrile (Pr)	Benzene, 1,4-dichloro-(PHA)	Benzonitrile (Pr)	Acetic acid (PS,AS)	Benzonitrile (Pr)	1,2-Benzenedicarboxylic acid (PHA)	2,3-Butanedione (PS)	Acetonitrile, dichloro-(Pr)
5	Benzene, 1,4-dichloro-(PHA)	Benzonitrile (Pr)	Benzene (PHA)	1H-Isoindole-1,3(2H)-dione (Pr)	Benzene (PHA)	Benzoic acid, 2-chloro-(PHA)	Phthalic anhydride (PHA)	Benzene (PHA)	Benzenecarboxylic acid (PHA)	Benzoic acid, 2-chloro-(PHA)
6	Benzoic acid, 4-chloro-(PHA)	Benzene, 1,4-dichloro-(PHA)	Benzoic acid, 4-chloro-(PHA)	Acetic acid (PS,AS)	1H-Isoindole-1,3(2H)-dione (Pr)	Dodecanoic acid (Lp)	2(5H)-Furanone, 3,5,5-trimethyl-(PS)	Benzene (PHA)	Benzonitrile (Pr)	
7	Acetamide (PS,AS)	2,5-Pyrrolidinedione (Pr)	n-Hexadecanoic acid (Lp)	Benzenecarboxylic acid (PHA)	Benzenecarboxylic acid (PHA)	Furan, 2-methyl-(Pr)	n-Hexadecanoic acid (Lp)	Acetic acid (PS,AS)		
8	Benzonitrile (Pr)	n-Hexadecanoic acid (Lp)	1H-Isoindole-1,3(2H)-dione (Pr)	Benzoic acid, 2,4-dichloro-(PHA)	Phthalic anhydride (PHA)		2,5-Pyrrolidinedione (Pr)	1,2-Benzenedicarbonitrile (Pr, PHA)		
9	Phenol (Pr,PHA)	1,4-Benzenedicarbonitrile (Pr,PHA)	2,5-Pyrrolidinedione (Pr)	Benzonitrile (Pr)	2,5-Pyrrolidinedione (Pr)		Benzene, 1-chloro-2-ethoxy-(PHA)	Furan, 2-methyl-(PS)		
10	2(5H)-Furanone, 3,5,5-trimethyl-(PS)	Octadecanoic acid (Lp)	Acetamide (PS,AS)	1,2-Benzenedicarbonitrile (Pr, PHA)	Furan, 2-methyl-(PS)		Tetradecanoic acid (Lp)	Formic acid, ethenyl ester (Lp)		

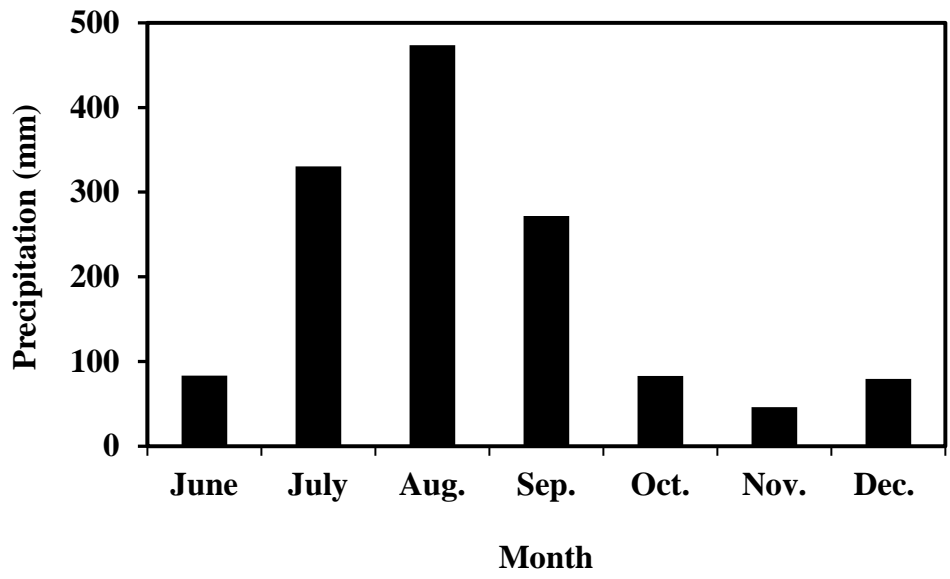
Ranking	Pyrolysis fragments							
	Aug 23–24	Aug 27–28 (Typhoon-Bolaven)	Aug 30 (Typhoon-Tevin)	Sep 12	Oct 22	Nov 5–11	Nov 13–26	Dec 12
1	1H-Isoindole-1,3(2H)-dione (PR)	Benzene (PHA)	Acetic acid (PS, AS)	Acetic acid (PS, AS)	1,2-Benzenedicarboxylic acid (PHA)	Benzonitrile (Pr)	Benzonitrile (Pr)	Acetaldehyde (PS)
2	Phthalic anhydride (PHA)	Acetic acid (PS, AS)	Phthalic anhydride (PHA)	o-Cyanobenzoic acid (PHA)	1H-Isoindole-1,3(2H)-dione (Pr)	Phthalic anhydride (PHA)	1H-Isoindole-1,3(2H)-dione (Pr)	Acetaldehyde (PS)
3	Benzoic acid, 4-(1-methylethyl)-(PHA)	Phenol (Pr,PHA)	Benzonitrile (Pr)	1,2-Benzenedicarboxylic acid (PHA)	Acetic acid (PS, AS)	Acetic acid (PS, AS)	Acetic acid (PS, AS)	1H-Isoindole-1,3(2H)-dione (Pr)
4	Acetic acid (PS,AS)	Benzene (PHA)	Benzene (PHA)	Benzonitrile (Pr)	Benzonitrile (Pr)		Benzene (PHA)	
5	Benzoic acid, 4-chloro-(PHA)	Styrene (Pr)	2-Pentenoic acid, 4-methyl-(Pr)	Benzene (PHA)			Phthalic anhydride (PHA)	
6	Benzoic acid, 4-methyl-(PHA)	.alpha.-D-Glucopyranose, 4-O-.beta.-D-galactopyranosyl-(PS)	Styrene (Pr)				Furan, 2,5-dimethyl-(PS)	
7	Benzonitrile (Pr)	1H-Isoindole-1,3(2H)-dione (Pr)	Pyridine (Pr)				Benzonitrile, 4-[2-(methylsulfonyl)ethenyl]-(Pr)	
8	Benzenecarboxylic acid (PHA)	2H-Pyran, 3,4-dihydro-4-methyl-(PS)	Benzenecarboxylic acid (PHA)				Benzenecarboxylic acid (PHA)	
9	Furan, 2-methyl-(PS)	2-Dodecenal, (E)-(Lp)	Benzene, 1-methyl-4-(1-methylethenyl)-(PHA)				1,2-Benzenedicarbonitrile (Pr, PHA)	
10	Benzoic acid, 4-(1-methylethyl)-(PHA)		Benzaldehyde (Lg)					

1 Pr=protein; PS=polysaccharides; AS=amino sugars; PHA=polyhydroxy aromatics; Lg=lignins; Lp=lipid



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2 Figure 1. Location of the sampling site for this study.



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2 Figure 2. Monthly integrated precipitation at Gwangju during 2012.

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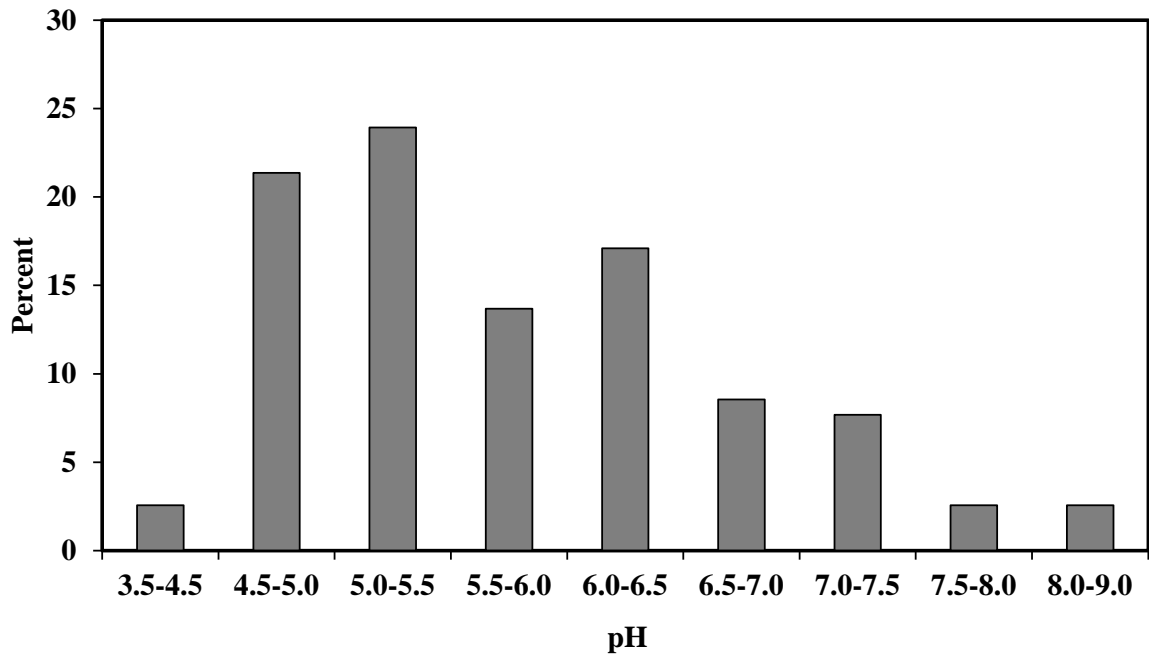
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2 Figure 3. Distribution of pH in rainwater samples collected from Gwangju.

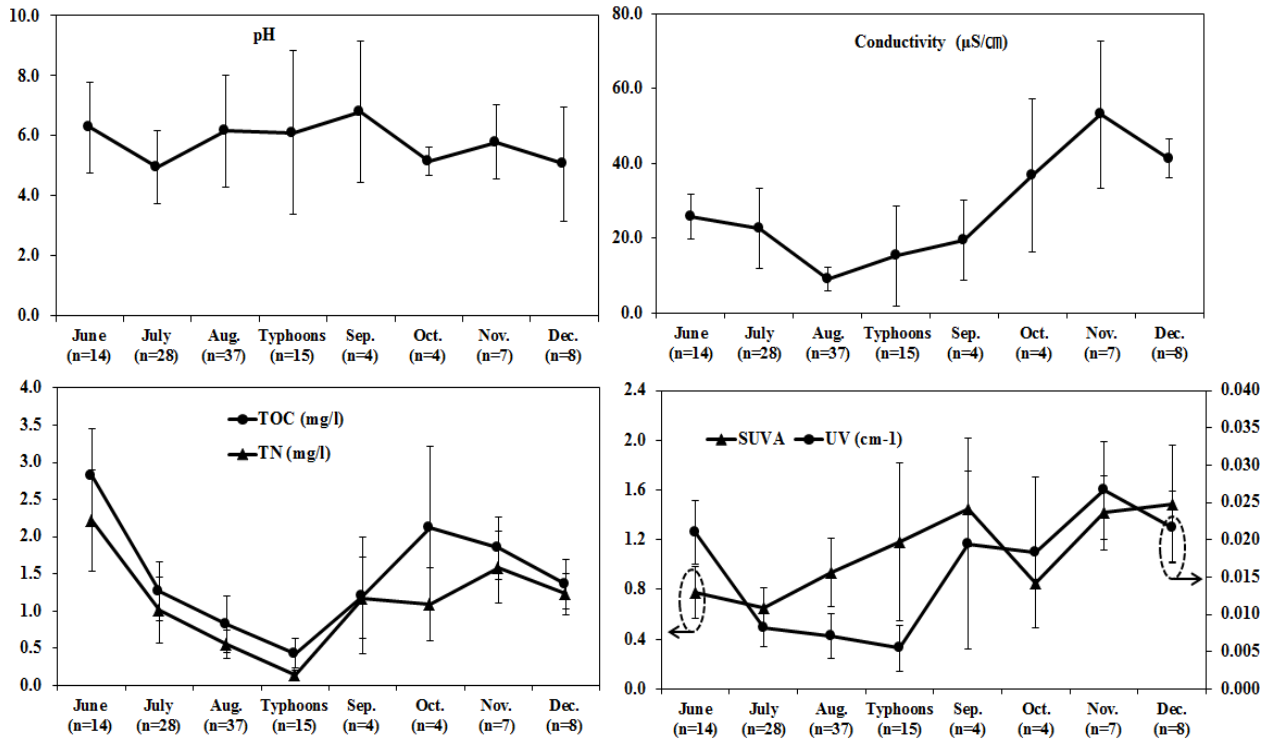
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2 Figure 4. Monthly variation of volume-weighted mean value of pH, Conductivity, TOC, TN,  
 3 SUVA, and UV in rainwater samples collected in Gwangju during 2012.

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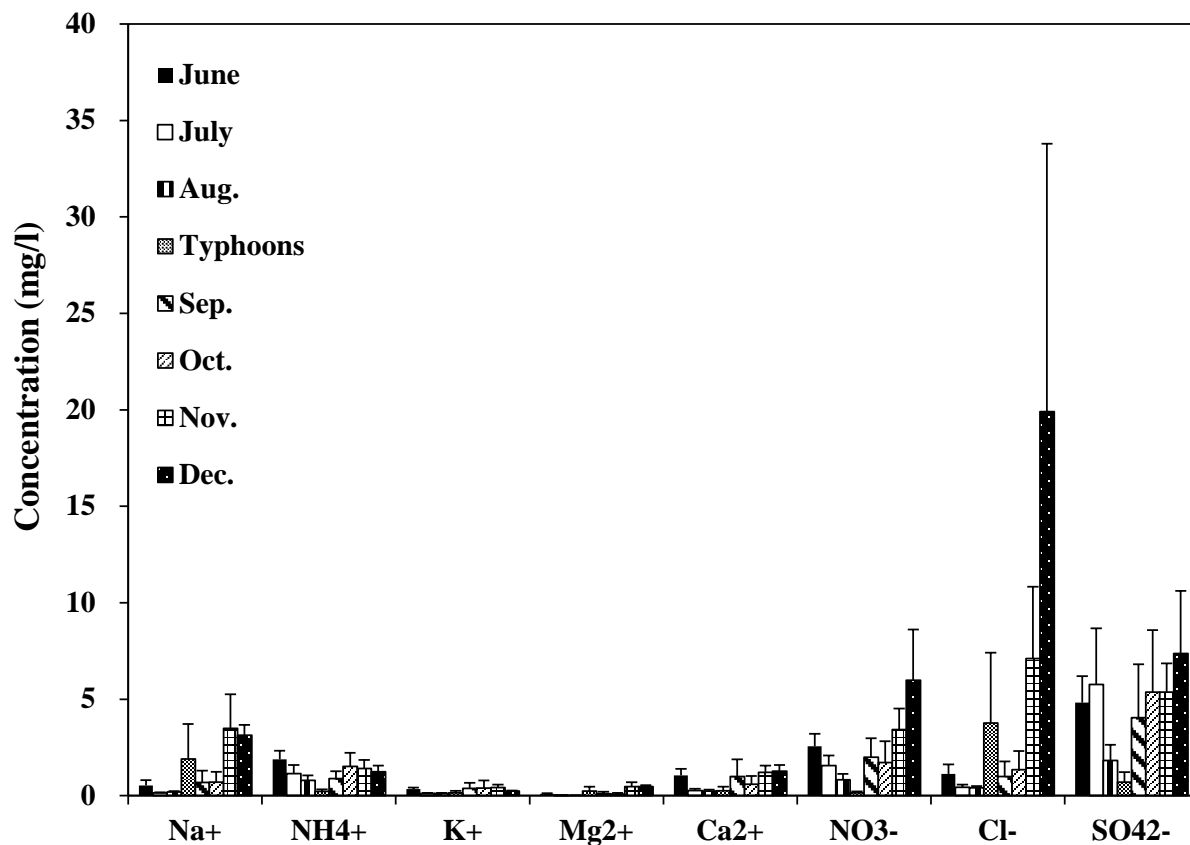
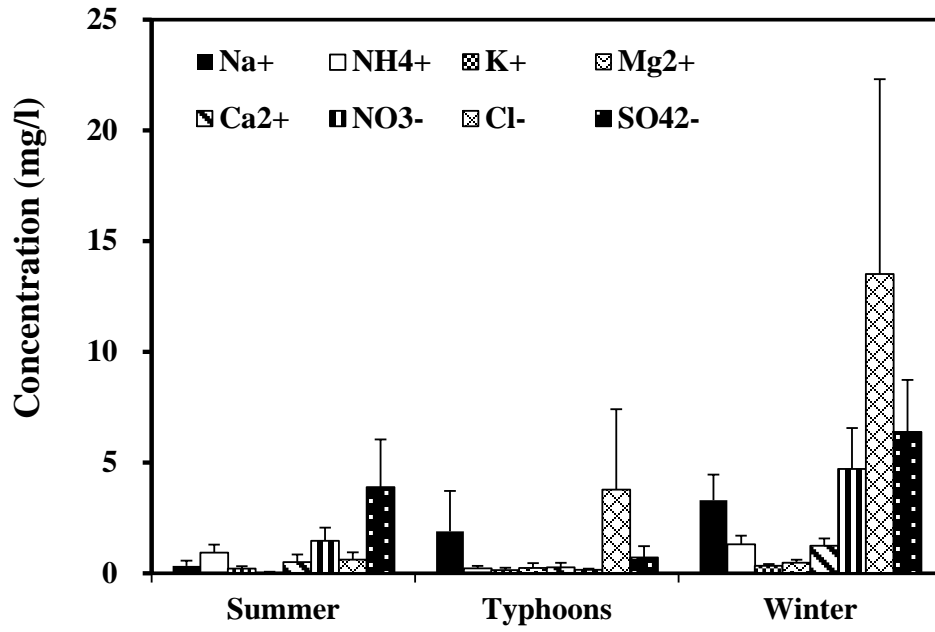


Figure 5. Monthly variation of VWMC of major ions in rainwater samples during 2012.

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2 Figure 6. Mean concentration of major ions in rainwater samples during summer (July–  
 3 September), typhoons, and winter (November–December).

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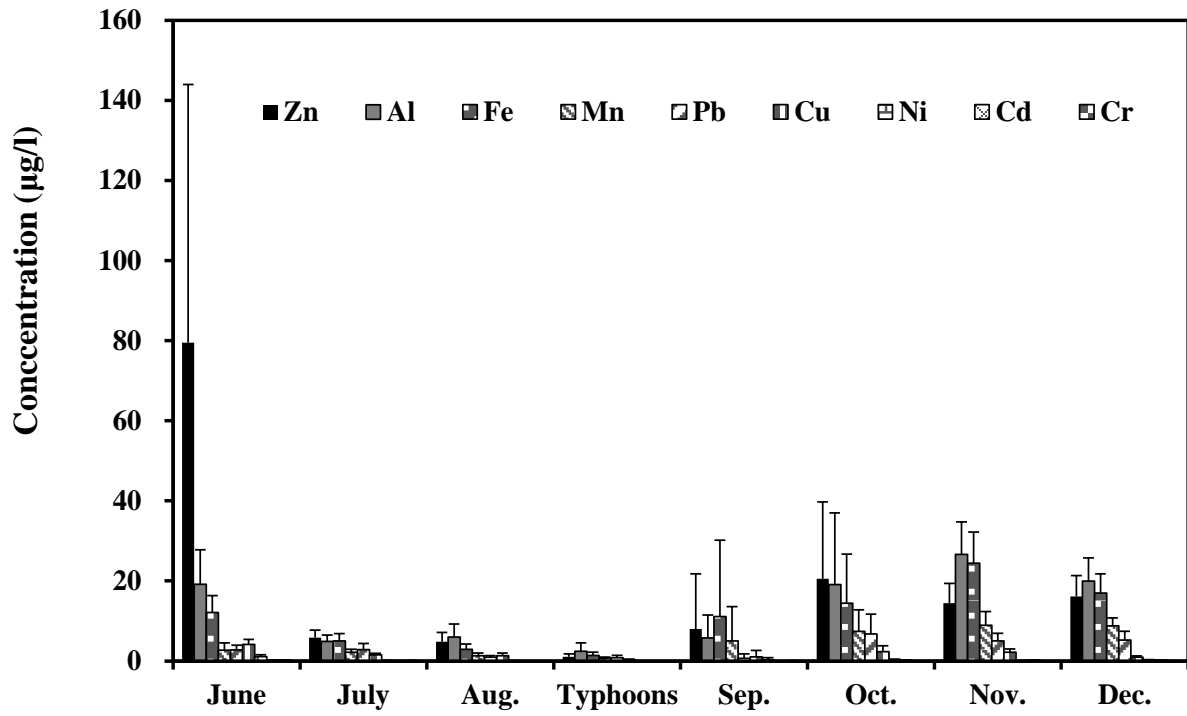
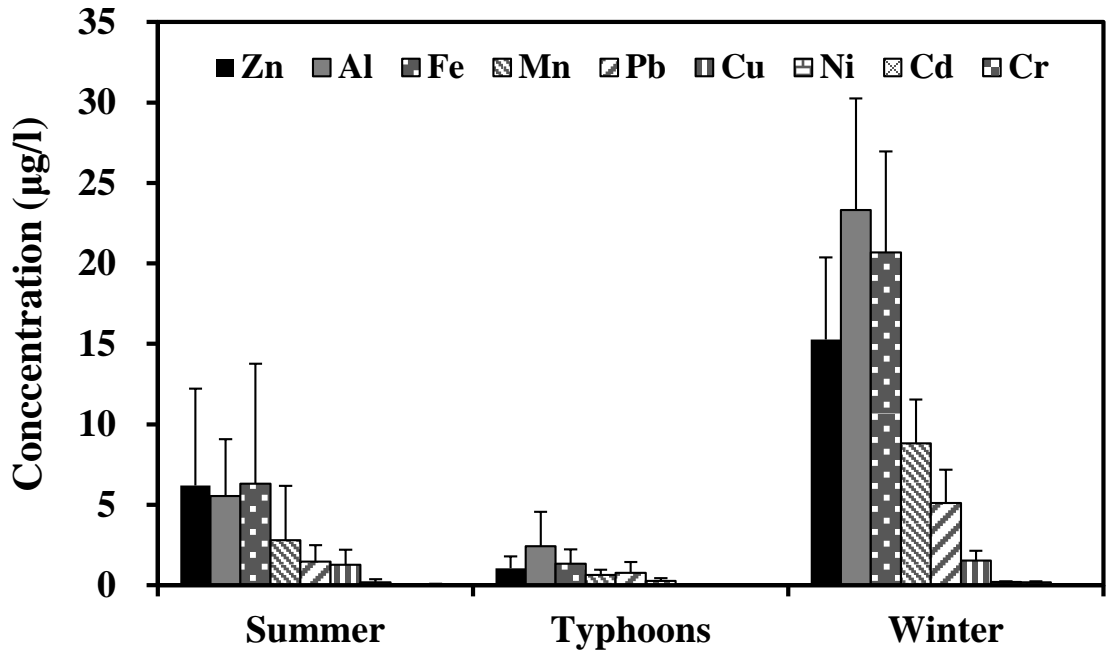


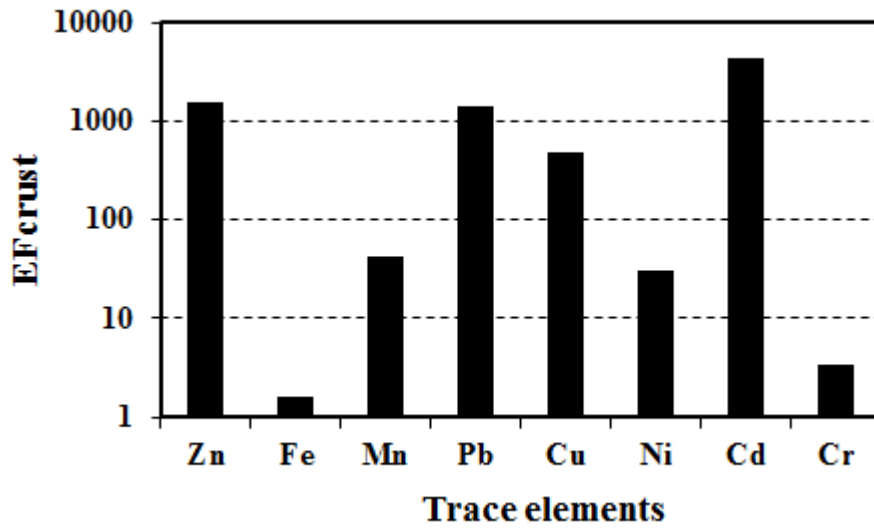
Figure 7. Monthly variation of VWMC of trace metals in rainwater samples during 2012.

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Figure 8. Mean concentration of trace metals in rainwater samples during summer (July–September), typhoons, and winter (November–December).



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2 Figure 9. Average EFs of trace metals in rainwater at Gwangju area during 2012.

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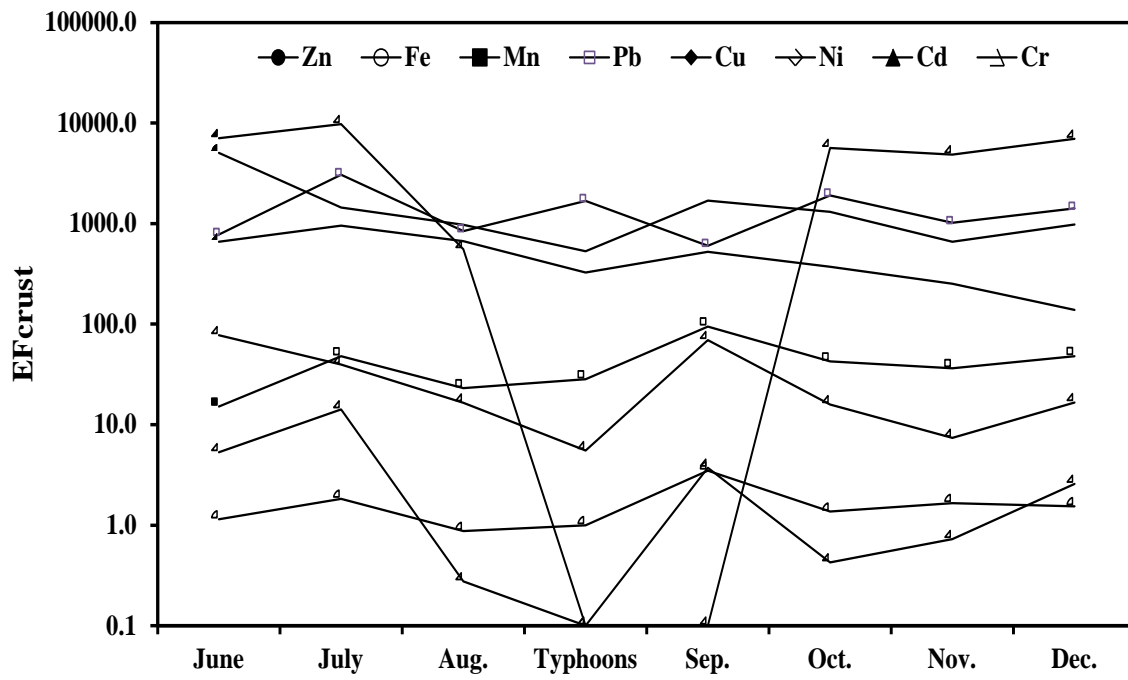
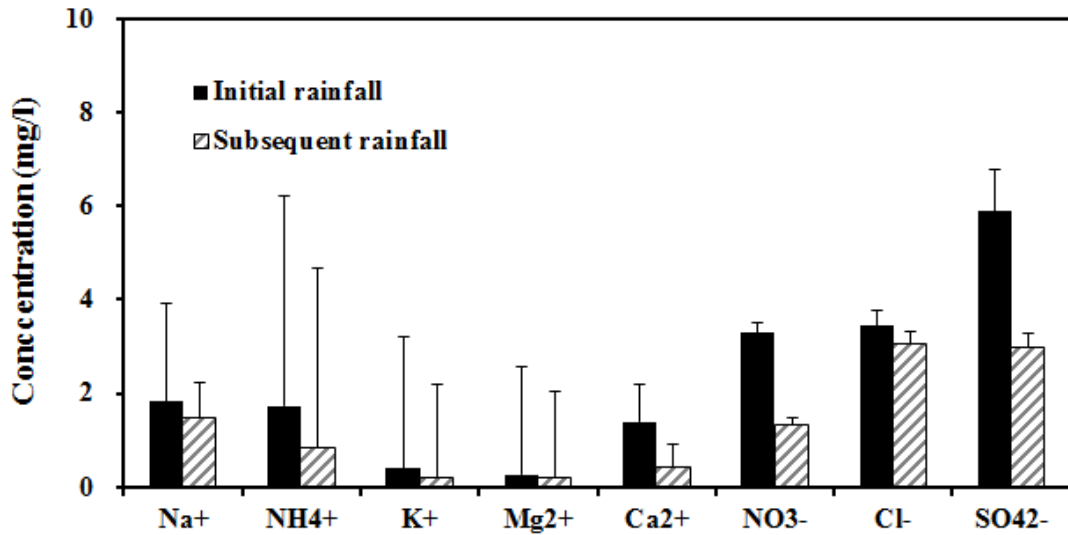


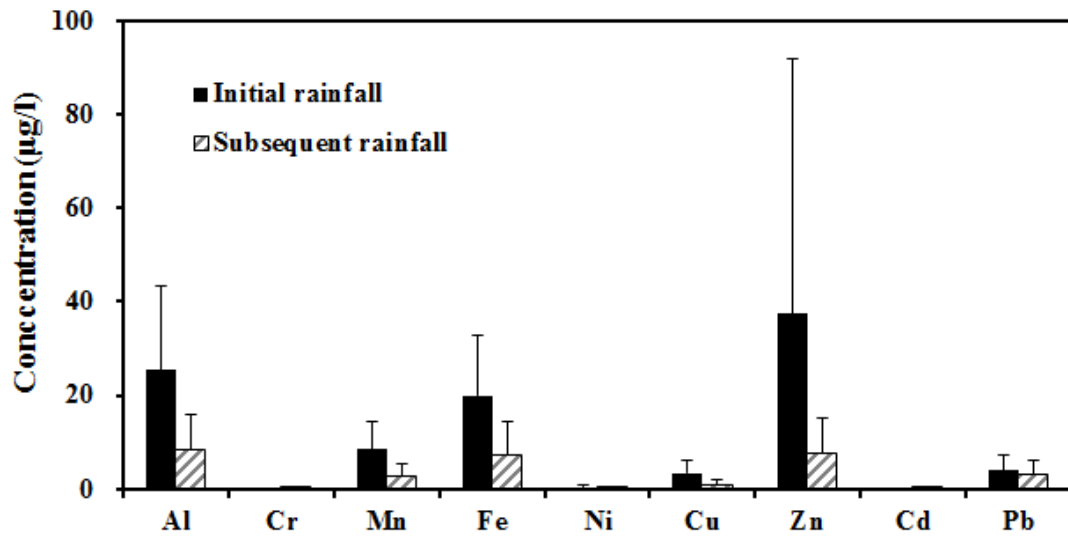
Figure 10. Monthly variation of EF<sub>crust</sub> of trace metals in rainwater at Gwangju area during 2012.

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3 Figure 11. Comparison of mean concentration of major ions and trace metals in initial (n = 40)  
 4 and subsequent (n = 73) rainfall during 2012.