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

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Abstract

The chemical composition and organic compounds of rainwater were investigated from June to December 2012 at Gwangju in Korea. The volume weighted mean of pH ranged from 3.83 to 8.90 with an average of 5.78. 50 % of rainwater samples had pH values below 5.6. The volume-weighted mean concentration (VWMC) of major ions followed the order: $Cl^- > SO_4^{2-} > NH_4^+ > Na^+ > NO_3^- > Ca^{2+} > Mg^{2+} > K^+$. The VWMC of trace metals decreased in the order as follows Zn > Al > Fe > Mn > Pb > Cu > Ni > Cd > Cr. The VWMCs of major ions and trace metals were higher in winter than in summer. The high enrichment factors indicate that Zn, Pb, Cu, and Cd originated predominantly from anthropogenic sources. Factor analysis (principal component analysis) indicates the influence of anthropogenic pollutants, sea salt, and crustal materials on the chemical compositions of rainwater. Benzoic acids, 1H-Isoindole-1,3(2H)-dione, phthalic anhydride, benzene, acetic acids, 1,2-benzenedicarboxylic acids, benzonitrile, acetaldehyde, and acetamide were the most prominent pyrolysis fragments for rainwater organic compounds identified by pyrolysis gas chromatography/mass spectrometry (Py-GC/MS). The results indicate that anthropogenic sources are the most important factors affecting the organic composition of rainwater in urban area.

1 Introduction

Rain is an efficient scavenging process for pollutants in the air and is becoming a source of pollution to the environment (Santos et al., 2011). The emission of SO_2 and NO_X from fossil fuel combustion and industrial processes has rapidly increased in East Asia due to its fast growing economy. These gases are converted into sulfuric and nitric acids before precipitating as acid rain (Lee et al., 2000; Báez et al., 2006). Consequently, there have been adverse environmental effects on aquatic, biological, and terrestrial systems (Bard, 1999; Başak and Alagha, 2004). Thus, the chemical composition of precipitation has been investigated all around the world during the last decade (Lara et al., 2001; Mouli et al., 2010; Santos et al., 2011).

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

Dissolved organic carbon (DOC) is a major component of both continental (161 µM) and marine rain (23 µM) (Willey et al., 2000). DOC is a mixture of simple substances such as alkanes, carbohydrates, and fatty acids, and of complex polymeric molecules, such as aromatic, aliphatic, and carboxylic carbons (Muller et al., 2008). Rainwater DOC plays a significant role in the atmospheric carbon cycle, and the global rainwater flux of DOC is $430 \times 10^{12}\,\mathrm{g\,C\,yr^{-1}}$ (Willey et al., 2000). Sources of DOC compounds in rainwater are primary anthropogenic and biogenic emissions, and photochemical transformations of precursors (Klouda et al., 1996). While numerous studies have been conducted on the inorganic chemistry of rainwater, little attention has been paid to organic compounds. Kawamura et al. (1983) initiated the identification and distribution of organic compounds in rainwater. The role of organic compounds in atmospheric processes has gained much attention in the last few years, and knowledge of organic compounds has improved with various analytical methods (Kieber et al., 2002; Seitzinger et al., 2003). However, the organic compounds in the atmosphere are very complicated and chemical characterization of organic matter in precipitation requires further work (Santos et al., 2009).

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

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

2 Materials and methods

2.1 Study site

Rainwater samples were collected at the Gwangju Institute of Science and Technology campus (35°13′ N, 126°50′ E) in Gwangju city in Korea (Fig. 1) from June to December in 2012. Gwangju has an area of 501.34 km^2 and a population of around 1 480 000. The annual average of temperature is 13.5 °C and the average precipitation is 1368 mm year^{-1}.

2.2 Sample collection and analysis

Rainwater samples were collected per event using a Teflon-coated collector designed to manually take samples with time. Samples from initial precipitation events were collected with care not to be mixed with later precipitation samples. All the initial and later samples were transported to the laboratory, and pH and electrical conductivity (EC) measured. The remaining samples were filtered through 0.45 µm filters (mixed cellulose ester, Advantec, Japan) and then stored at 4 °C until further chemical analyses were performed within one week. pH and EC were measured using a pH meter and an EC meter, respectively (Orion 3-Star, Thermo Scientific, USA).

Major ions were quantified using a suppressed type ion chromatograph (DX-120, ICS-90, Dionex, Sunnyvale, CA, USA). Ion Pac AS14 and an Ion Pac CS12A column (Dionex, Sunnyvale, CA, USA) were used for measurements of major anions

(NO_3^-, SO_4^{2-}, and Cl^-) and the cations (NH_4^+, Ca^{2+}, Mg^{2+}, Na^+, and K^+), respectively. The concentrations of trace metals were measured using inductively coupled plasma mass spectrometry (ICP-MS) (7500ce, Agilent, Santa Clara, CA, USA). All the samples were acidified to a final nitric acid concentration of 2 % using 70 % nitric acid solution. The levels of DOC and total nitrogen (TN) contents of rainwater samples were determined using a total organic carbon analyzer (TOC-V CPH, Shimadzu, Japan) equipped with a TN analyzer (TNM-1, Shimadzu, Japan). The UV absorbance of the samples at 254 nm (UV_{254}) was measured using a UV-vis spectrophotometer (UV-1601, Shimadzu, Japan). The specific UV absorbance (SUVA) value (an indicator of aromaticity) was calculated from the ratio of UV_{254} to DOC concentration. Rainwater samples were concentrated to a final DOC concentration of approximately 100 $mg\,C\,L^{-1}$ with a rotary evaporator (Eyela, Japan). Approximately 20 mL of concentrated samples was freeze-dried using a freeze dryer (Ilshin, Korea) prior to pyrolysis gas chromatography/mass spectrometry (Py-GC/MS) analysis. Approximately 0.5–1.0 mg of freeze-dried sample powders were pyrolyzed at 590 °C for 5 s in the pyrofoil (Pyrofoil F590, Japan Analytical Industry, Tokyo, Japan) within a curie point pyrolyzer (JCI-22, Japan Analytical Industry, Tokyo, Japan) coupled with an Agilent 7890A gas chromatograph coupled to a 5975C quadrupole mass spectrometer (ion source temperature 220 °C, scanning from 40 to 500 amu, electron energy 70 eV). Pyrolysis fragments were separated by GC equipped with a DB-5MS (Agilent Technologies, USA) column and identified using a mass spectrometer. Helium was used as the carrier gas. The temperature program of the GC oven was initially maintained at 40 °C for 5 min, then increased at 7 $^{\circ}C\,min^{-1}$ to a final temperature of 300 °C, and maintained there for 10 min, giving a total run time of 52.14 min. The interpretation of the pyrochromatograms was conducted according to the methods described in Bruchet et al. (1990).

3 Results and discussion

3.1 Variation of pH value and precipitation amount

The average monthly rainfall from June to December during 2012 was 195.4 mm and the highest amount of rain fall (473.5 mm) was observed in August in 2012 (Fig. 2). 79 % of the total rainfall was concentrated during summer (July–September). The percent frequency distribution of pH for the rainwater samples is presented in Fig. 3. The volume weighted mean of pH was 5.78. The lowest pH value was observed on 11 July with a pH of 3.83, while the highest was on 22 August 2012 with a pH value of 8.90. Most pH values ranged between 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 samples had pH values below 5.6, which is the value of unpolluted water equilibrated with atmospheric CO_2 (Charlson and Rodhe, 1982). On the other hand, approximately 12 % of the samples had pH above 7.0, suggesting strong inputs of alkaline substances to rainwater in this area.

3.2 Ionic composition of rainwater

The volume-weighted mean concentration (VWMC), standard deviation of the VWMC (SDVWMC), and minimum (Min) and maximum (Max) concentrations of the rainwater chemical components are summarized in Table 1. The VWMC of major ions in rainwater follows the order: $Cl^- > SO_4^{2-} > NH_4^+ > Na^+ > NO_3^- > Ca^{2+} > Mg^{2+} > K^+$. Among all the ions, Cl^- was the most abundant with an average of 123.5 µeq L^{-1}, accounting for 28.5 % of the ionic concentration. SO_4^{2-} was the second highest anion with an average of 91.9 µeq L^{-1}, accounting for 21.2 % of total ions. The contribution of NO_3 was 8.5 % (concentration of 36.8 µeq L^{-1}). The high value of SO_4^{2-} and highest of Cl^- can be attributed to emissions from fossil fuel combustion and typhoons and sea salts, respectively. As for cation species, NH_4^+ made the highest contribution at 63. µeq L^{-1}, accounting for 14.5 % of the total ions. Meanwhile, Na^+ was the second highest cation accounting for 13.5 % of the total ions. The concentration of Ca^{2+}, Mg^{2+} and K^+ ions accounted for 8.5, 3.5, and 1.8 %, respectively. The high level of NH_4^+ in Gwangju city was comparable to Seoul (with a mean concentration of 66.4 µeq L^{-1}, Lee et al., 2000). Wastes from agricultural and domestic activities as well as the use of fertilizers are believed to be the main sources of the emission of gaseous ammonia (Dianwu and Anpu, 1994; Panyakapo and Onchang, 2008). Ca^{2+} may originate from wind-blown dust and calcareous soil, Mg^{2+} from sea salts and dusts in the atmosphere, while Na^+ from sea salts. EC of rainwater ranged from 0.87 to 169.00 µS cm^{-1}, with a VWM value of 27.82 µS cm^{-1}. The VWMs of UV and SUVA in rainwater were 0.0160 and 1.09, respectively. Organic matter in rainwaters exhibit relatively hydrophilic characteristic, with SUVA values less than two generally indicating a high fraction of hydrophilic non-humic matter with low UV absorbance.

The VWMC of major ions in rainwater at Gwangju were compared to those reported in other urban areas around the world (Table 2). The pH value measured in our study is lower than that in Tirupati, India, but higher than those reported for other sites. The concentration of Na^+ is comparable to that in Shanghai, but lower than Istanbul and higher than other areas. The Cl^- value is comparable to that in Istanbul and much higher than those reported for other sites. The high concentration of marine elements was likely due to typhoons during summer seasons. The value of NO_3^- is higher than that in Southeast Brazil and close to that in other sites. Regarding SO_4^{2-}, its concentration is higher than that in Seoul, Mexico and Brazil and lower than in other areas. Shanghai shows the highest value of NO_3^- and SO_4^{2-} indicating severe air pollution problems in China. Both of these ions were mainly derived from the high coal/fuel consumption and mobile sources. The concentration of K^+, Ca^{2+}, Mg^{2+} are higher than those in Seoul, Mexico, Brazil and lower than ones in other sites. The concentrations of these ions are comparatively higher in Istanbul than in other areas. The value of NH_4^+ is comparable to that in Seoul and higher than that in India, Turkey, and Brazil.

3.3 Seasonal variation

Figure 4 displays the monthly variation of VWM of pH, conductivity, TOC, TN, SUVA and UV of rainwater samples. pH values measured during summer seasons (June–September) with greater rainfall were higher than those during the winter season (October–December). This is consistent with previous studies (Cerón et al., 2013). Lee et al. (2000) also mentioned that the amount of rainfall influences pH. Conductivity values increased from summer to winter seasons, in agreement with the seasonal trend of major ions. Less conductivity during summer was caused by the dilution effect of higher rainfall. The values of TOC show similar monthly trends to TN, increasing with decreasing rainfall amounts. Similar seasonal variations of TOC have been reported in other studies (Pan et al., 2010; Yan and Kim, 2012). DOC in the atmosphere is known to vary with the seasons due to biogenic emission form vegetation. Kieber et al. (2002) reported relatively higher levels of DOC in rainwater in warmer seasons. In contrast, Yan and Kim (2012) indicated that it was due to the prevailing anthropogenic contributions (mostly fossil fuel burning) and low precipitation in the relatively dry winter season. They also found that DOC in precipitation over Seoul was mainly produced by incomplete combustion of fossil fuel. The values of TN display similar monthly trends with TOC. It was higher in spring, fall, and winter, which are relatively dryer than summer. As expected, this is consistent with the monthly variation of NO_3^- and NH_4^+. The value of UV_{254} measured during winter season (November–December) is higher than in summer season (July–September). SUVA values higher than 1.4 were measured in September, November and December, but in the other months were lower than 1.0. The monthly VWMC of major ions in rainwater samples are depicted in Fig. 5. The mean concentration of major ions in samples during summer (July–September), typhoons, and winter (November–December) are illustrated in Fig. 6. More than half of the total rainfall is concentrated in summer, while in the winter, precipitation is less than 10 % of the total in Korea (Lee et al., 2000). Thus, seasonal variations of ionic concentration in rainwater were mainly affected by precipitation patterns and monsoonal winds (Lee et al., 2000). The major ions had relatively higher concentrations in the winter, which is a pattern opposite to the trend in rainfall. The ionic concentrations showed decreasing trends with increasing rainfall amounts, suggesting a dilution effect of rainwater on precipitation chemistry. The lowest ion concentrations were observed during typhoon periods, except Na^+ and Cl^-, which are typical marine components.

3.4 Correlation analysis

To investigate and identify potential correlation between major ions in rainwater samples, Pearson correlation analysis was applied (Table 3). A strong correlation was found between Na^+ and Mg^{2+} ($R^2 = 0.99$), and between Na^+ and Cl^- ($R^2 = 1.00$) suggesting a marine source. The high correlation between Mg^{2+} and Cl^- ($R^2 = 0.99$) also corresponds to salts of marine origin. Relatively high correlations between NO_3^- and NH_4^+ ($R^2 = 0.86$), and between SO_4^{2-} and NH_4^+ ($R^2 = 0.82$), may reveal co-occurrence of NH_4^+ with SO_4^{2-} and NO_3^- in rainwater. This was probably due to dissolution of secondary inorganic aerosols ($(NH_4)_2SO_4$ and NH_4NO_3) in rainwater (Panyakapo and Onchang, 2008). Among the compounds of ammonium, ammonium sulfate is known to predominate in the atmosphere (Seinfield, 1986). However, our study showed slightly higher correlation between NH_4^+ and NO_3^- ($R^2 = 0.86$) than between NH_4^+ and SO_4^{2-} ($R^2 = 0.82$), indicating that NH_4NO_3 dominates over $(NH_4)_2SO_4$. The dominance of NH_4NO_3 has also been reported previously (Saxena et al., 1996). The high correlation between SO_4^{2-} and NO_3^- suggests a common source origin, due to the co-emission of precursors (SO_2 and NO_x) from the same sources, such as fossil fuel burning, and the similarity of their behavior in precipitation. Correlations were also found between NO_3^- and Ca^{2+} ($R^2 = 0.78$), and between SO_4^{2-} and Ca^{2+} ($R^2 = 0.66$), suggesting that $Ca(NO_3)_2$ and $CaSO_4$ are formed from the neutralization reactions of acidity in rainwater (Zhao et al., 2013). Moderate correlation was found between K^+ and Ca^{2+}, indicating a common origin in marine aerosol. K^+ and SO_4^{2-} were somewhat correlated ($R^2 = 0.61$), suggesting the occurrence of reactions between the acid H_2SO_4 and the alkaline compounds carried into the atmosphere by windblown sea salts/dusts (Huang et al., 2008).

3.5 Trace metals

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

3.6 Variations in trace metal levels in rainwater

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

3.7 Correlation analysis

Table 6 lists the matrix correlation between ions and trace metals (correlation coefficients greater than 0.5 are marked in bold letters). Moderate correlation was found among the trace metals and NH_4^+, NO_3^-, and SO_4^{2-}, with the exception of Cr and Zn, suggesting anthropogenic origin of the species. These correlations were also observed in previous studies (Garcia et al., 2006; Jung et al., 2011). Significant correlations between SO_4^{2-} and trace metals in rainwater were observed in Clarke and Radojevic (1987).

3.8 Enrichment factor analysis

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

$$\mathrm{EF} = (C_X/C_{\mathrm{Al}}\ \mathrm{sample})/(C_X/C_{\mathrm{Al}}\ \mathrm{crust}),$$

where (C_X/C_{Al} sample) is the ratio of the concentration of an element X and Al in the rainwater sample and (C_X/C_{Al} crust) is the same ratio in crustal material, adapted from Wedepohl (1995).

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

3.9 Comparison of chemical components in initial and subsequent rainfall

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

3.10 Factor analysis

Factor analysis (principal component analysis) has been widely applied in previous studies to investigate the influence of different sources on the chemical components in precipitation (Báez et al., 2006; Garcia et al., 2006; Panyakapo and Onchang, 2008). A varimax-rotated principal component analysis (PCA) was performed using Minitab version 16 for Windows. Table 8 presents the result of the factor analysis that identified three factors that explained approximately 73.1 % of the total variance. Factor 1 explained 27.1 % of the total variance with high loadings for SO_4^{2-}, NO_3^-, and NH_4^+, and moderate loadings for K^+, Ca^{2+}, and Cu. This factor indicates marine sources for K^+ and Ca^{2+}, with an anthropogenic source for Cu, as is indicated by EF. Cu is a typical metal contaminant emitted from industrial processes (Wong et al., 2003). The loadings of SO_4^{2-}, NO_3^-, and NH_4^+ suggest that these ions come from anthropogenic sources associated with precursor gases such as SO_2 and NO_x. The co-occurrence of NH_4^+

Title Page
Abstract Introduction
Conclusions References
Tables Figures
◀| |▶
◀ ▶
Back Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

with NO_3^- and SO_4^{2-} are caused by dissolution of aerosols and secondary pollutants containing $(NH_4)_2SO_4$ and NH_4NO_3 in rainwater. Factor 2 accounted for 22.4 % of the total variance with high loading for Na^+, Mg^{2+}, and Cl^-, indicating the influence of sea spray. Factor 3, which explained 22.2 % of the total variance, proposed moderate loadings of most of the trace metals. This factor indicates the contribution of anthropogenic sources and significant crustal contributions for Al, Cr, and Fe, as indicated by EF. Overall, the anthropogenic pollutants, sea salts, and crustal materials were the main sources of the chemical species in rainwater in Gwangju.

3.11 Organic compounds in rainwater

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

1H-Isoindole-1,3(2H)-dione was one of the major pyrolysis organic compounds from precipitation in Konigstein, Germany (Laniewski et al., 1998) and found to be from tire derived aggregates. Phthalic anhydride originates from agricultural crop burning and open burning of scrap tires (Lemieux et al., 2004). Benzene is an important aromatic compound from gasoline, automobile exhaust, and urban atmosphere (Sigsby et al., 1987). Benzene was generally found as the major compound of volatile organic carbons in rainwater from Yokohama, Japan (Sato et al., 2006). 1,2-benzenedicarboxylic acids were the most abundant compound in October, which have been identified to be from particulate automobile exhaust emissions, cigarette combustion, production of plastics degradation, and products of lignin-type material metabolized by microorganisms (Johnstone and Plimmer, 1959; Simoneit, 1985; Kawamura and Kaplan, 1987). Benzonitrile was the most abundant species during November, which has been found in accidental vehicle fires (Estrellan and Lino, 2010) and biomass combustion in improved stoves in rural China (Wang et al., 2009). Acetaldehyde was the most abundant compound in December, probably derived from primary incomplete combustion of fossil fuel and secondary photochemical reactions of hydrocarbons emitted from anthropogenic sources (Sakugawa et al., 1993). Acetaldehyde was also detected in Los Angeles (Kawamura et al., 2001) and Spain (Peña et al., 2002). Among fatty acids, n-hexadecanoic acid (C_{16}), octadecanoic acid (C_{18}), and tetradecanoic acid (C_{14}) were found in the top 10 organic compounds during June and July. This is in agreement with previous work (Kawamura and Kaplan, 1986), where lower molecular fatty acids (C_{12}–C_{19}) are major compounds while higher molecular weight fatty acids (C_{20}–C_{30}) are minor. A major source of fatty acids ($C < 20$) is known to be from cooking and biomass combustion in urban areas (Xu et al., 2008). All results in the present study indicate that anthropogenic sources were significant contributors to the organic compounds present in rainwater.

4 Conclusion

Rainwater samples collected from Gwangju, Korea during June to December 2012 were analyzed to determine the chemical composition and organic compounds present in rainwater. The VWM of pH was 5.78 (ranging from 3.83 to 8.90) and acid rain ($pH < 5.6$) frequency was 50 %. The VWMC of major ions and trace metals followed the order: $Cl^- > SO_4^{2-} > NH_4^+ > Na^+ > NO_3^- > Ca^{2+} > Mg^{2+} > K^+$ and $Zn > Al > Fe > Mn > Pb > Cu > Ni > Cd > Cr$. The higher VWM values of TOC, TN, UV, SUVA, pH, conductivity, major ions, and trace metals appeared in initial rainfall than in subsequent rainfalls. The VWMCs of major ions and trace metals were relatively lower in summer due to the dilution effect. The lowest VWMCs of ions (except Na^+ and Cl^-) and trace metals were observed during typhoons. Based on EF values, Zn, Pb, Cu, Ni, Cd, and Mn were emitted mainly from anthropogenic sources whereas Fe and Cr originated from crustal sources. The factor analysis (principal component analysis) revealed that the anthropogenic pollutants, sea salts, and crustal materials were the main sources of ionic species and trace metals in rainwaters. The most abundant pyrolysis fragments for rainwater organic compounds were benzoic acids, 1H-Isoindole-1,3(2H)-dione, phthalic anhydride, benzene, acetic acids, 1,2-benzenedicarboxylic acids, benzonitrile, acetaldehyde, and acetamide, indicating that anthropogenic pollutants are significant contributors to rainwater organic compounds.

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Table 1. Volume-weighted mean concentration (VWMC), standard deviation of the VWMC (SDVWMC), and minimum (Min) and maximum (Max) concentrations of chemical 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	$\mu S\,cm^{-1}$	27.82	11.13	0.87	169.00
TOC	$mg\,C\,L^{-1}$	1.49	0.53	0.15	6.90
UV	cm^{-1}	0.0160	0.0061	0.0006	0.0972
SUVA		1.09	0.30	0.03	2.42
TN	$mg\,N\,L^{-1}$	1.13	0.40	N.D.	8.62
Na^+	$mg\,L^{-1}$	1.4	0.7	0.0	19.65
	$\mu eq\,L^{-1}$	58.5	30.7	1.2	854.50
NH_4^+	$mg\,L^{-1}$	1.1	0.4	0.0	5.9
	$\mu eq\,L^{-1}$	63.	22.1	1.6	327.1
K^+	$mg\,L^{-1}$	0.3	0.1	0.0	1.9
	$\mu eq\,L^{-1}$	7.7	4.1	0.3	53.0
Mg^{2+}	$mg\,L^{-1}$	0.2	0.1	N.D.	2.5
	$\mu eq\,L^{-1}$	15.3	7.5	N.D.	208.6
Ca^{2+}	$mg\,L^{-1}$	0.7	0.4	N.D.	6.7
	$\mu eq\,L^{-1}$	36.7	17.7	N.D.	337.1
NO_3^-	$mg\,L^{-1}$	2.28	0.9	N.D.	12.4
	$\mu eq\,L^{-1}$	36.8	14.8	N.D.	199.2
SO_4^{2-}	$mg\,L^{-1}$	4.4	2.1	0.0	19.5
	$\mu eq\,L^{-1}$	91.9	42.6	0.9	405.4
Cl^-	$mg\,L^{-1}$	4.4	3.0	0.0	39.3
	$\mu eq\,L^{-1}$	123.5	83.7	1.0	1106.4

N = number of samples.
WHO drinking water guidelines: pH: 6.5–8.5, NH_4^+: 1.5 $mg\,L^{-1}$, NO_3^-: 50 $mg\,L^{-1}$, SO_4^{2-}: 250 $mg\,L^{-1}$, Cl^-: 250 $mg\,L^{-1}$

Table 2. Comparison of VWMC of major ions (μeq L^{-1}) in precipitation in Gwangju with that at other sites.

Location	Period	pH	Na$^+$	NH$_4^+$	K$^+$	Mg^{2+}	Ca^{2+}	NO$_3^-$	SO$_4^{2-}$	Cl$^-$	References
This study	Jun~Dec 2012	5.78	58.5	63.	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)

Title Page
Abstract Introduction
Conclusions References
Tables Figures
◀| |▶
◀ ▶
Back Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

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

Variables	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	NO_3^-	Cl^-
NH_4^+	0.19 0.04						
K^+	0.50 0.00	0.50 0.00					
Mg^{2+}	**0.99** 0.00	0.23 0.01	0.53 0.00				
Ca^{2+}	0.41 0.00	0.55 0.00	**0.67** 0.00	0.48 0.00			
NO_3^-	0.39 0.00	**0.86** 0.00	0.59 0.00	0.44 0.00	**0.78** 0.00		
Cl^-	**1.00** 0.00	0.19 0.04	0.49 0.00	**0.99** 0.00	0.39 0.00	0.38 0.00	
SO_4^{2-}	0.29 0.00	**0.82** 0.00	**0.61** 0.00	0.32 0.00	**0.66** 0.00	**0.81** 0.00	0.29 0.00

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

Trace metals	VWMC	SDVWMC	Min	Max
Zn	18.78	14.08	N.D.	567.20
Al	12.99	6.64	N.D.	104.60
Fe	11.00	6.55	N.D.	74.51
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
Ni	0.28	0.18	N.D.	8.04
Cd	0.09	0.05	N.D.	1.14
Cr	0.06	0.03	N.D.	0.47

WHO drinking water guidelines: Zn: 3 mg L^{-1}, Al: 0.2 mg L^{-1}, Fe: 0.3 mg L^{-1}, Mn: 0.5 mg L^{-1}, Pb: 0.01 mg L^{-1}, Cu: 2 mg L^{-1}, Ni: 0.07 mg L^{-1}, Cd: 0.03 mg L^{-1}, 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 Balasubarmanian (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)

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

	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	NO_3^-	Cl^-	SO_4^{2-}
Al	0.32	**0.60**	0.44	0.36	**0.51**	**0.66**	0.33	**0.59**
	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	**0.52**	**0.57**	0.36	0.38
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe	0.36	**0.53**	0.39	0.41	0.49	**0.64**	0.37	**0.53**
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ni	0.02	**0.53**	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	**0.67**	0.35	0.07	0.35	**0.58**	0.06	**0.58**
	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	**0.59**	0.42	0.36	**0.50**	**0.61**	0.33	**0.64**
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Pb	**0.50**	**0.56**	0.44	**0.54**	0.39	**0.63**	**0.51**	**0.63**
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

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

	Initial rainfall		Subsequent rainfall	
	Mean	SD	Mean	SD
TOC (mg C L^{-1})	2.18	1.41	1.11	0.68
TN (mg N L^{-1})	1.95	1.19	0.79	0.47
UV (cm^{-1})	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^{-1})	38.17	25.67	25.72	19.07

SD: standard deviation.

Table 8. Factor analysis of chemical constituents in rainwater.

Variable	Factor 1	Factor 2	Factor 3
Na^+	0.12	**0.97**	0.10
NH_4^+	**0.88**	0.03	0.27
K^+	**0.61**	0.46	0.11
Mg^{2+}	0.15	**0.96**	0.15
Ca^{2+}	**0.67**	0.39	0.19
NO_3^-	**0.85**	0.29	0.28
Cl^-	0.11	**0.96**	0.12
SO_4^{2-}	**0.85**	0.18	0.23
Al	0.51	0.20	**0.71**
Cr	0.14	0.08	**0.79**
Fe	0.41	0.28	**0.76**
Ni	0.44	−0.18	**0.50**
Zn	0.04	0.02	**0.62**
Cd	0.47	0.24	**0.63**
Pb	0.44	0.42	**0.59**
Mn	0.36	0.35	**0.50**
Cu	**0.75**	−0.14	0.41
% Total variance	28.5	22.4	22.2

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

Ranking	Pyrolysis fragments									
	2 Jun	8 Jun	18 Jun	19 Jun	29 Jun	30 Jun	12 Jul	18 Jul (Typhoon-Khanun)	6 Aug	10–15 Aug
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-Benzene dicarbonitrile (Pr,PHA)	Phthalic anhydride (PHA)	Phthalic anhydride (PHA)
3	2,5-Pyrrolidine dione (Pr)	2,4-Dichloro benzamide (PHA)	Benzene carboxylic acid (PHA)	2,4-Dichloro benzamide (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	Benzene carboxylic acid (PHA)	Benzene carboxylic acid (PHA)	Benzonitrile (Pr)	Benzene, 1,4-dichloro- (PHA)	Benzonitrile (Pr)	Acetic acid (PS,AS)	Benzonitrile (Pr)	1,2-Benzene dicarboxylic 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)	Benzene carboxylic 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-Pyrrolidine dione (Pr)	n-Hexa decanoic acid (Lp)	Benzene carboxylic acid (PHA)	Benzene carboxylic acid (PHA)	Furan, 2-methyl-(Pr)	n-Hexa decanoic acid (Lp)		Acetic acid (PS,AS)	
8	Benzonitrile (PR)	n-Hexa decanoic acid (Lp)	1H-Isoindole-1,3(2H)-dione (Pr)	Benzoic acid, 2,4-dichloro- (PHA)	Phthalic anhydride (PHA)		2,5-Pyrrolidine dione (PR)		1,2-Benzene dicarbonitrile (Pr, PHA)	
9	Phenol (PR,PHA)	1,4-Benzene dicarbonitrile (Pr,PHA)	2,5-Pyrrolidine dione (Pr)	Benzonitrile (Pr)	2,5-Pyrrolidine dione (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-Benzene dicarbonitrile (Pr, PHA)	Furan, 2-methyl- (PS)		Tetradecanoic acid (Lp)		Formic acid, ethenyl ester (Lp)	

Table 9. Continued.

Ranking	Pyrolysis fragments							
	23–24 Aug	27–28 Aug (Typhoon-Bolaven)	30 Aug (Typhoon-Tenvin)	12 Sep	22 Oct	5–11 Nov	13–26 Nov	12 Dec
1	1H-Isoindole-1,3(2H)-dione (PR)	Benzene (PHA)	Acetic acid (PS, AS)	Acetic acid (PS, AS)	1,2-Benzene dicarboxylic 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-Benzene dicarboxylic 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	Benzene carboxylic acid (PHA)	2H-Pyran, 3,4-dihydro-4-methyl-(PS)	Benzene carboxylic acid (PHA)				Benzene carboxylic acid (PHA)	
9	Furan, 2-methyl-(PS)	2-Dodecenal, (E)-(Lp)	Benzene, 1-methyl-4-(1-methylethenyl)-(PHA)				1,2-Benzene dicarbonitrile (Pr, PHA)	
10	Benzoic acid, 4-(1-methylethyl)-(PHA)		Benzaldehyde (Lg)					

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

Title Page
Abstract
Introduction
Conclusions
References
Tables
Figures
◀I
▶I
◀
▶
Back
Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

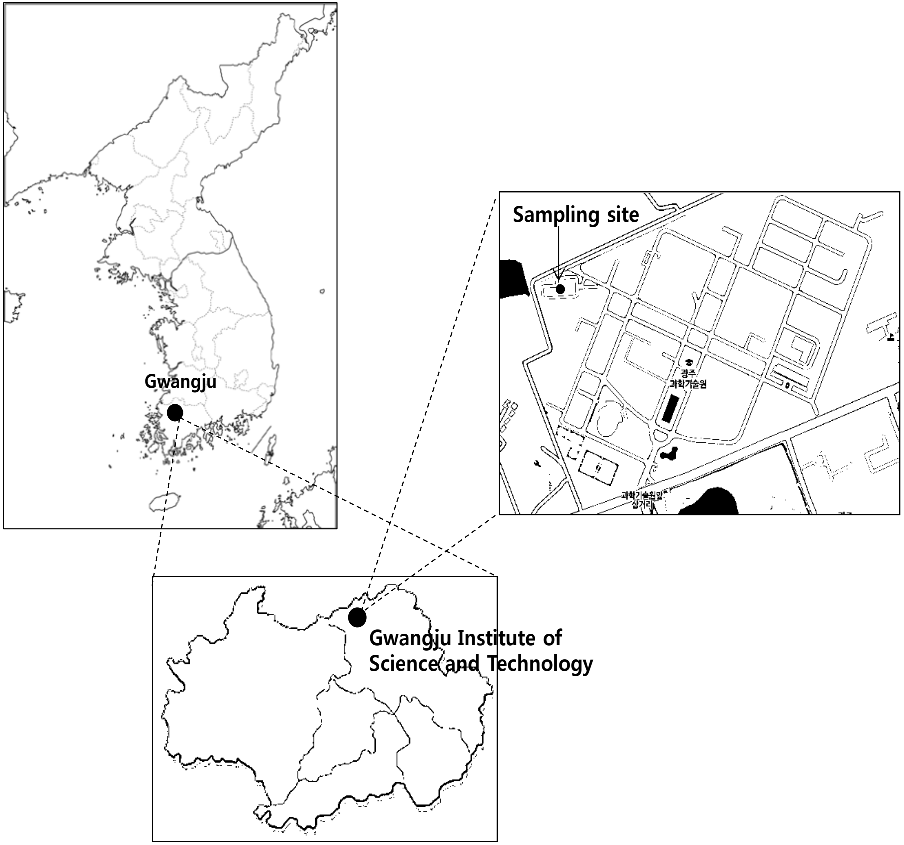

Figure 1. Location of the sampling site for this study.

Title Page
Abstract | Introduction
Conclusions | References
Tables | Figures
◄ | ►
◄ | ►
Back | Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

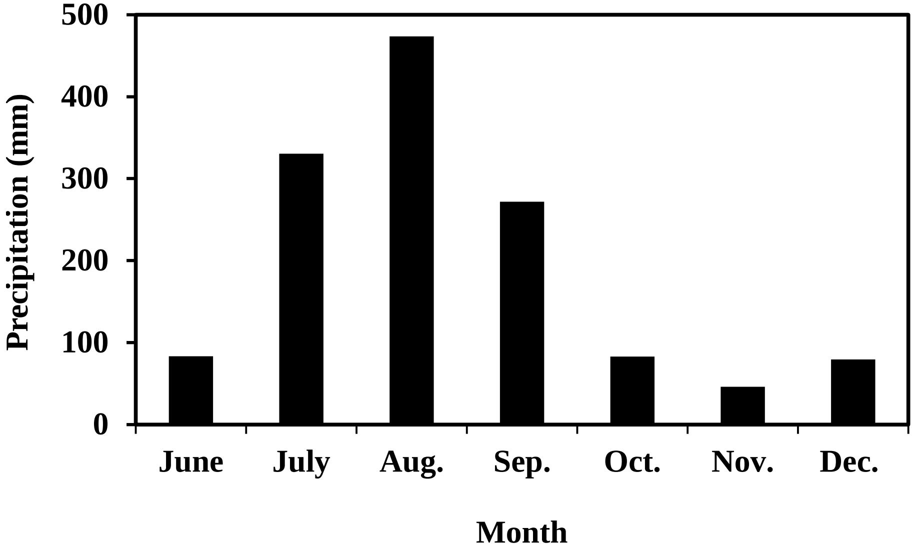

Figure 2. Monthly integrated precipitation at Gwangju during 2012.

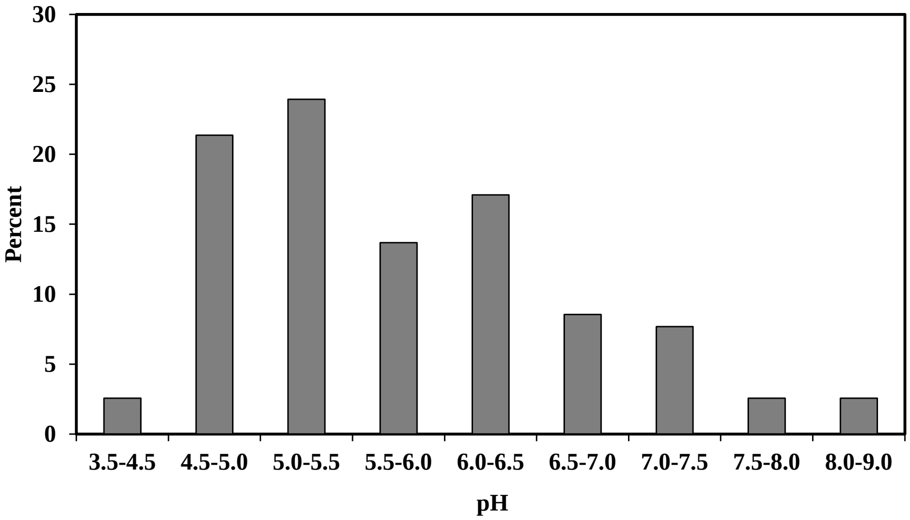

Figure 3. Distribution of pH in rainwater samples collected from Gwangju.

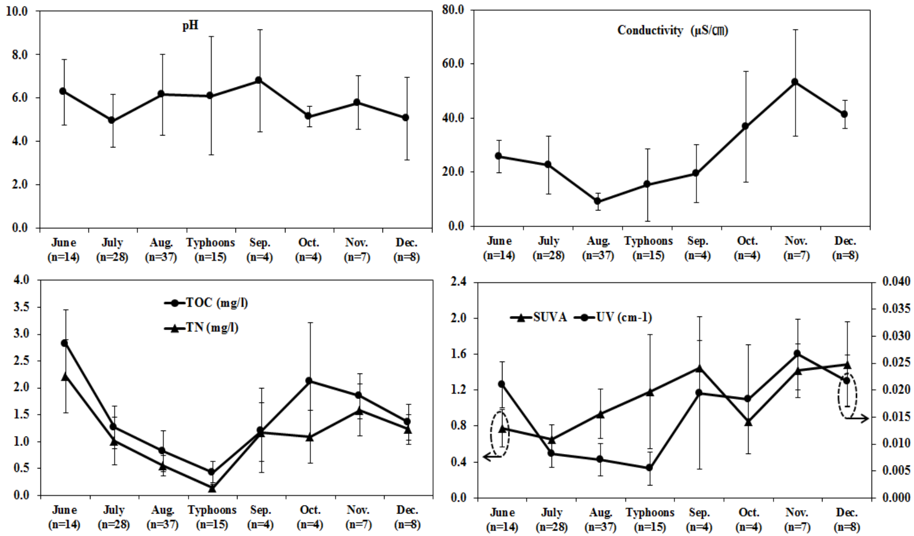

Figure 4. Monthly variation of volume-weighted mean value of pH, Conductivity, TOC, TN, SUVA, and UV in rainwater samples collected in Gwangju during 2012.

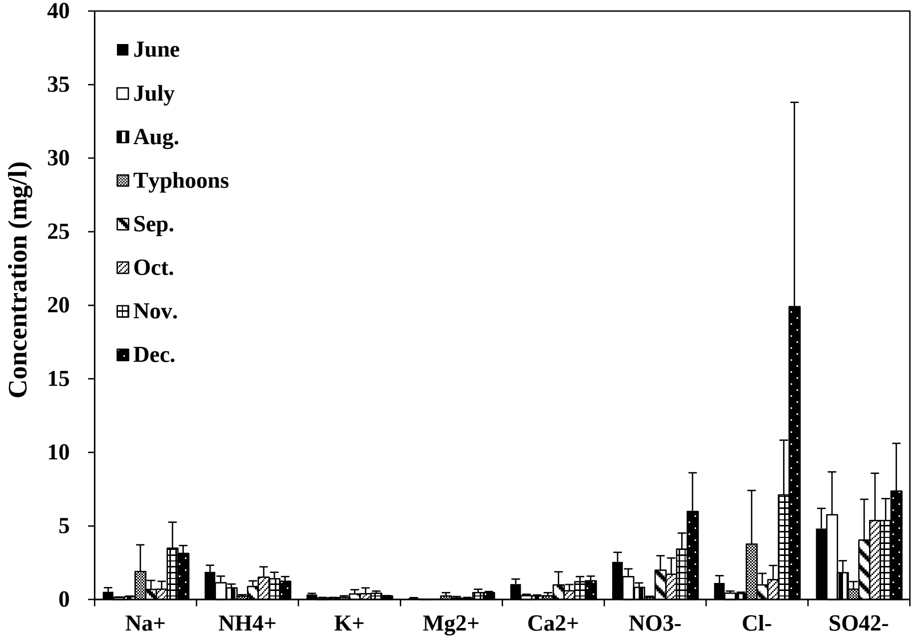

Figure 5. Monthly variation of VWMC of major ions in rainwater samples during 2012.

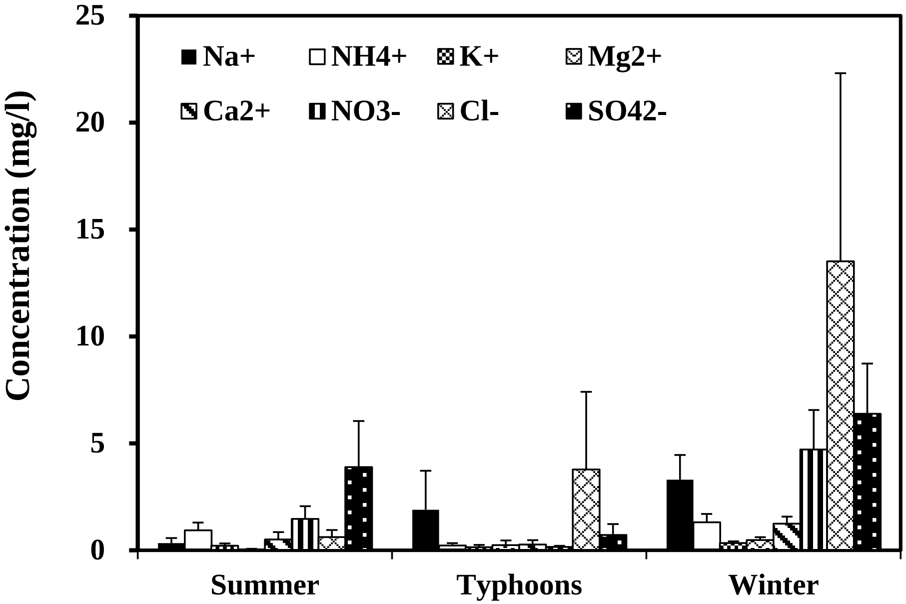

Figure 6. Mean concentration of major ions in rainwater samples during summer (July–September), typhoons, and winter (November–December).

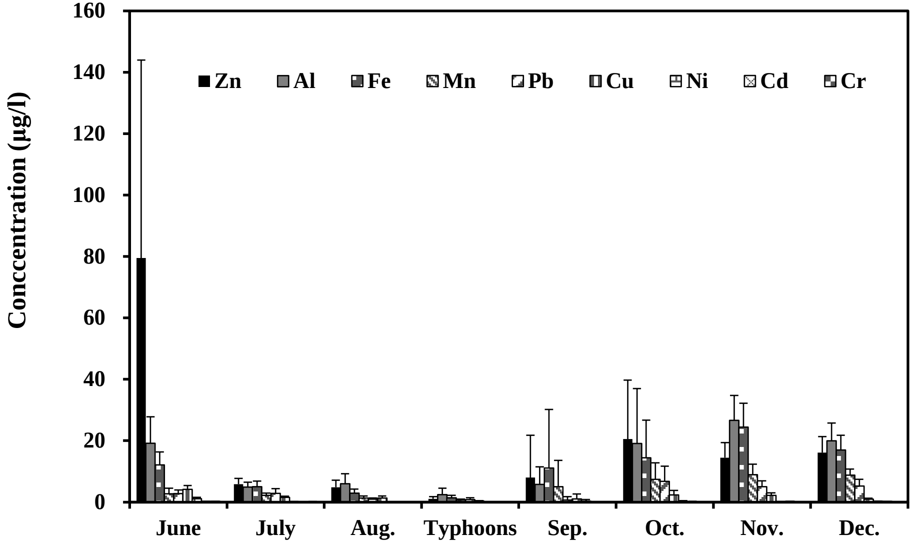

Figure 7. Monthly variation of VWMC of trace metals in rainwater samples during 2012.

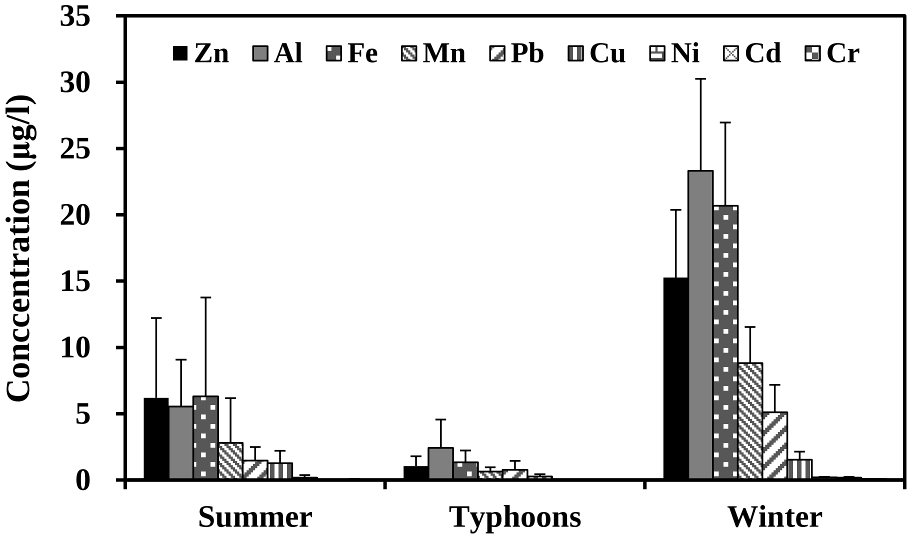

Figure 8. Mean concentration of trace metals in rainwater samples during summer (July–September), typhoons, and winter (November–December).

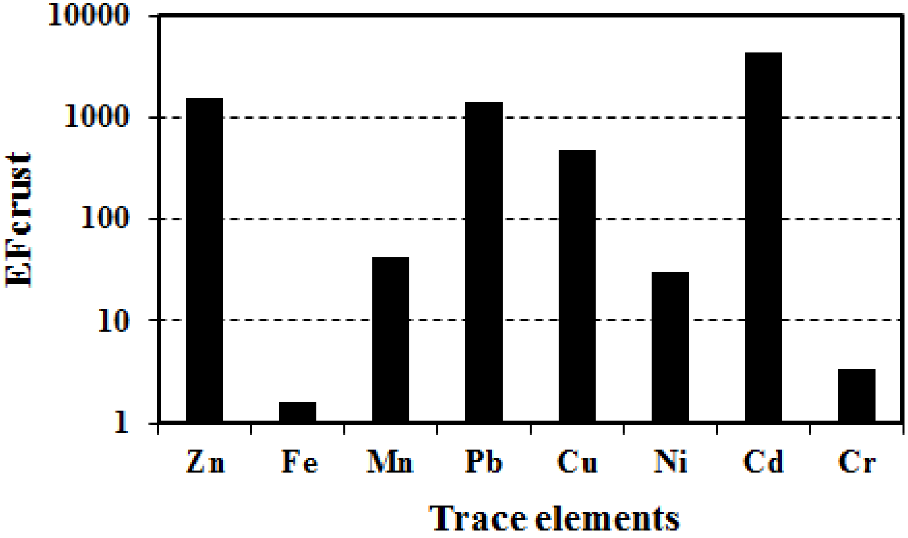

Figure 9. Average EFs of trace metals in rainwater at Gwangju area during 2012.

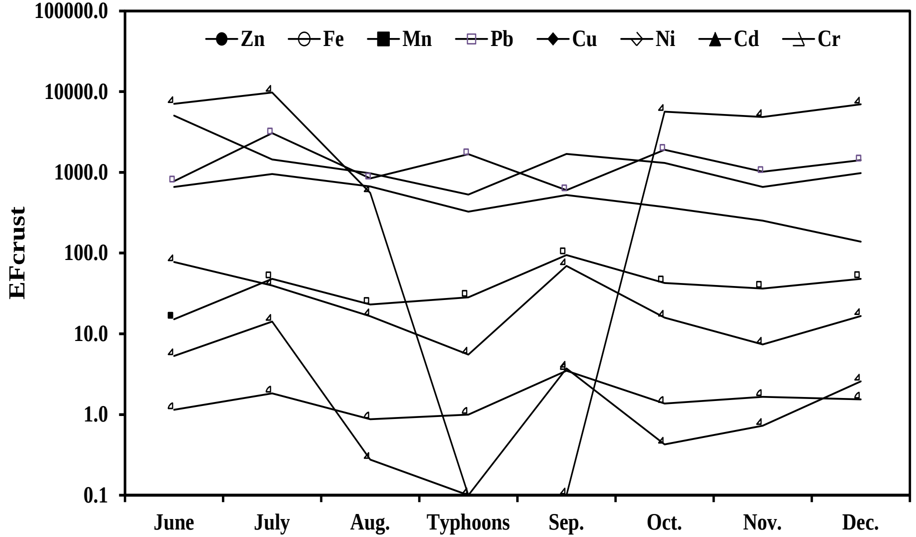

Figure 10. Monthly variation of EFs of trace metals in rainwater at Gwangju area during 2012.

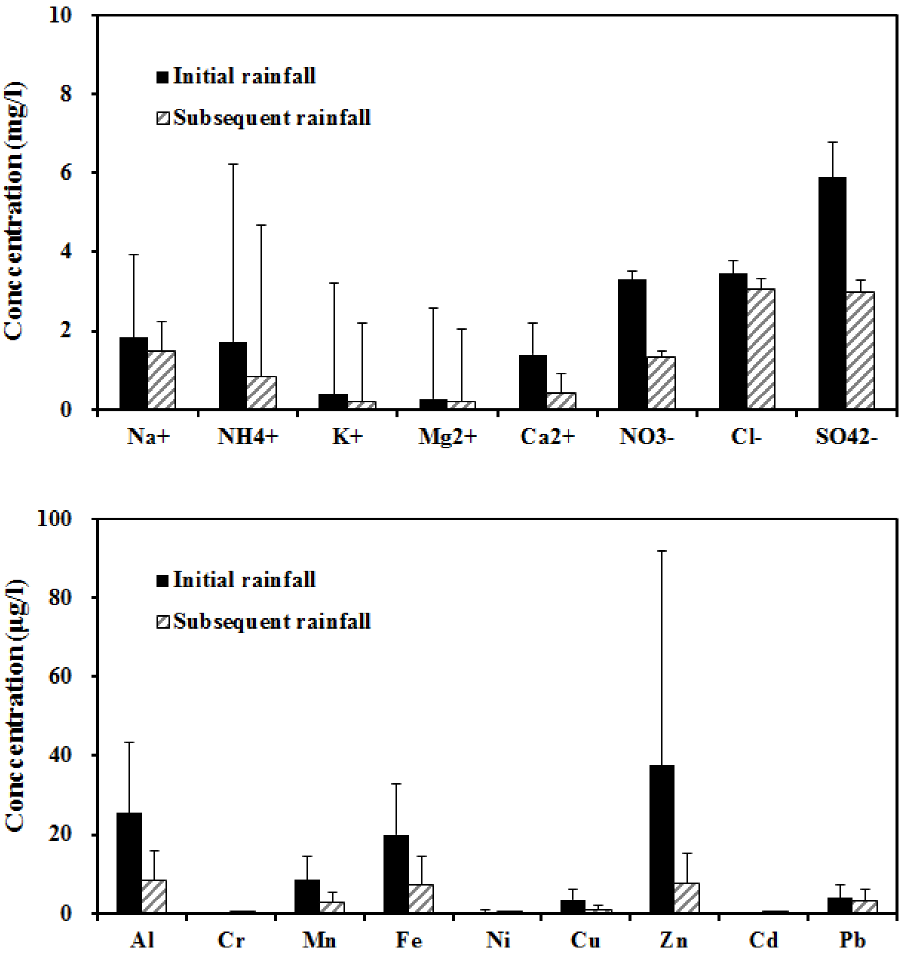

Figure 11. Comparison of mean concentration of major ions and trace metals in initial ($n = 40$) and subsequent ($n = 73$) rainfall during 2012.