Source Identification and Variation in the Chemical Composition of Rainwater in Southern-Eastern Region of Bangladesh

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Abstract

The present study portrayed a better understanding of the chemical characteristics of rainwater in South-Eastern region of Bangladesh (e.g. Chattogram) as well as to identify the potential sources of different precipitation constituents in the study region that were often unexplored and not well understood. Rainwater pH, major ions, and trace metals were measured in samples collected from five different locations with different land use patterns of Chattogram Metropolitan area (CMA) during the two rainy seasons. The samples were tested following standard protocols. The results of this study exhibit variability in rainwater quality across the sites signifying site-specific influences. The mean concentration of all measured physicochemical parameters, ions and trace metals in rainwater samples were found significantly lower compared to the drinking water quality standard of Bangladesh. In context of ionic constituents, the higher concentrations of nitrate (NO_3^-) and sulphate (SO_4^{2-}) were generally in commercial area. The correlation matrix and principal component analysis (PCA) indicated that NO_3^- and SO_4^{2-} were from anthropogenic sources, e.g. automobile exhaust, incomplete fuel combustions, and industrial emissions. The average concentration of trace metals in rainwater was followed a decreasing order: Zn ⊠ Cu ⊠ Fe ⊠ Cr ⊠ Mn ⊠ Pb ⊠ Cd. Trace metals concentration, especially copper (Cu) and zinc (Zn) were found maximum in the industrial catchment area. The resulting outcomes of this study could be useful to investigate the influences of industrial, urban, and agricultural emissions that elaborate the physical processes regulating the chemical characteristic of the atmosphere in the investigated area.

1. Introduction

Rainwater is considered blessings and is found generally safe and common alternative sources of water around the world that got huge attention of its culture in relation to quality uses in particularly developing countries. Although, rainwater is safe, the chemical compositions at the point of collection is seen altered influenced by local environment and atmospheric condition; hence, different places might see different elemental concentrations in place that is often key to define suitability of uses. Rainwater chemistry is formed through a dynamic interaction between the atmospheric (e.g. cloud) dynamics and the microphysical actions in together with a sequence of ‘rainout and washout atmospheric chemical reactions’ [1–4]. Rainwater chemistry signifies the chemical characteristics of the atmosphere through which it falls, helps to understand and investigate the soluble elements exists in rainwater as noted by Wang and Han [5]. Rainwater compositions provide insight into the relative contributions of different atmospheric pollutants, and their regional dispersion [6–7]. Additionally, it also helps to investigate the site-specific characteristics, such as influences of emissions from industrial, urban, and agricultural sectors, and the biogeochemical factors that elaborate the physical processes regulating the chemical characteristic of the atmosphere in regional areas and natural biogeochemical cycle [8–9].

Chattogram, a commercial capital and one of the largest port cities in Bangladesh is situated in the eastern coastal zone of Bangladesh [10]. The city is a home of nearly 4.5 million people and the sources of water are in mixed modes of surface and groundwater. However, ground water near the coastal belt see substantially high salinity in dry period due to little or no rainfall along with arsenic in few cases in shallow tube wells at household scale [11–12]. Therefore, people mostly depend on the water supplied by Chattogram Water Supply and Sewerage Authority (CWASA) both for domestic and drinking purposes that are intermittent and fall short in coverage fulfilling around 69% demand for city dwellers. In absence of wastewater treatment facilities and poor solid waste management system, the river water quality near city area is found unsuitable, hence, CWASA has to go further upstream covering the great distance for searching comparatively less polluted surface water suitable for treatment for its connected [13–14]. Taking poor quality surface water and groundwater with high salinity and arsenic in consideration, the rainwater culture is an only option left and is seen as blessing due to the volume of precipitation received during monsoon in Bangladesh.

While the potential rainwater harvesting methods and opportunities across Bangladesh are increasingly being studied [15–17], the chemical characteristics of rainwater and the variation of relative contributions of different atmospheric pollutants with respect to different land uses remain generally unexplored considering its merit for suitability of uses. There have been surprisingly very few studies devoted to investigating the chemical composition of rainwater around the globe. In Bangladesh particularly in Southern-Eastern region of the country e.g. Chattogram, no such study is found at present. These knowledge gaps are contributed to this study, which describes the results of a comprehensive experimental investigation on rainwater chemistry in Chattogram region across various social and economic zones of the city, e.g. industrial, residential, and urban area. The main purpose of this study to obtain a better understanding of the chemical composition of rainwater across varying geographical locations of Chattogram as well as to identify the potential sources of different precipitation constituents in the study region.

2. Materials And Methods

The rainwater chemistry was identified by comprehensive field and laboratory tests on various water quality parameters, e.g. pH, turbidity, alkalinity, hardness, major ions, trace metals, etc. The resulting chemical composition of rainwater obtained in this study are then compared with the existing standards of water quality parameters that are applicable to the study region.

2.1. Study Area

The city Chattogram is a noteworthy coastal city and commercial hub located in the south-eastern sides of Bangladesh. Chattogram Metropolitan area (CMA) is four times greater than the Chattogram City Corporation (CCC) area, situated as shown in Fig. 1 (22°6'41"N-22°33'38"N, 90°41'E-92°2'E). The city is bounded by the Bay of Bengal on the west, by Halda River on the north-east and, by Karnaphuli River on the south-east. The busiest seaport of Bangladesh is located at the estuary of the Karnafuli River [18]. Due to this port facility, the city is business friendly that’s why more than hundreds of oldest and largest industries of Bangladesh established here [19]. The CMA is one of the critical coastal regions of the country with around 4.5 million inhabitants (density 6000/km^2) with a growth rate of 2.06% per annum [20].

Geographically, the core city area is plain land and low height hillocks mainly towards the north with a peak elevation of 351 m in Sitakunda [21]. The tropical monsoon climate mostly dominates the weather characteristics of the city. According to the available data from Chattogram station of Bangladesh Meteorological Department (BMD), 2400 mm and 3000 mm annual rainfall occurs in Chattogram region of which 80% of total occurs between May and September (Fig. 2). In which, the mean annual relative humidity is 73.7% and mean monthly relative humidity varies from 58% in January to 86% in August [22]. During dry weather usually mild cold wind blows from the north to the south of the country with very little precipitation. The average maximum and minimum air temperature are 32.3 °C and 13 °C, in summer and winter, respectively [22]. In this study, five locations are selected addressing different land uses for collecting rainwater samples in which three of them are in the city centre (Fig. 1), while the remaining two sites are outsides of city centre, one of which is an industrial area named Kumira and another one is a sub-urban residential area named Pahartali. Generally, in a field, there exist residential, commercial and industrial characteristics, that's why in this study, all of the city based on their land use for specific purposes are selected, e.g. Figure 1. Rainwater parameters of GEC and Agrabad locations particularly belong to commercial land use might have been influenced by the road traffic environment as of high traffic volume.

Meanwhile, the highest traffic-induced noise pollution was recorded in the commercial areas (e.g. GEC intersection and Agrabad circle in Fig. 1.) [18, 23]. The growing concern for city dwellers is air pollution, mostly caused by automobile emission as the number of vehicles are increasing day by day, in 2010 registered vehicles was 84,391. Still, besides that, there are several thousands of non-registered vehicles [24]. Suspended Particulate Matter (SPM), sulphur dioxide (SO_2) and nitrogen oxides (NOx) are the three major components of air pollution in Chattogram city with SPM being the most concentrated [18, 25]. Pahartali site is mainly residential in nature where most of the Bangladesh Railway residence is situated. Kumira is an industrial area located in the north of the CMA one side of which is the Bay of Bengal and other side is hills. Besides, various cement, glass and steel manufacturing industries, South Asian one of the famous ships breaking industry situated here. The soil, water and also air around the ship breaking industries is greatly polluted by toxic substances [26–28]. On the other hand, Chittagong University of Engineering & Technology (CUET) is situated in Raozan Upazila very different from other sites and can be considered pristine site with little or no significant pollution, which is not part of CMA. The area is sub-urban with relatively clean environment where agricultural land use persists on top of academic activities.

2.2. Sample Collection

The samples of rainwater were taken on an event basis. Total ninety-five wet-only rainwater samples were collected from two rainy seasons (June 2018 to October 2018 and June 2019 to October 2019). Rainwater collector shown in Fig. 3 was placed on the roof of building at each of the rainwater sampling sites described above with varying heights ranged 10 to 20 m. First flush tank was incorporated to sperate the rainwater after first flush by using ballcock. In this study, the water from rainwater tank was used to analyse. In rainwater tank, there also a ballcock used to prevent passing of remaining rainwater stayed in catchment after filling up rainwater tank. It’s because, during the time between rainfall and collection there is a chance of contamination by birds and insects since the catchment was open whereas rainwater tank was closed. In this study, first flush water was not considered for testing since in most of the study it was suggested to let the first flush water go as it is considered polluted [29–31]. Between two rain events, the rainwater tank was cleaned manually while the dry deposition of pollutants primarily influenced by atmospheric fall out cannot be avoided. Immediately after each rainfall events the rainwater samples were collected by using 500 ml polypropylene bottle. Before collecting, the bottles were washed by using distilled water to avoid cross contamination.

2.3. Sample Collection

Table 1 summarizes the analytical parameters and methods used for determining rainwater quality. Potential of hydrogen (pH), electrical conductivity (EC) and TDS were measured at in situ by using Smart Digital pH meter and HQ40D Multi-meter. The pH meter has been calibrated using 4.0, 7.0, and 10.0 pH buffer solutions. All the samples were stored at 4 °C until analysis. Prior to analysis, samples were filtered by using No. 1 Whatman® filter paper to remove the insoluble particles. The standard analytical protocol following quality control and quality assurance has been maintained for the experiments conducted in the Environmental Engineering Laboratory at CUET.

Table 1
Analytical methods used for the determination of the rainwater quality

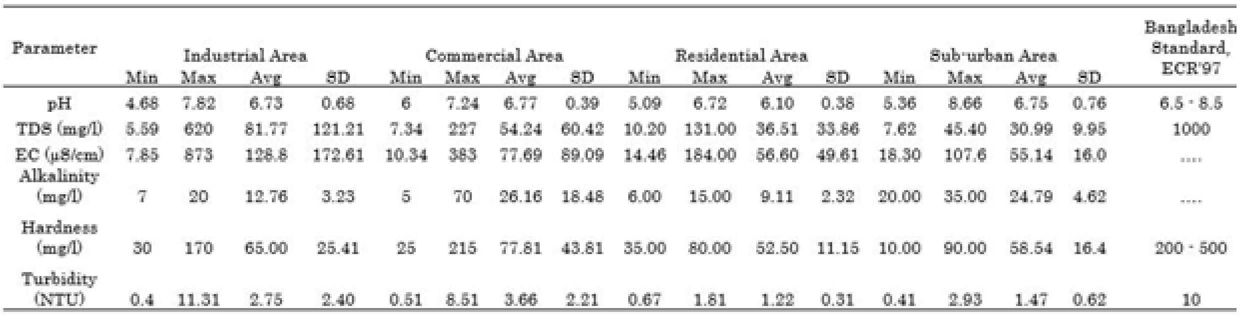
Parameters	**Analytical Method**
pH	Smart Digital pH Tester
Electrical Conductivity (EC)	HQ40D Multi Meter
Total dissolved solids (TDS)	HQ40D Multi Meter
Turbidity	2100Q Portable Turbidimeter
Alkalinity (as $CaCO_3$)	Titration with 0.02 N H_2SO_4 using methyl orange
Hardness (as CaCO3)	Titration with 0.02 N NaOH using 0.1 EDTA
Ions [Nitrate (NO_3^-), Sulphate (SO_4^{2-}), Phosphate (PO_4^{3-}) and Ammonium (NH_4^+)]	DR1900 Portable Spectrophotometer
Trace Metals (Fe, Cu, Zn, Pb, Mn, Cr & Cd)	AA-6200 Atomic Absorption Spectrophotometer

3. Results And Discussion

3.1. Physicochemical analysis

All the physicochemical parameters investigated in this study were found well below than the Bangladesh standard in all selected land use locations. The descriptive statistics of physicochemical parameters tabulated in Table 2, while for ease of understanding the average concentrations of the parameters are kept in bar chart plot in. The average pH values ranged from 6.07 to 6.75 in all tested samples which is in slightly acidic range. The EC and TDS were recorded higher in industrial area, indicating presence of more ions dissolved in the rainwater at that location (Fig. 4). Turbidity were found in similar range in all locations slightly higher in commercial area due to the presence of high quantity of dust particles in air of that region, although turbidity is not inevitably a health threat, it may possibly create a health hazard if the suspended particles have adsorbed toxic organic or inorganic compounds [30]. Average concentration of alkalinity and hardness were found somewhat higher in commercial area.

Table 2 Descriptive statistics of physicochemical parameters of rainwater



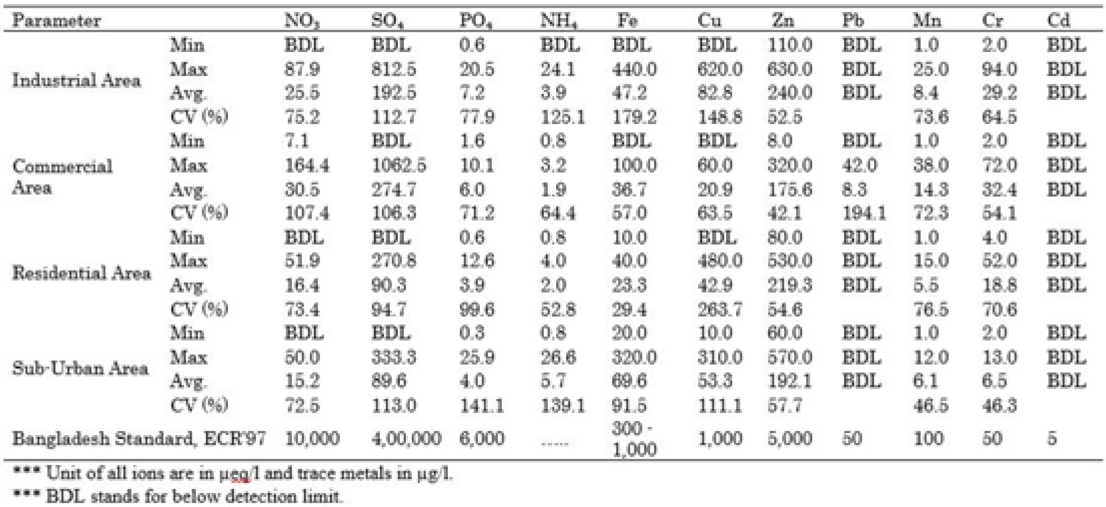
Parameter	Industrial Area				Commercial Area				Residential Area				Sub-urban Area				Bangladesh Standard, ECR'97
	Min	Max	Avg	SD	Min	Max	Avg	SD	Min	Max	Avg	SD	Min	Max	Avg	SD	
pH	4.68	7.82	6.73	0.68	6	7.24	6.77	0.39	5.09	6.72	6.10	0.38	5.36	8.66	6.75	0.76	6.5 - 8.5
TDS (mg/l)	5.59	620	81.77	121.21	7.34	227	54.24	60.42	10.20	131.00	36.51	33.86	7.62	45.40	30.99	9.95	1000
EC (μS/cm)	7.85	873	128.8	172.61	10.34	383	77.69	89.09	14.46	184.00	56.60	49.61	18.30	107.6	55.14	16.0	....
Alkalinity (mg/l)	7	20	12.76	3.23	5	70	26.16	18.48	6.00	15.00	9.11	2.32	20.00	35.00	24.79	4.62	....
Hardness (mg/l)	30	170	65.00	25.41	25	215	77.81	43.81	35.00	80.00	52.50	11.15	10.00	90.00	58.54	16.4	200 - 500
Turbidity (NTU)	0.4	11.31	2.75	2.40	0.51	8.51	3.66	2.21	0.67	1.81	1.22	0.31	0.41	2.93	1.47	0.62	10

3.2. pH value and ionic composition

Natural rainwater is normally considered to be weakly acidic with a pH value of 5.6 when the atmosphere is free from pollution [32–33]. Statistical variation of pH at different land use locations is shown in Fig. 5. The maximum pH (8.66) was recorded in residential (sub-urban) area whereas minimum value (4.68) was found in industrial area. Considering the variability and anthropogenic input at different sites, the residential catchment in Pahartali relatively clean with no surrounding input sources, exhibit the wide range of pH compared to other sites with urban, commercial and industrial surroundings. The relatively smaller variation in other rial catchment in comparison to sub urban catchment illustrate site-specific characteristics influenced by the anthropogenic input (road traffic and industrial emission) during precipitation followed by dry deposition between rain events. The similar variations are also seen in studies elsewhere [34–35].

Descriptive statistics for major ions in rainwater of different locations are given in Table 3. For the all four sampling locations, SO_4^{2-} was the highest dominant major ion, with an average concentration of 192.5, 274.7, 90.3 and 89.6 μeq/l, for industrial, commercial, residential (urban) and residential (sub-urban) area, respectively. The maximum concentration of NO_3^- and SO_4^{2-} were found in commercial area where rainwater quality might be influenced by vehicular emission than other locations. Most of the time vehicles are in traffic congestion in that location which increases vehicular emission [24]. Contribution of NO_3^- and SO_4^{2-} in commercial area are 36% and 41%, respectively, among all locations as depict in Fig. 6. The percentages of NH_4^+ in residential (sub-urban) area was recorded maximum (38%) around where agricultural activities are seen to be performed, whereas the highest mean concentration (7.2 μeq/l) of PO_4^{3-} was found in industrial area. The presence of PO_4^{3-} in rainwater may be a sign of bird or insect faces contamination as noted by Huston et al. [36].

Table 3 Statistical representation of different ions and trace metals in rainwater samples



Parameter		NO_3	SO_4	PO_4	NH_4	Fe	Cu	Zn	Pb	Mn	Cr	Cd
Industrial Area	Min	BDL	BDL	0.6	BDL	BDL	BDL	110.0	BDL	1.0	2.0	BDL
	Max	87.9	812.5	20.5	24.1	440.0	620.0	630.0	BDL	25.0	94.0	BDL
	Avg.	25.5	192.5	7.2	3.9	47.2	82.8	240.0	BDL	8.4	29.2	BDL
	CV (%)	75.2	112.7	77.9	125.1	179.2	148.8	52.5		73.6	64.5	
Commercial Area	Min	7.1	BDL	1.6	0.8	BDL	BDL	8.0	BDL	1.0	2.0	BDL
	Max	164.4	1062.5	10.1	3.2	100.0	60.0	320.0	42.0	38.0	72.0	BDL
	Avg.	30.5	274.7	6.0	1.9	36.7	20.9	175.6	8.3	14.3	32.4	BDL
	CV (%)	107.4	106.3	71.2	64.4	57.0	63.5	42.1	194.1	72.3	54.1	
Residential Area	Min	BDL	BDL	0.6	0.8	10.0	BDL	80.0	BDL	1.0	4.0	BDL
	Max	51.9	270.8	12.6	4.0	40.0	480.0	530.0	BDL	15.0	52.0	BDL
	Avg.	16.4	90.3	3.9	2.0	23.3	42.9	219.3	BDL	5.5	18.8	BDL
	CV (%)	73.4	94.7	99.6	52.8	29.4	263.7	54.6		76.5	70.6	
Sub-Urban Area	Min	BDL	BDL	0.3	0.8	20.0	10.0	60.0	BDL	1.0	2.0	BDL
	Max	50.0	333.3	25.9	26.6	320.0	310.0	570.0	BDL	12.0	13.0	BDL
	Avg.	15.2	89.6	4.0	5.7	69.6	53.3	192.1	BDL	6.1	6.5	BDL
	CV (%)	72.5	113.0	141.1	139.1	91.5	111.1	57.7		46.5	46.3	
Bangladesh Standard, ECR'97		10,000	4,00,000	6,000	.....	300 - 1,000	1,000	5,000	50	100	50	5

*** Unit of all ions are in μeq/l and trace metals in μg/l.

*** BDL stands for below detection limit.

3.3. Trace Metals

A statistical summary of trace metal concentrations in rainwater samples of different selected sites is presented in Table 3. It is observed that the average concentrations of all selected trace metals are well below than the Bangladesh drinking water standard. Elevated concentration of Zn was found in all analyzed samples, although the limiting value of Zn also much higher than other metals. Comparatively, the higher concentration of Zn and Cu was found in industrial area. The mean concentration of copper (Cu) in industrial area was 74.7%, 48.2% and 35.6% greater than the commercial, residential (urban) and residential (sub-urban) area, respectively. Industrial areas are usually influenced by metal intensive activities, and the widespread use of metals, such as Fe, Cu and Zn in industries, are reflected in higher concentrations in rainwater of these metals [37–38]. The average concentration of Fe was recorded 47.2 μg/l, 36.7 μg/l, 23.3 μg/l and 69.6 μg/l in industrial, commercial, residential (urban) and residential (sub-urban) area, respectively. Pb was only found in the rainwater of commercial area. Highest average concentration (32.3 μg/l) of Cr found in commercial area while lowest average concentration (6.5 μg/l) recorded in residential (sub-urban) area. Mn was found in elevated concentration in commercial area while Cd was found below detection limit in all sampling sites. Atmospheric deposition is one of the significant pathways of trace metals presence in urban rainwater and is mostly impacted by site-specific emissions [37]. As vehicular emissions in the commercial area are ample than those of residential area, this pathway (atmospheric deposition) could contribute to the elevated concentration of trace metals in the commercial site [39].

It is observed that the average concentration of trace metals in all analyzed samples followed a decreasing order of Zn Cu Fe Cr Mn Pb Cd. The percentages of total concentration for selected trace metals in different land use locations are shown in Fig. 7. Cu and Zn, together accounted 80% of total concentration in industrial area while 67% for commercial area, 84% for residential (urban) area and 74% for residential (sub-urban) area.

3.4. Worldwide comparison

The precipitation analysis of this study is compared with the data from other areas of Bangladesh as well as worldwide. In Table 4, the physicochemical characteristics of rainwater measured for this study area have been compared with those observed worldwide in other studies. The pH of rainwater samples was in the range from 4.68 to 7.82, with a mean value of 6.63 ± 0.62, i.e. is in the acidic range, reveals the similar characteristics as reported in other parts of the world. The concentrations of TDS and EC were found lower within this work when compared to those observed in other areas, but smaller than Korea. The measured values of alkalinity and hardness for the tested area were higher than those reported in other parts of the world, see Table 4. The concentration of turbidity was much lower than those observed in worldwide but slightly higher than those in another city of Bangladesh, i.e. Sylhet. In general, it is seen that the differences and variability among different sites within city, country, region and globe are reflected in the results, as expected, that signify the in-depth investigation prior to rainwater harvesting potential at sites. The mean concentrations of ions and trace metals in the study area for all samples are presented in Table 5 in conjunction with those reported for other regions around the world. Overall, the concentration of nitrate (NO_3^-) was found much lower in the investigated area in comparison to those observed in other sampling sites in the world, as shown in Table 5. The sulphate concentration (161.8 μeq/l) was observed to be slightly high, when compared with those reported in the literature for similar sampling locations around the world, except for the Taiwan in the republic of China (238.2 μeq/l). The observed values of NH_4^+ were much lower in precipitation reported here compared to those observed in the sampling sites around the world. The PO_4^{3-} concentration was slightly lower than that of India.

Table 4

Comparison of physicochemical characteristics of rainwater between this study and worldwide other studies

Parameter	**This study**	**Sylhet, Bangladesh**(a)	**Haryana, India**(b)	**Loess Plateau, China**(c)	**Jeju, Korea**(d)
pH	6.63 ± 0.62	7.6	6.85	7.48	5.2
TDS	52.3 ± 73.2	80	105	61.3	23.4
EC	81.3 ± 105.6	……	195	94.28	36
Alkalinity	19.3 ± 13.01	13.2	……	……	……
Hardness	65.3 ± 30.7	23	32	……	……
Turbidity	2.5 ± 2.02	0.56	11	4.5	4.8

*** All units are in mg/L, except pH, EC (μS/cm) and turbidity (NTU)

(a) Alam et al. [16]; (b) Bharti et al. [40] (c) Wu et al. [41] (d) Moon et al. [42]

Table 5
Comparison of ions (μeq/l) and trace metals (μg/l) in rainwater between Chattogram, Bangladesh and other locations

Parameter	**This study**	**Ghore El-Safi, Jordan(a)**	**Mexico City, Mexico(b)**	**Lucknow, India(c)**	**Tai'an, China(d)**	**Suburb, Japan(e)**
NO_3^-	21.9 ± 22.9	67.3	42.6	58.5	64.3	9.8
SO_4^{2-}	161.8 ± 220	112.4	61.9	104.2	238.2	24.4
PO_4^{3-}	5.3 ± 5.2	……	……	6.9	……	……
NH_4^+	3.4 ± 5.7	75.4	92.4	42.4	167.1	11.1
Fe	45.1 ± 56.2	430	……	69.2	41.2	7.5
Cu	48.5 ± 85.6	73	……	0.37	7.9	2.5
Zn	203.7 ± 108	210	……	17.6	85.2	18
Pb	5.1 ± 12.9	66	58.7	1.2	5.9	……
Mn	9.2 ± 7.7	……	79.7	6.9	14.2	11
Cr	22.7 ± 18.0	3.1	46.2	9.5	0.06	……
Cd	BDL	52	80.5	BDL	0.61	……

*** BDL stands for Below Detection Limit

(a) Al-Khashman [1]; (b) Báez et al. [43] (c) Singh et al. [44] (d) Li et al. [45] (e) Hou et al. [46]

Table 6
Enrichment factors of trace metals at different locations

Locations	**Cu**	**Zn**	**Pb**	**Mn**	**Cr**
Industrial area	2443.4	3098.5	……..	7.3	262.6
Commercial area	795.4	2918.9	516.2	16.1	374.2
Residential (urban)	1794.3	4010.5	……..	6.8	239.4
Residential (sub-urban)	1067.6	1682.2	……..	3.6	39.6

The trace metal concentrations reported here (Fe, Cu, Zn, Pb, Mn, Cr, and Cd) were overall somewhat higher than those reported worldwide, see Table 5. It is evident from Table 5 that the concentration of Zn

(203.7 µg/l) was found to be one of the highest concentrations of trace metals in the study area, which was also considerably higher than those found in Mexico, India, and Japan, except for the Jordan (210 µg/l). The Fe concentration (45.1 µg/l) was much lower in the investigated area when compared with those reported in Jordan, and India, but higher than China and Korea. The concentration of Cu (48.5 µg/l) within this study was moderately higher than that reported in Mexico, India, and Japan, but lower than that of Jordan. The mean Pb value was found close to those observed in other sampling sites in Asia, i.e. India and China, but much smaller than those in Jordan and Mexico. Overall, the concentrations of Mn and Cd were reported lower in this work compared to the data worldwide. The Cr value was found somewhat higher than those reported around the world, except for Mexico.

3.5. Enrichment factor of trace metals

Enrichment factors (EFs) are generally practiced to find the source of ions and metals in rainwater [47–48]. Crustal enrichment factor (EF_{crust}) was used in this study to identify the non-crustal or anthropogenic sources of trace metals in rainwater. EF_{crust} was calculated by using the following equation i.e. Eq. 1 [49]:

$$EF_{crust} = \frac{\left(\frac{X}{REF}\right)_{rain}}{\left(\frac{X}{REF}\right)_{crust}} \qquad (1)$$

Where, in Eq. (1) $[X]_{rain}$ is the concentrations of specific metals in rainwater and $[REF]_{rain}$ is the concentrations of reference metals in rainwater. Similarly, $[X]_{crust}$ and $[REF]_{crust}$ are the concentrations in crustal material. In this study iron (Fe) is taken as a reference metals because “iron is the most abundant element, by mass, in the earth, constituting about 80% of the inner and outer cores of earth” [50]. The enrichment factors were calculated by using the composition of continental crustal elements from Rudnick and Gao [51]. In general, an element with an enrichment factor (EF) value significantly greater or drastically lower than 1 is assumed to be enriched or diluted relative to the reference source [52–53]. Average enrichment factors for selected trace metals in rainwater are presented in Table 6 for all locations. EF of different metals were found more or less like this study by Uygur et al. [54] and Báez et al. [43]; while they have used Al and Mg as a reference metal. Every metal shows too much higher enrichment factor (especially Cu and Zn) which suggesting the presence of anthropogenic sources. Enrichment of Zn in rainwater like this study has been reported by others, also [44, 46]. Mn had much smaller EF values compared to the remainder of the metals, that were also observed greater than one, exhibiting 16 at commercial area, 7.3 at industrial area, 6.8 at residential (urban) area and 3.6 at residential (sub-urban) area, respectively.

3.6. Correlation matrix

The correlation matrix is a helpful way to characterize the relationship among the species present in rainwater samples. To investigate the relationship within the rainwater quality parameters, Spearman's rank correlation analysis was done and shown in Fig. 8. The electrical conductivity (EC) is a comprehensive indicator of the total dissolved solids in precipitation [55], offering a robust correlation with TDS. No apparent correlations between pH value and NO_3^- indicated that NO_3^- present as salt (NH_4NO_3), since somewhat good relation present in NH_4^+ and NO_3^- (-0.42) [32]. Nitrates may potentially transfer from the air to various water sources (e.g. ground, lakes, and surface water) using rainwater [56–57]. SO_4^{2-} mostly dominates pH in this study and PO_4^{3-} rather than SO_4^{2-} and NO_3^- since somewhat significant correlation exists among pH, SO_4^{2-} and PO_4^{3-} (-0.57). NO_3^- and SO_4^{2-} showed good correlation (0.48) in samples whereas PO_4^{3-} and NO_3^- (0.74) and PO_4^{3-} and SO_4^{2-} (0.68) exhibit strong associations. In relation to source apportion, it has been found that the combustion processes with the use of fuel oil with a sulphur content that occur in industry and thermoelectric power plants are the sources of SO_4^{2-} and NO_3^- [8, 43]. Nitrate and phosphate come from natural decomposition of rocks and minerals, atmospheric deposition, agricultural and industrial activities [58]. A strong correlation between SO_4^{2-} and NH_4^+ (-0.56) indicates that the available NH_3 in the atmosphere will principally react with H_2SO_4 to form $(NH_4)_2SO_4$ and NH_4HSO_4 referred by Seinfed [59].

3.7. Principal component analysis (PCA)

Principal Component Analysis (PCA) is a useful multivariate statistical method that used to identify the effect of probable sources of contaminants presents in rainwater samples [60–61]. In this study PCA was performed by using IBM SPSS Statistics 25. PCA of the rainwater quality parameters (Table 7) showed three PCs with eigenvalues greater than 1 explaining about 69% of the data variability. The parameters which were correlated significantly in correlation analysis also shows strong loading in PCA analysis. The three components were rotated using Varimax rotation procedure. A three-dimensional plot for all the variables in the component1, component2, and component3 is illustrated by Fig. 9. The first component (PC1) described 36% of the total variance and revealed strong loading among TDS (0.943), conductivity (0.930) and hardness (0.819), also moderate loading between pH (0.503) and turbidity (0.730). This clustering of variables points to a common origin and these are in rainwater likely related to environmental conditions.

Table 7
Varimax rotation for principal component analysis of selected parameters

Variables	PC1	PC2	PC3
pH	.503	− .196	.422
TDS	.943	.129	− .087
Conductivity	.930	.193	− .066
Alkalinity	.105	− .100	.773
Hardness	.819	.104	.142
Turbidity	.730	.126	− .003
NO_3^-	.141	.839	.056
SO_4^{2-}	.068	.890	− .025
PO_4^{3-}	.142	.837	− .081
NH_4^+	− .108	.098	.658
Eigenvalue	3.62	2.06	1.19
% of Variance	36	21	12
Cumulative Variance (%)	36	57	69

The second component (PC2) consisting of nitrate (NO_3^-), sulphate (SO_4^{2-}) and phosphate (PO_4^{3-}) accounted for approximately 21%of the total variance. PC2 revealed strong loading of 0.839, 0.890 and 0.837 of the photochemical species NO_3^-, SO_4^{2-} and PO_4^{3-}, respectively. Anthropogenic activities are major sources of NO_3^- and PO_4^{3-}pollution in rainwater as discussed earlier and same also reported by Fung and Lau, (1998). NO_3^- and SO_4^{2-} ions also define anthropogenic influences, such as incomplete fuel combustions, automobile exhaust, coal combustion, and industrial emissions discussed Xiao [32] and Zhang et al. [62].

The third and final component represented 12% of the total variance, having loadings of 0.422, 0.773 and 0.658 of pH, alkalinity and NH_4^+, respectively. The existence of NH_4^+ in the atmosphere may attribute to the utilization of fertilizers, volatilization of animal waste, human excreta, cattle farming, and also emitted from burning of fossil fuels [63–64]. The theoretical response shows that for oxidizing one milligram of ammonia, around 7.14 mg of alkalinity (as CaCO3) is extracted [65]. As noted by Colt et al. [66], insufficient alkalinity could lead to incomplete nitrification and lower pH values in the sites.

4. Conclusions

Detailed measurements have been undertaken to investigate the rainwater quality across different locations in the South-eastern region of Bangladesh. Based on this study, the following conclusions were made –

- The mean concentration of all tested physicochemical parameters, ions and trace metals in rainwater was found significantly lower compared to the drinking water quality standard of Bangladesh.
- The concentration of nitrate (NO_3^-) was found much lower in the investigated area in comparison to those observed in other sampling sites in the world. For the sampled locations, the mean concentration of nitrate (NO_3^-) and sulphate (SO_4^{2-}) was recorded highest in the commercial area. The observed values of NH_4^+ within this study were much lower in precipitation compared to those observed in the sampling sites around the world.
- The trace metal concentrations (Fe, Cu, Zn, Pb, Mn, Cr, and Cd) of our study area were overall somewhat higher than those reported worldwide. Higher enrichment factor of metals suggesting the presence of anthropogenic sources. The mean concentration of trace metals in rainwater was followed a decreasing order: Zn ▯ Cu ▯ Fe ▯ Cr ▯ Mn ▯ Pb ▯ Cd in almost every sampling location.
- Trace metals concentration, especially copper (Cu) and zinc (Zn) were found maximum in the industrial area. The mean concentration of copper (Cu) in industrial area was 74.7%, 48.2% and 35.6% greater than the commercial area, residential (urban) and residential (sub-urban) area, respectively.
- Principal component analysis was performed to find possible sources of the major species in rainwater. The parameters which were correlated significantly in correlation analysis also shows reliable loading in PCA analysis. The results showed that incomplete fuel combustions, industrial emissions, agricultural activities, and also environmental conditions were the dominant sources of the chemical composition in rainwater of Chattogram region.

Prior to this experimental investigations, limited knowledge was available in the chemical composition of rainwater in the southern-eastern region of Bangladesh, which has been attributed in this paper. Consequently, the data and findings of this extensive laboratory study would be useful to the engineers and researchers working in the sustainable use of water resources in Bangladesh, but particularly in southern-eastern region of the country.

Declarations

Availability of data and materials

Data will be available from the corresponding author on request.

Competing interests

The authors declare they have no competing interests.

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Authors' contributions

MAH and AH designed the study and performed the experiments. MGM and HJ fabricated the rainwater sample collection and conceived the original idea. MAH and MS wrote the first draft of the manuscript with the input from SKP. AH supervised the project. All authors read and approved the final manuscript.

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Figures

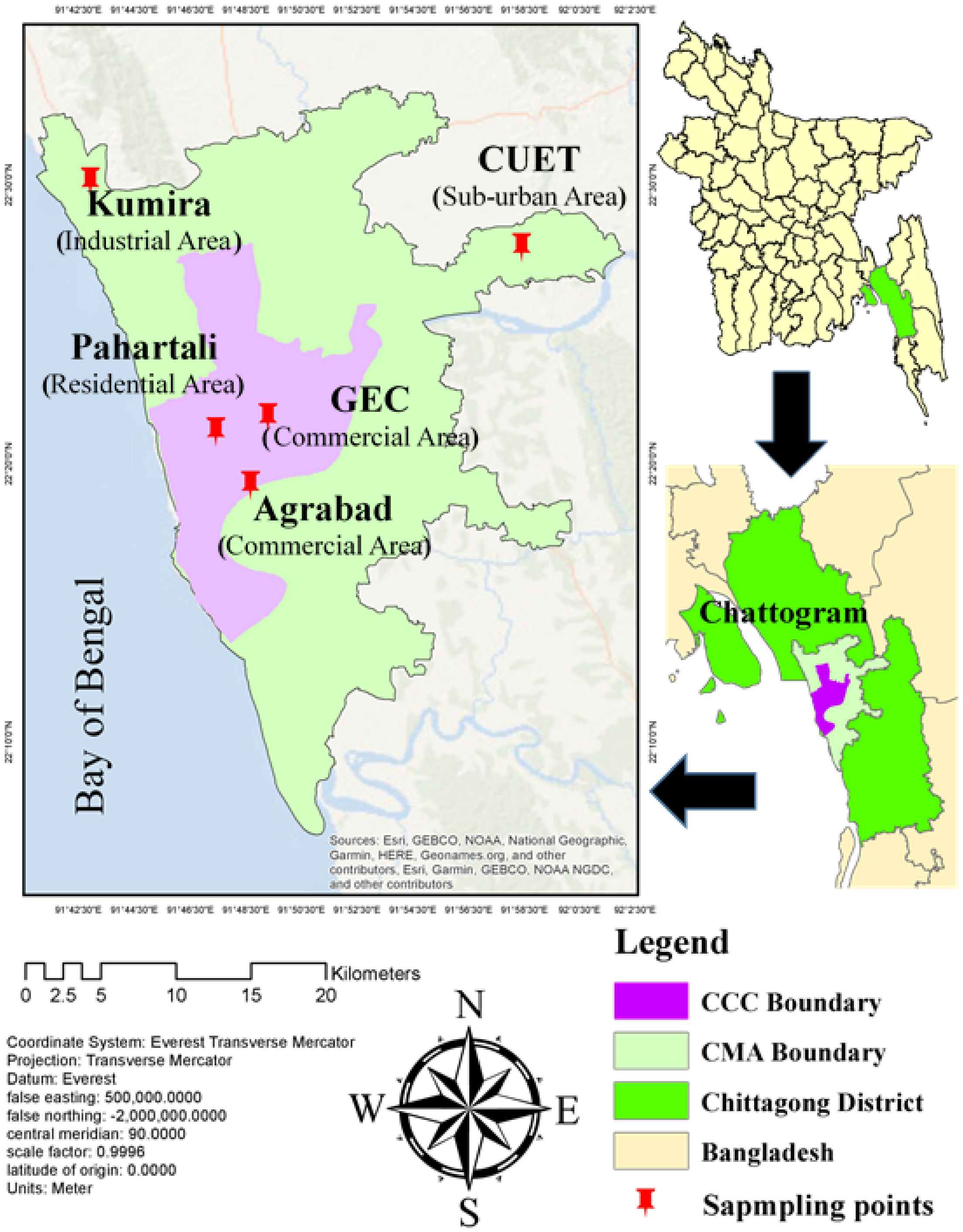

Figure 1

Study area map indicating sampling locations Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.

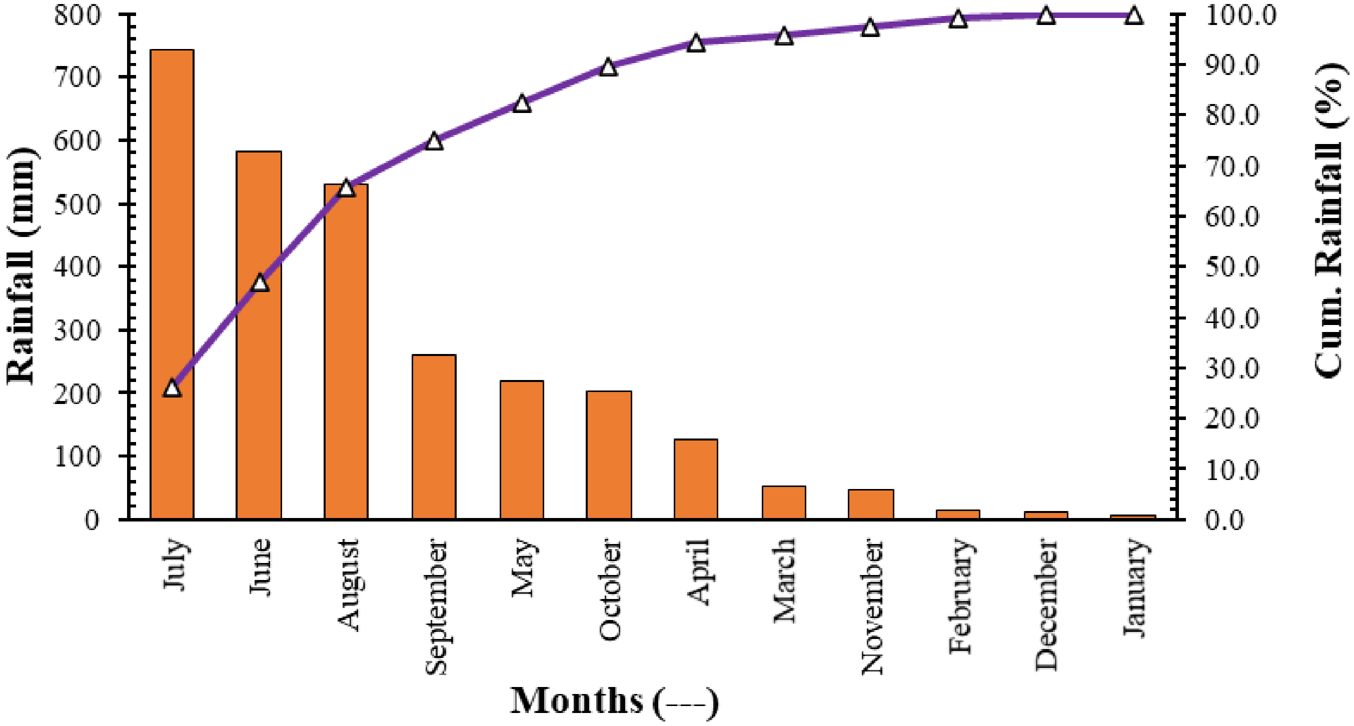

Figure 2

The monthly average rainfall scenario in the study area during the period (1982 – 2017)

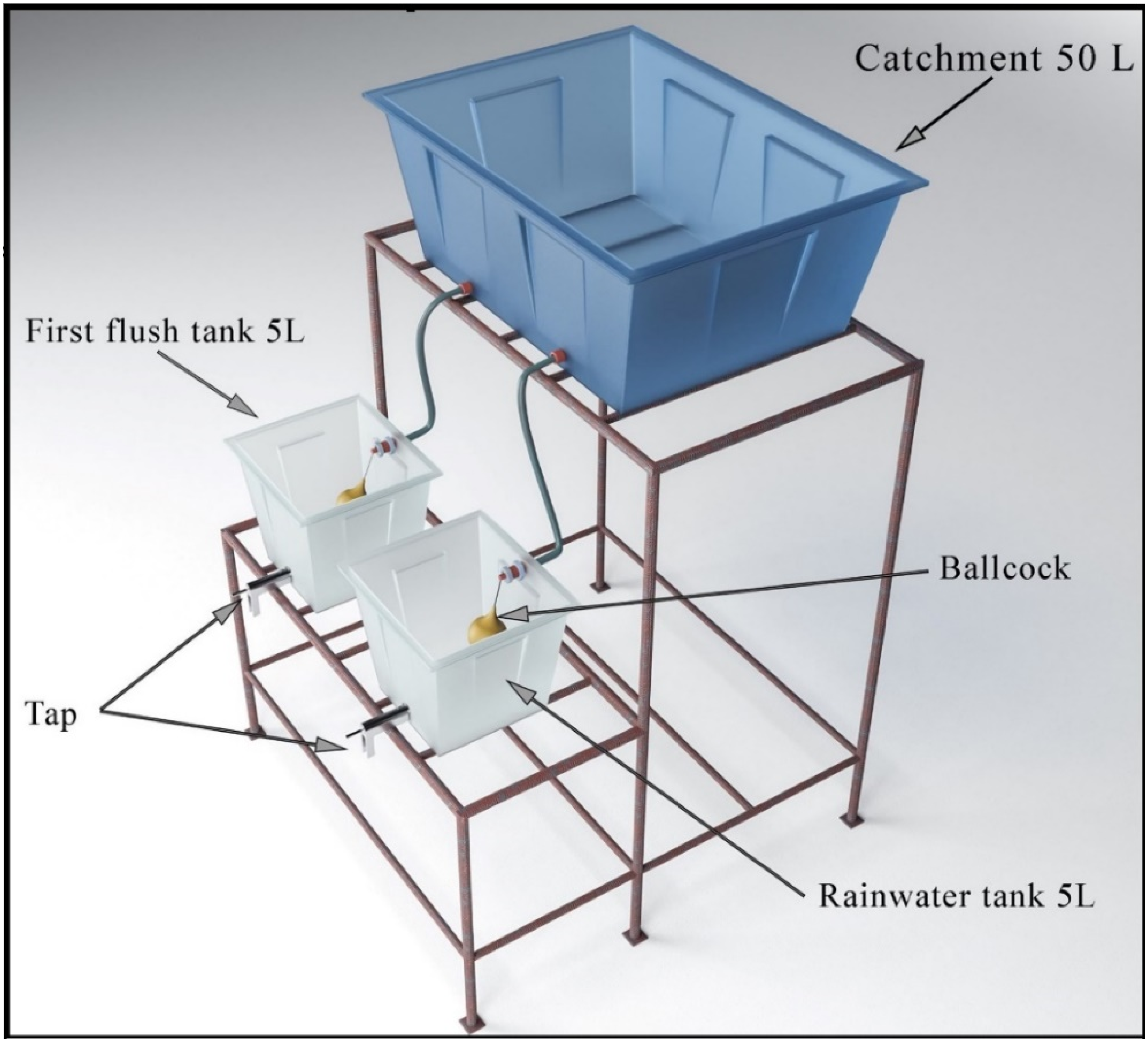

Figure 3

Schematic diagram of rainwater sample collection designed and used in this study

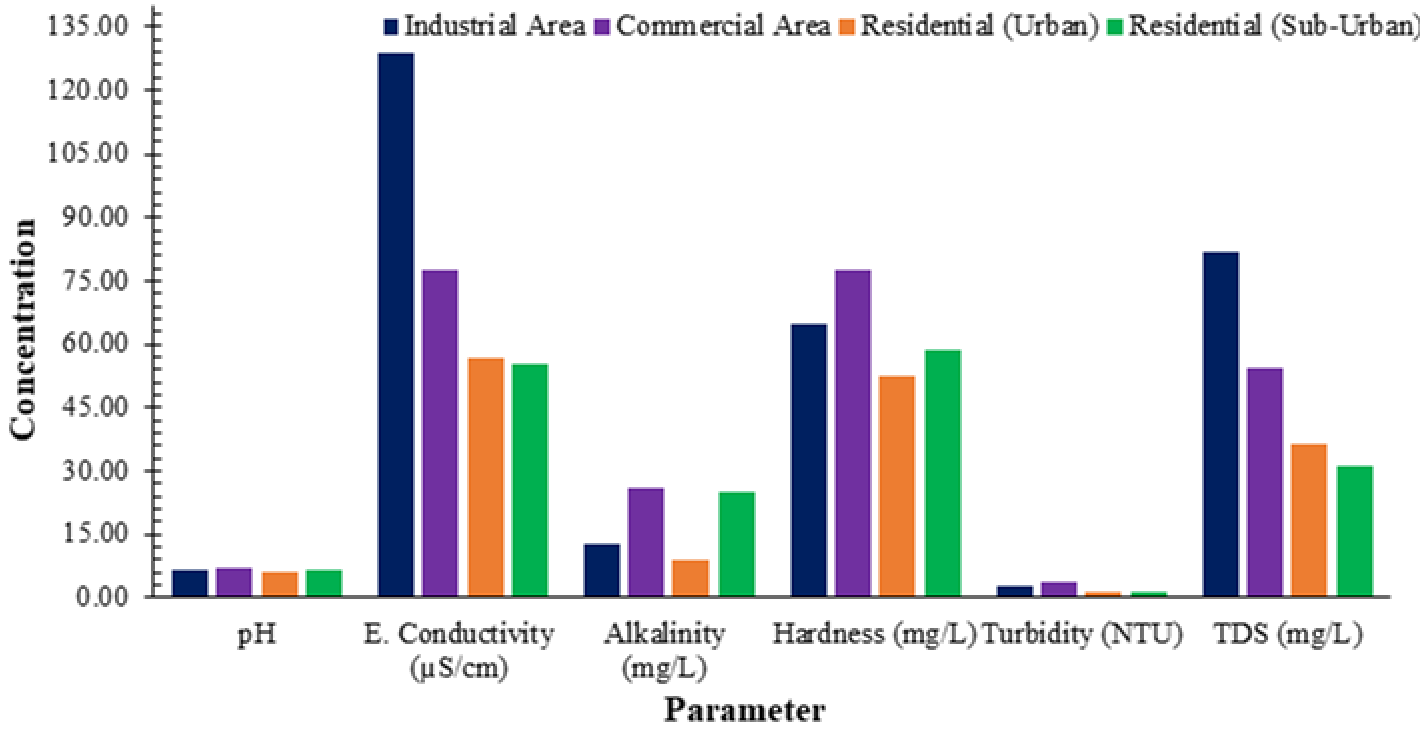

Figure 4

Average value of physicochemical parameters

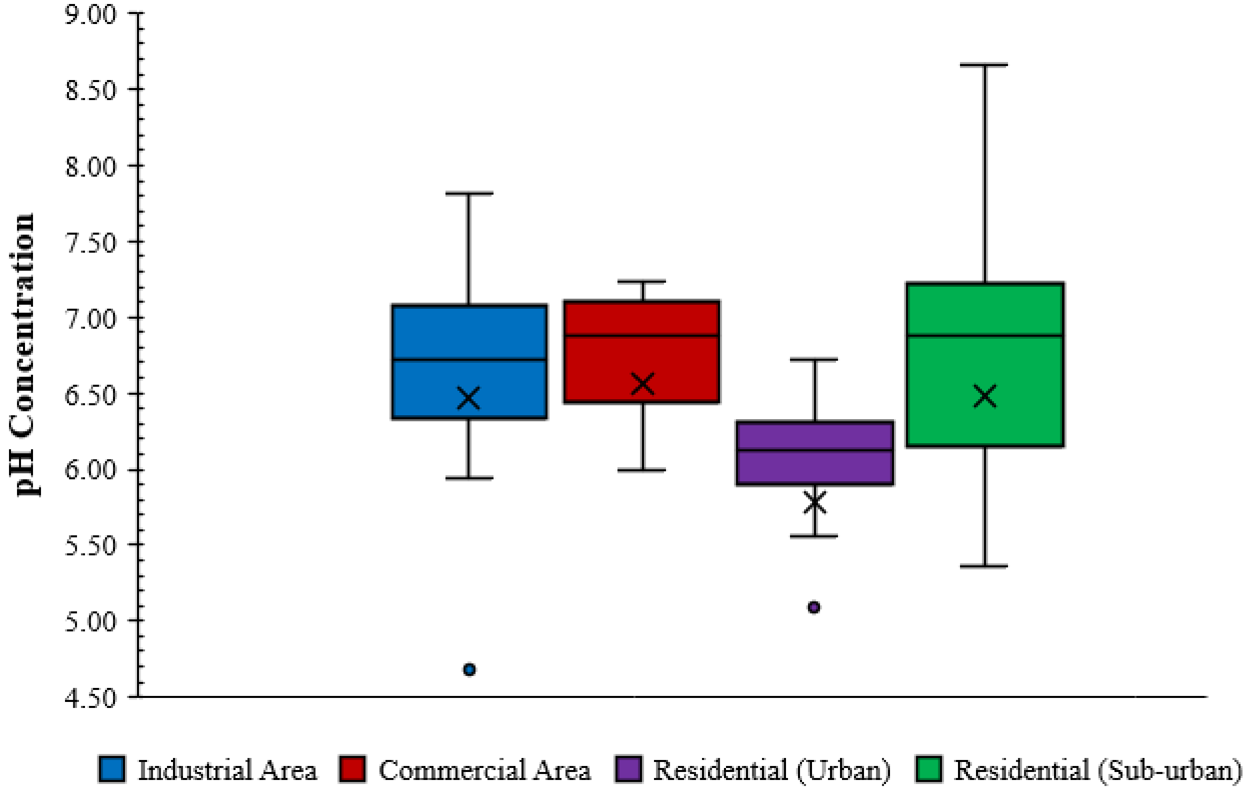

Figure 5

Box plot diagram of pH in rainwater at different locations

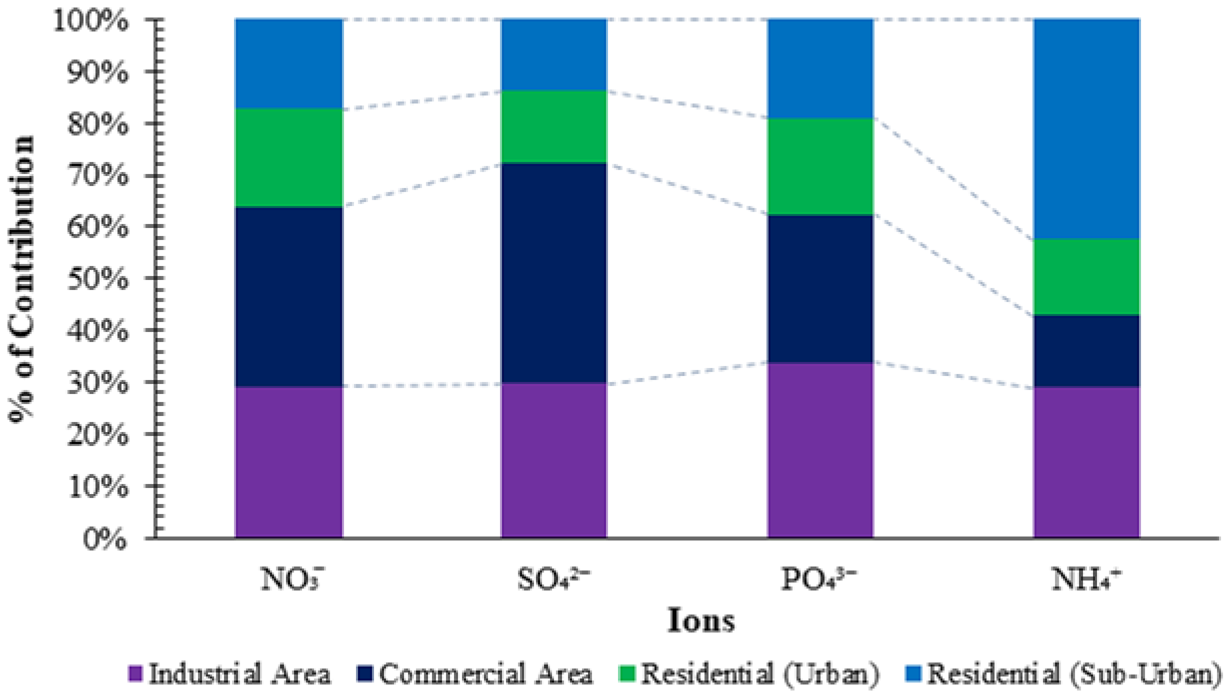

Figure 6

Frequency distribution of major ions in rainwater

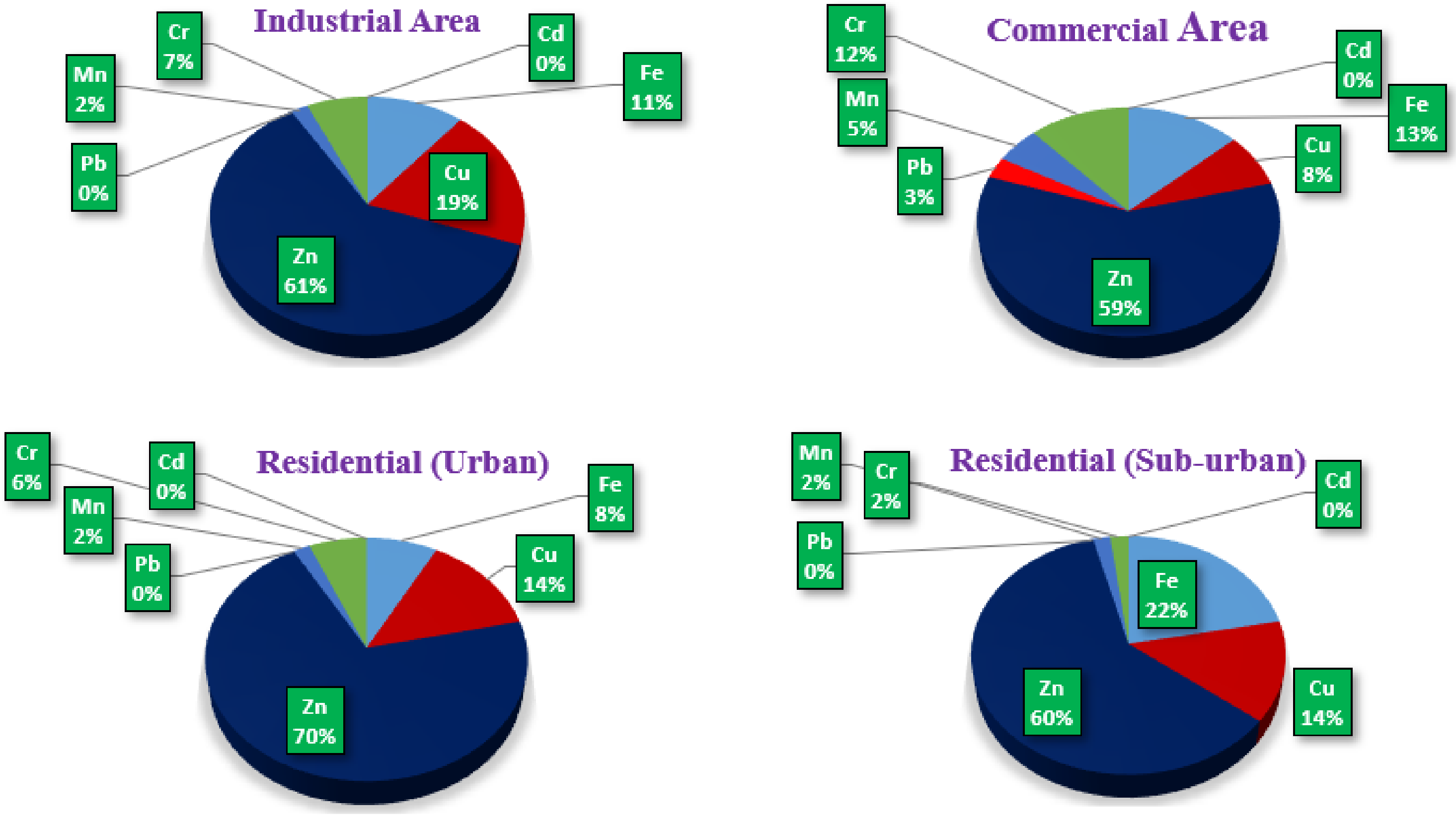

Figure 7

The contribution of metals in rainwater at different land use locations

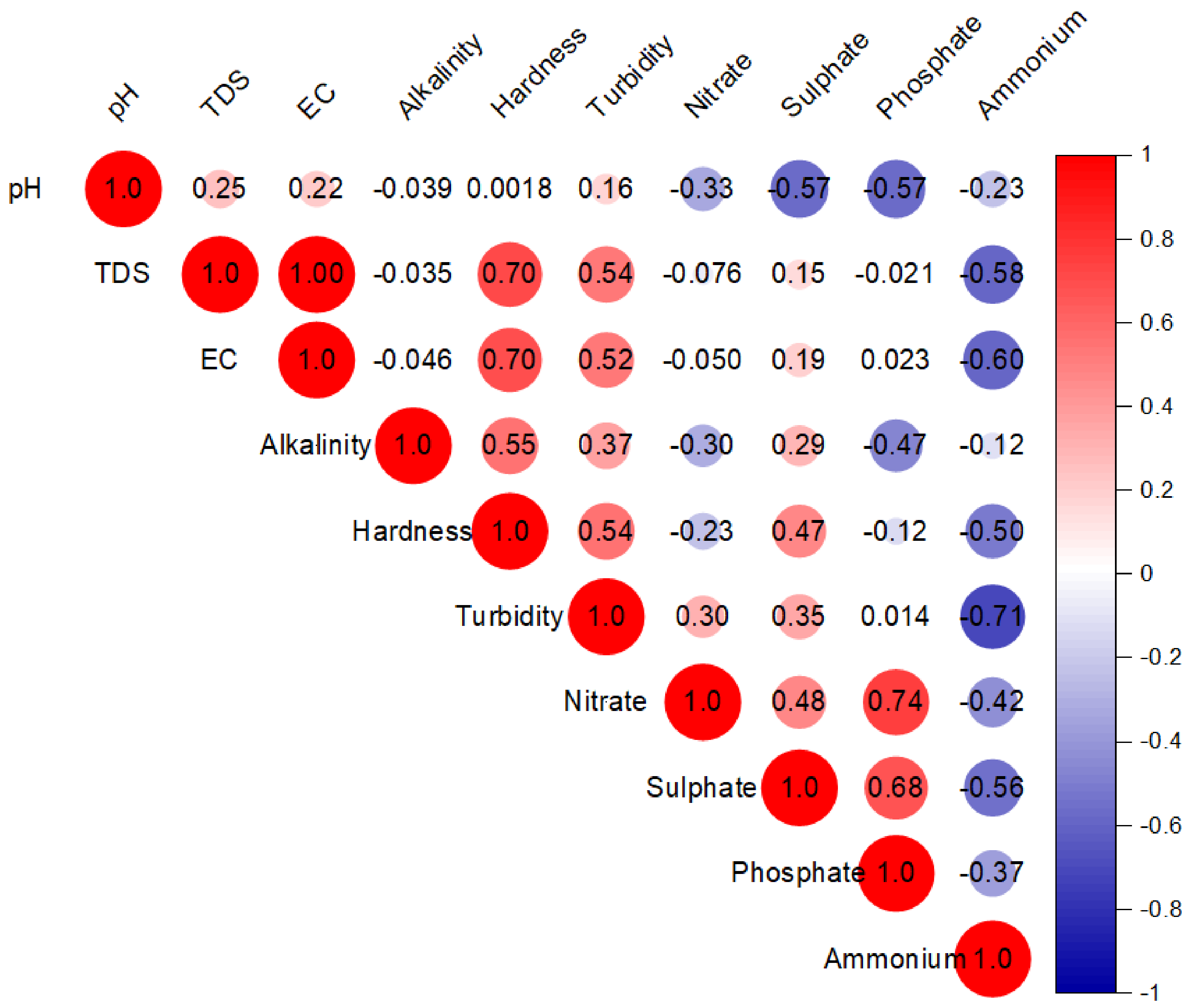

Figure 8

Correlation matrix among selected rainwater quality parameters

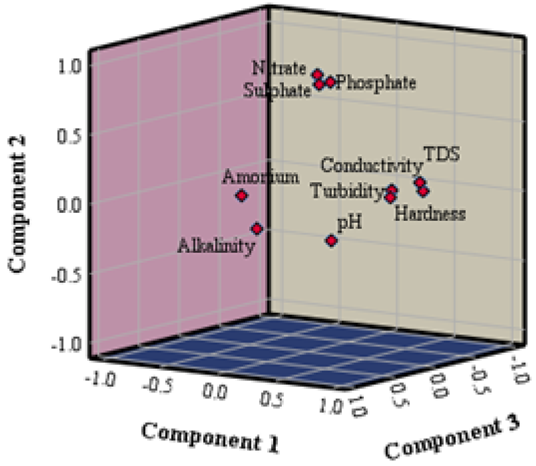

Figure 9

Component plot of different factors