



# Heavy Metal and Major Ionic Contamination Level in Effluents, Surface and Groundwater of an Urban Industrialised City: A Case Study of Rangpur City, Bangladesh

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## Authors' contributions

This work was carried out in collaboration with all authors. Authors HMZ and MSA designed the study, managed the literature and supervised the work. Author RY performed the experiment, sample collection and data recording. Author SM helped in manuscript preparation. All authors read and approved the final manuscript.

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## ABSTRACT

Industrialisation and unplanned urbanisation in different city areas of Bangladesh have greatly distorted the natural water resources. The present study was undertaken to evaluate ionic contamination level including heavy metals in effluents, surface and groundwater of Rangpur city, Bangladesh. Total 29 samples (24 effluents and surface water and 5 groundwater) were collected from the city area and analysed for various physicochemical parameters at the Department of Agricultural Chemistry, Bangladesh Agricultural University, Mymensingh during January to September 2017. The concentrations of heavy metals (Fe, Mn, Cu, Pb, Cr, and Zn) in water samples were measured by an atomic absorption spectrophotometer (AAS). Major cation chemistry showed their dominance in the order of  $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} = \text{K}^+$  and  $\text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+$  for effluents and surface and groundwater, respectively. Most of the water samples were rated as unsuitable for

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irrigation due to a higher concentration of  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$  and  $\text{Cl}^-$ , although  $\text{SO}_4^{2-}$  was the dominating anion. In the context of heavy metals, the amounts of Mn, Cu and Pb in effluents and surface water were comparatively higher than the standard limits. Enhanced concentration of Mn made 50% effluents and surface water and 80% of groundwater samples unsuitable for irrigation and drinking, respectively. Similarly, 21 effluents and surface water and all groundwater samples of the study area exceeded the freshwater toxicity reference value for Cu as prescribed by the US EPA. The study results concluded that these metals might release into the water as a consequence of natural weathering of soil, discharges from domestic and industrial effluents, and sewage treatment plants. Finally, the study suggested that one should not discharge and/ or dispose of any waste containing chemical substances without proper treatment which may ultimately contaminate both surface and groundwater.

*Keywords: Surface and groundwater contamination; urbanisation and industrialization; heavy metal; Rangpur; Bangladesh.*

## 1. INTRODUCTION

Urbanisation and industrialisation are closely related with each other. Industrialisation is the initiator of urbanisation and urbanisation is the inevitable result of industrialisation. Industrialisation and unplanned urbanisation have greatly transformed the natural environment. In recent times, the environment has become hostile, posing threat to health and welfare due to the release of pollutants from industries and urban sewage [1]. The effluents discharged from industries and urban sewage may find their way into surface water bodies via canals and surface run-off, and groundwater aquifers through leaching. Due to increasing contamination and scarcity of surface water resources, a major stress has been shifted to groundwater resources. Despite its importance, water is the most poorly managed resource in the developing world [2]. In many countries, including Bangladesh the wastewater is released into rivers, lakes and other water bodies. This further leads to many environmental issues including eutrophication, depletion of dissolved oxygen, fish mortality and others [3]. Therefore, the unchecked and uncontrolled disposal of wastewater into water bodies is degrading the water resources and ultimately affects the public health.

The existing tendency of industrialisation and urbanisation in developing countries has an enormous impact on natural and man-made environments. As a result, pollution sources increase with the development of cities and cause contamination of water and disrupts both the surface and groundwater qualities through indiscriminate disposal of domestic, agricultural, municipal and industrial waste and effluents, solid waste and other toxic substances which are the major environmental issues posing threats to

the existence of human being [4-5]. With the advent of industrialisation, not only surface water but groundwater has also been degraded up to a level at which it has become unsuitable for human consumption. Due to recent industrialisation and ever-increasing urbanisation, the quality of groundwater has become a matter of major concern because of metallic contamination [6-10].

An excess amount of ionic constituents including heavy metals lead to contamination of both surface and groundwater, and such contamination is a serious problem all over the world including Bangladesh. The common identifiable contaminants in both surface and groundwater of Bangladesh are Pb, Cd, Cr, Cu, As, Zn, Mn, Fe,  $\text{K}^+$ ,  $\text{HCO}_3^-$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ , which have significant adverse effects on water qualities [11-19]. Rangpur is a newly emerging divisional city which is located at the northern part of Bangladesh. The city is one of the oldest municipalities in Bangladesh. There are several types of industrial units in Rangpur including food processing, cast iron and aluminium, plastic, cold storage, tobacco, distilleries and chemical company and others [20]. Since last decade the city is also experiencing the pressure of industrialisation and urbanisation like other cities of Bangladesh. Considering the fact stated above, this study was undertaken to assess the degree of contamination of heavy metal and major ionic constituents in effluents, surface and groundwater of Rangpur city of Bangladesh.

## 2. METHODOLOGY

### 2.1 Description of the Study Area

The study area is located at the northern part of Bangladesh, which lies between 25°40' to 25°50' N latitude and 89°06' to 89°19' E longitude (Fig. 1). The climate of Rangpur is generally marked

with monsoons, high temperature, considerable humidity and rainfall. The average annual temperature in Rangpur is 24.9°C and rainfall is 2192 mm [20]. The soil composition is mainly alluvial soil of the Tista river basin. Geologically, the study area lies on the north-northwestern part of the Bengal basin. The surficial of the area is classified as recent floodplain deposits [21]. The recent floodplain deposit consists of clay, silt, fine and medium grain sand and are of relatively loose and more friable in nature [22].

## 2.2 Water Sampling and Processing

Total 29 samples, effluents and surface (24) and groundwater (5) were randomly collected from Rangpur city, Bangladesh during January 2017 following the sampling techniques as outlined by APHA [23]. The collected water samples were stored in 500 mL preconditioned clean, high-density plastic bottles and use for the different analysis. During collection of water samples, bottles were well rinsed using the same water. All effluents and surface water samples were filtered through Whatman No.1 filter paper to remove

unwanted solid and suspended material, but groundwater samples were clean, colourless and odourless. After filtration, 3-4 drops of nitric acid were added to the samples to avoid any fungal and other pathogenic growth. In the laboratory, the samples were kept in a clean, cool and dry place. The chemical analyses of water samples were done as quickly as possible on arrival at the laboratory of the Department of Agricultural Chemistry, Bangladesh Agricultural University, Mymensingh-2202, Bangladesh. The locations and detailed information about the sampling sites have been presented in Fig. 1 and Table 1, respectively.

## 2.3 Analytical Methods

Collected surface and groundwater samples were analysed for various physicochemical parameters. The pH, electrical conductivity (EC) and total dissolved solids (TDS) were measured within a few hours after collection by using a pH meter (Jenway 3505, UK) and a conductivity meter (SensION™+ EC5, HACH, USA), respectively. Contents of calcium and magnesium in water samples

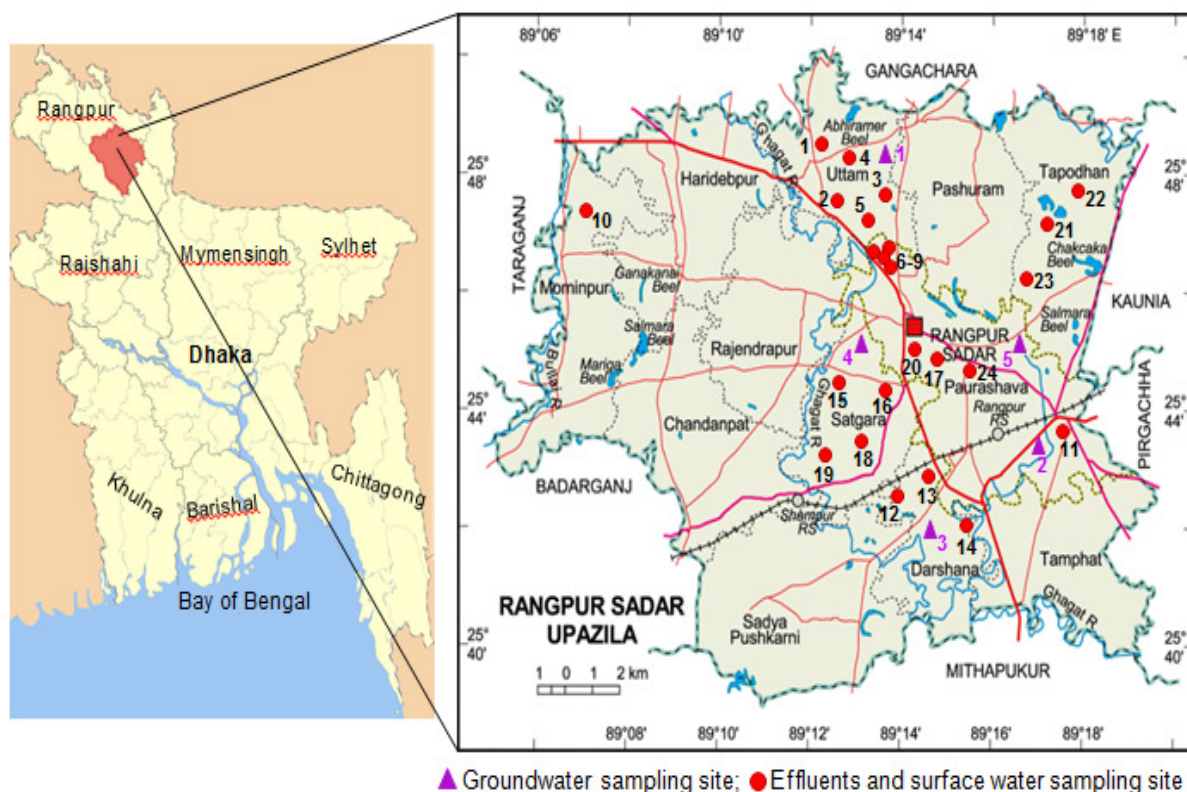


Fig. 1. Map showing effluents and surface water and groundwater sampling sites of Rangpur city, Bangladesh

**Table 1. List of effluents and surface water and groundwater sampling sites along with possible contamination sources collected from Rangpur city, Bangladesh**

Type of water	Sample no.	Sampling area	Water sources	Possible sources of contamination
Effluents and surface water	1	Uttom hasna bazar industry area	Drain	Industrial wastewater mainly from Partex Foundary
	2	Uttom hasna bazar industry area	Drain	Industrial wastewater mainly from Diamond Partex Board
	3	Hajirhat area	Drain	Industrial wastewater mainly from Akiz Company
	4	Uttom Hajirhat area	Drain	Industrial wastewater mainly from Vai-Vai Paper Mill
	5	Hasna bazar area	Drain	Industrial wastewater mainly from Abul Khair Leaf Tobacco Industry
	6	BSCIC area	Drain	Industrial wastewater mainly from RFL Company
	7	D.R. Metal Industry, BSCIC area	Drain	Industrial wastewater discharge from BSCIC area
	8	Silver Industry	Drain	Industrial wastewater discharge from BSCIC area
	9	BSCIC area	Drain	Industrial wastewater discharge from BSCIC area
	10	Sonic Food Industry, Fotkapur	Drain	Plastic material and industrial wastewater
	11	Fire service, D.L. Ray Road	Pond	Municipal and household waste
	12	Crematory, Dokhigong	Pond	Municipal sewage, chemicals and household waste
	13	Rail Station, Khamarpara	Drain	Municipal sewage, wastewater and plastic
	14	Darshana area	Pond	Municipal sewage and household waste water
	15	Terminal area	Pond	Domestic effluents and municipal sewage
	16	Bangladesh Open University, Terminal road	Drain	Municipal sewage, household waste and plastic
	17	Samasundori, masterpara	Canal	Fertilizer, pesticide and municipal wastewater
	18	Khalifapara	Pond	Municipal sewage and household waste
	19	Samasundori, checkpoint	Canal	Household materials and municipal sewage
	20	Rangpur Medical	Drain	Medical waste, sewage waste
	21	Amasu, bottola	Pond	Household, fertilizer and municipal waste
	22	Tails company, fulamtola	Drain	Industrial and agricultural waste
	23	Topodhon area	Pond	Household waste materials
	24	Honumantola area	Drain	Market waste, dust and sewage waste
Ground-water	1	Uttom hajirhat area	Hand tubewell	-
	2	Kamal kachna area	Hand tubewell	-
	3	Lalbag area	Hand tubewell	-
	4	Tarminal area	Hand tubewell	-
	5	Dhap jail road area	Hand tubewell	-

were determined titrimetrically using standard Na<sub>2</sub>-EDTA. Sodium and potassium concentrations in water were measured flame photometrically using a flame photometer (Jenway PFP7, UK). Chloride concentration in both surface and groundwater samples was determined by silver nitrate titration. Carbonate and bicarbonate concentrations were measured by acid-base titration. Contents of Sulphate, borate and phosphate in water samples were determined colourimetrically using a spectrophotometer (T60 UV-Visible, PG Instrument, UK). Determination of different heavy metals (Fe, Mn, Cu, Pb, Cr and Zn) in water samples were done by using an atomic absorption spectrophotometer (AAS) (SHIMADZU, AA-7000; Japan). Mono element hollow cathode lamp was employed for the determination of each heavy metal of interest.

## 2.4 Evaluation of Irrigation Quality

To evaluate the suitability of water samples for irrigation purpose, the following water quality parameters were considered. The ionic concentrations were interpreted and calculated with irrigation indices using the following formulas of different parameters as follow:

- i) Sodium adsorption ratio (SAR) =  $\frac{Na^+}{\sqrt{(Ca^{2+} + Mg^{2+})/2}}$
- ii) Soluble sodium percentage (SSP) =  $\frac{[Na^+ + K^+]}{[Ca^{2+} + Mg^{2+} + Na^+ + K^+]} \times 100$
- iii) Residual sodium carbonate (RSC) =  $(CO_3^{2-} + HCO_3^-) - (Ca^{2+} + Mg^{2+})$
- iv) Hardness (H<sub>T</sub>) =  $2.5 \times Ca^{2+} + 4.1 \times Mg^{2+}$

Where, all ionic concentrations were expressed as meqL<sup>-1</sup> but in case of hardness, cationic concentrations were expressed as mgL<sup>-1</sup>.

## 3. RESULTS AND DISCUSSION

### 3.1 Quality on the Basis of pH, EC and TDS

The pH values of effluents and surface water samples were within the range of 1.89 to 9.40 with the mean value of 6.87 (Table 2). Such a high fluctuation in pH of effluents and surface water samples might be due to the presence of major cations such as Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup> and Na<sup>+</sup> in water [24]. On the other hand, pH values of groundwater samples were varied from 6.25-7.93 with an average value of 6.92 (Table 2). The pH of most raw waters lies in the range of 6.5-9.5

[25]. Biological activities and anthropogenic sources such as nutrient cycling and industrial effluent discharge, respectively, can give rise to pH fluctuations. Acid-forming substances released into the atmosphere such as oxides of sulphur and nitrogen may ultimately alter the acid-base equilibria in natural waters and result in a reduced acid-neutralising capacity, and hence a lowering of the pH. The pH strongly influences corrosion and scaling processes which may cause considerable damage to industrial equipment and structures [25]. According to proposed Bangladesh Standards and Bangladesh Environment Conservation Rule (ECR) the acceptable range of pH for irrigation water is 6.50 to 8.50 [26-27]. The pH values on either side of 6.5-8.0, may cause mild to severe damage to industrial equipments due to corrosion or scaling [25]. Considering this range as the standard for industrial usage, 8 effluents and surface water, and 1 groundwater samples were found as problematic (Table 2).

Electrical conductivity values of effluents and surface water and groundwater samples were varied from 157 to 11240 and 264 to 845 μScm<sup>-1</sup> with the mean value of 1191 and 507 μScm<sup>-1</sup>, respectively (Table 2). According to Richards [28], among the effluents and surface water samples 2 were rated in the category C1 (EC <250 μScm<sup>-1</sup>), 12 samples were in the class C2 (EC= 250-750 μScm<sup>-1</sup>), 8 samples were in the class C3 (EC= 750-2250 μScm<sup>-1</sup>) and the rest 2 samples were in the class C4 (EC >2250 μScm<sup>-1</sup>) indicating low to very high salinity classes. Medium salinity class water might be applied for irrigation with a moderate level of permeability and leaching. But higher EC value reflected the higher amount of salt concentration which affected irrigation water quality related to salinity hazard [29]. The EC more than the range of 300-700 μScm<sup>-1</sup>, may cause moderate damage to industrial equipment's and structures through corrosion, scaling or fouling [25]. Considering this range as standard, 10 effluents and surface water and 1 groundwater samples were rated as unsuitable for industrial usage (Table 2).

The natural processes causing TDS are enhanced through anthropogenic activities such as domestic and industrial effluent discharges, surface runoff from urban, industrial and cultivated areas, irrigation and other return flows [25]. The maximum and minimum values of measured TDS of effluents and surface water samples in the investigated area were 6060 and 99 mgL<sup>-1</sup>, respectively, and the mean value of

TDS was  $654.13 \text{ mgL}^{-1}$  (Table 2). A sufficient quantity of bicarbonate, sulphate and chloride of Ca, Mg and Na caused high TDS values [30]. High levels of TDS can indirectly interfere with the proper functioning of several industrial processes. The higher the TDS level, the greater the potential for precipitation of salts, which may alter working conditions and result in the inefficient and improper operation of industrial processes [25]. The TDS values of groundwater samples were within the range of 127 to  $465 \text{ mgL}^{-1}$  with the mean value of  $283.40 \text{ mgL}^{-1}$  (Table 2). According to South African industrial water use guideline [25], TDS  $>450 \text{ mgL}^{-1}$  may cause significant to major damage likely as a result of corrosion, scaling or fouling to industrial equipments and structures for category 1 industrial processes. The values are  $>800 \text{ mgL}^{-1}$  for category 2 industrial processes and  $>1600 \text{ mgL}^{-1}$  for categories 3 and 4 industrial processes [25]. Considering these values as standard, 2 effluents samples (IDs # 6 and 7) were found unsuitable for all categories of industrial processes (Table 2).

### 3.2 Quality on the Basis of Anionic Constituents

Ions which commonly contribute to the alkalinity of water are  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$  and  $\text{OH}^-$ . The minimum and maximum concentration of  $\text{CO}_3^{2-}$  ion in collected effluents and surface water samples was trace and  $4.80 \text{ meqL}^{-1}$ , respectively with the mean value of  $3.07 \text{ meqL}^{-1}$ . In case of groundwater samples the range was 3.20 to  $5.60 \text{ meqL}^{-1}$  with an average value of  $4.16 \text{ meqL}^{-1}$  (Table 2). It is apparent from Fig. 2b and 2d that  $\text{CO}_3^{2-}$  ions are contributed 15 and 18% to the total anionic mass balance of effluents and surface water and groundwater, respectively. According to Ayers and Westcot [31], the recommended maximum concentration of  $\text{CO}_3^{2-}$  for irrigation water is  $0.10 \text{ meqL}^{-1}$ . As per this limit,  $\text{CO}_3^{2-}$  status in 19 effluents and surface water and all groundwater samples were exceeded the standard, thus hazardous for irrigating crops and soils. In case of industrial equipment's (vacuum pumps, heating baths, steam-heated drying drums and tanks), scaling is mainly due to the deposition of insoluble calcium carbonate, which is a major problem wherever heating of water or heat exchange reactions takes place [25].

Effluents and surface water and groundwater samples collected from Rangpur city area contained  $\text{HCO}_3^-$  ranging from a trace to  $9.20$

and  $1.60$  to  $2.80 \text{ meqL}^{-1}$  with the mean value of  $2.37$  and  $2.24 \text{ meqL}^{-1}$ , respectively (Table 2). It is evident from Fig. 2b and 2d that  $\text{HCO}_3^-$  ions are contributed 12 and 10% to the total anionic mass balance of effluents and surface water and groundwater, respectively. Waters, generally contained  $\text{HCO}_3^- <1.50 \text{ meqL}^{-1}$  are rated as suitable for irrigation [31], and considering this value as standard,  $\text{HCO}_3^-$  status in 17 effluents and surface water and all groundwater samples were exceeded the limit, thus hazardous for irrigating crops and soils. On the other hand, according to WHO [32], the acceptable limit of  $\text{HCO}_3^-$  in drinking water is  $<500 \text{ mgL}^{-1}$  ( $8.2 \text{ meqL}^{-1}$ ). Considering this value as standard, all groundwater samples were rated as suitable for drinking. Bicarbonates are derived mainly from the soil zone  $\text{CO}_2$  and dissolution of carbonates and reaction of silicates with carbonic acid [33]. High bicarbonate and carbonate levels in water can cause calcium to precipitate from the soil. This reduces the soil's exchangeable calcium content and increases soil sodicity. Magnesium can also be lost in this way. In extreme cases, the loss of soil calcium and magnesium will affect plant growth [34].

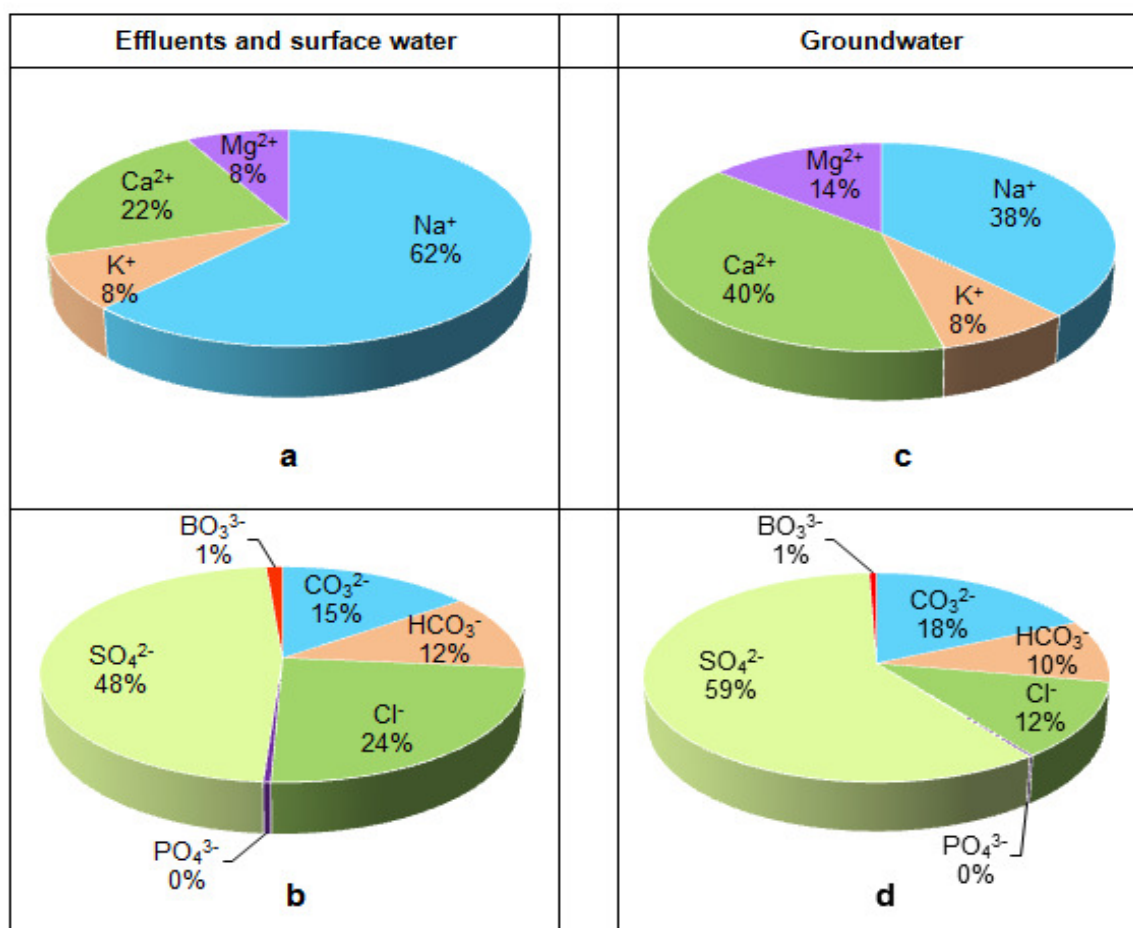
Chloride is a common constituent of water, which is highly soluble and once in solution tends to accumulate. Typically, the concentrations of  $\text{Cl}^-$  in freshwater range from a few to several hundred  $\text{mgL}^{-1}$  [25]. Effluents and surface water sample collected from the study area contained  $\text{Cl}^-$  ion ranging from 0.99 to  $13.25 \text{ meqL}^{-1}$  with the mean value of  $4.98 \text{ meqL}^{-1}$  (Table 2) and it contributed 24% to the total anionic mass balance (Fig. 2b). On the other hand, in case of groundwater  $\text{Cl}^-$  content varied from 1.27 to  $5.22 \text{ meqL}^{-1}$  with an average value of  $273 \text{ meqL}^{-1}$  (Table 2). The study results inferred that 11 effluents and surface water and 1 groundwater samples of the study area could be rated as unsuitable for irrigation in context of  $\text{Cl}^-$  content as because these samples contained a higher amount of  $\text{Cl}^-$  than the recommended limit ( $4.0 \text{ meqL}^{-1}$ ) [31]. High concentration of  $\text{Cl}^-$  in water is considered to be the indicator of pollution by high organic wastes of animal or industrial origin [35]. Most of the  $\text{Cl}^-$  in water was present as NaCl but  $\text{Cl}^-$  content may exceed sodium due to the base exchange phenomena [30]. Chlorides are particularly aggressive to stainless steel, causing stress and cracking corrosion. Its content  $>200 \text{ mgL}^{-1}$  ( $5.63 \text{ meqL}^{-1}$ ) may cause moderate to major damage as a result of corrosion to industrial equipment and structures up to category 3 industrial processes [25]. Effluents



and surface water and groundwater samples collected from Rangpur city contained  $\text{PO}_4^{3-}$  ranging from 0.03-0.18 and 0.01-0.12  $\text{mgL}^{-1}$  and the mean values were 0.09 and 0.05  $\text{mgL}^{-1}$ , respectively (Table 2). The maximum acceptable limit of  $\text{PO}_4^{3-}$  in water used for irrigation is 2.00  $\text{mgL}^{-1}$  [31]. On the basis of this limit, all water samples under investigation area were found suitable for irrigating crops and soils.

The occurrence of  $\text{SO}_4^{2-}$  in water mainly due to results from the dissolution of mineral sulphates in soil and rock, particularly calcium sulphate and other partially soluble sulphate minerals. Typically, the concentration of  $\text{SO}_4^{2-}$  in surface water is 5  $\text{mgL}^{-1}$ , although it exceeds of several hundred  $\text{mgL}^{-1}$  where the dissolution of sulphate minerals or discharge of sulphate-rich effluents from acid mine drainage takes place [25]. Most of the water samples contained the highest amount

of  $\text{SO}_4^{2-}$  compared to other anions, and the content ranged between 0.31-36.38 and 2.13-23.38  $\text{mgL}^{-1}$  with the mean value of 9.80 and 13.66  $\text{mgL}^{-1}$  for effluents and surface water and groundwater, respectively (Table 2). It is apparent from Fig. 2b and 2d that  $\text{SO}_4^{2-}$  ions are contributed 48 and 59% to the total anionic mass balance of effluents and surface water and groundwater, respectively. According to Ayers and Westcot [31], the acceptable limit of  $\text{SO}_4^{2-}$  in irrigation water is <20  $\text{mgL}^{-1}$ . As per this limit, 21 effluents and surface water and 4 groundwater samples were found suitable for irrigating soils and crops. Precipitation of sulphates can cause damage to equipment through the formation of calcium sulphate scale. At high concentrations, precipitation of  $\text{SO}_4^{2-}$  may interfere with the efficiency of dyeing operations in leather tanning and finishing industries [25].



**Fig. 2. Contribution of individual major ions towards the total cationic (a for effluents and surface water and c for groundwater) and anionic (b for effluents and surface water and d for groundwater) mass balance in waters collected from Rangpur city, Bangladesh.**

**Table 2. Physicochemical properties (pH, EC, TDS and major anions) of effluents and surface water and groundwater samples collected from Rangpur city, Bangladesh**

Type of water	Sample ID	pH	EC ( $\mu\text{Scm}^{-1}$ )	TDS ( $\text{mgL}^{-1}$ )	$\text{CO}_3^{2-}$ ( $\text{meL}^{-1}$ )	$\text{HCO}_3^-$ ( $\text{meL}^{-1}$ )	$\text{Cl}^-$ ( $\text{meL}^{-1}$ )	$\text{PO}_4^{3-}$ ( $\text{mgL}^{-1}$ )	$\text{SO}_4^{2-}$ ( $\text{mgL}^{-1}$ )	$\text{BO}_3^{3-}$ ( $\text{mgL}^{-1}$ )
Effluents and surface water	1	8.65	429	238	Trace	2.80	3.10	0.17	7.25	0.22
	2	7.05	660	358	4.80	2.40	3.95	0.13	10.31	0.71
	3	7.16	262	119	Trace	5.60	2.26	0.12	19.19	0.19
	4	9.40	862	470	3.20	3.60	5.22	0.08	4.98	0.19
	5	7.69	318	143	4.00	1.60	2.40	0.10	6.19	0.19
	6	9.10	3810	2110	Trace	9.20	10.15	0.03	4.50	0.50
	7	1.89	11240	6060	Trace	trace	13.25	0.05	7.40	0.33
	8	4.60	1821	1000	Trace	2.00	2.82	0.10	7.23	0.49
	9	5.40	1355	762	1.60	0.80	2.82	0.18	7.18	0.46
	10	6.15	255	162	3.20	1.60	0.99	0.06	6.19	0.25
	11	6.32	458	266	2.40	2.00	2.82	0.07	15.00	0.15
	12	6.60	164	109	4.00	2.40	1.27	0.08	0.31	0.19
	13	6.60	953	524	2.40	4.00	4.09	0.11	36.38	0.19
	14	7.00	283	162	4.00	1.20	3.53	0.14	0.50	0.19
	15	7.05	527	316	3.20	2.00	8.04	0.16	0.56	0.28
	16	7.02	1105	639	1.60	1.20	9.45	0.11	5.38	0.41
	17	7.15	794	369	4.00	2.00	8.88	0.08	15.69	0.19
	18	7.31	297	183	3.20	1.20	5.64	0.09	6.15	0.19
	19	7.05	848	491	1.60	2.40	8.04	0.05	5.65	0.13
	20	7.01	431	253	3.20	1.20	2.82	0.04	31.63	0.12
	21	7.34	157	99	3.20	1.20	5.64	0.09	2.50	0.09
	22	7.18	378	220	3.20	2.40	3.38	0.11	21.63	0.18
	23	7.23	405	225	2.40	2.00	5.78	0.05	0.69	0.16
	24	6.90	774	421	3.20	2.00	3.10	0.04	12.69	0.13
	Mean	6.87	1191	654.13	3.07	2.37	4.98	0.09	9.80	0.26
	Max.	9.40	11240	6060	4.80	9.20	13.25	0.18	36.38	0.71
	Min.	1.89	157	99	trace	trace	0.99	0.03	0.31	0.09
Ground-water	1	7.93	264	127	4.00	2.80	1.27	0.04	2.13	0.19
	2	6.25	495	281	3.20	2.00	1.83	0.01	17.31	0.15
	3	6.63	845	465	4.80	2.40	3.38	0.12	17.44	0.15
	4	7.07	287	176	3.20	1.60	1.97	0.05	8.06	0.06
	5	6.71	644	368	5.60	2.40	5.22	0.02	23.38	0.12
	Mean	6.92	507	283.40	4.16	2.24	2.73	0.05	13.66	0.13
	Max.	7.93	845	465	5.60	2.80	5.22	0.12	23.38	0.19
Min.	6.25	264	127	3.20	1.60	1.27	0.01	2.13	0.06	

The natural  $\text{BO}_3^{3-}$  content of groundwater and surface water is usually small. The  $\text{BO}_3^{3-}$  content of surface water can be significantly increased as a result of wastewater discharges because borate compounds are ingredients of domestic washing agents [36]. Furthermore, the amount of boron in fresh water depends on such factors as the geochemical nature of the drainage area, proximity to marine coastal regions, and inputs from industrial and municipal effluents [37]. The concentration of borate in effluents and surface water samples varied from 0.09 to 0.71  $\text{mgL}^{-1}$  with the mean value of 0.26  $\text{mgL}^{-1}$ . In case of groundwater,  $\text{BO}_3^{3-}$  content varied from 0.06 to 0.19  $\text{mgL}^{-1}$  with an average value of 0.13  $\text{mgL}^{-1}$

(Table 2). The acceptable limit of  $\text{BO}_3^{3-}$  in irrigation water is  $<0.75 \text{ mgL}^{-1}$  and as per this limit, all water samples were found suitable for irrigating soils and crops. On the other hand, concentrations of boron in drinking-water have wide ranges, depending on the source of the drinking water, but for most of the world, the range is judged to be between 0.1 and 0.3  $\text{mgL}^{-1}$  [38].

### 3.3 Quality on the Basis of Major Cationic Constituents

Sodium salts are found in virtually all foods and drinking water. Sodium levels in the latter are



typically less than 20 mgL<sup>-1</sup> but can markedly exceed this in some countries [39]. The content of Na<sup>+</sup> in effluents and surface water and groundwater samples collected from Rangpur city was within the range of 0.14-22.14 and 0.12-8.86 meqL<sup>-1</sup> with the mean value of 7.05 and 3.30 meqL<sup>-1</sup>, respectively (Table 3), and Na<sup>+</sup> contributed 68 and 32% to the total cationic mass balance, respectively (Fig. 2a and 2c). A huge amount of Na<sup>+</sup> in effluents and surface water might be due to the discharge of domestic and sewage effluents from urban areas, use water treatment chemicals, mineral deposits and salt used in different industrial units. Water generally contained <40 meqL<sup>-1</sup> Na<sup>+</sup> is suitable for irrigation [31] and all effluents and surface water had Na<sup>+</sup> less than this limit. On the other hand, according to WHO [32], the maximum guideline limit of Na<sup>+</sup> for drinking water is 200 mgL<sup>-1</sup> (8.7 meqL<sup>-1</sup>). The recorded Na<sup>+</sup> content in all groundwater samples under investigation area was less than this the limit. Potassium content in effluents and surface water and groundwater samples varied from 0.13-2.32 and 0.07-2.06 meqL<sup>-1</sup>, respectively (Table 3). The mean values of K<sup>+</sup> were 0.91 and 0.73 meqL<sup>-1</sup> for effluents and surface water and groundwater, respectively, which contributed 8% to the total cationic mass balance in both cases (Fig. 2a and 2c). The recommended concentration of K<sup>+</sup> in irrigation water is 2.0 mgL<sup>-1</sup> (0.05 meqL<sup>-1</sup>) [31]. Considering this value as standard, all effluents and surface water and groundwater samples collected from Rangpur city were rated as problematic for long-term irrigation. On the other hand, the highest acceptable limit of K<sup>+</sup> for drinking water is 12 mgL<sup>-1</sup> (0.3 meqL<sup>-1</sup>) [32]. Considering this value as standard, 3 groundwater samples were found within the limit and could safely be used for drinking.

The concentrations of Ca<sup>2+</sup> in effluents and surface water and groundwater samples were within the range of 1.20- 4.80 and 1.80-5.20 meqL<sup>-1</sup> with the average values of 2.50 and 3.48 meqL<sup>-1</sup>, respectively (Table 3). Calcium content in effluents and surface and groundwater samples contributed 22 and 40%, respectively to the total cationic mass balance (Fig. 2a and 2c). The study results inferred that Ca<sup>2+</sup> content in groundwater was higher, which might be due to washing out of Ca<sup>2+</sup> from bedrock. The contribution of Ca<sup>2+</sup> content in groundwater was largely dependent on the solubility of CaCO<sub>3</sub>, CaSO<sub>4</sub> and rarely on CaCl<sub>2</sub> [30]. Calcium

concentrations up to and exceeding 100 mgL<sup>-1</sup> (5.0 meqL<sup>-1</sup>) are common in natural sources of water, particularly groundwater [40]. The mineral contents of water from most Asian drinking-water supplies are generally in the range of 2.0-80.0 mg Ca<sup>2+</sup> L<sup>-1</sup> [41]. The maximum acceptable limit of Ca<sup>2+</sup> for drinking water is 10.0 meqL<sup>-1</sup> (200 mgL<sup>-1</sup>) [32]. Considering this limit as standard, all groundwater samples could safely be used for drinking.

Effluents and surface water and groundwater samples collected from Rangpur city contained Mg<sup>2+</sup> within the range of 0.20-2.20 meqL<sup>-1</sup> with the mean values of 0.89 and 1.20 meqL<sup>-1</sup>, respectively (Table 3). Magnesium content in effluents and surface and groundwater samples contributed 8 and 14%, respectively to the total cationic mass balance (Fig. 2a and 2c). Present study results revealed a higher amount of Mg<sup>2+</sup> in groundwater, which might be due to washing out of Mg<sup>2+</sup> from bedrock. Magnesium is present in natural groundwater usually at lower concentrations and the content usually varied from negligible to about 50 mgL<sup>-1</sup> and rarely above 100 mgL<sup>-1</sup> [40]. Similarly, according to WHO [41], the Mg<sup>2+</sup> contents of water from most Asian drinking-water supplies are generally below 20 mgL<sup>-1</sup>. However, the maximum acceptable limit of Mg<sup>2+</sup> for drinking water is 150 mgL<sup>-1</sup> (12.3 meqL<sup>-1</sup>) [32]. Considering this limit as standard, all groundwater samples were found suitable for drinking usage.

### 3.4 Quality on the Basis of Heavy Metal Content

Ionic constituents including heavy metals in water don't depend on the type of water sources, but it depends on the characteristics of the aquifers. Zinc content in effluents and surface water and groundwater samples collected from Rangpur city ranged from 0.05-0.47 and 0.05-0.98 mgL<sup>-1</sup> with the average values of 0.14 and 0.27 mgL<sup>-1</sup>, respectively (Table 3). Water is generally a minor contributor to the total daily oral intake of Zn but the areas in which Zn naturally occur in groundwater is mobilized, the Zn contribution from water may be significant [42]. Waters generally having less than 2.0 mgL<sup>-1</sup> Zn is safe for irrigating crops and soils [31]. High natural levels of Zn in water are usually associated with higher concentrations of other

**Table 3. The concentration of heavy metals and major cations in effluents and surface water and groundwater samples collected from Rangpur city, Bangladesh**

Type of water	Sample No.	Major cation (meqL <sup>-1</sup> )				Heavy metal (mgL <sup>-1</sup> )					
		Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Zn	Fe	Cu	Mn	Cr	Pb
Effluents and surface water	1	14.17	1.81	1.40	1.75	0.05	0.15	nd	0.05	nd	8.47
	2	10.63	1.29	2.00	2.20	0.06	0.02	nd	0.69	nd	8.41
	3	7.08	0.77	2.20	0.40	0.07	0.06	nd	0.06	nd	8.47
	4	12.40	1.03	1.20	0.80	0.09	0.28	0.01	0.14	nd	nd
	5	0.14	0.17	2.40	1.00	0.07	0.10	0.02	0.16	nd	nd
	6	22.14	2.06	3.00	1.40	0.07	0.13	0.02	0.43	nd	8.39
	7	0.16	0.14	1.80	0.80	0.47	2.09	0.10	2.20	nd	8.33
	8	0.37	0.18	3.00	0.40	0.17	0.06	0.02	1.21	nd	8.38
	9	0.28	0.21	2.60	0.20	0.43	0.92	0.04	1.12	nd	nd
	10	0.14	0.13	2.20	1.20	0.47	2.18	0.03	0.06	nd	nd
	11	0.16	0.23	2.40	0.80	0.08	0.05	0.04	0.09	nd	nd
	12	0.14	0.24	1.60	0.20	0.07	0.11	0.03	0.07	nd	nd
	13	15.94	1.55	4.60	0.60	0.07	0.22	0.03	0.66	nd	nd
	14	0.14	0.24	1.80	0.40	0.07	0.12	0.04	0.09	nd	nd
	15	7.97	2.32	3.00	1.00	0.07	0.39	0.03	0.13	nd	nd
	16	0.16	0.21	3.40	1.20	0.36	0.54	0.06	0.58	nd	nd
	17	18.15	1.94	2.40	2.20	0.18	5.99	0.06	0.42	nd	nd
	18	12.84	1.16	1.40	1.60	0.13	1.00	0.05	2.13	nd	nd
	19	18.60	1.55	4.80	0.20	0.09	2.23	0.05	0.96	nd	nd
	20	0.28	0.20	2.80	0.40	0.07	0.50	0.06	0.75	nd	nd
	21	0.53	0.21	2.20	0.40	0.08	0.19	0.05	0.13	nd	nd
	22	14.17	1.94	3.00	0.20	0.05	0.18	0.04	0.08	nd	nd
	23	12.40	2.06	2.00	1.00	0.07	0.92	0.04	0.08	nd	nd
	24	0.27	0.25	2.80	1.00	0.08	0.10	0.04	1.11	nd	nd
Mean		7.05	0.91	2.50	0.89	0.14	0.77	0.04	0.56	-	-
Max.		22.14	2.32	4.80	2.20	0.47	5.99	0.10	2.20	Trace	8.47
Min.		0.14	0.13	1.20	0.20	0.05	0.02	Trace	0.05	Trace	Trace
Ground-water	1	0.12	0.07	1.80	2.20	0.05	0.83	0.01	1.07	nd	nd
	2	0.14	0.12	4.80	0.20	0.98	0.11	0.02	0.63	nd	nd
	3	8.86	2.06	3.20	1.00	0.07	0.16	0.05	0.46	nd	nd
	4	7.08	0.10	2.40	1.40	0.14	0.20	0.04	1.10	nd	nd
	5	0.28	1.29	5.20	1.20	0.10	0.61	0.03	0.08	0.04	nd
	Mean		3.30	0.73	3.48	1.20	0.27	0.38	0.03	0.67	-
Max.		8.86	2.06	5.20	2.20	0.98	0.83	0.05	1.10	0.04	Trace
Min.		0.12	0.07	1.80	0.20	0.05	0.11	0.01	0.08	Trace	Trace

*nd = not detected.*

metals such as lead and cadmium. Mostly, the Zn is introduced into water by artificial pathways such as by-products of steel production, or coal burning, or from the burning of waste materials. Industries that discharge large quantities of Zn directly to water include iron and steel, zinc smelting, plastics, and electroplating. Urban

runoff, mine drainage, and municipal and industrial effluents are smaller but more concentrated sources of Zn in water [43].

The dissolved Fe concentration in water is dependent on the pH, redox potential, turbidity, suspended matter, the aluminium concentration

and the occurrence of several heavy metals, notably manganese. Typically, the concentration of dissolved Fe in unpolluted surface water is between 1 and 500 mgL<sup>-1</sup> [25]. Fe content in effluents and surface water and groundwater samples of the study area varied from 0.02-5.99 and 0.11-0.83 mgL<sup>-1</sup> with the average values of 0.77 and 0.38 mgL<sup>-1</sup>, respectively (Table 3). The present study revealed that sample IDs 7, 10, 17 and 19 contained a higher amount of Fe (ranged from 2.09-5.99 mgL<sup>-1</sup>) and those samples were collected from drains close to metal and food industries, and canals (Table 1), which usually carries urban and industrial wastes. Ayers and Westcot [31] reported the highest acceptable limit of Fe in irrigation water is 5.00 mgL<sup>-1</sup>. On the other hand, the maximum acceptable limit of Fe for drinking water is 0.30 mgL<sup>-1</sup> [44]. Considering this limit as standard, 60% of groundwater samples were found suitable for drinking. Iron may cause damage to industrial equipment and structures in a number of ways. On precipitation, it contributes to the sediment deposits which foul boilers, heat exchangers and pipelines. Iron can interfere with the efficient and effective operation of processes in various ways. It can form dark-coloured precipitates during tanning, which subsequently reduce tanning efficiency. In dyeing operations, iron may form complexes with acid dyes, rendering them inactive and resulting in discolouration, colour changes and dulling of shades [25].

Manganese is present in >100 common salts and mineral complexes that are widely distributed in rocks, soils and on the floors of lakes and oceans. Industrial emissions are the principal source of manganese in the atmosphere. In 1984, total atmospheric emission of Mn from anthropogenic sources in India was estimated 1225 ton and 78.5% of this originated from industrial processes, mainly related to metal alloy production [43]. Manganese concentration in effluents and surface water and groundwater samples of the study area varied from 0.05 to 2.20 and 0.08-1.10 mgL<sup>-1</sup> with the mean values of 0.56 and 0.67 mgL<sup>-1</sup>, respectively (Table 3). Typically, the median concentration of Mn in freshwater is 8.0 µgL<sup>-1</sup> with a range of 0.02-130 µgL<sup>-1</sup> [25]. The maximum permissible limit of Mn in water used for irrigation is 0.20 mgL<sup>-1</sup> [31]. Considering this limit as standard, 50 and 80% of effluents and surface water and groundwater samples were rated as unsuitable for irrigation, respectively. Similarly, 80% groundwater samples were also found as unsuitable for drinking as recommended by WHO [45]. In the

pulp and paper industry, Mn can form complexes with lignin and additives used in paper manufacture, hindering removal of lignin from crude pulp during washing and interfering with the proper function of the additives [25].

Copper is a micronutrient for aquatic life in all natural waters and sediments. Although this is a minor nutrient at low concentration, they can become toxic to aquatic life at higher concentrations. The concentrations of Cu in effluents and surface water and groundwater samples were within the range of not detectable to 0.10 and 0.01 to 0.05 mgL<sup>-1</sup> with the average values of 0.04 and 0.03 mgL<sup>-1</sup>, respectively (Table 3). According to US EPA [45], freshwater toxicity reference value for Cu is 0.009 mgL<sup>-1</sup>. Most of the effluents and surface water (87.5%) and all groundwater samples of the study area exceeded this reference value. Waters generally having less than 0.20 mgL<sup>-1</sup> Cu is safe for irrigating crops and soils [31]. Copper is released into the water as a result of natural weathering of soil and discharges from industries and sewage treatment plants. Copper compounds which are used in electroplating industries such as cupric sulphate and cupric acetate and paint industries such as cuprous oxide, ceramics and glass industries such as cupric acetate, cuprous and cupric oxides used as pigments and for making glazes were discharged through the treated industrial effluents. Other than this copper released through domestic activities such as human wastes flushed through the toilets, washing and bathing water etc. [43].

Water is rarely an important source of lead (Pb) exposure to human. The lead compound tetraethyl lead is applied as an additive in fuels. This organic lead compounds are quickly converted to inorganic lead and ends up in water, sometimes even in drinking water [43]. Lead concentration in effluents and surface water samples varied from trace to 8.47 mgL<sup>-1</sup>, while in case of groundwater Pb content was negligible (Table 3). According to US EPA [45], freshwater toxicity reference value for Pb is 0.0025 mgL<sup>-1</sup> and Pb content in 6 effluents samples was several thousand times higher than this limit. Pb in effluents might originate from municipal sewerage and industrial wastes. Different manufactured goods, e.g. paints, cosmetics, automobile tyres, batteries and fertiliser might also be a source of Pb into the environmental compartments [42]. According to Proposed Bangladesh Standards, Pb content for irrigation water is 0.01 mgL<sup>-1</sup> [26]. Considering this limit as

standard, Pb concentrations in 6 effluents samples collected from the study area were rated as unsuitable for irrigation. The content of Cr in effluents and surface water and groundwater samples were trace except for 1 groundwater sample (Table 3). So in the context of Cr, all samples of the study area could be used safely for all purposes.

### 3.5 Suitability of Water for Irrigation Usage

#### 3.5.1 Sodium adsorption ratio (SAR)

The computed SAR values of effluents and surface water and groundwater samples were within the limit of 0.11 to 14.93 and 0.08 to 6.11 with the mean value of 5.23 and 2.32, respectively (Table 4). Water used for irrigation with SAR <10 might not be harmful and considered as excellent and SAR ranged from 10-18 categorised as good for irrigating agricultural crops [46]. Considering this classification, 16 effluents and surface water and all groundwater samples were graded as an excellent category and the rest 8 effluents and surface water samples were considered as a good category for irrigation purpose. The present study results revealed that a good proportion of Ca and Mg existed in all water samples. According to the US salinity diagram as described by Richards [28], in which EC was taken as salinity hazard and SAR as alkalinity hazard showed that out of 24 effluents and surface water samples, 02 were in the category of C1S1; 8 were in the category of C2S1; each of 04 samples were in the category of C2S2, C3S1 and C3S2, and each of 1 water samples were in the category of C4S1 and C4S4, indicating low to very high salinity and low to very high alkali hazard. On the other hand, 04 groundwater samples were in the category of C2S1 and only 1 sample was in the category of C3S1, indicating medium to high salinity and low alkali hazard (Table 4). Very high salinity water cannot be used for irrigation with restricted drainage and it requires special management for salinity control (such as good drainage, high leaching and organic matter addition) and plants with good salt tolerance should be selected for such area. Low sodium water (S1) and medium sodium water (S2) can be used for irrigation on almost all soils with little danger of the development of harmful levels of exchangeable sodium. But very high (S4) sodium water is not suitable for irrigation.

#### 3.5.2 Soluble sodium percentage (SSP)

The suitability of water for irrigation depends mostly on the Na percentage. Saleh et al. [50] described that high Na in irrigation water causes exchange of Na in water for Ca and Mg in soil reduces permeability and eventually results in soil with poor internal drainage. The calculated SSP values of effluents and surface water and groundwater samples were varied from 7.36 to 87.04% and 4.53 to 72.22% with an average value of 46.50 and 33.36%, respectively (table 4). According to water classification proposed by Wilcox [47], 11 effluents and surface water samples were classified as excellent (SSP < 20%), 1 sample was rated as good (SSP = 20-40%), 4 samples were rated as doubtful (SSP = 61-80%) and the rest 8 samples were rated as unsuitable (SSP = >80%) for irrigation. On the other hand, among the groundwater samples, 3 and 2 samples were rated as excellent and doubtful category, respectively (Table 4).

#### 3.5.3 Residual sodium carbonate (RSC)

To quantify the effects of carbonate and bicarbonate, RSC has been computed. The quantity of bicarbonate and carbonate in excess of alkaline earths influence the suitability of water for irrigation, because precipitation of Ca and Mg may occur if the sum of carbonates and bicarbonates is in excess of Ca and Mg. A high RSC value in water leads to an increase in the adsorption of Na on soil. Irrigation water having RSC values >5.0 meqL<sup>-1</sup> are considered harmful to the growth of plants, while water with RSC value above 2.50 meqL<sup>-1</sup> are not considered suitable for irrigation. Hence, continued usage of high RSC water will affect the yields of crop [48]. The computed RSC values of effluents and surface water and groundwater samples were ranged from -2.60 to 4.80 and 0.20 to 3.00 meqL<sup>-1</sup> with the mean value of 1.41 and 1.72 meqL<sup>-1</sup>, respectively (Table 4). According to Ghosh et al. [48], 10 effluents and surface water samples were found as suitable (RSC= <1.25 meqL<sup>-1</sup>), 8 samples were categorized as marginal (RSC= 1.25-2.50 meqL<sup>-1</sup>) and the rest 6 water samples were rated as unsuitable (RSC= >2.50 meqL<sup>-1</sup>) for irrigation. On the other hand, incase of groundwater, 2, 1 and 2 samples were rated as suitable, marginal and unsuitable category for irrigation, respectively (Table 4).

**Table 4. Quality classification and suitability of water samples used for irrigation**

Type of water	Sample No.	SAR	SSP (%)	RSC (meqL <sup>-1</sup> )	H <sub>T</sub> (mgL <sup>-1</sup> )	SAR <sup>1</sup>	SSP <sup>2</sup>	RSC <sup>3</sup>	H <sub>T</sub> <sup>4</sup>	Alkalinity & salinity hazard class <sup>5</sup>
Effluents and surface water	1	11.29	83.53	-0.35	157.36	Good	Unsuit.	Suitable	Hard	C2S2
	2	7.34	73.95	3.00	209.83	Ex.	Doubtful	Unsuit.	Hard	C2S1
	3	6.21	75.12	3.00	130.15	Ex.	Doubtful	Unsuit.	MH	C2S1
	4	12.40	87.04	4.80	99.98	Good	Unsuit.	Unsuit.	MH	C3S2
	5	0.11	8.36	2.20	170.04	Ex.	Ex.	Unsuit.	Hard	C2S1
	6	14.93	84.62	4.80	220.04	Good	Unsuit.	Unsuit.	Hard	C4S4
	7	0.14	10.34	-2.60	130.03	Ex.	Ex.	Suitable	MH	C4S1
	8	0.28	13.92	-1.40	170.23	Ex.	Ex.	Suitable	Hard	C3S1
	9	0.24	14.89	-0.40	140.21	Ex.	Ex.	Suitable	MH	C3S1
	10	0.11	7.36	1.40	170.00	Ex.	Ex.	Marginal	Hard	C2S1
	11	0.13	10.86	1.20	160.08	Ex.	Ex.	Suitable	Hard	C2S1
	12	0.15	17.43	4.60	90.11	Ex.	Ex.	Unsuit.	MH	C1S1
	13	9.89	77.08	1.20	260.34	Good	Doubtful	Suitable	Hard	C3S2
	14	0.13	14.73	3.00	110.10	Ex.	Ex.	Unsuit.	MH	C2S1
	15	5.64	72.01	1.20	200.12	Ex.	Doubtful	Suitable	Hard	C2S1
	16	0.11	7.44	-1.80	230.13	Ex.	Ex.	Suitable	Hard	C3S1
	17	11.97	81.37	1.40	229.86	Good	Unsuit.	Marginal	Hard	C3S2
	18	10.48	82.35	1.40	149.85	Good	Unsuit.	Marginal	MH	C3S2
	19	11.76	80.12	-1.00	250.44	Good	Unsuit.	Suitable	Hard	C2S2
	20	0.22	13.04	1.20	160.20	Ex.	Ex.	Suitable	Hard	C2S1
	21	0.46	22.16	1.80	130.15	Ex.	Good	Marginal	MH	C1S1
	22	11.20	83.43	2.40	160.26	Good	Unsuit.	Marginal	Hard	C2S2
	23	10.12	82.82	1.40	150.02	Good	Unsuit.	Marginal	Hard	C2S2
	24	0.20	12.04	1.40	190.09	Ex.	Ex.	Marginal	Hard	C3S1
	Mean	5.23	46.50	1.41	169.57	-	-	-	-	-
	Max.	14.93	87.04	4.80	260.34	-	-	-	-	-
	Min.	0.11	7.36	-2.60	90.11	-	-	-	-	-
Ground-water	1	0.08	4.53	2.80	199.81	Ex.	Ex.	Unsuit.	Hard	C2S1
	2	0.09	4.94	0.20	250.44	Ex.	Ex.	Suitable	Hard	C2S1
	3	6.11	72.22	3.00	210.14	Ex.	Doubtful	Unsuit.	Hard	C3S1
	4	5.14	65.39	1.00	189.97	Ex.	Doubtful	Suitable	Hard	C2S1
	5	0.16	19.70	1.60	320.30	Ex.	Ex.	Marginal	VH	C2S1
		Mean	2.32	33.36	1.72	234.13	-	-	-	-
	Max.	6.11	72.22	3.00	320.30	-	-	-	-	-
	Min.	0.08	4.53	0.20	189.97	-	-	-	-	-

Legend: Ex.= Excellent; Unsuit.= Unsuitable; MH= Medium hard; VH= Very hard; C1= Low salinity; C2= Medium salinity; C3= High salinity; C4= Very high salinity and S1= Low alkalinity; S2= Medium alkalinity. <sup>1,2,3,4</sup> and <sup>5</sup> = Todd [46]; Wilcox [47]; Ghosh et al. [48]; Sawyer and McCarty [49] and Richards [28], respectively.

### 3.5.4 Hardness (H<sub>T</sub>)

Hardness of water resulted due to the abundance of divalent cations like Ca and Mg [46]. The calculated H<sub>T</sub> of effluents and surface water samples varied from 90.11 to 260.34 mgL<sup>-1</sup> with the mean value of 169.57 mgL<sup>-1</sup> and the range was 189.97 to 320.30 mgL<sup>-1</sup> with an average value of 234.13 mgL<sup>-1</sup> for groundwater (Table 4). A classification for irrigation water based on hardness as reported by Sawyer and McCarty [49], 16 and 8 effluents and surface

water samples were hard (H<sub>T</sub> = 150-300 mgL<sup>-1</sup>) and medium hard (H<sub>T</sub> < 150 mgL<sup>-1</sup>) category while incase of groundwater 4 samples were hard and only 1 was classified as very hard (H<sub>T</sub> = >300 mgL<sup>-1</sup>).

## 4. CONCLUSION

Industrialisation and unplanned urbanisation have greatly distorted the natural water resources in Bangladesh. Different ionic constituents including heavy metals lead to

contamination of both surface and groundwater, and such contamination of water restrict their different usage. The present study revealed that  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{K}^+$ ,  $\text{Mn}$ ,  $\text{Cu}$  and  $\text{Pb}$  were the major contaminants in effluents and surface water of Rangpur city, Bangladesh. Major cation chemistry of effluents and surface water showed their dominance in the order of  $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} = \text{K}^+$ , while in case of groundwater the sequence was  $\text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+$ . The study inferred that huge amount of  $\text{Na}^+$  in effluents and surface water might originate from the discharge of sewage effluents of urban areas, use of water treatment chemicals and salts used in different industrial units. In case of groundwater, the presence of higher content of  $\text{Ca}^{2+}$  might be due to washing out of this metal from bedrock. On the other hand, the anion chemistry of effluents and surface water in the study area were found to decrease in the order of  $\text{SO}_4^{2-} > \text{Cl}^- > \text{CO}_3^{2-} > \text{HCO}_3^- > \text{BO}_3^{3-} > \text{PO}_4^{3-}$  and for groundwater the sequence was  $\text{SO}_4^{2-} > \text{CO}_3^{2-} > \text{Cl}^- > \text{HCO}_3^- > \text{BO}_3^{3-} > \text{PO}_4^{3-}$ . The study results showed that most of the groundwater samples were suitable for drinking in the context of major cations and anions. Higher content of  $\text{Cl}^-$  in effluents and surface water samples might cause moderate to major damage as a result of corrosion to the industrial equipments up to category 3 industrial processes. Heavy metal concentrations in the effluents and surface water and groundwater samples were found to decrease in the sequence of  $\text{Fe} > \text{Mn} > \text{Zn} > \text{Cu} > \text{Pb} > \text{Cr}$  and  $\text{Mn} > \text{Fe} > \text{Zn} > \text{Cu} > \text{Cr} > \text{Pb}$ , respectively. The study results rated most of the effluents and surface water and groundwater samples as unsuitable for irrigation and drinking as regards to Mn content. Furthermore, most of the effluents and surface water (87.5%) and all groundwater samples of the study area exceeded the freshwater toxicity reference value for Cu as prescribed by the US EPA. Electrical conductivity and SAR reflected that effluents and surface water samples were low to very high salinity (C1-C4) and low to very high alkalinity (S1-S4) hazards classes, while groundwater samples were medium to high salinity (C2-C3) and low alkali (S1) hazard classes. As regards to hardness, out of 24 effluents and surface water samples, 8 were medium hard and 16 were hard, while in case of groundwater 4 samples were hard and only one was very hard in quality. Finally, we should not discharge and/ or dispose of any type of waste containing chemical substances without treatment which may ultimately contaminate both surface and groundwater.

## COMPETING INTERESTS

Authors have declared that no competing interests exist.

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