Original Research Article

Heavy metal and major ionic contamination level in surface and groundwater of an urban industrialised city: a case study of Rangpur city, Bangladesh

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ABSTRACT

Industrialisation and unplanned urbanisation in different city areas of Bangladesh have greatly distorted the natural water resources. Present study was undertaken to evaluate ionic contamination level including heavy metals in both surface and groundwater of Rangpur city, Bangladesh. Total 24 surface and 5 groundwater samples 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 Na > Ca > Mg = K and Ca > Na > Mg > K for surface and groundwater, respectively. Although SO_4 was the dominating anion in both surface and groundwater, but most of the water samples were rated as unsuitable for irrigation due to higher amount of CO_3, HCO_3 and Cl. In context of heavy metals, the amounts of Mn, Cu and Pb in surface water were comparatively higher than the standard limits. Enhanced concentration of Mn made 50% surface water and 80% groundwater samples unsuitable for irrigation and drinking, respectively. Similarly, 21 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 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 any type of waste containing chemical substances without proper treatment which may ultimately contaminate both surface and groundwater.

Keywords: Surface & groundwater contamination, urbanisation & industrialisation, heavy metal, Rangpur, Bangladesh

1. INTRODUCTION

Urbanisation and industrialisation are closely connected with each other. Industrialization 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 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 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 industrial 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].

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, K, HCO_3, Cl and SO_4, 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 aluminum, plastic, cold storage, tobacco, distilleries and chemical company and others [20]. Since last decade the city is also experiencing 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 both 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 is lies on the north-northwestern part of the Bengal basin. The surficial of the area is classified as recent flood plain deposits [21]. The recent flood plain deposit consist 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 twenty nine (29) surface (24) and groundwater (5) samples 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 uses for the different analysis. During collection of water samples, bottles were well rinsed using the same water. All 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 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 has been presented in Fig. 1 and Table 1, respectively.

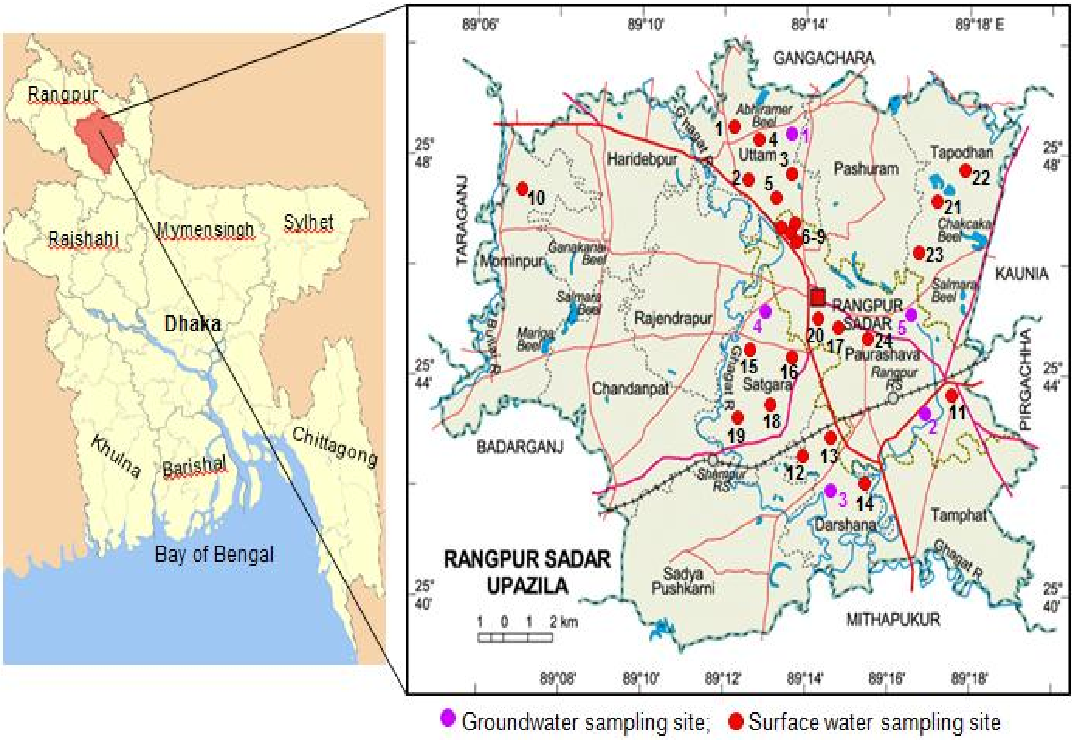

Fig. 1. Map showing surface and groundwater sampling sites of Rangpur city, Bangladesh

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^{TM}+EC5, HACH, USA), respectively. Contents of calcium and magnesium in water samples were determined titrimetrically using standard Na_2-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 colorimetrically using a spectrophotometer (T60UV-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.

Table 1. List of surface 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
	1	Uttom hasna bazar industry area	Drain	Industrial waste water mainly from Partex Foundary
	2	Uttom hasna bazar industry area	Drain	Industrial waste water mainly from Diamond Partex Board
	3	Hajirhat area	Drain	Industrial waste water mainly from Akiz Company
	4	Uttom hajirhat area	Drain	Industrial waste water mainly from Vai-Vai Paper Mill
	5	Hasna bazar area	Drain	Industrial waste water mainly from Abul Khair Leaf Tobacco Industry
	6	BSCIC area	Drain	Industrial waste water mainly from RFL Company

Surface water	7	D.R. Metal Industry, BSCIC area	Drain	Industrial waste water discharge from BSCIC area
	8	Silver Industry	Drain	Industrial waste water discharge from BSCIC area
	9	BSCIC area	Drain	Industrial waste water discharge from BSCIC area
	10	Sonic Food Industry, Fotkapur	Drain	Plastic material and industrial waste water
	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, waste water and plastic
	14	Darshana area	Pond	Municipal sewage and household waste water
	15	Tarminal area	Pond	Domestic effluents and municipal sewage
	16	Bangladesh Open University, Tarminal road	Drain	Municipal sewage, household waste and plastic
	17	Samasundori, masterpara	Canal	Fertilizer, pesticide and municipal waste water
	18	Khalifapara	Pond	Municipal sewage and household waste
	19	Samasundori, chekpost	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	-

3. RESULTS AND DISCUSSION

3.1 Quality on the Basis of pH, EC and TDS

The pH values of 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 surface water samples might be due to the presence of major cations such as Ca, Mg, K and Na 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. 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 equipment's due to corrosion or scaling [25]. Considering this range as standard for industrial usage, 8 surface and 1 groundwater samples were found as problematic (Table 2).

Electrical conductivity (EC) values of surface and groundwater samples were varied from 157 to 11240 and 264 to 845 µS cm^{-1} with the mean value of 1191.08 and 507 µS cm^{-1}, respectively (Table 2). According to Richards [28], 2 surface water samples were rated in the category C1 (EC= <250 µS cm^{-1}), 12 samples were in the class C2 (EC= 250-750 µS cm^{-1}), 8 samples were in the class C3 (EC = 750-2250 µS cm^{-1}) and the rest 2 samples were in the class C4 (EC >2250 µS cm^{-1}) indicating low to very high salinity classes. Medium salinity class water might be applied for irrigation with 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 μS cm^{-1}, may cause moderate damage to industrial equipments and structures through corrosion, scaling or fouling [25]. Considering this range as standard, 10 surface 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 total dissolved solids (TDS) of surface water samples in the investigated area were 6060 and 99 mg L^{-1}, respectively, and the mean value of TDS was 654.13 mg L^{-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 mg L^{-1} with the mean value of 283.40 mg L^{-1} (Table 2). According to South African industrial water use guideline [25], TDS >450 mg L^{-1} may cause significant to major damage likely as a result of corrosion, scaling or fouling to industrial equipment's and structures for category 1 industrial processes. The values are >800 mg L^{-1} for category 2 industrial processes and >1600 mg L^{-1} for categories 3 & 4 industrial processes [25]. Considering these values as standard, 2 surface water samples were found unsuitable for all categories of industrial processes (Table 2).

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

Type of water	Sample ID	pH	EC (μS cm^{-1})	TDS (mg L^{-1})	CO$_3$ (meL^{-1})	HCO$_3$ (me L^{-1})	Cl (meL^{-1})	PO$_4$ (mg L^{-1})	SO$_4$ (mg L^{-1})	BO$_3$ (mg L^{-1})
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	1191.08	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

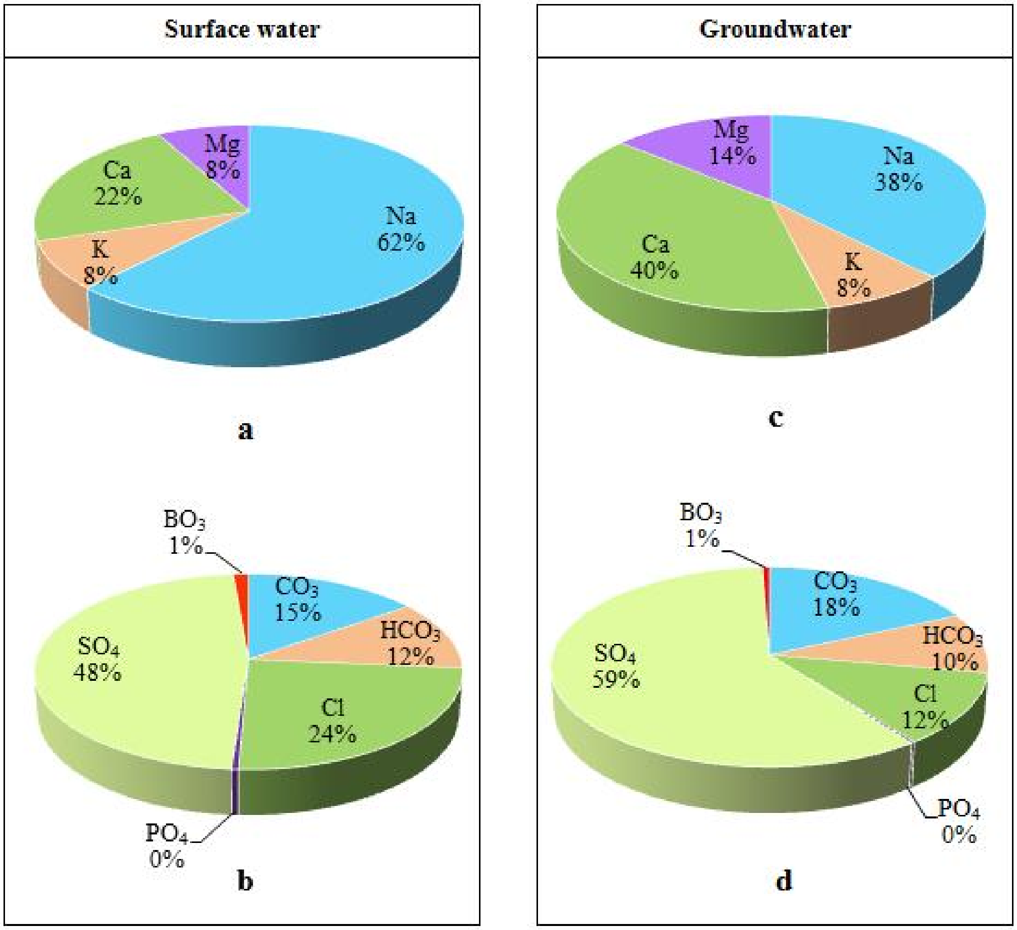

Fig. 2. Contribution of individual major ions towards the total cationic (a for surface and c for groundwater) and anionic (b for surface and d for groundwater) mass balance in waters collected from Rangpur city, Bangladesh.

3.2 Quality on the Basis of Anionic Constituents

Ions which commonly contribute to the alkalinity of water are bicarbonate (HCO_3), carbonate (CO_3) and hydroxide (OH). The minimum and maximum concentration of CO_3 ion in collected surface water samples was trace and 4.80 me L^{-1}, respectively with the mean value of 3.07 me L^{-1}. Incase of groundwater samples the range was 3.20 to 5.60 me L^{-1} with an average value of 4.16 me L^{-1} (Table 2). It is apparent from Fig. 2b & 2d that CO_3 ions are contributed 15 and 18% to the total anionic mass balance of surface and groundwater, respectively. According to Ayers and Westcot [31], the recommended maximum concentration of CO_3 for irrigation water is 0.10 me L^{-1}. As per this limit, CO_3 status in 19 surface and all groundwater samples were exceeded the standard, thus hazardous for irrigating crops and soils. Incase of industrial equipments (vacuum pumps, heating baths, steam-heated drying drums and tanks), scaling is mainly the deposition of insoluble calcium carbonate, which is a major problem wherever heating of water or heat exchange reactions takes place [25].

Surface and groundwater samples collected from Rangpur city area contained HCO_3 ranging from trace to 9.20 and 1.60 to 2.80 me L^{-1} with the mean value of 2.37 and 2.24 me L^{-1}, respectively (Table 2). It is evident from Fig. 2b & 2d that HCO_3 ions are contributed 12 and 10% to the total anionic mass balance of surface and groundwater, respectively. Waters, generally contained HCO_3 <1.50 me L^{-1} are rated as suitable for irrigation [31], and considering this value as standard, HCO_3 status in 17 surface 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 HCO_3 in drinking water is <500 mg L^{-1} (8.2 me L^{-1}). Considering this value as standard, all groundwater samples were rated as suitable for drinking. Bicarbonates are derived mainly from the soil zone 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 (Cl) is a common constituent of water, which is highly soluble and once in solution tends to accumulate. Typically, the concentrations of chloride in fresh water range from a few to several hundred mg L^{-1} [25]. Surface water sample collected from the study area contained Cl ion ranging from 0.99 to 13.25 me L^{-1} with the mean value of 4.98 me L^{-1} (Table 2) and it contributed 24% to the total anionic mass balance (Fig. 2b). On the other hand, incase of groundwater chloride content varied from 1.27 to 5.22 me L^{-1} with an average value of 273 me L^{-1} (Table 2). Among the waters, 11 surface and 1 groundwater samples of the study area could be rated as unsuitable for irrigation in context of Cl content as because these samples contained higher amount of Cl than the recommended limit (4.0 me L^{-1}) [31]. High concentration of chloride in water is considered to be the indicator of pollution by high organic wastes of animal or industrial origin [35]. Most of the chloride in water was present as sodium chloride (NaCl) but chloride 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 mg L^{-1} (5.63 me L^{-1}) may cause moderate to major damage as a result of corrosion to industrial equipment's and structures upto category 3 industrial processes [25]. Surface and groundwater samples collected from Rangpur city contained phosphate (PO_4) ranging from 0.03-0.18 and 0.01-0.12 mg L^{-1} and the mean values were 0.09 and 0.05 mg L^{-1}, respectively (Table 2). The maximum acceptable limit of PO_4 in water used for irrigation is 2.00 mg L^{-1} [31]. On the basis of this limit, all water samples under investigation area were found suitable for irrigating crops and soils.

Occurrence of sulphate (SO_4) in water mainly due to results from the dissolution of mineral sulphates in soil and rock, particularly calcium sulphate (gypsum) and other partially soluble sulphate minerals. Typically, the concentration of SO_4 in surface water is 5 mg L^{-1}, although it exceeds of several hundred mg L^{-1} where the dissolution of sulphate minerals or discharge of sulphate rich effluents from acid mine drainage takes place [25]. Both surface and groundwater samples contained the highest amount of SO_4 and ranged between 0.31-36.38 and 2.13-23.38 mg L^{-1} with the mean value of 9.80 and 13.66 mg L^{-1}, respectively (Table 2). It is apparent from Fig. 2b & 2d that SO_4 ions are contributed 48 and 59% to the total anionic mass balance of surface and groundwater, respectively. According to Ayers and Westcot [31], the acceptable limit of SO_4 in irrigation water is <20 mg L^{-1}. As per this limit, 21 surface 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 sulphates may interfere with the efficiency of dyeing operations in leather tanning and finishing industries [25].

The natural borate (BO_3) content of groundwater and surface water is usually small. The borate 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 surface water samples varied from 0.09 to 0.71 mg L^{-1} with the mean value of 0.26 mg L^{-1}, but incase of groundwater BO_3 content ranged between 0.06 to 0.19 mg L^{-1} with an average value of 0.13 mg L^{-1} (Table 2). The acceptable limit of BO_3 in irrigation water is <0.75 mg L^{-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 mg L^{-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 mg L^{-1} but can markedly exceed this in some countries [39]. The content of Na in surface and groundwater samples collected from Rangpur city was within the range of 0.14-22.14 and 0.12-8.86 me L^{-1} with the mean value of 7.05 and 3.30 me L^{-1}, respectively (Table 3), and Na contributed 68 and 32% to the total cationic mass balance, respectively (Fig. 2a & 2c). Huge amount of Na in surface water might be due to discharge of sewage effluents from urban areas, use water treatment chemicals, mineral deposits and salt used in different industrial units. Water generally contained <40 me L^{-1} Na is suitable for irrigation [31]. On the other hand, according to WHO [32], the maximum guideline limit of Na for drinking water is 200 mg L^{-1} (8.7 me L^{-1}). The recorded Na content in all water samples under investigation area was less than both the limits. Potassium content in surface and groundwater samples varied from 0.13-2.32 and 0.07-2.06 me L^{-1}, respectively (Table 3). The mean values of K were 0.91 and 0.73 me L^{-1} for surface and groundwater, respectively, which contributed 8% to the total cationic mass balance in both cases (Fig. 2a & 2c). The recommended concentration of K in irrigation water is 2.0 mg L^{-1} (0.05 me L^{-1}) [31]. Considering this value as standard, all surface 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 for drinking water is 12 mg L^{-1} (0.3 me L^{-1}) [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 in surface and groundwater samples were within the range of 1.20- 4.80 and 1.80-5.20 me L^{-1} with the average values of 2.50 and 3.48 me L^{-1}, respectively (Table 3). Ca content in surface and groundwater samples contributed 22 and 40%, respectively to the total cationic mass balance (Fig. 2a & 2c). The study results inferred that Ca content in groundwater was higher, which might be due to wash out of Ca from bedrock. The contribution of Ca content in groundwater was largely dependent on the solubility of $CaCO_3$, $CaSO_4$ and rarely on $CaCl_2$ [30]. Calcium concentrations up to and exceeding 100 mg L^{-1} (5.0 me L^{-1}) 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 L^{-1} for calcium [41]. The maximum acceptable limit of Ca for drinking water is 10.0 me L^{-1} (200 mg L^{-1}) [32]. Considering this limit as standard, all groundwater samples could safely be used for drinking.

Table 3. Concentration of heavy metals and major cations in surface and groundwater samples collected from Rangpur city, Bangladesh

Type of water	Sample No.	Major cation (me L^{-1})				Heavy metal (mg L^{-1})					
		Na	K	Ca	Mg	Zn	Fe	Cu	Mn	Cr	Pb
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	nd	8.47
	Min.	0.14	0.13	1.20	0.20	0.05	0.02	nd	0.05	nd	nd
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.

Both surface and groundwater samples collected from Rangpur city contained Mg within the range of 0.20-2.20 me L^{-1} with the mean values of 0.89 and 1.20 me L^{-1}, respectively (Table 3). Mg content in surface and groundwater samples contributed 8 and 14%, respectively to the total cationic mass balance (Fig. 2a & 2c). Present study results revealed higher amount of Mg in groundwater, which might be due to wash out of Mg from bedrock. Magnesium is present in natural groundwater usually at lower concentrations and the content usually varied from negligible to about 50 mg L^{-1} and rarely above 100 mg L^{-1} [40]. Similarly, according to WHO [41], the Mg contents of water from most Asian drinking-water supplies are generally below 20 mg L^{-1}. However, the maximum acceptable limit of Mg for drinking water is 150 mg L^{-1} (12.3 me L^{-1}) [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 the water sources, but it depends on the characteristics of the aquifers. Zinc (Zn) content in surface and groundwater samples collected from Rangpur city ranged from 0.05-0.47 and 0.05-0.98 mg L^{-1} with the average values of 0.14 and 0.27 mg L^{-1}, 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 mg L^{-1} Zn is safe for irrigating crops and soils [31]. High natural levels of Zn in water are usually associated with higher concentrations of other 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 iron (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 mg L^{-1} [25]. Fe content in surface and groundwater samples of the study area varied from 0.02-5.99 and 0.11-0.83 mg L^{-1} with the average values of 0.77 and 0.38 mg L^{-1}, respectively (Table 3). Present study revealed that sample IDs 7, 10, 17 and 19 contained higher amount of Fe (ranged from 2.09-5.99 mg L^{-1}) 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 mg L^{-1}. On the other hand, the maximum acceptable limit of Fe for drinking water is 0.30 mg L^{-1} [44]. Considering this limit as standard, 60% 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 surface and groundwater samples of the study area varied from 0.05 to 2.20 and 0.08-1.10 mg L^{-1} with the mean values of 0.56 and 0.67 mg L^{-1}, respectively (Table 3). Typically, the median concentration of Mn in freshwater is 8.0 µg L^{-1} with a range of 0.02-130 µg L^{-1} [25]. The maximum permissible limit of Mn in water used for irrigation is 0.20 mg L^{-1} [31]. Considering this limit as standard, 50 and 80% of surface 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 (Cu) 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 surface and groundwater samples were within the range of not detectable to 0.10 and 0.01 to 0.05 mg L^{-1} with the average values of 0.04 and 0.03 mg L^{-1}, respectively (Table 3). According to US EPA [45], freshwater toxicity reference value for Cu is 0.009 mg L^{-1}. Most of the surface water (87.5%) and all groundwater samples of the study area exceeded this reference value. Waters generally having less than 0.20 mg L^{-1} Cu is safe for irrigating crops and soils [31]. Copper is released into 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 the 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 is quickly converted to inorganic lead, and ends up in water, sometimes even in drinking water [43]. Lead concentration in surface water samples varied from not detectable to 8.47 mg L^{-1}, while incase of groundwater Pb content was negligible (Table 3). According to US EPA [45], freshwater toxicity reference value for Pb is 0.0025 mg L^{-1} and Pb content in 6 surface water samples were several thousand times higher than this limit. Pb in surface water might originate from domestic and industrial effluents. Different manufactured goods e.g. paints, cosmetics, automobile tyres, batteries and fertilizer 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 mg L^{-1} [26]. Considering this limit as standard, Pb concentrations in 6 surface water samples collected from the study area were rated as unsuitable for irrigation. The content of Cr in both surface and groundwater samples were trace except 1 groundwater sample (Table 3). So in context of Cr, all samples of the study area could be used safely for all purposes.

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. Present study revealed that CO_3, HCO_3, Cl, K, Mn, Cu and Pb were the major contaminants in surface water of Rangpur city, Bangladesh. Major cation chemistry of surface water showed their dominance in the order of Na > Ca > Mg = K, while incase of groundwater the sequence was Ca > Na > Mg > K. The study inferred that huge amount of Na in surface water might originate from discharge of sewage effluents of urban areas, use of water treatment chemicals and salts used in different industrial units. Incase of groundwater, presence of higher content of Ca might be due to wash out of this metal from bedrock. On the other hand, the anion chemistry of surface water in the study area were found to decrease in the order of $SO_4 > Cl > CO_3 > HCO_3 > BO_3 > PO_4$ and for groundwater the sequence was $SO_4 > CO_3 > Cl > HCO_3 > BO_3 > PO_4$. The study results showed that most of the groundwater samples were suitable for drinking in context of major cations and anions. But higher content of chlorides in surface water samples might cause moderate to major damage as a result of corrosion to industrial equipment's upto category 3 industrial processes. Heavy metal concentrations in the surface and groundwater samples were found to decrease in the sequence of Fe > Mn > Zn > Cu > Pb > Cr and Mn > Fe > Zn > Cu > Cr > Pb, respectively. The study results rated most of the surface and groundwater samples as unsuitable for irrigation and drinking as regards to Mn content. Furthermore, most of the 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. Finally, we should not discharge and/ or dispose any type of waste containing chemical substances without treatment which may ultimately contaminate both surface and groundwater.

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