ASSESSING IONIC COMPOSITION AND POLLUTION LEVEL OF SURFACE WATER AND GROUNDWATER IN NORTHERN BANGLADESH

MOHAMMAD JAHIDUL ISLAM[*], MOHAMMAD SHAZADUR RAHMAN, MOHAMMAD MAHAMUDUL HASSAN, KHELARAM CHANDRA ROY, MST NASRIN ZAHAN, MOHAMMAD AL-MAMUN, MOHAMMAD SHARIFUL ISLAM

Department of Agricultural Chemistry, Hajee Mohammad Danesh Science and Technology University, Dinajpur-5200, Bangladesh
*Corresponding author's email: jahidul@hstu.ac.bd

ABSTRACT

Surface and groundwater samples were collected from Parbatipur Upazila, Dinajpur, Bangladesh in dry season of the year 2014, were analyzed to identify the geochemical processes influencing water quality and suitability for agricultural and domestic uses. A total of 40 groundwater and surface water samples were collected from tubewells, ponds, canals and rivers and analysed for pH, EC, cations and anions. Based on TDS (total dissolved solids) and SAR (sodium adsorption ratio) values, both surface and groundwater were classed as 'freshwater' and 'excellent' categories. All samples were within 'soft' class regarding hardness with 'suitable' RSC (residual sodium carbonate). Based on Zn^{2+}, Mn^{2+}, Fe^{3+}, SO_4^{2-}, NO_3^- and Cl^-, all groundwater samples were within the 'safe' limit for drinking but unsuitable for some industries for specific ions. In both surface water and groundwater, trace metals including Cu^{2+}, Cr^{3+} and Pb^{2+} were within the recommended limit except Cd^{2+} while arsenic concentrations ranged from 0.01 to 0.04 mg/L and were below the permissible limit (> 0.05 mg/L). Cation exchange and silicate weathering are the dominant processes controlling the chemical composition of the groundwater in the area studied. It could be deduced from the present results that the groundwater and surface water are mainly $Ca–Mg–HCO_3$ water type regardless of the geology and water contamination. The study results indicate that groundwater and surface water in the Parbatipur Upazila might be suitable for drinking and irrigation purposes.

Key words: Groundwater, surface water, summer season, irrigation, water quality

INTRODUCTION

The surface and groundwater quality is an important issue, and a major factor affecting the human health as well as ecological systems [1]. The surface water quality is controlled by anthropogenic factors such as urbanizations, industrial and agricultural practices, and also by natural processes like soil erosion and the regional climatic conditions [2]. Likewise, the groundwater quality depends on many factors such as soil characteristics, manner of groundwater circulation through rock types, topography of the region and anthropogenic activities on the ground [3]. Increasing populations, food insecurity, growing economies and poor water management are putting unprecedented pressure on the world's freshwater resources. Demands of groundwater and surface water resources are increasing worldwide in arid and semi-arid regions with the

increasing population density. However, water pollution causes different problem in Bangladesh including Parbatipur Upazilla in Dinajpur district. Moreover, the increased use of agrochemicals such as insecticides, pesticides and chemical fertilizers to accelerate the crop productions is intensifying the water pollution of the present study area. The human health hazards caused by heavy metals associated with polluted water have been known for a long time, exposure to heavy metals is increasing in particular in less developed countries like Bangladesh. For example, manganese is a known mutagen. The chronic ingestion of Mn in drinking water is associated with neurologic damage [4]. Lead is considered as a possible human carcinogenic due to the inconclusive evidence of human and sufficient evidence of animal carcinogenicity [5]. Acute exposure to lead is known to cause renal failure and liver damage [6]. Moreover, recent research has shown that prolonged low-level exposure to lead may diminish the intellectual capacity of children [7]. Cadmium in our environment is a matter of concern since 1960s, when a painful bone disease "itai-itai" was reported in Japan. Moreover, it has recently been shown that Cd acts as an endocrine-disturbing substance and may lead to the development of prostate cancer and breast cancer [8]. Arsenic, a deadly poisonous metal, is unique among the metalloids and oxyanion-forming elements (e.g., Se, Mo) in its susceptibility to mobilization in various forms under the pH conditions of 6.5-8.5. The arsenic contamination of groundwater is among the most challenging environmental problems nowadays, threatening the well-being and livelihood of millions of people in South and Southeast Asia [9]. In Bangladesh, 30 million people drink arsenic-contaminated water without having alternative resources [10]. According to the estimate of the WHO, in the future, chronic consumption of such toxic water may lead to 1 in every 10 adult deaths caused by arsenic-related cancer [11]. Arsenic-contamination of natural water leads to the development of cancer, cardiovascular disease and inhibits the mental development of children [12].

Several researchers revealed that HCO_3^-, Na^+, Ca^{2+}, Mg^{2+} and Cl^- were the dominant ions in groundwater collected from different regions of Bangladesh [13, 14]. A substantial amount of Fe was present in groundwater which appeared unsuitable for baking, brewing and distilling, carbonated beverages, confectionery, paper and pulp, tanning, textile, laundering, synthetic rubber, ice manufacture sugar and dairy industries [15]. The ratio of groundwater use is much higher than surface water in northwestern districts compared to other parts of the country. All the rivers and cannels of the area dry up during the dry season and the people depend on groundwater. The objectives of this study were: to assess the chemical properties and heavy metals concentrations of surface and groundwater resources in Parbotipur upazila and to extract information relating to the influence of possible sources (natural or anthropogenic) on water quality parameters using multivariate statistical analysis.

MATERIALS AND METHODS

Sampling location and geological settings

Parbatipur Upazilla is located under Dinajpur district has an area of 395 km² having 10 unions. The lithology of most northern region of Bangladesh, especially this study area, consists predominantly of medium to coarse grained, poorly sorted sands and gravels with thin surface clays. A previous UNDP study classified the groundwater aquifers of Bangladesh into three zones, namely the upper aquifer, main aquifer and deep aquifer [16]. We collected the water samples from the main aquifer. The aquifer is comprised of medium and coarse-grained sediments, in places inter-bedded with gravel [16]. These sediments occur to depths of about 140 m below ground surface. The main water-bearing zone is either semi-confined or leaky or consists of stratified interconnected, unconfined water bearing formations. Presently, groundwater is drawn predominantly from these strata.

Water sampling and analysis

Both the surface water and groundwater samples were collected in March to May, 2014 from Parbatipur Upazila when water levels are generally lower relative to other seasons of the year [17]. Water samples were collected monthly from 7 deep tubewells, 7 shallow tubewells, 6 hand tubewells, 8 ponds, 4 Beels and 8 samples from rivers (3 of Kharkharia river, 2 of little Jamuna river, 1 of Naisisa river and 2 of Chirnai river) . Groundwater and surface water samples were collected in 5 liter plastic bottles that had been cleaned with hydrochloric acid (1:1) and then rinsed with tap water followed by rinsing with distilled water. Before collecting each sample, bottles were rinsed 3 to 4 times with sample. Water samples will be collected following the techniques outlined by Hunt and Wilson [18] and APHA [19]. All reagents used in chemical analysis were of analytical grade. All bottles and glasswares used were cleaned with P-free detergent (Extrans), rinsed three times with ultra-pure water (Milli-Q), soaked in 10% (v/v) HCl for at least 24 h, and finally rinsed three times with ultra-pure water. Samples were analyzed in Department of Agricultural Chemistry, Hajee Mohammad Danesh Science and Technology University, Dinajpur.

For assessing the quality of groundwater and surface waters, we measured pH, EC, TDS, Ca^{2+}, Mg^{2+}, Na^+, K^+, Zn^{2+}, Cu^{2+}, Mn^{2+}, Fe^{3+}, Cr^{3+}, Cd^{2+}, Pb^{2+}, PO_4^{3-}, As^{3+}, CO_3^{2-}, HCO_3^-, SO_4^{2-}, NO_3^- and Cl^-. Temperature was measured by thermometer. The pH (HANNA pH 211) and electrical conductivity (EC) were determined electrometrically [19]. The pH and electrical conductivity (EC) were determined electrometrically [19]. Inorganic phosphate was determined by ascorbic acid method. Nitrate was determined by Cd reduction method [19]. Total dissolved solids (TDS) were measured by drying and weighing method. K^+ and Na^+ were estimated by flame emission spectrophotometry. Ca^{2+} and Mg^{2+} were analyzed by complexometric titration. Chloride was estimated by argentometric titration [19] and PO_4^{3-} and NO_3^- were determined colorimetrically [19]. SO_4^{2-} was determined turbidimetrically. CO_3^{2-} and HCO_3^- were analyzed titrimetrically. A Perkin–Elmer Analyst 100 atomic absorption spectrophotometer equipped with a FIAS-100-flow injection hydride generation system was used for arsenic measurements. Zn^{2+}, Cu^{2+}, Mn^{2+} and Fe^{3+} were analyzed by atomic absorption spectrophotometry [19] in the Soil Resources Development Institute, Dinajpur, Bangladesh. Cr^{3+}, As^{5+}, Cd^{2+} and Pb^{2+} were analyzed by atomic absorption spectrophotometer in the Soil Resources Development Institute, Dhaka [19].

Table 1. The techniques/apparatus, book references used to measure the parameters

Parameters	Unit	Techniques/apparatus	References
Temperature	^oC	Centigrade Mercury Thermometer	Ramesh and Anbu, [20]
pH	-	Microprocessor pH meter (HANNA instruments, pH 211)	and APHA, [19]
EC	µs/cm	TDS meter (H1-9635, portable water proof Multirange Conductivity/TDS meter, HANNA)	
TDS	mg/L	TDS meter (H1-9635, portable water proof Multirange Conductivity/TDS meter, HANNA)	
Ca^{2+}	mg/L	Titrimetric method	Ramesh and Anbu,
Mg^{2+}	mg/L	Titrimetric method	[20]
Cl^-	mg/L	Titrimetric method	and APHA, [19]
Na^+	mg/L	Flame photometric method	
K^+	mg/L	Flame photometric method	
HCO_3^-	mg/L	Titrimetric method	
PO_4^{3-}	mg/L	Ascorbic acid method (Thermospectronic, UV-	

		visible Spectrophotometers, Helios 9499230 45811)
NO^{3-}	mg/L	Ultraviolet spectrophotometric screening method (Thermospectronic, UV-visible Spectrophotometers, Helios 9499230 45811)
SO_4^{2-}	mg/L	Turbidimetric method
Zn, Mn, Fe, As, Cr, Cd, Pb	mg/L	Atomic Absorption Spectrophotometer (Model: Perkin–Elmer Analyst 100)

Using identical methods the measured parameters were: pH, EC, TDS, Ca^{2+}, Mg^{2+}, Na^+, K^+, Zn^{2+}, Cu^{2+}, Mn^{2+}, Fe^{3+}, PO_4^{3-}, CO_3^{2-}, HCO_3^-, SO_4^{2-}, NO_3^- and Cl^- (Table 1). To classify water samples for irrigation, following equations were used in calculating water class rating parameters:

a)   Sodium adsorption ratio (SAR):
$$SAR = \frac{Na+}{\sqrt{\dfrac{Ca^{2+} + Mg^{2+}}{2}}}$$

b)   Soluble sodium percentage (SSP):
$$SSP = \frac{Soluble\ Na\ concentration\ (meq/L)}{Total\ cation\ concentration\ (meq/L)} \times 100$$

c)   Residual sodium carbonate (RSC):
$$RSC = (CO_3^{2-} + HCO_3^-) - (Ca^{2+} + Mg^{2+})$$

d)   Hardness or Total hardness (H_T):
$$H_T = 2.5 \times Ca^{2+} + 4.1 \times Mg^{2+} ;\ Freeze\ and\ Cherry,\ [9]$$

e)   Potential salinity (PS) = $Cl^- + (SO_4^{2-}/2$

f)   Permeability index (PI)= $\dfrac{Na^+ + \sqrt{HCO_3^-}}{Ca^{2+} + Mg^{2+} + Na^+}$

g)   Kelly's ratio = $Na^+/(Ca^{2+} + Mg^{2+})$

h)   Gibbs ratio 1 for anion = $Cl^- / (Cl^- + HCO_3^-)$ and Gibbs ratio 2 for cation = $(Na^+ + K^+) / (Na^+ + K^+ + Ca^{2+})$, Here concentrations for all ionic constituents for calculating all parameters are in meq/L except hardness (mg/L).

Figure 1. Map of sampling sites of the Parbatipur Upazila (20 groundwaters and 20 surface waters) under the district of Dinajpur along with the map of Bangladesh

RESULTS AND DISCUSSION

Table 2. Sampling information and chemical constituents of groundwater

Sl. No.	Parameters	Unit	Standard limit	Groundwater				Surface water			
				Min.	Max.	Mean	SD	Min.	Max.	Mean	SD
1	Depth	M		20	140	86.75	43.93	1.3	2	1.81	0.26
2	pH	-	6.5-8.0	6.8	7.7	7.33	0.25	6.7	7.8	7.34	0.36
3	Hardness	mg/L	500	47	311	129.2	65.52	37	170	94.25	36.27
4	Ca	meq/L	75	0.15	1.93	0.690	0.44	0.1	1	0.483	0.23
5	Mg	meq/L	30	0.81	4.35	1.92	0.93	0.66	2.43	1.42	0.50
6	Na	meq/L	200	0.2	0.3	0.23	0.04	0.09	0.41	0.269	0.08
7	K	meq/L	30	0.06	0.14	0.10	0.02	0.07	0.17	0.12	0.02
8	Cl	meq/L	250	0.35	1.5	0.76	0.31	0.25	1	0.61	0.23

MOHAMMAD JAHIDUL ISLAM et al.,

9	HCO_3	meq/L	200	0.65	4.2	1.70	0.89	0.7	2.7	1.28	0.52
10	SO_4^{2-}	meq/L	200	0.009	0.135	0.02	0.03	0.007	0.12	0.03	0.03
11	NO_3^-	mg/L	45	4.75	6.99	5.99	0.69	6.8	9.9	8.71	1.09
12	PO_4^{3-}	mg/L	-	0.006	0.289	0.109	0.08	0.02	0.426	0.17	0.13
13	Cu	mg/L	-	0.005	0.03	0.012	0.01	0.017	0.42	0.18	0.11
14	Zn	mg/L	-	0.024	0.042	0.029	0.01	0.025	0.84	0.23	0.08
15	Mn	mg/L	400	0.024	0.21	0.06	0.06	0.038	1.12	0.46	0.17
16	Fe	mg/L	-	0.001	0.287	0.099	0.09	0.055	2.15	1.11	0.06
17	Cr	mg/L	-	0.005	0.018	0.011	0.01	0.019	1.12	0.62	0.10
18	Cd	mg/L	-	0.011	0.036	0.02	0.01	0.013	0.056	0.02	0.08
19	Pb	mg/L	-	0.032	0.065	0.05	0.01	0.024	1.38	0.72	0.11
20	As	mg/L	-	0.01	0.04	0.02	0.0	0.011	0.025	0.02	0.04
21	EC		750	271	919	455.1	175.3	320	1149	511.3	219.9
22	TDS	mg/L	500	162	548	277.2	105.2	188	705	307.9	134.6
23	SAR		-	0.15	0.36	0.21	0.061	0.088	0.41	0.28	0.071
24	SSP		-	0.05	0.16	0.08	0.035	3.89	22.12	12.42	3.914
25	RSC		-	-2.08	-0.31	-0.91	0.47	-	-	-	-
26	KR		-	0.048	0.20	0.104	0.04	0.043	0.329	0.155	0.061
27	Cl/Anions		-	0.044	0.12	0.08	0.02	0.023	0.082	0.057	0.019
28	Na/(Na+Cl)		-	0.167	0.364	0.24	0.06	0.101	0.500	0.318	0.089

The results obtained from the chemical and heavy metals analyses of ground and surface water samples in Parbatipur Upazilla in Bangladesh are presented in Table 1.

Chemical properties

The observed pH ranges of the surface and groundwater in the study area are 6.7-7.8 and 6.8-7.7, respectively (Table 1). While pH usually has no direct impact on consumers, it is one of the most important operational water quality parameters. The recorded pH values of ground water and surface water samples were well within the WHO prescribed standard for pH of 6.5-8.5. According to environmental quality standards (EQS) for Bangladesh, [21] the maximum permissible value of pH in industrial water, fishing water, and drinking water are 6.0-9.5, 6.5-8.5, and 6.5-8.5, respectively. So the present values of pH indicated that the examined samples of groundwater were not objectionable for drinking, fish culture and irrigation, industrial and other purposes. The values of EC were ranged between 320 and 1149 µS/cm for surface water and from 271 to 919 µS/cm for groundwater indicate that high mineralization of surface water compared to groundwater (Table 1). However, no studied samples were beyond the WHO recommended maximum EC level of 1,500 µS/cm in drinking water [22]. High TDS (188-705 mg/L) was observed for surface water and low TDS (162-548 mg/L) for groundwater, could be due to the higher contact period of with rock surface water than that of groundwater. According to WHO, the maximum acceptable concentration of TDS in natural water for domestic purpose is 500 mg/L and the highest permissible limit is 1,500 mg/L. All the studied samples were within the permissible limit of WHO [23]. The TDS indicates the salinity behaviors of water and based on TDS, study water can be classified as fresh (TDS <1,000 mg/L) [24]. However, water with extremely low concentrations of TDS may also be unacceptable because of its flat, insipid taste.

The concentrations of chloride in surface water showed lower chloride concentration (0.25-1.00 mg/L) than that of groundwater (0.35-1.5 mg/L). Chloride in drinking water originates from natural sources, sewage and industrial effluents, urban runoff and saline intrusion. However, chloride concentrations in excess of about 250 mg/L can give rise to detectable taste in water [25]. The nitrate concentration in groundwater and surface water is normally low but can reach high levels because of agricultural runoff, refuse dump runoff, or contamination with human or animal wastes. The NO_3^- concentrations varied from 6.80-9.90 mg/L (surface water) and from 4.75-6.99 mg/L (groundwater). In natural conditions, concentration of NO_3^- does not exceed 10 mg/L in the water. All the analyzed samples contained nitrate concentrations within the tolerance limit of 45 mg/L.

The SAR values ranged from 0.088 to 0.41 (Table 2). The irrigation water with SAR less than 1 might not be harmful for agricultural crops [26]. Based on SAR, all samples were rated as 'low' alkalinity hazard (S1) class for irrigation (Table 5). According to Wilcox [27], the sodium hazard or SAR for all water samples is expressed in terms of classification of irrigation water as 'low' (S1 < 20). All water samples contained SSP value ranged from 0.05 to 22.12 (Table 2). According to Eaton [28], all samples were considered as 'excellent' for irrigation. The value of RSC values for all water samples were considered as 'suitable' for irrigation and other purposes according to Wilcox (Table 5). The level of Na^+ measured against Ca^{2+} and Mg^{2+} is known as Kelly's ratio (KR), based on which irrigation water can be rated. The Kelly's ratio for all water samples ranged from 0.043 to 0.329 (Table 2). Groundwater having Kelly's ratio more than one is generally considered as unfit for irrigation. Kelly's ratio for the tested samples indicates their suitability for irrigation purpose.

Heavy metals

The manganese concentrations were varied from 0.038-1.12 to 0.024-0.21 mg/L in surface and groundwater accordingly. The maximum permissible limit of Mn concentration in drinking water is 500 mg/L set by WHO. Potable water quality standard in terms of Mn is 100 mg/L set by Bangladesh Centre for Advanced Studies [29]. Mn concentrations of the present study were several folds lower than both WHO and BCAS suggested values. The maximum permissible limits of Pb suggested by WHO and USEPA are 10 and 15 µg/L respectively. Table 2 revealed that all surface water samples and groundwater samples contained the WHO recommended guideline value; have no demonstrating anthropogenic impact. The permissible concentration of Cd in drinking water is 3 µg/L set by WHO. Results showed that all surface water and groundwater samples were beyond the permissible limit [30]. Arsenic concentrations varied from 0.011 to 0.025 mg/L in surface water and from 0.01-0.04 mg/L in groundwater at different sampling locations (Table 2). Arsenic enters into the water naturally from rocks and sediments by coupled biogeochemical and hydrologic processes, some of which are presently affected by human activity. The WHO and USEPA [31] recommended limits of arsenic in water is 10 µg/L. Considering WHO guideline, all the water samples in the present study area were free from arsenic-contamination.

Trace metals such as Cu^{2+}, Zn^{2+}, Fe^{3+} and Cr^{3+} concentrations were low in groundwater except Cd^{2+} and considered to be suitable for crop production and the soil environment [3]. However, the average concentrations of Cu^{2+}, Zn^{2+}, Fe^{3+}, and Cr^{3+} were 0.012 mg/L, 0.029 mg/L, 0.099 mg/L, 0.011 mg/L respectively where as the average concentrations of Cr^{3+}, Cu^{2+}, Zn^{2+}, and Fe^{3+} of the surface water samples were found 0.62 mg/L, 0.18 mg/L, 0.23 mg/L, 1.11 mg/L respectively. The recommended concentrations of Cu^{2+}, Zn^{2+}, Fe^3 and Cr^{3+} were 0.20 mg/L, 2.0 mg/L, 5.0 mg/L, and 0.10 mg/L respectively and all the samples within the safe limit for drinking and irrigation purposes. The result also suggests that heavy metals and other pollutants pollute the surface water comparatively more than the groundwater. So the surface water is harmful for drinking and recreational purposes.

In Figure 2, Gibb's ratios (for anions and cations) of water samples were plotted against the total dissolved solids. This diagram is used to determine the mechanism controlling the water chemistry which occurs due to the evaporation dominance, rock dominance and precipitation dominance. From these diagrams, all the samples fall into the precipitation dominance in both the surface water and groundwater. As the study area has a higher rate of evapotranspiration characterized by tropical climate and restricted fresh water exchange, salt layers may form near the evaporating surface [32].On the other hand, human activities in areas of groundwater withdrawal might lead to future changes in groundwater chemical composition. For instance, intensive and long-term irrigation can leach salts from the soil/weathered rock zone, because of the availability of water. Piper diagrams are the combinations of anion and cation triangles that lie on a common baseline. Diamond shape between them can be used to make a tentative conclusion as to the origin of the water represented by the analysis and to categorize different water types. In both the surface water and groundwater, most of the samples were in the left corner of the diamond shape rich in Ca^{2+} + Mg^{2+} and HCO_3^- and is the region of water of temporary hardness (Fig. 3).

Table 3. Pearson's correlation matrix for the chemical constituents of groundwater and surface water (n=40)

Groundwater

	pH	EC	TDS	Hard	Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	HCO_3^-	SO_4^{2-}	NO_3^-	PO_4^{3-}
pH	1.00												
EC	-0.28	1.00											
TDS	-0.13	0.30	1.00										
Hard	-0.13	0.38	0.63	1.00									
Ca^{2+}	0.23	0.31	0.62	0.85	1.00								
Mg^{2+}	0.23	0.31	0.62	0.85	1.00	1.00							
Na^+	0.19	0.30	0.25	0.30	0.41	0.41	1.00						
K^+	0.19	0.30	0.25	0.30	0.41	0.41	1.00	1.00					
Cl^-	0.12	0.19	0.39	0.84	0.77	0.77	0.41	0.41	1.00				
HCO_3^-	-0.15	0.49	0.63	0.97	0.84	0.84	0.32	0.32	0.74	1.00			
SO_4^{2-}	-0.30	0.01	0.26	0.20	-0.11	-0.11	0.17	0.17	0.09	0.11	1.00		
NO_3^-	-0.34	-0.34	-0.21	-0.29	-0.40	-0.40	0.13	0.13	-0.24	-0.28	0.00	1.00	
PO_4^{3-}	-0.35	0.11	0.45	0.16	0.07	0.07	-0.13	-0.13	-0.08	0.18	0.19	-0.09	1.00

Surface water

	pH	EC	TDS	Hard	Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	HCO_3^-	SO_4^{2-}	NO_3^-	PO_4^{3-}
pH	1.00												
EC	-0.11	1.00											
TDS	-0.11	1.00	1.00										
Hard	-0.27	0.76	0.76	1.00									
Ca^{2+}	-0.31	0.75	0.75	0.99	1.00								
Mg^{2+}	-0.26	0.77	0.76	1.00	0.98	1.00							
Na^+	-0.23	0.24	0.24	0.58	0.55	0.59	1.00						
K^+	-0.27	0.38	0.38	0.19	0.21	0.18	0.05	1.00					
Cl^-	-0.16	0.69	0.69	0.82	0.79	0.83	0.42	0.20	1.00				
HCO_3^-	-0.33	0.63	0.63	0.92	0.92	0.92	0.67	0.20	0.58	1.00			
SO_4^{2-}	-0.01	-0.38	-0.38	-0.25	-0.25	-0.24	-0.33	-0.25	-0.43	-0.22	1.00		
NO_3^-	0.14	0.05	0.05	-0.16	-0.16	-0.16	0.23	0.12	-0.06	-0.20	-0.17	1.00	
PO_4^{3-}	-0.44	0.25	0.25	0.04	0.02	0.06	0.06	0.15	-0.07	0.21	-0.09	0.05	1.00

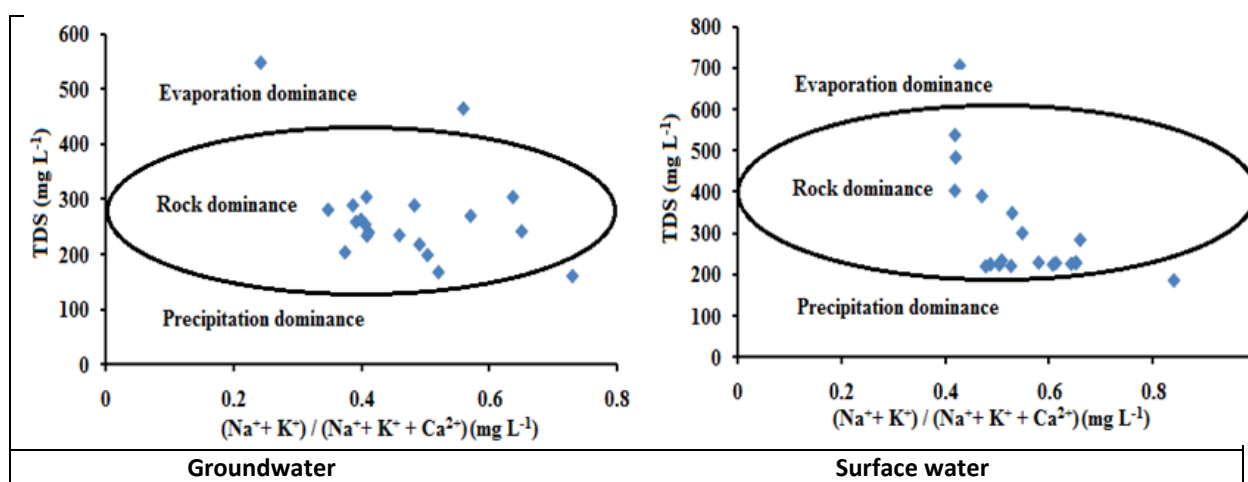Values are significant at p = 0.05 where r ≥0.43

To find out the interrelations among various water quality parameters, Pearson's correlation matrix was done (Table 3). According to Table 3, EC showed strong significant correlation with Ca^{2+}, Mg^{2+}, Cl^-, and

HCO_3^- with p value 0.05 and r ≥ 0.433. The result attributed to the alkalinity in nature of both the groundwater and surface water samples. In additions, H_T had significant correlation with EC, TDS, Ca^{2+}, Mg^{2+}, HCO_3^- and Cl^- in both the surface water and groundwater.

Table 4. Classification of groundwater quality based on suitability of water for irrigation or drinking purposes

Parameters	Reference	Range	Classification	Number of sample within standard range	
				Surface water	Groundwater
Electrical Conductivity	Wilcox [27]	<250 µScm^{-1}	Low salinity	0	0
		250-750 µScm^{-1}	Medium salinity	20	20
Sodium Adsorption ratio	Richards [26]	<10 mg/l	Excellent	20	20
Total Dissolved Solids	Freeze and Cherry [33]	0-1000 mg/l	Freshwater	20	20
Hardness	Sawyer and McCarty [34]	0-75 mg/l	Soft	2	6
		75-150 mg/l	Moderately hard	15	12
		150-300 mg/l	Hard	3	2
Residual Sodium Carbonate	Eaton [28]	<1.25meq/l	Suitable	20	20
Kelly's Ratio	Kelly [35]	<1	Suitable	20	20
Percentage of Na	Wilcox [27]	<20	Excellent	0	0
		20-40	Good	18	17
		40-60	Permissible	2	3

Groundwater

Surface water

MOHAMMAD JAHIDUL ISLAM et al.,
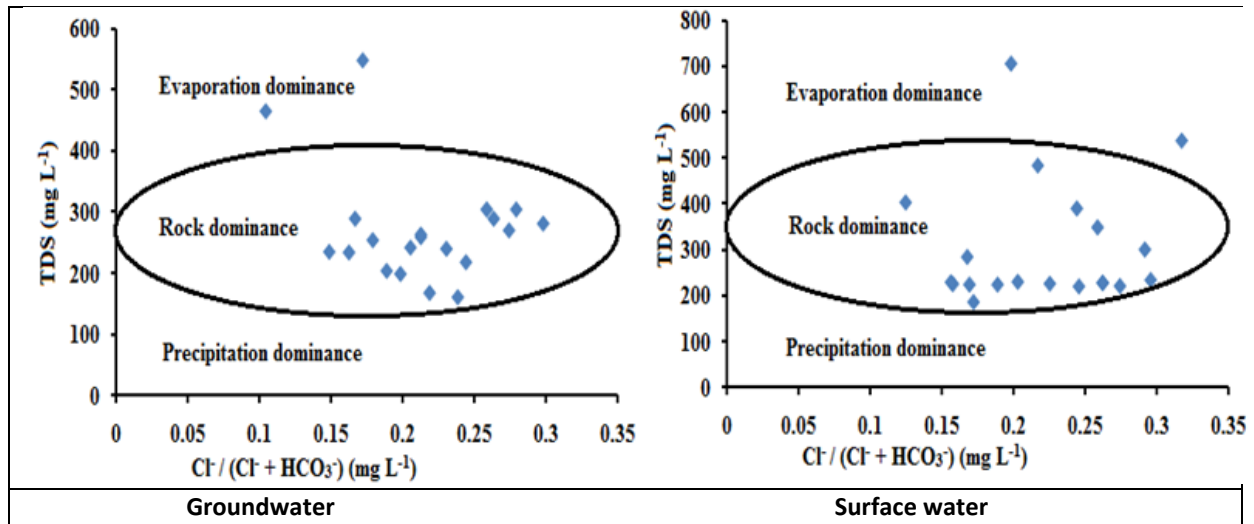
| Groundwater | Surface water |

Figure 2. The Gibb's Ratios (weight ratio) of **a.** TDS versus $(Na^+ + K^+) / (Na^+ + K^+ + Ca^{2+})$ and **b.** TDS and $Cl^- / (Cl^- + HCO_3^-)$
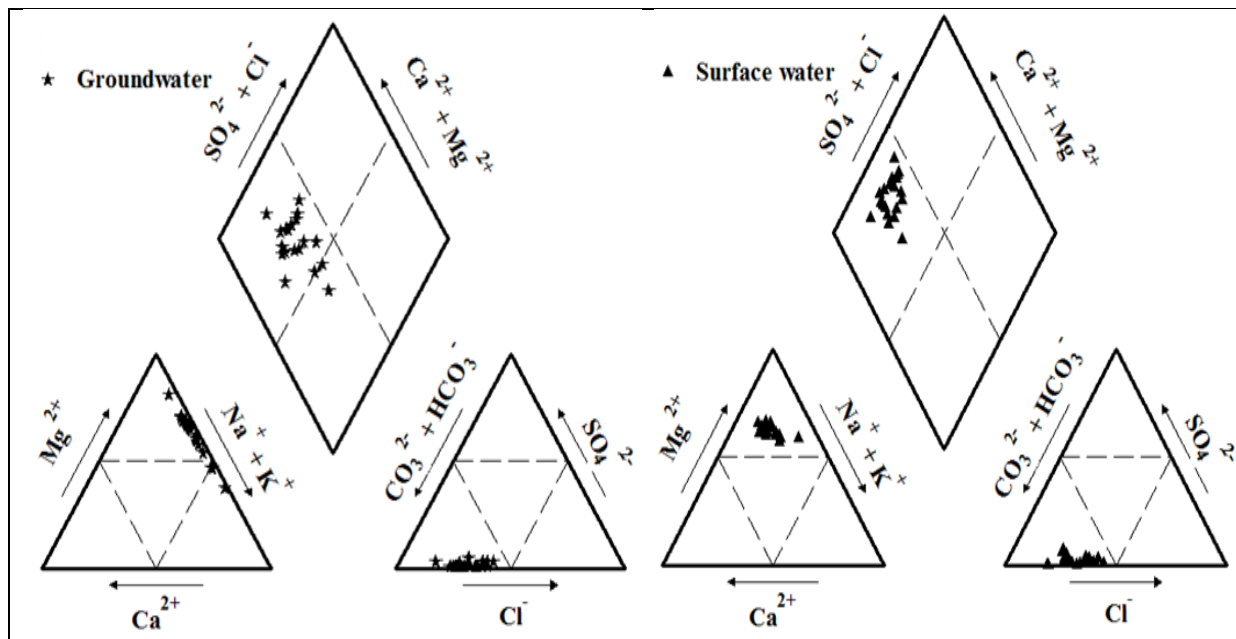

Figure 3. Piper diagram of the groundwater samples in the study area(1) $Na^+-K^+-SO_4^{2-}-Cl^-$ type, (2) $Ca^{2+}-Mg^{2+}-SO_4^{2-}-Cl^-$ type, (3)$Ca^{2+}-Mg^{2+}-CO_3^{2-}-HCO_3^-$ type, and (4) $Na^+-K^+-CO_3^{2-}-HCO_3^-$ type

The plot of equiline (Fig. 4) for the various ions shows the characteristics of the ions and their affinities. The plot of $Na^+ + K^+$ versus total cations of both surface and groundwater samples shows that most of the values are on the equiline suggesting that the alkali ions are not balanced by the total cations. Moreover, the correlations between the $Ca^{2+} + Mg^{2+}$ versus total cations in both surface water and groundwater were also found 0.981 and 0.990 respectively, indicating that the most of the ions were balanced by total cations. Among the alkalis, Na and K concentration were apparently low. Relatively, the subsequent dissolution and chemical weathering of minerals of local sedimentary rocks and igneous rocks and clay minerals were the source of

natural origin potassium in water [36]. In both the surface water and groundwater, the ratio of Cl^- versus total anions was 0.08 (Table 2) and the equilines between HCO_3^- versus total anions were very close to unity (Fig. 4) clearly showing the bicarbonate dominance over the alkaline metal ions.
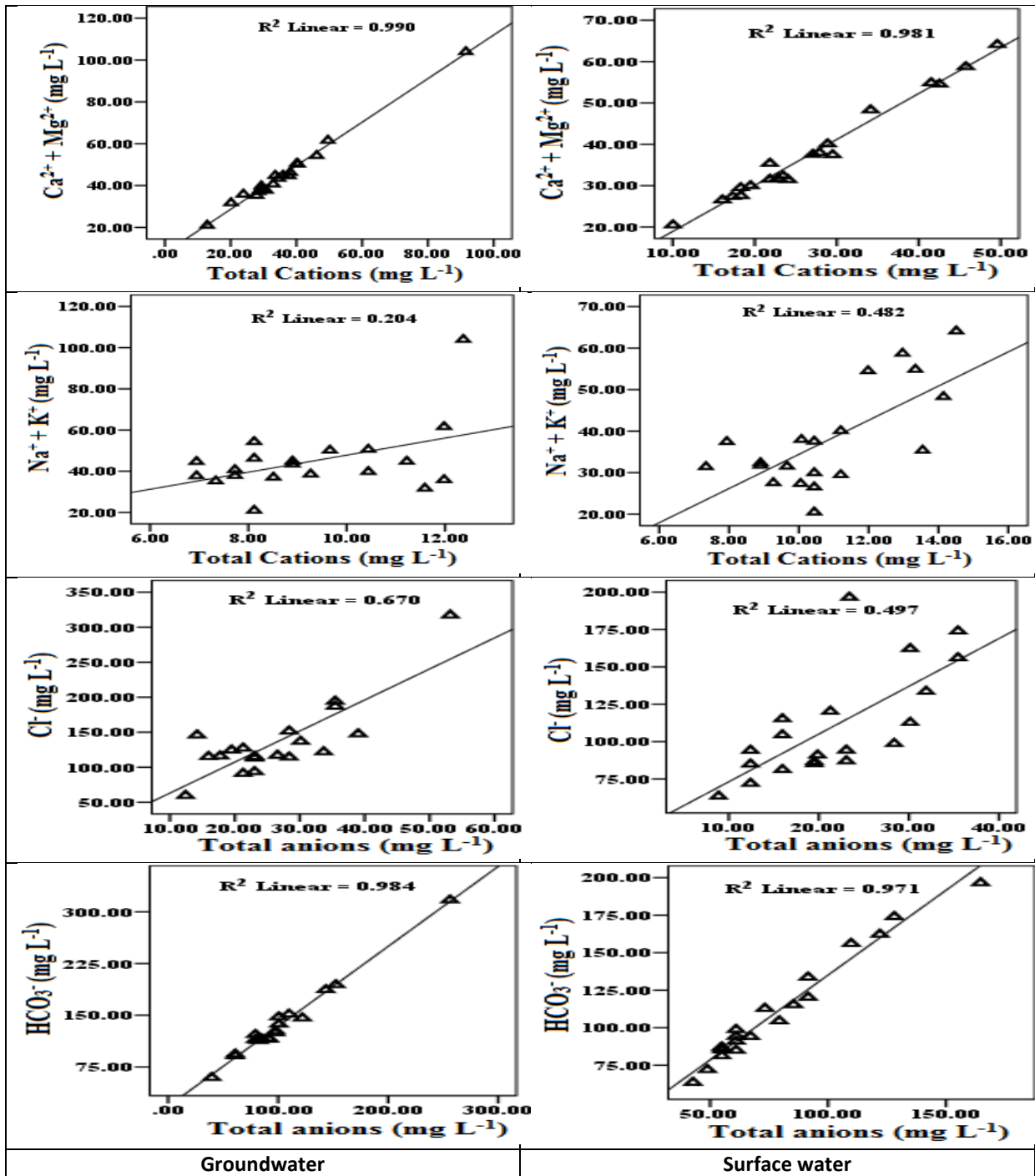

Figure 4. Scatter diagram showing relationships among major ions in the study samples of the study area (solid line denotes 1:1)

MOHAMMAD JAHIDUL ISLAM et al.,

CONCLUSIONS

Groundwater samples were belonged to the category of soft whereas surface water samples were moderately hard. The trace metals except Cd in surface water samples exceeded the recommended standards by WHO indicating the influence of anthropogenic activities. However, As and Mn concentrations were well within the recommended limits. In conclusion, one can view that surface and groundwater contamination occurred throughout the area to little extent and is likely to continue in the future. In general, the surface and groundwater samples in Parbatipur Upazilla of Dinajpur district were suitable for drinking and irrigation purposes.

REFERENCES

1. Wang Y, Wang P, Bai Y, Tian Z, Li J, Shao X, *et al*. Assessment of surface water quality via multivariate statistical techniques: A case study of the Shoghua River Harbin region, China. J Hydro Environ Res. 2013; 7:30-40.

2. Rahman MS, Saha N, Molla AH. Potential ecological risk assessment of heavy metal contamination in sediment and water body around Dhaka export processing zone, Bangladesh. Environ Earth Sci 2014; 71:2293-308.

3. Arslan H. Application of multivariate statistical techniques in the assessment of groundwater quality in seawater intrusion area in Bafra Plain, Turkey. Environ Monit Assess 2013; 185:2439-52.

4. Kondakis XG, Makris N, Leotsinidis M, Prinou M, Papapetropoulos T. Possible health effects of high manganese concentration in drinking water. Arch Environ Health. 1989; 44:175-8.

5. Frisbie SH, Ortega R, Maynard DM, Sarkar B. The concentrations of arsenic and other toxic elements in Bangladesh's drinking water. Environ Health Perspect. 2002; 110:1147-53.

6. Rahman MS, Molla AH, Saha N, Rahman A. Study on heavy metals levels and its risk assessment in some edible fishes from Bangshi River, Savar, Dhaka, Bangladesh. Food Chem 2012;134:1847-54.

7. Jarup L. Hazards of heavy metal contamination. Br Med Bull. 2003; 68:167-82.

8. Pan J, Plant JA, Voulvoulis N, Oates CJ, Ihlenfeld C. Cadmium levels in Europe: Implications for human health. Environ Geochem Health 2010;32:1-12.

9. Phuong NM, Kang Y, Sakurai K, Sugihara M, Kien CN, Bang ND, *et al.* Arsenic contamination in groundwater and its possible sources in Hanam, Vietnam. Environ Monit Assess 2012;184:4501-15.

10. Nordstrom DK. Public health. Worldwide occurrences of arsenic in ground water. Sci. 2002; 296:2143-5.

11. Chetia M, Chatterjee S, Banerjee S, Nath MJ, Singh L, Srivastava RB, *et al.* Groundwater arsenic contamination in Brahmaputra river basin: A water quality assessment in Golaghat (Assam), India. Environ Monit Assess 2011; 173:371-85.

12. Fendorf S, Michael HA, van Geen A. Spatial and temporal variations of groundwater arsenic in South and Southeast Asia. Sci. 2010; 328:1123-7.

13. Rahman MM, Zaman MW. Quality assessment of river and groundwater for irrigation at Shahzadpur in Bangladesh. Progress Agric. 1995; 6: 89-96.

14. Quddus KG, Zaman MW Irrigation water and quality in some selected villages of Meherpur in Bangladesh. Ban. J. of Agril. Sci.1996; 23(2): 51-57.

15. Islam MJ, Zaman MW, Rahman MM, Wadia R, Sahadat HM. Relative suitability of water quality in Dhaka city. Ban. J. of Environ. Sci. 1998; 4: 116-120.

16. UNDP. Groundwater Survey: the Hydrogeological Conditions of Bangladesh. UNDP Technical Report DP/UN/BGD-74-009/1, 1982; 113.

17. Shamsudduha, M, Chandler, RE, Taylor, RG and Ahmed, KM. Recent trends in groundwater levels in a highly seasonal hydrological system: the Ganges-Brahmaputra-Meghna Delta. Hydr. Earth Sys. Sci. Disc. 2009; 6:4125-4154.

18. Hunt DTE and Wilson AL. The Chemical Analysis of Water-General Principles and Techniques. 2nd ed., The Royal Society of Chemistry, Cambridge, 1986; 29-43.

19. APHA. Standard methods for the examination of water and wastewater. 21th ed., American Public Health Association, Wahsington, D. C. 2005.

20. Ramesh, R. and M. Anbu. 1996. Chemical Methods for Environmental Analysis:Water and Sediments.Macmillan Publishers, India. p. 180.

21. Environmental Quality Standards for Bangladesh (EQS). Department of Environment, Government of the People's Republic of Bangladesh; 1991.

22. Tiri A, Boudoukha A. Hydrochemical analysis and assessment of surface water quality in Koudiat Medouar reservoir, Algeria. Eur J Sci Res. 2010; 41:273-85.

23. WHO. Guidelines for Drinking-Water Quality. 2nd ed., Vol. 1. Geneva: World Health Organization; 1997.

24. Todd, D.K. and Mays, L. Groundwater Hydrology.Wiley, USA. 2005.

25. WHO. Guidelines for Drinking-Water Quality. Geneva: World Health Organization; 2004.

26. Richards, L. A. (Ed). 1968. Diagnosis and Improvement of Saline and Alkali Soils. Agricultural hand book 60, USDA and IBH. Publishing Co. Ltd. New Delhi, India. p. 98.

27. Wilcox, LV. Classification and use of irrigation water. United Status Department of Agriculture Circular No. 969.Washington D.C. 1955; p 19.

28. Eaton, FM. Significance of carbonate in irrigation waters. Soil Sci. 1950; 67: 12-133.

29. BCAS. Guide to the Environmental Conservation Act 1995 and rules 1997. Bangladesh Centre for Advanced Studies; 1998.

30. WHO. Guidelines for Drinking-Water Quality. 2nd ed., Vol. 1. Geneva: World Health Organization; 1993.

31. USEPA. Drinking Water Regulations and Health Advisories. Washington DC, USA: U.S. Environmental Protection Agency; 1996.

32. Karanth KR. Groundwater Assessment Development and Management, McGraw-Hill Publishing Co. Ltd., New Delhi, 1994.

33. Freeze, AR and JA Cherry. Groundwater. Prentice Hall Inc. England Cliffs. New Jersey. 1979; 84-87.

34. Sawyer, CN and McCarty, PL. Chemistry for Sanitary Engineers. 2nd ed. McGraw Hill, New York, 1967; p. 518.

35. Kelly WP. Permissible Composition and Concentration of Irrigated Waters. 1940; Proc A S C F 66, p. 607.

36. Sarin MM, Krishnaswamy S, Dilli K, Somayajulurd BLK, Moore WS. Major-ion chemistry of the Ganga-Brahmaputra river system: weathering processes and fluxes to the Bay of Bengal. Geochem Cosmochim Acta. 1989; 53:997–1009.