

## Original Article

# Surface and groundwater quality assessment based on multivariate statistical techniques in the vicinity of Mohanpur, Bangladesh

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## ABSTRACT

**Aims:** This work evaluated the surface and groundwater quality of Mohanpur area, Rajshahi district, Bangladesh. Multivariate statistical techniques were also applied to determine the possible sources of water contamination.

**Materials and Methods:** Water samples were collected from randomly selected ten different sampling sites for analyzing the chemical parameters including pH, electrical conductivity, total dissolved solids, total hardness, total alkalinity,  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and some heavy metals such as Mn, Pb, Cd, and As concentrations. Concentrations of heavy metals were determined using atomic absorption spectrometer (AAS).

**Results:** Based on hydrochemical characteristics, surface and groundwater in the study area were, in general, fresh, hard, and alkaline in nature. All chemical parameters were within the WHO water quality guidelines. Whereas, among four analyzed heavy metals Pb, and Cd concentrations exceeded the WHO recommended values. Pearson correlation matrix showed a number of statistically significant associations ( $P < 0.01$  and  $P < 0.05$ ) among the examined water quality parameters. Moreover, principal component (PC) analysis (PCA) and cluster analysis (CA) were used to analyze the water quality dataset. PCA analysis identified two PCs as responsible for the data structure explaining 72.53% of the total variance in water quality. PCA indicated that the water quality variations were mainly of anthropogenic origin through agricultural and municipal discharges. Results of CA revealed three significant groups of similarity among the 10 sampling sites.

**Conclusions:** It could be deduced from the present results that water contamination was occurred to some extent throughout the area, and is likely to be continued in the near future. Improvement of local sanitation system along with frequent training and awareness programs can help in developing water quality in the studied area.

**Key words:** Groundwater, hierarchical cluster analysis, multivariate statistics, principal component analysis, surface water

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## INTRODUCTION

The surface and groundwater quality is a very sensitive issue, and a major factor affecting the human health as well as ecological systems.<sup>[1]</sup> The surface water quality is controlled

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by anthropogenic factors such as urbanizations, industrial and agricultural practices, and also by natural processes like erosion and the regional climatic conditions.<sup>[2]</sup> Likewise, the groundwater quality depends on many factors such as soil characteristics, manner of groundwater circulation through rock types, topography of the region and human activities on the ground.<sup>[3]</sup> However, water pollution is a critical problem in Bangladesh including Rajshahi city and the surrounding areas like Mohanpur. Most of the surface water bodies in the Mohanpur area are linked with drains, which are connected with the latrines. 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.<sup>[4]</sup> According to the Rajshahi development authority report,<sup>[5]</sup> release of untreated urban effluent into the surrounding water bodies and the subsequent use of this polluted water in agricultural fields is immensely affecting the public health. Although 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.<sup>[6]</sup> Lead is considered as a possible human carcinogenic due to the inconclusive evidence of human and sufficient evidence of animal carcinogenicity.<sup>[7]</sup> Acute exposure to lead is known to cause renal failure and liver damage.<sup>[8]</sup> Moreover, recent research has shown that prolonged low-level exposure to lead may diminish the intellectual capacity of children.<sup>[9]</sup> 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.<sup>[10]</sup> 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.<sup>[11]</sup> In Bangladesh, 30 million people drink arsenic-contaminated water without having alternative resources.<sup>[12]</sup> 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.<sup>[13]</sup> Arsenic-contamination of natural water leads to the development of cancer, cardiovascular disease and inhibits the mental development of children.<sup>[14]</sup>

It is worth noting here that depending on the geological formation, the quality of water varies from place to place. Thus, a number of physicochemical parameters that results in a large data matrix need a complex data interpretation. Principal component (PC) analysis (PCA) and cluster analysis (CA) coupled with Pearson's product moment correlation

analysis allow us to resolve this complex data matrices. These multivariate approaches help to identify possible factors/sources that influence the water systems and offers a valuable tool for reliable management of water resources, as well as a rapid solution on pollution problems.<sup>[15-17]</sup> In general, CA groups the samples based on inter-sample similarities and illustrates the overall similarity of variable data set. On the other hand, PCA identify the most important factors contributing to the data structure by transforming many original, interrelated variables into fewer, uncorrelated variables named PCs. Usually, the minor PCs are not taken into consideration in order to simplify the analysis because of their poor interpretation of data structure.<sup>[1]</sup> A number of reports emphasize on the importance of multivariate statistical analysis as a tool in the treatment of analytical and environmental data.<sup>[18,19]</sup>

With these views, the present work was designed and carried out for the following purposes: To study the chemical properties and heavy metals concentrations of surface and groundwater resources in Mohanpur area of Rajshahi, Bangladesh; to compare the present status of water quality parameters with the recommended guidelines; and to extract information relating to the influence of possible sources (natural or anthropogenic) on water quality parameters using multivariate statistical analysis.

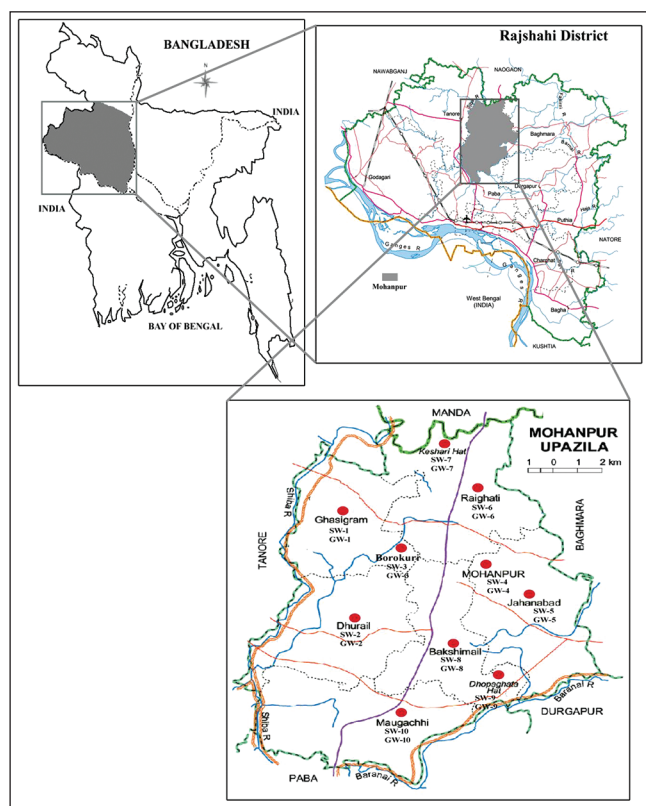
## MATERIALS AND METHODS

### Site description

The present study area, Mohanpur, belongs to Rajshahi district is situated on the northern bank of the Padma River, Bangladesh. The distance between Rajshahi city and Mohanpur town is about 30 km. It covers an area-extent of 163 km<sup>2</sup> and is distributed in 24,828 units of household. It experiences a tropical wet and dry climate and is generally marked with monsoon, high temperature, considerable humidity, and moderate rainfall. Ten villages were selected for the present study and the area map indicating the sampling sites is shown in Figure 1.

### Sampling methodology

Twenty water samples (10 groundwater samples from hand tube-wells and ten surface water samples from different ponds or canals) were collected from predetermined sampling sites in the month of April to December, 2010. Samples were collected from Ghasigram, Dhurail, Borokuri, Mohanpur, Jahanabad, Raighati, Keshari Hat, Bakshimai, Dhopaghata Hat, and Maugachhi. The tube-wells water around the study area was mostly used for drinking purposes. Clean and dry 500-ml polyethylene bottles were used to collect surface and groundwater samples. Before the collection of the groundwater samples, tube-wells were pumped for 5 min to wash out the stagnant water inside the tube-wells and to get fresh groundwater. After rinsing with fresh water, the sample water was poured into bottles. Prior to collection of



**Figure 1:** Sampling spots showing Mohanpur Upazila (sub-district), Rajshahi district, Bangladesh

the surface water samples, the surface of the ponds or canals were cleaned, and the bottles were rinsed with cleaned surface water. The sample bottles were then labeled, tightly packed, transported immediately to the laboratory, and stored at 4°C for chemical analyses. A portion of collected water samples were acidified (2 ml concentrated HNO<sub>3</sub> per L) and used in the determination of metallic constituents.

### Sample analysis

Water samples were analyzed for the chemical parameters including pH, electrical conductivity (EC), total dissolved solids (TDS), total hardness (TH), total alkalinity (TALK), chloride (Cl<sup>-</sup>), nitrate (NO<sub>3</sub><sup>-</sup>), and also for the heavy metals such as Mn, Pb, Cd, and As. pH of the samples were measured at the sites of collection using a portable pH meter (KPK, KP-5Z, Japan), previously standardized through pH 4, 7, and 10 standard buffer solutions (procured from Merck, India). EC of the water samples were measured as soon as possible after collection using a digital EC meter (HANNA instruments HI 9033, Singapore), previously calibrated through 0.01 M, 0.1 M and 1.0 M KCl solution. The TDS (EC × 0.7) of the samples were recorded by the TDS probe of the EC meter. After determining the pH, EC, and TDS on the sites, the samples were carried to the laboratory for remaining analyses. TH as CaCO<sub>3</sub>, TALK, and Cl<sup>-</sup> were determined following standard methods recommended by American Public Health Association.<sup>[20]</sup> NO<sub>3</sub><sup>-</sup> contents were analyzed by a UV-Visible spectrophotometer (WPA S104,

England). The concentrations of Mn, Pb, Cd, and As were determined by an atomic absorption spectrophotometer (AAS; Model AA-6800, Shimadzu Corporation, Japan) at their respective wavelength in the central science laboratory, Rajshahi university. Due to expected low concentrations of the metals in the water samples and limited instrument sensitivity, preconcentration of the water samples were done by evaporating 100 ml of water to 8 ml on a hot plate. The samples were then digested by adding 5 ml of 11.1 M HNO<sub>3</sub> and heated on the hot plate for 30 min. Thereafter, 10 ml of 16.3 M HCl was added, and digestion was continued until the solution turned into light brown or colorless, and the volume was then adjusted to 25 ml with double distilled water. In order to assure the precision of the measurement, reference standard solutions with a known concentration of each measured element were used as control samples. After every ten samples, the control sample was analyzed to check the accuracy of analysis. Each sample was measured at least two times in order to assess the reproducibility of the measurement. Samples were reanalyzed if the relative standard deviation of the measurement exceeded 10%. The reagents, including indicators and buffers, were of Analytical Reagent grade. The aqueous solutions were prepared using deionized water.

### Statistical tests

Analysis of variance (ANOVA) test was performed to evaluate the inter-sample locations variation of chemical parameters, as well as heavy metals concentrations. Moreover, to identify the relationship among the examined water quality parameters in the studied samples and to infer their sources (natural or anthropogenic), Pearson's correlation coefficient analysis, PCA, and CA were performed. In Pearson's correlation coefficient analysis, the values of correlation coefficients indicate the strength of inter-relationship between two chemical parameters. PCA and CA are the most common multivariate statistical methods for classification and interpretation of large datasets from environmental monitoring programs that allow the reduction of the dimensionality of the data and the extraction of information.<sup>[21]</sup> Data were processed using Statistical Package for Social Science (SPSS 17.0 for Windows; IBM, USA). Besides this, the STATISTICA 8.0 (StatSoft, Inc., USA) software package was employed for CA.

## RESULTS

The results obtained from the chemical and heavy metals analyses of ground and surface water samples in Mohanpur Upazila (sub-district); Bangladesh are presented in Table 1. One-way ANOVA analysis showed that the examined parameters in surface and groundwater samples differ significantly (at 95% confidence interval) except Mn ( $F = 0.045$ ,  $P = 0.834$ ) and As ( $F = 0.172$ ,  $P = 0.683$ ). Pearson's correlation coefficient analysis identified significant association between measured water quality parameters and

**Table 1: Chemical properties of surface and GW of Mohanpur area**

Sampling locations	Sample ID	pH	EC (µS/cm)	TDS (mg/L)	TH (mg/L)	TAlk (mg/L)	Cl <sup>-</sup> (mg/L)	NO <sub>3</sub> <sup>-</sup> (mg/L)	Mn (µg/L)	Pb (µg/L)	Cd (µg/L)	As (µg/L)
Ghasigram	SW-1	8.5	377	263.9	112.0	398.2	97.1	3.95	2.86	8.34	2.0	1.72
	GW-1	6.9	867	606.9	222.0	393.3	52.3	0.08	0.72	13.96	6.7	3.15
Dhurail	SW-2	8.2	645	451.5	124.0	500.7	131.8	5.154	0.90	7.97	1.0	2.59
	GW-2	7.1	766	536.2	301.6	416.8	23.9	0.30	1.20	15.90	3.7	3.13
Borokuri	SW-3	8.4	382	267.4	116.0	519.2	98.8	2.20	1.04	8.35	8.2	1.79
	GW-3	7.0	910	637.0	323.2	373.8	22.2	0.09	3.66	15.49	3.6	2.97
Mohanpur	SW-4	7.7	560	392.0	174.0	528.9	92.6	2.85	2.68	11.80	2.9	2.41
	GW-4	6.9	701	490.7	360.0	394.3	27.3	0.09	2.64	13.95	6.8	2.08
Jahanabad	SW-5	8.3	233	161.1	181.0	484.9	93.2	4.53	1.65	5.34	6.70	2.44
	GW-5	6.9	950	665.0	279.2	432.4	13.1	0.10	1.16	15.17	7.70	2.26
Raighati	SW-6	7.9	290	203.0	112.8	539.7	120.9	2.10	1.49	10.91	8.90	2.76
	GW-6	6.9	920	644.0	364.0	446.0	41.5	0.24	1.91	15.20	6.70	2.25
Keshari Hat	SW-7	8.3	470	329.0	138.4	481.2	151.2	3.35	1.54	11.06	4.1	2.79
	GW-7	7.0	810	567.0	337.6	402.1	30.2	0.15	1.82	13.63	4.1	2.15
Bakshimail	SW-8	8.6	390	273.0	128.8	534.9	106.7	5.20	1.91	6.47	1.50	3.09
	GW-8	6.9	750	525.0	400.0	421.0	36.4	2.80	1.88	15.31	15.30	3.16
Dhopaghata	SW-9	8.6	555	388.5	164.8	509.5	81.8	2.40	1.97	12.86	5.50	3.35
Hat	GW-9	7.1	956	669.2	396.0	495.8	57.4	0.28	1.80	14.51	19.00	2.41
Maugachhi	SW-10	8.4	488	341.6	120.0	499.7	116.4	5.20	1.59	13.60	2.0	2.54
	GW-10	6.9	987	690.9	272.0	373.8	38.6	0.25	1.54	15.79	16.90	2.81
SW	Mean	8.3	439	307.1	137.2	499.7	109.1	3.69	1.76	9.67	4.28	2.55
	(minimum-maximum)	(7.7-8.6)	(233-645)	(161.1-451.5)	(112.0-181.0)	(398.2-539.7)	(81.8-151.2)	(2.10-5.20)	(0.90-2.86)	(5.34-13.60)	(1-8.9)	(1.72-3.35)
GW	Mean	6.9	861.7	603.2	325.6	414.9	34.3	0.438	1.83	14.91	9.05	2.64
	(minimum-maximum)	(6.9-7.1)	(701-987)	(490.7-690.9)	(222.0-400.0)	(373.8-495.8)	(13.1-57.4)	(0.08-2.80)	(0.72-3.66)	(13.63-15.90)	(3.6-19)	(2.08-3.16)

\*SW: Surface water, GW: Groundwater

the results are given in Table 2. Moreover, PCA extracted two PCs controlling the variability of examined parameters in this study [Table 3].

## DISCUSSION

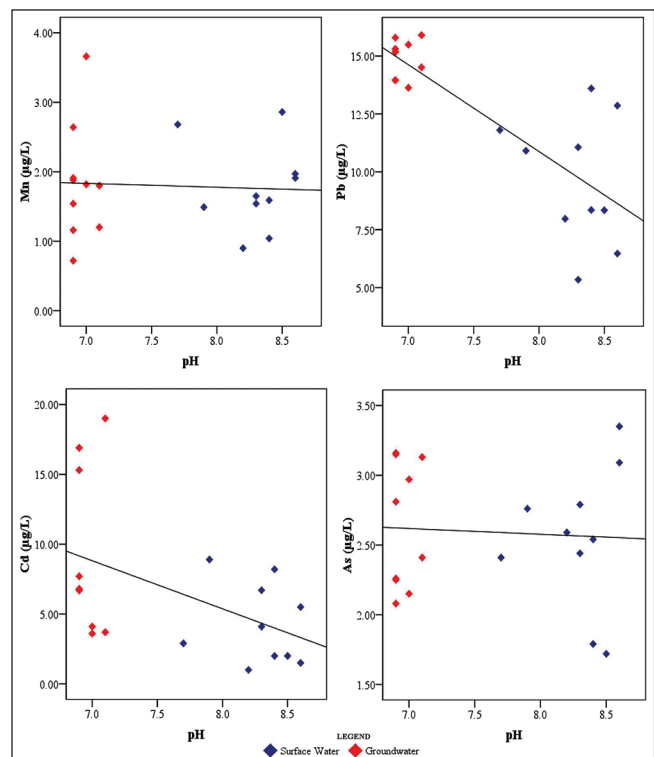
### Chemical properties

The observed pH ranges of the surface and groundwater in the study area are 7.7-8.6 and 6.9-7.1, respectively [Table 1]. The higher pH value of surface water than that of groundwater could be due to increased photosynthetic assimilation of dissolved inorganic carbon by plankton. 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 samples were well within the WHO<sup>[22]</sup> prescribed standard for pH of 6.5-8.5. Whereas, surface water pH values were in line with the upper end of the WHO recommended standard limit for pH. According to environmental quality standards (EQS) for Bangladesh,<sup>[23]</sup> 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, irrigation, industrial and other purposes. However, 80% of surface water samples were in line with the permissible limits of pH recommended by EQS. Scatter plots [Figure 2] have been used for illustrating how the metals solubility varies with water pH and their concentrations as well. The solubility plots indicate a general decrease in heavy metals solubility with increasing pH, which is the usual trend with cationic metals.

In this study, the values of EC were ranged between 233 and 645  $\mu\text{S}/\text{cm}$  for surface water and from 701 to 987  $\mu\text{S}/\text{cm}$  for groundwater indicating high mineralization of groundwater compared to surface water [Table 1]. However, no studied samples were beyond the WHO<sup>[24]</sup> recommended maximum EC level of 1,500  $\mu\text{S}/\text{cm}$  in drinking water.

Total dissolved solids values were varied between 161.1 and 690.9 mg/L [Table 1]. Low TDS (161.1-451.5 mg/L) was observed for surface water and high TDS (490.7-690.9 mg/L)

for groundwater, could be due to the higher contact period of groundwater with rock than that of surface water. According to WHO,<sup>[25]</sup> 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.<sup>[25]</sup> The TDS indicates the salinity behaviors of water and based on TDS, natural water quality can be classified as fresh (if TDS < 1,000 mg/L), brackish (if TDS = 1,000-10,000 mg/L), saline (if TDS = 10,000-1,000,000 mg/L) and brine (if TDS > 1,000,000 mg/L).<sup>[26]</sup> According to this classification, the surface and groundwater of the studied area were in the fresh category. However, water with extremely low concentrations of TDS may also be unacceptable because of its flat, insipid taste.



**Figure 2:** Solubility plots show the relationship between the pH and heavy metal concentrations in surface and groundwater samples

**Table 2: Pearson correlation between chemical parameters of water samples**

	pH	EC	TDS	TH	TAlk	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	Mn	Pb	Cd	As
pH	1	-0.858**	-0.858**	-0.875**	0.686**	0.858**	0.846**	-0.055	-0.802**	-0.484*	-0.063
EC	-0.858**	1	1.000**	0.785**	-0.626**	0.774**	0.764**	0.010	0.828**	0.423	0.143
TDS	-0.858**	1.000**	1	0.784**	-0.626**	0.774**	0.764**	0.010	0.828**	0.423	0.143
TH	-0.875**	0.785**	0.784**	1	-0.587**	-0.846**	-0.726**	0.217	0.728**	0.540*	0.052
TAlk	0.686**	-0.626**	-0.626**	-0.587**	1	0.730**	0.602**	-0.249	-0.562**	-0.161	0.025
Cl <sup>-</sup>	0.858**	0.774**	0.774**	-0.846**	0.730**	1	0.812**	-0.197	-0.726**	-0.364	-0.036
NO <sub>3</sub> <sup>-</sup>	0.846**	0.764**	0.764**	-0.726**	0.602**	0.812**	1	-0.065	-0.763**	-0.441	0.018
Mn	-0.055	0.010	0.010	0.217	-0.249	-0.197	-0.065	1	0.098	-0.155	-0.134
Pb	-0.802**	0.828**	0.828**	0.728**	-0.562**	-0.726**	-0.763**	0.098	1	0.406	0.253
Cd	-0.484*	0.423	0.423	0.540*	-0.161	-0.364	-0.441	-0.155	0.406	1	0.067
As	-0.063	0.143	0.143	0.052	0.025	-0.036	0.018	-0.134	0.253	0.067	1

\*\*Correlation is significant at the 0.01 level (two-tailed), \*Correlation is significant at the 0.05 level (two-tailed)

**Table 3: Rotated component matrix for data of surface and GW samples**

Variable	Component	
	1	2
pH	-0.951	-0.059
EC	0.923	0.159
TDS	0.923	0.159
TH	0.902	-0.022
TAlk	-0.750	0.313
Cl <sup>-</sup>	-0.915	0.125
NO <sub>3</sub> <sup>-</sup>	-0.880	-0.013
Mn	0.160	-0.786
Pb	0.870	0.158
Cd	0.495	0.440
As	0.079	0.588
Eigenvalues	6.629	1.349
% variance explained	60.266	12.264
% cumulative variance	60.266	72.530

Extraction method: Principal component analysis, Rotation method: Varimax with Kaiser normalization

The acceptable limit of TH (as CaCO<sub>3</sub>) is 200 mg/L, which can be extended up to 600 mg/L in case of non-availability of any alternate water source.<sup>[25]</sup> The TH in the studied samples were ranged from 112 to 181 mg/L in surface water and from 222 to 400 mg/L in groundwater. Based on TH, Dufor and Becker<sup>[27]</sup> classified water as soft (if TH = 0-60 mg/L), moderately hard (if TH = 61-120 mg/L), hard (if TH = 121-180 mg/L), and very hard (if TH >180 mg/L). According to this classification, about 40% of surface water samples were belonged to moderately hard type, 50% were belonged to hard type and the rest (surface water sample collected from Jahanabad with TH = 181 mg/L) corresponded to very hard type water. Whereas, all the examined samples of groundwater were under the category of very hard water [Table 1].

The values of TAlk in the present study were measured from 398.2 to 539.7 mg/L in surface water and from 373.8 to 495.8 mg/L in groundwater [Table 1]. In natural water, most of the alkalinity is caused due to dissolution of CO<sub>2</sub> in water. However, all the surface and groundwater samples contained TAlk more than TH, which is indicative of excess water alkalinity (EA).<sup>[28]</sup> It is also noted that the EA varied from 21 to 171 mg/L (not mentioned in the table), which could be due to the salt of NaHCO<sub>3</sub>.

The concentrations of chloride in the examined water samples were between 13.1 and 151.2 mg/L [Table 1]. Surface water showed higher chloride concentration (81.8-151.2 mg/L) than that of groundwater (13.1-57.4 mg/L). Chloride in drinking water originates from natural sources, sewage and industrial effluents, urban runoff and saline intrusion. No health-based guideline value has been proposed for chloride in drinking-water. However, chloride concentrations in excess of about 250 mg/L can give rise to detectable taste in water.<sup>[22]</sup>

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<sub>3</sub><sup>-</sup> concentrations were varied from 2.10 to 5.20 mg/L (surface water) and from 0.08 to 2.80 mg/L (groundwater). In natural conditions, concentration of NO<sub>3</sub><sup>-</sup> does not exceed 10 mg/L in the water.<sup>[29]</sup> All the analyzed samples contained nitrate concentrations within the tolerance limit of 45 mg/L.<sup>[25]</sup>

### Heavy metals

The manganese concentrations were varied from 0.90-2.86 to 0.72-3.66 µg/L in surface and groundwater accordingly. The average concentration (1.83 µg/L) of Mn in groundwater was slightly higher than the average Mn content (1.76 µg/L) of surface water. The maximum permissible limit of Mn concentration in drinking water is 500 µg/L set by WHO.<sup>[30]</sup> Potable water quality standard in terms of Mn is 100 µg/L set by Bangladesh Centre for Advanced Studies.<sup>[31]</sup> 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<sup>[30]</sup> and USEPA<sup>[32]</sup> are 10 and 15 µg/L respectively. Table 1 revealed that about 50% of surface water samples and almost all the groundwater samples contained higher Pb concentrations than the WHO recommended guideline value; clearly demonstrating anthropogenic impact.

The maximum permitted concentration of Cd in drinking water is 3 µg/L set by WHO.<sup>[30]</sup> Results showed that five surface water samples out of ten satisfied the WHO permissible level. On the other hand, all the groundwater samples were beyond the permissible limit.

In this study, arsenic-concentrations were varied from 1.72 to 3.35 µg/L in surface water and from 2.08 to 3.16 µg/L in groundwater at different sampling locations [Table 1]. 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.<sup>[14]</sup> The WHO<sup>[30]</sup> and USEPA<sup>[32]</sup> recommended limit 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.

### Interrelations of water quality parameters

The interrelations among the chemical parameters were evaluated using Pearson correlation coefficient (*r*) model [Table 2]. Correlation coefficient is commonly used to measure and to establish the relationship between two variables. It is a simplified statistical tool to show the degree of dependency of one variable to the other.<sup>[33]</sup> The results showed that the parameters in the water samples were correlated to each other at *P* < 0.01 and *P* < 0.05 level. A significant positive correlations were found between pH and TAlk (*r* = 0.686), Cl<sup>-</sup> (*r* = 0.858), NO<sub>3</sub><sup>-</sup> (*r* = 0.846) at *P* < 0.01 levels, whereas pH was negatively correlated with EC (*r* = -0.858), TDS (*r* = -0.858), TH (*r* = -0.857), Pb

( $r = -0.802$ ) at  $P < 0.01$  levels and with Cd ( $r = -0.484$ ) at  $P < 0.05$  levels. The negative correlation between heavy metals and pH suggested that release of heavy metals to water might be enhanced by acidic pH and oxidizing conditions. EC and TDS ( $r = 1.00, P < 0.05$ ) showed highly positive correlation with TH ( $r = 0.785$  and  $0.784$ ),  $Cl^-$  ( $r = 0.774$  and  $0.774$ ),  $NO_3^-$  ( $r = 0.764$  and  $0.764$ ), and Pb ( $r = 0.828$  and  $0.828$ ). The positive correlation indicated that the water was mainly controlled by TH (i.e.,  $Ca^{2+}$  and  $Mg^{2+}$ ),  $Cl^-$ , and  $NO_3^-$  ions, which depend upon the mineral dissolution, mineral solubility, ion exchange, evaporation, and anthropogenic activities. TALK exhibited good positive correlation with  $Cl^-$  ( $r = 0.730$ ),  $NO_3^-$  ( $r = 0.602$ ), and negative correlation with EC ( $r = -0.626$ ), TDS ( $r = -0.626$ ), TH ( $r = -0.587$ ), Pb ( $r = 0.562$ ) at  $P < 0.01$  levels. Mn and As showed no significant correlation between them and with other chemical parameters. However, some correlations were also observed between Pb and other parameters.

### Multivariate analysis

#### Principal component analysis

Principal component analysis is a multivariate statistical technique used for deciphering patterns within large sets of data and to explain the variance of a large dataset of inter-correlated variables with a smaller set of independent variables (PCs) by orthogonal transformation.<sup>[34]</sup> PCA is a powerful tool for the characterization of anthropogenic and geogenic loads. In this study, each dataset was subjected to PCA using the correlation matrix in order to standardize each variable, meaning the analysis was not influenced by the differences in data magnitude and measurement scales.<sup>[3-37]</sup> A varimax rotation was applied to aid interpretation of the results; this works by loading variables more strongly on fewer PCs. Significant PCs were then selected based on the Kaiser principal.<sup>[38]</sup> Under this principal, only component with eigenvalues  $\geq 1$  would be accepted as possible sources of variance in the data, with the highest priority ascribed to component that has the highest eigenvector sum. Table 3

shows the results of the PC loadings with a varimax rotation, as well as the eigenvalues, % variance explained and % cumulative variance. The results indicated that two PCs were obtained with eigenvalues  $> 1$  summing almost 72.53% of the total variance in the water datasets [Table 3]. The scree plot [Figure 3] was used to identify the number of PCs to be retained in order to comprehend the underlying data structure. The scree plot indicated that first two components captured the most significant variation in the data. However, the elbow occurred at PC 2, therefore, up to PC 2 was accepted to account for the variation in the data. The first PC, accounting for 60.266% of the total variance was correlated with pH, EC, TDS, TH, TALK,  $Cl^-$ ,  $NO_3^-$ , Pb, and Cd. PC 1 may be interpreted as representing influences of anthropogenic point and nonpoint sources such as land use change, municipal waste, agricultural runoff and atmospheric deposition. The second PC described 12.264% of the total variance, showed a high negative loading on Mn and moderate positive loading for As. Water samples in the study area were found to be below the WHO<sup>[30]</sup> recommended guideline values in terms of Mn and As. Thus, it could be stated that PC 2 represented natural soil leaching processes. The negative loading on Mn indicated that as the As concentration increases, Mn level decreases showing existence of the inverse relation with As in the water. However, Figure 4 shows the score plot for the two PCs explaining 72.53% of the total variance. Two groups of water (groundwater and surface water), could be classified through the diagram of the scores for PC 1 versus PC 2, where groundwater samples showed more variations than the surface water samples.

#### Cluster analysis

CA comprises a series of multivariate methods that are used to find true groups of data.<sup>[39]</sup> Hierarchical CA that has been used in this study is the most widely applied technique for analyzing water quality data. Hierarchical clustering joins the most similar observations and then successively the next most similar observations. The levels of similarity at which observations are merged are used to construct a dendrogram. In this study, hierarchical agglomerative CA was performed

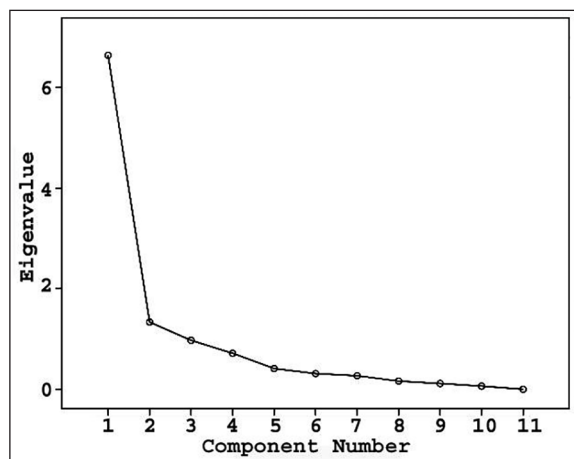


Figure 3: Scree plot showing point (principal component 2) at which the factor extraction is terminated

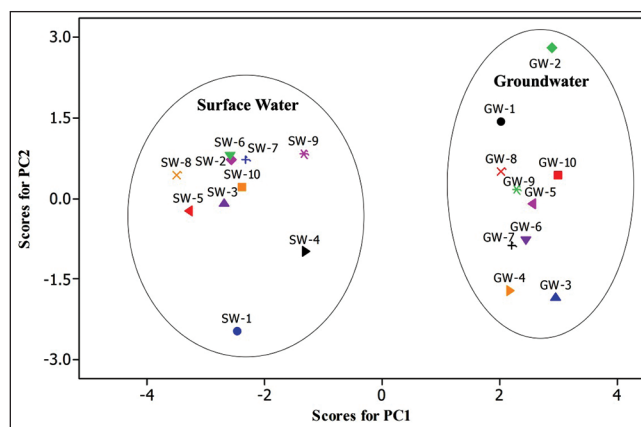
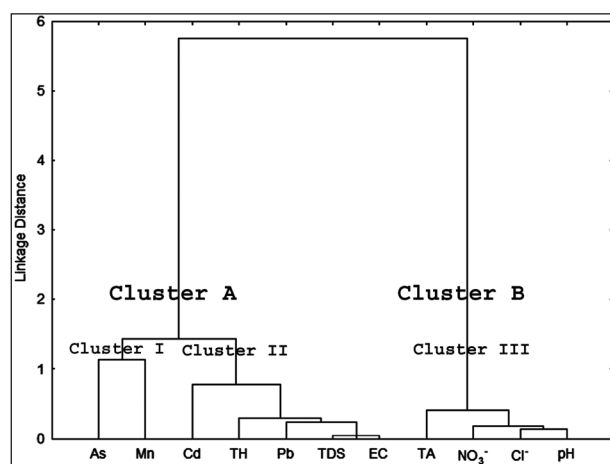


Figure 4: Principal component scores for the surface and ground water samples

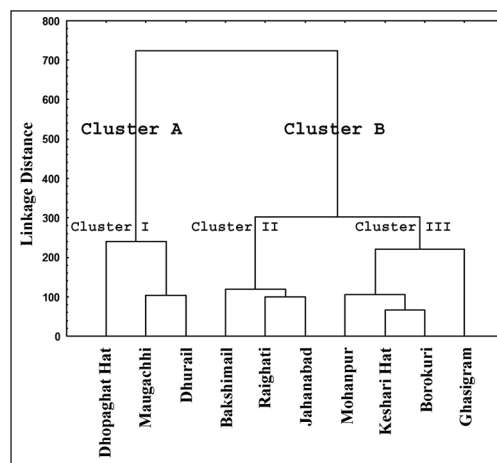
on the data set by means of City-block (Manhattan) distance as similarity measurement and Ward's method as the amalgamation rule. The Dendrogram of the clustering of 11 chemical parameters shows in Figure 5. It exhibited that the chemical parameters could be initially grouped into two main clusters, cluster A and cluster B. Nevertheless, in our opinion it would be possible to distinguish among three secondary clusters labeled as clusters I to III in Figure 5. Cluster I showed a close association between As and Mn. This finding corroborates the result of PCA and CA. Cluster II formed by Cd, TH, Pb, TDS and EC. TDS and EC exhibited very close association and completely accordance with the correlation analysis ( $r = 1.00, P < 0.05$ ). Cluster III formed by TAlk,  $\text{NO}_3^-$ ,  $\text{Cl}^-$  and pH. Moreover, the CA was also used to identify the spatial similarity between 10 sampling sites based on the level of chemical concentration and three statistically significant clusters were obtained [Figure 6]. Cluster I consisted of Dhopaghat Hat to Dhurail; cluster II consisted of Bakshimail to Jahanabad; and cluster III from Mohanpur to Ghasigram. The clustering procedure revealed the groups of similar sites in a quite convincing way. These clusters included sampling sites with similar characteristics and natural background that were affected by similar types of sources. The CA carried out using our data indicates that this approach could be used to design future spatial sampling strategy in an optimal way in the Mohanpur area. For instance, the number of the sampling sites could be optimized in such a way that for rapid quality assessment studies only the representative sites from each cluster (not all monitoring sites) can be used. This will reduce the number of analysis and also the cost of the risk assessment procedure. However, two distinct clusters (cluster A and cluster B) emerged from the grouping of ground and surface water samples [Figure 7]. Cluster A consisted of groundwater samples whereas cluster B consisted of surface water samples, which is completely identical to the PC score plot for ground and surface water samples [Figure 4].

## CONCLUSIONS

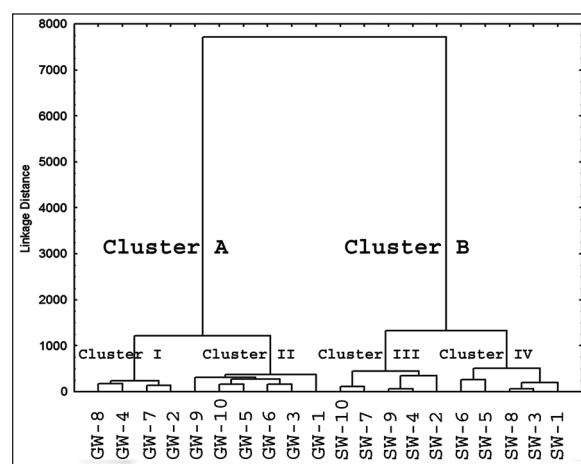
In general, the surface and groundwater samples in Mohanpur area of Rajshahi district were alkaline in nature that could be due to the salt of  $\text{NaHCO}_3$ . Groundwater samples were belonged to the category of very hard, whereas surface water samples were moderately hard to very hard. The pH values and the concentrations of EC, TDS, chloride, and nitrate in the examined water samples were less than the WHO recommended maximum values. The trace metals, Pb and Cd, in 50% surface water samples and all groundwater samples exceeded the recommended standards by WHO indicating the influence of anthropogenic activities. However, As and Mn concentrations were well within the recommended limits. Pearson correlation coefficients among the chemical parameters showed a number of strong associations. Multivariate statistical methods were applied to the water quality data set. The two PCs explaining 60.27 and 12.26% respectively of the total variance were obtained from PCA.



**Figure 5:** Dendrogram of clustering of water quality parameters using City-block (Manhattan) distance and Ward's agglomerative method



**Figure 6:** Dendrogram of clustering of sampling sites using City-block (Manhattan) distance and Ward's agglomerative method



**Figure 7:** Dendrogram of clustering of samples using City-block (Manhattan) distance and Ward's agglomerative method; SW = Surface water and GW = Ground water

The PC 1 demonstrated the anthropogenic impacts on water quality, whereas the PC 2 was related to natural activities.



Hierarchical CA helped to group the 10 sampling sites into three clusters of similar water quality characteristics. Based on obtained information, it is possible to design a future optimal sampling strategy, which could reduce the number of sampling sites and associated cost. In addition, the dendrogram of 11 chemical parameters was plotted and grouped into three main clusters.

In conclusion, one can view that surface and groundwater contamination occurred throughout the area to some extent and is likely to continue in the future. We are still in a position to make choices on how best to use, manage, and protect the valuable resource, water. It is our obligation to try our utmost to check the misuses of water as every drop of it is highly precious. Prevention of water contamination is a more effective strategy than cure. Improvement of local sanitation system along with training and awareness programs (on hygiene, water handling and system maintenance) can help in improving surface and groundwater quality in the studied area.

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